



Etude structurale de fluides complexes

Marianne Impéror-Clerc

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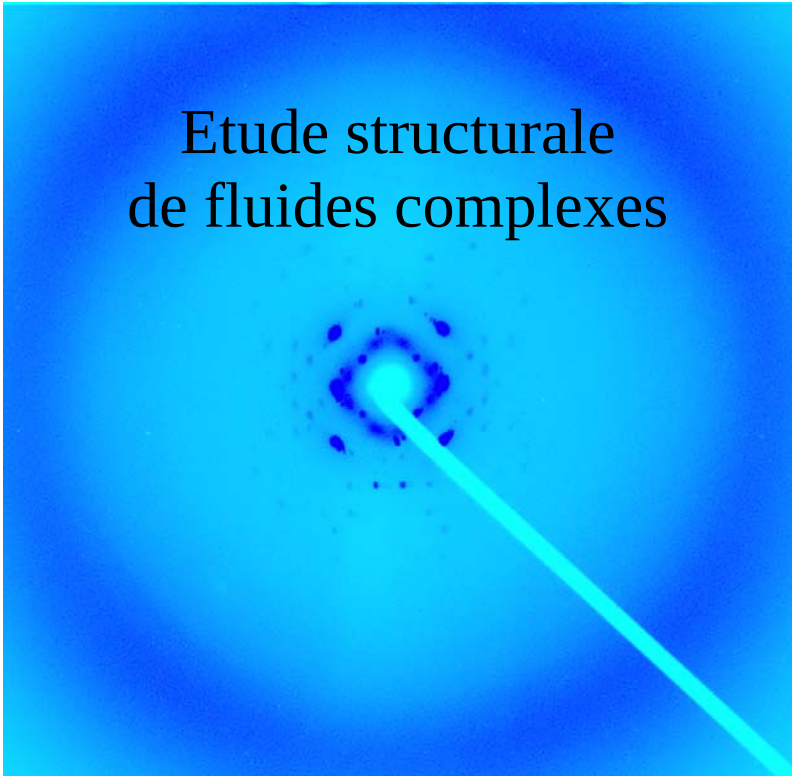
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HABILITATION A LA DIRECTION DE RECHERCHE

de l'Université Paris-Sud



Etude structurale de fluides complexes

Marianne Impérator-Clerc

Soutenue le 5 juin 2007

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Introduction

Ce manuscrit comporte une introduction à l'étude structurale des fluides complexes et des matériaux mésoporeux, puis expose les principaux résultats obtenus dans ce domaine.

Ce sujet bien spécifique s'inscrit dans une thématique de recherche plus large, celle des phases ordonnées formées par auto-organisation moléculaire. Les molécules mises en jeu sont des tensioactifs ou des lipides en solution aqueuse, des molécules de cristaux-liquides (thermotropes), des copolymères, des dendrimères. Un des objectifs de ce manuscrit est de souligner que les phases ordonnées qu'elles forment ont un peu leur existence propre, indépendamment du choix des briques moléculaires.

Une partie importante du manuscrit est consacrée à répondre à la question suivante : comment, à partir de quelques pics de Bragg mesurés aux petits angles, sait-on déterminer la structure d'une phase ? C'est finalement la question qui revient le plus souvent, et même si une bonne partie de la réponse est connue depuis longtemps, le but est d'expliquer le mieux possible les méthodes utilisées.

Cette thématique bénéficie largement de l'utilisation des grands instruments : le rayonnement synchrotron (L.U.R.E., E.S.R.F., HASY lab) et plus ponctuellement les sources de neutrons (I.L.L., L.L.B.). Egalement, les collaborations avec des groupes de chimie, que ce soit pour la synthèse de nouveaux cristaux liquides ou celle de matériaux mésoporeux sont tout aussi indispensables pour progresser dans ce domaine.

Après un bilan de mon activité de chercheur (chapitre 1), une première partie rassemble des connaissances utiles dans le domaine. Tout d'abord une introduction aux molécules et aux phases qu'elles forment (chapitres 2-5), puis des notions de diffusion (chapitres 6-12). La particularité de cette partie sur la diffusion réside dans le fait que l'on décrit la matière à l'échelle moléculaire. Au lieu d'une assemblée d'atomes ponctuels, on utilise une fonction continue, la densité électronique, qui est de plus périodique dans le cas des phases organisées.

La seconde partie présente les principaux résultats obtenus, regroupés par thématique : les relations d'épitaxie (chapitre 13), la détermination de structures (chapitres 14 et 15), la modélisation des intensités de diffraction (chapitres 16 et 17), les fluctuations et la dynamique (chapitres 18 et 19), et enfin les propriétés de facettage (chapitre 20).

Le dernier chapitre (chapitre 21) est consacré aux perspectives de cette thématique.

Chapitre 1

Bilan de l'activité

Depuis mon doctorat, je me suis spécialisée dans l'étude structurale des fluides complexes. Il s'agit soit de déterminer des structures, soit de suivre en temps réel des modifications structurales lors d'expériences de cinétique. La technique expérimentale que j'utilise principalement est la diffusion des rayons X, ainsi que des neutrons. De nombreux résultats ont été obtenus grâce à l'utilisation du rayonnement synchrotron (L.U.R.E. (Orsay), E.M.B.L. (Hamburg) et E.S.R.F. (Grenoble)) ainsi que de la diffusion des neutrons (I.L.L. (Grenoble), L.L.B. (Saclay)). Ces études sont réalisées en collaboration avec différents groupes de chimie, que ce soit pour la synthèse de nouveaux cristaux liquides (collaboration notamment avec *Michèle Veber* au LPS, avec *Robert Deschenaux* à l'Université de Neuchatel) ou celle de nouveaux matériaux (collaboration notamment avec *Anne Davidson* au LRS -Paris VI-, avec *Florence Babonneau* au LCMC -Paris VI-). En parallèle à cette spécialisation, j'ai élargi progressivement le champ des techniques expérimentales utilisées, avec toujours une prédilection pour les aspects structuraux. Il s'agit de la microscopie à force atomique (facettage des phases cubiques), de la rhéologie (utilisation d'un rhéomètre en parallèle aux expériences en cellule de Couette couplée à la diffusion des rayons X) et de la microscopie électronique (imagerie de nanoparticules).

Tout d'abord, ma thématique de recherche a été consacrée aux **phases cubiques** dites **bicontinues**. Lors des études structurales par RX et neutrons [2,3,4,8,9,13,16,19,20,22,29 collaboration au LPS avec *Elisabeth Dubois-Violette*, *Yolande Hendriks*, *Anne-Marie Levelut* et *Jean-François Sadoc*, à l'EMBL avec *Gert Rapp* et *Peter Laggner*, à L'ILL avec *Bela Farago*], l'originalité a été de montrer que ces phases peuvent croître en monocristaux de quelques mm³. La différence avec les cristaux atomiques usuels est, qu'à l'intérieur de ces monocristaux, l'ordre cristallin ne se réalise plus de manière discrète à l'échelle atomique, mais s'établit de manière continue à l'échelle moléculaire. En parallèle, les propriétés remarquables de facettage macroscopique de ces monocristaux ont été mises en évidence,

notamment par microscopie à force atomique, et sont encore à l'étude [12,15,26,29,32, collaboration au LPS avec *Catherine Even, Pawel Pieranski, Paul Sotta et Michèle Veber*].

Deux résultats originaux concernent la détermination de deux structures. Tout d'abord, j'ai montré que la symétrie des empilements 3D de micelles de molécules de tensioactifs dans l'eau n'était pas nécessairement cubique, comme admis couramment, puisque ces phases sont souvent dénommées phases cubiques micellaires. J'ai en effet démontré l'existence d'un **empilement** de symétrie hexagonale, **de type hexagonal compact** (hcp) [6]. Le deuxième résultat concerne **une phase cubique tri-continue** de grande maille, de groupe d'espace Im3m, dont la structure a finalement été élucidée en 2005, plus de 20 ans après l'obtention des premières données de rayons X [9,19,29,30, collaboration au LPS avec *Anne-Marie Levelut*, et avec *Goran Ungar et Xiangbing Zeng* à l'Université de Sheffield, UK].

J'ai aussi étudié des **phases hexagonales bidimensionnelles**, en mettant l'accent sur l'alignement de ces phases et l'instabilité en zig-zag de cet alignement, inhérente à ces phases [5, 11, 17, 18, collaboration au LPS avec *Patrick Davidson*].

Depuis 1999, j'ai commencé une nouvelle thématique concernant les **matériaux mésoporeux**. La synthèse de ces matériaux fait en effet appel aux propriétés d'auto-association des molécules de tensioactifs qui conduisent aux phases organisées (phases cubiques, hexagonales 2D, hexagonale 3D ...) que j'étudie en détails. Ainsi, la structure d'un matériau mésoporeux est une réplique solide de celle d'un fluide complexe. Ces matériaux sont le plus souvent constitués de silice amorphe. Le résultat principal que j'ai obtenu dans ce domaine est la déduction de **la taille des pores d'une phase hexagonale 2D** d'un matériau mésoporeux à partir des données de diffraction X [14, collaboration avec *Anne Davidson* au LRS -Paris VI-]. Pour ce type de matériau, cette méthode constitue une alternative avantageuse à la méthode d'adsorption/désorption d'azote, qui nécessite d'être réalisée à basse température et qui est utilisée couramment pour caractériser la porosité d'un matériau. Cette méthode a aussi été appliquée avec succès à des expériences de synthèse in-situ de ces matériaux, permettant ainsi de **suivre en temps réel l'auto-assemblage des micelles** [31,34 collaboration avec *Dominique Durand* (IBBMC, UPS), *Andrei Khodakov* (Unité de Catalyse et de Chimie du Solide, Université de Lille), *Vladimir Zholobenko* (Université de Keele, Chemistry Dpt, UK et *Isabelle Grillo*, ILL, Grenoble)].

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Publications jointes

Autant que possible, les résultats sont présentés en utilisant directement les publications. Voici la liste de celles jointes au manuscrit avec les chapitres correspondants:

Chapitre 4

[29] Imperor-Clerc, M. Thermotropic cubic mesophases. *Current Opinion in Colloid & Interface Science* **2005**, 9 (6), 370-376.

Chapitre 14

[6] Clerc, M. A new symmetry for the packing of amphiphilic direct micelles. *Journal de Physique II* **1996**, 6 (7), 961-968.

Chapitre 15

[19] Imperor-Clerc, M.; Veber, M.; Levelut, A. M. Phase transition between single crystals of two thermotropic cubic phases from a mixture of 3,5-didodecyloxybenzoic acid and C-18-ANBC. *Chemphyschem* **2001**, 2 (8-9), 533-+.

[30] Zeng, X. B.; Ungar, G.; Imperor-Clerc, M. A triple-network tricontinuous cubic liquid crystal. *Nature Materials* **2005**, 4 (7), 562-567.

Chapitre 16

[3] Clerc, M.; Duboisviolet, E. X-Ray-Scattering by Bicontinuous Cubic Phases. *Journal de Physique II* **1994**, 4 (2), 275-286.

Chapitre 17

[14] Imperor-Clerc, M.; Davidson, P.; Davidson, A. Existence of a microporous corona around the mesopores of silica-based SBA-15 materials templated by triblock copolymers. *Journal of the American Chemical Society* **2000**, 122 (48), 11925-11933.

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Chapitre 18

[11] Imperor-Clerc, M.; Davidson, P. An X-ray scattering study of flow-aligned samples of a lyotropic liquid-crystalline hexagonal phase. *European Physical Journal B* **1999**, 9 (1), 93-104.

Chapitre 19

[8] Clerc, M.; Hendrikx, Y.; Farago, B. Dynamics of a lyotropic cubic phase. *Journal de Physique II* **1997**, 7 (9), 1205-1214.

Première partie

A- Molécules et phases

Chapitre 2

Les tensioactifs et leurs diagrammes de phase

Les molécules de tensioactifs étudiées sont issues de l'industrie des détergents. Historiquement, les premiers détergents connus sont les savons, dont l'emploi remonte au début de notre ère. Ce sont des sels d'acides gras de sodium, comme le savon de Marseille, ou de potassium, comme le savon noir, préparés par saponification de corps gras naturels. Entre les deux guerres, sont apparus les premiers détergents synthétiques, les alkyl-benzène-sulfonates de sodium, fabriqués à partir du benzène et d'hydrocarbures tirés du kérosène. Depuis, de très nombreux détergents synthétiques ont été développés, avec notamment les non-ioniques.

Les molécules de tensioactifs sont dites amphiphiles, car elles possèdent deux parties d'affinités opposées :

- Une chaîne alkyl, hydrophobe, ayant de l'affinité pour les huiles
- Une partie hydrophile, la tête polaire, leur apportant le caractère de solubilité dans l'eau

Cette conformation conduit tout naturellement les tensioactifs à se rassembler aux interfaces huile-eau, solide-eau, air-eau, lorsqu'ils sont en solution aqueuse. Ils abaissent les tensions superficielles, d'où leur nom de "tensioactif" ou encore d'agent de surface.

Les différentes familles de tensioactifs

Suivant la nature de la tête polaire, il existe quatre familles de tensioactifs :

- Les tensioactifs anioniques, avec une tête polaire chargée négativement et un contre-ion de charge positive
- Les tensioactifs cationiques, avec une tête polaire chargée positivement et un contre-ion de charge négative
- Les tensioactifs non-ioniques, avec une tête polaire ne portant pas de charge, sans contre-ion associé

- Les tensioactifs zwitterioniques, avec une tête polaire portant deux charges compensées entre elles, sans contre-ion associé

Tensioactifs anioniques

Cette famille contient les savons, c'est-à-dire les sels d'acides gras, obtenus par saponification, où le cation est le plus souvent un ion sodium ou potassium. Un exemple classique est celui du laurate de sodium (**Fig 2-1**).

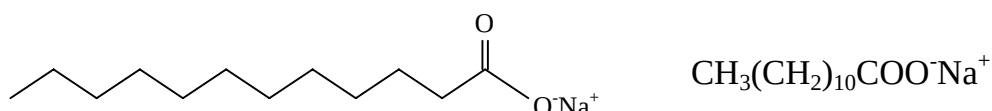


Figure 2-1. *Le laurate de sodium.*

La saponification est souvent réalisée à partir d'un mélange d'acide gras. Ainsi, la composition de l'huile de noix de coco (**Fig 2-2**) donne une idée des longueurs de chaînes usuelles.

Acide caprylique C8	8.86
Acide caprique C10	6.17
Acide laurique C12	48.83
Acide myristique C14	19.97
Acide palmitique C16	7.84
Acide stéarique C18	3.06
Acide oléique C18:1	0.76
Acide linoléique C18:2	4.44
Acide arachidique C20	0.05

Figure 2-2. *Composition en acides gras de l'huile de noix de coco (%)*

Les diagrammes de phase dans l'eau sont en général connus et l'ouvrage de référence dans le domaine est le livre de R. Laughlin.¹ Les principaux groupes polaires pour les tensioactifs anioniques de synthèse sont donnés dans le tableau de la **Figure 2-3**.

Alkanesulfonate salts	$\text{RSO}_3^-, \text{M}^+$
Alkyl sulfate salts	$\text{ROSO}_3^-, \text{M}^+$
N-Alkylsulfamate salts	$\text{RNHSO}_3^-, \text{M}^+$
Alkylsulfinates salts	$\text{RSO}_2^-, \text{M}^+$
S-Alkylthiosulfate salts	$\text{RSSO}_3^-, \text{M}^+$
Phosphonate salts	$\text{RPO}_3^-, 2\text{M}^+$
Phosphate monoester salts	$\text{ROPO}_4^-, 2\text{M}^+$
Phosphinate salts	$\text{R(R')PO}_2^-, \text{M}^+$
Nitroamide salts	$\text{RN}^-\text{NO}_2, \text{M}^+$
Trisulfonylmethide salts	$\text{RSO}_2(\text{CH}_3\text{SO}_2)_2\text{C}^-, \text{M}^+$
Xanthate salts	$\text{RSCS}_2^-, \text{M}^+$

Figure 2-3. Tensioactifs anioniques : M^+ , désigne le contre-ion, les plus courants étant Na^+ et K^+ .¹

Le SDS, sodium dodecyl sulfate, est un des tensioactifs les plus utilisés pour les études en physico-chimie. Son diagramme de phase de l'eau est de plus remarquable (**Figure 2-4**), car il présente un grand nombre de phases intermédiaires entre la phase hexagonale et la phase lamellaire^{2,3}.

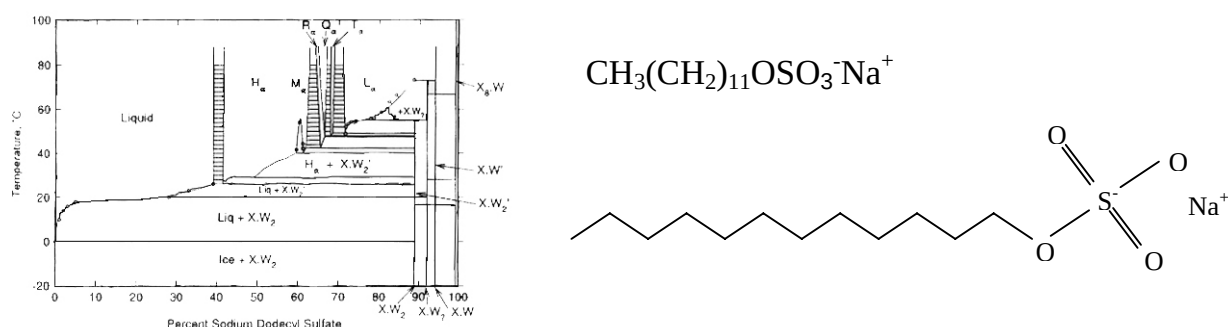


Figure 2-4. Le SDS, sodium dodecyl sulfate, et son diagramme de phase dans l'eau.

Tensioactifs cationiques

Les principaux groupes polaires sont donnés dans le tableau de la **Figure 2-5**.

Quaternary ammonium salts	$\text{RN}^+(\text{CH}_3)_3, \text{X}^-$
Primary, secondary, tertiary ammonium salts	$\text{RN}^+\text{H}_n(\text{CH}_3)_{3-n}, \text{X}^-$
N-Alkylpyridinium salts	$\text{RNC}_5\text{H}_5^+, \text{X}^-$
Quaternary phosphonium salts	$\text{RP}^+(\text{CH}_3)_3, \text{X}^-$
Ternary sulfonium salts	$\text{RS}^+(\text{CH}_3)_2, \text{X}^-$
Ternary sulfoxonium salts	$\text{RS}^+(\rightarrow\text{O})(\text{CH}_3)_2, \text{X}^-$
Bis(phosphoranylidyl)ammonium salts	$[\text{R}(\text{CH}_3)_3\text{P} \rightarrow \text{N} \leftarrow \text{P}(\text{CH}_3)_3\text{R}]^+, \text{X}^-$

Figure 2-5. Tensioactifs cationiques : X^- , désigne le contre-ion, les plus courants étant Br^- et Cl^- .¹

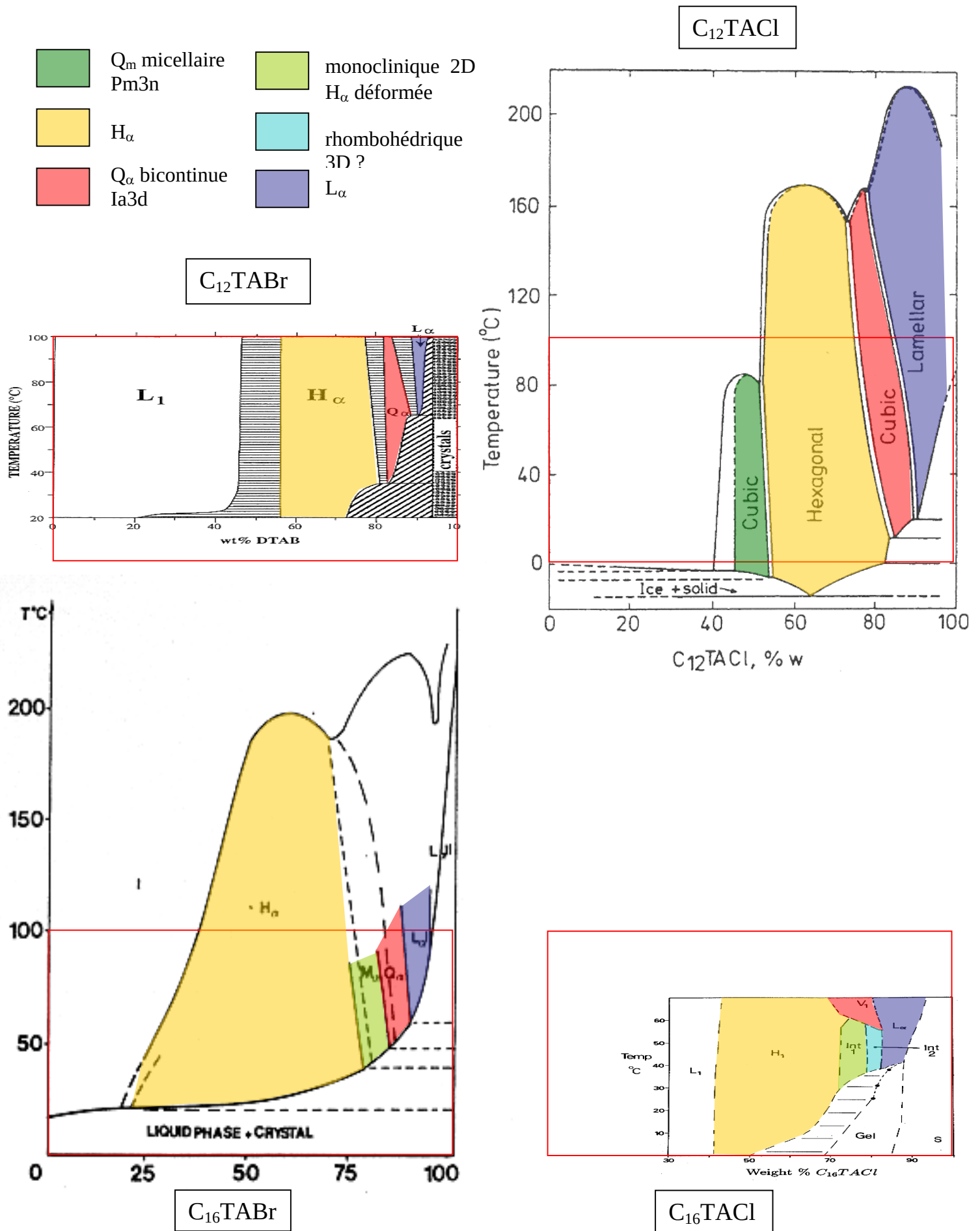


Figure 2-6. Diagrammes de phase de tensioactifs cationiques illustrant l'effet de longueur de chaîne et de contre-ion $C_{12}TABr$ ⁴⁻⁵

Les sels d'ammonium quaternaire sont parmi ceux les plus étudiés en physico-chimie. De plus, le CTAB (hexadecyl trimethylammonium bromide) (**Figure 2-7**) est la molécule avec laquelle ont été découverts les premiers matériaux mésoporeux par Mobil (chapitre 5).

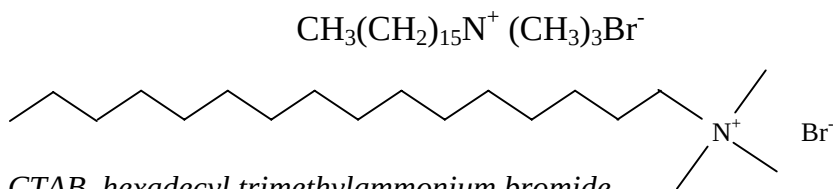


Figure 2-7. Le CTAB, hexadecyl trimethylammonium bromide.

Les contre-ions sont le plus souvent du brome ou du chlore. A l'aide des diagrammes de phase connus pour les ammonium quaternaires ($\text{C}_{12}\text{TABr}^4$, $\text{C}_{12}\text{TACl}^{6,7}$, $\text{C}_{16}\text{TABr}^5$ et $\text{C}_{16}\text{TACl}^8$), on peut mettre en évidence les effets de la longueur de chaîne ainsi que de la nature du contre-ion (**Figure 2-6**). L'effet de la longueur de chaîne est le principal. Comme attendu, l'allongement de la chaîne de C_{16} à C_{12} favorise la phase hexagonale au détriment de la phase cubique micellaire. Le remplacement du brome par le chlore modifie peu les frontières des phases, et permet surtout de stabiliser les mésophases à température ambiante.

Tensioactifs nonioniques

Trois familles de molécules sont présentées, où la partie hydrophile est formée par plusieurs groupements oxyéthylènes, EO.

Les C_nEO_m

Ces tensioactifs sont constitués d'une chaîne alkyl de n carbones liée à un polyoxyéthylène comportant m groupes oxyéthylène, $\text{EO} = \text{OCH}_2\text{CH}_2$ (**Fig 2-8**).

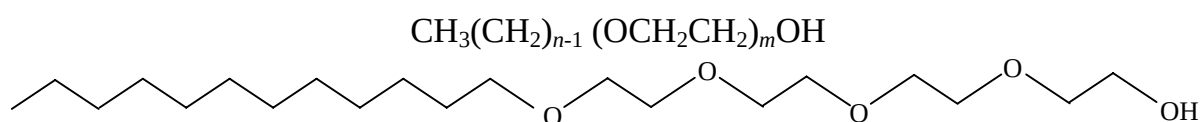


Figure 2-8. Le C_{12}EO_4

Ils sont disponibles commercialement avec de nombreuses combinaisons des valeurs de n et m , ce qui conduit à une grande variété de mésophases dans l'eau. Les diagrammes de phase (**Figure 2-9**) sont connus depuis les années 80 pour les plus courants d'entre-eux.⁹

Chapitre 2

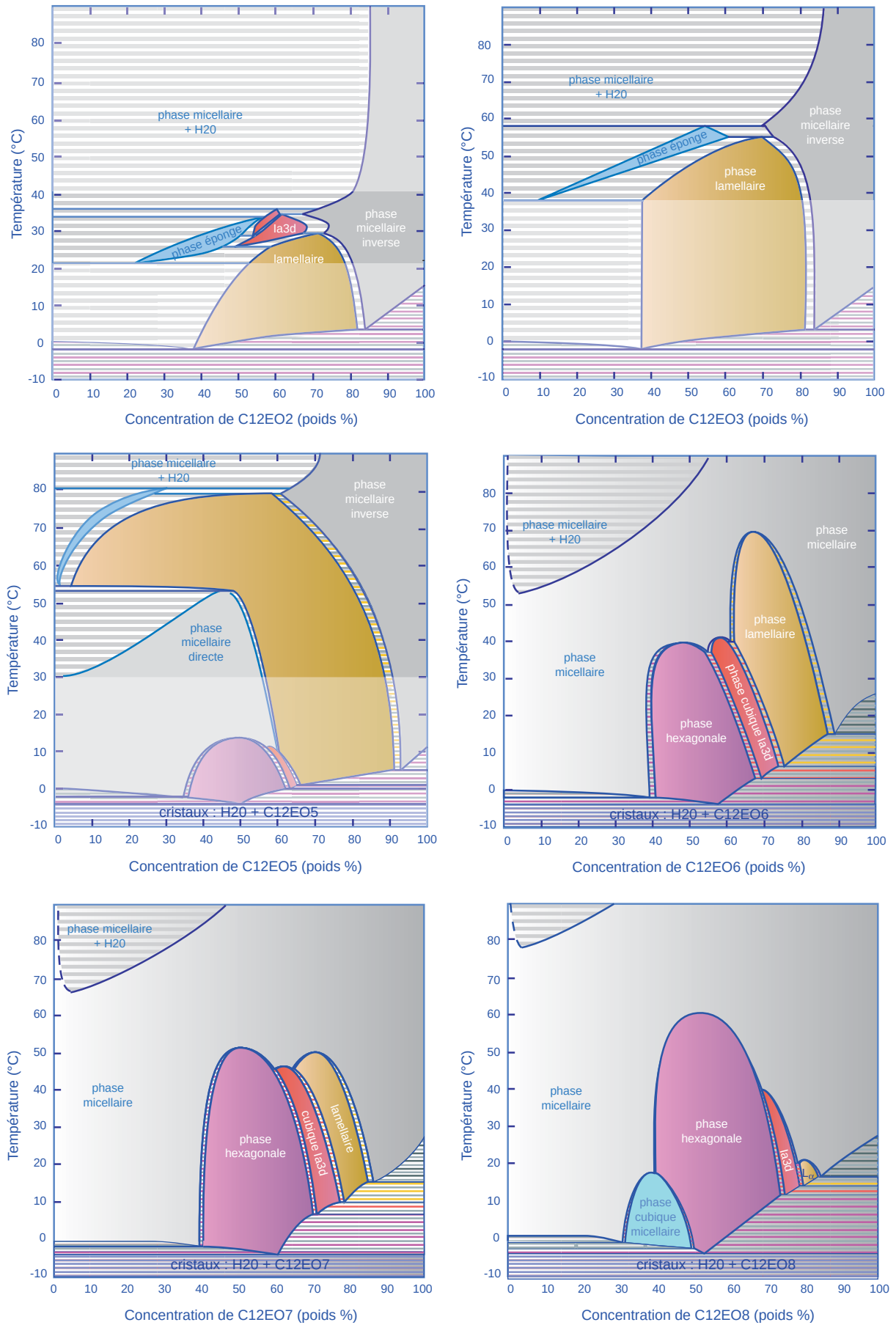


Figure 2-9. $C_{12}EO_2$ ¹⁰, $C_{12}EO_3$ ¹¹, $C_{12}EO_5$, $C_{12}EO_6$, $C_{12}EO_7$ ^{12,13} et $C_{12}EO_8$.

Lorsque le nombre de groupes EO augmente, à longueur de chaîne fixée (chaîne en C₁₂), on observe deux phénomènes (**Fig 2-9**). Tout d'abord, l'importance du domaine de stabilité des mésophases suit la séquence attendue : phase lamellaire, phase cubique directe bicontinue, phase hexagonale directe et phases micellaires directes (voir le chapitre 3). En chauffant, les groupes EO se déshydratent (voir aussi la **figure 2-12**) et une zone de démixtion de la phase isotrope est observée à haute température et pour les faibles concentrations en tensioactif. Plus le nombre de groupes EO est important, et plus la zone de démixtion apparaît à des températures de plus en plus hautes (**Fig 2-9**). La « rencontre » de la zone de démixtion avec celle des mésophases conduit à la stabilisation d'une phase éponge pour les petits nombres de groupes EO (C₁₂EO₂ - C₁₂EO₅).

La zone de la phase cubique micellaire du C₁₂EO₈ a été étudiée en détail et comporte plusieurs phases, notamment une phase hexagonale compacte 3D (voir les chapitres 3 et 14).

Les Pluronic

Ces molécules sont apparentées aux tensioactifs, mais comportent deux extrémités hydrophiles. Ce sont des bloc-copolymères, synthétisés par BASF [<http://www.basf.com>]. Ils interviennent dans la synthèse de matériaux mésoporeux (chapitres 5 et 17). Ils comportent un cœur hydrophobe en polyoxypropylène (PPO) et deux extrémités identiques hydrophiles en polyoxyéthylène (PEO) (**Fig 2-10**). Leur formule générale s'écrit : EO_mPO_nEO_m.

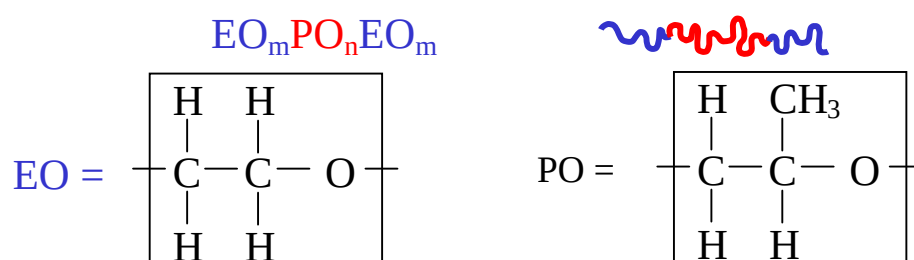


Figure 2-10. Les copolymères tri-blocs Pluronic.

Différents tri-blocs sont commercialisés, pour différentes valeurs de n et m (**Fig 2-11**). La lettre du nom commercial indique l'aspect à température ambiante : L pour liquide, P pour pâteux et F pour solide. Le premier chiffre du nom (ou les deux premiers pour ceux contenant trois chiffres) permettent de connaître approximativement la masse molaire du bloc de PPO, en multipliant ce chiffre par 300. Le dernier chiffre, multiplié par 10, donne le pourcentage en poids de PEO (entre 10 et 80 %).

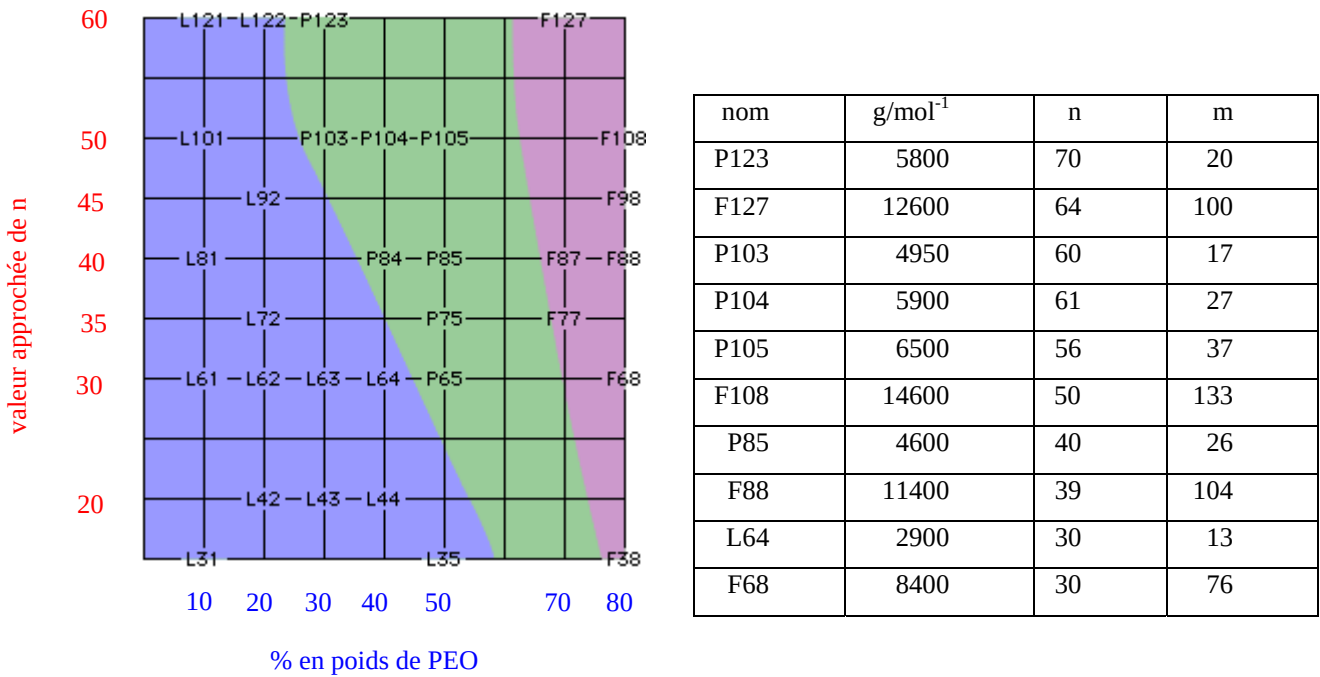


Figure 2-11. Les différents tri-blocs Pluronic. Les valeurs de n et m sont à une ou deux unités près.

Le caractère hydrophobe et hydrophile des deux types de bloc dépend en fait fortement de la température (**Fig 2-12**). En-dessous de la température ambiante, le PPO est soluble dans l'eau et le tri-bloc est soluble sous forme d'unimères. Au-dessus d'une température critique, le PPO devient plus hydrophobe que le PEO, et il y a formation de micelles. En augmentant la température, le cœur de PPO se déshydrate progressivement et la concentration en unimère chute. A des températures nettement au-dessus de la température ambiante, le PEO devient à son tour de plus en plus hydrophobe et la couronne de PEO se déshydrate progressivement. A haute température, il y a démixtion, le PEO devenant à son tour hydrophobe

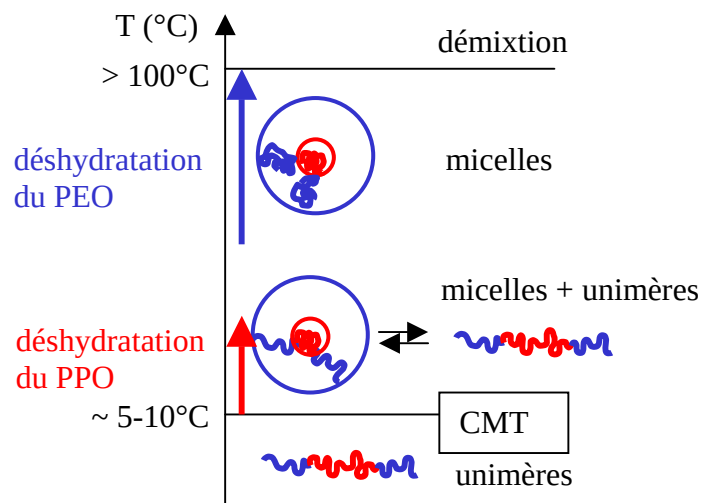


Figure 2-12. Effet de la température sur un Pluronic en solution dans l'eau

Les diagrammes de phase binaires des Pluronic dans l'eau sont connus pour les plus courants d'entre-eux.¹⁴ Un exemple de diagramme de phase ternaire Pluronic/éthanol/eau est donné ci-dessous (**fig 2-13**).¹⁵

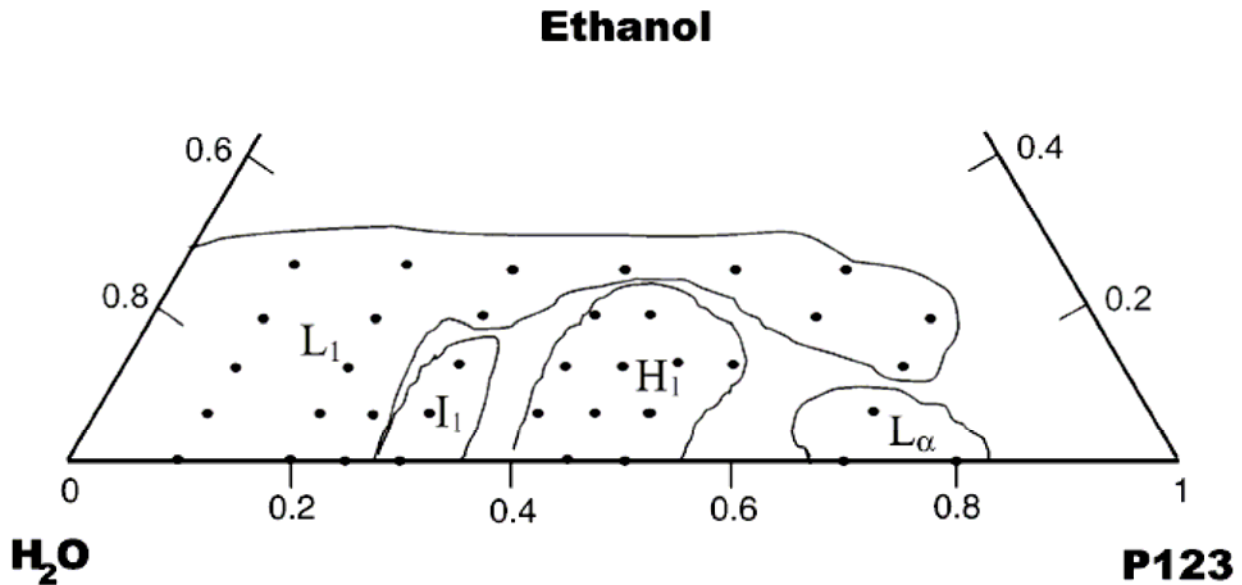


Figure 2-13. Diagramme de phase ternaire du P123/eau/éthanol à 23°C. L_1 est la phase isotrope, I_1 une région comportant des phases micellaires (cubique et hcp), H_1 une phase hexagonale 2D et L_α une phase lamellaire.¹⁵

Les EO_mBO_n

Ces bloc-copolymères diblocs ne sont pas commerciaux^{16,17}, donc moins répandus que les autres composés non-ioniques précédents (**Fig 2-14**). Leur formule générale s'écrit : EO_mBO_n . Le bloc hydrophobe est un polyoxybutylène (PBO), au caractère hydrophobe intermédiaire entre le polyoxypropylène des Pluronic et les chaînes alkyls des C_nEO_m .

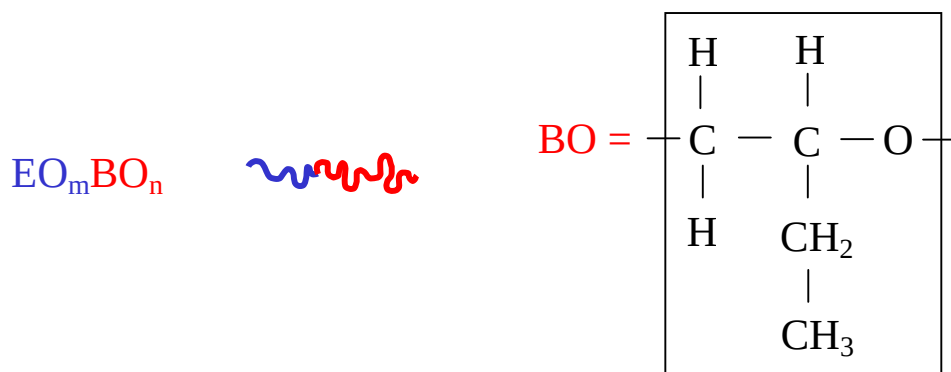


Figure 2-14. Blocs copolymères EO_mBO_n .

Chapitre 2

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Chapitre 3

Les phases organisées

Dans ce chapitre, on présente d'abord la séquence d'observation des différentes phases organisées. Puis on introduit les différentes phases micellaires 3D, en montrant qu'elles sont de deux types : les empilements de sphères et les empilements compacts de tétraèdres (tcp, abréviation de tetrahedrally close-packed). On discute aussi les contraintes géométriques d'empilement qui conduisent à ces phases. Le cas de la phase hexagonale compacte (hcp) est aussi abordé au chapitre 14. Les phases hexagonales 2D sont traitées dans les chapitres 8 et 17 et celui des phases cubiques bicontinues dans les chapitres 4, 9 et 16.

Séquence de phases

Comme cela a été introduit au chapitre 2 pour les diagrammes binaires de molécules de tensioactif, les phases organisées sont observées toujours suivant la même séquence dans un diagramme de phase. Ainsi, on peut établir une séquence générale (**Fig 3-1**), valable pour les tensioactifs, mais aussi pour les composés thermotropes possédant deux affinités, généralement apolaire et polaire ou encore des bloc-copolymères possédant deux types de blocs. Au milieu de cette séquence se situe la phase lamellaire, où l'interface entre les deux milieux est constituée par des plans et a donc une courbure nulle. Lorsque la courbure moyenne de cette interface est positive (le milieu des chaînes ayant une forme convexe), on parle de phases directes. La séquence d'observation des phases directes lorsque la valeur de cette courbure augmente est la suivante :

- phase lamellaire (courbure nulle, 1D)
- phases intermédiaires (3D ou 2D)
- phase hexagonale (2D)
- phases micellaires (3D)

Entre la phase lamellaire (ordre 1D) et la phase hexagonale (ordre 2D), on observe des phases intermédiaires, 2D ou 3D. Le plus fréquemment, il s'agit de la phase cubique bicontinue de

groupe d'espace $Ia\bar{3}d$, aussi bien pour les phases directes et inverses. Mais d'autres phases intermédiaires existent, telles que des phases rhomboédriques (3D) ou des phases 2D autres qu'hexagonale (rectangle ou oblique).¹ Par exemple, les diagrammes de phase des tensioactifs cationiques $C_{16}TABr$ et $C_{16}TACl$ (**Fig 2-6**) présentent plusieurs phases intermédiaires.

La séquence est la même pour les phases dites inverses, où la courbure de l'interface est cette fois-ci négative. Pour passer des phases directes aux phases inverses, on échange les rôles des deux milieux, polaire et apolaire.

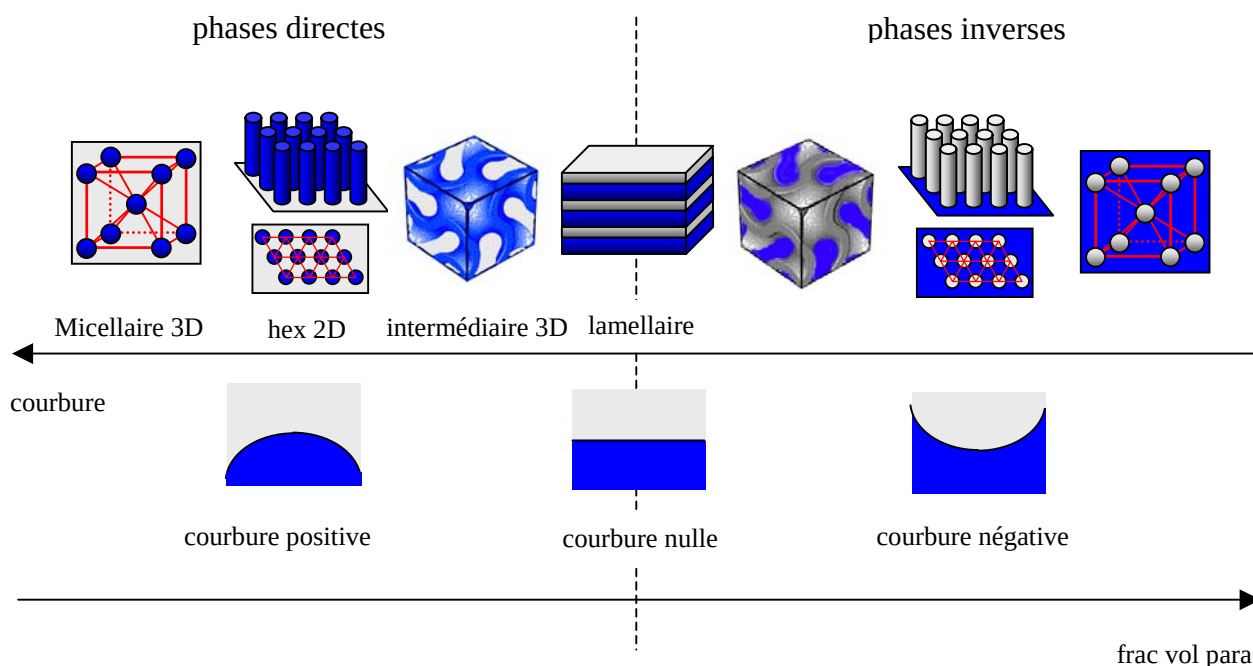


Figure 3-1. Séquence des phases organisées. En bleu les régions occupées par les chaînes alkyles et en gris les régions polaires.

Les différentes phases micellaires :

Les phases micellaires résultent de la mise en ordre de micelles de forme sphéroïdale. Dans le cas de phases directes, le cœur des micelles contient les chaînes aliphatiques. Pour les phases inverses, il s'agit de nano-gouttelettes d'eau. Il existe plusieurs types de phases micellaires, comme détaillé ci-après, mais, comme on le verra à plusieurs occasions, il est difficile de prédire pour un système expérimental donné leurs stabilités relatives dans un diagramme de phase. A partir des données expérimentales actuelles, il est intéressant de constater que ces phases micellaires se regroupent en deux catégories, détaillées ci-après :

- Les phases bcc, fcc, hcp, où les micelles sont toutes identiques et à symétrie sphérique
- Les phases tcp, avec des micelles sphéroïdales qui ne sont pas toutes identiques

Dans un diagramme binaire dans un solvant, l'apparition d'une phase micellaire correspond à la cristallisation à une fraction de volume critique occupée par ces micelles. Cette fraction de volume critique est connue dans le cas idéal d'un liquide de sphères dures, et a été établie à partir de simulations numériques². Il a été montré dans ce cas que lorsque la fraction de volume augmente, la phase cristalline ordonnée devient thermodynamiquement plus stable que la phase liquide désordonnée. Plus précisément, il y a une transition de phase du premier ordre entre la phase liquide et la phase cristallisée, la zone de coexistence correspondant à une fraction de volume occupée par les sphères comprise entre 0.494 et 0.545. Pour comparaison, une phase bcc a une compacité de 0.68 et les phases fcc et hcp une compacité de 0.74. Ainsi, en raisonnant avec un modèle de sphères dures, on peut dire que l'ordre de grandeur de la fraction de volume critique pour la formation d'une phase micellaire est de 0.5.

La compréhension exacte des stabilités relatives de ces différentes phases micellaires dépend du détail des interactions entre les micelles, qui diffère d'un système à l'autre. Un seul modèle quantitatif a été élaboré pour l'instant, dans le cas des dendrimères thermotropes.^{3,4} Il peut se transposer également au cas des systèmes lyotropes, bien qu'un solvant soit alors présent entre les micelles. Ce modèle montre que la phase de type tcp appelée $Pm\bar{3}n$ (figs 3-8 et 3-12) est plus favorable par rapport aux empilements bcc et fcc, lorsque l'on tient compte d'une interaction effective répulsive à courte portée entre les chaînes qui forment la couronne des micelles de dendrimères. L'interaction proposée est d'origine entropique. Lorsque l'aire de contact entre les micelles (aire des cellules de Voronoi associées aux micelles) est minimale, l'entropie d'orientation des chaînes de la couronne est maximisée.

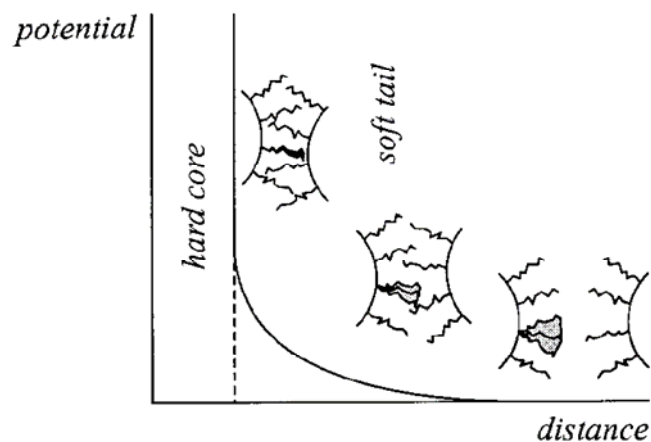


Figure 3-2. Potentiel d'interaction utilisé dans le modèle de Ziherl.^{3,4}

Nous allons maintenant détailler la structure des différentes phases micellaires.

Empilement de sphères (bcc, fcc, hcp):

Dans ce premier cas, les micelles sont toutes identiques, et à symétrie sphérique. On observe la phase cubique centrée (bcc) et les empilements compacts de sphères : cubique face centré (fcc), hexagonal compact (hcp), ou encore un mélange aléatoire de ces deux derniers empilements.

- Phase cubique centrée (bcc)

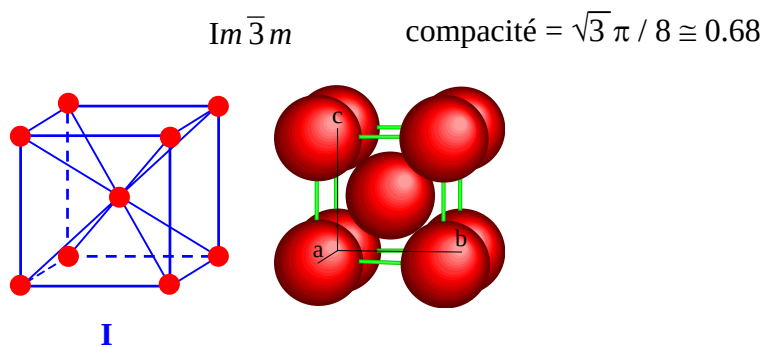


Figure 3-3. Empilement cubique centré (bcc)

- Empilement compact de sphères (fcc et hcp)

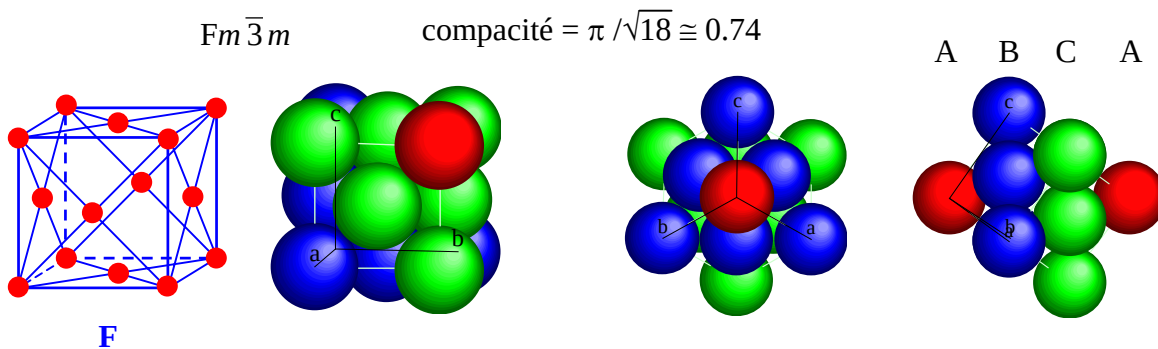


Figure 3-4. Empilement cubique face centré (fcc)

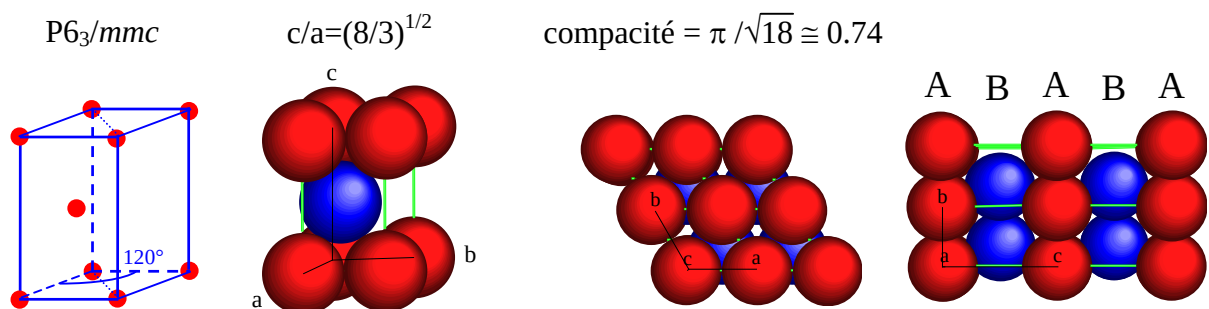


Figure 3-5. Empilement hexagonal compact (hcp)

La question se pose de savoir dans quel cas se forme une de ces phases plutôt qu'une autre. Voici quelques éléments de réponse.

- Phase fcc ou hcp ?

Ces deux structures sont des arrangements compacts de sphères, qui ne diffèrent que par la séquence des plans d'empilements : séquence ABC pour fcc et séquence AB pour hcp. Ils ont la même compacité, 0.74. La conjecture dite de Kepler, datant de 1611, affirme que cette compacité est la plus grande possible pour un empilement de sphères identiques à 3D.⁵ Il est remarquable que la preuve mathématique de cette conjecture soit encore d'actualité. En effet, en 1998, le mathématicien Thomas C. Hales¹ a donné une preuve de cette conjecture,⁶ mais dont la vérification ultime devrait encore nécessiter plusieurs années, tant le sujet est complexe et fait appel à des moyens numériques lourds ! En tout cas, du point de vue de la compacité, les deux types d'empilements sont identiques. Ce qui les différencie est l'environnement des 12 premiers voisins de chaque sphère (**Fig 3-6**).

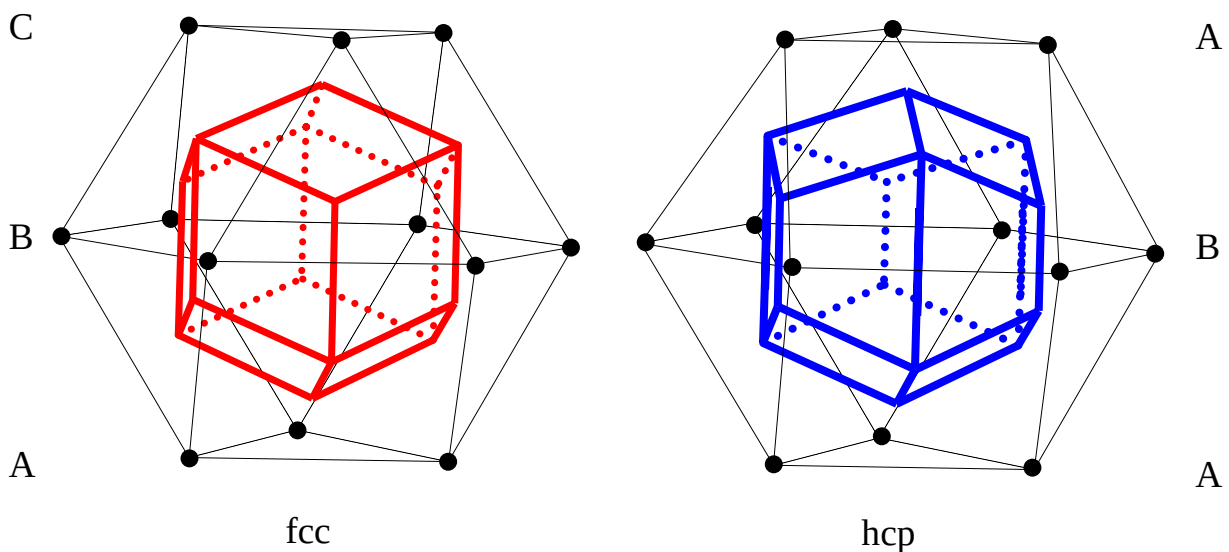


Figure 3-6. Polyèdre des 12 premiers voisins et cellule de Voronoï des empilements fcc et hcp.

En considérant uniquement un potentiel d'interaction de type sphère dure, plusieurs travaux numériques récents montrent qu'il existe une très faible différence d'entropie en faveur de la phase fcc par rapport à la phase hcp.^{7,8} Cette différence d'entropie est de l'ordre de $+ 10^{-3} k_B$ par sphère.⁷ Il n'y a donc qu'une différence infime entre les phases fcc et hcp.

¹ (<http://www.math.pitt.edu/articles/cannonOverview.html>)

- Phase bcc ou fcc ?

L'observation d'une phase bcc semble plus étonnante que celle des empilements compacts dans la mesure où la compacité est plus faible (0.68 au lieu de 0.74). Son apparition est liée à l'existence d'un potentiel d'interaction différent de celui d'un potentiel de sphères dures. Une étude expérimentale des phases micellaires des tensioactifs E_mB_n (voir le chapitre 2) du groupe de I. W. Hamley permet d'illustrer ce point (**Fig 3-7**).⁹ A faible concentration dans l'eau et pour un rapport m/n petit, donc une couronne hydrophile petite, on observe la phase fcc. Par contre, lorsque la concentration dans l'eau augmente, ainsi que le rapport m/n , on observe une phase bcc. L'interprétation donnée⁹ est que la phase bcc correspond au cas d'un potentiel d'interaction entre les micelles à plus longue portée que le potentiel de sphères dures. L'origine proposée pour ce potentiel est une interaction entre les couronnes constituées de groupements EO longs (m/n grand) et son effet est plus notable lorsque la concentration augmente. L'origine de ce potentiel est ainsi analogue à celui introduit par Zihlerl dans le cas des dendrimères.^{3,4}

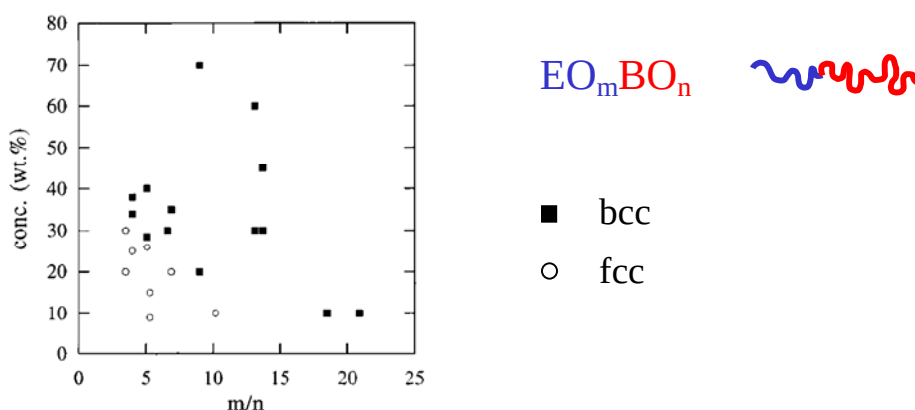


Figure 3-7. Phases micellaires des E_mB_n dans l'eau. La phase fcc est observée à faible concentration et pour un rapport m/n petit, lorsque la couronne hydrophile est courte. A plus forte concentration dans l'eau, et lorsque m/n est plus grand, on observe la phase bcc.⁹

Empilement de micelles sphéroïdales : les phases tcp

Contrairement aux empilements de sphères précédents, d'autres phases micellaires sont spécifiques à l'empilement d'objets déformables tels que des micelles. Dans ces phases coexistent plusieurs types de micelles, dont la forme s'écarte légèrement de celle d'une sphère. Pour l'instant, trois phases tcp ont été découvertes dans les systèmes tensioactif/eau et dans les phases thermotropes de dendrimères (**Figs 3-8 et 3-9**).

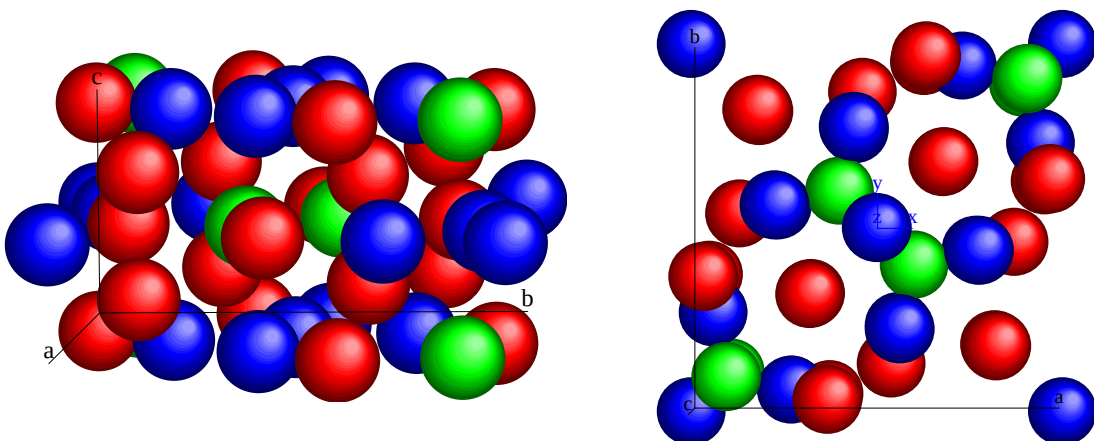
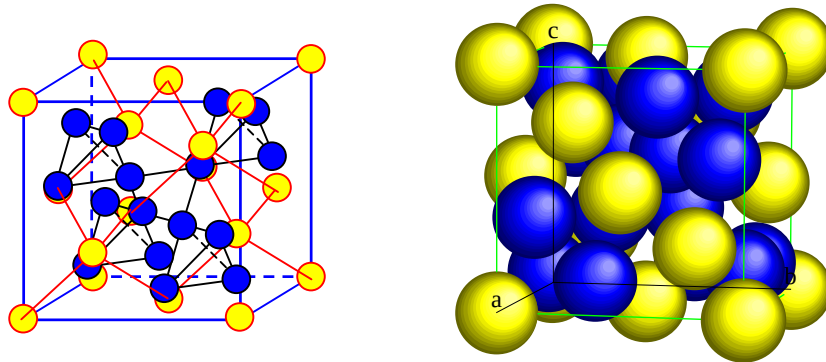
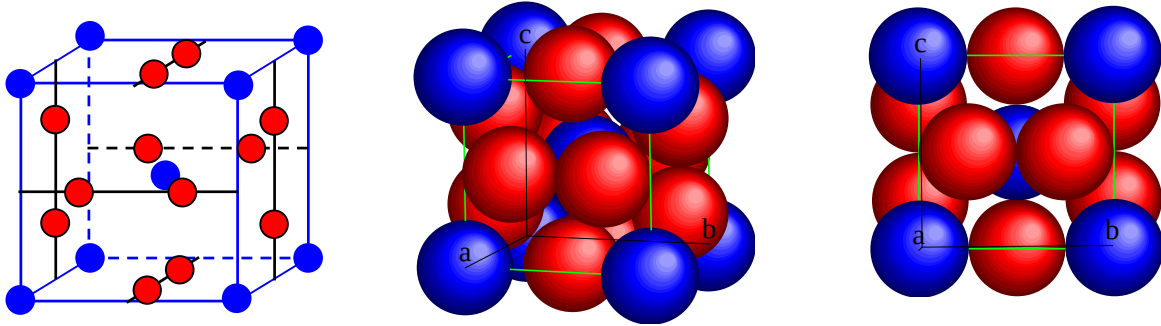


Figure 3-8. Phases micellaires de type tcp (ou Frank-Kasper) observées expérimentalement : $Pm\bar{3}n$, $Fd\bar{3}m$ et $P4_2/mnm$. La couleur correspond au type de sites qu'occupe une micelle : $Z = 12$ en bleu, $Z = 14$ en rouge, $Z = 15$ en vert et $Z = 16$ en jaune (voir aussi **Fig 3-11**).

Space-group	tcp phase	exemple	N	Z = 12	Z = 14	Z = 15	Z = 16	<Z>
$Pm\bar{3}n$	A15	β -tungstène	8	2	6	-	-	13.5
$P4_2/mnm$	σ	β -uranium	30	10	16	4	-	13.467
$Cmmm$	H	complex	30	10	16	4	-	13.467
$Pmmm$	K'	complex	82	28	42	12	-	13.463
$P6_3/mmm$	F	complex	52	18	26	8	-	13.462
$Pmmm$	J	complex	22	8	10	4	-	13.455
$Immm$	v	$Mn_{81.5}Si_{18.5}$	186	74	80	20	12	13.441
$P6_3/mmm$	Z	Zr_4Al_3	7	3	2	2	-	13.428
$Pbnm$	P	$Mo_{42}Cr_{18}Ni_{40}$	56	24	20	8	4	13.428
$P2_12_12_1$	δ	MoNi	56	24	20	8	4	13.428
C2	K	$Mn_{77}Fe_4Si_{19}$	220	100	76	16	28	13.418
$R\bar{3}$	R	$Mo_{31}Co_{18}Cr_{51}$	159	81	36	18	24	13.396
$R\bar{3}m$	μ	Mo_6Co_7	39	21	6	6	6	13.385
$P6_3/mmc$	-	K_7Cs_6	26	14	4	4	4	13.385
$Pbam$	p σ	$W_6(Fe,Si)_7$	26	14	4	4	4	13.385
$Pnam$	M	$Nb_{48}Ni_{39}Al_{15}$	52	28	8	8	8	13.385
Cc	I	$V_{41}Ni_{36}Si_{23}$	228	132	24	24	48	13.369
$C2/m$	C	$V_2(Co,Si)_3$	50	30	4	4	12	13.360
$Im\bar{3}$	T	$Mg_{32}(Zn,Al)_{49}$	162	98	12	12	40	13.358
$Pnnm$	X	$Mn_{45}Co_{40}Si_{15}$	74	46	4	4	20	13.351
$C2/m$	-	Mg_4Zn_7	110	70	4	4	32	13.345
$P6_3/mmc$	C14	$MgZn_2$	12	8	-	-	4	13.333
$Fd\bar{3}m$	C15	$MgCu_2$	24	16	-	-	8	13.33

Figure 3-9. Phases de Franck et Kasper ou tcp. N est le nombre de sites par maille et <Z> la coordinance moyenne des sites. Les phases observées dans des systèmes micellaires sont notées en gras.¹⁰

Dans les phases micellaires, plusieurs exemples des phases $Pm\bar{3}n$ et $Fd\bar{3}m$ sont connus, la plus fréquemment observée étant la phase $Pm\bar{3}n$.¹¹ La phase $Fd\bar{3}m$ semble spécifique aux phases inverses.¹² Par contre, la phase $P4_2/mnm$ n'a été observée pour l'instant qu'une seule

fois, dans une phase thermotrope de dendrimères.¹³ Ce résultat remarquable a été accompagné de l'observation d'une phase quasicristalline.¹⁴ Nous reviendrons à la fin de cette partie sur le lien entre les phases tcp et les quasi-cristaux. Un exemple de phase $P4_2/mnm$ pour un matériau mésoporeux a été aussi trouvé très récemment.¹⁵

La formation de ces phases peut se comprendre par des arguments géométriques, comme résultant de la mise en ordre des micelles, avec la contrainte de minimiser l'aire totale des cellules de Voronoï entourant chaque micelle.^{11,16}

En termes mathématiques, cette minimisation est connue comme la conjecture de Kelvin. Le problème posé est de trouver la partition de l'espace en cellules de même volume qui minimise l'aire totale des cellules. La meilleure solution connue à ce jour avec des cellules identiques est l'empilement de type bcc de polyèdres dit de Kelvin (1887). Ces polyèdres sont des octaèdres tronqués, dont les faces sont légèrement courbées. Mais il n'existe pas de réalisation « expérimentale » de cet empilement. En 1994, D. Weaire et R. Phelan ont montré que la phase tcp la plus simple (phase $Pm\bar{3}n$ avec deux types de cellules) est une meilleure solution que celle de Kelvin, avec une surface d'aire environ 0.3% plus petite.¹⁷ La question ultime de la meilleure structure possible reste actuellement non résolue et il a été proposé que d'autres structures tcp plus complexes pourraient être envisagées, telle que la phase $P4_2/mnm$.¹⁰ On peut remarquer en passant que l'analogue de la conjecture de Kelvin à deux dimensions est le réseau hexagonal en nid-d'abeille. Ce résultat intuitif, jusqu'à présent admis, n'a été prouvé mathématiquement complètement qu'en 2001, par T. C. Hales, déjà cité à propos de la conjecture de Kepler.¹⁸

Expérimentalement, cette problématique a été rencontrée en premier non pas dans le domaine des phases micellaires qui nous intéresse ici, mais dans deux domaines apparemment éloignés l'un de l'autre : celui des films et mousses de savon, et, à l'échelle atomique, celui des phases de certains métaux et alliages métalliques (phases de Franck et Kasper). Les phases de Franck et Kasper, introduites pour les métaux et les alliages métalliques, sont aussi appelées empilements compacts de tétraèdres (tcp, abréviation de tetrahedrally close-packed).

La **figure 3-10** illustre le lien existant entre ces deux domaines. A trois dimensions, la minimisation de l'aire de films de savon, ou la maximisation de la fraction d'empilement de sphères dures (atomes à symétrie sphérique), conduit au même optimum **local**. Les quatre sphères au contact forment un empilement tétrahédrique. Les faces représentées sont celles des cellules de Voronoï associées. Ces faces s'assemblent en suivant les règles de Plateau (angles entre arêtes de $109^{\circ}28'$ et angle dièdre entre faces de 120°), établies grâce à

l'observation des films et mousses de savon. Cet optimum est uniquement local, car il n'est pas possible de remplir l'espace à 3D avec des tétraèdres réguliers. C'est là l'origine des phases tcp, qui sont un compromis entre cet optimum local et un remplissage périodique de l'espace, compromis réalisé par différents motifs d'empilement des tétraèdres.¹⁶

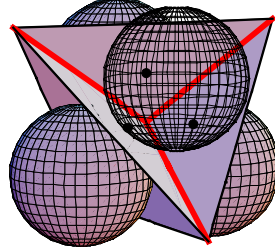


Figure 3-10. Relation entre la minimisation de l'aire et une phase tcp : l'empilement tétraédrique de quatre sphères, le plus compact localement, correspond à des faces de cellule vérifiant les règles de Plateau.

Franck et Kasper ont décrit pour des phases métalliques 24 types de ces empilements compacts de tétraèdres, dites phases tcp (**Fig 3-9**).¹⁰ Dans ces structures, tous les sites ne sont pas identiques. Dans une maille, il y a deux, trois ou quatre types de sites différents (type de cellule de Voronoi), que l'on distingue suivant le nombre de voisins Z du site : cellule de Voronoi dodécaédrique ($Z = 12$), ou polyèdres à plus de faces ($Z = 14$, $Z = 15$ et $Z = 16$) :

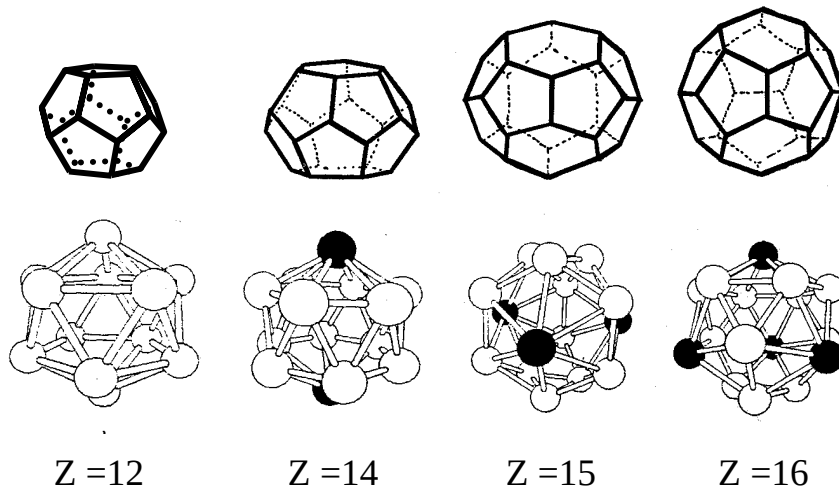


Figure 3-11. Les quatre types de sites rencontrés dans les phases tcp : $Z = 12$, 14 , 15 et 16 . En haut, la cellule de Voronoi, en bas, le polyèdre dont les sommets sont les premiers voisins. Pour $Z = 12$, la cellule de Voronoi est un dodécaèdre régulier, et, pour les autres sites, plusieurs faces hexagonales (2, 3 ou 4) sont ajoutées au polyèdre.^{10,16}

Il est ainsi remarquable que la phase dites $Pm\bar{3}n$ soit la réplique exacte de la phase métallique β du tungstène et la phase dites $P42/mnm$ celle de la phase β de l'uranium (**Fig 3-9**). Le résultat de la minimisation globale (celle de l'aire totale de la surface des cellules) conduit à faire coexister des cellules de formes différentes. Néanmoins, cette minimisation peut se faire à volume constant pour chaque cellule.

Ainsi, si l'on revient maintenant au cas des phases micellaires, on peut penser que les micelles peuvent garder approximativement la même taille, et ne se différencient que par de légères déformations par rapport à une sphère suivant le site qu'elles occupent. Par exemple, une micelle au centre d'une cellule de Voronoi dodécaédrique ($Z = 12$) est de symétrie sphérique, alors qu'une micelle au centre d'une cellule de type $Z = 14$ est légèrement ellipsoïdale. On aboutit ainsi à la représentation de la phase $Pm\bar{3}n$ (**Fig 3-12**).

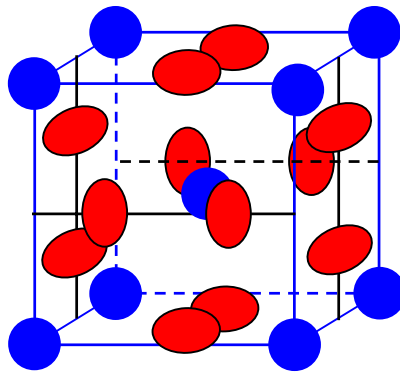


Figure 3-12. Représentation de la phase $Pm\bar{3}n$, avec les micelles des sites $Z = 14$ (en rouge) de forme ellipsoïdale.

En conclusion, l'importance des arguments géométriques pour expliquer les empilements observés dans les phases micellaires semble claire. Ces arguments sont basés sur l'optimisation de la fraction d'empilement et de la minimisation de l'aire des cellules.

Mais tout n'est pas encore compris en ce domaine, notamment les stabilités relatives des différentes phases. L'utilisation de simulations par des potentiels d'interaction adéquats devrait apporter certaines réponses. La découverte récente d'une phase quasi-cristalline liée aux phases tcp, constitue une autre piste, quant à la recherche des solutions optimales d'empilement de micelles (**Fig 3-13**).¹⁴

Enfin, on peut rajouter que, dans cette recherche d'empilement optimum, les phases micellaires constituent un meilleur système expérimental que les mousses de savon, dans la

mesure où il n'est pas possible de réaliser des mousses de savon périodiques à 3D sur de grandes échelles.

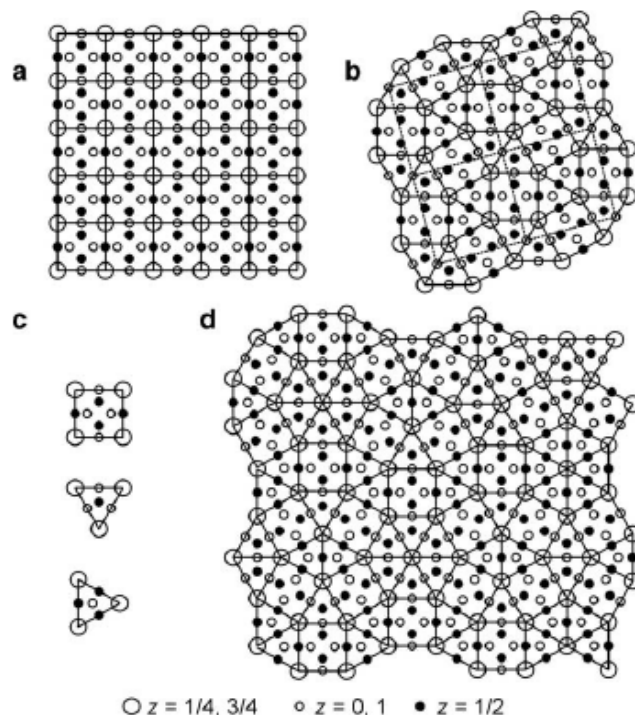


Figure 3-13. Modèle proposé pour le lien entre les phase tcp, ici les phases $Pm\bar{3}n$ et $P4_2/mnm$, et la phase quasi-cristalline, toutes observées avec des dendrimères thermotropes.¹⁴

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Chapitre 4

Phases cubiques de molécules thermotropes

Ce chapitre reprend un article de revue consacré aux phases cubiques formées par des molécules thermotropes (publication [29] jointe¹). Les premières phases cubiques thermotropes ont été découvertes dans les années 60, en même temps que celles des systèmes lyotropes. Grâce au nombre croissant de molécules synthétisées, les exemples de phases cubiques thermotropes se sont multipliés. On peut ainsi dresser un inventaire des principales molécules thermotropes formant des phases cubiques. Comme pour les systèmes lyotropes, la phase la plus fréquente est la phase bicontinue de groupe d'espace $Ia\bar{3}d$. Ce chapitre permet d'introduire la structure de cette phase, qui a été proposée puis vérifiée par le groupe de V. Luzzati.²⁻⁴ Le chapitre 16 est également consacré à cette même phase bicontinue, et concerne la modélisation de la structure à partir des intensités des pics de diffraction. Une autre phase cubique de structure plus complexe, de groupe d'espace $Im\bar{3}m$, apparaît jusqu'à maintenant spécifique aux molécules thermotropes. L'élucidation de la structure de cette phase comme une phase tri-continue est discutée en détails au chapitre 15.

La structure bicontinue de groupe d'espace $Ia\bar{3}d$:

La structure admise pour cette phase est une structure bicontinue (**Fig 4-1**). Comme dans toute mésophase, les molécules individuelles ne sont pas cristallisées : elles sont à l'état liquide et diffusent à grande échelle au cours du temps. Par contre, la nano-ségrégation entre les deux parties incompatibles des molécules (chaînes alkyl et cœurs polaires) engendre une partition de l'espace. Certaines régions sont occupées uniquement par les chaînes, et d'autres par les parties polaires des molécules.

Dans le cas d'une phase inverse, la région occupée par les chaînes alkyl est continue et est centrée sur une surface particulière, la surface minimale G. Cette région sépare deux régions équivalentes contenant les parties polaires des molécules thermotropes. Ces deux régions ont

la forme de deux labyrinthes 3D. Dans le cas des phases directes, ce sont les parties polaires qui séparent les deux labyrinthes contenant les chaînes alkyls.

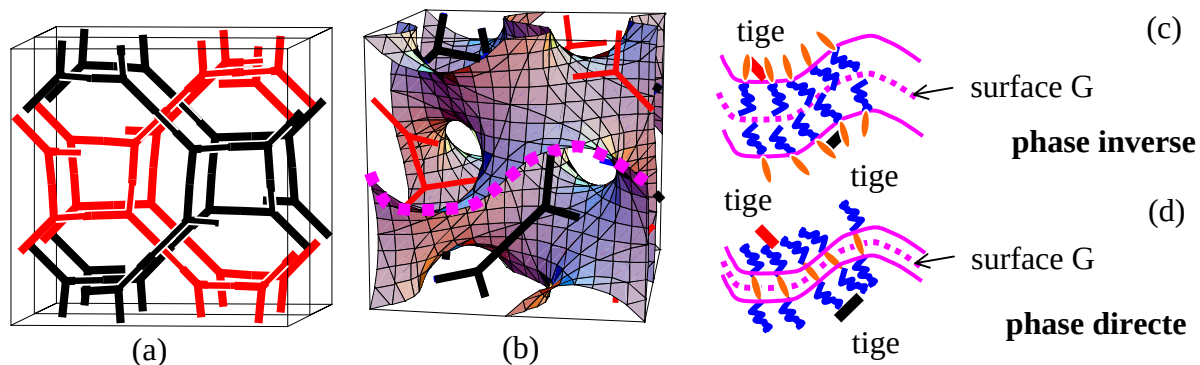


Figure 4-1 (a) Les deux réseaux 3D de tiges. Les tiges sont connectées trois par trois à chaque nœud des réseaux. (b) La surface minimale G, qui sépare l'espace en deux sous-volumes équivalents, chacun contenant l'un des deux réseaux de tiges. (c) phase inverse thermotrope (d) phase directe thermotrope.

La position exacte de la séparation entre les différentes régions n'est pas connue exactement, mais est seulement estimée à l'aide d'une modélisation. Il s'agit essentiellement de déterminer l'épaisseur du milieu continu qui sépare les deux labyrinthes. Ce point est discuté en détails au chapitre 16.

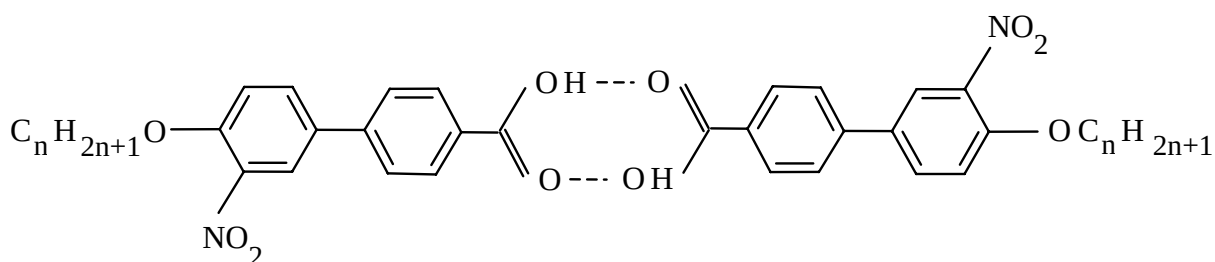
Les molécules :

On donne ici la liste des principaux composés thermotropes connus formant des phases cubiques. Les numérotations des références et des figures sont relatives à l'article de revue.¹

Famille des acides carboxyliques nitrophenyl : ANBC- n : $n = 11-25$

[1,2,5,8,34] (Figure 2)

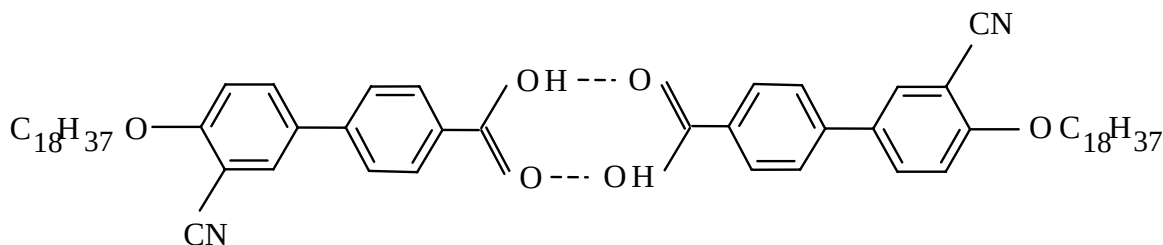
Cette famille est particulièrement intéressante car de nombreuses longueurs de chaîne ont été synthétisées. Les deux phases cubiques $Ia\bar{3}d$ et $Im\bar{3}m$ sont formées par ces composés.



Acide carboxylique cyanobiphenyl : $n = 18$

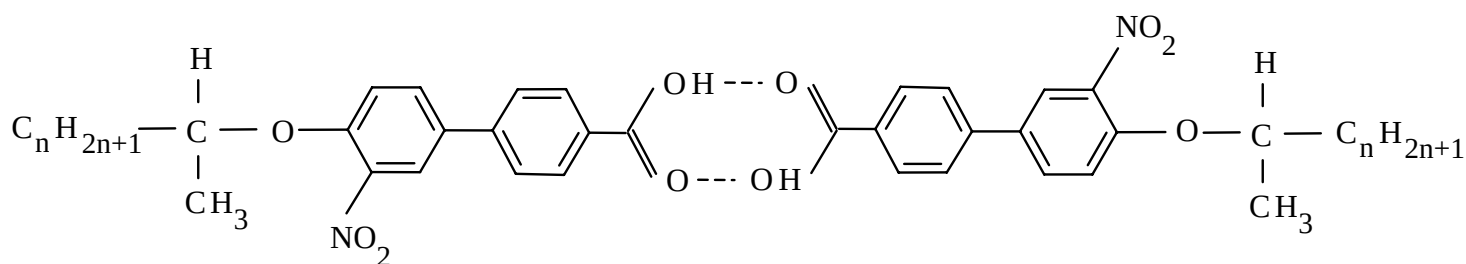
[6]

Le seul changement du groupe latéral nitro en un groupe cyano transforme la phase $Ia\bar{3}d$ en phase $Im\bar{3}m$.



Acide carboxylique nitrobiphenyl avec une chaîne alkyl ramifiée : $n = 9,10,12,14$

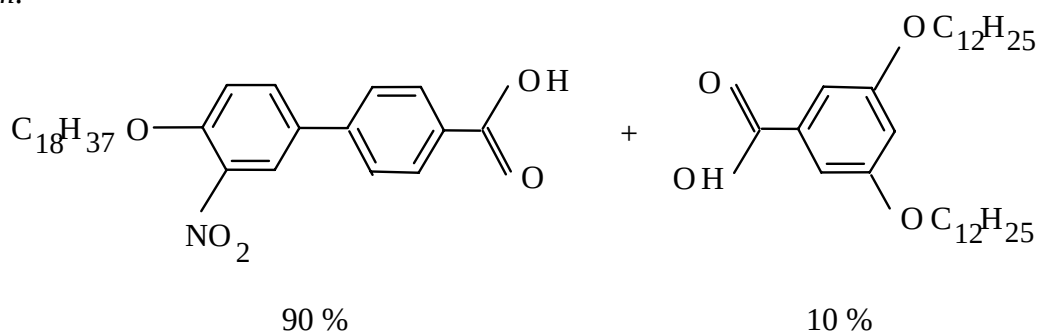
[54] ($n = 9$ in figures 5 and 6) ¹



Mélange de l'ANBC-18 avec l'acide 3,5-didodecyloxybenzoïque

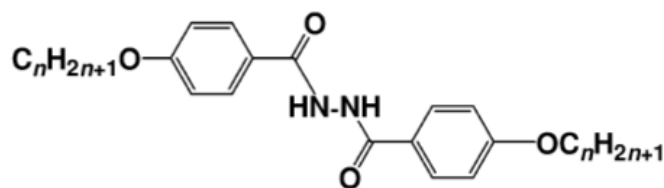
[37,52] (figure 3b) ^{1,5}

Ce mélange présente une transition en température entre les deux phases cubiques $Ia\bar{3}d$ et $Im\bar{3}m$.



Dérivés de l'hydrazine BABH- n : $n = 8,9,10$

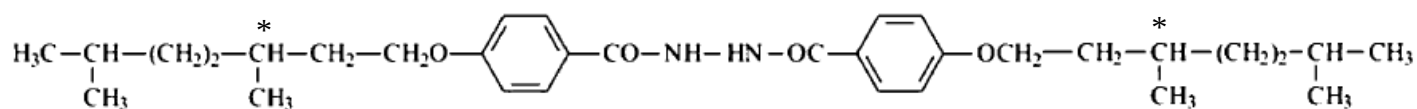
[7,12,44,45]



Dérivé chiral de l'hydrazine :

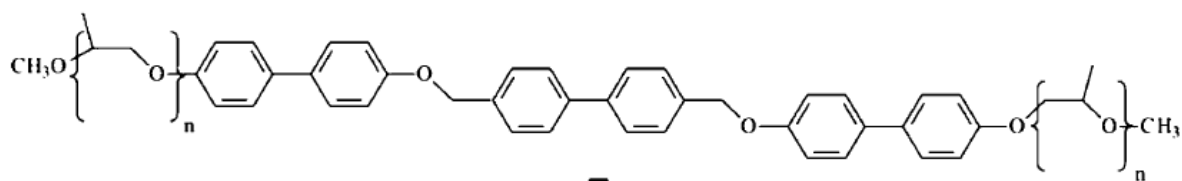
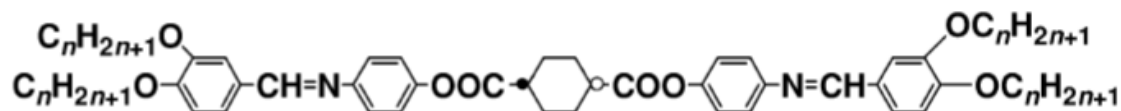
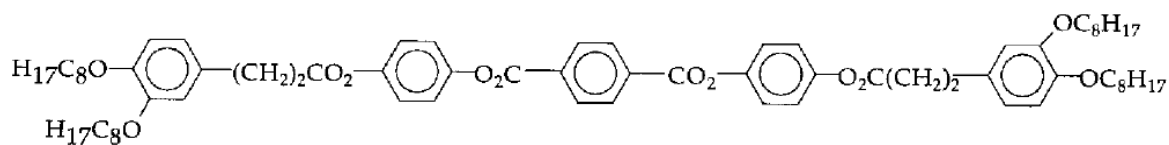
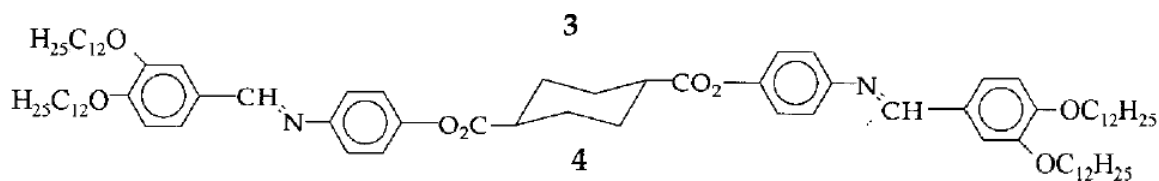
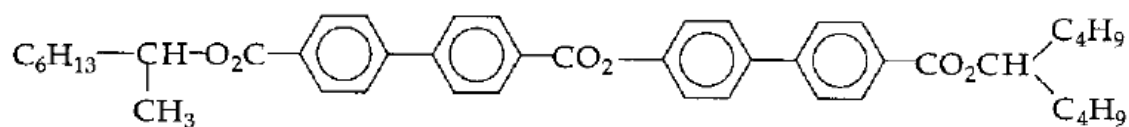
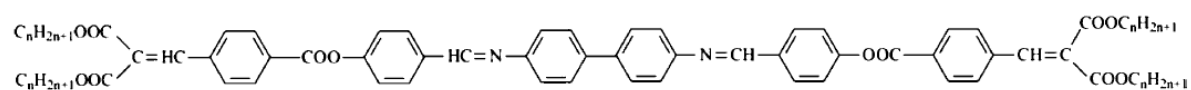
[12]

Cette molécule forme probablement une phase cubique $Im\bar{3}m$.

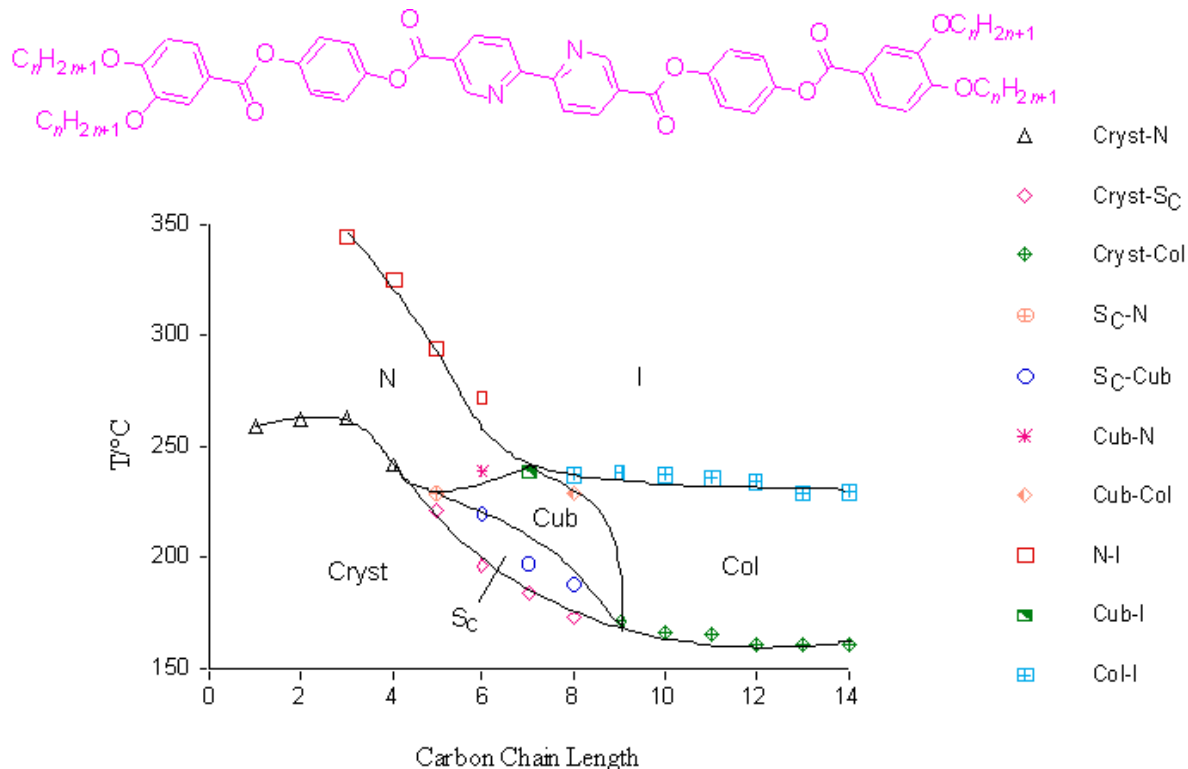


Mésogènes polycatenaires :

[6,7,8]



[Duncan Bruce's homepage : <http://www.ex.ac.uk/chemweb/research/staff/dwb/dwb.htm>]:

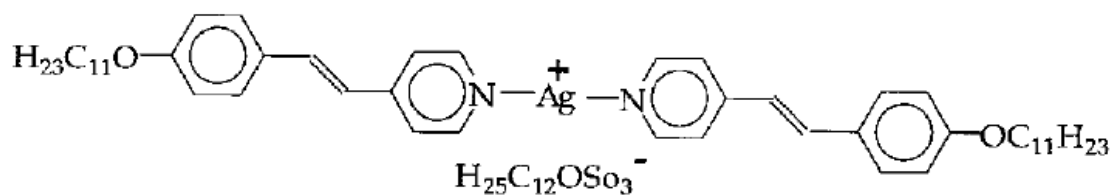


Métallomésogènes polycaténaires :

Avec de l'argent :

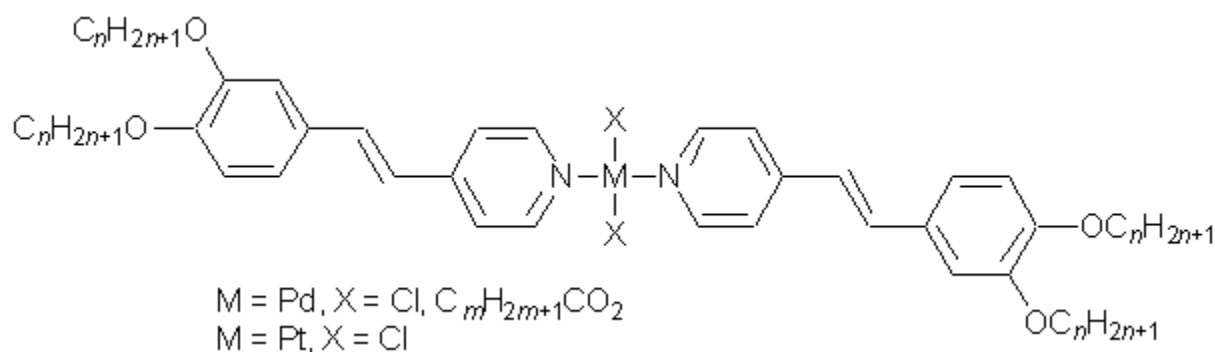
[27,28]

L'unique observation par microscopie électronique d'une phase cubique thermotrope a été réalisée avec cette molécule.



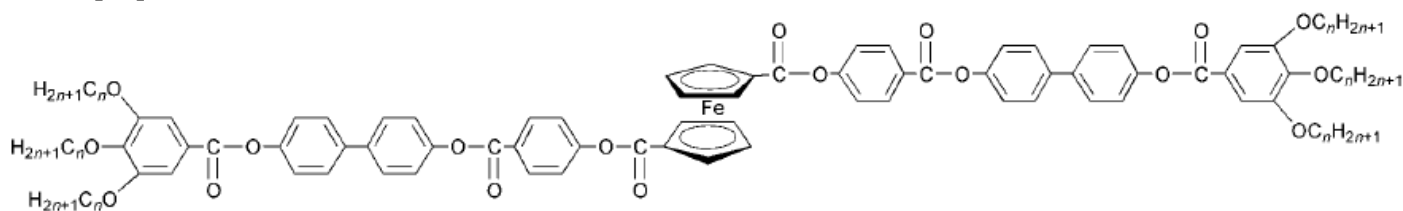
Avec du platine et du palladium :

[21]

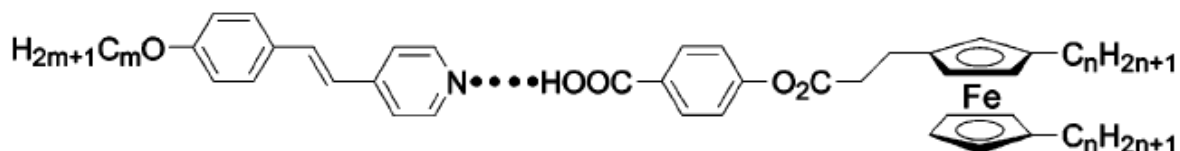


Avec un groupe ferrocene : $n = 8, 10$

[24]



[25]



1a ($m = 6, n = 8$)

2a ($m = 10, n = 8$)

1b ($m = 6, n = 10$)

2b ($m = 10, n = 10$)

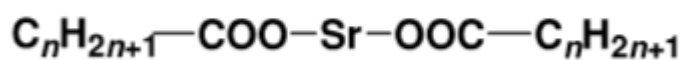
1c ($m = 6, n = 12$)

2c ($m = 10, n = 12$)

Amphiphiles ioniques :

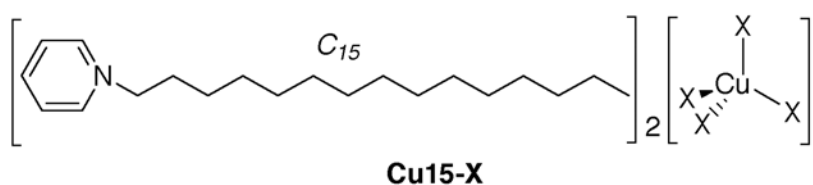
Le stéarate de strontium :

[3,4,50]



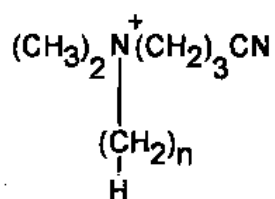
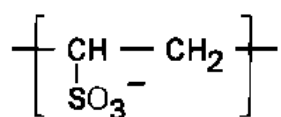
Alkylpyridinium tetrahalocuprates : $X = \text{Cl}$ ou Br

[23]



Alkylammonium poly(vinylsulfonate)s : $n = 12, 14$

[17]

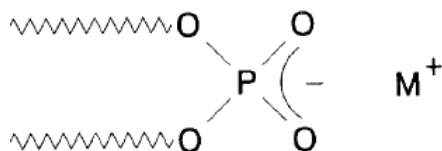


Alkali metal dialkylphosphate salts :

M = K avec $n = 8,10,12,14,16,18$

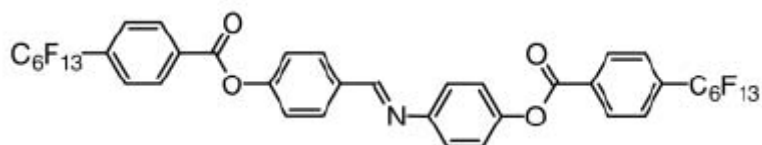
M = K, Rb ou Cs avec $n = 16$

[18]

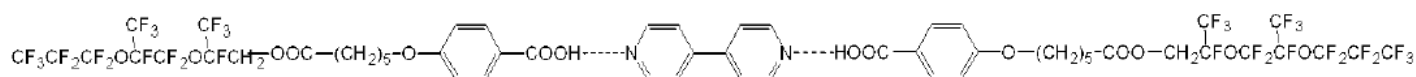


Chaines perfluorées :

[9]

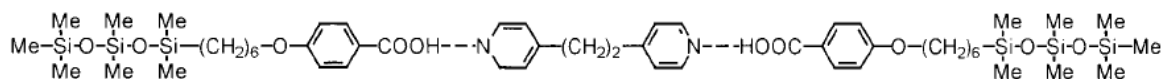
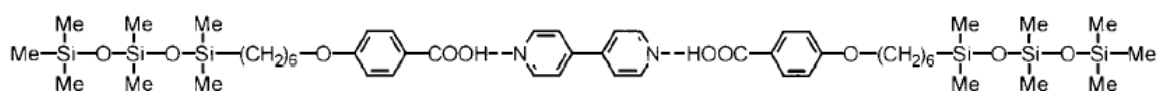


[20]



Oligosiloxane units :

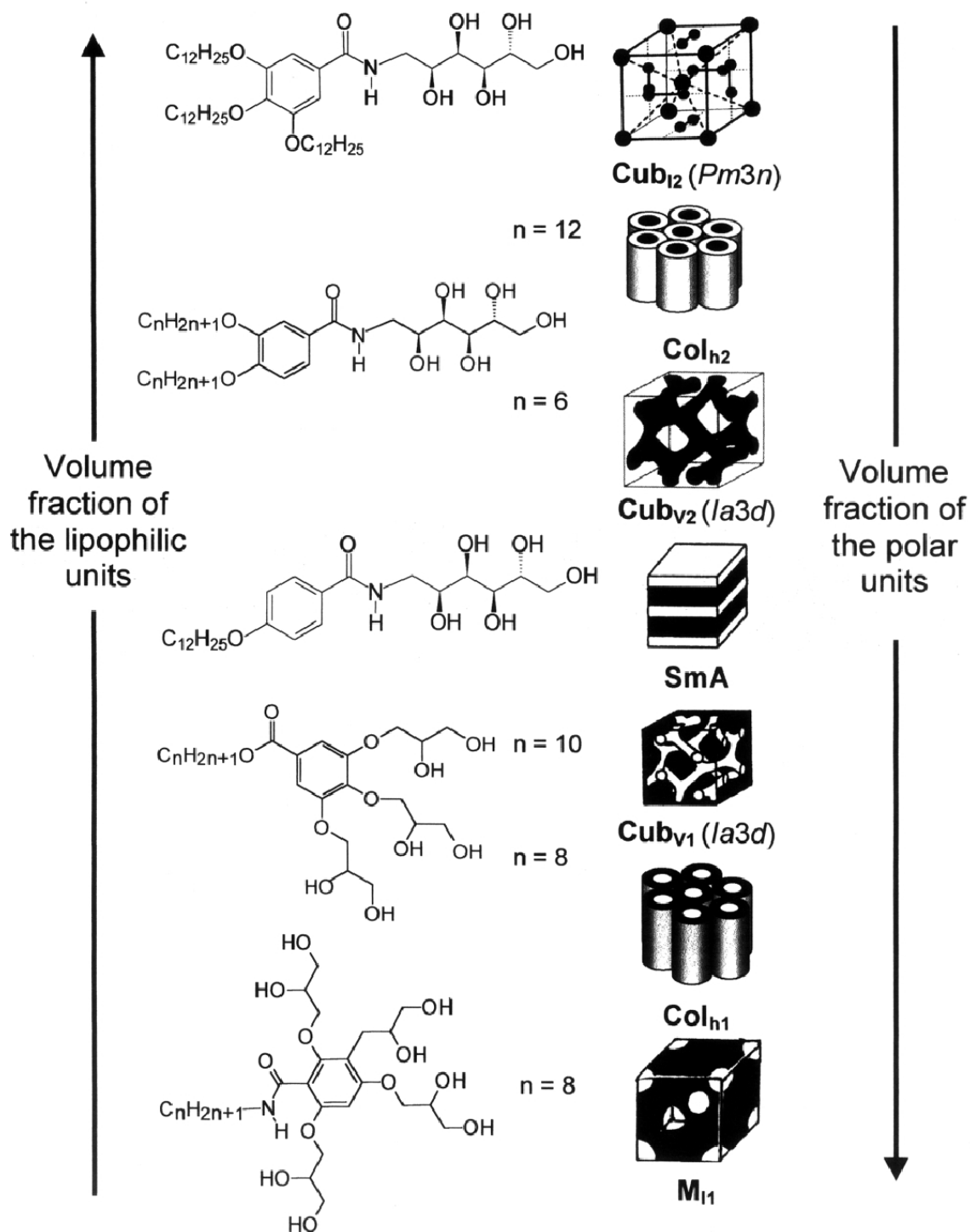
[9,19]



Polyhydroxy amphiphiles :

[9,11]

Cette famille de composés remarquable permet d'obtenir toutes les phases, à la fois de types direct et inverse.



Chapitre 4

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Thermotropic cubic mesophases

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Abstract

Thanks to important recent progress in the synthesis of mesomorphic molecules, thermotropic cubic phases have become more and more widespread. Many new examples of the $Ia\bar{3}d$ bicontinuous cubic phase have been discovered. Moreover, a multi-continuous $Im\bar{3}m$ cubic phase is up to now specific to thermotropic mesophases, and its exact structure is still under debate. Spectacular architectures built by the packing of supramolecular soft spheres have also been recently discovered. Studies of the macroscopic properties of these soft materials are just beginning, including their stability under pressure or their ability to form numerous facets.

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1. Introduction

Thermotropic cubic phases were discovered [1,2] during the 1960s in parallel to the cubic phases of lyotropic materials. The famous bicontinuous model from *V. Luzzati* applied successfully, both for lyotropic [3^{''},4^{''}] and the first thermotropic cubic phases [5^{''}]. Thanks to important progress in the synthesis of mesomorphic molecules during the last ten years, the panorama of cubic structures offered by thermotropic compounds is now as rich as the one for lyotropics. This recent evolution has been reviewed by several authors [6^{''}–11] and, in particular, *C. Tschierske* makes clear that thermotropics can offer even more complex mesophase morphologies [9^{''}–11].

In this review, we will focus only on thermotropic mesophases which appear because of the nano-segregation of two amphipatic building-blocks (like polar and apolar blocks), and which exhibit 3D-long range order, almost always of cubic symmetry. We will not discuss mesophases resulting of the combination of long range order with chirality, which leads to various beautiful

molecular arrangements (like blue phases, twist grain boundaries phases or quadratic ‘smectic Q’ phases ...) [7^{''},12^{''}–14]. However, this combination is an important specificity of thermotropic mesophases compared to lyotropic ones.

We will review some recent results in the following order. Starting from the frequently encountered bicontinuous $Ia\bar{3}d$ phase, we will show that a second cubic arrangement of the space group $Im\bar{3}m$ seems to be specific to thermotropic mesophases, and that its detailed structure is not completely elucidated. Then, we will briefly introduce spectacular structures recently found in the packing of spherical objects. The last part will be devoted to recent studies concerning macroscopic properties of thermotropic cubic mesophases: modification under an external field (electric field or pressure), viscoelastic behaviour and formation of faceted droplets.

2. Bicontinuous $Ia\bar{3}d$ cubic phase

As for lyotropic materials, the most widespread thermotropic cubic phase is the bicontinuous $Ia\bar{3}d$ phase. Recent studies have given many new examples of thermotropic $Ia\bar{3}d$ cubic phases, varying the chemical nature of the two amphipatic blocks [9^{''}–11,15^{''}–25]. Selected examples are

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available in the *electronic supplementary material*. Its famous structure with two equivalent interwoven subspaces is recalled in Fig. 1.

Electron microscopy analysis of freeze-fractured samples combined with appropriate image analysis is a powerful technique in order to visualise cubic phases [26]. Unfortunately, to our knowledge, there is only one electron microscopy study concerning a thermotropic $Ia\bar{3}d$ cubic phase [27^{''},28^{*}].

Thus, cubic phases are mainly identified using X-ray scattering. The X-ray signature of a bicontinuous $Ia\bar{3}d$ cubic phase is the presence of two very strong Bragg reflections on a powder diagram corresponding to the 211 and 220 reticular distances. In several cases, single crystals data have been obtained, so that the $Ia\bar{3}d$ space group is unambiguously identified [12^{*},20,23].

With X-ray, the intensity of the Bragg peaks is sensitive to the position in the cubic unit cell of the polar/apolar interfaces, because the electron density contrast comes mainly from two different electron density levels, inside the polar regions on one part and inside the apolar regions on the other part. Then, in order to determine the dimensions of these two regions (polar and apolar), modelisation of the diffraction intensities are needed [29^{*}–31^{*}].

With the increasing number of examples of thermotropic $Ia\bar{3}d$ cubic phases, the question of the existence of both types (direct and inverse) of cubic phases arises. It is now clear that they both exist, as for lyotropic materials [9^{''}–11,15^{*},17^{*},23]. The Bragg intensities alone are not sufficient to discriminate between the two types of phases, because they are not sensitive to the position of the alkyl-chains region with respect to the apolar/polar interfaces (Babinet's theorem for diffraction). The best way to determine the type of the structure is then by comparing compounds with different chain lengths that exhibit either lamellar or columnar phases. Then, the following sequence on increasing the alkyl-chain volume fraction is used: direct micellar, direct hexagonal, direct bicontinuous (or type I), lamellar,

inverse bicontinuous (or type II), inverse hexagonal, inverse micellar [9^{''}].

Then, the best way to visualise the bicontinuous structure is probably to use the *Schoen* Gyroid infinite periodic minimal surface. This surface has the appropriate $Ia\bar{3}d$ space group symmetry and separates the space into two equivalent subspaces, with each 3D-network of rods located in the middle of each of these two subspaces [29^{*}]. By comparing with a lamellar phase, which is a stacking of layers with flat polar/apolar interfaces, a bicontinuous cubic phase corresponds to a packing of similar layers but with curved interfaces. More precisely, it has been argued that a bicontinuous cubic phase appears as one possibility to make a compromise between a local curvature of the polar/apolar interface and a long range order of layers [32^{''},33^{*}].

Then, the two types of bicontinuous cubic phase are expected in the following situations. Starting from a lamellar phase and increasing the alkyl-chain volume fraction, an inverse bicontinuous $Ia\bar{3}d$ cubic phase (type II) is expected, because the polar/apolar interface is curved towards the core regions, and the alkyl chains are forming a continuous layer around the Gyroid IPMS. Conversely, on decreasing the alkyl-chain volume fraction, the polar/apolar interface is curved towards the alkyl-chain regions and the cores are forming a continuous layer around the Gyroid IPMS.

The thermal behaviour of the thermotropic $Ia\bar{3}d$ cubic phase has also been recently investigated [25,27^{''},34^{''},35^{''}]. The cubic unit cell volume varies only very slightly with temperature. In several cases, the cubic unit cell is very slightly decreasing on heating with an average value of $(1/a^3)da^3/dT \approx -10^{-3} \text{ K}^{-1}$. Only very few dilatometry experiments have been performed in order to understand better this result [27^{''},35^{''}]. In these recent studies, it has been established that this little contraction of the unit cell is balanced by a decrease of the number of molecules per unit cell, because, as expected, the measured molecular volume

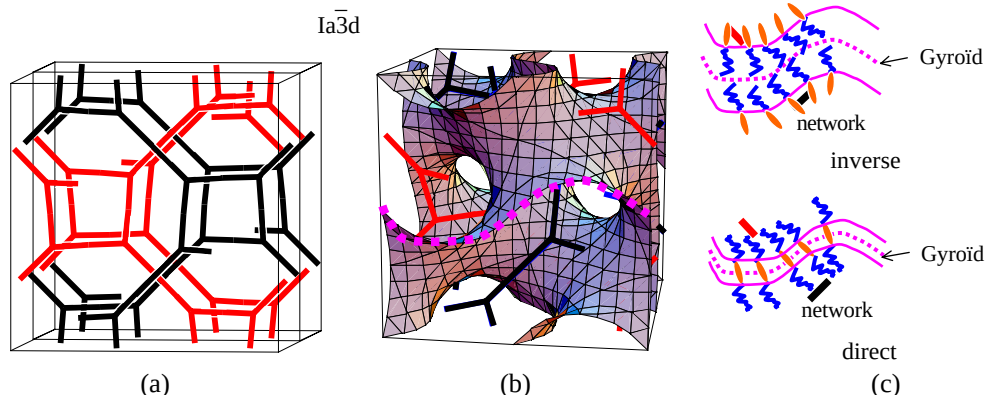


Fig. 1. Bicontinuous $Ia\bar{3}d$ cubic phase. Two equivalent networks of 3-connected nodes (in red and black) (a) are at the centre of two subspaces separated by the *Schoen* Gyroid infinite periodic minimal surface (b). In an inverse structure, the alkyl chains form an infinite layer around the Gyroid surface (dotted line) that separates the two networks where the cores are located. For a direct structure, the layer is made of the cores and the two networks contain the alkyl chains. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

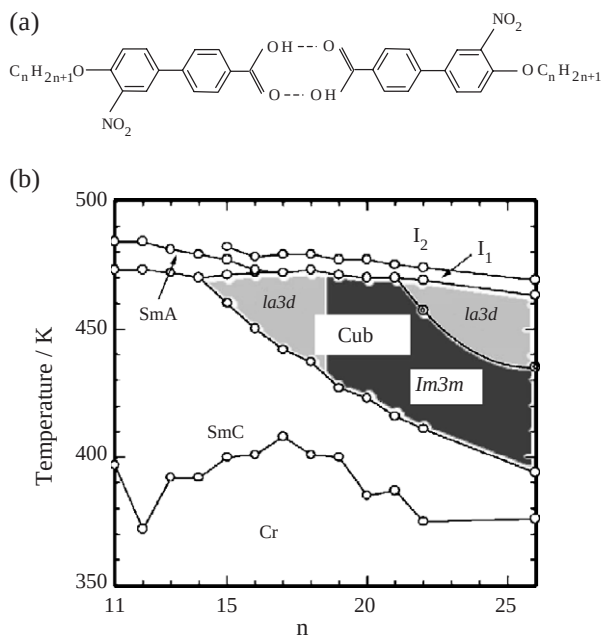


Fig. 2. Phase behaviour of the ANBC- n compounds. These molecules form dimers (a). On increasing the chain length n of their alkyl chains, two cubic phases of space groups $Ia\bar{3}d$ and $Im\bar{3}m$ are progressively favoured instead of smectic A and smectic C phases (b). (reproduced from *Liquid Crystals* 2002, 29:1447–1458, by permission of the Taylor and Francis group).

is increasing with temperature. It confirms the fact that the relevant structural unit is the layer and not the individual molecules. The fact that the lattice parameter is slightly

changing with temperature is probably related to the little discrepancies between the thermal dilatation coefficients of the alkyl chains on one part and of the cores on the other part [35].

3. Multi-continuous $Im\bar{3}m$ cubic phase

In contrast with lyotropic cubic phases, the bicontinuous phase based on the Schwarz D surface with space group $Pn\bar{3}m$ has never been observed for thermotropic compounds. But interestingly, a more complex cubic phase is now well identified, and is specific to thermotropic materials. At the moment, one has to be careful that these specificities may only be due to the small number of investigated compounds up to now.

This second cubic phase is formed by several quite different thermotropic compounds, and is identified using X-ray scattering [6–8,12,13]. As an example, the remarkable behaviour of the ANBC- n family is recalled in Fig. 2 [34–36]. Depending on the alkyl-chain length, the $Ia\bar{3}d$ and this other cubic phase are observed. The behaviour of these compounds is quite complex, especially on cooling. The kinetics influences the mesophase sequence and a metastable 3D-tetragonal mesophase can also form depending on the cooling rate [6,8,52]. Thus the exact stability regions of each cubic phase are difficult to determine.

Even if other space groups are compatible with the X-ray data, the space group is often taken as $Im\bar{3}m$ because it has

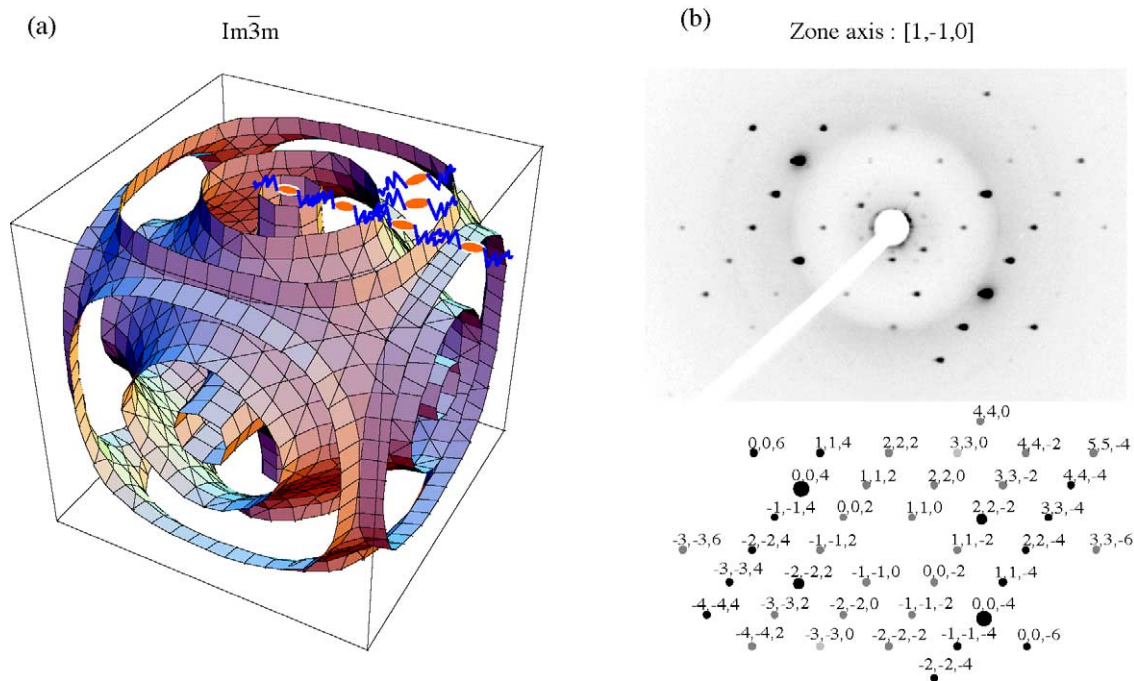


Fig. 3. Multi-continuous $Ia\bar{3}d$ cubic phase. Model of the cubic unit cell with three layers made of alkyl chains separated by four core regions (a). The shape of the layers is based on the P Schwarz infinite periodic minimal surface (adapted from *Liquid Crystals* 1998, 24:105–115, by permission of the Taylor and Francis group). An X-ray diffraction pattern of a single crystal (b) from this complex structure gives strong reflections for relatively high Miller indices (reproduced from *Chemphyschem* 2001, 2:533–535 by permission of Wiley-VCH Verlag GmbH).

more symmetry elements than the other ones. The X-ray signature of this $Im\bar{3}m$ phase is the same for the different examples and is the way to identify this phase [6'',7'',12',34'']. The Bragg peaks with strong intensities have quite large Miller indices like 321 and 400, and correspond to reticular distances similar to d_{211} or d_{220} of an $Ia\bar{3}d$ bicontinuous cubic phase. This means that the cubic unit cell contains more structural units than in the case of the $Ia\bar{3}d$ phase. Moreover, when the $Im\bar{3}m$ cubic phase appears as a “companion” phase of the $Ia\bar{3}d$ bicontinuous phase, then the lattice parameter a is always equal to about 1.5 times the $Ia\bar{3}d$ lattice parameter. This suggests that close structural relationships exist between these two phases.

This phase is believed to be a multi-continuous structure, and even if its detailed structure is not fully elucidated, a scheme of it is given in Fig. 3 [6'']. This scheme is based on the infinite periodic minimal Schwarz P surface which has the $Im\bar{3}m$ symmetry and on the estimation that three alkyl-chains continuous regions are needed in order to provide enough area to the polar/apolar interfaces. A related model also based on the P surface has been proposed by S. Kutsumizu, with only two alkyl-chains regions inside the unit cell that separate three independent core regions [8'']. However, both models do not show strong structural relations with the $Ia\bar{3}d$ bicontinuous structure, as one might expect from the experimental results.

Recently, single crystal X-ray data of the $Im\bar{3}m$ phase have been obtained, which allows to measure many individual Bragg peak intensities as illustrated in Fig. 3b [37']. By performing an electron density reconstruction of these data, it should be possible to elucidate precisely the shape of the polar/apolar interfaces. This method has been recently applied successfully to different micellar cubic

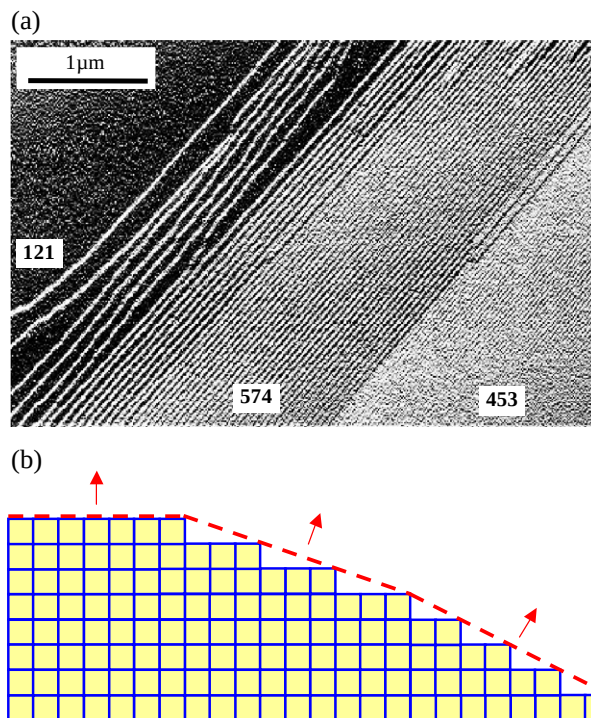


Fig. 5. AFM observation of facets. Used in tapping mode, AFM allows to visualise the surface of a faceted droplet. Molecular steps (about 3 nm in height) appear as white lines (a). A (121) principal facet is essentially flat, whereas vicinal facets—(574) and (453)—are made of a succession of equally spaced steps (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

phases (Section 4). Lastly, one notices that electron microscopy on cryofractured samples could also be of great help in order to visualise this structure.

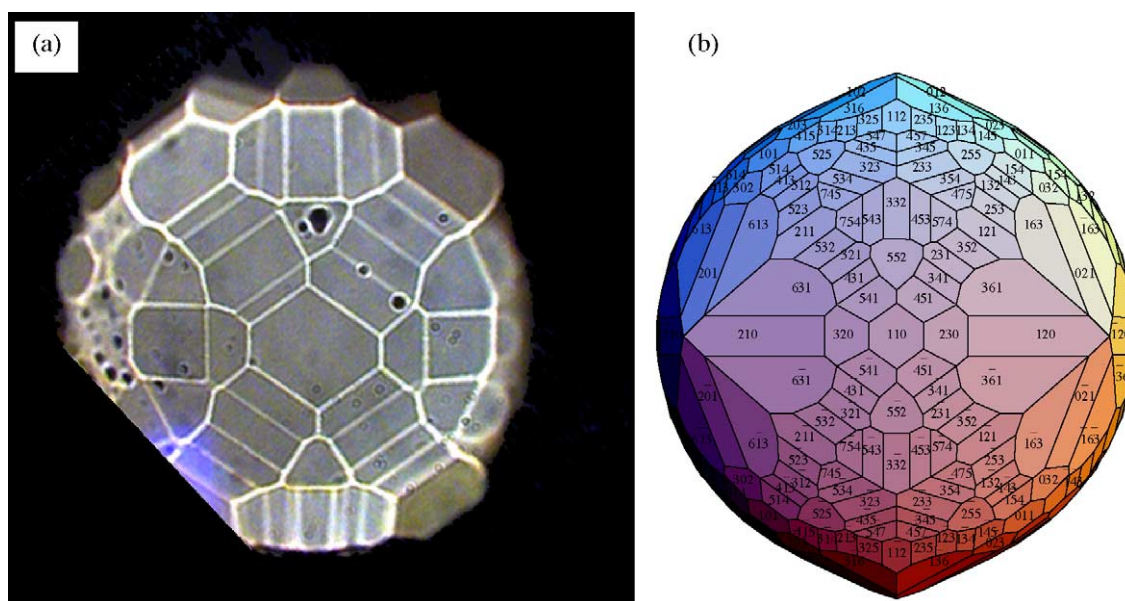


Fig. 4. Faceted droplet of an $Ia\bar{3}d$ bicontinuous cubic phase. The droplet (which size is a few hundred microns) is deposited on a substrate and observed under an optical microscope (a). Its surface presents a large number of facets, corresponding to a single cubic crystal, as shown by the shape reconstruction (b).

The thermal behaviour of the $Im\bar{3}m$ phase has also been investigated and the results are similar to the case of the $Ia\bar{3}d$ bicontinuous phase (Section 2) [8'',34''–36].

4. Micellar cubic phases

In the previously described bicontinuous or multi-continuous cubic phases, the structural units are made of layers with curved interfaces. Micellar cubic phases exhibit also a cubic long range order but their structural units are much more simple, made of spheroidal shaped objects.

Simple packing (b.c.c. and f.c.c.) already encountered in lyotropics or copolymers assemblies is now also observed with thermotropic phases [9'',10'']. Thanks to great progress in the synthesis of dendrimers that form supramolecular assemblies [38] and to electron density reconstruction methods in the analysis of single crystal X-ray data [39'',40''], spectacular new assemblies have been discovered very recently. A remarkable sequence of more and more complex architectures has been found: the cubic $Pm\bar{3}n$ phase (8 micelles per unit cell) [10'',11,39''], the $P4_2/mnm$ quadratic phase (30 micelles per unit cell) [40''] and a 2D-quasicrystalline phase [41'']. This sequence reveals that tetrahedrally close packed structures are involved [33',40'',41''] and draws a remarkable parallel between liquid crystals and metallic alloys.

5. Macroscopic properties of cubic phases

In this last part, we will focus on macroscopic physical properties rather than on structural aspects.

A first idea is to study the behaviour when an external field is applied, namely an electric field or a pressure field. Under AC electric field, it is possible to induce and control a smectic C to a cubic $Im\bar{3}m$ phase transition (ANBC-22), with possible applications in stress transferring devices [42]. Under pressure [43–48], temperature–pressure phase diagrams have been established for some members of two families of thermotropic compounds, BABH(*n*) and ANBC-*n*. Pressure experiments can be coupled either to optical microscopy or to X-ray diffraction. On increasing pressure, cubic phases can be destabilised and a smectic phase favoured, like the BABH(8) compounds, where the cubic phase exists up to 10–20 MPa [44,45]. For ANBC-*n* compounds, the behaviour is more complex, especially on cooling, as already seen for the behaviour at usual pressure (Section 2). However, on heating, the cubic phase can be stable up to 300 MPa, with an increased stability on increasing the chain length [47].

All cubic phases are viscoelastic materials. In order to quantify this property, rheology measurements can be performed, but relatively large quantities (usually a few cubic centimeters) are needed so that lyotropic materials are rather used. Concerning thermotropic phases, it has been possible to measure the elastic moduli for some members of the ANBC-*n* family, both for the $Ia\bar{3}d$ and the $Im\bar{3}m$ cubic

phases [8'',34'',35'',49'']. These data are the only available ones for thermotropic cubic phases with data concerning dry strontium stearate [50]. The order of magnitude of the shear elastic moduli found for these cubic phases is $G' \approx 10^6$ Pa with $G' \approx 10 G''$, where G' is the storage modulus and G'' the loss modulus [49'']. This value of G' is characteristic of a soft material ($G' \approx 10^9$ – 10^{12} Pa for solid materials), and compares well with values obtained for bicontinuous lyotropic cubic phases [51]. The ratio between G' and G'' reveals a strong elastic component, as expected for a 3D-ordered material. An interesting observation is a significant jump of the elastic moduli at the $Im\bar{3}m$ to $Ia\bar{3}d$ phase transition.

The last new development is the discovery of original faceting properties of cubic phases [52–54]. As seen in Fig. 4, a droplet deposited on a substrate that contains only one single crystal of an $Ia\bar{3}d$ thermotropic cubic phase (ANBC-*n* derivative) presents a high number of different facets at the air/cubic phase interface. This phenomenon has also been observed in the case of lyotropic cubic phases [53'']. In contrast, in the case of atomic crystalline solids, only a few different facets are usually observed. In comparison, cubic phases have a much larger unit cell and lower elastic moduli. These two facts are believed to explain the formation of a very large number of facets. The type of facets is linked to the crystallographic point group, so that each type of cubic phase gives a characteristic set of facets. In some way, this very simple optical observation of droplets could generalise the notion of optical texture widely used for non-cubic liquid crystals.

Using an ANBC-*n* derivative for which an $Ia\bar{3}d$ bicontinuous cubic phase is metastable at room temperature (during several weeks for small droplets), the surface of these facets could be imaged using atomic force microscopy [54]. In Fig. 5, the topography of the facets reveals that principal facets (211 or 220 for the $Ia\bar{3}d$ space group) are essentially flat, whereas the numerous vicinal facets with high Miller indices are made of a succession of parallel and equally spaced molecular steps, which is also called a “devil’s staircase” [53''].

6. Conclusion

In this review, we have shown that many new thermotropic compounds have been recently discovered that form cubic phases. Among them, many examples of the $Ia\bar{3}d$ bicontinuous structure are found. Moreover, a second type of cubic phase, the multi-continuous $Im\bar{3}m$ phase, is up to now specific to thermotropic compounds. We focus our attention on these two phases because we believe that they mainly derive from the presence of two amphipatic building-blocks. However, thermotropic liquid crystals offer much more auto-organisation possibilities by their ability to combine nano-segregation with other molecular properties, like for example chirality. In the near future, one can expect

that new complex architectures will be obtained by generalising the nano-segregation to the case of three different building-blocks [9^{••},55].

The case of thermotropic micellar cubic phases is remarkable because many different assemblies of soft spherical objects have been very recently discovered.

Studies of the macroscopic behaviour of thermotropic cubic phases are just beginning. We present some results that should help to understand better the properties of this particular class of soft materials, which will be probably more and more widespread, as for example in the templating of porous materials [56].

Selected examples of thermotropic compounds are available in the electronic supplementary material.

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Chapitre 5

Matériaux mésoporeux

Ces matériaux ont été découverts très récemment au début des années 90. Ce sont des matériaux solides, le plus souvent en silice (SiO_2), dont la porosité est calibrée et ordonnée à l'échelle nanométrique. Nous nous intéressons à ces matériaux car les propriétés remarquables de leur porosité résultent de leur mode de synthèse, qui utilise les propriétés d'auto-association des molécules de tensioactifs. Ainsi, la structure de ces matériaux est une réplique solide des phases hexagonales et cubiques. Dans ce chapitre, après quelques généralités, nous introduisons les différentes voies de synthèse utilisées et qui conditionnent la mise en forme du matériau final.

Généralités

Les premiers matériaux mésoporeux ont été synthétisés par la société Mobil au début des années 90, en utilisant des tensioactifs cationiques (famille des CTAB, voir le Chapitre 2). Ils ont été brevetés sous le sigle MCM (**M**obil **C**omposition of **M**atter). En 1994, un autre brevet, de l'Université de Santa-Barbara en Californie a été déposé pour des matériaux apparentés, sous le sigle SBA (**S**anta **B**Arbara). Par rapport aux MCM, la nouveauté a été d'utiliser des copolymères non-ioniques (Pluronic, Chapitre 2), comme agent structurant. Ces matériaux donnent lieu actuellement à de très nombreuses publications dans le domaine de la chimie des matériaux, et d'autres brevets sont déposés régulièrement, comme par exemple les matériaux MSU (**M**ichigan **S**tate **U**niversity). Au-delà de leurs nombreuses applications potentielles, l'engouement pour ces matériaux s'explique entre autre par le fait que l'on arrive à structurer la matière à l'échelle nanométrique uniquement par un phénomène d'auto-association, et en utilisant des synthèses simples issues de la « chimie douce », réalisées à température ambiante et en solution aqueuse.

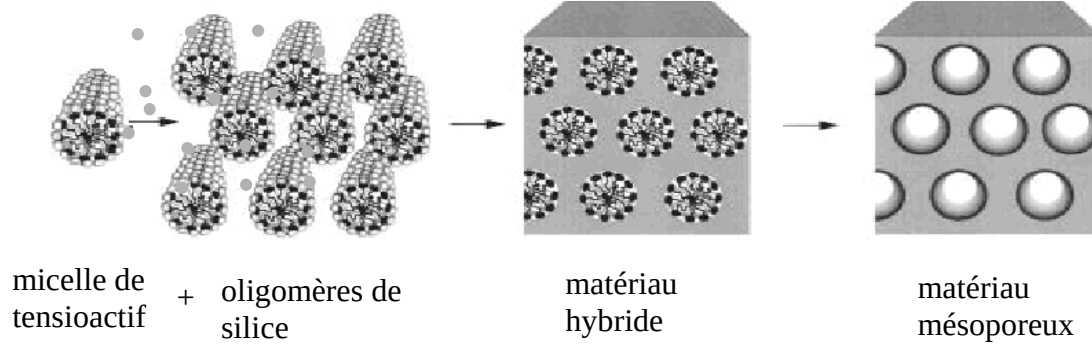


Figure 5-1. Schéma de la synthèse d'un matériau mésoporeux : auto-assemblage, formation d'un matériau hybride et calcination.

Schématiquement (**Fig 5-1**), l'auto-assemblage en solution aqueuse de micelles de tensioactif en présence d'oligomères de silice conduit à un matériau hybride ordonné, où les micelles sont entourées d'un milieu aqueux où la silice polymérise. La calcination du matériau hybride à haute température (400°C) permet d'éliminer par combustion les molécules organiques et de condenser entièrement les espèces de silice. Un matériau poreux en silice amorphe est obtenu, dont la porosité structurée est l'empreinte des micelles dans le matériau hybride.

Le premier domaine d'application concerné est celui de la catalyse, où ces matériaux constituent une alternative aux zéolithes comme supports poreux contenant des catalyseurs. Par rapport aux zéolithes, l'intérêt des matériaux mésoporeux est d'augmenter la taille des pores dans la gamme de quelques nanomètres (**Fig 5-2**), avec des surfaces poreuses (quelques centaines de m² par gramme) et des volumes poreux (de l'ordre d'un cm³ par gramme) importants.

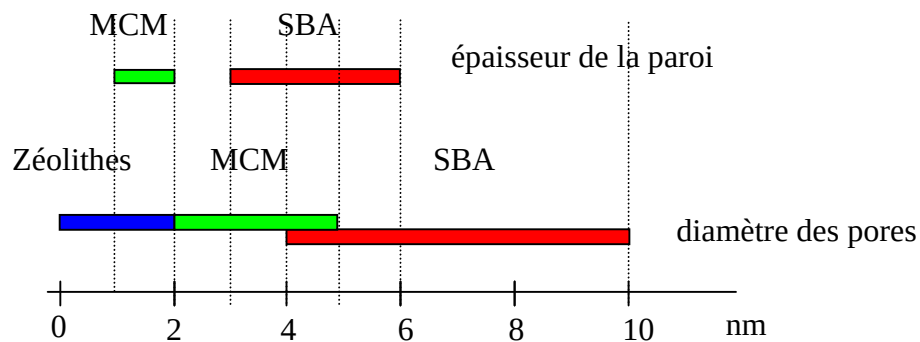


Figure 5-2. Taille des pores et des épaisseurs de parois.

La très bonne calibration en taille des pores obtenue grâce au phénomène d'empreinte des micelles de tensioactif permet de réaliser des membranes de filtration. Cela nécessite alors de mettre en forme le matériau sous forme de films bi-dimensionnels. Sous forme de films déposés sur du verre, ils sont aussi testés comme revêtement de surface.

La plupart des applications nécessitent néanmoins de doper ces matériaux. On peut ainsi synthétiser des nano-particules calibrées en taille à l'intérieur de la porosité. Il peut s'agir de nano-particules métalliques, d'oxydes métalliques ou encore de semi-conducteurs. Le matériau peut alors acquérir des propriétés nouvelles une fois dopé par ces nano-particules (propriétés optiques, magnétiques ...).¹ Il est aussi possible de redissoudre le moule de silice et de récupérer uniquement les nanoparticules, comme des nano-fils métalliques à partir d'une phase hexagonale 2D.² Quelques exemples remarquables illustrent ces possibilités dans les **figures 5-3 et 5-4**.

Enfin, afin d'étendre la gamme des applications de ces matériaux, une autre voie actuelle de recherche est de varier la nature du matériau à d'autres oxydes que la silice (SiO_2) comme l'oxyde de titane (TiO_2) ou l'oxyde d'aluminium (Al_2O_3).

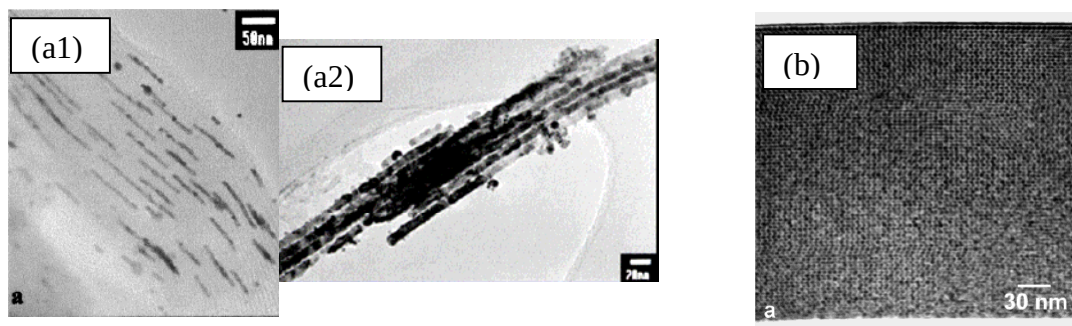


Figure 5-3. Deux exemples remarquables dans le domaine de la synthèse de nano-particules : (a) Nano-tiges de platine synthétisées à l'intérieur d'un grain de silice mésoporeuse 2D-hexagonale SBA-15 (a1) puis extraites après dissolution de la silice dans une solution de HF (a2).² (b) Coupe d'un film mince mésoporeux de 300 nm d'épaisseur. La matrice de silice (en gris) a une structure hexagonale 3D et les pores sphériques contiennent des nanoparticules de CdS de 4 nm de diamètre (en noir).¹

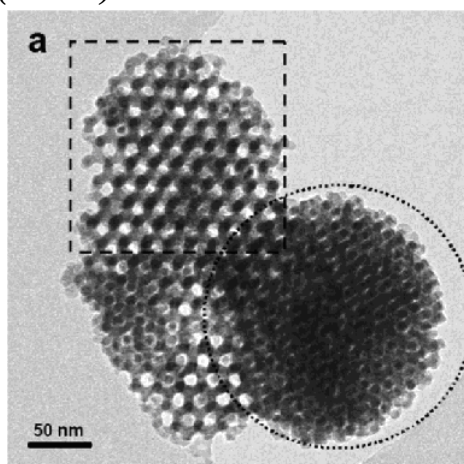


Figure 5-4. Image d'une réplique d'oxyde métallique d'un matériau mésoporeux en phase cubique bicontinue $Ia3d$ (voir aussi le chapitre 16). On distingue les deux labyrinthes imbriqués l'un dans l'autre en bas à droite. En haut à gauche, un seul des deux labyrinthes subsiste.³

Procédé sol/gel :

Le procédé sol/gel utilisé pour synthétiser la silice est bien connu en absence de tensioactif.⁴ Un précurseur moléculaire en solution aqueuse, le plus souvent le TEOS, Si(Et)₄, ou le TMOS, s'hydrolyse en des espèces de silice qui polymérisent entre elles pour former des oligomères de silice. Les cinétiques de ces réactions sont contrôlées essentiellement par le pH. Suivant le pH, on obtient plutôt une suspension colloïdale de particules sphériques (catalyse basique), ou un gel polymérique linéaire (catalyse acide).

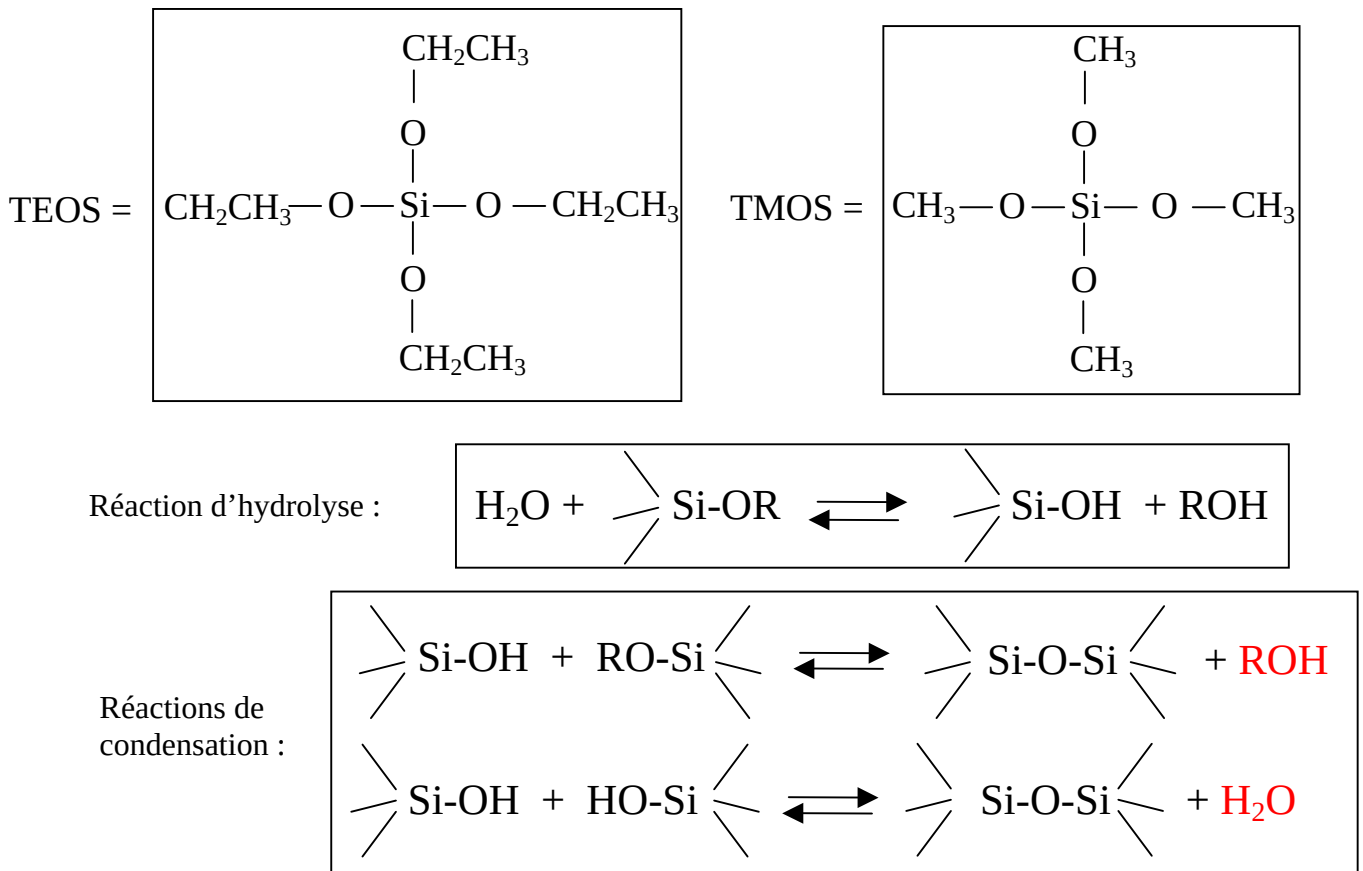


Figure 5-5. Les précurseurs moléculaires de la silice , le TEOS et le TMOS, ainsi que les réactions d'hydrolyse et de condensation.

Voies de synthèse et mise en forme du matériau :

La mise en forme du matériau se fait au moment de la synthèse, puisque la condensation de la silice donne un caractère solide au matériau hybride. Trois types de mises en forme sont développées : les poudres (grains de taille nano ou micrométriques), les films 2D et les monolithes (mono-domaine de taille millimétrique). Seuls les films et les monolithes permettent de conserver macroscopiquement l'anisotropie du matériau (phase hexagonale), ce qui pourra être très important pour les applications.

- synthèse en mésophase

Il s'agit de la voie directe où l'on se place en mésophase.⁵ La concentration en précurseur étant importante, il faut évaporer rapidement l'alcool résultant de la réaction de condensation afin de conserver la mésophase au cours du temps. On utilise alors le TMOS comme précurseur afin d'évaporer du méthanol plutôt que de l'éthanol. Il s'agit d'un véritable phénomène de moulage de la structure et l'on peut obtenir par cette voie des monolithes de taille millimétrique.

Cette méthode a surtout été appliquée en utilisant des tensioactifs non-ioniques de type C_nE_m ou Pluronic⁶ (voir le chapitre 2).

Les deux méthodes suivantes restent néanmoins les plus répandues :

- Synthèse de poudre par précipitation

C'est la méthode la plus simple pour sa mise en œuvre, et elle est donc très utilisée. L'inconvénient est que le matériau est obtenu sous forme de poudre, dont la morphologie des grains n'est pas forcément bien contrôlée. On ajoute à une solution micellaire diluée de tensioactif le précurseur de la silice. En quelques minutes, en maintenant une agitation permanente de la solution, le matériau hybride précipite sous forme de poudre. La poudre est souvent maintenue en solution aqueuse pendant quelques heures en chauffant pour améliorer la structure (traitement hydrothermal) puis est filtrée et calcinée pour libérer la porosité.

Suivant la nature du tensioactif, cationique (type CTAB) ou non-ionique (type Pluronic), l'interaction entre les oligomères de silice avec le tensioactif est de nature différente. Le rôle du pH est là-aussi primordial pour contrôler les charges de surfaces. Dans le cas du CTAB en milieu basique, les espèces de silice sont chargées négativement (I^-), et une interaction

électrostatique directe notée (S^+I^-) entre le tensioactif et les espèces de silice pilote l'association organique/inorganique. Pour les non-ioniques, en milieu acide (ex : HCl), deux hypothèses sur la nature de l'interaction existent. Soit l'interaction est aussi de type électrostatique, mais médiée par des contre-ions, elle est notée ($S^0H^+ClI^+$). Soit l'interaction fait intervenir des liaisons hydrogène entre les groupes polaires EO et les espèces de silice, notée alors S^0I^0 .

Depuis 2005, nous réalisons des expériences de cinétiques par SAXS et SANS, afin de suivre en temps réel l'association des micelles et des espèces de silice lors de la précipitation du matériau hybride. Cette activité est abordée dans les chapitres 17 et 21.

La **figure 5-6** donne quelques exemples de matériaux calcinés obtenus par précipitation, où la morphologie des grains est remarquable. En phase cubique $Pm3n$ (**Fig 5-6-a**), la surface des grains est facettée.⁷ Cette observation est à rapprocher des études sur le facettage présentée au chapitre 20.

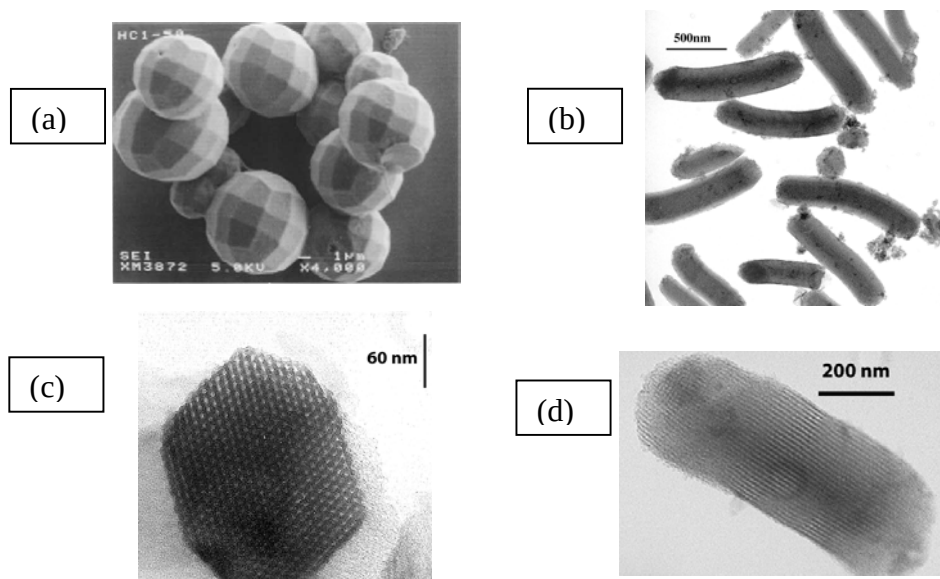


Figure 5-6. Exemples de grains obtenus par précipitation et observés par microscopie électronique. (a) Grains facettés d'une phase cubique $Pm3n$.⁷ Grains cylindriques d'une phase hexagonale 2D. (b,c,d).⁸

En phase hexagonale 2D (matériau SBA-15, préparé à partir du Pluronic P123), des grains cylindriques sont observés (**Fig 5-6-b**). Les zooms sur un grain unique (**Fig 5-6-c,d**) montrent le réseau 2D hexagonal des pores.⁸

- Synthèse de film par évaporation de solvant

Cette méthode est développée en vue d'applications nécessitant de synthétiser un film bidimensionnel. Une goutte de solution contenant le tensioactif et les précurseurs inorganiques est déposée rapidement sur un substrat par spin-coating ou dip-coating. Le film s'auto-organise rapidement (quelques minutes) lors de l'évaporation du solvant au contact de l'air. En jouant sur les paramètres du taux d'évaporation, (humidité de l'atmosphère, température ...), méthode dite EISA (pour **E**vaporation **I**nduced **S**elf-**A**ssembly),⁹ on peut contrôler la structure du film mésoporeux final.

- Synthèse de monolithes par séchage lent

Cette dernière voie de synthèse, encore très peu explorée, consiste à fabriquer des monolithes macroscopiques (cm^3) et constitue une alternative à la méthode de synthèse directe en mésophase. Elle s'apparente à la méthode EISA pour les films 2D, dans la mesure où l'évaporation du solvant pilote l'organisation du matériau. Les temps de préparations sont par contre beaucoup plus longs (plusieurs semaines ou jours). Une évaporation très lente du solvant permet d'obtenir un matériau ne contenant que très peu de domaines, et ayant une taille millimétrique.^{10,11}

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Première partie

B- Notions de diffusion

Chapitre 6

Mesure des intensités

Ce chapitre rassemble les expressions utiles lorsque l'on réalise des mesures d'intensités, afin de les confronter à des modèles de structure. On commence par introduire l'expression de l'intensité absolue, dans le cadre de ce qu'il est convenu d'appeler la diffusion aux petits angles. Puis, pour les phases organisées, on introduit l'intensité intégrée d'un pic de Bragg, qui est la bonne quantité à mesurer. On discute alors les différentes corrections, essentiellement géométriques, à apporter aux intensités mesurées avant de les comparer à un modèle de structure.

Intensité absolue :

Il peut être utile de connaître l'expression en unités absolues de l'intensité. Elle a la forme générale suivante :

$$I^{abs}(\vec{k}) = I_e T I_0 I(\vec{k})$$

$$\text{avec } I(\vec{k}) = |A(\vec{k})|^2 = A(\vec{k})A^*(\vec{k}) \text{ et } A(\vec{k}) = \int_{\text{échantillon}} \rho(\vec{x}) e^{-2i\pi\vec{k}\cdot\vec{x}} d\vec{x}$$

Elle est proportionnelle à l'intensité du faisceau incident I_0 , à la transmission T de l'échantillon, et au terme de diffusion par un électron, I_e .

$\rho(\vec{x})$ est la densité électronique, soit un nombre d'électrons par unité de volume. Dans le cas des phases organisées, on décrit la matière à l'échelle moléculaire, comme un milieu continu, et $\rho(\vec{x})$ est alors une fonction continue. C'est cette description qui est adoptée ici. Elle n'est valable que pour les petits vecteurs de diffusion, où la décroissance des facteurs de diffusion atomique avec l'angle de Bragg est négligeable. Autrement dit, le facteur de diffusion atomique est pris égal à Z , le nombre d'électrons de l'atome considéré.

On voit que cette description de la matière diffère de celle à l'échelle atomique, où $\rho(\vec{x})$ est une somme discrète de pics de Dirac, localisés sur les atomes, et où l'on tient compte des facteurs de diffusion atomique.

Correction de polarisation :

L'expression de la diffusion par un électron I_e est la suivante (diffusion cohérente) ^{1,2} :

$$I_e = \frac{r_0^2}{r^2} CP \quad \text{avec} \quad r_0 = \frac{1}{4\pi\epsilon_0} \frac{e^2}{mc^2} = 2.82 \cdot 10^{-15} \text{ m}$$

r_0 est le rayon classique de l'électron et r la distance échantillon-détection. CP, la correction de polarisation dépend de l'angle de diffusion θ ($k = \frac{2\sin\theta}{\lambda}$).

I_e est un flux d'énergie par unité de surface à la distance r . Dans un angle solide $d\Omega$, l'énergie diffusée vaut : $I_e dS = \frac{r_0^2}{r^2} CP dS = r_0^2 CP d\Omega$.

Aux petits angles, on néglige la correction de polarisation car $CP=1$. On donne ici néanmoins son expression, suivant les situations utilisées ³ :

- rayonnement non polarisé (cas du rayonnement d'un générateur de RX) :

$$CP = \frac{1 + \cos^2(2\theta)}{2}$$

- rayonnement synchrotron, polarisé dans le plan de l'anneau (β étant l'angle entre le plan de diffraction et le plan de polarisation) :

$$CP = \sin^2(\beta) + \cos^2(\beta)\cos^2(2\theta)$$

RQ : pour $\beta = \pi/2$, le plan de diffraction est vertical et la correction de polarisation vaut 1.

- rayonnement polarisé en sortie d'un monochromateur (α étant l'angle d'incidence du faisceau sur le monochromateur) :

$$CP = \frac{1 + \cos^2(2\alpha)\cos^2(2\theta)}{1 + \cos^2(2\alpha)}$$

Finalement, on a l'expression complète :

$$I^{abs}(\vec{k}) = \frac{r_0^2}{r^2} (CP)(T) I_0 I(\vec{k})$$

Diffuseur de référence :

Une façon de déterminer en unité absolue une intensité est d'utiliser un échantillon diffuseur de référence de taille connue, en gardant les mêmes conditions d'expérience (intensité du faisceau incident, distance échantillon-détection ...). On s'affranchit ainsi de la mesure de l'intensité du faisceau I_0 , et l'on doit mesurer seulement les transmissions des échantillons.

Dans le domaine des petits angles, on peut utiliser la diffusion par un liquide tel que l'eau. En effet, dans la gamme de vecteur d'onde appropriée, un liquide donne un signal constant, relié aux fluctuations de densité excitées thermiquement⁴ :

$$I(\vec{k}) = V_{tot} k_B T \langle \rho \rangle^2 \kappa_T$$

où V_{tot} est le volume de l'échantillon, k_B la constante de Boltzmann, T la température absolue, $\langle \rho \rangle$ la densité électronique moyenne et κ_T la compressibilité isotherme du liquide. Dans le cas de l'eau comme référence aux petits angles^{5 6}, on a :

$$I(\vec{k}) = V_{tot} k_B T \langle \rho \rangle^2 \kappa_T = 6.37 N_{eau} \quad \text{et} \quad I_{eau}^{abs}(\vec{k}) = \frac{r_0^2}{r^2} (CP)(T) I_0 6.37 N_{eau}$$

où N_{eau} est le nombre de molécules d'eau contenues dans l'échantillon de volume V_{tot} .

Intensité intégrée d'un pic de Bragg :

Pour des échantillons présentant un ordre à grande distance, des pics de Bragg sont obtenus, dont la largeur mesurée est fixée par la résolution expérimentale (taille du faisceau) et non par la taille des domaines diffractants. Pour les mesures quantitatives d'intensité, on utilise alors l'intensité intégrée de ces pics. La réalisation pratique des mesures se fait dans trois situations différentes, suivant la « qualité » de l'échantillon.

Soit on obtient une configuration de « **poudre** » de bonne qualité, où l'approximation d'une assemblée de petits domaines possédant toutes les orientations possibles de manière isotrope est bonne. Ceci se fabrique facilement avec un échantillon solide que l'on prépare en broyant des grains suffisamment fins. Ce n'est pas souvent le cas pour les échantillons rencontrés en matière molle qui présentent souvent des orientations partielles dues à des phénomènes d'orientation sous écoulement.

On cherche alors à obtenir au contraire un seul monocristal, ce qui est souvent possible pour les phases cubiques. Les mesures d'intensités des pics sont alors réalisées dans une configuration de « **cristal tournant** », en faisant tourner l'échantillon autour d'un axe vertical, soit en mode continu, soit en mode oscillant.

Quelques mesures ont aussi été réalisées sur monocristal en utilisant un diffractomètre et un détecteur ponctuel.

Dans la suite, on note $I_{mono}^{int}(\vec{k}^*) = \int_{dV^*} I(\vec{k}) d\vec{k}$, l'intensité intégrée d'un pic de Bragg dans l'espace réciproque dans un volume dV^* entourant le pic.

Cas d'une poudre :

On considère formellement que l'espace réciproque s'obtient en faisant tourner autour de l'origine l'espace réciproque d'un seul cristal, en lui faisant prendre toutes les orientations. L'intensité de chaque réflexion de Bragg se répartit à la surface d'une sphère de rayon k^* dans l'espace réciproque (**Fig 6-1**). On obtient des sphères concentriques pour tous les modules de k^* différents. On aboutit à la relation suivante entre l'intensité d'une raie de poudre et l'intensité d'une réflexion de Bragg individuelle :

$$I_{poudre}^{int}(k^*) = \frac{M(k^*) I_{mono}^{int}(\vec{k}^*)}{4\pi k^{*2}}$$

Les intensités des réflexions de Bragg dont les modules du vecteur de diffusion sont égaux s'additionnent. Le nombre de ces réflexions pour une valeur de k^* est la multiplicité de la raie de poudre, $M(k^*)$.

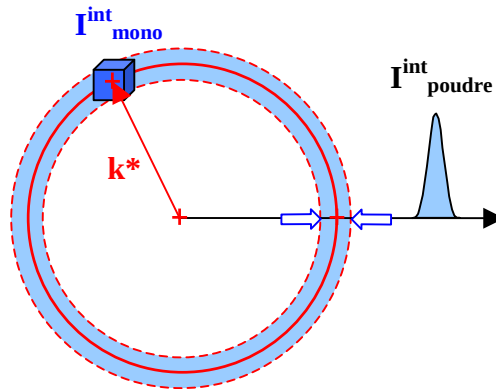


Figure 6-1. Espace réciproque d'une poudre.

$I_{mono}^{int}(\vec{k}^*)$ est une intensité intégrée sur un volume de l'espace réciproque entourant un pic de Bragg individuel. $I_{poudre}^{int}(k^*)$ est l'intensité intégrée du pic obtenu le long d'une ligne radiale passant par l'origine de l'espace réciproque.

Pour un réseau hexagonal 2D, la multiplicité vaut 6 (raies $h0$ et $h = k$) ou 12 (voir chapitre 8). Pour un réseau cubique, les multiplicités sont rappelées dans le tableau de la **figure 6-2**.⁷

hkl	raies équivalentes	$M(hkl)$
$h00$	$h00, 0h0, 00h, \bar{h}00, 0\bar{h}0, 00\bar{h}$	6
hhh	$hhh, \bar{h}hh, h\bar{h}h, hh\bar{h}, \bar{h}\bar{h}\bar{h}, h\bar{h}\bar{h}, \bar{h}h\bar{h}, \bar{h}\bar{h}h$	8
$hh0$	$hh0, h\bar{h}0, \bar{h}h0, \bar{h}\bar{h}0$ $h0h, h0\bar{h}, \bar{h}0h, \bar{h}0\bar{h}$ $0hh, 0h\bar{h}, 0\bar{h}h, 0\bar{h}\bar{h}$	12
$hk0$	$hk0, h\bar{k}0, \bar{h}k0, \bar{h}\bar{k}0, k0h, k0\bar{h}, \bar{k}0h, \bar{k}0\bar{h}$ $0hk, 0h\bar{k}, 0\bar{h}k, 0\bar{h}\bar{k}, kh0, k\bar{h}0, \bar{k}h0, \bar{k}\bar{h}0$ $h0k, h0\bar{k}, \bar{h}0k, \bar{h}0\bar{k}, 0kh, 0k\bar{h}, 0\bar{k}h, 0\bar{k}\bar{h}$	24
hhl	$hhl, h\bar{h}l, \bar{h}hl, \bar{h}\bar{h}l, hlh, h\bar{l}h, \bar{h}lh, \bar{h}\bar{l}h,$ $lhh, lh\bar{h}, \bar{l}hh, \bar{l}h\bar{h}, hh\bar{l}, h\bar{h}\bar{l}, \bar{h}h\bar{l}, \bar{h}\bar{h}\bar{l},$ $hh\bar{l}, h\bar{l}h, \bar{h}l\bar{h}, \bar{h}\bar{l}h, hhl, \bar{l}hh, \bar{l}h\bar{h}, \bar{l}h\bar{h}$	24
hkl	signes + permutations circulaires	48

Figure 6-2. Multiplicité $M(hkl)$ d'un réseau cubique.

Cas d'un cristal tournant :

L'espace réciproque s'obtient en faisant tourner autour de l'axe de rotation l'espace réciproque du cristal (**Fig 6-2**). L'intensité de chaque réflexion de Bragg se répartit sur un cercle de rayon k^*_{perp} (composante perpendiculaire à l'axe de rotation du vecteur $\vec{k}^*$). Certaines réflexions de Bragg s'additionnent : ce sont celles de même module du vecteur de diffusion et qui se trouvent dans la même strate (plan perpendiculaire à l'axe de rotation dans l'espace réciproque). Le nombre de ces réflexions est noté $m(k^*)$.

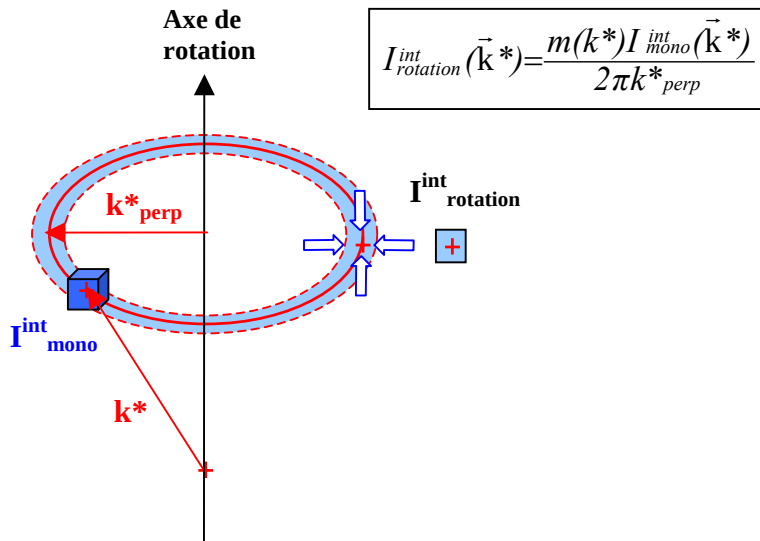


Figure 6-3. Espace réciproque d'un cristal tournant.

$I_{rotation}^{int}(\vec{k}^*)$ est l'intensité intégrée à 2D de la section du pic dans un plan perpendiculaire au cercle de rayon k_{perp}^* .

Un pic de Bragg situé sur l'axe de rotation n'est pas mesurable par cette méthode. En effet, même pour des petits angles de diffraction, il faut tenir compte dans ce cas de l'intersection avec la sphère d'Ewald. Tout ce qui est sur l'axe de rotation n'est pas en position de réflexion et n'est donc pas mesurable. En pratique, l'alignement de l'axe de rotation avec un axe cristallographique n'est pas parfait. On peut alors observer des pics de Bragg sur l'axe, mais la mesure de leur intensité ne peut être exploitée quantitativement.

Intersection avec la sphère d'Ewald, mesure sur film plan ou sur film cylindrique :

Jusqu'ici, les intégrations ont été faites dans l'espace réciproque, sans tenir compte de l'intersection avec la sphère d'Ewald. En effet, pour les petits angles de diffraction, on fait souvent l'approximation que la sphère d'Ewald se confond avec le plan perpendiculaire au faisceau direct. Cette approximation est valable pour des angles de Bragg tels que $\cos\theta \cong 1$, soit encore θ plus petit qu'environ 5° . Une détection sur un film plan donne directement l'intensité dans le plan de l'espace réciproque perpendiculaire au faisceau direct (**Fig 6-4**). On utilise alors les formules précédentes pour les intensités intégrées d'une poudre ou d'un cristal tournant.

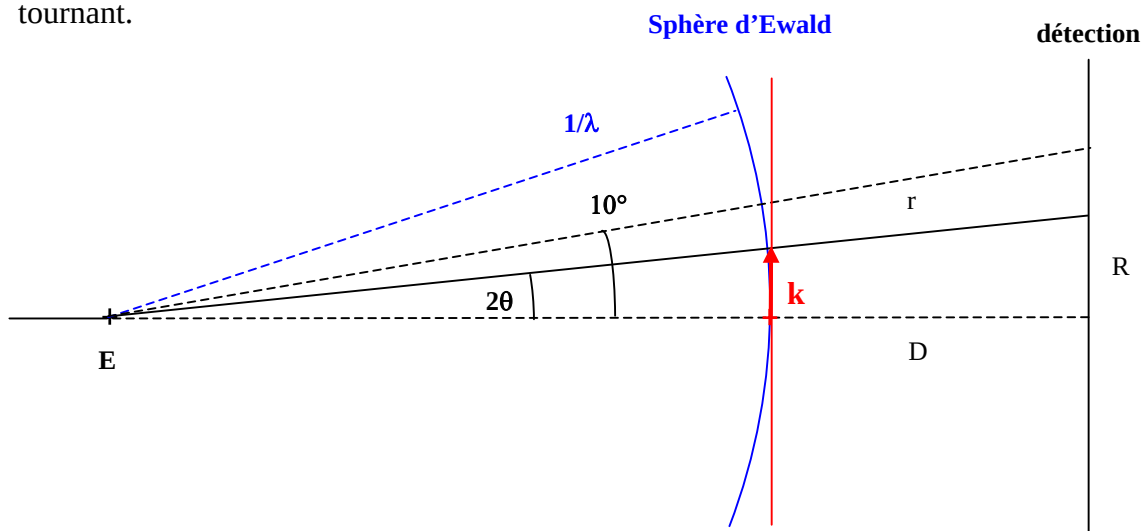


Figure 6-4. Détection dans un plan.

On utilise une détection dans un plan placé à une distance D de l'échantillon. Un signal enregistré une distance R du centre, correspond au vecteur de diffusion suivant :

$$k = \frac{2}{\lambda} \sin \left(\frac{1}{2} \arctan \left(\frac{R}{D} \right) \right) \approx \frac{R}{\lambda D}$$

En unités absolues (par unité de surface dans le plan de détection), on a :

$$I^{abs}(\vec{k}) = \frac{r_0^2}{D^2} T I_0 I(\vec{k})$$

Ainsi, l'intensité I_{ij} d'un pixel ij d'aire Δ , pour une efficacité de détection E , vaut :

$$I_{ij} = \frac{r_0^2}{D^2} T I_0 I(\vec{k}) \Delta E$$

On a donc une proportionnalité directe entre les intensités I_{ij} mesurées et l'intensité $I(\vec{k})$ calculée dans l'espace réciproque. En pratique, on ne réalise pas de mesures en unités absolues, et les formules de correction à appliquer sont finalement les suivantes :

$$I_{poudre}^{int}(k^*) \propto \frac{M(k^*) I_{mono}^{int}(\vec{k}^*)}{k^{*2}}$$

$$I_{rotation}^{int}(\vec{k}^*) \propto \frac{m(k^*) I_{mono}^{int}(\vec{k}^*)}{k_{perp}^*}$$

Lorsque l'angle de Bragg θ est supérieur à approximativement 5° , il faut introduire le facteur de Lorentz, correction géométrique prenant en compte l'effet d'intersection avec la sphère d'Ewald.

Facteur de Lorentz pour une poudre :

Dans l'espace réciproque d'une poudre, la coquille sphérique de rayon k^* et d'épaisseur dk^* contient une intensité total intégrée égale à $M(k^*) I_{mono}^{int}(\vec{k}^*)$.

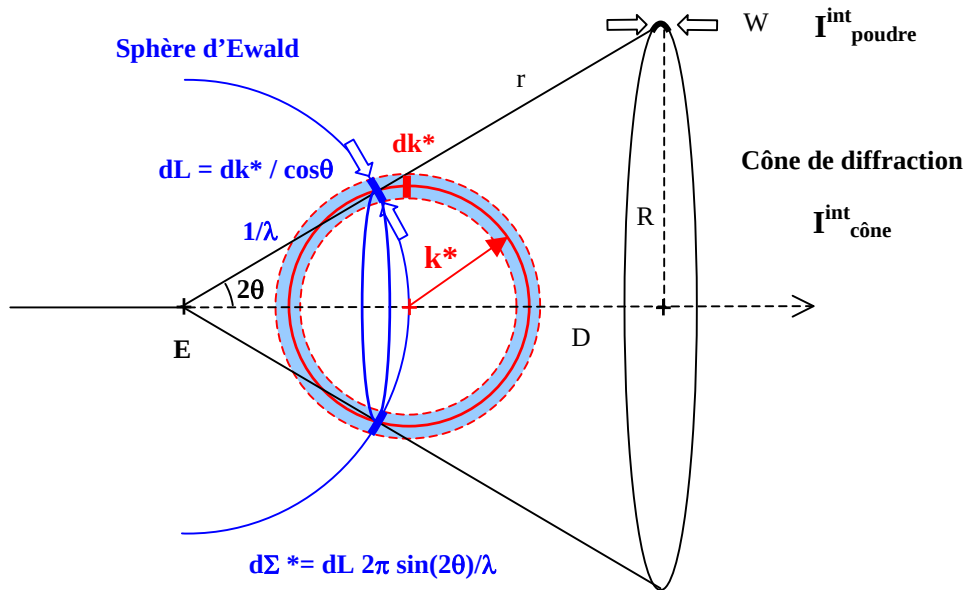


Figure 6-5. Correction de Lorentz pour une poudre.

Le facteur de Lorentz tient compte du fait que le cône de diffraction contient l'intensité provenant uniquement de l'intersection de la sphère d'Ewald avec la coquille sphérique. Ce facteur géométrique est égale à $d\Sigma^*/dV^*$, rapport entre la surface intersectée par la sphère d'Ewald et le volume de la coquille sphérique ($dV^*=4\pi k^{*2}dk^*$). L'intensité totale contenue dans le cône de diffraction, en intégrant sur l'angle solide correspondant, $d\Omega=\lambda^2 d\Sigma^*$, vaut :

$$I_{c\acute{o}ne}^{int}(k^*) = \int_{c\acute{o}ne} Id\Omega = \frac{\lambda^2 d\Sigma^* M(k^*) I_{mono}^{int}(\vec{k}^*)}{4\pi k^{*2} dk^*} = \frac{\lambda^3 M(k^*) I_{mono}^{int}(\vec{k}^*)}{4 \sin(\theta)}$$

Une autre façon d'obtenir ce résultat est de déterminer la proportion de domaines diffractants en position de réflexion dans l'échantillon, c'est-à-dire ceux ayant une famille de plans réticulaires à l'angle de Bragg avec le faisceau direct.

Suivant le dispositif expérimental, on ne détecte pas forcément l'ensemble de l'intensité provenant du cône de diffraction, mais seulement une partie. A une distance r entre l'échantillon et le point de détection, si l'on mesure sur un détecteur de largeur W dans le plan perpendiculaire au plan de diffraction, on obtient :

$$I_{poudre}^{int}(k^*) = \frac{W}{2\pi R} I_{c\acute{o}ne}^{int}(k^*) = \frac{W \lambda^3 M(k^*) I_{mono}^{int}(\vec{k}^*)}{16\pi r \cos(\theta) \sin^2(\theta)}$$

En revenant aux unités absolues, on obtient le facteur dit « Lorentz-polarisation », $\frac{CP}{\cos(\theta)\sin^2(\theta)}$, qui regroupe les termes angulaires en $\cos(\theta)$ et $\sin(\theta)$ ³ :

$$I_{poudre}^{abs}(k^*) = r_0^2(T) I_0 \frac{\lambda^3}{16\pi} \frac{W}{r} \frac{CP}{\cos(\theta)\sin^2(\theta)} M(k^*) I_{mono}^{int}(\vec{k}^*)$$

Pour faire des mesures comparatives d'intensité sur une large gamme de grands angles de Bragg, il est préférable de fixer la distance r . On a ainsi la même distance parcourue par les faisceaux diffractés, ce qui évite d'introduire des corrections d'absorption dans l'air. On utilise un film cylindrique dans le plan équatorial (Chambre de Debye-Sherrer de rayon r) ou un détecteur ponctuel se déplaçant à une distance r fixe autour de l'échantillon (diffractomètre).

En pratique, on ne réalise pas de mesures en unités absolues, et la formule de correction à appliquer est finalement la suivante :

$$I_{poudre}^{int}(k^*) \propto \frac{CP}{\cos(\theta)\sin^2(\theta)} M(k^*) I_{mono}^{int}(\vec{k}^*)$$

Pour les petits angles, le facteur $\frac{CP}{\cos(\theta)\sin^2(\theta)}$ est égal à $1/\sin^2(\theta)$, équivalent au terme en $1/k^{*2}$.

Si l'on détecte néanmoins sur un film plan, en négligeant les corrections d'absorption dans l'air (détection sous vide), $r=D/\cos(2\theta)$, et la correction devient :

$$I_{poudre}^{int}(k^*) \propto \frac{CP\cos(2\theta)}{\cos(\theta)\sin^2(\theta)} M(k^*) I_{mono}^{int}(\vec{k}^*)$$

Agitation thermique : facteur de Debye-Waller

Sous l'effet de la température, les atomes dans un cristal se déplacent autour d'une position moyenne, ce qui diminue l'intensité des pics de diffraction, et ceci plus l'angle de diffusion est grand. Le modèle le plus fréquemment utilisé pour décrire cette diminution est un terme exponentiel appelé facteur de Debye-Waller. La même expression est utilisée par analogie à l'échelle moléculaire, pour rendre compte des déplacements sous l'effet de l'agitation thermique de micelles (par exemple : micelles sphériques dans une phases cubique micellaire ou micelles cylindriques dans une phase hexagonale).

L'expression du terme exponentiel de Debye-Waller est la suivante. On considère pour simplifier un ensemble d'objets identiques, cristallisés sur un réseau aux positions moyennes R_i , de vecteurs déplacements u_i sous l'effet de l'agitation thermique. La moyenne temporelle (notée $\langle \rangle$) de l'amplitude de diffusion est modifiée comme suit :

$$\langle A(\vec{k}) \rangle = \langle \sum_i e^{-2i\pi\vec{k}(\vec{R}_i + \vec{u}_i)} \rangle = \sum_i e^{-2i\pi\vec{k} \cdot \vec{R}_i} (1 - 2\pi^2 \langle (\vec{k} \cdot \vec{u}_i)^2 \rangle + \dots) = \sum_i e^{-2i\pi\vec{k} \cdot \vec{R}_i} e^{-2\pi^2 \langle (\vec{k} \cdot \vec{u}_i)^2 \rangle}$$

Si on note $\langle u^2 \rangle$ l'amplitude moyenne des déplacements, en supposant que ces déplacements se font de manière isotrope dans toutes les directions de l'espace, on obtient l'expression finale :

$$A_{3D} : \langle A(\vec{k}) \rangle = \left(\sum_i e^{-2i\pi\vec{k} \cdot \vec{R}_i} \right) e^{-\frac{2}{3}\pi^2 k^2 \langle u^2 \rangle} \quad \text{et} \quad \boxed{\langle I(\vec{k}) \rangle = I(\vec{k}) e^{-\frac{4}{3}\pi^2 k^2 \langle u^2 \rangle}}$$

A 2D (déplacements dans deux dimensions, cas d'une phase 2D hexagonale) :

$$\langle A(\vec{k}) \rangle = \left(\sum_i e^{-2i\pi \vec{k} \cdot \vec{R}_i} \right) e^{-\pi^2 k^2 \langle u^2 \rangle} \quad \text{et} \quad \boxed{\langle I(\vec{k}) \rangle = I(\vec{k}) e^{-2\pi^2 k^2 \langle u^2 \rangle}}$$

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Chapitre 7

Facteurs de forme

Cette partie rassemble les expressions utiles du facteur de forme de différents objets. On commence par rappeler l'expression classique du facteur de forme d'une sphère et l'on introduit dans ce cas le modèle à deux densités (sphères pleines), puis le modèle à trois densités (modèle cœur/couronne). On donne ensuite les formes d'objets anisotropes, ellipsoïde de révolution et cylindre.

Pour les objets à symétrie sphériques, le facteur de forme se factorise toujours dans l'amplitude de diffusion. Par contre, pour les objets anisotropes, on ne peut pas dissocier le facteur de forme de la distribution d'orientation.

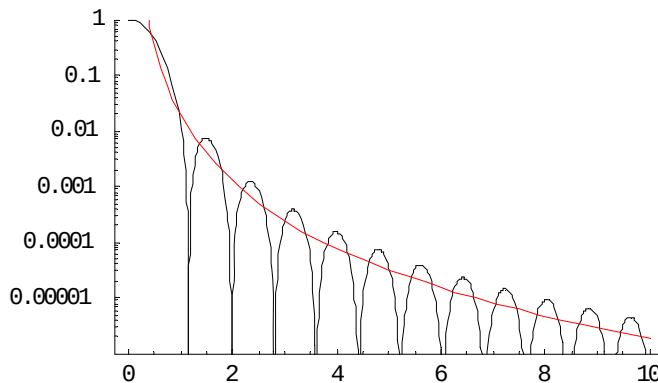
Facteur de forme d'une sphère

L'expression du facteur de forme d'une sphère de rayon R s'intègre facilement en coordonnées sphériques :

$$F_{\text{sphère}}(\vec{k}, R) = \int_{\text{sphère}} e^{-2i\pi\vec{k}\vec{r}'} d^3\vec{r}' = \left(\frac{4}{3}\pi R^3\right) 3 \frac{\sin(2\pi kR) - (2\pi kR)\cos(2\pi kR)}{(2\pi kR)^3}$$

$$I_{\text{sphère}}(k, R) = (F_{\text{sphère}}(k, R))^2 = \left(\frac{4}{3}\pi R^3\right)^2 \left(3 \frac{\sin(2\pi kR) - (2\pi kR)\cos(2\pi kR)}{(2\pi kR)^3}\right)^2$$

L'observation de nombreuses oscillations n'a lieu que pour des sphères très monodisperses.

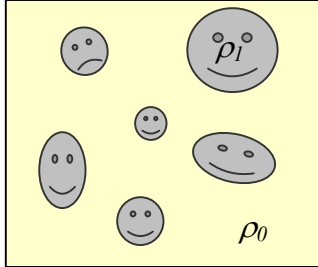


$$\lim_{k \rightarrow +\infty} I_{\text{sphère}}(k, R) = (4\pi R^2) \frac{2\pi}{(2\pi k)^4}$$

Intensité diffusée par une sphère. En rouge, le comportement asymptotique de Porod en $1/k^4$.

Modèle à deux niveaux

Dans un modèle à deux niveaux de densité, on considère des objets de densité ρ_1 dans un milieu continu de densité ρ_0 . L'intégrale s'étend sur tout l'espace, de volume macroscopique V . L'intégration sur ce volume V se décompose de la façon suivante :



$$F_V(\vec{k}) = \int_V \rho(\vec{r}) e^{-2i\pi\vec{k}\vec{r}} d^3\vec{r} = (\rho_1 - \rho_0) \int_{\text{objets}} e^{-2i\pi\vec{k}\vec{r}} d^3\vec{r} + \rho_0 \int_V e^{-2i\pi\vec{k}\vec{r}} d^3\vec{r}$$

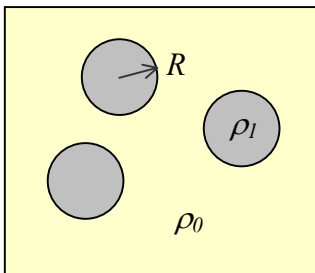
La deuxième intégrale ne contribue que pour des valeurs du module k inférieures à l'inverse d'une dimension de l'échantillon, donc pour des valeurs non mesurables en diffraction X.

Aussi, seules les régions contrastées par rapport au milieu continu de densité ρ_0 contribuent au signal. Ce résultat est général, quel que soit la forme des objets.

$$F_V(\vec{k}) = (\rho_1 - \rho_0) \int_{\text{objets}} e^{-2i\pi\vec{k}\vec{r}} d^3\vec{r}$$

Modèle à deux niveaux d'une assemblée de sphères identiques

C'est une situation simple, où l'amplitude de diffusion se factorise en un produit de trois termes d'origines distinctes :



- le contraste de densité électronique ($\rho_1 - \rho_0$) (ceci est toujours valable pour un modèle à deux niveaux)
- le facteur de forme des objets $F_{\text{sphère}}$ (qui se factorise grâce à la symétrie sphérique et à l'hypothèse de sphères identiques)
- le facteur de structure, sensible aux positions relatives des centres des sphères.

$$F_V(\vec{k}) = (\rho_1 - \rho_0) F_{\text{sphère}}(|\vec{k}|, R) \sum_{\{i\}} e^{-2i\pi\vec{k}\vec{R}_i}$$

Dans le cas où les centres de sphères sont répartis aléatoirement (système dilué, sphères sans interactions), le facteur de structure se réduit au nombre d'objets N et le terme d'interférence est nul. L'intensité diffusée est égale à :

$$I(\vec{k}) = F_V(\vec{k}) F_V^*(\vec{k}) = N (\rho_1 - \rho_0)^2 F_{\text{sphère}}^2(|\vec{k}|, R)$$

Ce cas est en fait un cas idéal, et le plus souvent, la répartition des centres n'est pas totalement aléatoire. Le terme d'interférence est non nul, et le facteur de structure reflète la corrélation entre les positions $\{\vec{R}_i\}$ des centres des sphères.

$$I(\vec{k}) = F_V(\vec{k}) F_V^*(\vec{k}) = (\rho_1 - \rho_0)^2 F_{\text{sphère}}^2(\vec{k}, R) \sum_{\{i\}} e^{-2i\pi\vec{k}\vec{R}_i} \sum_{\{j\}} e^{2i\pi\vec{k}\vec{R}_j}$$

On distingue alors le cas cristallin du cas liquide. Dans le cas d'un cristal (sphères ordonnées sur un réseau, corrélation à longue portée des positions), le facteur de structure donne des pics de Bragg. Connaissant le type du réseau, l'intensité des pics est reliée au facteur de forme des sphères. Si un nombre suffisant de pics de Bragg sont mesurés, on peut même déterminer ce facteur de forme.

Dans le cas d'un liquide, avec un ordre de position à courte portée, il est souvent plus difficile de séparer dans un spectre expérimental la contribution du facteur de forme de celle du facteur de structure. On essaie alors de déterminer indépendamment le facteur de forme, par exemple par une mesure en milieu dilué. On peut aussi distinguer des domaines en k où la contribution de l'un des deux facteurs prédomine.

Le régime de Porod correspond à la limite de $k \rightarrow +\infty$. Dans ce régime, le terme d'interférence peut être considéré constant et égal à 1, et l'expression de l'intensité est celle de sphères indépendantes. En unités absolues (voir chapitre 1), l'intensité s'écrit :

$$I^{abs}(\vec{k}) = \frac{r_0^2}{r^2} (CP)(T) I_0 N (4\pi R^2) (\rho_1 - \rho_0)^2 \frac{2\pi}{(2\pi k)^4} = \frac{r_0^2}{r^2} (CP)(T) I_0 \Sigma (\rho_1 - \rho_0)^2 \frac{2\pi}{(2\pi k)^4}$$

Pour les grandes valeurs de k , l'intensité est proportionnelle à $\Sigma = N (4\pi R^2)$ qui est l'aire totale de la surface qui sépare les deux milieux de densités ρ_1 et ρ_0 .

On rencontre souvent l'expression normalisée suivante, qui a la dimension de l'inverse d'une longueur, où V est le volume d'échantillon et Σ/V la surface par unité de volume :

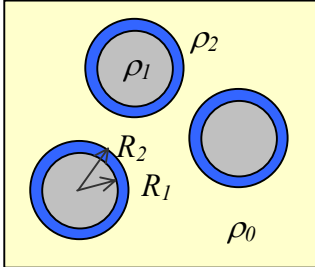
$$I^{norm}(\vec{k}) = I^{abs}(\vec{k}) r^2 \frac{1}{(CP)(T) I_0} \frac{1}{V} = r_0^2 \frac{\Sigma}{V} (\rho_1 - \rho_0)^2 \frac{2\pi}{(2\pi k)^4}$$

Rq : Dans le cas de la diffusion par les neutrons (voir chapitre 12), l'expression fait intervenir les densités de longueur de diffusion des deux milieux :

$$\text{Neutrons : } I^{norm}(\vec{k}) = \frac{\Sigma}{V} (\rho_{n1} - \rho_{n0})^2 \frac{2\pi}{(2\pi k)^4}$$

Modèle à trois niveaux de sphères : modèle cœur/couronne

De nombreux objets à symétrie sphériques nécessitent au moins un modèle à trois niveaux pour être correctement décrits (micelles, particules habillées en surface ...). On se placera toujours dans l'hypothèse de particules identiques.



$$F_V(\vec{k}) = \left((\rho_2 - \rho_0) F_{\text{sphère}}(\vec{k}, R_2) + (\rho_1 - \rho_2) F_{\text{sphère}}(\vec{k}, R_1) \right) \sum_{\{i\}} e^{-2i\pi\vec{k}\vec{R}_i}$$

L'intégration sur tout le volume de la quantité ρ_0 est négligée comme dans le cas d'un modèle à deux niveaux.

On conserve la factorisation du facteur de forme à cause de la symétrie sphérique. Par contre, les effets de contraste de densité électronique et des dimensions de l'objet (les deux rayons R_1 et R_2 de la couronne) sont combinés. Dans le cas d'un fit de données, on a trois paramètres ajustables, les deux rayons R_1 et R_2 et un rapport de contrastes de densités, par exemple :

$$\alpha = \frac{(\rho_1 - \rho_2)}{(\rho_2 - \rho_0)}$$

Coquille sphérique

C'est le cas où le contraste provient uniquement de la couronne, et l'on a : $\rho_1 = \rho_0$. Le terme de contraste de densité électronique se factorise à nouveau puisque l'on est ramené à un modèle à deux niveaux de densité :

$$F_V(\vec{k}) = (\rho_2 - \rho_0) \left(F_{\text{sphère}}(\vec{k}, R_2) - F_{\text{sphère}}(\vec{k}, R_1) \right) \sum_{\{i\}} e^{-2i\pi\vec{k}\vec{R}_i}$$

Si la coquille sphérique est fine, d'une épaisseur ΔR petite devant son rayon R , on a :

$$F_{\text{sphère}}(\vec{k}, R_2) - F_{\text{sphère}}(\vec{k}, R_1) = \Delta R F_{\text{coquille}}(\vec{k}, R)$$

$$F_{\text{coquille}}(\vec{k}, R) = 4\pi R^2 \frac{\sin(2\pi kR)}{2\pi kR}$$

Facteur de forme d'un ellipsoïde de révolution

On considère un ellipsoïde de révolution, de demi-axes R et vR . Pour $v < 1$, l'ellipsoïde est aplati et allongé pour $v > 1$. Le facteur de forme se déduit de celui d'une sphère. En effet, on obtient l'ellipsoïde en multipliant par un coefficient v les longueurs suivant l'axe $z'z$ d'une sphère de rayon R . D'où :

$$F_{\text{ellipsoïde}}(\vec{k}, R, v) = v F_{\text{sphère}}(\vec{k}_{\text{perp}} + v \vec{k}_z, R)$$

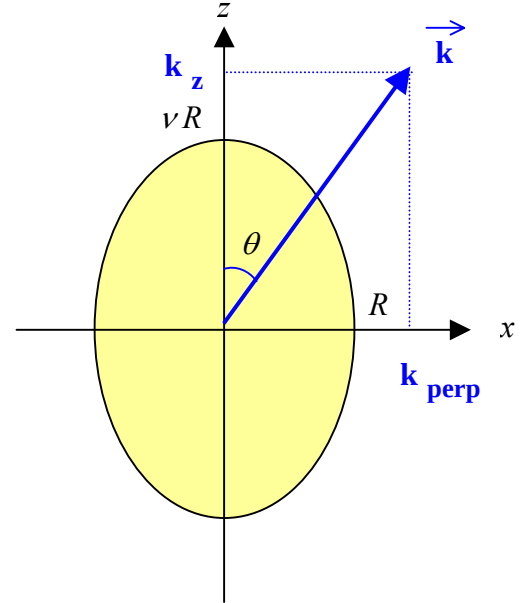
car :

$$\vec{k} \cdot \vec{r} = (\vec{k}_{\text{perp}} + \vec{k}_z) \cdot (\vec{r}_{\text{perp}} + \vec{z}) = \vec{k}_{\text{perp}} \cdot \vec{r}_{\text{perp}} + v \vec{k}_z \cdot \vec{z}'$$

avec $\vec{k}' = \vec{k}_{\text{perp}} + v \vec{k}_z$

$$k' = \sqrt{k_{\text{perp}}^2 + v^2 k_z^2} = k \sqrt{\frac{k_{\text{perp}}^2 + v^2 k_z^2}{k_{\text{perp}}^2 + k_z^2}} = k \sqrt{1 + \cos^2(\theta)(v^2 - 1)}$$

$$F_{\text{ellipsoïde}}(\vec{k}, R, v) = v F_{\text{sphère}}(k \sqrt{1 + \cos^2(\theta)(v^2 - 1)}, R)$$

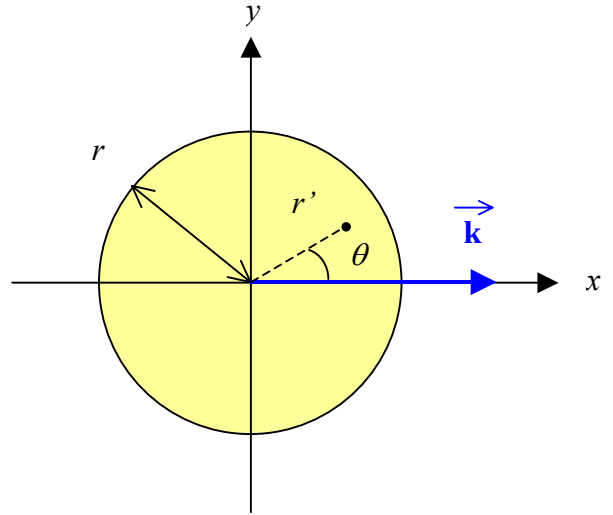


$$F_{\text{ellipsoïde}}(\vec{k}, R, v) = \left(\frac{4}{3} \pi v R^3 \right) \frac{3 \left[\sin(2\pi k R \sqrt{1 + \cos^2(\theta)(v^2 - 1)}) - (2\pi k R \sqrt{1 + \cos^2(\theta)(v^2 - 1)}) \cos(2\pi k R \sqrt{1 + \cos^2(\theta)(v^2 - 1)}) \right]}{(2\pi k R \sqrt{1 + \cos^2(\theta)(v^2 - 1)})^3}$$

Facteur de forme d'un disque

Soit l'expression du facteur de forme d'un disque :

$$F(\vec{k}) = \int_{\text{disque}} e^{-2i\pi\vec{k}\vec{r}'} d^2\vec{r}'$$



On intègre en coordonnées polaires, en choisissant l'axe de référence de l'angle polaire θ le long de la direction du vecteur $\vec{k}$.

$$F(\vec{k}) = \int_0^r r' \left(\int_0^{2\pi} e^{-2i\pi k r' \cos(\theta)} d\theta \right) dr' = 2 \int_0^r r' \left(\int_0^{\pi} \cos(2\pi k r' \cos(\theta)) d\theta \right) dr'$$

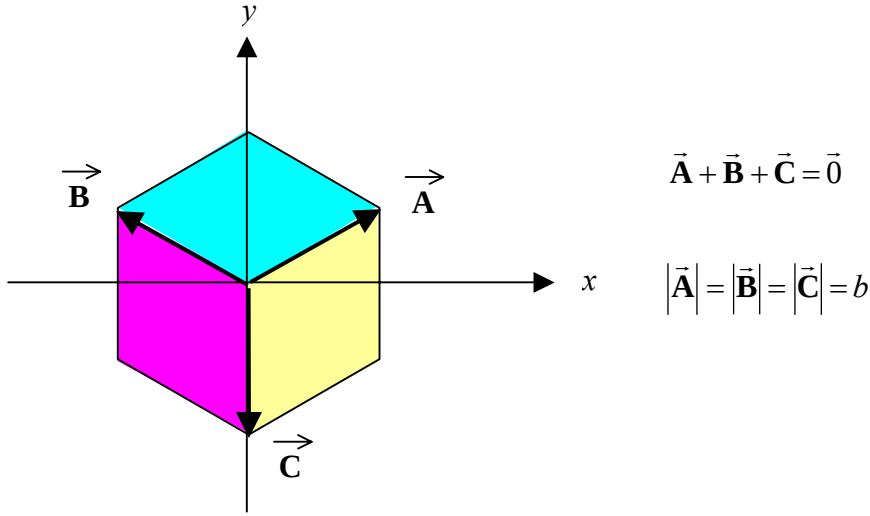
$$F(\vec{k}) = 2\pi \int_0^r r' J_0(2\pi k r') dr' \quad \text{car} \quad J_0(y) = \frac{1}{\pi} \int_0^{\pi} \cos(y \cos(\theta)) d\theta$$

où J_0 est la fonction de Bessel d'ordre 0.

Le facteur de forme fait intervenir la fonction de Bessel d'ordre 1, notée J_1 :

$$F_{\text{disque}}(\vec{k}) = \pi r^2 \frac{J_1(2\pi k r)}{\pi k r} \quad \text{car} \quad y J_1(y) = \int_0^y y' J_0(y') dy'$$

Facteur de forme d'un hexagone



Le facteur de forme d'un hexagone peut se décomposer en trois intégrales :

$$F(\vec{k}) = \int_{S_{AB}} e^{-2i\pi\vec{k}\vec{r}} d^2\vec{r} + \int_{S_{BC}} e^{-2i\pi\vec{k}\vec{r}} d^2\vec{r} + \int_{S_{CA}} e^{-2i\pi\vec{k}\vec{r}} d^2\vec{r} = F_{AB}(\vec{k}) + F_{BC}(\vec{k}) + F_{CA}(\vec{k})$$

$$F_{AB}(\vec{k}) = \int_{S_{AB}} e^{-2i\pi\vec{k}\vec{r}} d^2\vec{r} = \int_0^1 \int_0^1 \sin\left(\frac{2\pi}{3}\right) b^2 e^{-2i\pi\vec{k}\cdot(X\vec{A}+Y\vec{B})} dXdY$$

avec $\vec{r} = X\vec{A} + Y\vec{B}$ $0 \leq X \leq 1$ et $0 \leq Y \leq 1$

$$F_{AB}(\vec{k}) = \frac{\sqrt{3}}{2} b^2 e^{i\pi\vec{k}\cdot\vec{C}} \frac{\sin(\pi\vec{k}\cdot\vec{A})}{(\pi\vec{k}\cdot\vec{A})} \frac{\sin(\pi\vec{k}\cdot\vec{B})}{(\pi\vec{k}\cdot\vec{B})}$$

Le facteur de forme est une fonction réelle, qui s'écrit :

$$F_{\text{hexagone}}(\vec{k}) = \frac{\sqrt{3}}{2} b^2 \left(\begin{aligned} &\cos(\pi\vec{k}\cdot\vec{C}) \frac{\sin(\pi\vec{k}\cdot\vec{A})}{(\pi\vec{k}\cdot\vec{A})} \frac{\sin(\pi\vec{k}\cdot\vec{B})}{(\pi\vec{k}\cdot\vec{B})} + \cos(\pi\vec{k}\cdot\vec{A}) \frac{\sin(\pi\vec{k}\cdot\vec{B})}{(\pi\vec{k}\cdot\vec{B})} \frac{\sin(\pi\vec{k}\cdot\vec{C})}{(\pi\vec{k}\cdot\vec{C})} \\ &+ \cos(\pi\vec{k}\cdot\vec{B}) \frac{\sin(\pi\vec{k}\cdot\vec{C})}{(\pi\vec{k}\cdot\vec{C})} \frac{\sin(\pi\vec{k}\cdot\vec{A})}{(\pi\vec{k}\cdot\vec{A})} \end{aligned} \right)$$

Facteur de forme d'un cylindre

L'expression du facteur de forme d'un cylindre de rayon R et de longueur L est :

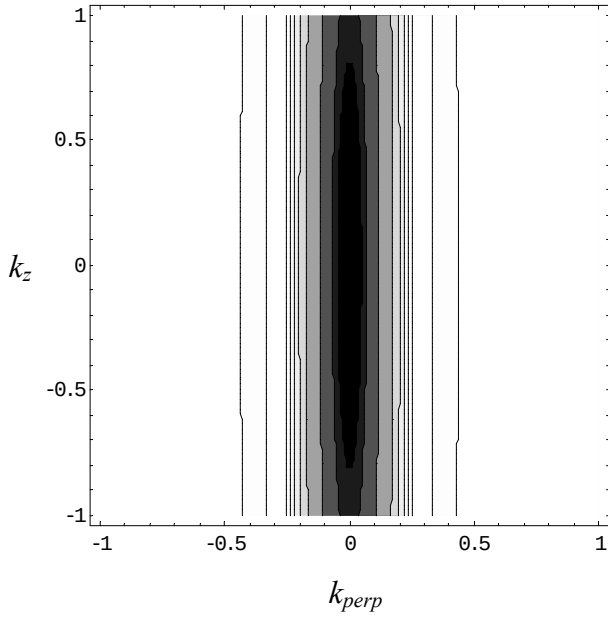
$$F_{cylindre}(\vec{k}, R, L) = \pi R^2 L \frac{J_1(2\pi k_{perp} R)}{\pi k_{perp} R} \frac{\sin(\pi k_z L)}{\pi k_z L}$$

où k_z est la composante du vecteur de diffusion le long de l'axe du cylindre et k_{perp} la composante perpendiculaire dans le plan de base. Le calcul pour la composante k_{perp} est celui d'un disque (page 62). La **figure 7-1** représente l'intensité diffusée par un cylindre de volume constant mais dont le rapport d'aspect (L/R) varie.

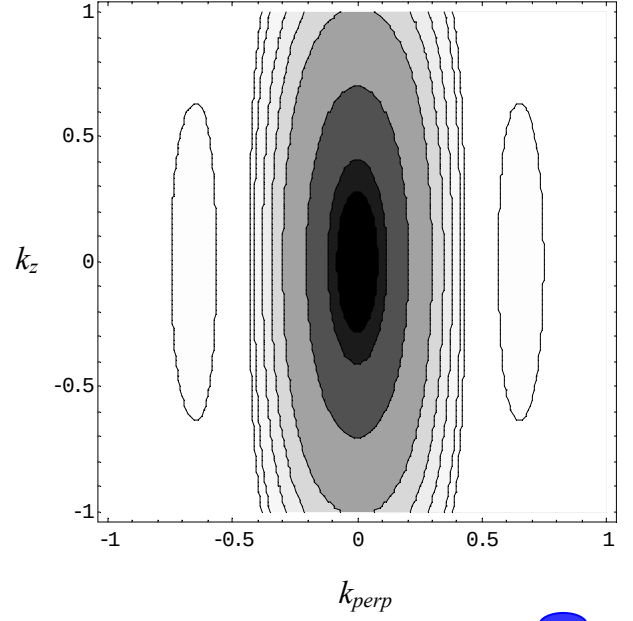
$$I_{cylindre}(\vec{k}, R, L) = V_{cylindre}^2 \left(\frac{J_1(2\pi k_{perp} R)}{\pi k_{perp} R} \right)^2 \left(\frac{\sin(\pi k_z L)}{\pi k_z L} \right)^2$$

Figure 7-1. (page 65) *Intensité diffusée par un cylindre de volume constant pour différents rapports d'aspect. Les lignes iso-intensités sont prises à 1%, 2%, 5%, 10%, 20%, 50%, 80% et 90% de l'intensité maximale à l'origine.*

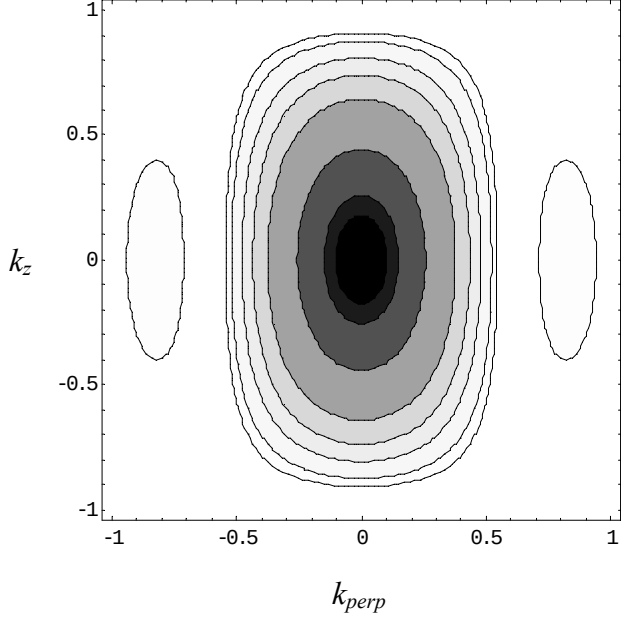
$L/R = 0.1$ $R = 2.154$ $L =$ 



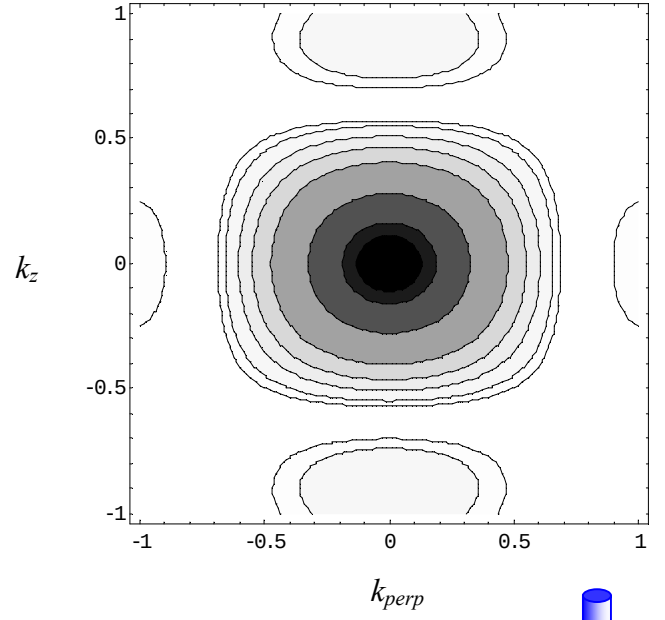
$L/R = 0.5$ $R = 1.260$ $L =$ 



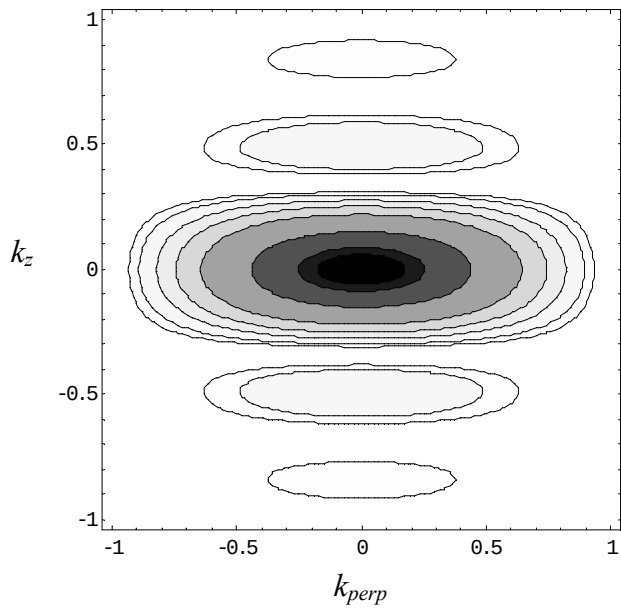
$L/R = 1$ $R = 1$ $L = 1$ 



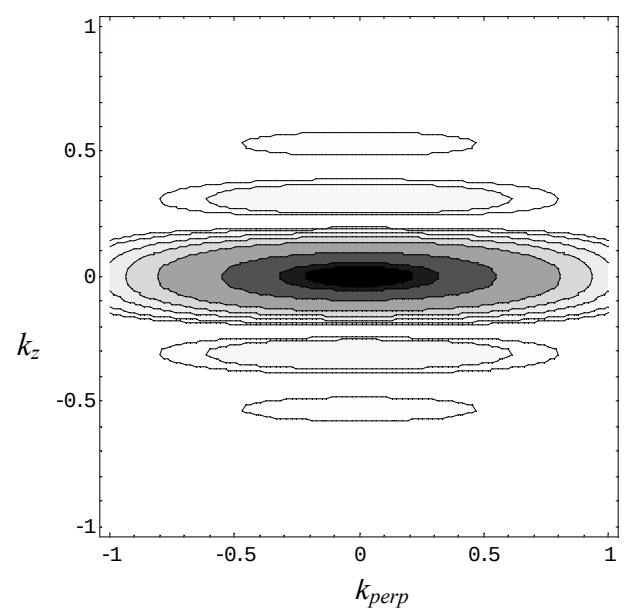
$L/R = 2$ $R = 0.794$ $L = 1.587$ 



$L/R = 5$ $R = 0.585$ $L = 2.924$ 



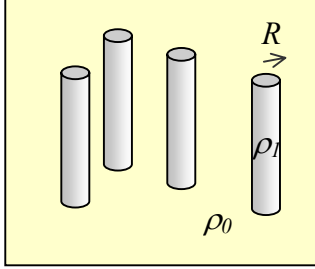
$L/R = 10$ $R = 0.464$ $L = 4.642$ 



Assemblée de cylindres parallèles

Par analogie avec les modèles à deux et trois niveaux d'une assemblée de sphère, on déduit les expressions ci-dessous :

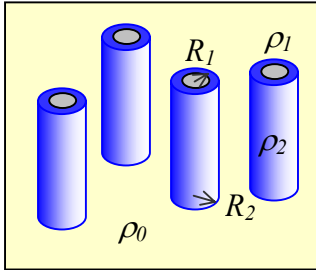
Modèle à deux niveaux



$$F_V(\vec{k}) = (\rho_1 - \rho_0) F_{cylindre}(\vec{k}, R) \sum_{\{i\}} e^{-2i\pi\vec{k}\vec{R}_i}$$

$$I(\vec{k}) = (\rho_1 - \rho_0)^2 V_{cylindre}^2 \left(\frac{J_1(2\pi k_{perp} R)}{\pi k_{perp} R} \right)^2 \left(\frac{\sin(\pi k_z L)}{\pi k_z L} \right)^2 \sum_{\{i\}} e^{-2i\pi\vec{k}_{perp}\vec{R}_i} \sum_{\{j\}} e^{2i\pi\vec{k}_{perp}\vec{R}_j}$$

Modèle à trois niveaux



$$F_V(\vec{k}) = \left((\rho_2 - \rho_0) F_{cylindre}(\vec{k}, R_2) + (\rho_1 - \rho_2) F_{cylindre}(\vec{k}, R_1) \right) \sum_{\{i\}} e^{-2i\pi\vec{k}\vec{R}_i}$$

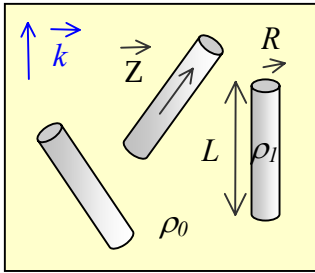
$$I(\vec{k}) = (\pi L)^2 \left((\rho_2 - \rho_0) R_2^2 \left(\frac{J_1(2\pi k_{perp} R_2)}{\pi k_{perp} R_2} \right) + (\rho_1 - \rho_2) R_1^2 \left(\frac{J_1(2\pi k_{perp} R_1)}{\pi k_{perp} R_1} \right) \right)^2 \left(\frac{\sin(\pi k_z L)}{\pi k_z L} \right)^2 \left(\sum_{\{i\}} e^{-2i\pi\vec{k}_{perp}\vec{R}_i} \sum_{\{j\}} e^{2i\pi\vec{k}_{perp}\vec{R}_j} \right)$$

Cylindres orientés aléatoirement

On fait l'hypothèse de cylindres diffusant indépendamment les uns des autres, et prenant toutes les orientations possibles dans l'espace. L'intensité diffusée est alors la somme des intensités diffusées par chaque cylindre. Comme pour les sphères, cette formule est un cas limite, et une telle répartition est rarement réalisée. Les objets étant anisotropes, elle nécessite une distribution aléatoire de leurs positions ainsi que de leurs orientations.

Modèle à deux niveaux

On réalise une moyenne sur l'orientation de la direction $\vec{Z}$ d'un cylindre :



$$I(k) = N (\rho_1 - \rho_0)^2 \int_{\vec{Z}} F_{cylindre}^2(\vec{k}, R) d\vec{Z}$$

avec :

$$F_{cylindre}(\vec{k}, R, L) = \pi R^2 L \frac{J_1(2\pi k_{perp} R)}{\pi k_{perp} R} \frac{\sin(\pi k_z L)}{\pi k_z L}$$

On fixe la direction du vecteur $\vec{k}$, parallèle à $\vec{Z}$, et le vecteur unitaire $\vec{Z}$ décrit la sphère unité (toutes les orientations sont possibles et équiprobables).

$$\vec{Z} = \cos(\theta) \vec{z} + \sin(\theta) \cos(\varphi) \vec{x} + \sin(\theta) \sin(\varphi) \vec{y}$$

$$I(k) = N (\rho_1 - \rho_0)^2 (\pi R^2 L)^2 \frac{1}{4\pi} \left(\int_0^\pi \left(\frac{J_1(2\pi k \sin(\theta) R)}{\pi k \sin(\theta) R} \right)^2 \left(\frac{\sin(\pi k \cos(\theta) L)}{\pi k \cos(\theta) L} \right)^2 \sin(\theta) d\theta \right) \left(\int_0^{2\pi} d\varphi \right)$$

$$I(k) = N (\rho_1 - \rho_0)^2 (\pi R^2 L)^2 \frac{1}{2} \left(\int_0^{\pi/2} \left(\frac{J_1(2\pi k \sin(\theta) R)}{\pi k \sin(\theta) R} \right)^2 \left(\frac{\sin(\pi k \cos(\theta) L)}{\pi k \cos(\theta) L} \right)^2 \sin(\theta) d\theta \right)$$

Le domaine d'intégration peut se réduire de 0 à $\pi/2$. En effet, les orientations θ et $\pi - \theta$ sont équivalentes.

$$I(k) = N (\rho_1 - \rho_0)^2 (\pi R^2 L)^2 \left(\int_0^{\pi/2} \left(\frac{J_1(2\pi k \sin(\theta) R)}{\pi k \sin(\theta) R} \right)^2 \left(\frac{\sin(\pi k \cos(\theta) L)}{\pi k \cos(\theta) L} \right)^2 \sin(\theta) d\theta \right)$$

Cette expression peut s'intégrer numériquement si besoin dans le cas général. Néanmoins, on effectue le plus souvent des hypothèses supplémentaires pour simplifier cette intégrale. En particulier, on distingue le cas des disques ($R > L$) et celui des cylindres ($R < L$).

Disque mince (limite $L = 0$ et $R \gg L$)

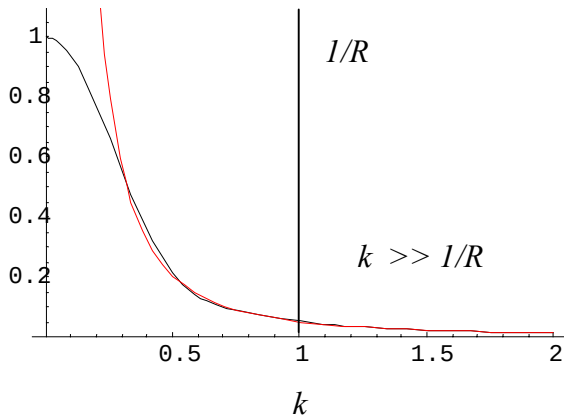
Dans le cas des disques minces, on aboutit à une expression analytique :

$$I_{disque}(k) = N (\rho_1 - \rho_0)^2 V_{disque}^2 \frac{2}{(2\pi k R)^2} \left(1 - \frac{J_1(4\pi k R)}{2\pi k R} \right)$$

Cette expression est utile pour décrire la courbe de diffusion pour $k < 1/R$. Pour des valeurs de k supérieures à $1/R$, on peut utiliser l'expression asymptotique suivante :

$$I_{disque}(k) = N (\rho_1 - \rho_0)^2 V_{disque}^2 \frac{2}{(2\pi k R)^2}$$

Cette seconde expression est valable tant que $k \ll 1/L$, pour rester dans l'approximation de disques minces. Au-delà, on est ramené au cas général. Ainsi, pour des disques d'épaisseur finie, on utilise les expressions précédentes tant que $k \ll 1/L$.



On a tracé ci-contre l'expression de I_{disque} (courbe en noir) et l'expression asymptotique en $1/k^2$ (courbe en rouge).

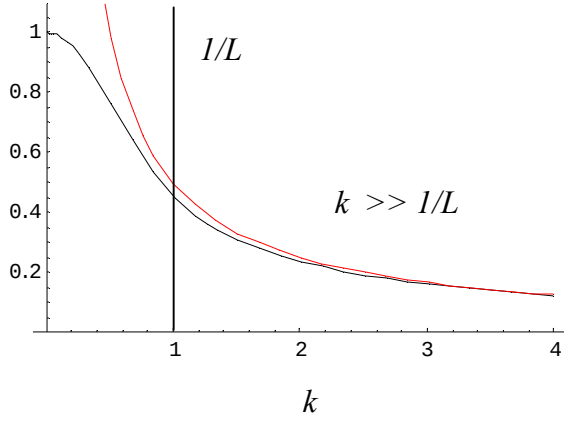
Ligne mince (limite $R = 0$ et $R \ll L$)

Dans le cas de lignes minces, on aboutit également à une expression analytique :

$$I_{ligne}(k) = N (\rho_1 - \rho_0)^2 V_{ligne}^2 \frac{1}{\pi k L} \left(\sin I(2\pi k L) - \frac{\sin^2(\pi k L)}{\pi k L} \right) \quad \text{avec :} \quad \sin I(x) = \int_0^x \frac{\sin u}{u} du$$

Lorsque $k \gg 1/L$, on obtient l'expression asymptotique suivante en $1/k$:

$$I_{ligne}(k) = N (\rho_1 - \rho_0)^2 V_{ligne}^2 \frac{1}{2kL}$$



On a tracé ci-contre l'expression de I_{ligne} (courbe en noir) et l'expression asymptotique en $1/k$ (courbe en rouge).

Cylindres ($R \ll L$)

Lorsque l'anisotropie est grande ($R \ll L$), on peut simplifier l'intégrale sur toutes les orientations comme une somme de deux termes, l'un dépendant de R et l'autre de L . Seuls contribuent les cylindres dont l'orientation est proche de la perpendiculaire au vecteur k . En considérant $\varepsilon = \cos\theta$ comme une quantité petite, on factorise l'intégrale de départ en une partie dépendante de R et l'autre de L . L'intégrale sur ε est étendue de 0 jusqu'à $+\infty$.

$$I(k) = N (\rho_1 - \rho_0)^2 (\pi R^2 L)^2 \left(\frac{J_1(2\pi k R)}{\pi k R} \right)^2 \left(\int_0^{+\infty} \left(\frac{\sin(\pi k \varepsilon L)}{\pi k \varepsilon L} \right)^2 d\varepsilon \right)$$

$$I(k) = N (\rho_1 - \rho_0)^2 (\pi R^2 L)^2 \left(\frac{J_1(2\pi k R)}{\pi k R} \right)^2 \frac{1}{2kL}$$

On retrouve bien l'expression d'une ligne lorsque R tend vers 0.

La **figure 7-2** montre comment se situe cette expression approchée par rapport au calcul exact par intégration sur toutes les orientations. Pour $R = 1$ et $L = 5$, les oscillations de la fonction de Bessel sont mieux évaluées par l'expression exacte. Lorsque $R = 0.05$, on est essentiellement ramené à la diffusion par une ligne.

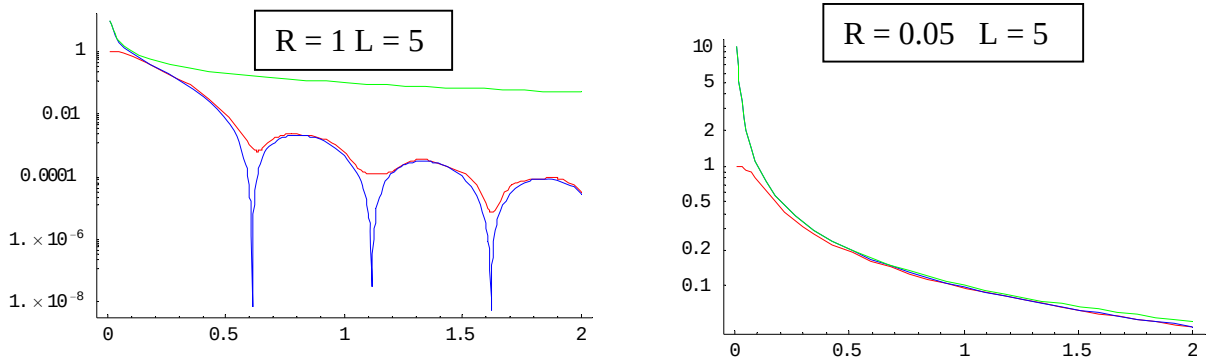
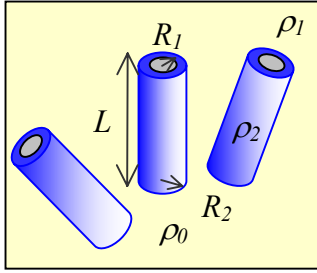


Figure 7-2. Expression exacte (en rouge, intégrale sur toutes les orientations) et expression approchée (en bleu, expression ci-dessus) – a : pour $R=1$ et $L=5$. – b : pour $R=0.05$ et $L=5$. La courbe en vert est l'expression de la diffusion par une ligne en $1/2kL$.

Modèle à trois niveaux

($R \ll L$) :



$$I(k) = N (\pi L)^2 \left((\rho_2 - \rho_0) R_2^2 \left(\frac{J_1(2\pi k R_2)}{\pi k R_2} \right) + (\rho_1 - \rho_2) R_1^2 \left(\frac{J_1(2\pi k R_1)}{\pi k R_1} \right) \right)^2 \frac{1}{2kL}$$

Cas général :

$$I(k) = N \int_0^{\pi/2} \left((\rho_2 - \rho_0) \left(\pi R_2^2 L \right) \frac{J_1(2\pi k \sin(\theta) R_2)}{\pi k \sin(\theta) R_2} + (\rho_1 - \rho_2) \left(\pi R_1^2 L \right) \frac{J_1(2\pi k \sin(\theta) R_1)}{\pi k \sin(\theta) R_1} \right)^2 \left(\frac{\sin(\pi k \cos(\theta) L)}{\pi k \cos(\theta) L} \right)^2 \sin(\theta) d\theta$$

Ellipsoïdes orientés aléatoirement

Modèle à deux niveaux

L'expression se déduit directement de la moyenne d'orientation comme pour les cylindres.

$$I_{\text{ellipsoïde}}(k, R, v) = N (\rho_1 - \rho_0)^2 \left(\frac{4}{3} \pi v R^3 \right)^2 \int_0^{\pi/2} 3 \frac{\sin(2\pi k R \sqrt{1+\cos^2(\theta)(v^2-1)}) - (2\pi k R \sqrt{1+\cos^2(\theta)(v^2-1)}) \cos(2\pi k R \sqrt{1+\cos^2(\theta)(v^2-1)})}{(2\pi k R \sqrt{1+\cos^2(\theta)(v^2-1)})^3}^2 \sin(\theta) d\theta$$

$$I_{\text{ellipsoïde}}(k, R, v) = N (\rho_1 - \rho_0)^2 \left(\frac{4}{3} \pi v R^3 \right)^2 \int_0^1 3 \frac{\sin(2\pi k R \sqrt{1+x^2(v^2-1)}) - (2\pi k R \sqrt{1+x^2(v^2-1)}) \cos(2\pi k R \sqrt{1+x^2(v^2-1)})}{(2\pi k R \sqrt{1+x^2(v^2-1)})^3}^2 dx$$

En conclusion sur cette partie, le cas simple et bien connu des sphères a permis d'introduire les modèles à deux et trois niveaux de densité, ainsi que la factorisation en facteur de forme et facteur de structure. Ces notions ont été étendues au cas des cylindres (ou des ellipsoïdes), moyennant des hypothèses supplémentaires puisque les objets ne sont plus à symétrie sphérique : cylindres infinis ou disques minces, alignement de tous les objets ou orientation aléatoire complète.

Chapitre 8

Phase hexagonale

Une phase hexagonale 2D résulte de l'assemblage d'objets longs. les objets assemblés sont le plus souvent considérés comme infinis suivant la direction d'assemblage et la diffraction est restreinte au plan perpendiculaire à cette direction.

On établit tout d'abord l'expression de la diffraction par un réseau 2D de ces objets. On donne ensuite la formule de l'intensité diffractée dans le cas d'une poudre.

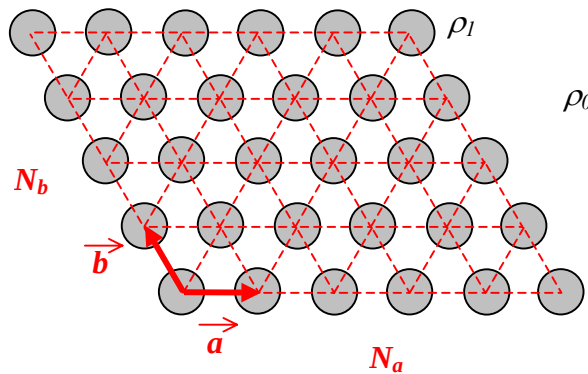
Enfin, l'effet de la forme de la section des objets est abordé et deux sections sont considérées, soit un disque, soit un hexagone.

Diffraction par un réseau hexagonal 2D de cylindres

On établit la formule générale de l'intensité diffusée pour une phase hexagonale de cylindres, dans un modèle à deux niveaux. Les cylindres sont tous parallèles entre eux, et l'on a :

$$A(\vec{k}) = (\rho_1 - \rho_0) V_{\text{cylindre}} \left(\frac{J_1(2\pi k_{\text{perp}} R)}{\pi k_{\text{perp}} R} \right) \left(\frac{\sin(\pi k_z L)}{\pi k_z L} \right) \sum_{\{i\}} e^{-2i\pi \vec{k}_{\text{perp}} \vec{R}_i}$$

On note $(\vec{a}, \vec{b})$ les vecteurs de base de la maille 2D. Les vecteurs $\vec{R}_i$ sont de la forme $n\vec{a} + m\vec{b}$, et l'on considère un cristal macroscopique contenant N_a mailles suivant $\vec{a}$ et N_b mailles suivant $\vec{b}$.



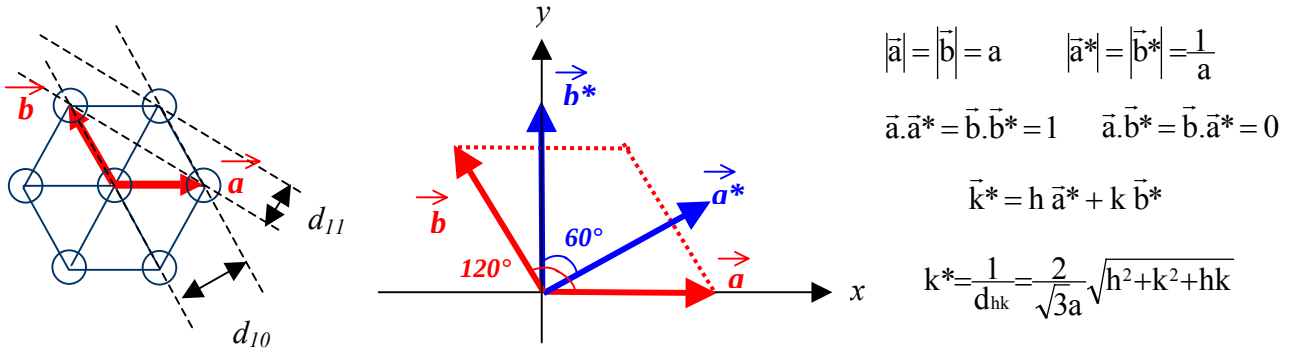
$$I(\vec{k}) = (\rho_1 - \rho_0)^2 V_{cylindre}^2 \left(\frac{J_1(2\pi k_{perp} R)}{\pi k_{perp} R} \right)^2 \left(\frac{\sin(\pi k_z L)}{\pi k_z L} \right)^2 \left(\frac{\sin(N_a \pi \vec{k}_{perp} \cdot \vec{a})}{\sin(\pi \vec{k}_{perp} \cdot \vec{a})} \right)^2 \left(\frac{\sin(N_b \pi \vec{k}_{perp} \cdot \vec{b})}{\sin(\pi \vec{k}_{perp} \cdot \vec{b})} \right)^2$$

où l'on utilise la sommation :

$$\sum_{\{i\}} e^{-2i\pi \vec{k}_{perp} \cdot \vec{R}_i} = \sum_{n=0}^{N_a-1} \sum_{m=0}^{N_b-1} e^{-2i\pi \vec{k}_{perp} \cdot (n\vec{a} + m\vec{b})} =$$

$$e^{-i\pi (N_a-1) \vec{k}_{perp} \cdot \vec{a}} e^{-i\pi (N_b-1) \vec{k}_{perp} \cdot \vec{b}} \frac{\sin(N_a \pi \vec{k}_{perp} \cdot \vec{a})}{\sin(\pi \vec{k}_{perp} \cdot \vec{a})} \frac{\sin(N_b \pi \vec{k}_{perp} \cdot \vec{b})}{\sin(\pi \vec{k}_{perp} \cdot \vec{b})}$$

On se place dans le cas d'un cristal macroscopique, de dimensions $N_a a$, $N_b a$ et L . En particulier, la longueur L des cylindres est comparable aux deux autres dimensions. L'intensité $I(\vec{k})$ est alors non nulle seulement au voisinage de pics de Bragg placé dans l'espace réciproque en : $\vec{k} = \vec{k}^* = h \vec{a}^* + k \vec{b}^*$. Par convention, en symétrie hexagonale, il y a un angle de 120° entre les vecteurs du réseau réel, et un angle de 60° entre ceux du réseau réciproque :



Réseau réciproque d'une phase hexagonale 2D

L'intensité mesurée dans une expérience est alors l'intensité intégrée autour de chaque pic de Bragg. Autour du pic de Bragg $\vec{k}^*$, le vecteur de diffusion s'écrit : $\vec{k} = \vec{k}^* + K_a \vec{a}^* + K_b \vec{b}^* + k_z \vec{z}$, et l'intensité vaut :

$$I(\vec{k}) = (\rho_1 - \rho_0)^2 V_{cylindre}^2 \left(\frac{J_1(2\pi k^* R)}{\pi k^* R} \right)^2 \left(\frac{\sin(\pi k_z L)}{\pi k_z L} \right)^2 \left(\frac{\sin(N_a \pi K_\alpha)}{\sin(\pi K_\alpha)} \right)^2 \left(\frac{\sin(N_b \pi K_\beta)}{\sin(\pi K_\beta)} \right)^2$$

On peut intégrer cette expression de $-\infty$ à $+\infty$ en K_a , K_b et k_z et en se ramenant à l'intégrale connue

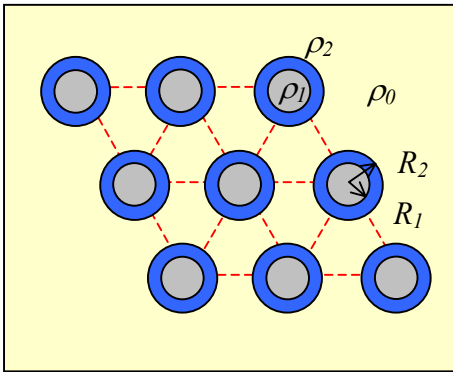
$$\int_{-\infty}^{+\infty} \left(\frac{\sin(x)}{x} \right)^2 = \pi.$$

Finalement, l'intensité intégrée mesurée en un pic de Bragg est :

$$I_{\text{mono}}^{\text{int}}(k^*) = (\rho_1 - \rho_0)^2 V_{\text{cylindre}}^2 \left(\frac{J_1(2\pi k^* R)}{\pi k^* R} \right)^2 \frac{1}{L} \frac{N_a N_b}{S_{\text{maille}}} = (\rho_1 - \rho_0)^2 \left(\frac{\pi R^2}{S_{\text{maille}}} \right)^2 V_{\text{cristal}} \left(\frac{J_1(2\pi k^* R)}{\pi k^* R} \right)^2$$

avec : $V_{\text{cristal}} = S_{\text{maille}} L N_a N_b$

Modèle à trois niveaux



Ce modèle à trois densités, avec une couronne de densité ρ_2 , a été introduit dans le chapitre 7. L'expression de l'intensité intégrée d'un pic se déduit aisément du cas précédent :

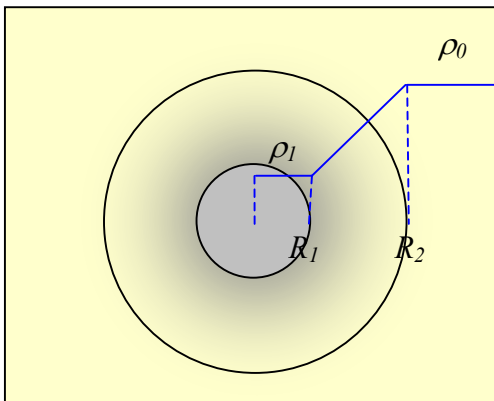
$$I_{\text{mono}}^{\text{int}}(k^*) = \left(\frac{\pi}{S_{\text{maille}}} \right)^2 V_{\text{cristal}} \left((\rho_2 - \rho_0) R_2^2 \left(\frac{J_1(2\pi k^* R_2)}{\pi k^* R_2} \right) + (\rho_1 - \rho_2) R_1^2 \left(\frac{J_1(2\pi k^* R_1)}{\pi k^* R_1} \right) \right)^2$$

On a également établi l'expression de l'intensité dans le cas d'un profil linéaire d'intensité dans la zone de la couronne.¹

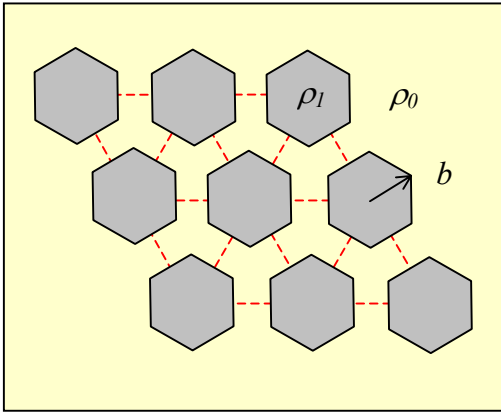
$$I_{\text{mono}}^{\text{int}}(k^*) = \left(\frac{\pi}{S_{\text{maille}}} \right)^2 V_{\text{cristal}} (\rho_1 - \rho_0)^2 \frac{1}{(R_2 - R_1)^2} \left(R_2^3 \left(\frac{J_1(2\pi k^* R_2)}{\pi k^* R_2} - \text{int}(2\pi k^* R_2) \right) - R_1^3 \left(\frac{J_1(2\pi k^* R_1)}{\pi k^* R_1} - \text{int}(2\pi k^* R_1) \right) \right)^2$$

Cette expression fait intervenir la fonction hypergéométrique suivante :

$$\text{int}(x) = \frac{2}{3} \text{HypergeometricPFQ}[\{3/2\}, \{1, 5/2\}, -\frac{x^2}{4}] \quad (\text{Ecriture en Mathematica de la fonction } {}_1F_2)$$



Cas d'une section hexagonale des objets



On a également cherché à déterminer l'influence de la forme des objets sur les intensités diffractées, en considérant des hexagones au lieu de disques. Le facteur de forme d'un hexagone $F_{\text{hexagone}}(\vec{k})$ est donné dans le chapitre 7. L'expression de l'intensité intégrée d'un pic se déduit aisément du cas du modèle à deux niveaux pour un disque :

$$I_{\text{mono}}^{\text{int}}(\vec{k}^*) = (\rho_1 - \rho_0)^2 \left(\frac{1}{S_{\text{maille}}} \right)^2 V_{\text{cristal}} \left(F_{\text{hexagone}}(\vec{k}^*) \right)^2$$

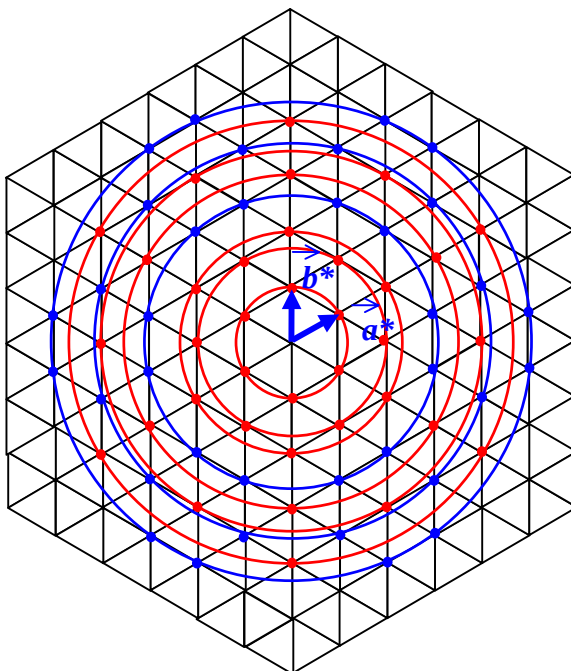
$$F_{\text{hexagone}}(\vec{k}^*) = \left(\frac{3\sqrt{3}}{2} b^2 \right) \frac{1}{3} \left(\cos(\vec{k}^* \cdot \vec{C}) \frac{\sin(\vec{k}^* \cdot \vec{A})}{(\vec{k}^* \cdot \vec{A})} \frac{\sin(\vec{k}^* \cdot \vec{B})}{(\vec{k}^* \cdot \vec{B})} + \cos(\vec{k}^* \cdot \vec{A}) \frac{\sin(\vec{k}^* \cdot \vec{B})}{(\vec{k}^* \cdot \vec{B})} \frac{\sin(\vec{k}^* \cdot \vec{C})}{(\vec{k}^* \cdot \vec{C})} + \cos(\vec{k}^* \cdot \vec{B}) \frac{\sin(\vec{k}^* \cdot \vec{C})}{(\vec{k}^* \cdot \vec{C})} \frac{\sin(\vec{k}^* \cdot \vec{A})}{(\vec{k}^* \cdot \vec{A})} \right)$$

Intensité pour une poudre

La relation entre l'intensité intégrée pour une poudre avec l'intensité intégrée dans le cas d'un monocristal a été discutée au chapitre 6.

$$I_{\text{poudre}}^{\text{int}}(k^*) \propto \frac{M(k^*) I_{\text{mono}}^{\text{int}}(\vec{k}^*)}{k^{*2}}$$

Pour un réseau hexagonal 2D, la multiplicité $M(k^*)$ vaut 6 (raies $h0$ et $h = k$) ou 12, comme illustré sur la figure. Dans le tableau sont données les premières valeurs :



hk	$h^2 + k^2 + hk$	$M(hk)$
10	1	6
11	3	6
20	4	6
21	7	12
30	9	6
22	12	6
31	13	12
40	16	6
32	19	12

Intensités dans le modèle à deux niveaux

Le tableau ci-après donnent les intensités relatives pour le modèle à deux niveaux avec des cylindres (section circulaire). Le paramètre est le rapport sans dimension R/a , R étant le rayon des cylindres et a le paramètre de maille hexagonal (distance entre deux cylindres). L'intensité de la raie 10 est prise comme référence et fixée à 10000. C'est toujours la raie la plus intense, et dès que le rapport R/a est supérieur à environ 0.1, seulement les 5 premières raies ont une intensité notable. Suivant la valeur de R/a , certaines raies ont une très faible intensité car elles sont situées sur un zéro du facteur de forme.

Comparaison disque/hexagone

On compare les intensités obtenues, toujours pour une poudre et le modèle à deux niveaux, mais avec une section hexagonale des objets. Le second tableau ci-après montre que l'effet de la forme des objets est peu sensible. Il est notable uniquement pour les fractions de volume importantes (> 0.6), lorsque les objets sont proches du contact et que leur forme joue alors de façon plus importante.

Ceci est également illustré pour des fractions de volume identique, en section circulaire ou hexagonale.

Chapitre 8

Intensités relatives pour une poudre. Modèle à deux niveaux pour une section circulaire

R/a	$S_{\text{disque}}/S_{\text{maille}}$	$I_{10}=10000$	I_{11}/I_{10}	I_{20}/I_{10}	I_{21}/I_{10}	I_{30}/I_{10}	I_{22}/I_{10}	I_{31}/I_{10}	I_{40}/I_{10}
rayon	fracvol	(10) 1	(11) 3	(20) 4	(21) 7	(30) 9	(22) 12	(31) 13	(40) 16
0.01	0.00036276	10000	3324	2490	2834	1099	821	1514	612
0.02	0.00145104	10000	3298	2460	2768	1065	786	1443	577
0.03	0.00326484	10000	3254	2412	2659	1009	730	1331	521
0.04	0.00580416	10000	3194	2345	2513	936	657	1187	451
0.05	0.009069	10000	3118	2261	2334	847	572	1019	372
0.06	0.0130594	10000	3027	2162	2129	748	480	841	290
0.07	0.0177752	10000	2921	2049	1905	643	387	662	213
0.08	0.0232166	10000	2802	1923	1670	536	297	495	144
0.09	0.0293835	10000	2671	1788	1430	432	216	346	89
0.1	0.036276	9999	2530	1644	1194	335	146	223	47
0.11	0.0438939	9999	2379	1496	968	247	90	128	20
0.12	0.0522374	10000	2221	1344	759	172	49	61	5
0.13	0.0613064	10000	2057	1191	571	111	21	21	0
0.14	0.0711009	10000	1889	1041	408	64	5	2	1
0.15	0.081621	10000	1719	894	273	31	0	0	6
0.16	0.0928665	9999	1548	753	166	10	1	8	11
0.17	0.104838	10000	1378	621	88	1	7	21	15
0.18	0.117534	10000	1211	498	36	0	14	34	16
0.19	0.130956	10000	1049	387	8	5	20	42	15
0.2	0.145104	9999	893	289	0	14	25	46	12
0.21	0.159977	10000	745	204	7	24	26	43	8
0.22	0.175576	9999	608	134	27	33	24	36	4
0.23	0.1919	10000	481	79	52	40	20	26	1
0.24	0.20895	10000	366	38	80	43	15	16	0
0.25	0.226725	10000	265	13	107	43	9	7	0
0.26	0.245226	9999	180	1	128	39	4	1	2
0.27	0.264452	9999	109	2	142	32	1	0	5
0.28	0.284404	10000	56	15	147	24	0	2	7
0.29	0.305081	10000	20	38	143	16	1	8	8
0.3	0.326484	10000	2	71	131	8	4	16	9
0.31	0.348612	10000	2	110	111	2	9	24	7
0.32	0.371466	10000	21	154	86	0	13	29	5
0.33	0.395046	10000	58	201	59	1	17	32	3
0.34	0.41935	10000	115	249	34	5	20	30	0
0.35	0.444381	10000	191	296	13	13	20	25	0
0.36	0.470137	10000	286	338	1	24	18	17	0
0.37	0.496618	10000	400	375	1	36	14	8	3
0.38	0.523825	10000	534	403	14	47	8	2	7
0.39	0.551758	9999	688	422	44	57	3	0	11
0.4	0.580416	10000	864	428	90	63	0	4	15
0.41	0.609799	10000	1062	422	154	65	0	15	16
0.42	0.639908	10000	1286	400	233	61	5	35	16
0.43	0.670743	10000	1540	362	327	51	16	60	12
0.44	0.702303	10000	1833	308	432	36	34	88	7
0.45	0.734589	9999	2178	239	546	19	58	116	2
0.46	0.7676	10000	2597	157	664	4	87	137	0
0.47	0.801337	10000	3134	71	784	0	121	146	5
0.48	0.835799	10000	3876	6	902	26	158	137	27
0.49	0.870986	10000	5018	37	1017	125	196	105	81
0.5	0.9069	10000	7114	435	1136	433	235	47	209

Chapitre 8

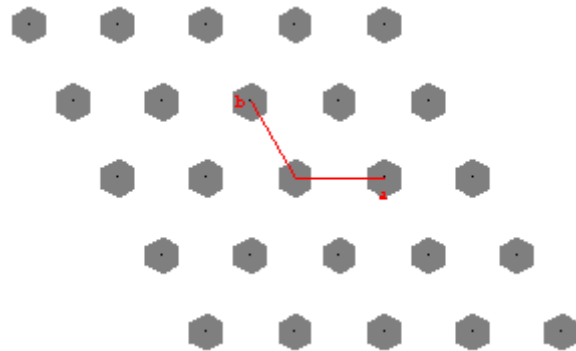
Intensités relatives pour une poudre. Modèle à deux niveaux pour une section hexagonale

b/a	$S_{\text{hexagone}}/S_{\text{maille}}$	$I_{10}=10000$	I_{11}/I_{10}	I_{20}/I_{10}	I_{21}/I_{10}	I_{30}/I_{10}	I_{22}/I_{10}	I_{31}/I_{10}	I_{40}/I_{10}
cote	fracvol	(10) 1	(11) 3	(20) 4	(21) 7	(30) 9	(22) 12	(31) 13	(40) 16
0.01	0.0003	10000	3326	2491	2838	1101	823	1518	614
0.02	0.0012	10000	3304	2467	2782	1072	793	1459	584
0.03	0.0027	10000	3267	2426	2691	1026	746	1364	537
0.04	0.0048	10000	3217	2370	2568	963	684	1240	477
0.05	0.0075	10000	3153	2300	2416	887	610	1095	407
0.06	0.0108	10000	3077	2216	2240	801	529	935	333
0.07	0.0147	10000	2987	2119	2044	708	444	771	259
0.08	0.0192	10000	2887	2012	1835	611	360	611	191
0.09	0.0243	10000	2775	1895	1619	514	280	462	132
0.1	0.03	10000	2654	1770	1401	419	207	330	83
0.11	0.0363	10000	2524	1639	1186	331	145	220	46
0.12	0.0432	10000	2387	1503	981	252	94	133	21
0.13	0.0507	10000	2244	1365	789	182	55	70	6
0.14	0.0588	10000	2095	1226	614	124	27	29	0
0.15	0.0675	10000	1943	1088	459	77	10	7	0
0.16	0.0768	10000	1788	952	327	42	2	0	4
0.17	0.0867	10000	1633	822	218	19	0	3	10
0.18	0.0972	10000	1478	697	133	5	2	13	15
0.19	0.1083	10000	1324	579	71	0	7	24	19
0.2	0.12	10000	1174	470	29	1	12	35	21
0.21	0.1323	9999	1028	371	6	7	16	42	20
0.22	0.1452	10000	888	282	0	17	18	45	18
0.23	0.1587	10000	754	205	5	27	18	43	14
0.24	0.1728	10000	629	140	20	37	15	38	10
0.25	0.1875	10000	512	88	40	46	12	29	6
0.26	0.2028	10000	406	47	62	52	7	20	3
0.27	0.2187	10000	310	20	84	56	3	11	1
0.28	0.2352	10000	227	4	102	56	0	4	0
0.29	0.2523	10000	155	0	115	54	0	0	0
0.3	0.27	10000	97	6	122	49	1	0	0
0.31	0.2883	10000	52	23	121	42	5	2	1
0.32	0.3072	10000	21	50	113	34	11	6	1
0.33	0.3267	10000	3	84	100	26	19	12	2
0.34	0.3468	10000	0	126	81	18	27	17	2
0.35	0.3675	10000	10	173	60	11	34	21	2
0.36	0.3888	10000	34	225	39	5	39	24	1
0.37	0.4107	10000	71	281	20	2	42	23	1
0.38	0.4332	10000	121	338	6	0	41	20	0
0.39	0.4563	10000	183	396	0	0	37	15	0
0.4	0.48	10000	256	453	4	1	30	9	0
0.41	0.5043	10000	340	509	21	4	21	4	0
0.42	0.5292	10000	433	562	51	8	12	0	0
0.43	0.5547	10000	535	611	97	12	4	0	0
0.44	0.5808	10000	643	655	158	16	0	4	0
0.45	0.6075	10000	759	694	234	19	1	14	0
0.46	0.6348	10000	878	727	324	22	11	30	0
0.47	0.6627	10000	1002	753	425	23	30	51	0
0.48	0.6912	10000	1127	772	536	23	58	77	1
0.49	0.7203	10000	1253	785	654	22	97	106	2
0.5	0.75	10000	1378	790	774	20	146	136	5
0.51	0.7803	10000	1501	789	893	17	201	164	8
0.52	0.8112	10000	1620	780	1007	13	262	190	12
0.53	0.8427	10000	1734	766	1113	9	325	210	17
0.54	0.8748	10000	1841	745	1207	6	387	225	22
0.55	0.9075	10000	1941	719	1285	3	443	231	27
0.56	0.9408	10000	2032	688	1345	1	490	231	32
0.57	0.9747	10000	2113	653	1384	0	525	222	36
0.58	1.0092	10000	2183	614	1402	0	545	207	39

cote de l'hexagone normalisé = 0.220

fraction de volume = 0.145

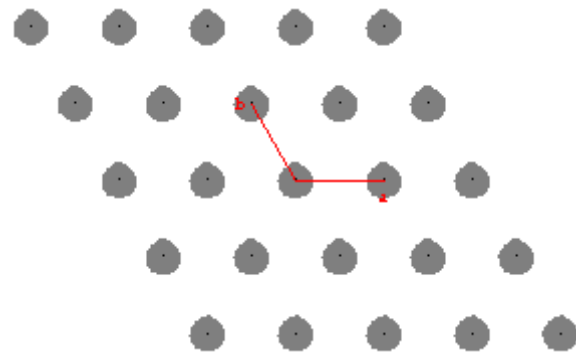
```
10 1 10000.
11 3 889
20 4 283
21 7 0.00
30 9 17
22 12 18
31 13 46
40 16 19
```



rayon du disque normalisé = 0.2

fraction de volume = 0.145

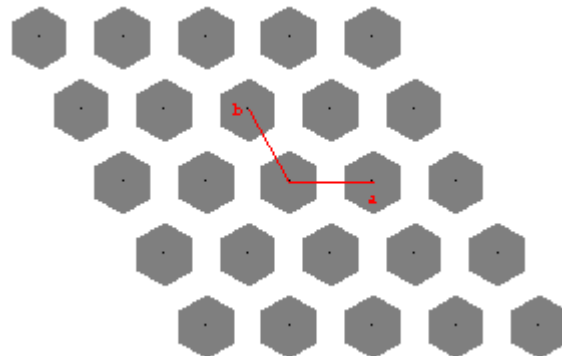
```
10 1 10000.
11 3 894
20 4 289
21 7 0.012
30 9 14
22 12 25
31 13 46
40 16 12
```



cote de l'hexagone normalisé = 0.385

fraction de volume = 0.444

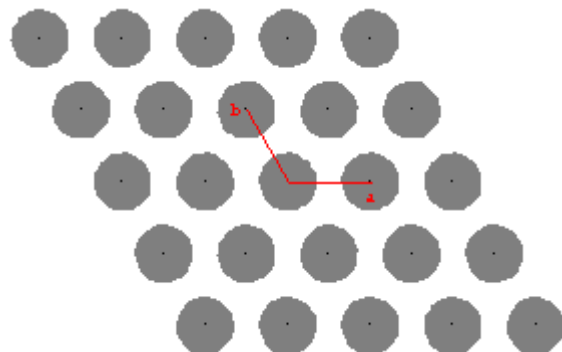
```
10 1 10000.
11 3 150
20 4 367
21 7 2.04
30 9 0
22 12 40
31 13 18
40 16 0.69
```



rayon du disque normalisé = 0.35

fraction de volume = 0.444

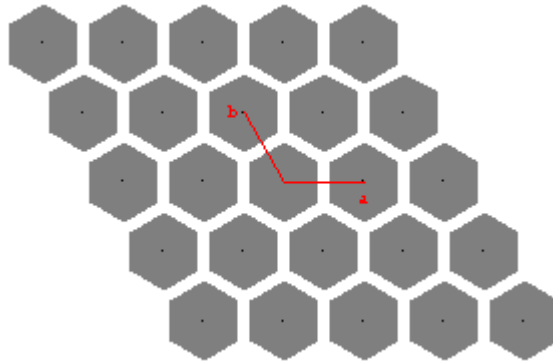
```
10 1 10000.
11 3 192
20 4 296
21 7 14
30 9 14
22 12 20
31 13 25
40 16 0.00
```



cote de l'hexagone normalisé = 0.495 fraction de volume = 0.735

```

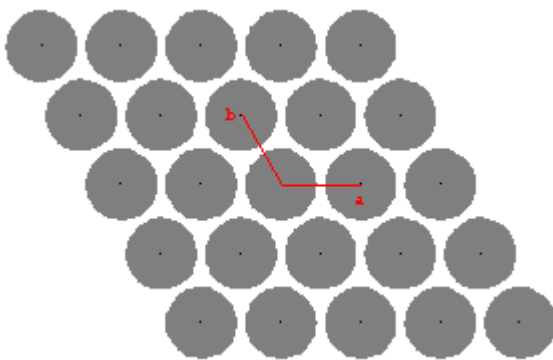
10  1  10000.
11  3  1314
20  4  789
21  7  712
30  9  21
22  12 120
31  13 121
40  16 3.79
    
```



rayon du disque normalisé = 0.45 fraction de volume = 0.735

```

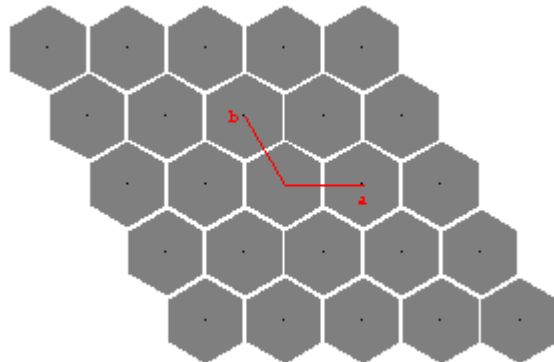
10  1  10000.
11  3  2178
20  4  239
21  7  546
30  9  20
22  12 58
31  13 116
40  16 2.35
    
```



cote de l'hexagone normalisé = 0.55 fraction de volume = 0.9075

```

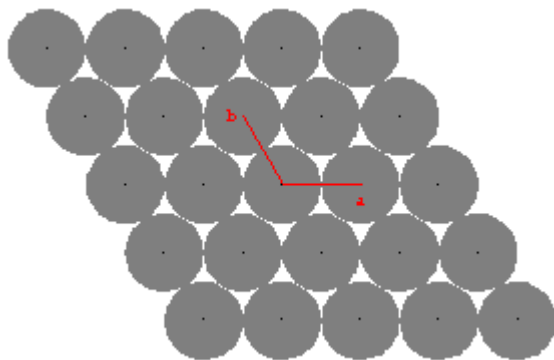
10  1  10000.
11  3  1942
20  4  719
21  7  1285
30  9  3.62
22  12 443
31  13 232
40  16 28
    
```



rayon du disque normalisé = 0.5 fraction de volume = 0.9069

```

10  1  10000.
11  3  7114
20  4  435
21  7  1136
30  9  434
22  12 235
31  13 48
40  16 209
    
```



Influence de la taille d'un grain :

Pour des grains suffisamment petits, les pics de Bragg sont élargis (chapitre 10). Pour une poudre de grains, l'élargissement est mesuré dans la direction longitudinale d'un pic de Bragg. Cela signifie que dans le cas d'une phase hexagonale 2D, on accède seulement aux dimensions des grains dans le plan perpendiculaire aux cylindres.

La mesure de la taille le long des cylindres n'est donc pas facilement accessible. Cette taille est en plus en général nettement plus grande que la taille perpendiculairement aux cylindres.

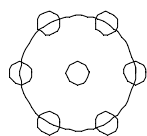
Pour des grains peu anisotropes, on peut espérer mesurer l'influence de la dimension le long des cylindres par des mesures en diffusion centrale aux très petits angles, autour de l'origine de l'espace réciproque. On est alors sensible à toutes les dimensions des grains.

Pour illustrer l'influence de la taille, on peut calculer directement la somme $\sum_{\{ij\}} e^{-2i\pi\vec{k}_{perp}\vec{R}_{ij}}$ sur un réseau hexagonal 2D pour des grains très petits, composés de quelques mailles. On suppose que ces grains sont cylindriques.

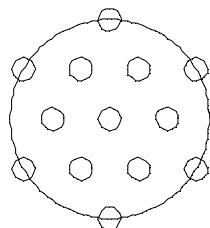
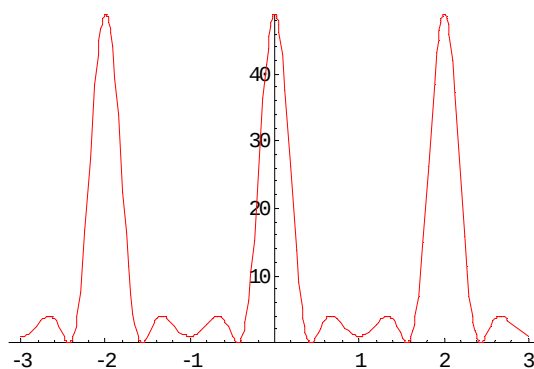
On voit que même pour de très petits grains (20 cylindres), l'intensité est entièrement concentrée dans les pics de Bragg. Ces pics sont élargis par la taille du grain, $R_{cristal}$. En bleu, une bonne approximation de la largeur des pics est donnée par le facteur de forme du grain lui-même :

$$\left(\frac{J_1(2\pi k_{perp} R_{cristal})}{\pi k_{perp} R_{cristal}} \right)^2$$

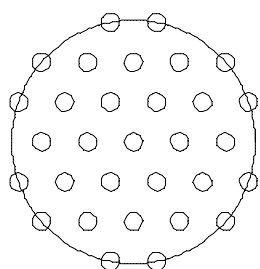
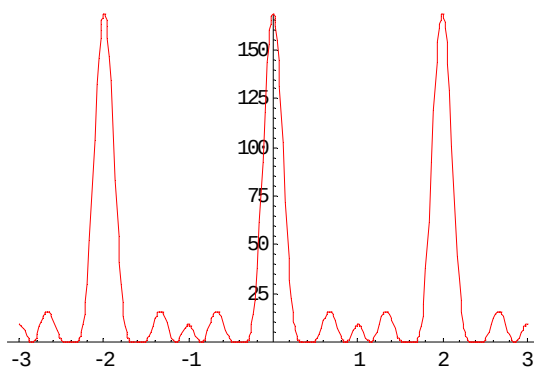
En conclusion, dès-que les cylindres sont ordonnés sur un réseau 2D, même en petit nombre, on a des pics de Bragg. Si les grains sont petits, ces pics ont un élargissement mesurable, donné par la valeur de $R_{cristal}$.



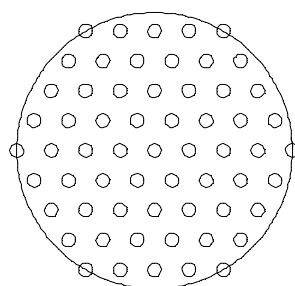
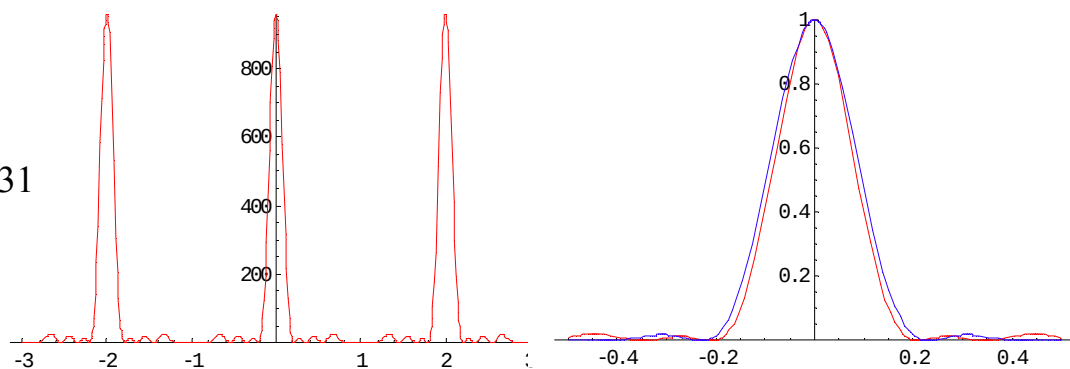
$N = 7$



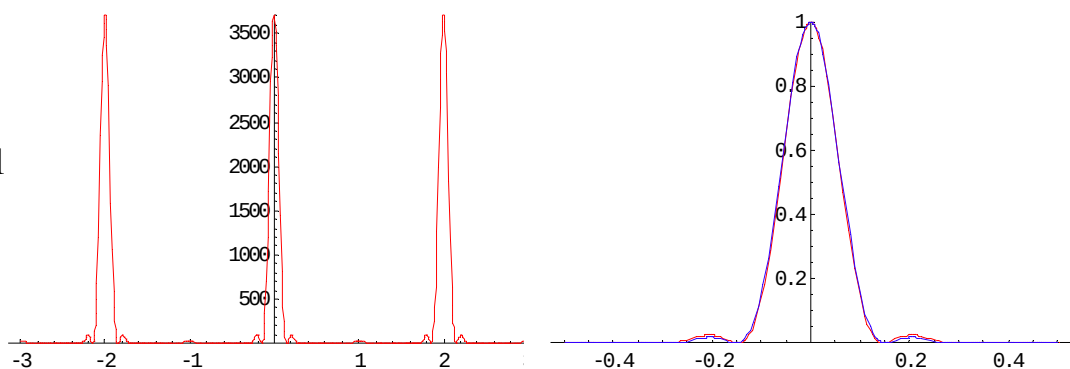
$N = 13$



$N = 31$



$N = 61$



Largeur des pics de Bragg pour de très petits nombres N de cylindres.

References

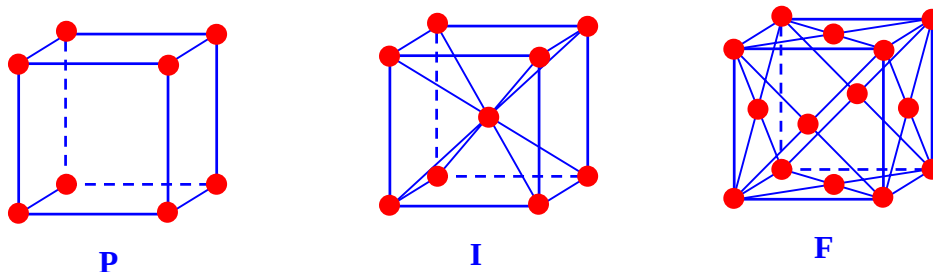
1. Imperor-Clerc, M.; Davidson, P.; Davidson, A. Existence of a microporous corona around the mesopores of silica-based SBA-15 materials templated by triblock copolymers. *Journal of the American Chemical Society* **2000**, *122* (48), 11925-11933.

Chapitre 9

L'identification d'un groupe d'espace cubique ¹

Il existe 36 groupes d'espace cubiques différents. Par une expérience de diffraction, on ne peut pas toujours déterminer entièrement le groupe d'espace, et l'on distingue seulement 17 classes de groupes cubiques. Les groupes d'espace appartenant à une même classe donnent les mêmes extinctions et ne sont donc pas discernables. Ceci est relié à la loi de Friedel, $I(\vec{k}^*) = I(-\vec{k}^*)$, qui fait que l'origine de l'espace réciproque est toujours un centre d'inversion. Cette loi est valable loin d'un seuil d'absorption. Ainsi, par une expérience de diffraction standard, on ne peut déterminer si le groupe d'espace est centro-symétrique ou pas.

Ces 17 classes sont énumérées dans les tableaux ci-dessous. On voit que les classes permettent de déterminer le réseau de Bravais (**P**, **I**, **F**), ainsi que la présence de miroirs à glissement (**a**, **c**, **d**, **n**) et d'axes hélicoïdaux (**2₁**, **4₁**, **4₂**). Ainsi, les groupes $Pm\bar{3}m$, $Pn\bar{3}m$, $Pm\bar{3}n$ et $Pn\bar{3}n$ sont chacun dans une classe différente. Enfin, dans une classe donnée, deux groupes d'espace diffèrent souvent l'un de l'autre par la présence d'un centre d'inversion ainsi que d'un miroir **m** perpendiculaire à un axe 4 ou 2, comme par exemple entre les groupes $P432$ et $Pm\bar{3}m$ dans la classe **P**...



Les trois réseaux de Bravais pour la symétrie cubique : primitif, *P*, centré, *I*, et face-centré, *F*.

Classes des groupes primitifs P :

groupe ponctuel	P...	P4₂.. P2₁..	P4₁..	Pn..	P..n	Pn.n	Pa..
$m\bar{3}m$	$Pm\bar{3}m$			$Pn\bar{3}m$	$Pm\bar{3}n$	$Pn\bar{3}n$	
432	P432	P4 ₂ 32	P4 ₁ 32 P4 ₃ 32				
$\bar{4}3m$	$P\bar{4}3m$				$P\bar{4}3n$		
$m\bar{3}$	$Pm\bar{3}$			$Pn\bar{3}$			$Pa\bar{3}$
23	P23	P2 ₁ 3					

Classes des groupes centrés I :

groupe ponctuel	I...	I4₁..	Ia..	I..d	Ia.d
$m\bar{3}m$	$Im\bar{3}m$				$Ia\bar{3}d$
432	I432	I4 ₁ 32			
$\bar{4}3m$	$I\bar{4}3m$			$I\bar{4}3d$	
$m\bar{3}$	$Im\bar{3}$		$Ia\bar{3}$		
23	I23 I2 ₁ 3				

Classes des groupes faces centrés F :

groupe ponctuel	F...	F4₁..	Fd..	F..c	Fd.c
$m\bar{3}m$	$Fm\bar{3}m$		$Fd\bar{3}m$	$Fm\bar{3}c$	$Fd\bar{3}c$
432	F432	F4 ₁ 32			
$\bar{4}3m$	$F\bar{4}3m$			$F\bar{4}3c$	
$m\bar{3}$	$Fm\bar{3}$		$Fd\bar{3}$		
23	F23				

Les raies de diffraction pour un cristal cubique s'indexent suivant trois indices entiers h,k,l. On a la relation suivante entre la distance inter-réticulaire d_{hkl} et le paramètre de maille

$$a : d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.$$

La classe **P...** correspond au cas où toutes les raies hkl sont observées car aucun élément de symétrie n'introduit d'extinctions. Mais en général, la maille contient des éléments de symétrie (translations de réseau -I ou F-, miroirs à glissement ou axes hélicoïdaux) qui introduisent des extinctions. Les séquences de raies observées sont différentes pour chacune des 17 classes cubiques ce qui permet leur identification (voir les tableaux ci-dessous). Un nombre suffisant de raies observées est toutefois nécessaire pour identifier complètement une classe.

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Raies observées pour les classes P :

$h^2+k^2+l^2$	hkl	P...	P4 ₂ .. P2 ₁ ..	P4 ₁ ..	Pn..	P.. _n	Pn.n	Pa..
1	100	+	-	-	-	-	-	-
2	110	+	+	+	+	+	+	-
3	111	+	+	+	+	-	-	+
4	200	+	+	-	+	+	+	+
5	210	+	+	+	-	+	-	x
6	211	+	+	+	+	+	+	+
8	220	+	+	+	+	+	+	+
9	300	+	-	-	-	-	-	-
	221	+	+	+	+	-	-	+
10	310	+	+	+	+	+	+	-
11	311	+	+	+	+	-	-	+
12	222	+	+	+	+	+	+	+
13	320	+	+	+	-	+	-	x
14	321	+	+	+	+	+	+	+
16	400	+	+	+	+	+	+	+
17	410	+	+	+	-	+	-	x
	322	+	+	+	+	-	-	+
18	411	+	+	+	+	+	+	+
	330	+	+	+	+	+	+	-
19	331	+	+	+	+	-	-	+
20	420	+	+	+	+	+	+	+
21	421	+	+	+	+	+	+	+
22	332	+	+	+	+	+	+	+
24	422	+	+	+	+	+	+	+
25	500	+	-	-	-	-	-	-
	430	+	+	+	-	+	-	x
26	510	+	+	+	+	+	+	-
	461	+	+	+	+	+	+	+
27	511	+	+	+	+	-	-	+
	333	+	+	+	+	+	+	+
29	520	+	+	+	-	+	-	x
	432	+	+	+	+	+	+	+
30	521	+	+	+	+	+	+	+
32	440	+	+	+	+	+	+	+
33	522	+	+	+	+	-	-	+
	441	+	+	+	+	-	-	+
34	530	+	+	+	+	+	+	-
	433	+	+	+	+	+	+	+
35	531	+	+	+	+	+	+	+

Classes des groupes primitifs P : (+) raies observées, (-) raies éteintes, (x) raies où la moitié des plans contribuent (hk0), (0hk) et (k0h) avec h pair.

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Raies observées pour les classes I :

Tous les groupes centrés ont comme règle de sélection : $h+k+l$ pair. C'est la seule règle de sélection pour la classe **I**....

$h^2+k^2+l^2$	hkl	I...	I4₁..	Ia..	I..d	Ia.d
1	100	-	-	-	-	-
2	110	+	+	-	-	-
3	111	-	-	-	-	-
4	200	+	-	+	-	-
5	210	-	-	-	-	-
6	211	+	+	+	+	+
8	220	+	+	+	+	+
9	300	-	-	-	-	-
	221	-	-	-	-	-
10	310	+	+	-	+	-
11	311	-	-	-	-	-
12	222	+	+	+	-	-
13	320	-	-	-	-	-
14	321	+	+	+	+	+
16	400	+	+	+	+	+
17	410	-	-	-	-	-
	322	-	-	-	-	-
18	411	+	+	+	-	-
	330	+	+	-	-	-
19	331	-	-	-	-	-
20	420	+	+	+	+	+
21	421	-	-	-	-	-
22	332	+	+	+	+	+
24	422	+	+	+	+	+
25	500	-	-	-	-	-
	430	-	-	-	-	-
26	510	+	+	-	+	-
	461	+	+	+	+	+
27	511	-	-	-	-	-
	333	-	-	-	-	-
29	520	-	-	-	-	-
	432	-	-	-	-	-
30	521	+	+	+	+	+
32	440	+	+	+	+	+
33	522	-	-	-	-	-
	441	-	-	-	-	-
34	530	+	+	-	+	-
	433	+	+	+	-	-
35	531	-	-	-	-	-

Classes des groupes centrés I : (+) raies observées, (-) raies éteintes.

Chapitre 9

Raies observées pour les classes F :

Tous les groupes faces centrés ont comme règle de sélection h, k, et l de même parité. C'est la seule règle de sélection pour la classe **F**....

$h^2+k^2+l^2$	hkl	F...	F4₁..	Fd..	F.. c	Fd.c
1	100	-	-	-	-	-
2	110	-	-	-	-	-
3	111	+	+	+	-	-
4	200	+	-	-	+	-
5	210	-	-	-	-	-
6	211	-	-	-	-	-
8	220	+	+	+	+	+
9	300	-	-	-	-	-
	221	-	-	-	-	-
10	310	-	-	-	-	-
11	311	+	+	+	-	-
12	222	+	+	+	+	+
13	320	-	-	-	-	-
14	321	-	-	-	-	-
16	400	+	+	+	+	+
17	410	-	-	-	-	-
	322	-	-	-	-	-
18	411	-	-	-	-	-
	330	-	-	-	-	-
19	331	+	+	+	-	-
20	420	+	+	-	+	-
21	421	-	-	-	-	-
22	332	-	-	-	-	-
24	422	+	+	+	+	+
25	500	-	-	-	-	-
	430	-	-	-	-	-
26	510	-	-	-	-	-
	461	-	-	-	-	-
27	511	+	+	+	-	-
	333	+	+	+	-	-
29	520	-	-	-	-	-
	432	-	-	-	-	-
30	521	-	-	-	-	-
32	440	+	+	+	+	+
33	522	-	-	-	-	-
	441	-	-	-	-	-
34	530	-	-	-	-	-
	433	-	-	-	-	-
35	531	+	+	+	+	+

Classes des groupes faces centrés F : (+) raies observées, (-) raies éteintes.

Application aux phases cubiques

La détermination du groupe d'espace se fait grâce aux raies observées sur les diagrammes de diffraction. L'étape d'indexation, c'est-à-dire l'attribution des indices hkl aux raies observées ainsi que le calcul du paramètre a , est en général facile pour un système cubique. On établit la symétrie cubique en vérifiant que toutes les raies observées correspondent à des distances inter-réticulaires de la forme $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$. Si la symétrie est différente (phase 3D, hexagonale ou quadratique) deux paramètres de maille (a et c) sont nécessaires pour indexer.

Pour les phases 2D (phases hexagonales, rectangles, obliques), les raies ne dépendent que de deux indices hk .

L'attribution du groupe d'espace ou de la classe auquel il appartient se fait en utilisant les tableaux précédents. Pour la plupart des phases, quelques raies suffisent pour reconnaître à quelle classe le groupe appartient. On peut l'illustrer sur deux exemples fréquents.

Phase bicontinue $Ia\bar{3}d$

La phase bicontinue la plus fréquemment observée est la phase de groupe d'espace $Ia\bar{3}d$. Ce groupe d'espace est entièrement identifié puisqu'il est le seul de la classe $Ia.d$. Ce groupe est facilement reconnaissable car c'est le seul (avec le groupe $I\bar{4}3d$) où les deux premières raies observées sont les raies 211 et 220. On remarque toutefois que c'est seulement l'absence de la raie 310 qui permet de le distinguer du groupe $I\bar{4}3d$.

Raies observées pour le groupe $Ia\bar{3}d$:

Règles de sélection : $h+k+l$ pair hhl : l pair et $2h+l=4n$ $hk0$: h et k pairs

$h^2+k^2+l^2$	hkl	$Ia.d$
6	211	+
8	220	+
14	321	+
16	400	+
20	420	+
22	332	+
24	422	+
26	510	-
	431	+
30	521	+
32	440	+

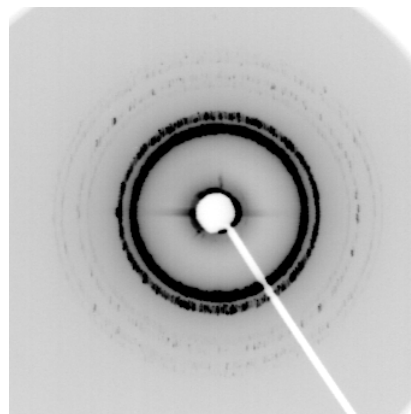


Diagramme de poudre typique de la phase $Ia\bar{3}d$. Il s'agit du composé thermotrope 18-ANBC (chapitre 4).²

Phase micellaire $Pm\bar{3}n$

La phase micellaire de groupe d'espace $Pm\bar{3}n$ se caractérise également par les premières raies de diffraction observées. La première raie est la raie 110 suivie d'un groupe de trois raies proches, les raies 200, 210 et 211. Ce groupe d'espace est dans la classe $P..n$ qui contient également le groupe $P\bar{4}3n$. Dans un tel cas, on privilégie le groupe $Pm\bar{3}n$ correspondant au groupe ponctuel le plus symétrique, $m\bar{3}m$ (au lieu de $\bar{4}3m$).

Raies observées pour le groupe $Pm\bar{3}n$:

Règles de sélection : hhl : l pair

$h^2+k^2+l^2$	hkl	$P..n$
2	110	+
4	200	+
5	210	+
6	211	+
8	220	+
10	310	+
12	222	+
13	320	+
14	321	+
16	400	+
17	410	+
	322	-
18	411	+
	330	+
20	420	+
21	421	+
22	332	+
24	422	+
25	500	-
	430	+
26	510	+
	461	+
27	511	-
	333	+
29	520	+
	432	+
30	521	+
32	440	+
34	530	+
	433	+
35	531	+

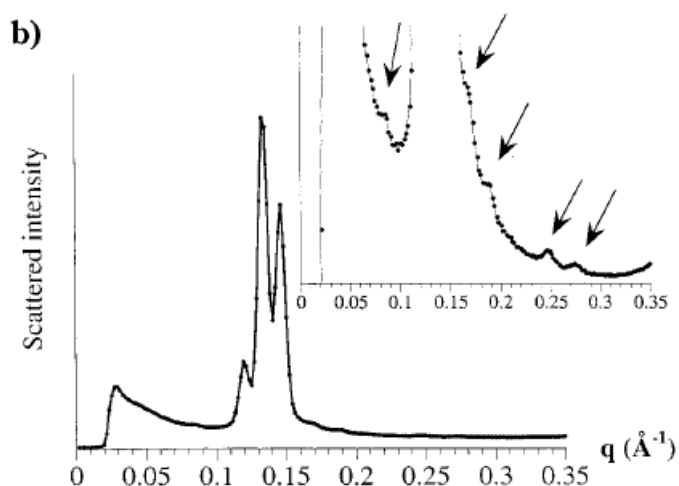


Diagramme de poudre typique de la phase $Pm\bar{3}n$. Il s'agit d'un surfactant cationique dans l'eau³.

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Enfin, on remarque que les phases cubiques connues sont des structures qui possèdent toutes le groupe ponctuel $m\bar{3}m$. Ce groupe correspond à la présence de miroirs perpendiculaires aux axes 4 et 2. Ainsi, en faisant l'hypothèse de ce groupe ponctuel, on aboutit à une liste simplifiée des groupes d'espaces envisageables :

groupe ponctuel	P...	Pn..	P..n	Pn.n	I...	Ia.d	F...	Fd..	F.. c	Fd.c
$m\bar{3}m$	$Pm\bar{3}m$	$Pn\bar{3}m$	$Pm\bar{3}n$	$Pn\bar{3}n$	$Im\bar{3}m$	$Ia\bar{3}d$	$Fm\bar{3}m$	$Fd\bar{3}m$	$Fm\bar{3}c$	$Fd\bar{3}c$

References

1. *International Tables for Crystallography*; Springer: 2005.
2. Levelut, A. M.; Clerc, M. Structural investigations on 'smectic D' and related mesophases. *Liquid Crystals* **1998**, 24 (1), 105-115.
3. Ilkkti, P.; Martin, T.; Cabane, B.; Piculell, L. Effects of polyelectrolytes on the structures and interactions of surfactant aggregates. *Journal of Physical Chemistry B* **1999**, 103 (45), 9831-9840.

Chapitre 10

Taille de grains ou de nano-particules

Dans le cas de petits cristaux ou de nano-particules cristallines, on observe un élargissement des raies de diffraction provenant de la structure cristalline (arrangement périodique des atomes). Cet élargissement est directement relié à la forme des petits domaines diffractants.

Dans le cas de nano-particules, se pose la question de savoir si elles sont monocristallines ou constituées de plusieurs domaines cristallins, et aussi quelle est l'orientation cristallographique de ces domaines par rapport à la forme de la nanoparticule si celle-ci est anisotrope. C'est la taille d'un domaine cristallin cohérent qui contribue à l'élargissement des raies de Bragg.

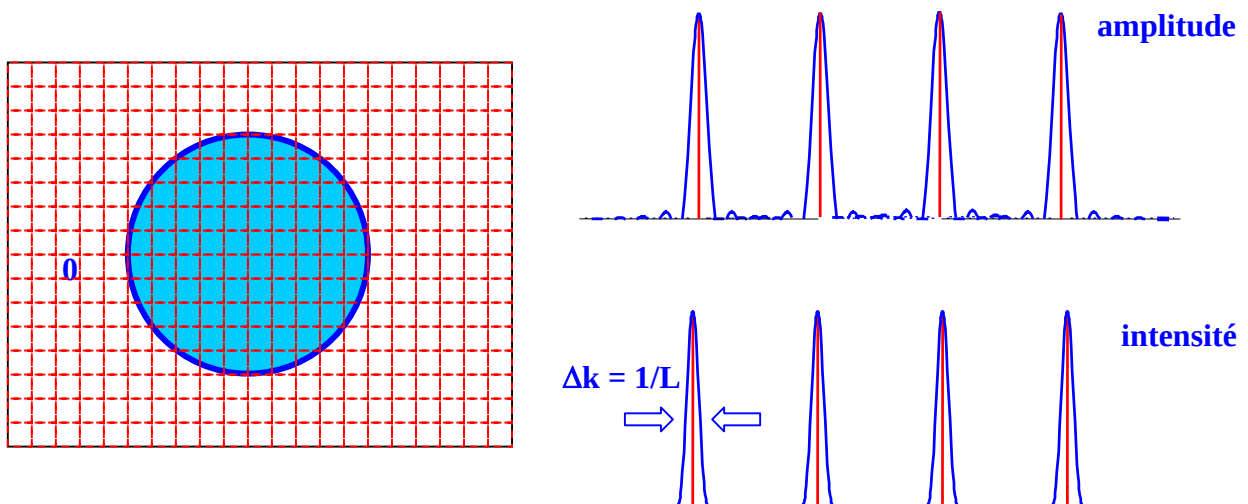


Figure 10-1. Exemple d'une particule sphérique monocristalline. En amplitude, chaque pic de Dirac est élargi par la transformée de Fourier d'une sphère. La largeur des pics en intensité est donnée par celle des maxima principaux.

Plus précisément, partant d'un cristal infini pour lequel les pics de Bragg sont des pics de Dirac dans l'espace réciproque, on obtient un cristal de taille finie en découpant une région ayant la forme du petit cristal dans le cristal infini (**Fig 10-1**). Ceci revient à multiplier dans l'espace réel par une fonction égale à 1 à l'intérieur de cette région et 0 à l'extérieur. Ce

produit de deux fonctions dans l'espace réel correspond dans l'espace réciproque au produit de convolution des transformées de Fourier de ces deux fonctions. D'où le résultat connu : chaque pic de Dirac est multiplié par la transformée de Fourier de la fonction de forme du petit cristal. Pour des formes usuelles, les amplitudes de Fourier sont réelles. On s'intéresse uniquement à la largeur des pics de Bragg, et donc uniquement aux maxima principaux, en utilisant l'intensité (carré de l'amplitude).

Pour le cas de particules très petites (quelques nanomètres), on observe le recouvrement de certaines raies de diffraction aux grands angles. Les pics de Bragg n'étant plus alors clairement séparés, on utilisera plutôt un calcul complet de l'intensité de diffraction à partir des coordonnées atomiques des atomes contenus dans le petit cristal.

Elargissement de raie

La taille apparente L est donnée par la relation $L = 1 / \Delta k$, où Δk est l'élargissement d'une raie de Bragg. Ceci constitue un bon ordre de grandeur de la taille des cristaux. Mais on peut aussi affiner cette relation pour différentes formes de particules, ou encore tenir compte d'une distribution de taille. Enfin, on peut mesurer soit la largeur à mi-hauteur, soit la largeur intégrale des pics de diffraction.

On donne ici seulement deux expressions utiles de Δk , pour une mesure de largeur à mi-hauteur :

- Pour des sphères de diamètre D , en utilisant le facteur de forme d'une sphère et sa largeur à mi-hauteur, on trouve la relation :

$$\Delta k_{FWHM} = 2k_{1/2} = \frac{1}{L} = \frac{1.16}{D} = \frac{1}{0.87D}$$

$$I_{\text{sphère}}(k, R) = \left(3 \frac{\sin(2\pi k R) - (2\pi k R) \cos(2\pi k R)}{(2\pi k R)^3} \right)^2$$

On trouve numériquement dans Mathematica la largeur à mi-hauteur : $2\pi k_{1/2} R = 1.8148$ en résolvant :

$$I_{\text{sphère}}(k_{1/2}, R) = \left(3 \frac{\sin(2\pi k_{1/2} R) - (2\pi k_{1/2} R) \cos(2\pi k_{1/2} R)}{(2\pi k_{1/2} R)^3} \right)^2 = 1/2$$

- Pour un ensemble de N plans distants de d , à partir de la fonction de Laue et de sa largeur à mi-hauteur, on obtient ¹ :

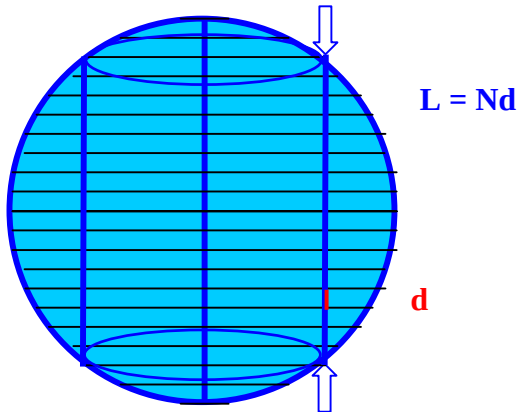
$$\Delta k_{FWHM} = 2k_{1/2} = \frac{1}{L} = \frac{0.89}{Nd} = \frac{1}{1.13Nd}$$

$$I_{\text{Laue}}(k_{1/2}, N, d) = \frac{1}{N^2} \left(\frac{\sin(N\pi k_{1/2} d)}{\sin(\pi k_{1/2} d)} \right)^2 = 1/2$$

Méthode de Guinier² :

On décompose la particule en assemblée de plans diffractants d'extension variable le long de la normale à ces plans. On effectue une moyenne volumique de cette extension, $\langle L \rangle_V$. Pour la largeur à mi-hauteur, on utilise l'expression précédente à partir de la fonction de Laue.

$$\Delta k_{FWHM} = 2k_{1/2} = \frac{1}{L} = \frac{0.89}{\langle L \rangle_V} \quad \langle L \rangle_V = \frac{1}{V} \int L dV$$



Pour une sphère, la moyenne volumique donne : $\langle L \rangle_V = \frac{3}{4}D$

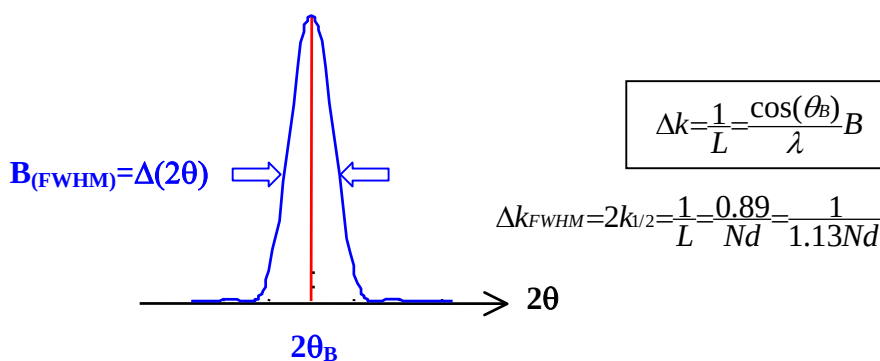
D'où :
$$\Delta k_{FWHM} = 2k_{1/2} = \frac{1}{L} = \frac{0.89}{\langle L \rangle_V} = \frac{1.19}{D} = \frac{1}{0.84D}$$

On retrouve une correction proche de celle obtenue précédemment en utilisant le facteur de forme de la sphère.

Dans le cas de sphères, l'élargissement est le même pour toutes les raies. Pour toutes les autres formes, l'élargissement est a priori différent pour les différentes raies hkl. On devra aussi distinguer la mesure pour un monocristal (élargissement anisotrope autour d'un pic de Bragg) et celle sur une poudre.

Passage en unité de 2θ

Pour les mesures sur poudre, il est usuel d'exprimer un élargissement de raie, noté B, en unités de 2θ : c'est l'expression classique de la formule de Scherrer^{2,3}. L est la largeur apparente de la raie de Bragg.

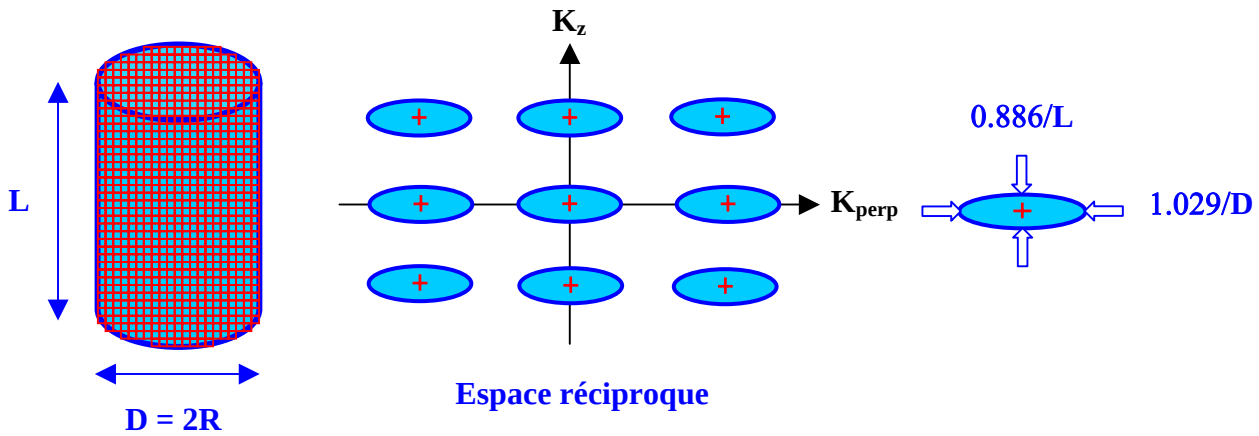


En différenciant la relation de Bragg, $k = \frac{2\sin(\theta)}{\lambda}$, au voisinage du pic, on obtient : $\Delta k = \frac{2\cos(\theta_B)}{\lambda} \Delta\theta$
Car la valeur de $\cos(\theta)$ est considérée constante, égale à $\cos(\theta_B)$.

En pratique, on doit soustraire à l'élargissement mesuré, B_{mes} , l'élargissement systématique dû à la taille du faisceau, B_{res} . Celui-ci est déterminé en remplaçant l'échantillon par une poudre de référence (par exemple, cristaux de quartz) dont les grains sont suffisamment gros. On utilise ensuite la relation : $B^2 = B_{mes}^2 - B_{res}^2$ (ou éventuellement : $B = B_{mes} - B_{res}$) pour tenir compte de la résolution.³

Particules anisotropes

Soit un monocristal ayant la forme d'un cylindre ou d'un disque, de longueur L et de diamètre $D = 2R$. Dans l'espace réciproque, les pics de Bragg provenant du réseau cristallin contenus dans l'objet sont élargis par le facteur de forme de la particule. Autour de l'origine, on a le même effet : c'est la diffusion centrale.



Elargissement des pics de Bragg d'un monocristal de forme anisotrope.

La forme des pics est donnée par le facteur de forme :

$$I(K_{perp}, K_z) \propto \left(\frac{\sin(\pi K_z L)}{\pi K_z L} \right)^2 \left(\frac{J_1(2\pi K_{perp} R)}{\pi K_{perp} R} \right)^2$$

On calcule numériquement la largeur à mi-hauteur du maximum principal de cette fonction dans différentes directions en utilisant la fonction FindRoot de Mathematica.

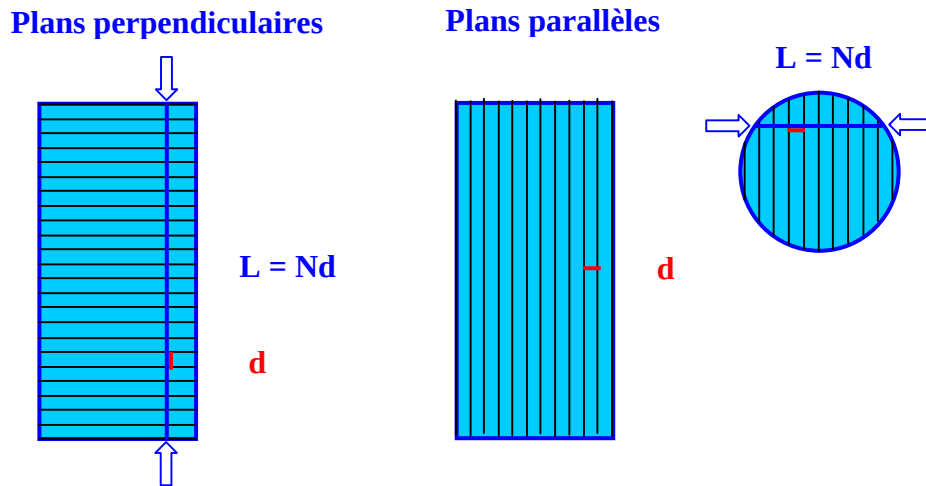
le long de l'axe z : $\Delta K_z = 2K_{z1/2} = \frac{0.886}{L}$

perpendiculairement à l'axe z : $\Delta K_{\text{perp}} = 2K_{\text{perp}1/2} = \frac{1.03}{D}$

le long d'une direction d'angle α avec l'axe z, l'élargissement a une valeur comprise entre ces deux valeurs, qui dépend du rapport d'anisotropie L/D.

Méthode de Guinier² :

Comme pour la sphère, on décompose la particule en assemblée de plans diffractants d'extension variable le long de la normale à ces plans, puis l'on effectue une moyenne volumique de cette extension, $\langle L \rangle_v$.



- Pour des plans diffractants perpendiculaires à l'axe, l'extension est constante et égale à L. On applique simplement la formule dérivée de la fonction de Laue :

$$\Delta k_{\text{FWHM}} = 2k_{1/2} = \frac{0.89}{\langle L \rangle_v} = \frac{0.89}{L}$$

- pour des plans diffractants contenant l'axe de la particule, la moyenne volumique $\langle L \rangle_v$ est égale à : $\langle L \rangle_v = \frac{8}{3\pi} D$

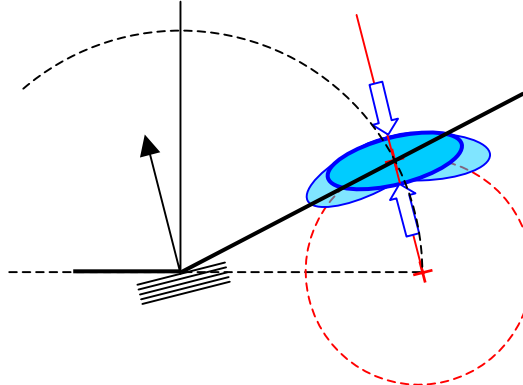
D'où : $\Delta k_{\text{FWHM}} = 2k_{1/2} = \frac{0.89}{\langle L \rangle_v} = \frac{1.05}{D}$

On trouve pratiquement les mêmes coefficients numériques qu'en utilisant le facteur de forme.

Poudre :

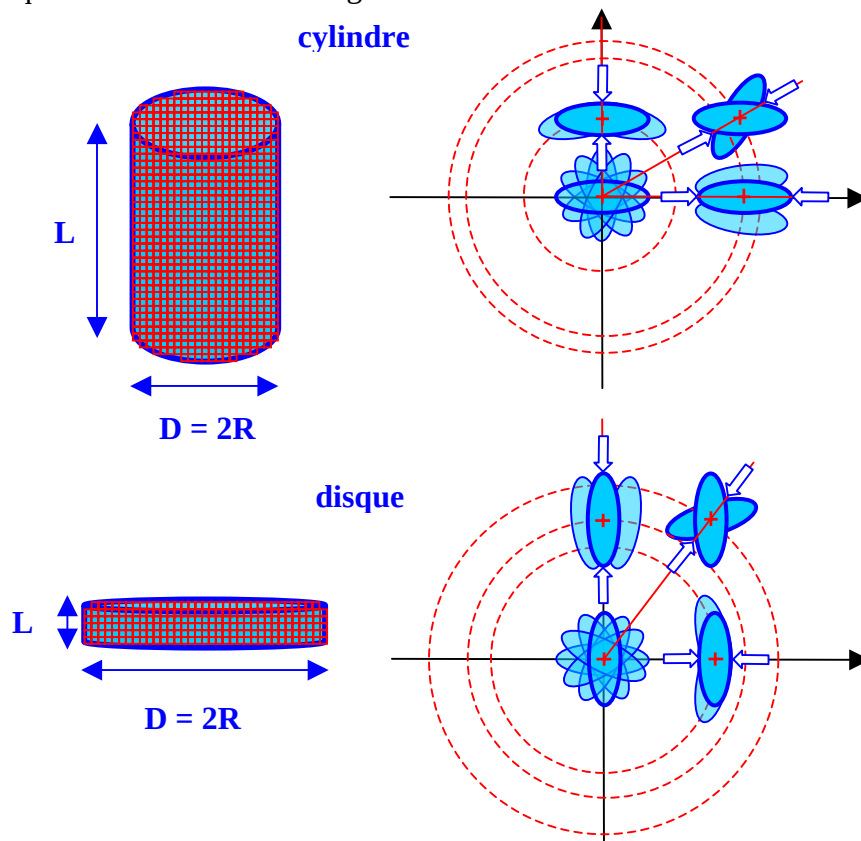
On fait ici l'hypothèse de particules toutes identiques : elles ont la même dimension, mais sont également toutes monocristallines, avec toujours la même orientation cristallographique par rapport à l'axe d'anisotropie. L'espace réciproque pour une poudre peut être obtenu en

faisant tourner l'espace réciproque du monocristal dans toutes les orientations spatiales (chapitre 6). Autour de l'origine, on moyenne directement le signal autour de l'origine. Pour un pic de Bragg, le signal parcourt une sphère de rayon k_{Bragg} . Dans le cas d'une poudre, on mesure uniquement l'élargissement dans la direction longitudinale d'un pic de Bragg.



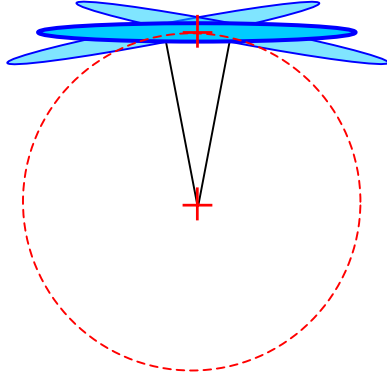
Mesure de l'élargissement longitudinal d'un pic de Bragg pour une poudre.

Ainsi, dans le cas de cylindres, les pics les plus élargis sont ceux correspondant à des familles de plan contenant l'axe de cylindre. Dans le cas de disques, le pic le plus élargi est celui correspondant à une famille de plans perpendiculaires à l'axe. Les familles de plans faisant un angle quelconque avec l'axe ont un élargissement intermédiaire.



Elargissement des pics de Bragg pour une poudre de cylindre ou de disques. Seul l'élargissement longitudinal est mesuré et dépend de l'orientation des familles de plans diffractants par rapport à l'axe des particules.

On voit qu'un effet d'asymétrie du profil longitudinal peut être obtenu, notamment dans le cas d'un élargissement transverse important. Si cet effet est négligeable, on considère que la largeur du pic dans la direction longitudinale est la même que pour un monocristal.



Effet d'asymétrie pour un élargissement transverse important.

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Chapitre 11

Reconstruction de la densité électronique

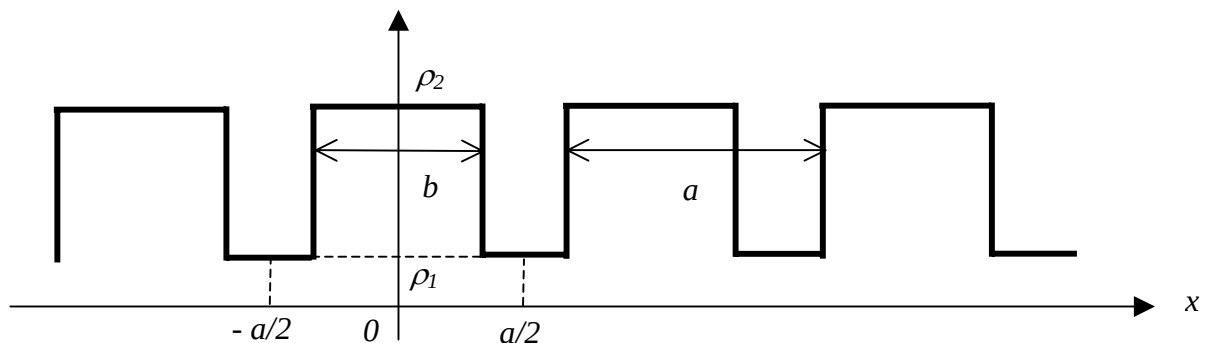
On utilise deux types de méthodes pour modéliser les intensités de diffraction, les méthodes dites directe et inverse. Par une méthode directe, on réalise un modèle de structure dans l'espace réel, comportant un certain nombre de paramètres (tailles des objets, contrastes de densité électronique), et l'on ajuste au mieux les valeurs de ces paramètres afin de rendre compte des données expérimentales.

Avec une méthode inverse, on réalise une transformation de Fourier à partir de l'espace réciproque vers l'espace réel, qui donne directement la forme de la fonction densité électronique. Cette méthode a l'avantage de ne pas supposer de modèle de structure au départ. Par contre, comme on mesure les intensités et non pas les amplitudes de diffusion, les phases sont a priori indéterminées pour réaliser la transformée de Fourier. C'est le problème des phases. Pour lever cette indétermination, on essaye les différentes combinaisons de phases possibles. Ensuite, on choisit parmi les différentes reconstructions de la densité électronique obtenues celles qui remplissent certains critères compatibles avec ce que l'on sait par ailleurs des objets (tailles, contraste).

Dans ce chapitre, on illustre par quelques exemples la méthode inverse.

Exemple à une dimension :

La densité électronique $\rho(x)$ est périodique à une dimension suivant x , de période a . On considère un modèle à deux niveaux, où des régions de largeur b et de densité ρ_1 alternent avec des régions de largeur $(a-b)$ et de densité ρ_2 .



L'amplitude de diffusion $A(k)$ s'écrit (où l'on intègre de $-L/2$ à $L/2$, avec $L = (2N+1)a$) :

$$A(k) = \int_{-\frac{L}{2}}^{\frac{L}{2}} \rho(x) e^{-2i\pi kx} dx = \left(\int_{-\frac{a}{2}}^{\frac{a}{2}} \rho(x) e^{-2i\pi kx} dx \right) \sum_{n=-N}^N e^{-2i\pi kna}$$

$$A(k) = a \left((\rho_2 - \rho_1) \frac{b}{a} \frac{\sin(\pi kb)}{\pi kb} + \rho_1 \frac{\sin(\pi ka)}{\pi ka} \right) \sum_{n=-N}^N e^{-2i\pi kna}$$

$A(k)$ est non nulle seulement pour les valeurs de $k^* = n/a$, où n est un entier. On note F_n les coefficients de Fourier :

$$F_n = \frac{1}{L} A\left(\frac{n}{a}\right) = (\rho_2 - \rho_1) r \frac{\sin(\pi nr)}{\pi nr} \quad \text{avec } r = \frac{b}{a} \quad \text{pour } n \neq 0$$

$$F_0 = \frac{1}{L} A(0) = (\rho_2 - \rho_1) r + \rho_1 = \langle \rho(x) \rangle$$

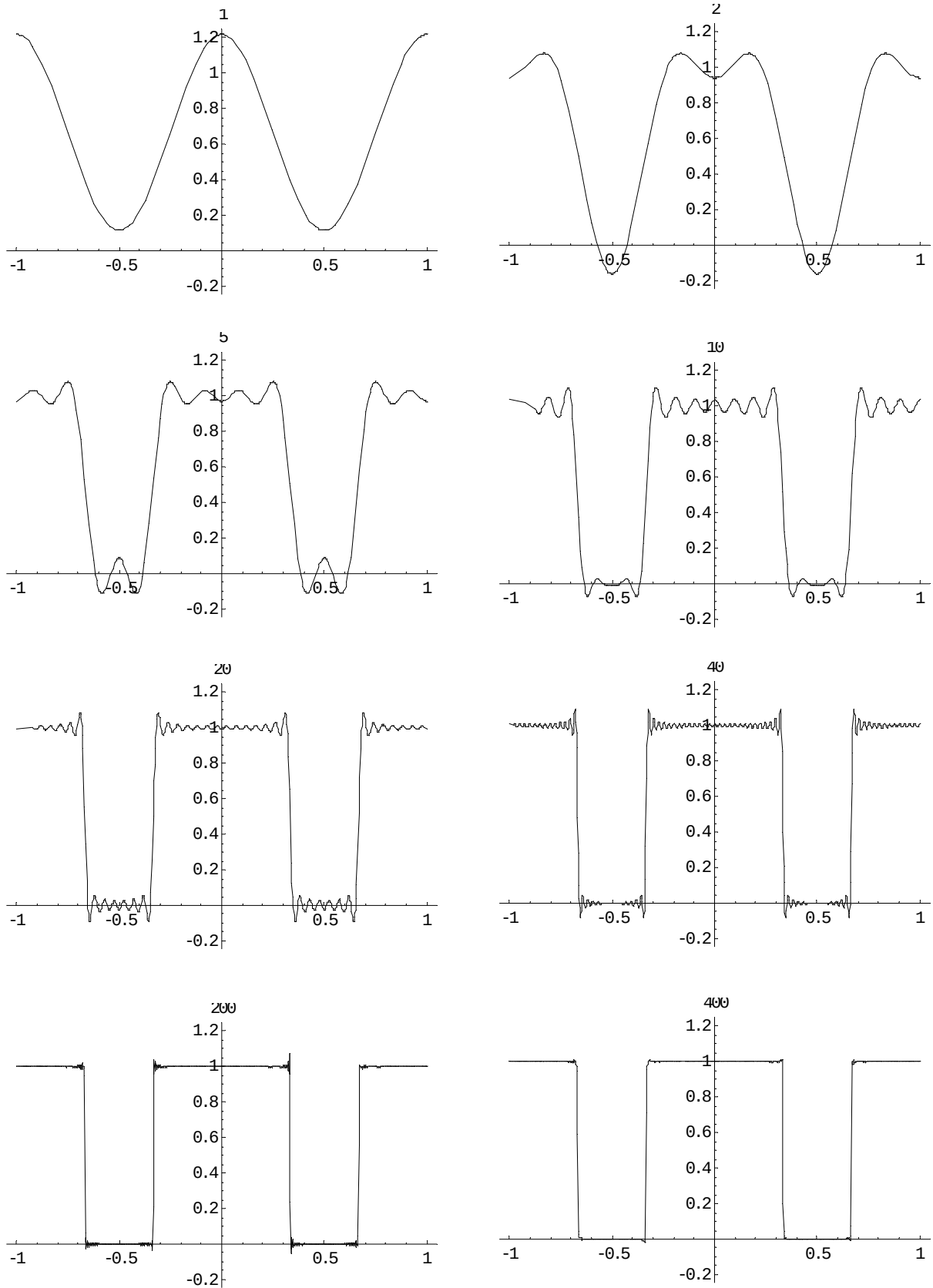
La décomposition en série de Fourier de $\rho(x)$ s'obtient par transformée de Fourier inverse. L'origine de l'axe des x est prise pour que $\rho(x)$ soit une fonction paire ($\rho(x) = \rho(-x)$), ce qui entraîne que $F_n = F_{-n}$.

$$\rho(x) = \sum_{n=-N}^{+N} F_n e^{2i\pi nx/a} = F_0 + 2 \sum_{n=1}^N F_n \cos\left(\frac{2\pi nx}{a}\right)$$

$$\rho(x) = \rho_1 + (\rho_2 - \rho_1) r \left(1 + 2 \sum_{n=1}^N \frac{\sin(\pi nr)}{\pi nr} \cos\left(\frac{2\pi nx}{a}\right) \right)$$

Si l'on reconstruit la fonction créneau périodique pour un nombre N de modes de Fourier, la reconstruction complète de la forme du créneau nécessite de l'ordre de 500 termes. Par contre, les valeurs de la largeur du créneau (rapport r) et de sa hauteur (1 pour cet exemple numérique) sont obtenues avec peu de termes, de l'ordre de 5, en faisant abstraction des oscillations résiduelles.

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Reconstruction d'un créneau ($r = b/a = 2/3$) en fonction du nombre N de modes de Fourier utilisés.

Expérimentalement, on mesure N ordres de diffraction, et l'on en déduit les valeurs absolues $|F_n|$ des coefficients de Fourier. Toujours dans l'hypothèse où $\rho(x)$ est une fonction paire, la densité reconstruite s'écrit comme précédemment, et seuls les signes relatifs des F_n sont inconnus.

$$\rho(x) = \langle \rho(x) \rangle + 2 \sum_{n=1}^N \pm |F_n| \cos\left(\frac{2\pi n x}{a}\right)$$

On reconstruit donc autant de cartes de densité électronique que de combinaisons de signes possibles, soit 2^{N-1} . Plus N est grand, plus la reconstruction est de bonne qualité, mais plus il est difficile de choisir parmi un grand nombre de cartes de densités électroniques, sans s'appuyer sur un modèle de structure.

Dans le cas où un modèle à deux niveaux est une bonne description, par exemple une phase lamellaire de copolymères di-blocs, un fit des données par les expressions des coefficients de Fourier d'une fonction créneau permet de déterminer la valeur de R . Le terme de contraste ($\rho_2 - \rho_1$) n'est connu qu'au signe près (Théorème de Babinet), puisque l'on ne mesure que les valeurs absolues $|F_n|$.

Reconstruction à 3D :

Les expressions précédentes se généralisent au cas d'une maille 3D, définie par les vecteurs $(\vec{a}, \vec{b}, \vec{c})$. La densité électronique $\rho(\vec{x})$ est périodique à 3 dimensions et se reconstruit avec les coefficients de Fourier F_{hkl} :

$$\rho(\vec{x}) = \sum_{hkl} F_{hkl} e^{+2i\pi(hx+ky+lz)}$$

avec : $F_{hkl} = \frac{1}{V_{\text{maille}} V_{\text{maille}}} \int \rho(\vec{x}) e^{-2i\pi(hx+ky+lz)} d\vec{x} = \frac{A(\vec{k}^*)}{N_{\text{maille}} V_{\text{maille}}}$

$$F_{000} = \frac{1}{V_{\text{maille}} V_{\text{maille}}} \int \rho(\vec{x}) d\vec{x} = \langle \rho(\vec{x}) \rangle$$

$$\vec{x} = x \vec{a} + y \vec{b} + z \vec{c} \quad \text{et} \quad \vec{k}^* = h \vec{a}^* + k \vec{b}^* + l \vec{c}^*$$

Expérimentalement, on mesure l'intensité intégrée d'un pic de Bragg dans l'espace réciproque, qui est proportionnelle à $|F_{hkl}|^2$ (chapitre 6) :

$$I_{\text{mono}}^{\text{int}}(\vec{k}^*) = \int_{dV^*} I(\vec{k}) d\vec{k} = N_{\text{maille}} V_{\text{maille}} |F_{hkl}|^2$$

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$$\text{avec : } F_{hkl} = \frac{1}{V_{\text{maille}}} \int \rho(\vec{x}) e^{-2i\pi(hx+ky+lz)} d\vec{x} = \frac{A(\vec{k}^*)}{N_{\text{maille}} V_{\text{maille}}}$$

En effet :

$$A(\vec{k}) = \int_{V_{\text{cristal}}} \rho(\vec{x}) e^{-2i\pi\vec{k}\vec{x}} d\vec{x} = \left(\int_{V_{\text{maille}}} \rho(\vec{x}) e^{-2i\pi\vec{k}\vec{x}} d\vec{x} \right) \sum_n e^{-2i\pi\vec{k}\vec{R}_n}$$

$$I(\vec{k}) = |A(\vec{k})|^2 = \left| \int_{V_{\text{maille}}} \rho(\vec{x}) e^{-2i\pi\vec{k}\vec{x}} d\vec{x} \right|^2 \left(\frac{\sin(N_x \pi \vec{k} \cdot \vec{a})}{\sin(\pi \vec{k} \cdot \vec{a})} \right)^2 \left(\frac{\sin(N_y \pi \vec{k} \cdot \vec{b})}{\sin(\pi \vec{k} \cdot \vec{b})} \right)^2 \left(\frac{\sin(N_z \pi \vec{k} \cdot \vec{c})}{\sin(\pi \vec{k} \cdot \vec{c})} \right)^2$$

Avec $N_x N_y N_z = N_{\text{maille}}$.

L'intensité intégrée autour d'un pic de Bragg dans l'espace réciproque vaut (chapitre 6):

$$I_{\text{mono}}(\vec{k}^*) = \left| \int_{V_{\text{maille}}} \rho(\vec{x}) e^{-2i\pi\vec{k}^* \cdot \vec{x}} d\vec{x} \right|^2 \frac{N_{\text{maille}}}{V_{\text{maille}}}$$

Les coefficients de Fourier sont a priori complexes, avec des phases φ_{hkl} indéterminées.

$$\rho(\vec{x}) = \sum_{hkl} |F_{hkl}| e^{i\varphi_{hkl}} e^{+2i\pi(hx+ky+lz)}$$

En utilisant la Loi de Friedel (valable loin d'un seuil d'absorption), $|F_{hkl}| = |F_{-h-k-l}|$ et

$\varphi_{hkl} = -\varphi_{-h-k-l}$, on obtient :

$$\rho(\vec{x}) - \langle \rho(\vec{x}) \rangle = 2 \sum_{hkl \text{ demi-espace}} |F_{hkl}| \left(\cos(\varphi_{hkl}) \cos(2\pi(hx+ky+lz)) - \sin(\varphi_{hkl}) \sin(2\pi(hx+ky+lz)) \right)$$

Dans le cas d'un groupe centro-symétrique, $\rho(\vec{x}) = \rho(-\vec{x})$ (avec l'origine sur le centre d'inversion), les coefficients de Fourier sont réels, et les phases valent soit 0 soit $\pm\pi$. On a aussi $F_{hkl} = F_{-h-k-l}$.

$$\rho(\vec{x}) - \langle \rho(\vec{x}) \rangle = 2 \sum_{hkl \text{ demi-espace}} |F_{hkl}| \cos(\varphi_{hkl}) \cos(2\pi(hx+ky+lz)) = \sum_{hkl \neq 000} |F_{hkl}| \cos(\varphi_{hkl}) \cos(2\pi(hx+ky+lz))$$

avec $\cos(\varphi_{hkl}) = \pm 1.$

On retrouve une expression similaire à l'exemple du créneau à une dimension. Pour N intensités mesurées, on a 2^{N-1} combinaisons de signe différentes.

Rq : On reconstruit la densité électronique par rapport à sa valeur moyenne $\langle \rho(\vec{x}) \rangle$. Le coefficient F_{000} n'est pas mesurable, car situé au centre de l'espace réciproque.

Cas des phases cubiques (groupe ponctuel $m\bar{3}m$) :

On explicite la somme précédente dans le cas d'une maille cubique, pour un groupe ponctuel $m\bar{3}m$. On a vu en effet que les phases cubiques que nous étudions ont toutes ce groupe ponctuel (chapitre 9). Les éléments de symétrie de la maille permettent de relier les valeurs des différents coefficients de Fourier F_{hkl} , pour des valeurs des indices hkl fixées (par exemple, une relation simple entre F_{hkl} et F_{-hkl}).

Tout d'abord, on choisit l'origine sur le centre d'inversion de la maille : $\rho(\vec{x}) = \rho(-\vec{x})$ et

$$F_{-h-k-l} = \frac{1}{V_{\text{maille maille}}} \int \rho(\vec{x}) e^{-2i\pi(-hx-ky-lz)} d\vec{x} = \frac{1}{V_{\text{maille maille}}} \int \rho(-\vec{x}) e^{-2i\pi(hx+ky+lz)} d\vec{x} = F_{hkl}$$

Ensuite, on a toujours un axe d'ordre trois passant par l'origine, ce qui donne la relation

$$F_{hkl} = F_{klh} = F_{lkh} \quad (\text{permutation circulaire des indices}) \quad \text{car} \quad \rho(x,y,z) = \rho(y,z,x) = \rho(z,x,y).$$

La relation $F_{-hkl} = F_{hkl}$ (changement de signe d'un indice) est toujours vérifiée seulement s'il y a un miroir perpendiculaire à un axe 4 passant par l'origine. De même, la relation $F_{khl} = F_{hkl}$ (permutations de deux indices) n'est toujours vérifiée que pour un miroir perpendiculaire à un axe 2 passant par l'origine. Ainsi, ces deux relations ne sont vérifiées toutes deux que pour le groupe $Im\bar{3}m$.

Dans le cas de miroirs à glissement (groupes $Pm\bar{3}n$ et $Ia\bar{3}d$), on a parfois un signe entre deux coefficients de Fourier, par exemple $F_{-hkl} = -F_{hkl}$.

On donne ci-dessous les expressions des termes de Fourier permettant de reconstruire la densité électronique à partir des coefficients de Fourier F_{hkl} pour différents groupes d'espace.

Rappel : on a un groupe centro-symétrique et $\cos(\varphi_{hkl}) = \pm 1$ avec $\varphi_{hkl} = 0$ ou $\pm\pi$.

Centre d'inversion + axe 3 :

hkl	Termes de Fourier	$M(hkl)$
$h00$	$2 F_{h00} \cos(\varphi_{h00})(\cos(2\pi hx) + \cos(2\pi hy) + \cos(2\pi hz))$	6
hhh	$2 F_{hhh} \cos(\varphi_{hhh})(\cos(2\pi h(x+y+z)))$ $+ 2 F_{h-hh} \cos(\varphi_{h-hh})(\cos(2\pi h(-x+y+z)) + \cos(2\pi h(x-y+z)) + \cos(2\pi h(x+y-z)))$	8
$hh0$	$2 F_{hh0} \cos(\varphi_{hh0})(\cos(2\pi h(x+y)) + \cos(2\pi h(y+z)) + \cos(2\pi h(z+x))) +$ $2 F_{h-h0} \cos(\varphi_{h-h0})(\cos(2\pi h(x-y)) + \cos(2\pi h(y-z)) + \cos(2\pi h(z-x)))$	12
$hk0$	$2 F_{hk0} \cos(\varphi_{hk0})(\cos(2\pi(hx+ky)) + \cos(2\pi(hy+kz)) + \cos(2\pi(hz+kx))) +$ $2 F_{h-k0} \cos(\varphi_{h-k0})(\cos(2\pi(hx-ky)) + \cos(2\pi(hy-kz)) + \cos(2\pi(hz-kx))) +$ $2 F_{k0} \cos(\varphi_{k0})(\cos(2\pi(kx+hy)) + \cos(2\pi(ky+hz)) + \cos(2\pi(kz+hx))) +$ $2 F_{k-h0} \cos(\varphi_{k-h0})(\cos(2\pi(kx-hy)) + \cos(2\pi(ky-hz)) + \cos(2\pi(kz-hx)))$	24
hhl	$2 F_{hhl} \cos(\varphi_{hhl})(\cos(2\pi(hx+hy+lz)) + \cos(2\pi(hy+hz+lx)) + \cos(2\pi(hz+hx+ly))) +$ $2 F_{h-hl} \cos(\varphi_{h-hl})(\cos(2\pi(hx-hy+lz)) + \cos(2\pi(hy-hz+lx)) + \cos(2\pi(hz-hx+ly))) +$ $2 F_{-hhl} \cos(\varphi_{-hhl})(\cos(2\pi(-hx+hy+lz)) + \cos(2\pi(-hy+hz+lx)) + \cos(2\pi(-hz+hx+ly))) +$ $2 F_{hh-l} \cos(\varphi_{hh-l})(\cos(2\pi(hx+hy-lz)) + \cos(2\pi(hy+hz-lx)) + \cos(2\pi(hz+hx-ly)))$	24
hkl	$2 F_{hkl} \cos(\varphi_{hkl})(\cos(2\pi(hx+ky+lz)) + \cos(2\pi(hy+kz+lx)) + \cos(2\pi(hz+kx+ly))) +$ $2 F_{-hkl} \cos(\varphi_{-hkl})(\cos(2\pi(-hx+ky+lz)) + \cos(2\pi(-hy+kz+lx)) + \cos(2\pi(-hz+kx+ly))) +$ $2 F_{h-kl} \cos(\varphi_{h-kl})(\cos(2\pi(hx-ky+lz)) + \cos(2\pi(hy-kz+lx)) + \cos(2\pi(hz-kx+ly))) +$ $2 F_{hk-l} \cos(\varphi_{hk-l})(\cos(2\pi(hx+ky-lz)) + \cos(2\pi(hy+kz-lx)) + \cos(2\pi(hz+kx-ly))) +$ $2 F_{khl} \cos(\varphi_{khl})(\cos(2\pi(kx+hy+lz)) + \cos(2\pi(ky+hz+lx)) + \cos(2\pi(kz+hx+ly))) +$ $2 F_{-khl} \cos(\varphi_{-khl})(\cos(2\pi(-kx+hy+lz)) + \cos(2\pi(-ky+hz+lx)) + \cos(2\pi(-kz+hx+ly))) +$ $2 F_{k-hl} \cos(\varphi_{k-hl})(\cos(2\pi(kx-hy+lz)) + \cos(2\pi(ky-hz+lx)) + \cos(2\pi(kz-hx+ly))) +$ $2 F_{kh-l} \cos(\varphi_{kh-l})(\cos(2\pi(kx+hy-lz)) + \cos(2\pi(ky+hz-lx)) + \cos(2\pi(kz+hx-ly)))$	48

groupe $Im \bar{3}m$:

hkl	Termes de Fourier	$M(hkl)$
$h00$	$2 F_{h00} \cos(\varphi_{h00})(\cos(2\pi hx) + \cos(2\pi hy) + \cos(2\pi hz))$	6
hhh	$2 F_{hhh} \cos(\varphi_{hhh})(\cos(2\pi h(x+y+z)))$ $+ (\cos(2\pi h(-x+y+z)) + \cos(2\pi h(x-y+z)) + \cos(2\pi h(x+y-z)))$	8
$hh0$	$2 F_{hh0} \cos(\varphi_{hh0})(\cos(2\pi h(x+y)) + \cos(2\pi h(y+z)) + \cos(2\pi h(z+x))) +$ $\cos(2\pi h(x-y)) + \cos(2\pi h(y-z)) + \cos(2\pi h(z-x)))$	12
$hk0$	$2 F_{hk0} \cos(\varphi_{hk0})(\cos(2\pi(hx+ky)) + \cos(2\pi(hy+kz)) + \cos(2\pi(hz+kx))) +$ $\cos(2\pi(hx-ky)) + \cos(2\pi(hy-kz)) + \cos(2\pi(hz-kx))) +$ $\cos(2\pi(kx+hy)) + \cos(2\pi(ky+hz)) + \cos(2\pi(kz+hx))) +$ $\cos(2\pi(kx-hy)) + \cos(2\pi(ky-hz)) + \cos(2\pi(kz-hx)))$	24
hhl	$2 F_{hhl} \cos(\varphi_{hhl})(\cos(2\pi(hx+hy+lz)) + \cos(2\pi(hy+hz+lx)) + \cos(2\pi(hz+hx+ly))) +$ $\cos(2\pi(hx-hy+lz)) + \cos(2\pi(hy-hz+lx)) + \cos(2\pi(hz-hx+ly))) +$ $\cos(2\pi(-hx+hy+lz)) + \cos(2\pi(-hy+hz+lx)) + \cos(2\pi(-hz+hx+ly))) +$ $\cos(2\pi(hx+hy-lz)) + \cos(2\pi(hy+hz-lx)) + \cos(2\pi(hz+hx-ly)))$	24
hkl	$2 F_{hkl} \cos(\varphi_{hkl})(\cos(2\pi(hx+ky+lz)) + \cos(2\pi(hy+kz+lx)) + \cos(2\pi(hz+kx+ly))) +$ $\cos(2\pi(-hx+ky+lz)) + \cos(2\pi(-hy+kz+lx)) + \cos(2\pi(-hz+kx+ly))) +$ $\cos(2\pi(hx-ky+lz)) + \cos(2\pi(hy-kz+lx)) + \cos(2\pi(hz-kx+ly))) +$ $\cos(2\pi(hx+ky-lz)) + \cos(2\pi(hy+kz-lx)) + \cos(2\pi(hz+kx-ly))) +$ $\cos(2\pi(kx+hy+lz)) + \cos(2\pi(ky+hz+lx)) + \cos(2\pi(kz+hx+ly))) +$ $\cos(2\pi(-kx+hy+lz)) + \cos(2\pi(-ky+hz+lx)) + \cos(2\pi(-kz+hx+ly))) +$ $\cos(2\pi(kx-hy+lz)) + \cos(2\pi(ky-hz+lx)) + \cos(2\pi(kz-hx+ly))) +$ $\cos(2\pi(kx+hy-lz)) + \cos(2\pi(ky+hz-lx)) + \cos(2\pi(kz+hx-ly)))$	48

Chapitre 11

Groupe $Pm\bar{3}n$: Centre d'inversion + axe 3 + axe 4 + miroir n

Pour le groupe $Pm\bar{3}n$, on a un miroir n perpendiculaire à un axe 2, et l'on a : $F_{khl} = (-1)^{h+k+l} F_{hkl}$

hkl	Termes de Fourier	$M(hkl)$
$h00$	$2 F_{h00} \cos(\varphi_{h00}) (\cos(2\pi hx) + \cos(2\pi hy) + \cos(2\pi hz))$	6
hhh	$2 F_{hhh} \cos(\varphi_{hhh}) (\cos(2\pi h(x+y+z)) + \cos(2\pi h(-x+y+z)) + \cos(2\pi h(x-y+z)) + \cos(2\pi h(x+y-z)))$	8
$hh0$	$2 F_{hh0} \cos(\varphi_{hh0}) (\cos(2\pi h(x+y)) + \cos(2\pi h(y+z)) + \cos(2\pi h(z+x)) + \cos(2\pi h(x-y)) + \cos(2\pi h(y-z)) + \cos(2\pi h(z-x)))$	12
$hk0$	$2 F_{hk0} \cos(\varphi_{hk0}) (\cos(2\pi(hx+ky)) + \cos(2\pi(hy+kz)) + \cos(2\pi(hz+kx)) + \cos(2\pi(hx-ky)) + \cos(2\pi(hy-kz)) + \cos(2\pi(hz-kx))) + (-1)^{h+k} (\cos(2\pi(kx+hy)) + \cos(2\pi(ky+hz)) + \cos(2\pi(kz+hx)) + \cos(2\pi(kx-hy)) + \cos(2\pi(ky-hz)) + \cos(2\pi(kz-hx)))$	24
hhl	$2 F_{hhl} \cos(\varphi_{hhl}) (\cos(2\pi(hx+hy+lz)) + \cos(2\pi(hy+hz+lx)) + \cos(2\pi(hz+hx+ly)) + \cos(2\pi(hx-hy+lz)) + \cos(2\pi(hy-hz+lx)) + \cos(2\pi(hz-hx+ly)) + \cos(2\pi(-hx+hy+lz)) + \cos(2\pi(-hy+hz+lx)) + \cos(2\pi(-hz+hx+ly)) + \cos(2\pi(hx+hy-lz)) + \cos(2\pi(hy+hz-lx)) + \cos(2\pi(hz+hx-ly)))$	24
hkl	$2 F_{hkl} \cos(\varphi_{hkl}) (\cos(2\pi(hx+ky+lz)) + \cos(2\pi(hy+kz+lx)) + \cos(2\pi(hz+kx+ly)) + \cos(2\pi(-hx+ky+lz)) + \cos(2\pi(-hy+kz+lx)) + \cos(2\pi(-hz+kx+ly)) + \cos(2\pi(hx-ky+lz)) + \cos(2\pi(hy-kz+lx)) + \cos(2\pi(hz-kx+ly)) + \cos(2\pi(hx+ky-lz)) + \cos(2\pi(hy+kz-lx)) + \cos(2\pi(hz+kx-ly))) + (-1)^{h+k+l} (\cos(2\pi(kx+hy+lz)) + \cos(2\pi(ky+hz+lx)) + \cos(2\pi(kz+hx+ly)) + \cos(2\pi(-kx+hy+lz)) + \cos(2\pi(-ky+hz+lx)) + \cos(2\pi(-kz+hx+ly)) + \cos(2\pi(kx-hy+lz)) + \cos(2\pi(ky-hz+lx)) + \cos(2\pi(kz-hx+ly)) + \cos(2\pi(kx+hy-lz)) + \cos(2\pi(ky+hz-lx)) + \cos(2\pi(kz+hx-ly)))$	48

Ia $\bar{3}d$: Centre d'inversion + axe 3 + miroirs à glissement perpendiculaires aux axes 4 et 2

$$F_{-hkl} = (-1)^{h+k} F_{hkl} \quad F_{khl} = (-1)^{(h+k+l)/2} F_{hkl}$$

hkl	Termes de Fourier	$M(hkl)$
$h00$	$2 F_{h00} \cos(\varphi_{h00}) (\cos(2\pi hx) + \cos(2\pi hy) + \cos(2\pi hz))$	6
hhh	$2 F_{hhh} \cos(\varphi_{hhh}) (\cos(2\pi h(x+y+z)) + \cos(2\pi h(-x+y+z)) + \cos(2\pi h(x-y+z)) + \cos(2\pi h(x+y-z)))$	8
$hh0$	$2 F_{hh0} \cos(\varphi_{hh0}) (\cos(2\pi h(x+y)) + \cos(2\pi h(y+z)) + \cos(2\pi h(z+x)) + \cos(2\pi h(x-y)) + \cos(2\pi h(y-z)) + \cos(2\pi h(z-x)))$	12
$hk0$	$2 F_{hk0} \cos(\varphi_{hk0}) (\cos(2\pi(hx+ky)) + \cos(2\pi(hy+kz)) + \cos(2\pi(hz+kx)) + \cos(2\pi(hx-ky)) + \cos(2\pi(hy-kz)) + \cos(2\pi(hz-kx))) + (-1)^{(h+k)/2} (\cos(2\pi(kx+hy)) + \cos(2\pi(ky+hz)) + \cos(2\pi(kz+hx)) + \cos(2\pi(kx-hy)) + \cos(2\pi(ky-hz)) + \cos(2\pi(kz-hx)))$	24
hhl	$2 F_{hhl} \cos(\varphi_{hhl}) (\cos(2\pi(hx+hy+lz)) + \cos(2\pi(hy+hz+lx)) + \cos(2\pi(hz+hx+ly)) + \cos(2\pi(-hx+hy+lz)) + \cos(2\pi(-hy+hz+lx)) + \cos(2\pi(-hz+hx+ly))) + (-1)^h (\cos(2\pi(hx-hy+lz)) + \cos(2\pi(hy-hz+lx)) + \cos(2\pi(hz-hx+ly)) + \cos(2\pi(hx+hy-lz)) + \cos(2\pi(hy+hz-lx)) + \cos(2\pi(hz+hx-ly)))$	24
hkl	$2 F_{hkl} \cos(\varphi_{hkl}) (\cos(2\pi(hx+ky+lz)) + \cos(2\pi(hy+kz+lx)) + \cos(2\pi(hz+kx+ly)) + (-1)^{h+k} (\cos(2\pi(-hx+ky+lz)) + \cos(2\pi(-hy+kz+lx)) + \cos(2\pi(-hz+kx+ly))) + (-1)^{k+l} (\cos(2\pi(hx-ky+lz)) + \cos(2\pi(hy-kz+lx)) + \cos(2\pi(hz-kx+ly))) + (-1)^{l+h} (\cos(2\pi(hx+ky-lz)) + \cos(2\pi(hy+kz-lx)) + \cos(2\pi(hz+kx-ly))) + (-1)^{(h+k+l)/2} (\cos(2\pi(kx+hy+lz)) + \cos(2\pi(ky+hz+lx)) + \cos(2\pi(kz+hx+ly)) + (-1)^{h+k} (\cos(2\pi(-kx+hy+lz)) + \cos(2\pi(-ky+hz+lx)) + \cos(2\pi(-kz+hx+ly))) + (-1)^{k+l} (\cos(2\pi(kx-hy+lz)) + \cos(2\pi(ky-hz+lx)) + \cos(2\pi(kz-hx+ly))) + (-1)^{l+h} (\cos(2\pi(kx+hy-lz)) + \cos(2\pi(ky+hz-lx)) + \cos(2\pi(kz+hx-ly)))$	48

Chapitre 11

Enfin, dans un cadre plus général, les expressions des fonctions trigonométriques sont tabulées dans les tables internationales de cristallographie pour tous les groupes d'espace.¹

Reference

1. *International Tables for Crystallography*; Kluwer Academic Publishers: 1995; Vol. B, section 1.4.

Chapitre 12

Contraste en diffusion des rayons X et des neutrons

Que l'on utilise les rayons X ou les neutrons, l'origine des signaux en diffusion provient des inhomogénéités de la matière : objets dans un solvant, fluctuations de densité excitées thermiquement. Encore faut-il que ces inhomogénéités correspondent à un contraste avec le rayonnement utilisé pour que l'on puisse les détecter.

Dans le cas des rayons X, on est sensible aux inhomogénéités de la densité électronique, qui suivent globalement celles de la densité de la matière. Ainsi, suivant la nature des objets en solution dans l'eau, le contraste pourra être faible (protéines, micelles), ou élevé (nanoparticules métalliques ou d'oxydes métalliques).

Lorsqu'il s'agit des neutrons, le contraste provient des longueurs de diffusion des différents noyaux, qui varient très aléatoirement en fonction de la masse atomique. Le contraste auquel on est sensible est celui de la densité de longueur de diffusion. En solution dans l'eau, on peut par contre modifier ce contraste en variant les proportions d'eau lourde (D_2O) et d'eau légère (H_2O) : c'est la méthode de variation de contraste.

Densités électroniques :

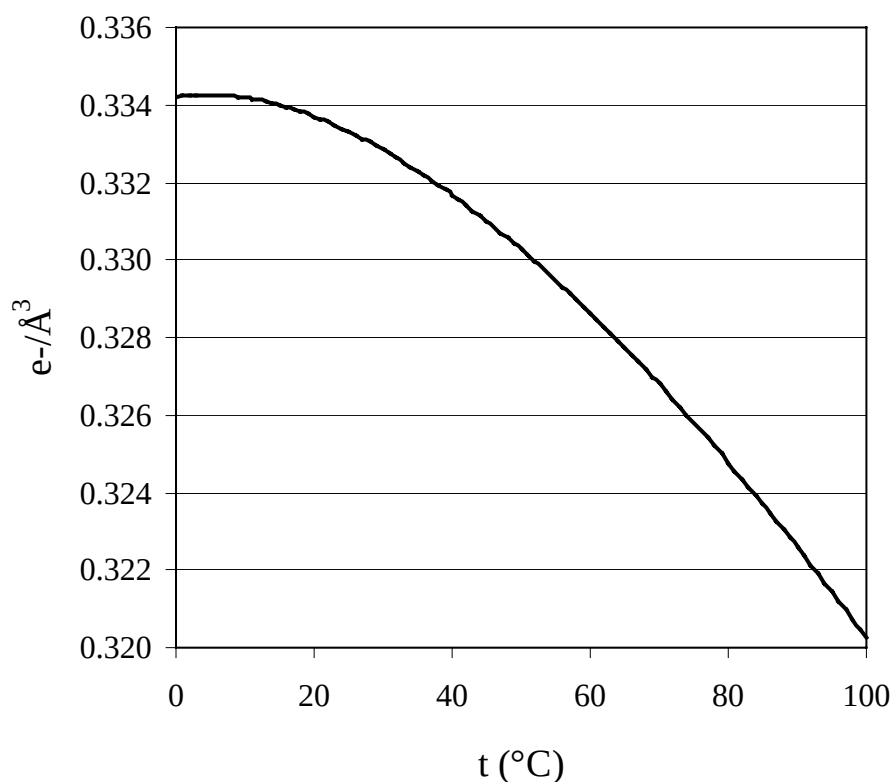
$\rho(\vec{x})$ est la densité électronique, soit un nombre d'électrons par unité de volume. Dans le cas des phases organisées, on décrit la matière à l'échelle moléculaire, comme un milieu continu, et $\rho(\vec{x})$ est alors une fonction continue. C'est cette description qui est adoptée ici. Elle n'est valable que pour les petits vecteurs de diffusion, pour lesquels la décroissance des facteurs de diffusion atomique avec l'angle de Bragg est négligeable. Autrement dit, le facteur de diffusion atomique est pris égal à Z , le nombre d'électrons de l'atome considéré.

On donne ici quelques valeurs de densités électroniques. Pour une molécule contenant N_e électrons dans un volume v , on a :

$$\rho \text{ (e-/\AA}^3\text{)} = \frac{N_e}{v(\text{\AA}^3)} = \frac{N_e N_A d \text{ (g/cm}^3\text{)}}{10^{24} M \text{ (g/mol)}}$$

N_A est le nombre d'Avogadro.

	M (g/mol)	N _e	densité (g/cm ³)	v (Å ³)	ρ (e ⁻ / Å ³)
H ₂ O	18.016	10	0.998	30.0	0.334
PO	58.078	32	1.004	96.1	0.333
EO	44.052	24	1.13	64.7	0.371
-CH ₂ (20°C)	14.026	8	0.860	27.1	0.295
-CH ₃ (20°C)	15.034	9	0.466	53.6	0.168
-C ₁₂ H ₂₅ (20°C)	169.32	97	0.800	351.4	0.276
SiO ₂	60.09	30	2.2	45.4	0.661
MnO ₂ (pyrolusite)	86.94	41	5.2	27.8	1.477
Pt	195.08	78	21.09	15.4	5.078



Densité électronique de l'eau en fonction de la température.

Chaînes alkyl

Pour les molécules thermotropes ou les molécules de tensioactif, on a besoin d'estimer la densité électronique des chaînes alkyl. Ceci est fait en estimant que leur densité est voisine de celle des alcanes à l'état liquide.

Pour les densités à 20°C, on utilise les densités connues des alcanes de 9 à 16 carbones. En utilisant une régression linéaire, on calcule les volumes moyens d'un groupe -CH₂ et d'un groupe -CH₃ : $v(\text{CH}_2)=27.1 \text{ Å}^3$ et $v(\text{CH}_3)=53.6 \text{ Å}^3$ à 20°C.

Ces volumes sont proche de ceux donnés par Tanford à température ambiante ($v(\text{CH}_2)=26.9 \text{ \AA}^3$ et $v(\text{CH}_3)=54.3 \text{ \AA}^3$)¹.

On en déduit alors la densité électronique moyenne pour des chaînes alkyls.

	M (g/mol)	N _e	densité (g/cm ³)	$v (\text{\AA}^3)$	$\rho (\text{e}^-/\text{\AA}^3)$
nonane	128.25	74	0.7176	296.8	0.249
decane	142.276	82	0.73	323.6	0.253
undecane	156.302	90	0.7402	350.6	0.257
dodecane	170.328	98	0.7487	377.8	0.259
tridecane	184.354	106	0.7564	404.7	0.262
tetradecane	198.38	114	0.7628	431.9	0.264
pentadecane	212.406	122	0.7685	459.0	0.266
hexadecane	226.432	130	0.7733	486.2	0.267
nonane	128.25	74	0.7176	296.8	0.249
-CH ₂ (20°C)	14.026	8	0.860	27.1	0.295
-CH ₃ (20°C)	15.034	9	0.466	53.6	0.168
-C ₉ H ₁₉ (20°C)	127.242	73	0.782	270.2	0.270
-C ₁₀ H ₂₁ (20°C)	141.268	81	0.789	297.3	0.272
-C ₁₁ H ₂₃ (20°C)	155.294	89	0.795	324.4	0.274
-C ₁₂ H ₂₅ (20°C)	169.32	97	0.800	351.4	0.276
-C ₁₃ H ₂₇ (20°C)	183.346	105	0.804	378.5	0.277
-C ₁₄ H ₂₉ (20°C)	197.372	113	0.808	405.6	0.279
-C ₁₅ H ₃₁ (20°C)	211.398	121	0.811	432.7	0.280
-C ₁₆ H ₃₃ (20°C)	225.424	129	0.814	459.7	0.281

Alcanes et chaînes alkyl à 20°C .

A partir des valeurs de la densité en fonction de la température des alcanes liquides, on obtient la densité électronique de ces mêmes alcanes en fonction de la température. Une bonne approximation est de considérer une variation linéaire en température de la forme :

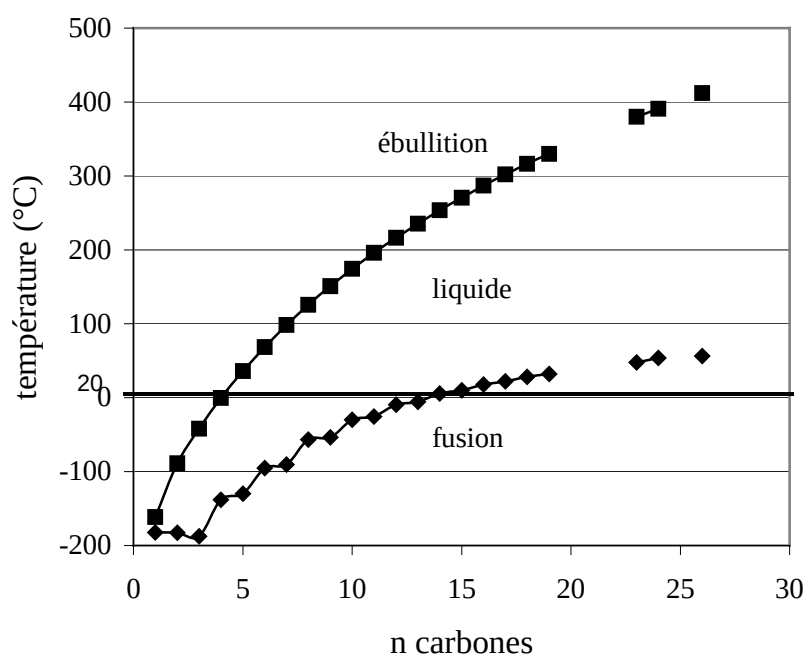
$$\rho (\text{e}^-/\text{\AA}^3)(t) = \rho (\text{e}^-/\text{\AA}^3) (20^\circ\text{C}) - 0.0003 (t(^\circ\text{C})-20) \text{ (pour les chaînes courtes, } n < 10)$$

$$\rho (\text{e}^-/\text{\AA}^3)(t) = \rho (\text{e}^-/\text{\AA}^3) (20^\circ\text{C}) - 0.00026 (t(^\circ\text{C})-20) \text{ (pour les chaînes longues, } 0 < n < 25)$$

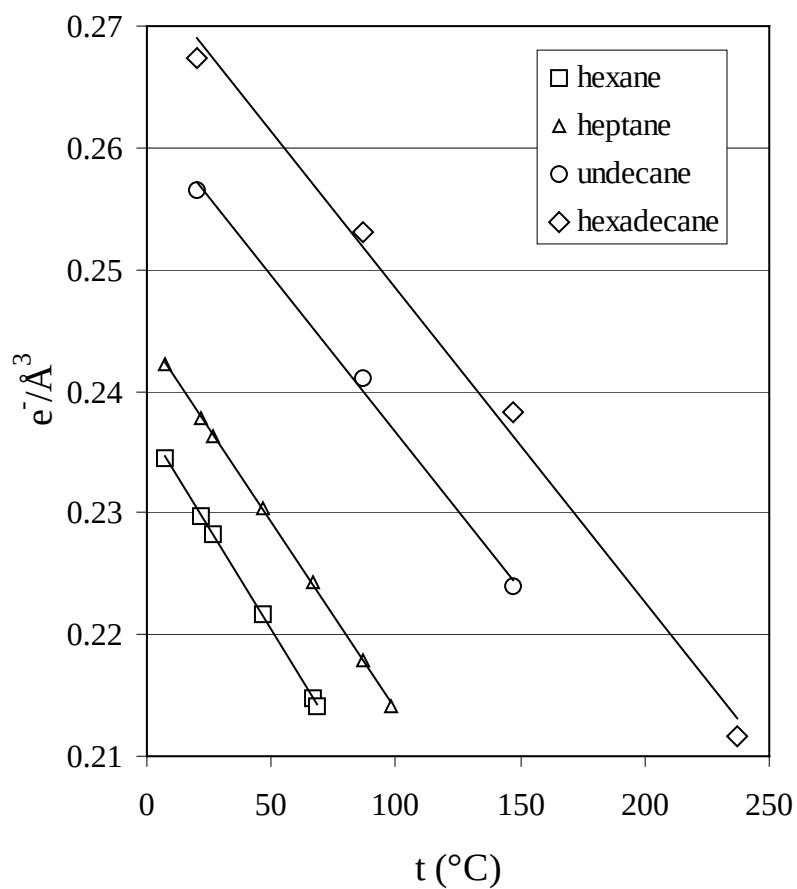
On peut également utiliser les valeurs données par F. Reiss-Husson et V. Luzzati² qui donne un coefficient de dilatation thermique légèrement différent pour les groupes CH₂ et CH₃.

$$\rho (\text{e}^-/\text{\AA}^3)(t) = 0.295 - 0.000172 (t(^\circ\text{C})-20) \text{ (pour un groupe CH}_2)$$

$$\rho (\text{e}^-/\text{\AA}^3)(t) = 0.168 - 0.000326 (t(^\circ\text{C})-20) \text{ (pour un groupe CH}_3)$$



Températures de la phase liquide des alcanes en fonction de leur longueur de chaîne.^{3,4}



Densité électronique d'alcanes liquides en fonction de la température.

Densités de longueur de diffusion en neutrons :

L'expression de l'intensité de diffusion cohérente des neutrons par un noyau de longueur de diffusion b_i est similaire à celle de la diffusion cohérente par un électron en rayons X (chapitre 6) :

$$I_n = \frac{b_i^2}{r^2} \quad (\text{au lieu de } I_e = \frac{r_0^2}{r^2} CP \quad \text{avec } r_0 = \frac{1}{4\pi\epsilon_0} \frac{e^2}{mc^2} = 2.82 \cdot 10^{-15} \text{ m})$$

En unités absolues (par unité de surface dans le plan de détection placé à la distance D, cas de la diffusion aux petits angles), on a :

$$I_n^{abs}(\vec{k}) = \frac{1}{D^2} T I_0 I(\vec{k})$$

$$\text{avec } I(\vec{k}) = |A(\vec{k})|^2 = A(\vec{k}) A^*(\vec{k}) \quad \text{et} \quad A(\vec{k}) = \int_{\text{échantillon}} \rho_n(\vec{x}) e^{-2i\pi\vec{k}\cdot\vec{x}} d\vec{x}$$

où $\rho_n(\vec{x})$ est la densité de longueur de diffusion cohérente, exprimée habituellement en cm^{-2} .

Pour une molécule contenant un ensemble de noyaux (i) de longueurs de diffusion cohérentes b_i , de volume v , on a :

$$\rho_n (\text{cm}^{-2}) = \frac{\sum_i b_i (\text{cm})}{v(\text{cm}^3)} = \sum_i b_i (\text{cm}) \frac{N_A d (\text{g/cm}^3)}{M (\text{g/mol})}$$

Rq : On retrouve formellement l'expression de l'intensité diffusée dans le cas des rayons X en utilisant $\rho_n(\vec{x})$ avec comme longueur de diffusion $b_e = Z r_0$.

		longueurs de diffusion	
	% isotopique	b cohérent (cm)	b incohérent (cm)
H		$-3.7390 \cdot 10^{-13}$	
1H	99.985	$-3.7406 \cdot 10^{-13}$	$2.5274 \cdot 10^{-12}$
2H (deuterium)	0.015	$6.6710 \cdot 10^{-13}$	$4.04 \cdot 10^{-13}$
3H (tritium)		$4.7920 \cdot 10^{-13}$	$-1.04 \cdot 10^{-13}$
Si		$4.1491 \cdot 10^{-13}$	
O		$5.8030 \cdot 10^{-13}$	
C		$6.6460 \cdot 10^{-13}$	
12C	98.9	$6.6511 \cdot 10^{-13}$	0
13C	1.1	$6.1900 \cdot 10^{-13}$	$-5.2 \cdot 10^{-14}$
Cl		$9.5770 \cdot 10^{-13}$	
35Cl	75.77	$1.1650 \cdot 10^{-12}$	
37Cl	24.33	$3.0800 \cdot 10^{-13}$	
Mn		$-3.7300 \cdot 10^{-13}$	$1.79 \cdot 10^{-13}$

Longueurs de diffusion neutroniques.⁵

	M (g/mol)	densité (g/cm ³)	v (Å ³)	ρ_n (cm ⁻²)
H ₂ O	18.016	0.998	30.0	-0.5589 10 ¹⁰
D ₂ O				6.361 10 ¹⁰
PO	58.078	1.004	96.1	0.344 10 ¹⁰
EO	44.052	1.13	64.7	0.639 10 ¹⁰
-CH ₂ (20°C)	14.026	0.860	27.1	-0.307 10 ¹⁰
-CH ₃ (20°C)	15.034	0.466	53.6	-0.853 10 ¹⁰
-C ₁₂ H ₂₅ (20°C)	169.32	0.800	351.4	-0.39 10 ¹⁰
-CD ₂ (20°C)	14.026	0.860	27.1	7.37 10 ¹⁰
-CD ₃ (20°C)	15.034	0.466	53.6	4.97 10 ¹⁰
-C ₁₂ D ₂₅ (20°C)	169.32	0.800	351.4	7.01 10 ¹⁰
SiO ₂	60.09	2.2	45.4	3.474 10 ¹⁰
MnO ₂ (pyrolusite)	86.94	5.2	27.8	2.837 10 ¹⁰

Densités de longueur de diffusion cohérente neutroniques.

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Deuxième partie

Chapitre 13

Relations d'épitaxie

L'étude des « relations d'épitaxie », dans le cas particulier du système binaire $C_{12}E_6$ /eau, a été le sujet principal de ma thèse de doctorat.¹ Ce système présente, autour d'une concentration de 65 % en poids de tensioactif, une séquence de trois phases en augmentant la température : hexagonale 2D, cubique bi-continue Ia3d puis lamellaire. Lorsqu'un mono-domaine d'une phase germe dans un mono-domaine d'une autre phase, des relations d'épitaxie entre les paramètres de maille des deux phases et leurs orientations cristallographiques relatives sont observées.

Dans ce chapitre, les relations d'épitaxie sont discutées de façon plus générale, pour les différents types de phases organisées, en les illustrant par des résultats sur des systèmes expérimentaux variés.

L'origine de ces relations d'épitaxie est vraisemblablement liée à des effets de croissance cristalline, avec des orientations préférentielles d'un cristal en croissance dans un autre (rôle de l'anisotropie de la tension de surface entre les deux phases). De plus, les transitions de phase s'accompagnent le plus souvent d'un changement de forme des micelles (sphérique/cylindrique par exemple). Aussi, on peut élaborer, à partir des relations d'épitaxie, des mécanismes pour les transitions de phase basés sur des fusions ou des redistributions de matière entre les micelles.

Phase hexagonale 2D / phase cubique

Comme il a été rappelé au chapitre 3, une phase hexagonale 2D peut transiter vers une phase bi-continue (le plus souvent une phase de groupe d'espace Ia3d) ou une phase micellaire (bcc, Pm3n et éventuellement fcc ou hcp).

Un argument simple de symétrie fait qu'une phase hexagonale 2D et une phase cubique ont toujours un axe en commun : l'axe c de la phase hexagonale, qui reste parallèle à un axe 3

(direction $[111]$) de la phase cubique lors d'une transition de phase. La phase hexagonale (**Fig 13-1**) contient trois familles de plans équivalents contenant l'axe c et faisant un angle de 60° entre elles : les plans (10) , (01) et $(1\bar{1})$.

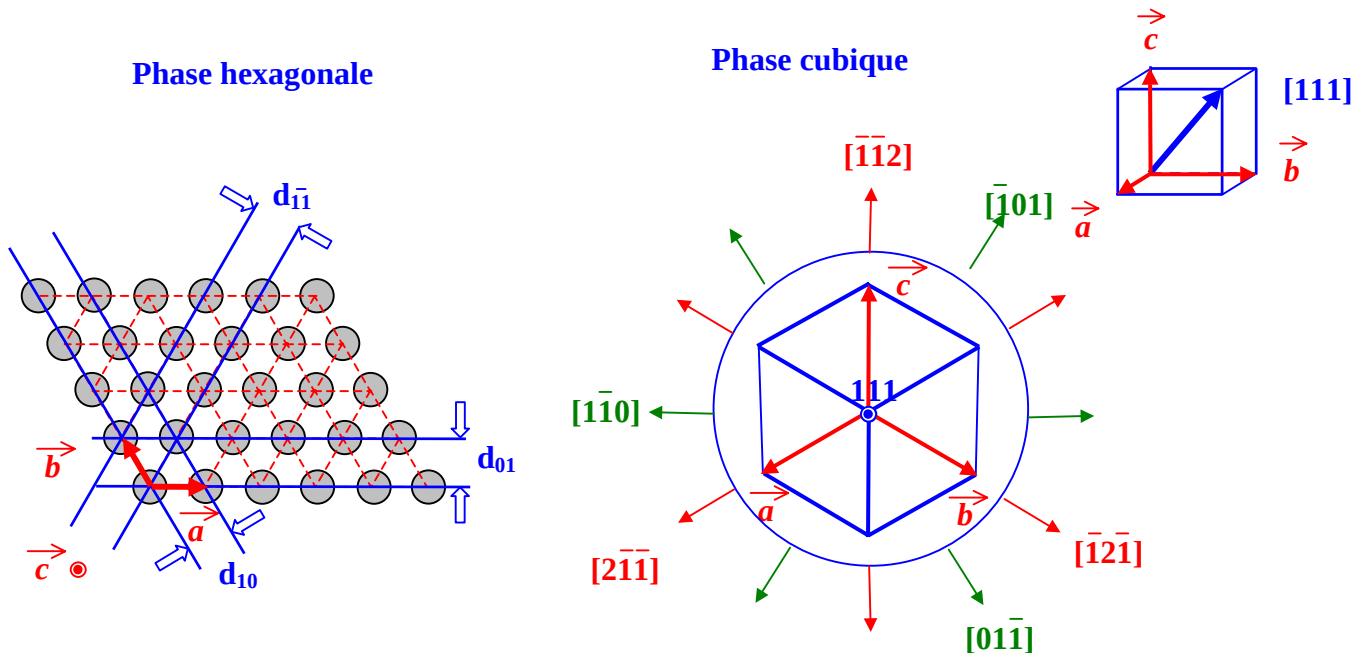


Figure 13-1. Projection suivant l'axe c d'une phase hexagonale 2D et projection suivant un axe $[111]$ d'une phase cubique.

En phase cubique, il y a deux familles de plans simples contenant une direction $[111]$ et où les plans font un angle de 60° entre eux : les plans $(1\bar{1}0)$, $(01\bar{1})$ et $(\bar{1}01)$ d'une part, et les plans $(\bar{1}\bar{1}2)$, $(2\bar{1}\bar{1})$ et $(\bar{1}2\bar{1})$ d'autre part. En projection suivant la direction $[111]$, les plans de type (110) apparaissent parallèles aux côtés du cube alors que les plans de type (211) apparaissent perpendiculaires à ces côtés (**Fig 13-1**). Dans chaque cas, les lignes d'intersection de ces plans le long d'un axe trois forment un réseau 2D hexagonal (**Fig 13-2**).

On peut remarquer également que l'on peut utiliser des plans d'espacement plus petit, tels que des plans (220) ou (422) , ce qui permet aussi de reconstruire une phase hexagonale 2D, mais de paramètre de maille plus petit.

Cette construction géométrique s'applique aux différents cas de phases cubiques, aussi bien celui des phases micellaires (phase bcc avec les plans (110) , phase fcc avec les plans (220) et phase $Pm\bar{3}n$ avec les plans (211)); que celui des phases bicontinues (phase $Ia\bar{3}d$ avec les plans (211)). Quelques exemples sont donnés juste après dans ce chapitre. L'épitaxie entre des plans peut s'établir à partir d'un diagramme de poudre. Néanmoins, seule une étude sur mono-domaine permet d'établir complètement l'orientation relative de deux phases.

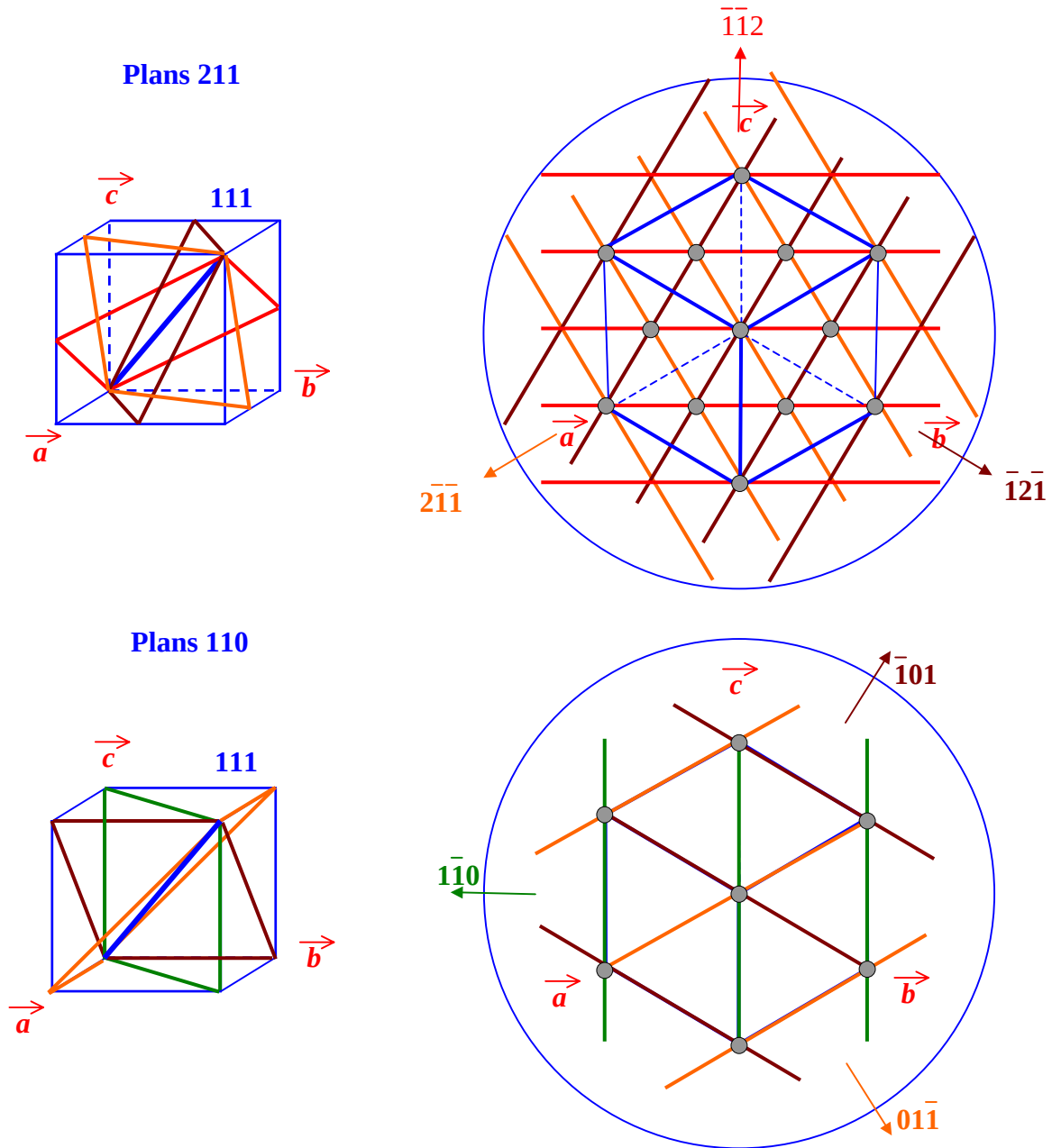


Figure 13-2. Familles de plans (211) et (110) d'une phase cubique. Les lignes d'intersection de ces plans le long d'un axe trois permettent de reconstruire le réseau d'une phase hexagonale 2D.

- épitaxie entre mono-domaines

Lorsqu'une phase hexagonale 2D croît dans un mono-domaine de phase cubique, les domaines hexagonaux ont 4 orientations possibles du directeur hexagonal, correspondant aux directions des 4 axes d'ordre 3 équivalentes par symétrie du domaine cubique initial (**Fig 13-3**).¹ L'orientation du réseau hexagonal 2D est ensuite fixée par le type de plans cubiques liés par épitaxie aux plans (10) de la phase hexagonale 2D.

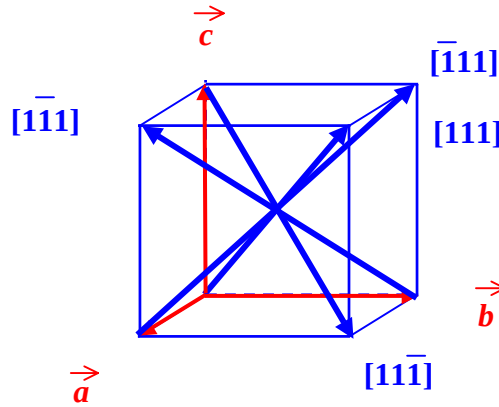


Figure 13-3. Les 4 orientations du directeur d'une phase hexagonale 2D en croissance dans un mono-domaine de phase cubique, suivant les 4 axes d'ordre 3.

Inversement, lorsque la transition se fait d'un mono-domaine hexagonal vers une phase cubique, deux orientations équivalentes « jumelles » (twins) peuvent coexister. Ces deux orientations se déduisent l'une de l'autre par un plan miroir perpendiculaire à l'axe c de la phase hexagonale 2D (**Fig 13-4**).

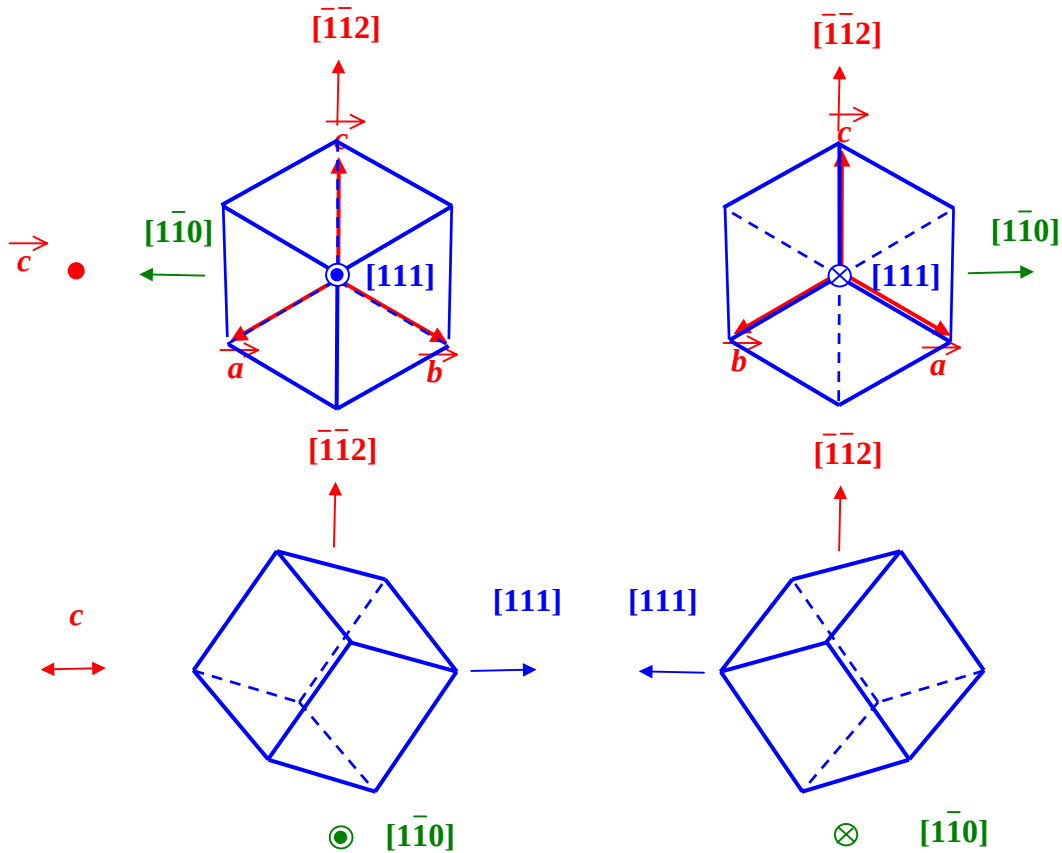


Figure 13-4. Les deux orientations jumelles d'une phase cubique en croissance dans un domaine orienté de phase hexagonale 2D (cylindres le long de l'axe c).

Dans une expérience de diffusion des rayons X, s'il y a coexistence des deux orientations « jumelles », les deux espaces réciproques se superposent donnant lieu à des diagrammes caractéristiques (Fig 13-5).²

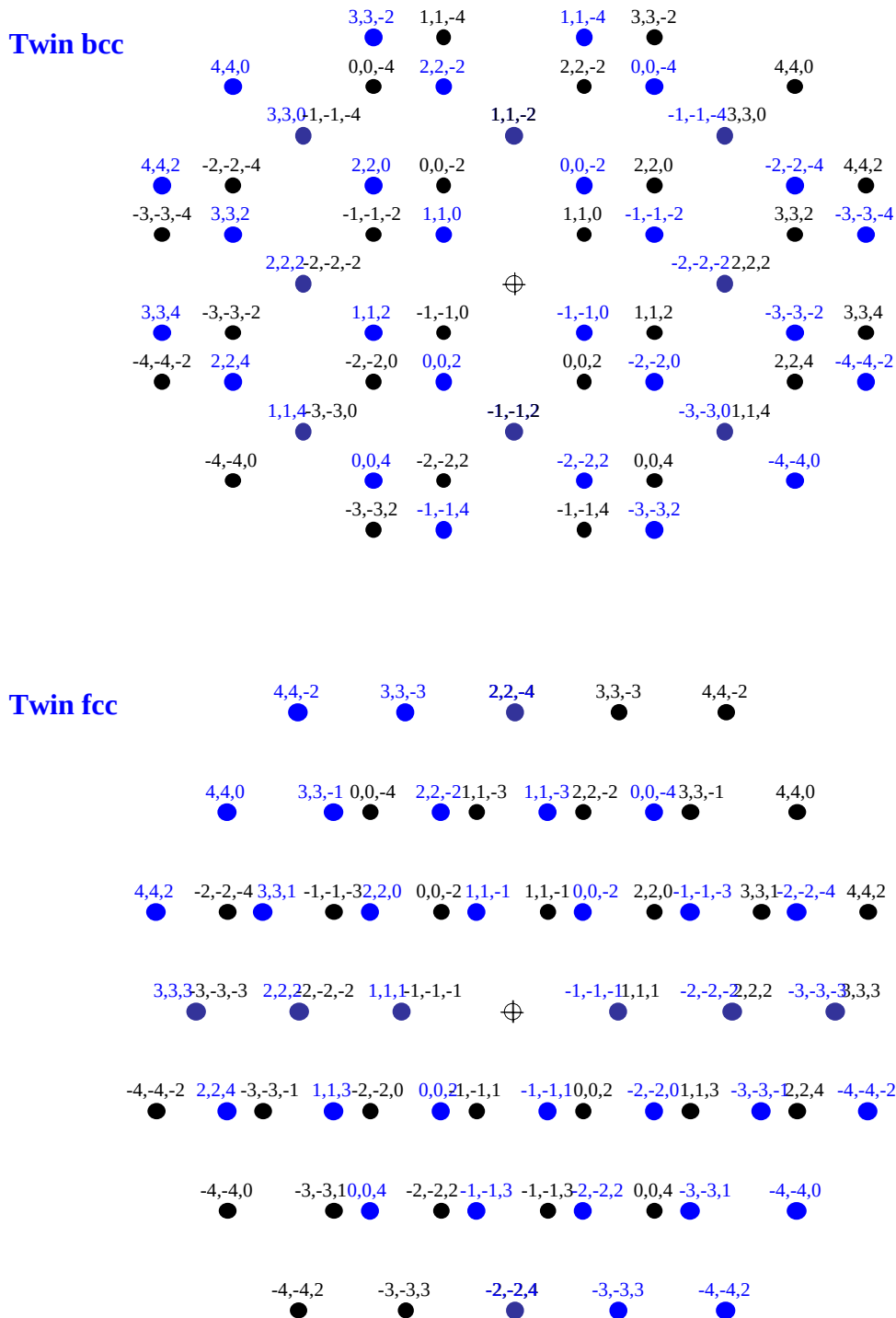


Figure 13-5. Superposition dans l'espace réciproque de deux orientations jumelles, pour les phases bcc et fcc, suivant un axe de zone 1-10. Les règles d'extinction sont différentes pour les phases bcc et fcc (chapitre 9).

- phase bcc

Le passage par épitaxie se fait suivant les plans 110 et on a la relation : $d_{10} = d_{110} = a/\sqrt{2}$. Cette relation a été observée dans des systèmes variés, tels que le système binaire $C_{12}E_{12}$ /eau³ (voir aussi le chapitre 14), des bloc-copolymères fondus,⁴ ou encore des films 2D de matériaux mésoporeux.⁵ A partir de cette relation, plusieurs auteurs ont proposé un mécanisme de fusion des micelles de la phase bcc pour former les cylindres de la phase hexagonale (**Fig 13-6**).

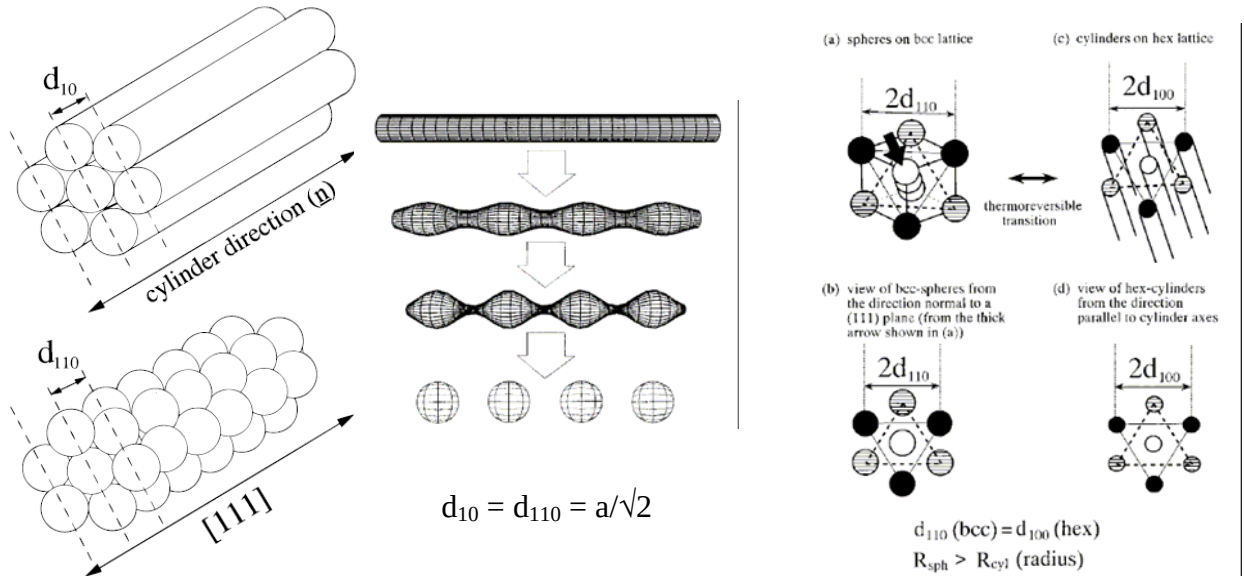


Figure 13-6. Relations d'épitaxie entre une phase hexagonale 2D et une phase bcc. (a) dans le système $C_{12}E_{12}$ /eau (voir aussi le chapitre 14).³ (b) dans un système de copolymères di-blocs (PS-PI) en température.⁴

Des résultats récents sur un copolymère tri-bloc PS-PI-PS, confirment ce mécanisme, par une étude in-situ par SAXS combinée à des observations par TEM (**Fig 13-7**).⁶

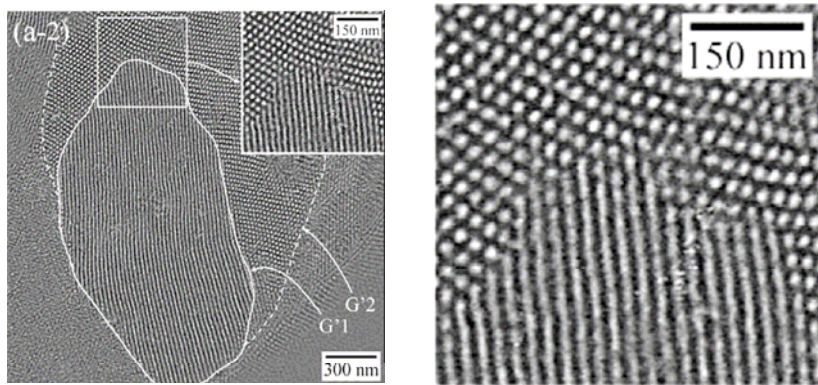


Figure 13-7. Tri-bloc PS-PI-PS.⁶ observation de la croissance d'un grain de phase hexagonale 2D dans une phase bcc. Le grain est anisotrope car la croissance est plus rapide le long de la direction des cylindres, et la fusion des micelles sphériques de la phase bcc pour former les cylindres est observée.

- phase fcc

Comme pour la phase bcc, la structure en projection suivant un axe 3 de la phase fcc donne des alignements de micelles suivant un réseau 2D hexagonal (**Fig 13-8**). Aussi, un passage par épitaxie vers une phase hexagonale 2D suivant les plans 220 avec la relation : $d_{10} = d_{220} = a/\sqrt{8}$ semble naturel. Il n'y a par contre pas à notre connaissance de confirmation expérimentale comme pour la phase bcc.

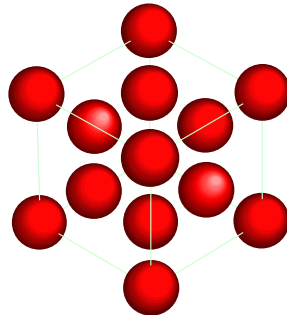


Figure 13-8. Projection suivant un axe trois de la phase fcc.

- phase hcp

Un passage par épitaxie entre cette phase et une phase hexagonale 2D ne semble pas aussi évident que dans les cas précédents, comme le montre la projection suivant l'axe c de la phase hcp (**Fig 13-9**). Il n'y a en tout cas à notre connaissance pas d'exemple d'une telle transition (voir aussi le chapitre 3).

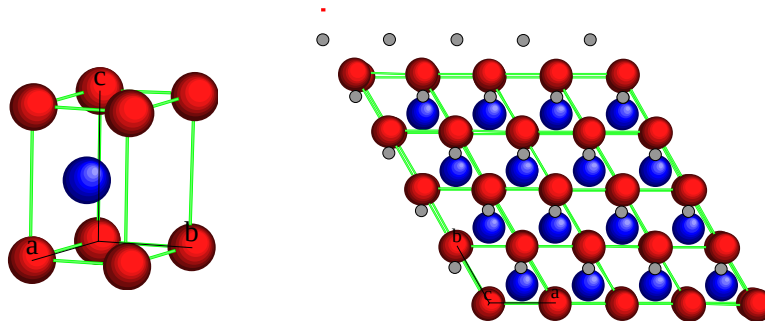


Figure 13-9. Projection suivant l'axe c de la phase hcp. Le passage le plus « naturel » vers une phase hexagonale 2D (réseau en gris clair) semble briser la symétrie 3 autour de l'axe c.

- phase Pm3n

Cette phase micellaire a été introduite au chapitre 3. Toujours en se basant sur la projection le long de l'axe trois, on peut proposer un passage par épitaxie vers une phase hexagonale 2D suivant les plans 211 avec la relation : $d_{10} = d_{211} = a/\sqrt{6}$.

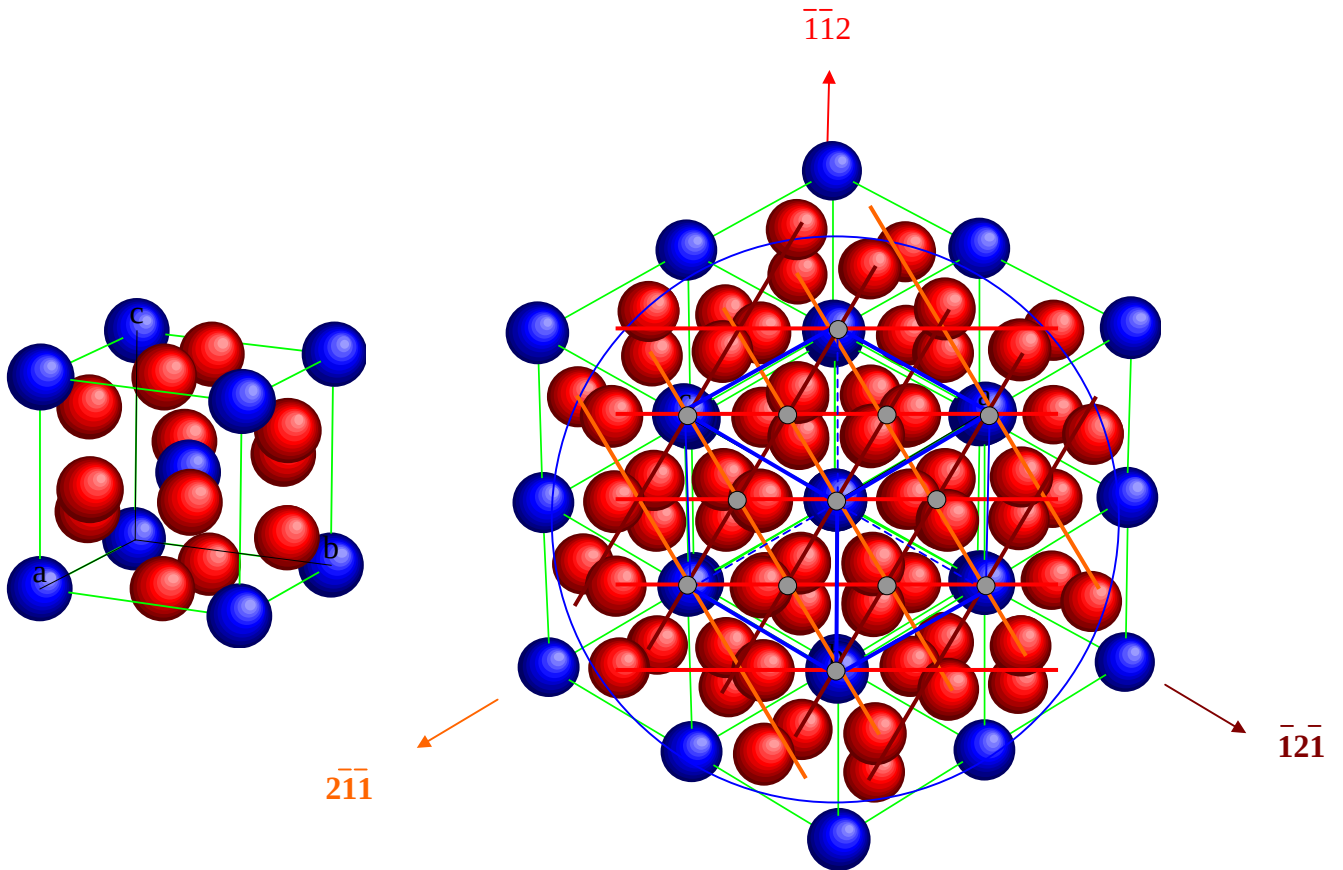
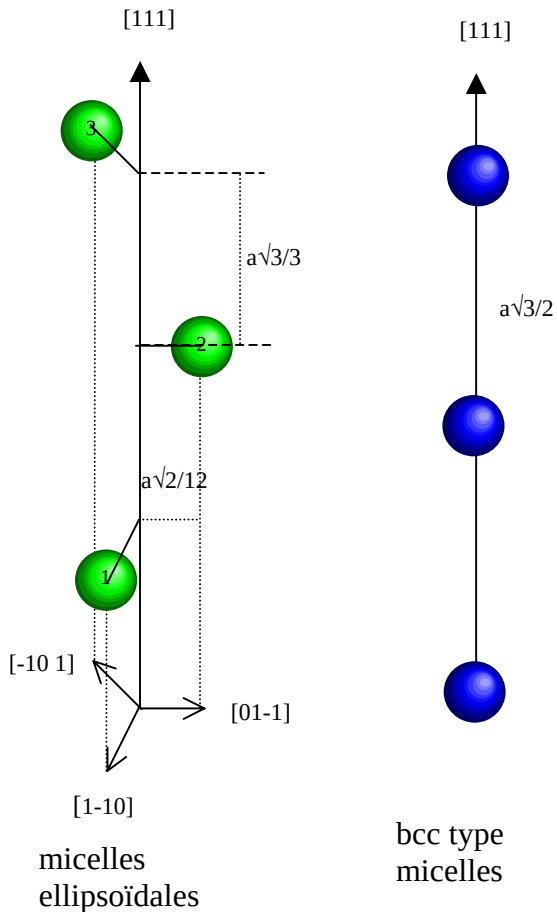


Figure 13-10. Relation d'épitaxie entre les plans 211 de la phase $Pm\bar{3}n$ et une phase hexagonale 2D.



Deux types de micelles sont présents dans cette phase (chapitre 3). En bleu, des micelles sphériques, réparties comme dans une maille bcc, et en rouge, des micelles légèrement ellipsoïdales, regroupées deux par deux sur chacune des faces (**Fig 13-10**).

Les micelles de type bcc forment des alignements réguliers le long d'un axe 3, avec un espacement de $a\sqrt{3}/2$. Les micelles ellipsoïdales sont réparties régulièrement autour d'axes parallèles à un axe trois, avec une période de $a\sqrt{3}/3$ en projection le long de l'axe d'enroulement (**Fig 13-11**). Elles sont décalées de $a\sqrt{2}/12$ par rapport à cet axe dans le plan perpendiculaire. La figure 13-12 montre en 3D ces regroupements de micelles.

Figure 13-11.

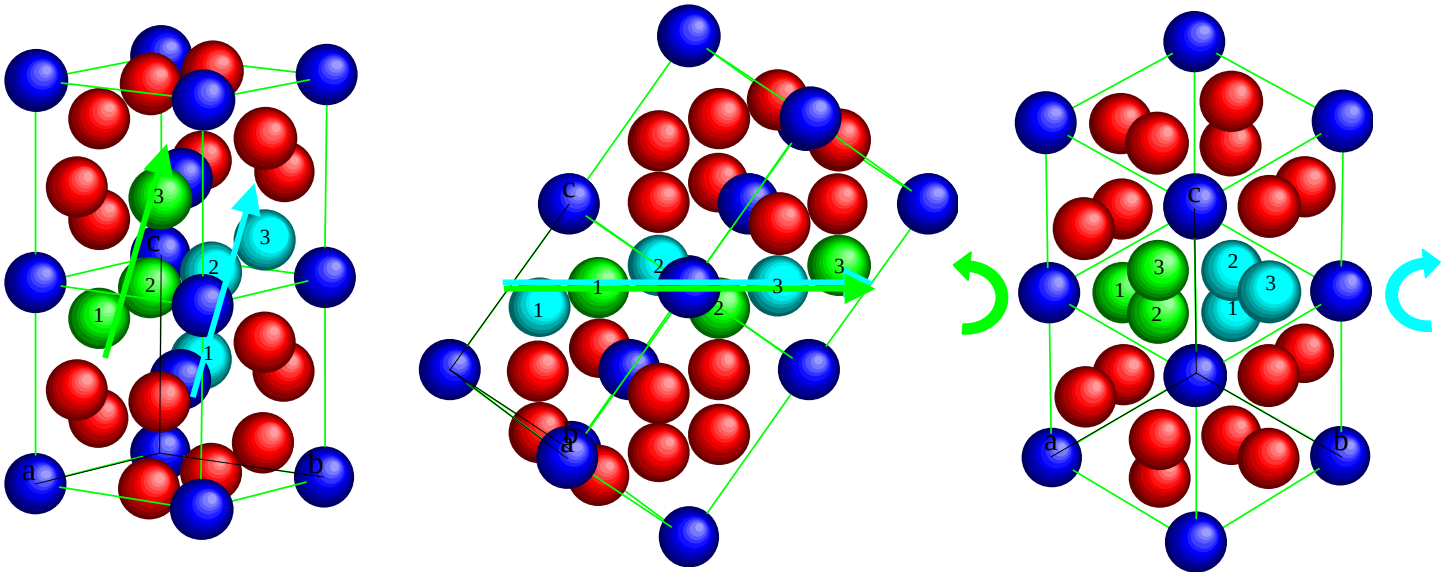


Figure 13-12. Deux mailles de la phase $Pm3n$ sont représentées. On distingue en bleu les micelles de type bcc et en rouge les micelles ellipsoïdales. En vert clair et bleu clair, deux « enroulements » de micelles ellipsoïdales sont détaillés. Ils ont des sens d'enroulement opposés.

A partir de cette analyse géométrique, on peut donc imaginer, comme pour une phase bcc, un processus de fusions des micelles de la phase cubique, menant à la formation des cylindres de la phase hexagonale 2D.

Expérimentalement, plusieurs études sur des matériaux mésoporeux ont montré une relation d'épitaxie entre les plans (211) et les plans (10) de la phase hexagonale 2D lors d'une transition de phase.^{7,8} Parmi elle, une seule⁷ contient une image de microscopie électronique montrant la croissance en épitaxie d'une phase hexagonale 2D (**Fig 13-13**). Le mécanisme suggéré est le même que celui que nous proposons.

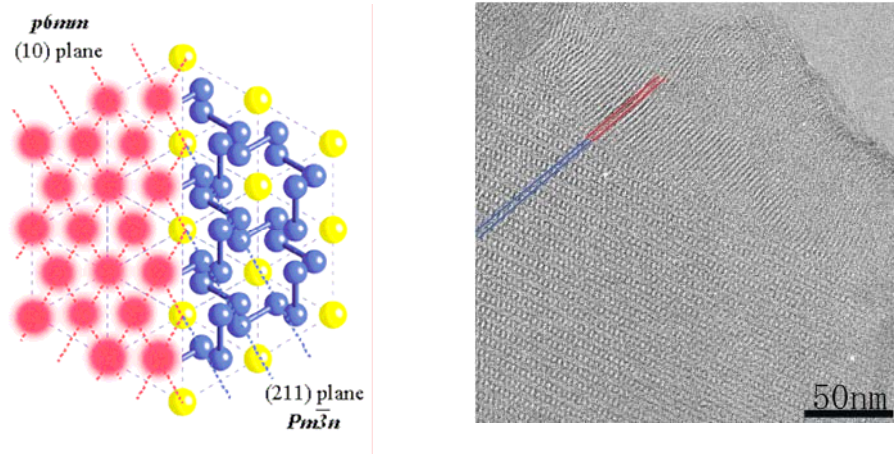


Figure 13-13. Croissance par épitaxie d'une phase hexagonale 2D dans une phase cubique micellaire d'un matériau mésoporeux.⁷ L'observation par microscopie électronique d'un grain montre la relation d'épitaxie entre des plans (211) de la phase $Pm\bar{3}n$ (en bleu) et des plans (10) de la phase hexagonale 2D (en rouge).

Phases bicontinue Ia3d

Nous avons étudié, lors de notre thèse de doctorat, les « relations d'épitaxie » entre la phase bicontinue (Ia3d) (voir aussi les chapitres 4 et 16) et la phase hexagonale 2D dans le système binaire $C_{12}E_6$ /eau.¹ On rappelle juste ici que ce sont les plans (211) de la phase cubique bicontinue (comme précédemment pour la phase $Pm\bar{3}n$) qui permettent une croissance en épitaxie (**Fig 13-14**). Nous avons proposé un mécanisme de transition de phase (« tours de Karcher ») s'appuyant sur ces relations.¹

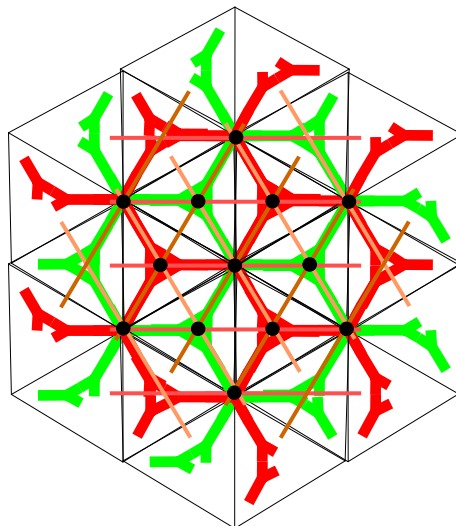


Figure 13-14. Relation d'épitaxie entre les plans 211 de la phase bicontinue Ia3d et une phase hexagonale 2D.¹

Ces relations ont été confirmées expérimentalement plusieurs fois, dans différents systèmes : des blocs-copolymères fondus⁹⁻¹² (**Fig 13-15**) et aussi des matériaux mésoporeux.¹³

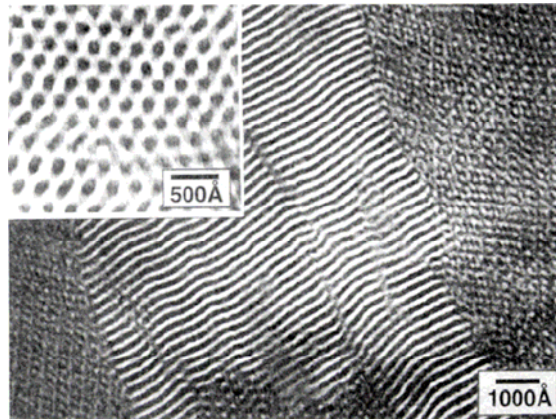


Figure 13-15. Croissance par épitaxie d'une phase hexagonale 2D dans une phase cubique bicontinue Ia3d d'un copolymère dibloc PS-PI.⁹

En conclusion de cette partie, on voit que plusieurs résultats expérimentaux, par diffusion des rayons X et par microscopie électronique, confirment les relations d'épitaxie établies géométriquement au début de ce chapitre. Même s'il est souvent tentant d'y associer un mécanisme local de fusion entre micelles, il reste difficile de prouver expérimentalement que cela est bien le cas. C'est par exemple le cas pour le mécanisme en « tour de Karcher » (phase bicontinue/phase hexagonale 2D) qui n'a pas de preuve expérimentale.

Phase tri-continue Im3m /phase bicontinue Ia3d

On a discuté jusqu'ici le cas d'une transition d'une phase hexagonale 2D vers une phase cubique. En guise d'introduction au chapitre 15, on peut citer ici un autre cas intéressant de relations d'épitaxie, cette fois-ci entre deux phases cubiques. Il s'agit de la phase cubique bicontinue Ia3d et de la phase tri-continue Im3m. Un résultat remarquable est que, là-aussi, des relations d'épitaxie semblent relier ces deux phases. Les paramètres de maille sont dans un rapport sensiblement constant pour les divers systèmes expérimentaux connus : $a_{\text{Im3m}} \cong 1.53 a_{\text{Ia3d}}$. Des expériences de diffusion des rayons X sur monocristaux ont permis de suivre la transition de phase en température entre ces deux phases cubiques dans un mélange de molécules thermotropes.¹⁴ Il est difficile d'interpréter les diagrammes de diffraction obtenus, dans la mesure où un seul mono-domaine d'une phase cubique génère plusieurs domaines équivalents par symétrie de l'autre phase cubique. Il est en particulier délicat de discerner les

relations d'orientations entre deux réseaux cubiques et une véritable épitaxie entre plans, avec superposition des taches de Bragg dans l'espace réciproque. Pour l'instant, à partir des mesures réalisées, les relations d'épitaxie en **figure 13-16** semblent les plus probables.

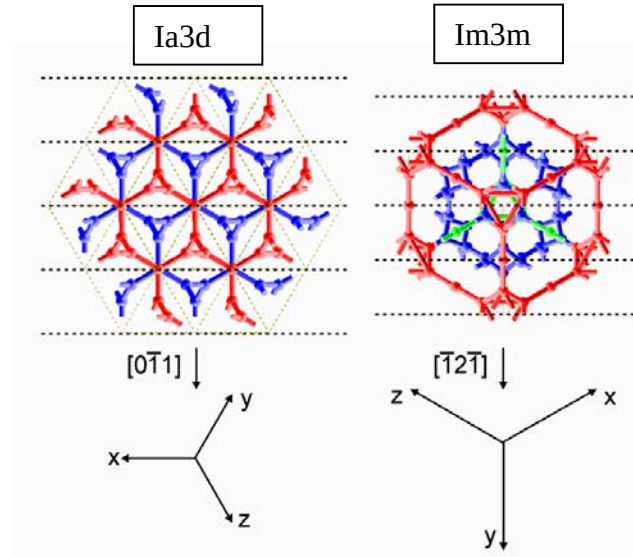


Figure 13-16. Relations d'épitaxie entre la phase cubique bi-continue $Ia3d$ et la phase cubique tri-continue $Im3m$.¹⁵

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Chapitre 14

Phase hexagonale 3D de micelles

Il existe différentes structures pour les phases micellaires, qui ont été introduites au chapitre 3. Ce chapitre est consacré au cas de l'empilement hexagonal compact. Nous avons en effet montré¹ (publication [6] jointe) qu'un tel arrangement existe dans un système binaire simple : le tensioactif non-ionique $C_{12}E_8$ dans l'eau. Une étude plus récente du même diagramme de phase par Imai² a confirmé cette structure. On donne dans ce chapitre les principaux résultats obtenus.

D'autre-part, plusieurs matériaux mésoporeux présentent une structure hcp (voir aussi le chapitre 5).^{3,4}

Phase hexagonale 3D et diagrammes de phase

Le système $C_{12}E_8$ /eau est le seul diagramme binaire où l'existence d'une phase micellaire de symétrie hexagonale 3D et non pas cubique a été montrée.¹ Au premier abord, ce résultat a été un peu déroutant, dans la mesure où les phases micellaires connues auparavant étaient toutes de symétrie cubique. Le point principal des analyses par rayons X de mono-domaines (publication [6] jointe) a été de démontrer l'existence d'une symétrie hexagonale 3D, avec un rapport c/a très proche de $(8/3)^{0.5}$, cette valeur correspondant au cas d'un empilement compact de sphères. La phase hexagonale 3D est donc une variante bien connue des empilements compacts de sphères. Comme on l'a vu au chapitre 3, la différence de stabilité entre cette phase et la phase cubique face centrée fcc est extrêmement faible. Il est donc difficile de comprendre pourquoi ce tensioactif particulier donne une phase hexagonale 3D, alors que par exemple un tensioactif très proche, le $C_{12}E_{12}$, donne une phase fcc (**Fig 14-2**).⁵ D'autre part, la zone des phases micellaires directes des tensioactifs de type C_nE_m n'a été pour l'instant étudiée en détail que pour le $C_{12}E_8$ et le $C_{12}E_{12}$, et il est donc possible que la phase hexagonale 3D soit observée pour d'autres tensioactifs de cette famille.

Le diagramme de phase dans l'eau lourde (D_2O) du $C_{12}E_8$ montre plusieurs phases micellaires en fonction de la concentration (**Fig 14-1**).^{1,2} La phase hexagonale 3D est observée autour de 35 % en poids de tensioactif, et en-dessous de la température ambiante. Autour de 39 % en

poids, on observe plus cette phase, mais une phase micellaire cubique Pm3n, de type tcp (voir le chapitre 3). Une phase de type bcc a également été observée, au-dessus de cette phase Pm3n en température, mais uniquement par Imai (**Fig 14-1b**).² Il y a donc un désaccord concernant l'existence d'une phase bcc entre les deux diagrammes, et il pourrait être utile de refaire des expériences pour lever cette contradiction.

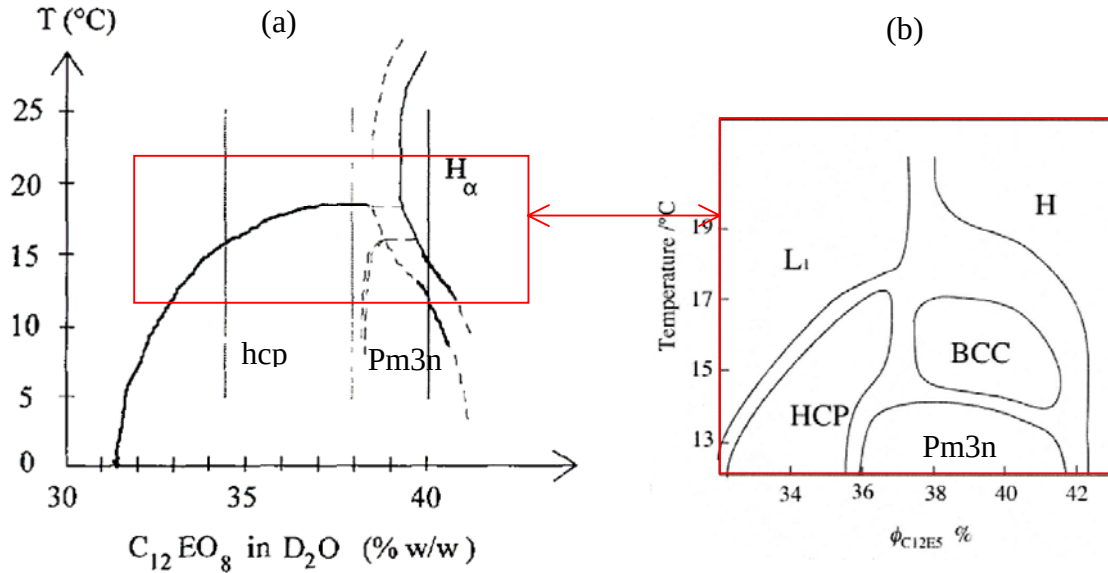


Figure 14-1. Diagramme de phase du $C_{12}E_8$ dans D_2O dans la zone des phases micellaires. (a) d'après la référence¹. (b) d'après la référence². La zone encadrée permet de comparer les deux diagrammes. Le diagramme complet dans l'eau est donné au chapitre 2.

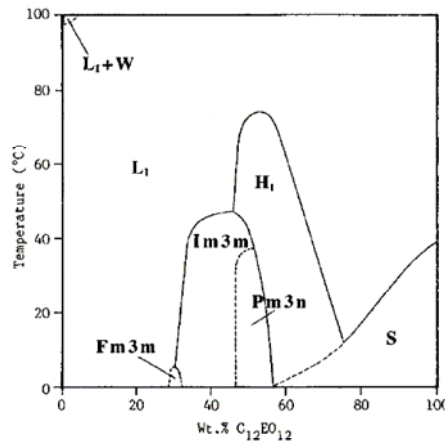


Figure 14-2. Diagramme de phase du $C_{12}E_{12}$ dans H_2O .⁵

Il est intéressant de comparer ce diagramme du $C_{12}E_8$ avec celui du tensioactif $C_{12}E_{12}$ (**Fig 14-2**),⁵ de formule très proche, mais non commercial comme le $C_{12}E_8$. La zone des phases micellaires est plus étendue dans le diagramme du $C_{12}E_{12}$ que dans celui du $C_{12}E_8$. En effet, le groupe hydrophile est plus grand, à longueur de chaîne égale (C_{12}), ce qui favorise les

micelles sphériques. Trois phases micellaires sont observées en fonction de la concentration. Autour de 30 % en poids, et à basse température, on observe une phase fcc, analogue à la phase hcp du $C_{12}E_8$. Autour de 40 % en poids et jusqu'à 40°C, une phase bcc (groupe $Im\bar{3}m$) est stabilisée. Puis, autour de 50 % en poids, on retrouve aussi une phase $Pm\bar{3}n$.

Reconstruction de la densité électronique

Récemment, nous avons réalisé, en collaboration avec X. Zeng, une nouvelle étude de la phase hexagonale 3D du $C_{12}E_8/H_2O$, à 34 % en poids de tensioactif.⁶ Cette étude a permis d'affiner la structure de cette phase (**Fig 14-3**).

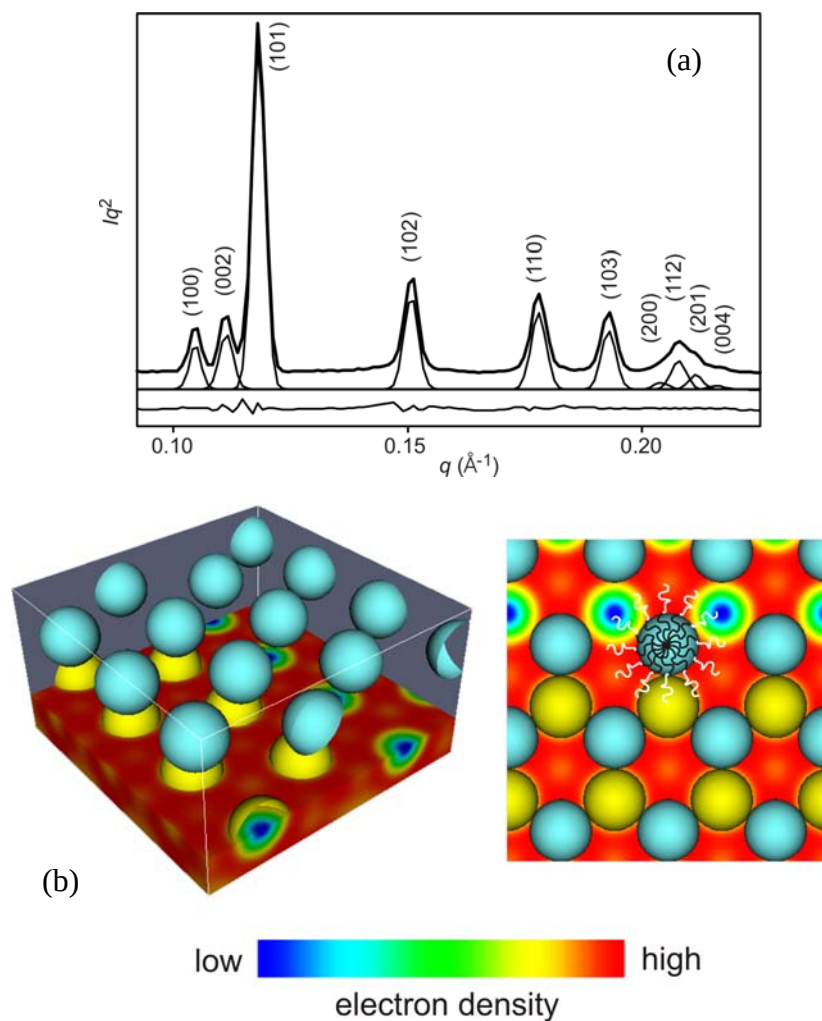


Figure 14-3. (a) : diagramme de poudre de diffusion des rayons X de la phase hexagonale 3D de $C_{12}E_8/H_2O$ à 34 % en poids. (b) : reconstruction de la densité électronique. Les régions de basse densité électronique, situées à l'intérieur de sphères de rayon 2 nm, contiennent principalement les chaînes en C_{12} . Elles sont représentées alternativement en jaune et bleu clair, suivant l'empilement AB de plans compacts.

A partir d'un diagramme de poudre (**Fig 14-3a**), les intensités relatives des pics de Bragg ont été mesurées. Ces données ont permis de reconstituer la densité électronique dans la maille (voir le chapitre 11 pour la méthode). On montre ainsi que les micelles sont de symétrie sphérique, et on peut aussi estimer leurs dimensions (taille du cœur hydrophobe et de la couronne hydrophile).

Ce type d'analyse pourra être étendu aux phases bcc et Pm3n de ces systèmes, ce qui donnera des renseignements utiles pour comprendre les stabilités relatives des différentes phases micellaires. Plus précisément, il sera intéressant de comparer les tailles des micelles en phases hcp/fcc et en phase bcc, notamment au niveau de l'extension dans l'eau de la couronne hydrophile (groupes EO). En phase Pm3n, les micelles ne sont plus à symétrie sphérique, et leur forme et leur taille pourront aussi être déduites d'une reconstruction de la densité électronique.

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A New Symmetry for the Packing of Amphiphilic Direct Micelles

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Abstract. — Thanks to X-ray scattering, we have studied the $C_{12}EO_8$ /water binary system in the region located between the isotropic phase and the direct hexagonal mesophase. We have discovered two 3D-periodic phases in this region: one with a cubic symmetry (space group $Pm\bar{3}n$), the other with a hexagonal symmetry (space group $P6_3/mmc$). Both phases consist in a regular packing of direct micelles build with the surfactant molecules in water. The cubic phase have already been observed in other lyotropic systems. On the other hand, the hexagonal phase is a new type of structure for such systems. We assume for this phase a hexagonal compact structure.

Résumé. — Nous avons étudié par diffraction des rayons X la région du système binaire $C_{12}EO_8$ /eau comprise entre la phase isotrope et la phase hexagonale directe. Nous y avons mis en évidence deux phases périodiques tridimensionnelles : l'une avec une symétrie cubique (groupe d'espace $Pm\bar{3}n$), l'autre avec une symétrie hexagonale (groupe d'espace $P6_3/mmc$). Ces deux phases résultent de l'arrangement périodique de micelles directes, formées par les molécules de surfactant dans l'eau. Ce type de phase cubique micellaire a déjà été observé dans d'autres systèmes lyotropes. Par contre, une telle phase hexagonale n'a jamais été observée précédemment. Nous proposons pour cette phase une structure hexagonale compacte.

1. Introduction

It is well known that micellar cubic phases appear in lyotropic systems [1,2]. They consist in a 3D regular arrangement either of direct micelles, formed by amphiphilic molecules in water, or of inverse micelles of water embedded in a continuous amphiphilic matrix. These phases have been studied thanks to NMR, X-ray scattering and electronic microscopy [1,2]. Two main space groups have been observed: $Pm\bar{3}n$ and $Fd\bar{3}m$. Models for these two space groups have been established. They all involve two different species of micelles inside the structure. Some geometrical arguments have explained why these two types of cubic arrangements are favourable for the packing of the micelles [3].

Recently, other cubic space groups for direct micellar phases have been observed in the ganglioside/water systems [4]. It was a clue that structures with space groups $Pm\bar{3}n$ and

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$Fd\bar{3}m$ are not the only possible ones. So the polymorphism of micellar phases had to be investigated deeper. In this paper, we display another periodic arrangement of direct micelles, this one having a new feature: a hexagonal symmetry!

The existence of a micellar cubic region in the binary mixture $C_{12}EO_8$ (octa-ethylene glycol mono n-dodecyl ether)/ H_2O was first reported in [5]. Our aim was to study the structure of this phase, to get a new set of experimental data, in order to improve the description of the micellar cubic phases. Our first surprise during these experiments was that there are two phases instead of one in the region indicated in [5]. If we look at the phase diagram of the $C_{14}EO_8/H_2O$ mixture [6], a very similar system, two distinct micellar cubic phases are also identified, unfortunately without any structural data available. Which strengthens our result.

Going further into our X-ray investigations, our second surprise was that one of the two phases has not a cubic symmetry, but a hexagonal one. It took us a long time to realize it, because, as far as we knew, a triply-periodic micellar phase was always cubic. In spite of numerous efforts, finding some cubic indexations of the powder patterns proved to be a failure. Fortunately, the single-crystals analysis gave an indisputable evidence of a hexagonal symmetry. Every X-ray pattern could then be easily interpreted; we will show it in Section 3.

2. Materials and Methods

$C_{12}EO_8$ was purchased from Nikko Chemical [7] and used without further purification. Deuterated water was mixed with the surfactant and equilibrated for a few weeks at room temperature. Concentrations between 30% and 43% (w/w) of $C_{12}EO_8$ in D_2O were used.

The mixtures were observed during the cooling from the room temperature down to 8 °C. First observations of the samples by optical microscopy were done between crossed polarizers. For the X-ray experiments the samples were placed in Lindeman cylindrical glass capillaries ($\varnothing$ 1 mm). The X-ray apparatus used for the single-crystals analysis was a Rigaku rotating anode generator (copper wavelength $\lambda = 1.54$ Å). The powders analysis were made on the synchrotron beam line D 43 at the LURE laboratory. Photographic films and image plates have been used as detection.

The best results concerning the single-crystals analysis were obtained with samples equilibrated in a refrigerator (8 °C) for several months.

3. Results

3.1. QUALITATIVE PHASE DIAGRAM (FIG. 1). — At room temperature, the samples are fluid and isotropic for concentrations up to about 39% (w/w). Beyond 39%, the samples become viscous; the texture of the direct hexagonal mesophase is clearly identified through optical microscopy. By cooling the samples which were under 39%, we observe a highly viscous isotropic phase (Fig. 1). For samples of concentration above 39%, a biphasic region between the hexagonal phase and a highly viscous isotropic phase is observed. Going on cooling, there remains only the isotropic phase.

3.2. X-RAY DATA: POWDER DIFFRACTION. — We wanted to determine the structure of the high viscous isotropic phase appearing at low temperature in our samples thanks to X-ray scattering. Two different kinds of X-ray patterns were obtained, depending on the concentration.

3.2.1. Concentration above 39%. — Several high-resolved powder diffraction patterns were obtained on the synchrotron beam line D 43 at the LURE laboratory. The diffraction rings are easily interpreted using a cubic unit cell, as detailed in Table I. A unit cell of parameter

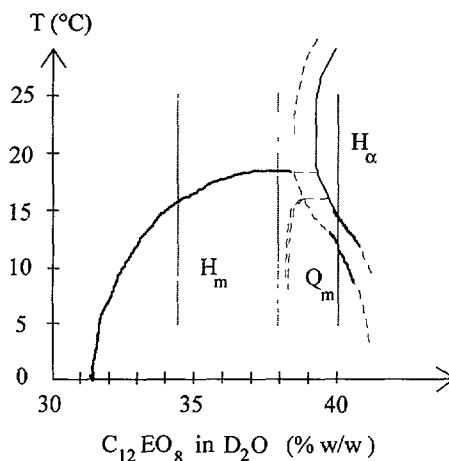


Fig. 1. — Qualitative phase diagram of the binary mixture $C_{12}EO_8$ in D_2O . The transition lines we determined during our study are drawn in heavy black lines. They correspond to changes in the viscosity and/or in the optical aspect between crossed polarizers of the samples. The dashed fine lines are extrapolated from the phase diagram of the $C_{14}EO_8$ /water system [6] and do not correspond to observations. Especially, we do not cross experimentally the coexistence region of the two micellar phases, which is probably narrow *versus* concentration. The vertical lines correspond to the samples used for the X-ray scattering analysis. H_α indicates the hexagonal direct phase, Q_m the cubic micellar phase and H_m the hexagonal micellar phase.

$a = 120.26 \pm 0.19 \text{ \AA}$ is measured. The observed reflections are compatible with the space group $Pm\bar{3}n$, usually observed for micellar direct cubic phases (see Sect. 1). The unit cell of this structure contains six ellipsoidal micelles and two quasi-spherical micelles [1–3]. We will see in Section 3.4 that this model with eight micelles per unit cell is compatible with the physico-chemical data. So we admit the space group $Pm\bar{3}n$ for this phase. We did measure the parameter of the direct hexagonal phase in coexistence with this cubic phase: $a_{H_\alpha} = 59.40 \pm 0.14 \text{ \AA}$ (Tab. I). No epitaxial relations between inter-reticular distances are observed between these two phases.

3.2.2. Concentration below 39%. — We manage to obtain several similar powder diffraction patterns in the range 34.3–38% (w/w). As stressed in the introduction (Sect. 1), we performed many unsuccessful indexations of these diagrams, assuming a cubic unit cell.

We also began to perform single-crystal diffraction patterns in the same concentration range. The interpretation of the reciprocal planes, still assuming a cubic unit cell, happen to be impossible.

As specified below, the single-crystal diffraction patterns could be interpreted by assuming a hexagonal unit cell. Coming back to the powder diffraction patterns, we found accurate indexations for them, assuming a hexagonal unit cell. Results are given in Table II. At 38% (w/w), we measure a hexagonal parameter $a = 68.81 \pm 0.14 \text{ \AA}$, and a ratio $R = c/a = 1.623$. Extinctions are compatible with the hcp structure factor, as detailed below.

3.3. X-RAY DATA: SINGLE-CRYSTAL ANALYSIS BELOW 39%. — We focused on the structure of the micellar phase below 39%, for which the assumption of a cubic unit cell did not give satisfactory results. We succeeded in growing sufficiently large single-crystals ($\sim 1 \text{ mm}^3$) in the Lindeman capillaries. In order to perform their analysis, we fixed them on a goniometric

Table I. — Powder diffraction data of the cubic phase (Q_m) and of the direct hexagonal mesophase (H_α). Results are given for a sample of concentration 40% (w/w), located in the biphasic region (Q_m/H_α). The parameter of the cubic phase is equal to $a = 120.26 \pm 0.19$ Å and the parameter of the hexagonal phase is equal to $a_{H_\alpha} = 59.40 \pm 0.14$ Å. The observed reflections for the cubic phase (values of $s^2 = h^2 + k^2 + l^2$) are compatible with the $Pm\bar{3}n$ space group.

d_{hkl} (Å)	s^2	a (Å) = $d_{hkl}s$
60.17	4	120.34
53.91	5	120.55
49.17	6	120.44
42.41	8	119.95
34.74	12	120.34
33.16	13	(119.56)
32.08	14	120.03
30.08	16	120.32
29.18	17	120.31
26.84	20	120.03

d_{hkl} (Å)	s^2	d_{100} (Å) = $d_{hkl}s$
51.43	1	51.43
29.71	3	51.46
25.72	4	51.44

40 % (w/w)

Cubic phase ($Pm\bar{3}n$): $a = 120.26 \pm 0.19$ Å

H_α phase: $a_{H_\alpha} = 59.40 \pm 0.14$ Å

head, movable around its vertical axis. Thus, all possible orientations of the single-crystals have been observed.

In pattern (a) of Figure 2, the X-ray beam is parallel to a symmetry axis of a single-crystal. Three types of reflection ($(1, \bar{1}, 0, 0)$, $(2, \bar{1}, \bar{1}, 0)$ and $(2, \bar{2}, 0, 0)$ in the hexagonal four indices notation) form a figure of diffraction with a six-fold symmetry. Starting from this position, we rotated continuously the sample around the vertical axis over 360° . Making the hypothesis of a cubic symmetry, the starting position of pattern (a) would correspond to the X-ray beam being parallel to a three-fold axis. As we know that four equivalent axes of three-fold symmetry exist in the case of a cubic symmetry, we expected to observe during the rotation the appearance of equivalent Bragg reflections to the ones observed on pattern (a). It never happened: all the reflections of pattern (a), excepting the ones located on the rotation axis, are observed only at the starting position. As a conclusion, the symmetry axis of pattern (a) is unique, and the symmetry is not cubic.

We regard this symmetry axis as the c^* axis of a hexagonal symmetry. In Figure 2, three reciprocal planes are shown, and their orientations respecting to the c^* axis are given. Then the indexation of the Bragg spots is obtained. Eventually, the whole reciprocal space has been reconstructed. We then observe some extinctions, for instance the $(0, 0, 0, 1)$ and $(0, 0, 0, 3)$

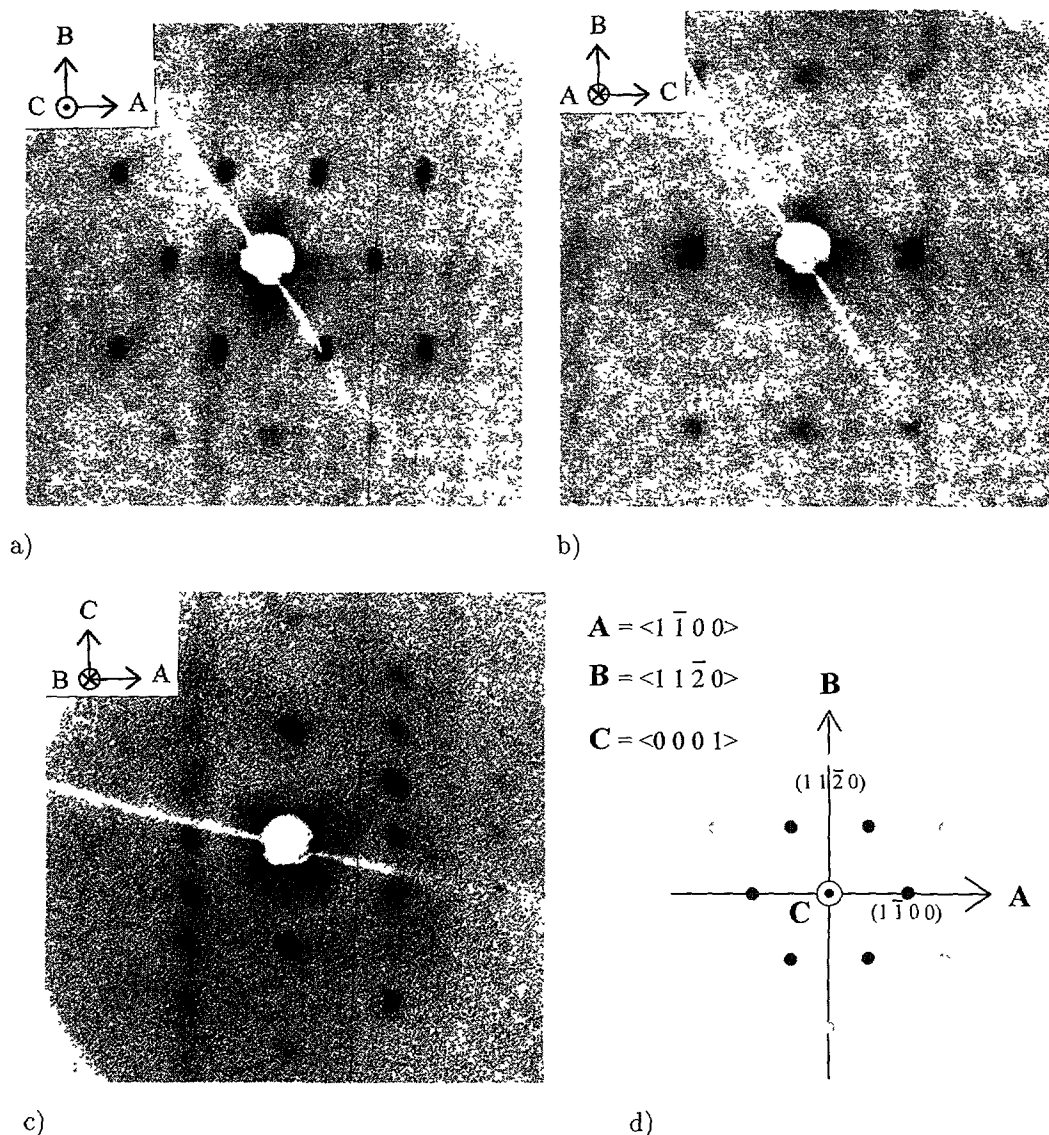


Fig. 2. — Single-crystal diffraction patterns of the hexagonal micellar phase. Three diffraction patterns obtained on image-plates are reproduced. The four indices hexagonal notation is used in this caption. a) X-ray beam along the c^* axis (exposure time of four hours): the $(1, \bar{1}, 0, 0)$, $(2, \bar{1}, \bar{1}, 0)$ and $(2, \bar{2}, 0, 0)$ reflections, plus the reflections obtained by the circular permutations of their first three indices form a six-fold symmetric pattern. b) X-ray beam along the $\langle 1, \bar{1}, 0, 0 \rangle$ reciprocal direction (exposure time of three hours): the $(0, 0, 0, 2)$ reflection (along the c^* axis), the $(1, 1, \bar{2}, 0)$ and the $(1, 1, \bar{2}, 2)$ are located on a rectangular 2D array of reflections. c) X-ray beam along the $\langle 1, \bar{1}, \bar{2}, 0 \rangle$ reciprocal direction (exposure time of three hours): one observes the $(0, 0, 0, 2)$ and the $(0, 0, 0, 4)$ reflections along the c^* axis. The $(1, \bar{1}, 0, 0)$, $(1, \bar{1}, 0, 1)$, $(1, \bar{1}, 0, 2)$ and $(1, \bar{1}, 0, 3)$ reflections are aligned in a row parallel to the c^* axis. d) Relative orientations of the different X-ray patterns in the reciprocal space.

Table II. — Powder diffraction data of the hexagonal phase. Indexation of the reflections assuming a hexagonal unit cell is given for two samples of concentrations 38% and 34.3% (w/w). hkl are the indices in the four indices notation and HKl are the indices in the three indices notation. a and c are the two unit cell parameters and R is equal to the ratio c/a . We use the following relation: $\frac{1}{d_{HKL}^2} = \frac{1}{d_{100}^2} (H^2 + K^2 + HK) + \frac{l^2}{c^2} = \frac{1}{a^2} \left(\frac{4}{3} (H^2 + K^2 + HK) + \frac{1}{R^2} l^2 \right) = \frac{s^2}{a^2}$. All the reflections are compatible with the structure factor of the hcp (3.3). Taking a value of R , we derive a value of a for all different reflections and calculate the average value of a and the corresponding statistical error. The best value of R is determined by minimizing this statistical error. Following this criterion, the best value of R and the associated average value of a are given for the two samples. The statistical error on a is about 0.15 Å for the two samples, and is of the same order of magnitude as for the cubic phase indexation (Tab. I). The value of the unit cell volume is greater for the sample of concentration 34.3% (w/w) than for the sample of concentration 38% (w/w). It is in agreement with our model assuming a constant volume of a micelle and a greater water volume fraction at 34.3% (w/w) than at 38% (w/w).

h	k	i	l	$H K l$	$s^2 = \frac{4}{3} (H^2 + K^2 + HK) + \frac{1}{R^2} l^2$	d_{HKL} (Å)	a (Å)	d_{HKL} (Å)	a (Å)
1	-1	0	0	1 0 0	4/3	59.57	68.79	60.97	70.40
0	0	0	2	0 0 2	4/R ²	55.92	68.91	-	-
1	-1	0	1	1 0 1	4/3 + 1/R ²	52.81	69.12	53.81	70.35
1	-1	0	2	1 0 2	4/3 + 4/R ²	40.74	68.80	41.69	70.22
2	-1	-1	0	1 1 0	4	34.36	68.72	35.07	70.14
1	-1	0	3	1 0 3	4/3 + 9/R ²	31.47	68.59	32.27	70.08
2	-2	0	0	2 0 0	16/3	29.82	68.87	30.34	70.07
2	-1	-1	2	1 1 2	4 + 4/R ²	29.29	68.81	30.06	70.52
2	-2	0	1	2 0 1	16/3 + 1/R ²	28.73	68.67	29.38	70.20

$$\begin{array}{ll}
 38\% \text{ (w/w)} & 34.3\% \text{ (w/w)} \\
 R = 1.623 & R = 1.6311 \\
 a = 68.81 \pm 0.14 \text{ Å} & a = 70.25 \pm 0.15 \text{ Å}
 \end{array}$$

reflections (Fig. 2). As a rule, here are the general conditions of extinction:

$$(h \ k \ i \ l) = (h \ h \ 2\bar{h} \ 2n + 1) \quad (\text{four indices notation}).$$

We propose a hexagonal compact structure for this phase, with a unit cell containing two identical micelles at positions $(1/3, 2/3, 1/4)$ and $(2/3, 1/3, 3/4)$. The structure factor is equal to (three indices notation):

$$F_{HKL} = e^{-2i\pi(\frac{H+2K}{3} + \frac{l}{4})} + e^{-2i\pi(\frac{2H+K}{3} + \frac{3l}{4})} = e^{-2i\pi(\frac{H+2K}{3} + \frac{l}{4})} \left(1 + (-1)^l e^{-2i\pi(\frac{H-K}{3})} \right)$$

Using the four indices notation, we obtain the following values for the intensity derived from this structure factor:

$$\begin{array}{ll}
 l = 2n & \text{if } h \ k \ i = h \ h \ 2\bar{h} \ \text{then } |F_{hkl}|^2 = 4 \quad \text{else } |F_{hkl}|^2 = 1 \\
 l = 2n + 1 & \text{if } h \ k \ i = h \ h \ 2\bar{h} \ \text{then } |F_{hkl}|^2 = 0 \quad \text{else } |F_{hkl}|^2 = 3
 \end{array}$$

This is consistent with the observed extinctions. The space group of this structure is: $P6_3/mmc$. Notice that this space group is not uniquely determined by the observed extinctions (two

other hexagonal space groups are compatible with the extinctions) but by the assumption of a hexagonal compact structure. In the following section, we will show that the structure we propose with two micelles per hexagonal unit cell is also consistent with the physico-chemical data.

3.4. AGGREGATION NUMBER OF THE MICELLES. — A crude estimation of the aggregation number of the micelles in both micellar phases will be now discussed.

We can simply estimate the density of the binary mixture by ignoring solvation effects on the molecular volumes. We know the densities of D_2O : $20/18 \text{ g cm}^{-3}$ and of $C_{12}EO_8$ [7]: 0.99 g cm^{-3} . No corrections *versus* temperature are included for this crude estimate. We will take for the density d of a binary mixture of weight fraction x in $C_{12}EO_8$:

$$\frac{1}{d} = \frac{1}{100} \left(\frac{x}{0.99} + \frac{100-x}{(20/18)} \right).$$

We calculate for the sample of concentration 38% a density of 1.062 g cm^{-3} . For this sample, the volume of the hexagonal unit cell is equal to: $V_{u.c.} = \frac{\sqrt{3}}{2} Ra^3 = 457\,934 \text{ Å}^3$ (Tab. II). Knowing the density of the mixture and the molecular weight of $C_{12}EO_8$ (538 g mol^{-1}), we derive $N_S = 207$, the number of surfactant molecules per unit cell. With two micelles per unit cell in the structure, we get an aggregation number $N = 103$.

A similar calculation is performed for the sample of concentration 40%, the one which exhibits a cubic micellar phase (Tab. I). We find a number of surfactant molecules per unit cell: $N_S = 824$. The structure contains eight micelles per unit cell, but with two different types of shape, so we can derive only an average aggregation number $\langle N \rangle = 103$.

A neutron scattering study [8] estimate the aggregation number of the direct micelles in the isotropic phase. This study has been performed for temperatures between 30 and 60 °C and for weight concentrations of $C_{12}EO_8$ in H_2O between 2.5% and 35%. Aggregation numbers are found between 90 and 140; they increase *versus* the concentration or *versus* the temperature. In this region of the phase diagram, the micelles are expected to be quite spherical.

In short, we can say that an aggregation number of 103 is convenient for quasi-spherical micelles formed by $C_{12}EO_8$ molecules. The models we propose with two micelles per unit cell for the hexagonal phase, and eight micelles per unit cell for the cubic phase appear to be consistent with the physico-chemical data. We also find that the average aggregation number is quite similar for both micellar phases.

4. Discussion

Thanks to the X-ray scattering analysis of single-crystals (3.3), we have identified a new type of micellar phase. We suggest it has a hexagonal compact structure with two micelles per unit cell (space group $P6_3/mmc$). This model is consistent with the aggregation number of quasi-spherical micelles (3.4).

There remains a puzzling question about this phase: the optical observation of the samples between crossed polarizers does not reveal any birefringence (3.1), as expected in the case of a hexagonal symmetry. This implies that the anisotropy of the dielectric tensor is very weak, and that only appropriate measurements of birefringence could be able to detect it. Of course, such a measure would be a confirmation of the hexagonal symmetry.

We also notice that the ratio $R = c/a$ of the hexagonal unit cell (Tab. II) is very close to the value corresponding to a hexagonal close compact packing of spheres: $R_{hcc} = \sqrt{8/3} = 1.6330$. In our opinion, it means that the micelles are rather quasi-spherical than anisotropic.

To conclude, we see that the $\text{Pm}\bar{3}\text{n}$ and $\text{Fd}\bar{3}\text{m}$ cubic structures are not the only solutions for direct micellar arrangements. The ganglioside/water systems [4] and now the C_{12}EO_8 /water binary system are two examples of different arrangements. They have several common features: a single type of micelle (instead of two types of shape in coexistence), having a quasi-spherical shape. All space groups correspond to compact arrangements of spheres: $\text{P6}_3/\text{mmc}$ for the hexagonal phase, $\text{Fm}\bar{3}\text{m}$ and $\text{Im}\bar{3}\text{m}$ in the case of [4], respectively the closest and second closest cubic packing of spheres. The nature of a micellar phase is obviously related to the shape of the micelles: quasi-spherical or ellipsoidal.

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Chapitre 15

Phase tri-continue $Im\bar{3}m$

Certaines molécules de cristaux-liquides forment par auto-association moléculaire des structures périodiques tri-dimensionnelles, à l'échelle de quelques dizaines de nanomètres. Un exemple maintenant bien connu de ce type d'architecture est celui des phases cubiques dites bi-continues, car constituées de deux labyrinthes imbriqués et séparés par une surface périodique (chapitres 4,16). Nous avons pu élucider la structure d'une autre phase cubique, qui constitue le premier exemple de phase tri-continue, formée cette fois-ci de trois labyrinthes imbriqués. Cette phase cubique à grande maille est pour l'instant rencontrée uniquement dans les systèmes de molécules thermotropes. Les exemples de molécules formant cette phase ont été introduits au chapitre 4. L'élucidation de la structure de cette phase tri-continue aura demandé beaucoup de ténacité.^{1,2} C'est finalement grâce à l'obtention de mono-cristaux de cette phase, et de la mesure des intensités relatives des pics de Bragg,³ qu'une bonne description de cette structure a pu être obtenue en 2005,⁴ en collaboration avec G. Ungar et X. Zeng (Sheffield University, UK). Cette résolution fait appel aux méthodes inverses de reconstruction de la densité électronique introduites au chapitre 11.

Ce chapitre est essentiellement constitué des deux publications jointes ([19] et [30]). Une partie de ce travail est également abordée dans la publication [29],² jointe au chapitre 4.

Données de diffraction par un monocristal

Publication [19]

Nous avons appliqué récemment avec succès la technique de croissance de monocristaux *in situ* et leur étude par diffraction des rayons X à un mélange de deux composés présentant deux phases cubiques différentes en fonction de la température.³ L'une de ces phases est une phase bicontinue de structure connue, $Ia3d$, alors que la seconde phase a une maille de plus grande taille, de groupe d'espace $Im\bar{3}m$, dont le contenu a finalement pu être élucidé tout récemment.

Reconstruction de la densité électronique

Publication [30]

La reconstruction de la densité électronique à partir des données de diffraction montre que cette phase comporte trois labyrinthes enchevêtrés, d'où son appellation de phase tri-continue (**Fig 15-1**). Ce résultat est remarquable, vu la complexité de cette phase. Cette structure est l'une des plus complexes formées par des molécules de cristaux-liquides et le « pourquoi » d'une telle architecture est loin d'être compris.

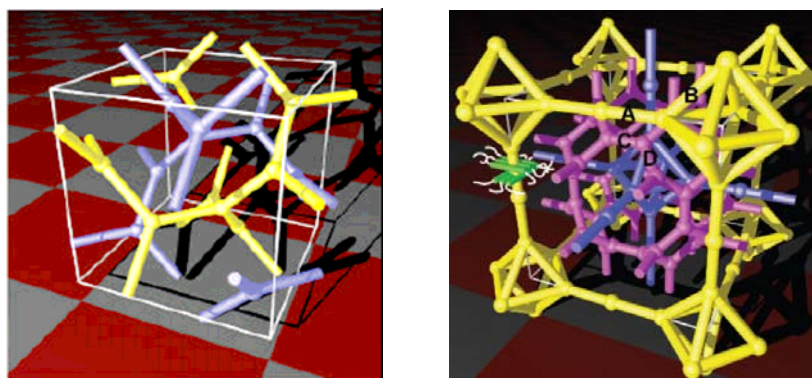


Figure 15-1. La figure représente une maille cubique de la phase tri-continue (de 18 nm de côté) qui contient environ 10000 molécules. Les trois labyrinthes sont représentés en jaune, violet et bleu. Chaque molécule contient un cœur aromatique (en vert) et une ou plusieurs chaînes alkyls (en blanc). La structure résulte de la ségrégation entre les cœurs et les chaînes alkyls, les molécules se déplaçant avec la contrainte que les cœurs se situent sur les labyrinthes.

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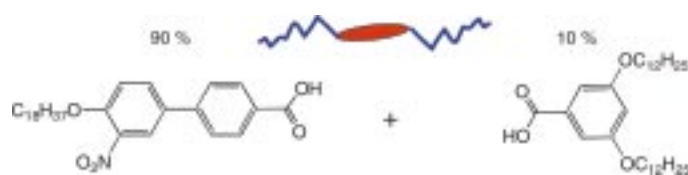
Phase Transition between Single Crystals of Two Thermotropic Cubic Phases from a Mixture of 3,5-Didodecyloxybenzoic Acid and C₁₈-ANBC

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KEYWORDS:

crystal growth · liquid crystals · phase transitions · X-ray scattering

Cubic phases are encountered in many lyotropic systems: lipids, surfactants or block copolymers in concentrated aqueous solutions.^[1a] Depending on the concentration, two classes of such phases, micellar and bicontinuous, are distinguished. Recently, new mesoporous materials have been synthesised by templating these cubic-phase architectures with amorphous silica walls.^[2] Over the same period, cubic phases have also been obtained in thermotropic systems: C₁₆-ANBC and



Scheme 1. Molecular composition of the mixture studied here, 3'-nitro-4'-n-octadecyloxybiphenyl-4-carboxylic acid (C₁₈-ANBC) plus 3,5-didodecyloxybenzoic acid.

C₁₈-ANBC (Scheme 1) compounds are among the first examples of them.^[3, 4, 5] Since then, several examples of thermotropic cubic phases have been identified, for a large variety of molecules:^[6] C_n-ANBC,^[6-9] amphiphilic derivatives,^[10, 11] phasmids,^[12, 13] hydrazine derivatives,^[14] silver salts^[15] and supramolecular dendrimers.^[16] Depending on temperature, length, positions and number of the grafted chains, micellar or bicontinuous cubic phases are obtained. If some of these cubic phases are the same as in lyotropic systems, specific cubic phases are observed only in thermotropic systems, due to more complex molecular interactions.

For instance, the *la3d* space group is reported for several of these thermotropic compounds,^[5, 6, 8, 11, 14] and is also widely

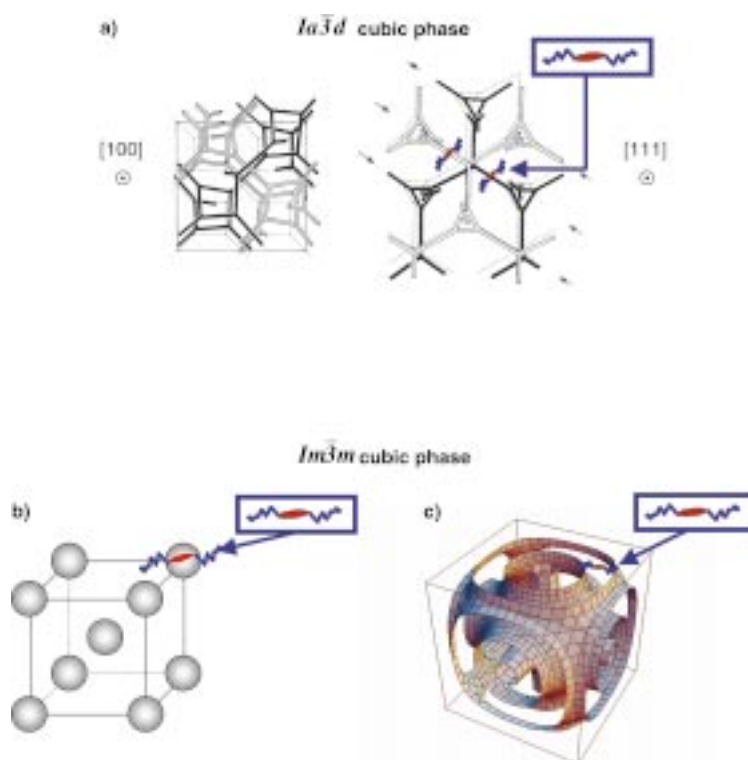


Figure 1. a) Schematic drawing of the *la3d* cubic phase (from Luzzati et al.^[1b]); b) *Im3m* micellar bcc phase; c) proposed model for the *Im3m* four-continuous phase.^[6]

encountered in lyotropic systems. This space group corresponds to a bicontinuous structure (Figure 1 a), made of two interwoven equivalent subspaces separated by a three-dimensional periodic surface, Schoen's gyroid (G) surface. In the case of thermotropic mesogens, the terminal methyl groups of the paraffinic chains are located on the G surface with the mesogenic cores inside the two subspaces.^[5] Supramolecular dendrimers^[16] and amphiphilic derivatives^[11] exhibit the first thermotropic examples of a *Pm3n* micellar phase, that is also observed in many lyotropic systems. A third space group, *Im3m*, is also reported in thermotropic compounds.^[6, 8, 9, 14] This space group is observed both with pure compounds and binary mixtures. Very similar structural data are obtained with these different systems and will be detailed below. They clearly indicate that this *Im3m* phase consists neither of a simple body-centred cubic (bcc) micellar phase (Figure 1 b) nor of a simple primitive (P) surface^[17] (both which have the same *Im3m* space group) as in lyotropic systems. Indeed, we proposed recently a four-continuous structural model for this phase which consists in a P surface surrounded by two parallel P-type surfaces (Figure 1 c),^[6] but its structure is still not fully established. This *Im3m* phase appears as a new type of cubic phase specific to thermotropic systems. This paper focuses on the study of a binary thermotropic mixture (Scheme 1) which exhibits a reversible phase transition between two cubic phases of *la3d* and *Im3m* symmetry, respectively. We present for the first time a complete set of single-crystal X-ray diffraction data of the *Im3m* phase, which will be very useful to elucidate its structure. The phase transition between these two cubic phases is followed

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Supporting information for this article is available on the WWW under <http://www.chemphyschem.com> or from the author.

both by X-ray diffraction on single-crystal samples and direct optical-microscopic observation of faceted droplets. Finally, the observation of a metastable tetragonal phase is also reported.

Pure C_{18} -ANBC exhibits an $la\bar{3}d$ cubic phase ($a = 11.7$ nm) in between its smectic C (SmC; $d = 4.5$ nm) and isotropic phases.^[6, 7, 9] Recently,^[9] we found that when 30% of 3,5-didodecyloxybenzoic acid is added to C_{18} -ANBC, only an $Im\bar{3}m$ cubic phase is obtained ($a = 17.3$ nm), between a SmC phase and the isotropic liquid. For the 10% mixture studied here, we observed the following phase sequence on heating:

Cr $\xrightarrow{120^\circ\text{C}}$ SmC $\xrightarrow{125^\circ\text{C}}$ $la\bar{3}d$ $\xrightarrow{175^\circ\text{C}}$ $Im\bar{3}m$ $\xrightarrow{200^\circ\text{C}}$ I. On cooling

from the $Im\bar{3}m$ phase, the $la\bar{3}d$ phase is reversibly obtained; supercooling is observed ($Im\bar{3}m \xrightarrow{145^\circ\text{C}} la\bar{3}d$). The transition temperatures are determined using optical microscopy observations coupled with X-ray diffraction data. The phase transition between the two cubic phases appears to be fully reversible with temperature, in a very reproducible way, contrary to the pure C_{26} -ANBC homologue.^[8]

Upon cooling from the isotropic liquid, the phase behaviour seems to be rather complex. In particular, Figure 3c (see later) shows a picture of small faceted droplets after fast cooling from the isotropic liquid. The droplets are birefringent and their shape indicate a possible tetragonal symmetry, specific to the thermotropic systems.^[6] Within minutes, the $Im\bar{3}m$ phase is recovered. The birefringence disappears and the facets become larger, proving the metastability of the tetragonal phase. In the following, the mixture's behaviour upon cooling from the isotropic phase will not be discussed further.

A single crystal of the $Im\bar{3}m$ phase (175–200 °C) is obtained reproducibly by slow heating (0.1 K min^{−1}) from room temperature. The typical size of such a single crystal, grown directly in a Lindemann capillary inside the X-ray oven, is a few cubic millimeters (see the Experimental Section). Figure 2a shows an X-ray pattern of such a single crystal with a three-fold axis aligned along the vertical axis. Oscillating patterns along this axis have been recorded in order to explore the whole reciprocal space. The indexation of two different reciprocal planes, $[1, \bar{2}, 1]$ and $[1, \bar{1}, 0]$, is given in the Supporting Information. The space group aspect (Laue symbol $I\cdots$) is fully confirmed by these data. The space group determination as $Im\bar{3}m$ is made under the usual assumption that mirror planes are expected both perpendicular to four-fold and two-fold axes. The lattice parameter $a_{Im\bar{3}m}$ is 17.3 nm and no significant variation of this value is registered in function of temperature. The first 20 hkl reflections (from (110) to (600)) were detected and their relative intensities measured (see the Table in Supporting Information). Compared to powder diffraction data, we measured with this single crystal about twice the number of reflections and especially the very weak ones, such as the (110) reflection. Moreover, the (330) and (411) reflections, with the same interreticular spacings, can be detected separately only with a single crystal. The relative intensities of the reflections reveal the signature of the complex structure factor of this phase. As already reported, the (400) and (321) are the strongest reflections.^[6, 8, 9, 14]

By very slow cooling (0.01 K min^{−1}) from this $Im\bar{3}m$ phase, small single crystals (typically 1 mm³) of the $la\bar{3}d$ phase are

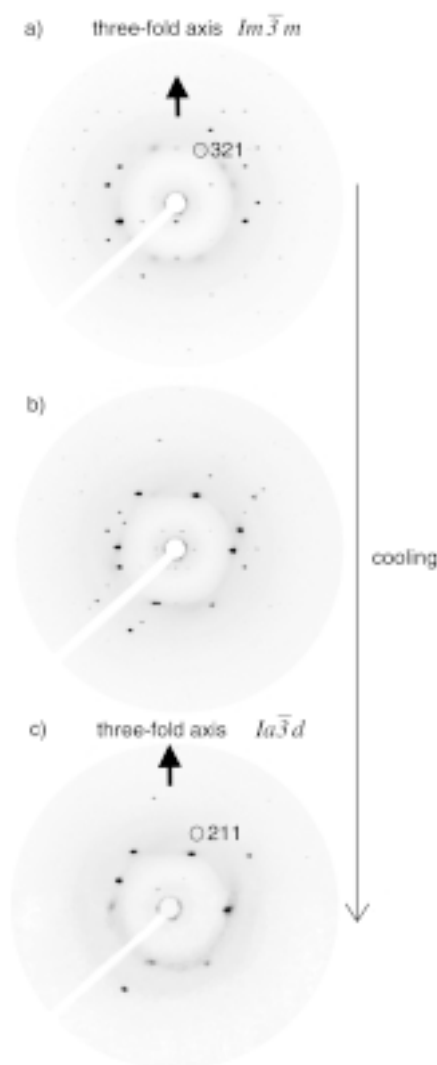


Figure 2. Phase transition from the $Im\bar{3}m$ cubic phase into the $la\bar{3}d$ cubic phase upon cooling at 0.01 K min^{−1}. An $Im\bar{3}m$ $[2, -3, 1]$ zone axis (a) transforms into a $la\bar{3}d$ $[0, -1, 1]$ zone axis (c) with a common vertical three-fold axis. In (b), the coexistence between the two phases is recorded. Weak powder rings in the background are probably due to a parasitic scattering.

obtained ($a_{la\bar{3}d} = 11.7$ nm at 140 °C). Figure 2 shows an example of this phase transformation in one reciprocal plane with a three-fold axis along the same direction for both single crystals (along the vertical axis in the Figure). The preservation of a three-fold axis during the transition was observed for all the $la\bar{3}d$ single crystals we obtained by this method.

The (211) reflection of the $la\bar{3}d$ phase ($d_{(211)} = 4.78$ nm) appears to be very close to the (321) reflection of the $Im\bar{3}m$ phase ($d_{(321)} = 4.62$ nm), as observed in other examples.^[6, 8, 14] Indeed, these two strong reflections can also be compared to the layer thickness of the SmC phase ($d = 4.6$ nm).

Finally, we observe an important difference between the single crystals of the two phases, already observed with hydrazine compounds.^[14] As usual, the $la\bar{3}d$ single crystals show intense diffuse scattering lines between Bragg spots,^[14, 15] which is not the case with $Im\bar{3}m$ cubic phase.

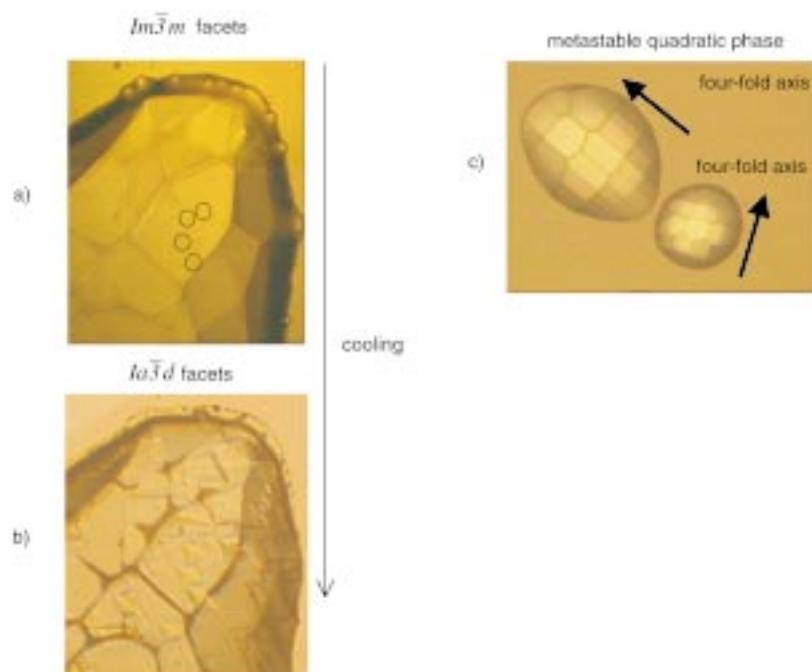


Figure 3. Phase transition from the $Im\bar{3}m$ cubic phase (a) into the $Ia\bar{3}d$ cubic phase (b) observed on a faceted droplet by optical microscopy. A photograph of the metastable birefringent phase, probably tetragonal, observed upon fast cooling from the isotropic liquid phase is shown in (c). The typical size of a droplet is about 50 microns.

Droplets of the mixture were also deposited on a hydrophobic substrate and their shapes observed with an optical microscope. Facets appear at the surface of these droplets by cooling into both cubic phases, as already reported in ref. [9]. Figure 3 shows a modification of these facets associated to the phase transition between the two cubic phases. In Figure 3a, large well-defined facets of the $Im\bar{3}m$ phase appear. Such large facets can be observed either for large or small droplets. By careful observation of the sample, small spots can be detected, indicated by circles on the picture. By further cooling of the mixture (0.1 K min^{-1}) into the $Ia\bar{3}d$ phase, the small spots transform into stepped diamond shapes (Figure 3b) with angles corresponding to (110) planes, as was the case for the growing of free drops of the $Ia\bar{3}d$ phase of pure C_{18} -ANBC compound.^[9]

We have shown it is possible to grow large single crystals of thermotropic cubic phases suitable for X-ray diffraction analysis. Moreover, the observation of these cubic phases by direct optical microscopy of faceted droplets is confirmed. The mixture studied, with only 10% of di-substituted carboxylic acid, is intermediate between pure C_{18} -ANBC ($Ia\bar{3}d$ phase) and the 30% mixture ($Im\bar{3}m$ phase).^[9] It was chosen on purpose to stabilise both phases and thereby allow the reversible observation of the transition between the two cubic phases. It should be noticed that a distance, directly related to the molecular length, is preserved in the three phases (SmC phase: layer thickness, $Ia\bar{3}d$ phase: $d_{(211)}$, $Im\bar{3}m$ phase: $d_{(321)}$). In all cases it gives rise to the most intense X-ray powder diffraction ring. The measured single crystals X-ray intensities relate to the modulus of the structure factor, and these new experimental results will help to elucidate the structure of the $Im\bar{3}m$ phase and its structural relations with the $Ia\bar{3}d$ phase.

Experimental Section

Pure C_{18} -ANBC and 3,5-didodecyloxybenzoic acid have been obtained as described.^[9] The molar composition of the mixture is 90% C_{18} -ANBC and 10% 3,5-didodecyloxybenzoic acid.

Single-crystal X-ray scattering data was taken from the D43 station at the LURE synchrotron (Orsay, France) at a wavelength of $1.45\text{ \AA}$. Detection was performed at 407.2 mm on an image-plate detector and required an exposure time of about five minutes. The mixture, introduced in Lindemann capillaries (diameter 1 mm) was held inside an home-made oven specifically designed to obtain large single crystals as it allows very slow (typically 0.01 K min^{-1}) heating or cooling rates, which are essential for growing single crystals. The oven is mounted on a motorised goniometric head. The investigation of the whole reciprocal space is achieved by a motorised rotation of the oven around its vertical axis.

Indexation from a unique single crystal was obtained using the crystallographic software CaRine.^[18]

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A triple-network tricontinuous cubic liquid crystal

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Soft matter such as surfactant–water systems, block copolymers or liquid crystals can form periodic structures on nanometre to micrometre scales. This property can be used for templating nanoporous ceramics, surface patterning for electronic devices, or generation of photonic materials. Much attention has been paid to structures appearing between the layer and cylinder phases, the three so-called bicontinuous cubic phases. These are formed by two continuous interpenetrating networks of channels. In this article we describe a related phase, which has the first reported structure consisting of three interpenetrating infinite networks. It is a thermotropic (solvent-free) liquid crystal of cubic symmetry $Im\bar{3}m$. The structure is one of the most complex in liquid crystals, and is determined by direct Fourier reconstruction of electron density. We discuss the possible rationale for the existence of such a phase, its structural relationship with the bicontinuous phases, and its position in the phase diagram.

Micro-phase separation between oil and water, or between hydrophilic and hydrophobic, or aliphatic and aromatic parts of the molecule, or between two blocks of a copolymer, leads to a variety of self-organized structures in soft condensed matter. The three bicontinuous cubic phases, found in lyotropic (that is, solvent-containing) liquid crystals^{1,2} and block copolymers^{3,4}, have space group symmetries $Ia\bar{3}d$, $Pn\bar{3}m$ and $Im\bar{3}m$ respectively⁵. Each of the two interwoven networks is made up of channel segments with junctions where three ($Ia\bar{3}d$), four ($Pn\bar{3}m$) or six ($Im\bar{3}m$) such segments join (Fig. 1). If one connects all the midway points between the two networks, one obtains a so-called infinite periodic minimum surface (IPMS). These are of type G ($Ia\bar{3}d$), D ($Pn\bar{3}m$), and P ($Im\bar{3}m$)⁶. The P and D surfaces were described mathematically by Schwartz already in the 19th century. In water-in-surfactant microemulsions ('inverse' lyotropic liquid crystals), water fills the channels and the middle of the surfactant double layer coincides with the IPMS.

The inverse bicontinuous cubic lyotropics form when the outer surface of the bilayer requires a larger area than the interior. Significant portions of the IPMS are saddle surfaces, with zero mean curvature and constant negative gaussian curvature. Note that, for the same reason, a saddle shape is adopted by a thinly cut potato chip when fried, as the surface becomes hot first and expands. If the inner and outer surface areas of a bilayer match, the layer is flat, and when one surface area is significantly larger than the other, the bilayer cleaves and the individual layers roll up into cylinders; hence the bicontinuous phases appear as intermediate between the lamellar and the hexagonal phase.

The intermediate phases, when found in triblock copolymers or polyphilic molecules, have sometimes been called 'tricontinuous' or 'multicontinuous', referring to the number of incompatible molecular moieties⁷. To avoid confusion, here we refer to them collectively as 'double-network' phases.

The G-, P- and D-type IPMSs most closely approximate the ideal situation in which everywhere on the surface gaussian curvature is constant and mean curvature is zero. Other surfaces exist, but they are slightly poorer approximations and the corresponding phases have not been observed⁵. More complex 'high genus' surfaces have been predicted^{8,9}, but also remain unobserved.

In thermotropic liquid crystals, cubic phases with space-group symmetry $Ia\bar{3}d$ (commonly known as smectic D phase)¹⁰

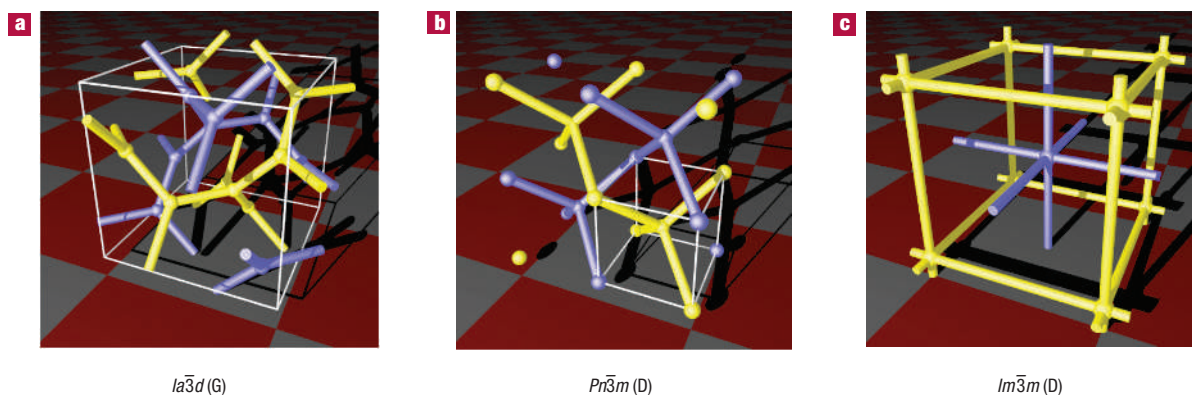
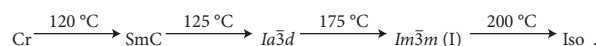


Figure 1 Network models of the three known bicontinuous cubic phases in soft matter. **a**, $Ia\bar{3}d$ (G). **b**, $Pr\bar{3}m$ (D). **c**, $Im\bar{3}m$ (P). The two interpenetrating networks are coloured blue and yellow. White lines delineate the unit cell.

and $Im\bar{3}m$ ¹¹ have also been identified in the phase diagram intermediate between the lamellar and columnar phases. The thermotropic $Ia\bar{3}d$ phase is consistent with the double-network structural model. In this case, the aromatic parts form two separate continuous interwoven networks of channels immersed in the aliphatic matrix, adopting an inverse type structure. However, the structure of the thermotropic $Im\bar{3}m$ cubic phase remains unclear^{12,13}. Compared with molecular dimensions, the unit cell parameter is too large to be explained by the P-type ‘bicontinuous’ structure. Another indication of the complexity of this structure is the fact that the dominant reflections observed in the powder X-ray diffraction pattern are (321) and (400), instead of the (110) as commonly observed in the lyotropic $Im\bar{3}m$ (P) phase. ‘Tricontinuous’¹¹ and ‘quadricontinuous’ models^{14,15}, based on the modification of the P-type IPMS, have been proposed in the past. However, these structural models raise serious questions, and, moreover, do not explain the observed diffraction intensities quantitatively. For clarity, we note here that another thermotropic $Im\bar{3}m$ liquid-crystal phase occurs in wedge-shaped molecules such as dendrons, representing a body-centred-cubic (b.c.c.) packing of isolated self-assembled dendrimer spheres engulfed in a matrix of terminal aliphatic chains (the ‘micellar’ $Im\bar{3}m$ phase)^{16,17}. To avoid confusion, we shall refer to the current phase as $Im\bar{3}m$ (I).

Significant progress has been made recently in the understanding of the $Im\bar{3}m$ (I) phase. High-quality single-domain diffraction data have been obtained from a mixture of two carboxylic acid compounds¹⁸. The study of a series of 4′-*n*-alkoxy-3′-nitrophenyl-4-carboxylic acids (ANBC-*n*, where *n* is the number of alkoxy carbons with *n* = 15–26) has also provided valuable information on the structure of the $Im\bar{3}m$ (I) phase and its relationship to smectic C and $Ia\bar{3}d$ phases on changing the temperature and alkoxy chain length¹⁹.

To resolve the structure of this intriguing phase, we resort to the method of direct reconstruction of electron-density distribution. Sample I used in this work is an asymmetric mesogen with one *n*-alkoxy chain at one end and two at the other (Fig. 2a)²⁰. At temperatures above 85 °C, this compound shows a single optically isotropic mesophase of $Im\bar{3}m$ symmetry up to 172.5 °C, at which point it transforms to a disordered liquid (Iso). Sample II used in this work is the 90/10 molar mixture of two carboxylic acids: ANBC-18 and 3,5-didodecyloxybenzoic acid (Fig. 2a)²¹. The following phase sequence is observed on heating:



On cooling from the $Im\bar{3}m$ phase, the $Ia\bar{3}d$ phase is reversibly obtained with supercooling:



Molecular dimensions of sample I and II, as well as their aromatic/aliphatic volume ratios, are calculated using Cerius² molecular modelling software and listed in Table 1.

A small-angle powder diffractogram of the $Im\bar{3}m$ (I) phase in sample I is shown in Fig. 2b. Consistent with previous results on the $Im\bar{3}m$ (I) phase, the two strongest reflections are (321) and (400). Intensity integration was carried out on the first nine visible diffraction peaks and these are listed in Table S1 of the Supplementary Information. The measured intensities are almost identical to those collected from single-crystal diffraction patterns of sample II (Fig. 2c). This indicates that both samples have similar aromatic/aliphatic volume ratios, as estimated in Table 1.

A reconstructed three-dimensional electron-density map, considered to represent the best combination of structure-factor phases, is shown in Fig. 3. The method and the choice of phases are described in the text and Fig. S2 of the Supplementary Information. Referring to the problem of selecting the correct combination of structure-factor phases, it should be noted that all conceivable

Table 1 Molecular dimensions of sample I and II. The listed values for sample II are those for the majority component ANBC-18. Cerius² molecular modelling software is used to calculate the molecular dimensions. Only C_{*n*}H_{2*n*+1} end groups are included in the calculation of the volume of the aliphatic parts, whereas all other parts are counted in the aromatic core.

Molecular dimensions	Sample I	ANBC-18 (major component of Sample II)
Extended molecular length	6.0 nm	3.5 nm
Length of aromatic core	3.0 nm	1.3 nm
$V_{ar}:V_{ali}$	43.6:56.4	40.6:59.4

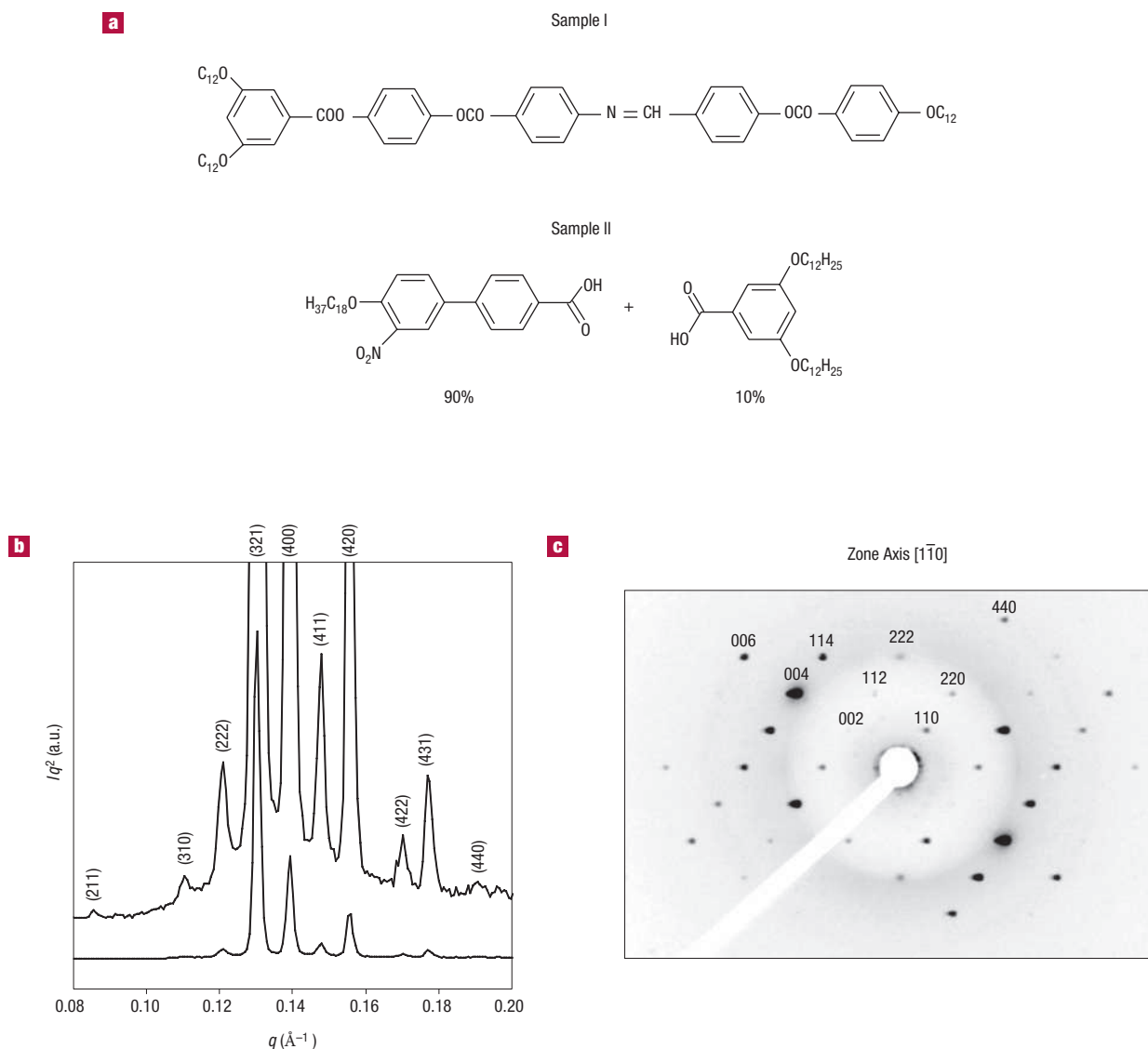


Figure 2 Chemical structures and X-ray diffraction patterns of the liquid-crystal phase under study. **a**, Structures of compound I and the mixture II. **b**, Small-angle X-ray powder diffractogram of sample I recorded at 100 °C using station 16.1 of the Daresbury Synchrotron Radiation Source. The curve on top is enhanced by a factor of 10. **c**, Single-domain diffraction pattern of sample II recorded at 175 °C.

structures compatible with the X-ray data have been investigated. Effectively the choice narrows down to the four structures in Fig. S2, the chosen one (Fig. S2c) being strongly favoured by physical considerations (also see the discussion relating to Fig. 4b).

The 'best' map is represented in Fig. 3a by the isoelectron surface that divides the unit cell volume into high-density regions (inside the channels) and low-density regions (outside). The volume ratio of the high-density to the low-density regions is chosen to be 40:60, which is close to the volume ratio of the aromatic–aliphatic parts of sample I (Table 1). The map is rather complex and does not support previous tricrystalline or quadricrystalline models (Fig. 3b). Instead, the high-density regions can be best described by a model consisting of three sets of interwoven networks as drawn in Fig. 4a. Two of the three networks (yellow and blue) are identical but mutually displaced by $(x/2, y/2, z/2)$. Each of these networks contains an octahedron which sits either at a corner (yellow network) or at the centre (blue network) of the unit cell.

The octahedra are connected by rods along the edges of the unit cell or from centre to centre of the cell. An octahedron is made up of 12 rod-like segments defining its edges. In between the two networks is the third 'middle' network (magenta in Fig. 4a), every node of which joins three rod-like segments, as in the *Ia3d* 'gyroid' (G) structure (Fig. 1a). Interestingly, the backbone of the 'middle' network follows closely the P minimum surface (Fig. 3c), although it does not cover the whole surface as suggested by the tricrystalline model¹¹. Moreover, the other two networks (termed 'inner' and 'outer', respectively) follow roughly the other two surfaces in the tricrystalline model (Fig. 3d). The three networks of high-density must be occupied by the aromatic mesogens lying across the rod-like network segments, with the surrounding low-density continuum made up of the tethered aliphatic chains (Fig. 4a). It must be noted though that the cross-sectional area of the rod-like segments of the inner and outer networks undulates, whereas that of the intermediate network is rather uniform.

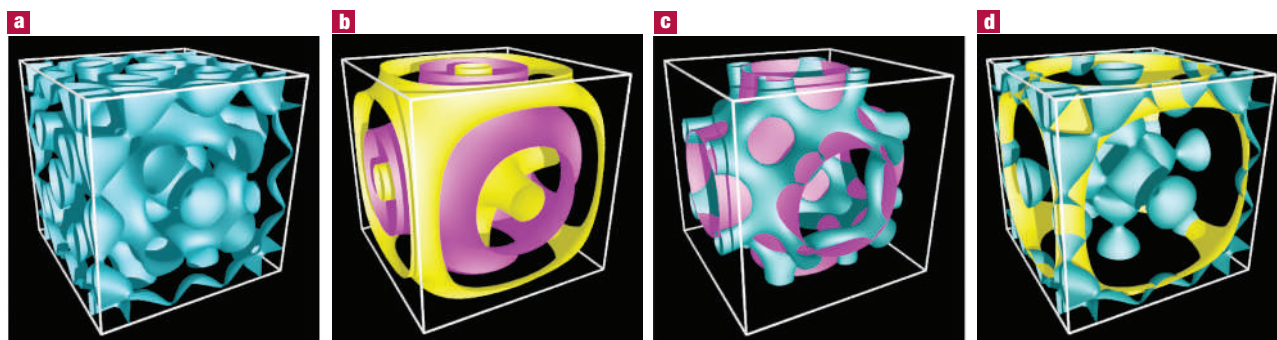


Figure 3 Isosurface representations of the reconstructed three-dimensional electron-density map. **a**, Complete map of the $Im\bar{3}m$ (I) structure reconstructed from the powder X-ray diffraction pattern. **b**, The three-surfaces model¹⁶. The surfaces are given by the general equation: $\cos(2\pi x/a) + \cos(2\pi y/a) + \cos(2\pi z/a) - \cos(2\pi x/a)\cos(2\pi y/a)\cos(2\pi z/a) = \beta$, with $\beta = 0$ (magenta, a good approximation of the IPMS surface P) and $\beta = \pm 1.7$ (yellow). **c**, The backbone of the intermediate network follows the P surface. For clarity only the isosurface of the intermediate network is shown, with the density level increased. **d**, The inner and the outer network follow the yellow $\beta = \pm 1.7$ surfaces.

Next we attempt to rationalize the existence of the triple network $Im\bar{3}m$ (I) structure. First of all, a structure based on a network of rod-like segments is compatible with the general position of the phase between smectic and columnar. A branched network of rods provides a mean curvature lower than that of linear rods (columnar) and higher than zero (smectics). In terms of molecular design, many compounds that form this phase have two alkyl chains at one or both ends of the aromatic core; related mesogens forming smectic phases have only one, whereas those forming columns have two or three chains at each end²². Regarding the structure of the network, for all three bicontinuous phases known previously, every rod segment is equivalent to another. In contrast, in the $Im\bar{3}m$ (I) structure there exist four crystallographically non-equivalent rod-like segment types (marked A, B, C and D in Fig. 4a). The method of determining the node positions is described in the Supplementary Information. The node positions of the octahedra constituting the inner and outer networks are found to be (0.23, 0, 0) and all crystallographic equivalents generated by $Im\bar{3}m$ symmetry. For the intermediate network the node positions are at (0.30, 0.30, 0.09) and the crystallographic equivalents. The segments of the intermediate network are all of the same lengths and the three adjoining rods at each junction are coplanar within the experimental error.

Some topographic data on the $Ia\bar{3}d$ (G) and the $Im\bar{3}m$ (I) structures are compared in Table 2. The characteristic distances are given first relative to the cell parameter, and then in nanometres as calculated for samples I and II. Despite the differences between the two structures in the lengths of the rod-like segments, the minimum distance between networks and the maximum distance of any point from the networks are surprisingly similar. However, the question still remains as to why thermotropic liquid crystals should prefer a complex structure over a simpler one.

The bicontinuous structures observed in lyotropic systems are often treated mathematically as films of constant thickness enclosing either the polar or the nonpolar region. Such models are primarily suited to phases where the thickness of the nonpolar bilayer is nearly constant. The system's free energy then depends largely on the thickness and the mean and gaussian curvatures of the film⁵. Space filling is not an issue, as water is available to fill gaps of any shape. However, in thermotropics no solvent is present, thus the whole space must be reachable by the mesogenic molecules. This space-filling requirement adds extra limitations to the structures that can be displayed by thermotropic liquid crystals.

To quantify the space-filling factor, we have calculated the average radial distribution of volume dV/dr for all four cubic

Table 2 Selected topographic data on $Im\bar{3}m$ (I) and $Ia\bar{3}d$ structures. The values are first given as fractions of cell parameter, and then in nanometres using the experimentally observed cell parameters. The node coordinates used are (0.23, 0, 0) a_i and (0.303, 0.303, 0.0915) a_i for $Im\bar{3}m$, and (0.125, 0.125, 0.125) a_i for $Ia\bar{3}d$. To enable comparison between the two structures, the ratio between the unit cell parameters a_i/a_e is set at 1.55, making the theoretical r_{ar} values for both phases equal (the experimental a_i/a_e ratio is ~ 1.53 at the $Im\bar{3}m$ – $Ia\bar{3}d$ transition).

Characteristic distances	$Ia\bar{3}d$ (G)	$Im\bar{3}m$ (I)
Experimental unit cell parameter a	11.7 nm (Sample II, 140 °C)	18.1 nm (Sample I, 100 °C) 17.3 nm (Sample II, 175 °C)
Lengths of rod segments between junctions	0.354 a_e 4.14 nm (Sample II)	0.270 a_i = 0.419 a_e (A)* 0.325 a_i = 0.504 a_e (B)* 0.183 a_i = 0.284 a_e (C, D)*
Sample I		
4.89 nm (A)		
5.88 nm (B)		
3.31 nm (C, D)		
Sample II		
4.67 nm (A)		
5.62 nm (B)		
3.17 nm (C, D)		
Minimum distance between networks	0.433 a_e 5.07 nm (sample II)	0.266 a_i = 0.412 a_e 4.81 nm (sample I) 4.60 nm (sample II)
Maximum distance of any point to the nearest network	0.299 a_e 3.50 nm (sample II)	0.204 a_i = 0.316 a_e 3.69 nm (sample I) 3.53 nm (sample II)
r_{ar} for volume ratio $v_{ar}/v_{all} = 40:60$	0.128 a_e 1.50 nm (sample II)	0.0828 a_i = 0.128 a_e 1.50 nm (sample I) 1.42 nm (sample II)

*There are four crystallographically distinct rod segments (marked A, B, C and D in Fig. 4a) in the $Im\bar{3}m$ (I) structure. The edge centre (0.5, 0, 0) a_i and the face centre (0.5, 0.5, 0) a_i of the unit cell are taken as junction points of the inner and outer networks.

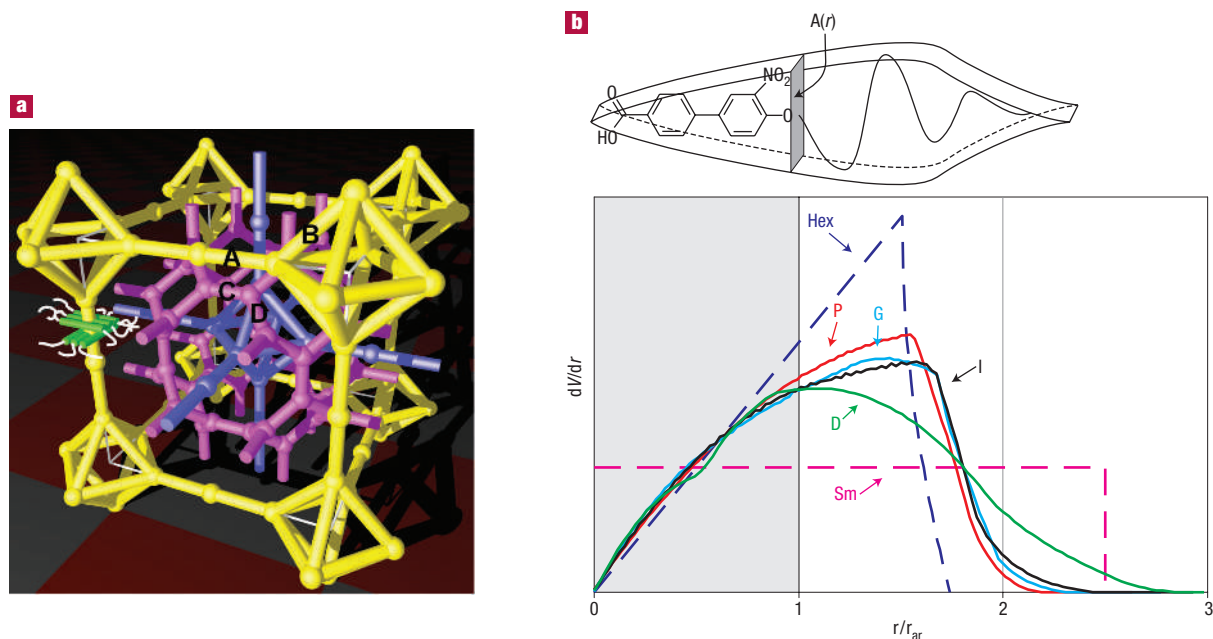


Figure 4 Network model of the $Im\bar{3}m$ (I) structure and the average radial distributions of volume for lamellar, columnar and different cubic structures.

a, Perspective view of the network representation of the $Im\bar{3}m$ (I) structure. Several molecules are also shown schematically. A, B, C and D are four crystallographically non-equivalent rod-like segment types. **b**, dV/dr plots for different liquid-crystal phases. The following abbreviations are used: I for the triple-network $Im\bar{3}m$ cubic phase; G, D and P for the double-network cubic phases $Ia\bar{3}d$, $Pn\bar{3}m$ and $Im\bar{3}m$, respectively; Sm for smectic and Hex for hexagonal columnar phase. Top: schematic drawing of molecular cross-sectional area profile, $A(r)$, which should match dV/dr for uniform filling of volume of a particular phase.

structures mentioned above, as well as for the smectic and the hexagonal columnar phases. Here r is the distance from the central axis of the rod-like segments (or the central plane of the layers in smectics). As r increases, the cylindrical surfaces enveloping adjacent rods impinge and the rods overlap increasingly, causing a reduction in the rate of growth of the enclosed volume dV/dr . The calculated dV/dr curves are shown in Fig. 4b.

The dV/dr curves in Fig. 4b are scaled horizontally and vertically to allow meaningful comparison. r scales are normalized specifically for the 40:60 aromatic/aliphatic volume ratio. For this purpose it is assumed that the aromatic parts occupy the space within a distance r_{ar} from the axis of the rod-like segments, and the aliphatic chains occupy the remaining volume. r in Fig. 4b is the reduced radius in units of r_{ar} . The ordinates are scaled to the same total volume (more information on the numerical calculation is given in Supplementary Information).

The link between the dV/dr curves and molecular packing is provided by assuming that the centre of each molecule (or the centre of the dimer in the case of ANBC- n) lies on the central axis of the rod-like segments, the molecule radiating outwards. Therefore the distance r_{ar} is expected to be half the length of the aromatic part of the molecules (or the dimers). The r_{ar} values for sample I and II, calculated according to this assumption, are 1.50 nm and 1.42 nm, using the observed unit cell parameter (Table 2). These are indeed consistent with the molecular dimensions: the half-length of the aromatic core for sample I is 1.5 nm, and the length of ANBC-18, the major component of sample II and half the dimer, is 1.3 nm (Table 1). More realistically, several rod-like molecular cores lie side-by-side and splay out near the core ends in a perpendicular section of a channel (see Fig. 4a), as proposed for the columnar phase of phasmids (rod-like molecules with multiple flexible chains at each end)²².

For uniform filling of volume of a particular phase, ideally the molecular cross-sectional area as a function of distance from the molecular centre, $A(r)$, should match dV/dr (see schematic drawing at the top of Fig. 4b). $A(r)$ refers to a weighted average over all conformations at a given temperature. In comparison, for smectic phases, $dV/dr = \text{constant}$, whereas for the hexagonal columnar (cylindrical) phase $dV/dr \propto r$ for r below the impingement threshold. As is seen in Fig. 4b, for the four 'intermediate' phases discussed here, initially $dV/dr \propto r^n$, where $0 < n < 1$. A similar analysis in terms of dV/dr has been applied in comparing the different three-dimensional micellar structures in thermotropic liquid crystals²³. There, initially $dV/dr \propto r^2$.

Figure 4b clearly shows that the ideal molecular shapes for the $Ia\bar{3}d$ (G) and the new $Im\bar{3}m$ (I) phase are very similar, probably the reason why, out of the four structures being considered, only these two have been observed in thermotropic liquid crystals so far. The dV/dr curves also give an indication of how the molecular shape should be changed in order to produce the other two structures. For the $Pn\bar{3}m$ (D) structure, the aliphatic chains should be longer and narrower relative to the core (for example, fewer or more extended). In contrast, for the simple $Im\bar{3}m$ (P) structure they need to be wider and shorter, for example, at a higher temperature.

From the network models of the $Ia\bar{3}d$ (G) and the $Im\bar{3}m$ (I) phase, the ratio of the unit cell parameters of the two phases at the transition point can be estimated. According to numerical calculations, $a_G = 7.79r_{ar}$ for the $Ia\bar{3}d$ structure, and $a_I = 12.1r_{ar}$ for the $Im\bar{3}m$ (I) structure when the aromatic/aliphatic volume ratio is 40:60 (the ratio is 44:56 for sample I and 40:60 for sample II, Table 1). Thus a_I/a_G can be estimated to be 1.55. This is in agreement with the experimental observations^{12,19} that, upon the transition between the $Ia\bar{3}d$ and $Im\bar{3}m$ (I) phases in the same compound, the a_I/a_G value is about 1.53, providing further support for the proposed structural model of the $Im\bar{3}m$ (I) phase.

Figure 4b could be used to explain the observed phase sequence smectic $\rightarrow Im\bar{3}m$ (I) $\rightarrow Ia\bar{3}d$ (G) with increasing temperature in the ANBC-*n* series. At higher temperatures the aliphatic chains expand laterally and consequently their radial length is reduced. According to Fig. 4b, this shift of volume to smaller *r* would indeed favour the $Ia\bar{3}d$ (G) structure. However, the temperature sequence of phases is reversed in the binary sample II: the $Im\bar{3}m$ (I) phase is observed at higher temperatures than the $Ia\bar{3}d$ (G) phase. No satisfactory explanation has been found for this observation so far, but considering that in this sample the mesogen is held together by hydrogen bonding of two components, other temperature-dependent effects may interfere.

As the dV/dr curves shown in Fig. 4b are averages over the entire unit cell, they do not provide information on the possible differences in molecular packing for the different networks, or for different positions on the same network.

It has been observed that upon the phase transition between the $Im\bar{3}m$ (I) and $Ia\bar{3}d$ phases, the orientation of the three-fold axis [111] is preserved¹⁸. Moreover, the (321) reflection of $Im\bar{3}m$ (I) is apparently^{18,19} transformed to the (211) reflection of $Ia\bar{3}d$. This suggests that $[\bar{1}2\bar{1}]$ axis of $Im\bar{3}m$ (I) becomes $[0\bar{1}1]$ axis of $Ia\bar{3}d$ (G). Models of both phases, viewed along the [111] axis, support such an orientational relationship between the two phases, as shown in Fig. S4 of the Supplementary Information. However, we should stress that the epitaxial relation between the $Im\bar{3}m$ (I) and $Ia\bar{3}d$ phases has not been fully elucidated.

The long-standing problem of the structure of the thermotropic $Im\bar{3}m$ (I) phase seems to have been resolved. Thus for the first time we have a liquid crystal consisting of three interpenetrating continuous networks. Furthermore, geometric calculations show that the shape requirements for molecules forming such a structure are very similar to those for the formation of the $Ia\bar{3}d$ phase. These calculations also help rationalize the observed phase sequence in a range of liquid-crystal phases as a function of temperature and molecular architecture. Further studies, experimental as well as theoretical, are now required for a better understanding of this unusually complex liquid crystal.

METHODS

Small-angle X-ray powder diffractograms were recorded using station 16.1 of the Daresbury Synchrotron Radiation Source. Monochromatic radiation of wavelength $\lambda = 1.4 \text{ \AA}$ was used. The detector was proportional multiwire (Rapid II). The powder samples in glass capillaries were held in a modified Linkam hot stage (TMS93; in which a hole for the capillary was drilled through the heating block) with temperature accuracy of $\pm 0.1 \text{ }^\circ\text{C}$. For temperature and geometry calibration, pure crystalline *n*-alkanes of known melting points and lattice parameters were used. The capillary was rotated during recording of the diffraction pattern.

Single-domain diffraction patterns were recorded using station D43 of the LURE synchrotron source. Monochromatic radiation of wavelength $\lambda = 1.45 \text{ \AA}$ was used. An image-plate detector (Storm 820, Molecular Dynamics) was used. The single-crystal samples were obtained in Lindeman glass capillaries (diameter 1 mm) using a home-made oven, allowing very low cooling and heating rates (typically $0.01 \text{ }^\circ\text{C min}^{-1}$). The oven was mounted on a motorized goniometric head. A motorized rotation of the oven around the vertical axis in an oscillating mode was used to record the diffraction about different zone axes of a single crystal.

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Competing financial interests

The authors declare that they have no competing financial interests.

A Triple-Network Tricontinuous Cubic Liquid Crystal

Supporting Information

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Reconstruction of Electron Density Map

Laue Class of the Diffraction Pattern

The space group determination of the new phase has been helped considerably by the recent single crystal x-ray diffraction work¹. Very weak diffraction peaks such as (110) and (200) were detected, confirming the general extinction rule $h + k + l = 2n$. From the single crystal diffraction patterns, the Laue class can be determined as $m\bar{3}m$, for the following reason. A general reflection (hkl), with $h \neq k \neq l$, is equivalent to (lkh) for Laue class $m\bar{3}m$ but not for $m\bar{3}$. Since no intensity difference between (hkl) and (lkh) reflections has been observed in the single crystal diffraction pattern (Figure S1), $m\bar{3}m$ is the correct Laue class. The choice of space group of the new phase can thus be narrowed down to $Im\bar{3}m$, $I432$ and $I\bar{4}3m$. The description of the final choice will be given further below.

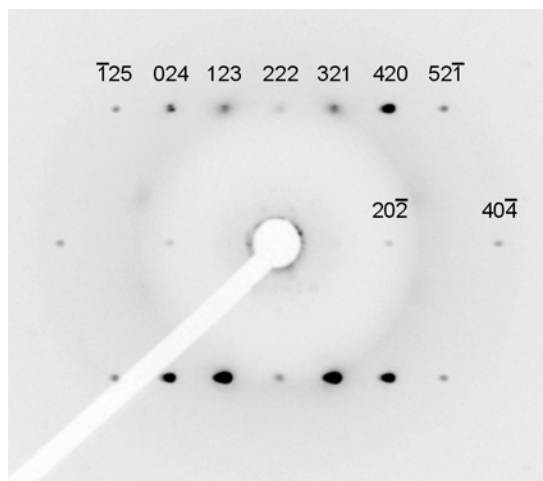


Figure S1. Single domain x-ray diffraction pattern of sample **II** along the $[1\bar{2}1]$ zone axis recorded at 175 °C.

Principle of Electron Density Map Reconstruction

The electron density of a liquid crystal in the unit cell $\rho(x,y,z)$ is related to the structure factor $F(hkl)$ by Fourier transformation:

$$\rho(x,y,z) = \frac{1}{V} \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)]$$

$F(hkl)$ is in turn related to the intensity of the (hkl) reflection $I(hkl)$ as

$$I(hkl) = \text{const.} \times |F(hkl)|^2$$

Thus the electron density $\rho(x,y,z)$ can be reconstructed from the intensities of x-ray reflections $I(hkl)$ using the general formula:

$$\rho(x,y,z) = \frac{1}{\text{const.}} \sum_{hkl} \sqrt{I(hkl)} \exp[-2\pi i(hx + ky + lz) + i\phi_{hkl}]$$

Here ϕ_{hkl} is the phase angle of the structure factor $F(hkl)$.

The diffraction intensities of the current phase, measured from the powder diffraction pattern of compound **I** and from the single crystal patterns of sample **II**, are provided in Table S1.

Table S1. Diffraction intensities and structure factor phases for samples **I** and **II**. Sample **I**: recording temperature 100 °C, lattice parameter $a = 18.1$ nm ($a = 17.6$ nm at 150 °C). Sample **II**: recording temperature 175 °C, lattice parameter $a = 17.3$ nm. For the powder pattern of sample **I** the intensities are corrected for multiplicity and the Lorentz factor. Integrated intensities for sample **II** are measured from single crystal oscillation patterns and are corrected using a rotating-crystal type term. In both cases, the intensities are normalized to that of the (400) reflection.

Index	$I(hkl)$ (sample I)	$I(hkl)$ (sample II)	Multiplicity	Phase
2 1 1	0.095	0.089	24	0
3 1 0	0.292	1.232	24	0
2 2 2	5.662	8.057	8	0
3 2 1	38.04	56.39	48	π
4 0 0	100.0	100.0	6	0
4 1 1* (3 3 0)	3.689*	2.997 (0.006)	24	π
4 2 0	10.75	12.66	24	0
4 2 2	0.689	0.688	24	0
4 3 1* (5 1 0)	0.823*	1.265 (not observed)	48	0

* The observed peak can not be uniquely indexed in the powder diffraction pattern. However, as shown by the intensities measured from the single crystal pattern, the intensity of the peak with the alternative index (in brackets) is so weak that it can be neglected.

Space Group Determination and Selection of Structure Factor Phases

The phase angle of the structure factor ϕ_{hkl} is not obtainable from x-ray experiments. However, for a centrosymmetric structure $\rho(x,y,z) = \rho(-x,-y,-z)$, and ϕ_{hkl} is either 0 or π . This significantly reduces the number of phase choices and allows for an “exhaustive” approach where the results from all possible phase combinations are compared. The “right” phase combination is then decided by the physical merit of the reconstructed map, aided by other knowledge of the system, such as chemical structure. This method works well when there are only a few strong reflections, which is almost always true for liquid crystals.

Among the three candidate space groups, $\text{Im}\bar{3}\text{m}$, $\text{I}432$ and $\text{I}\bar{4}3\text{m}$, only $\text{Im}\bar{3}\text{m}$ is centrosymmetric. Since reflections (321), (400) and (420) are by far the strongest (Table S1), preliminary reconstruction of $\rho(x,y,z)$ was carried out for all three space groups using only these three reflections. The phases of the (400) and (420) reflections can only be 0 or π for all three space groups. The phase of (321) can again be only 0 or π for space group $\text{Im}\bar{3}\text{m}$, but for $\text{I}432$ and $\text{I}\bar{4}3\text{m}$ it can have any value between 0 to 2π . We shall start by examining the centrosymmetric $\text{Im}\bar{3}\text{m}$. Eight phase combinations are possible for reflections (321), (400) and (420) in the case of $\text{Im}\bar{3}\text{m}$, but we need consider only combinations 000, 00π , $\pi 00$ and $\pi 0\pi$ (Figure S2), as the remaining four maps are simply their inverse. For $\pi 00$ we get the essential features of the triple-network model (Figure S2c). The difference from the final adopted structure in Figure 3a is mainly in details, such as the evenness of the rod-like segments. The reconstruction for combination 000 is given in Figure S2a. In this map the rod-like segments of each octahedron in figure S2c merge to form a hollow sphere; at the same time the connections between the octahedra (now spheres) are lost. The hollow spheres are completely enwrapped by the intermediate network, which now has extra junctions at the face and edge centres where four segments meet. This structure is rejected on the basis of the following arguments. Firstly, the inside and outside surfaces of the spheres are non-equivalent. Therefore, there would be more crowding for aliphatic chains on the inside than for those on the outside. Although in lyotropic systems vesicular structures do exist, the problem there is solved by (a) their much larger diameter, and (b) by the number of molecules at the inner and the outer surface often being different, which cannot apply to the current phase as it is observed mainly in symmetrical mesogens. Furthermore, the coexistence of hollow spheres and rod-like segments in the same structure formed by a single compound is hard to explain. Thirdly, the intermediate network becomes less well defined and more distorted, there is the presence of four-way junctions in addition to the 3-way junctions, etc. The other two phase combinations, 00π and $\pi 0\pi$, can be dismissed on similar grounds.

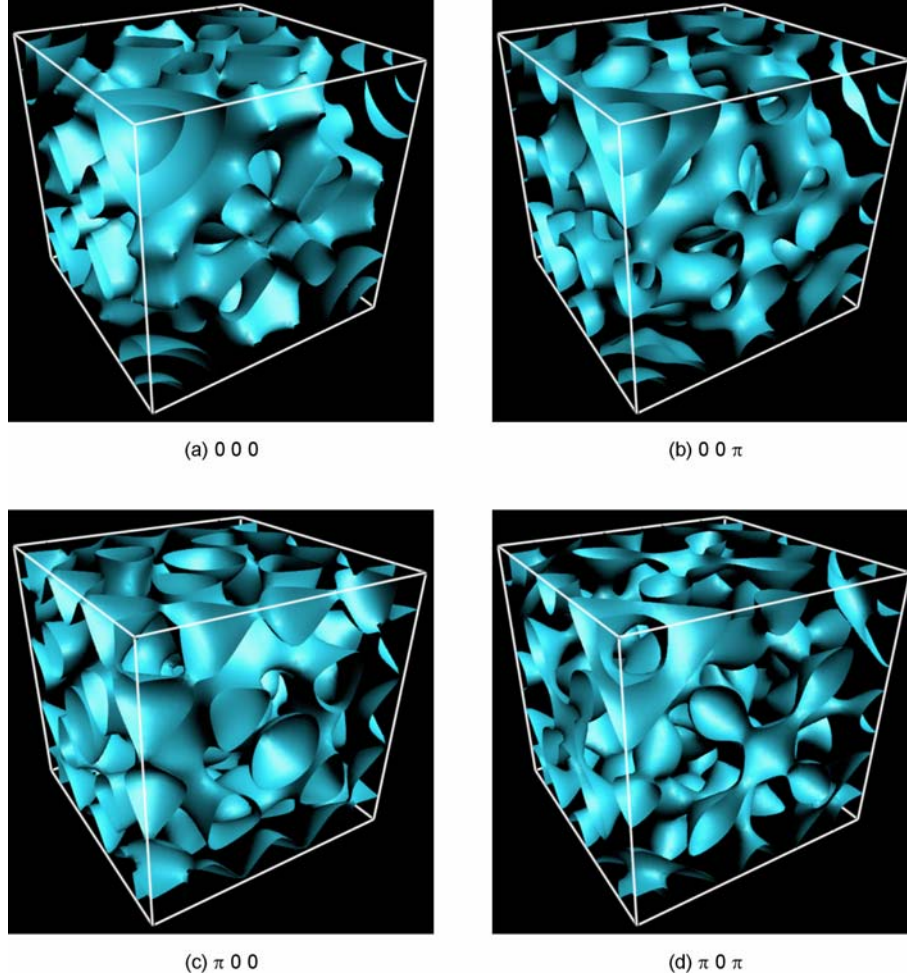


Figure S2. Reconstructed electron density maps for different phase combinations for space group $\text{Im}\bar{3}\text{m}$, using only the three strongest reflections (321), (400) and (420). (a) $\phi_{(321)} = 0$, $\phi_{(400)} = 0$, $\phi_{(420)} = 0$. (b) $\phi_{(321)} = 0$, $\phi_{(400)} = 0$, $\phi_{(420)} = \pi$. (c) $\phi_{(321)} = \pi$, $\phi_{(400)} = 0$, $\phi_{(420)} = 0$. (d) $\phi_{(321)} = \pi$, $\phi_{(400)} = 0$, $\phi_{(420)} = \pi$.

We now return to the non-centrosymmetric space groups $\text{I}432$ and $\text{I}\bar{4}3\text{m}$. The phase of the (321) structure factor has been varied in steps of 20° . Typical maps for the two space groups are presented in Figure S3. For all the maps shown the phase angles of reflections (400) and (420) are 0, while $\phi_{(321)} = \pi/3$ or $2\pi/3$. These maps are in fact closely related to those of the space group $\text{Im}\bar{3}\text{m}$, Figures S2a and S2c corresponding to the limiting cases of $\phi_{(321)} = 0$ and π , respectively. Intermediate values of $\phi_{(321)}$ introduce different degrees of distortion of the structural features, corresponding to a lowering of the system's symmetry. These distortions are not physically plausible (e.g. a large variety of junction geometries appear; the channel cross-section varies widely, etc). It was thus concluded that the space group of the new phase is indeed $\text{Im}\bar{3}\text{m}$. Because $\text{Im}\bar{3}\text{m}$ is centrosymmetric, it is then possible to use the first nine visible reflections, as listed in Table S1, to look for the “correct” phase combination and the most plausible electron density map. The final chosen structure is shown in Figure 3 of the main text. Varying the

phases of the six weak reflections only has an effect of fine tuning the density map. It should therefore be reiterated that all conceivable structures compatible with the X-ray data had been investigated and that effectively the choice was between the structures in Figures S2, with the one in Figure S2c strongly favoured by physical considerations (also see the discussion relating to Figure 4b).

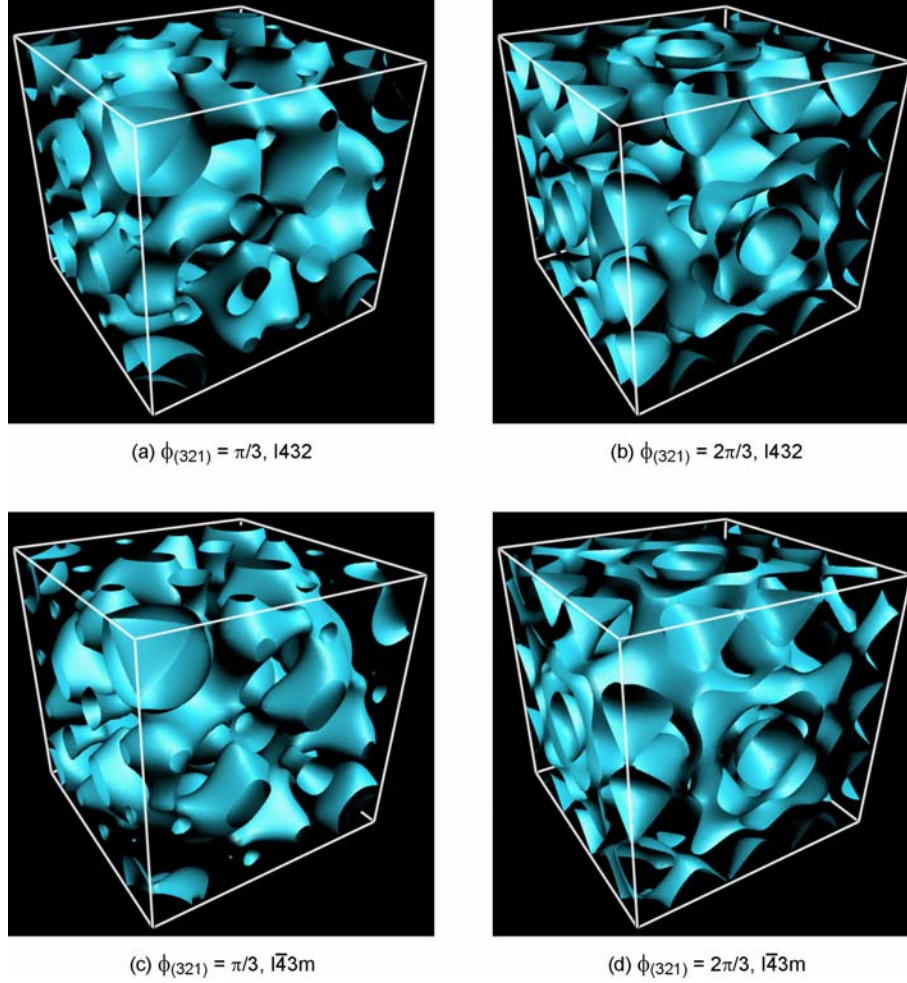


Figure S3. Reconstructed electron density maps for different space group assignments and phase combinations, using only the three strongest reflections (321), (400) and (420). (a) Space group $I432$, $\phi_{(321)} = \pi/3$, $\phi_{(400)} = 0$, $\phi_{(420)} = 0$. (b) Space group $I432$, $\phi_{(321)} = 2\pi/3$, $\phi_{(400)} = 0$, $\phi_{(420)} = 0$. (c) Space group $I\bar{4}3m$, $\phi_{(321)} = \pi/3$, $\phi_{(400)} = 0$, $\phi_{(420)} = 0$. (d) Space group $I\bar{4}3m$, $\phi_{(321)} = 2\pi/3$, $\phi_{(400)} = 0$, $\phi_{(420)} = 0$.

Construction of the Network Model

For the inner and the outer network, the positions of the nodes are chosen to be at the density maxima in the reconstructed electron density map. The node positions of the octahedra are thus found to be at position (0.23, 0, 0) and all its crystallographic equivalents generated by $Im\bar{3}m$ symmetry. For the intermediate network the electron

density maxima are less pronounced and the nodes were taken to be the points of intersection of the central axes of the three adjoining rod-like segments. The node positions are thus found to be (0.30, 0.30, 0.09) and its crystallographic equivalents. This position is in fact very close to the theoretical value (0.303, 0.303, 0.0915) obtained by assuming that all segments in the intermediate network have the same length, and that the three rod segments joining each node are coplanar. These seem to be reasonable assumptions to make and the theoretical values are used for the intermediate network.

Orientational Relationship between $\text{Im}\bar{3}\text{m}(\text{I})$ and $\text{Ia}\bar{3}\text{d}$ upon Phase Transition

It has been observed that upon the phase transition between the $\text{Im}\bar{3}\text{m}(\text{I})$ and the $\text{Ia}\bar{3}\text{d}(\text{G})$ phases the orientation of the 3-fold axis is preserved.¹ Moreover, upon the transition the (321) reflection of $\text{Im}\bar{3}\text{m}(\text{I})$ is apparently transformed to the (211) reflection of $\text{Ia}\bar{3}\text{d}(\text{G})$. This suggests that the $[\bar{1}2\bar{1}]$ axis of $\text{Im}\bar{3}\text{m}(\text{I})$ becomes the $[0\bar{1}1]$ axis of $\text{Ia}\bar{3}\text{d}(\text{G})$. Models of both phases, viewed along the $[111]$ axis, support such an orientational relationship between the two phases, as shown in Figure S4.

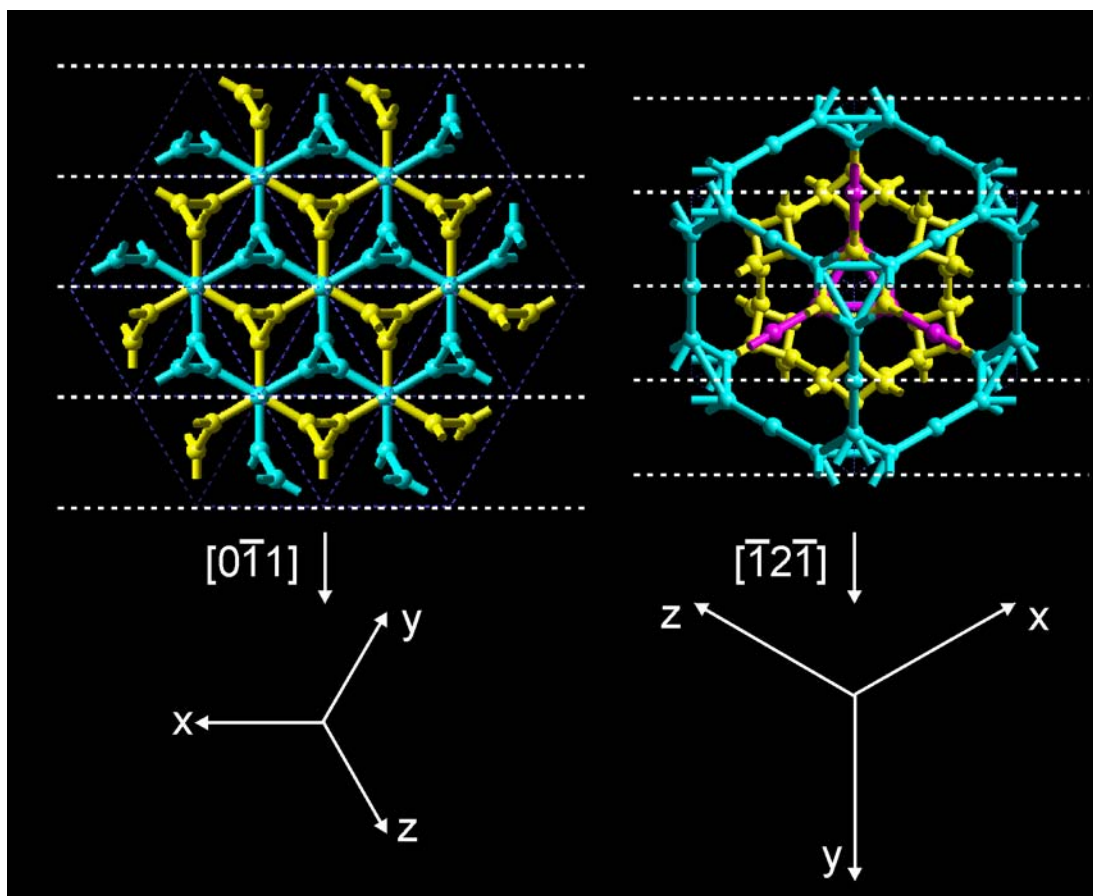


Figure S4. Network models of the $\text{Ia}\bar{3}\text{d}$ and $\text{Im}\bar{3}\text{m}(\text{I})$ structures viewed along the $[111]$ axis. The ratio of the unit cell parameters (a_I/a_G) in the picture is 1.5.

Numerical Calculation of the Radial Distribution of Volume dV/dr

For the four cubic phases, $Ia\bar{3}d$ (G), $Pn\bar{3}m$ (D), $Im\bar{3}m$ (P) and $Im\bar{3}m$ (I), points in the unit cell are sampled in steps of $0.002a$ in all three principal directions. For each point its shortest distance from the networks is calculated. The points falling within a distance interval r to $r + \Delta r$ are then counted and the dV/dr curve generated. The curves are normalized as described in the main text. The dV/dr curves for the smectic and hexagonal columnar phases are calculated analytically.

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Chapitre 16

Phase bicontinue $Ia\bar{3}d$: Structure déduite des intensités des pics de Bragg

La structure bicontinue de cette phase a été proposée puis vérifiée par le groupe de V. Luzzati¹⁻³. Cette structure est introduite au chapitre 4 en prenant l'exemple des molécules thermotropes. Au chapitre 9, on explique comment identifier le groupe d'espace $Ia\bar{3}d$ à partir des pics de diffraction. Le but de ce chapitre est de discuter de la position exacte de l'interface entre les parties polaire/apolaire ou hydrophobe/hydrophile dans cette structure. Plus précisément, on discute comment les mesures d'intensités des pics de Bragg permettent de décrire quantitativement le contenu de la maille, en comparant les différents modèles de structure (réseaux de tiges et surface minimale G). Les méthodes directes et inverses ont été introduites au chapitre 11. Tout d'abord, on montre ici comment la méthode inverse de reconstruction de la densité électronique permet de « retrouver » l'architecture bicontinue. Puis on introduit les méthodes directes, basées notamment sur le calcul du facteur de structure de la surface G ⁴, qui aboutissent à des résultats plus quantitatifs.

Méthode inverse :

On a vu au chapitre 9 que la phase $Ia\bar{3}d$ donne lieu essentiellement à deux pics de Bragg très intenses, les pics 211 et 220. Aussi, en utilisant le formalisme décrit au chapitre 11, on peut facilement reconstruire la densité électronique seulement à partir des deux coefficients de Fourier, F_{211} et F_{220} , dont l'amplitude est mesurée expérimentalement. Le groupe d'espace est centro-symétrique, ces deux coefficients sont donc réels, et seulement deux combinaisons de phase sont possibles : ++ ou +-. La combinaison ++ conduit à la bonne structure (**Fig 16-1**) et pas la combinaison +- (**Fig 16-2**).^{1,2} En effet, seul l'histogramme de la combinaison ++ est compatible avec la répartition de la densité électronique attendue. Entre les deux surfaces (**Fig 16-1**), on retrouve la région continue décrite habituellement par la surface minimale G (voir paragraphe suivant) et où la densité électronique est plus élevée. De part et d'autre des deux

surfaces, on obtient deux sous-volumes contenant les deux labyrinthes proposés initialement par le groupe de V. Luzzati.^{1,2}

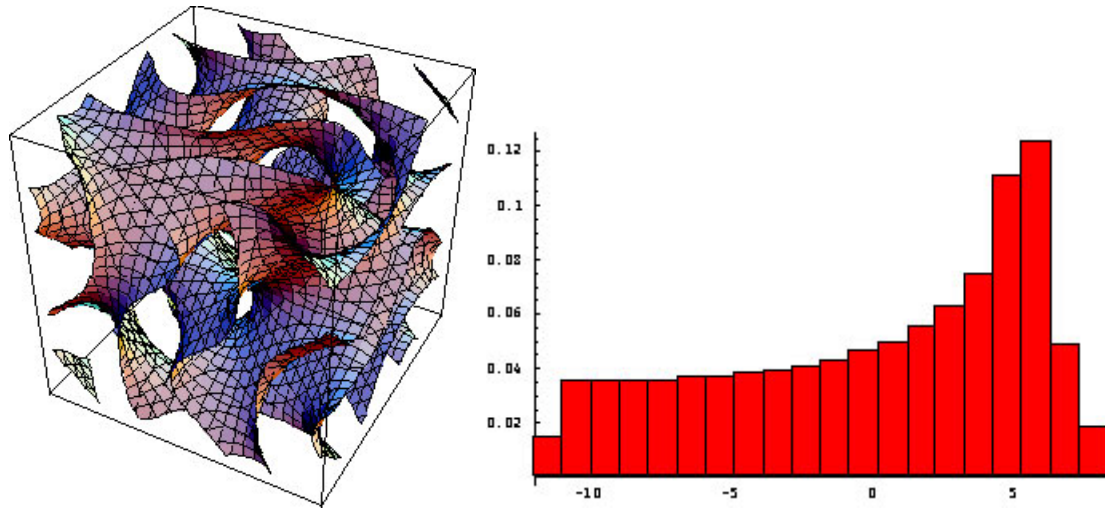


Figure 16-1. Reconstruction de la densité électronique avec $F_{211} = 1$ et $F_{220} = 0.7$ (++). Deux surfaces correspondent aux lieux où la densité électronique est égale à la densité moyenne. L'histogramme de la densité électronique comporte un maximum.

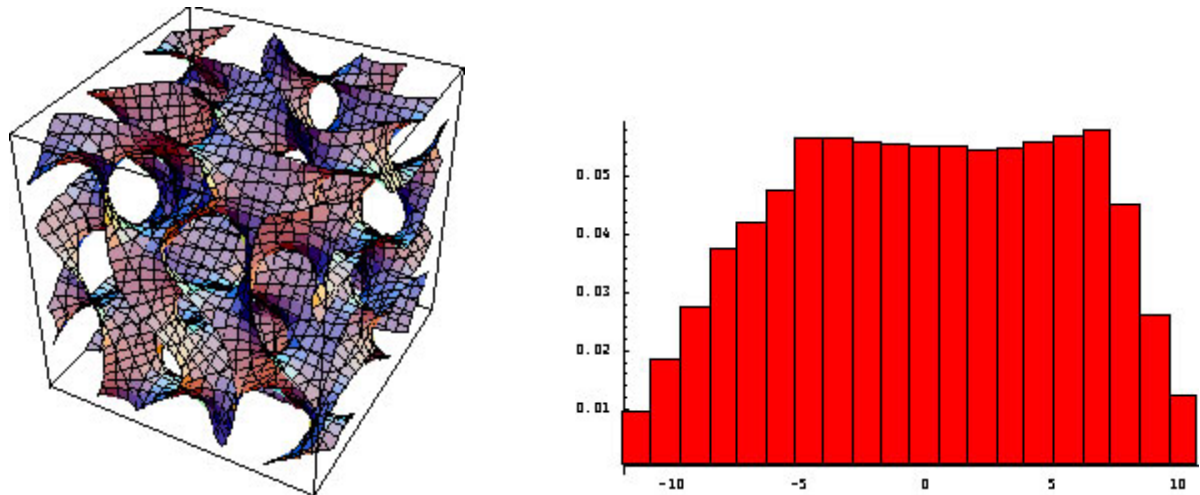


Figure 16-2. Reconstruction de la densité électronique avec $F_{211} = 1$ et $F_{220} = -0.7$ (+-). La surface correspond aux lieux où la densité électronique est égale à la densité moyenne. L'histogramme de la densité électronique ne comporte pas de maximum.

Cette reconstruction très simple permet de comprendre comment le modèle de la structure bicontinue a été élaboré initialement. On raffine ensuite la reconstruction en utilisant toutes les raies de Bragg mesurées, et l'on reconstruit le lieu de l'interface entre les parties polaires/apolaires dans la structure, en choisissant une surface iso-densité.³

Méthodes directes :

Deux types de modèles ont été développés, soit en se basant sur les deux labyrinthes (réseaux de tiges), soit en se basant sur la surface minimale G (**Fig 16-3**). Comme il s'agit de méthodes directes, on fixe la position de l'interface entre les parties polaires/apolaires. En général, on utilise un modèle à deux niveaux, avec des densités électroniques constantes dans les deux types de régions.

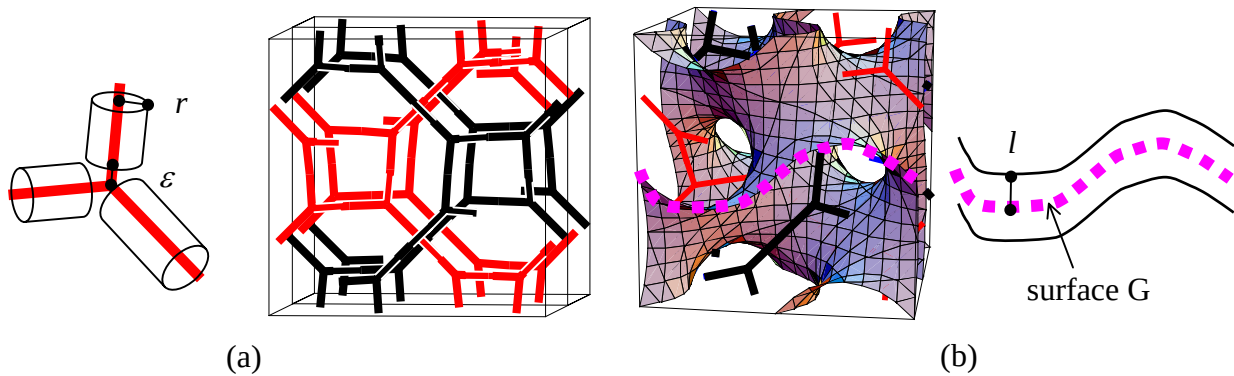


Figure 16-3. Modèles basés sur les réseaux de tiges (a) et modèles basés sur la surface minimale G (b).

Les premiers modèles à avoir été utilisés sont basés sur les labyrinthes. L'interface est à la surface de portions de cylindres de rayon r dont les axes sont les tiges des réseaux 3D. Afin de rendre compte des intensités mesurées, un paramètre ajustable ε est introduit, qui corrige la longueur des cylindres afin d'éviter les recouvrements trois par trois au niveau des nœuds. Ce modèle peut être utile pour estimer une taille via le rayon r ,⁵ mais les modèles basés sur la surface G sont nettement plus satisfaisants, car ils permettent de décrire une interface continue entre les régions polaires/apolaires.

Dans le cas des modèles basés sur la surface minimale G, il s'agit essentiellement de donner une épaisseur L au milieu continu qui sépare les deux labyrinthes. La première étape est de connaître le facteur de structure de la surface G.

Facteur de structure de la surface G :

Publication [3]

Notre contribution dans ce domaine a été de calculer, avec E. Dubois-Violette, le facteur de structure exact de la surface minimale Gyroïde, notée G.⁴ Les coordonnées des points sur cette surface ont été dérivés des équations dans le plan complexe de Weierstrass.

$$F_{hkl}^G = \frac{1}{a^2} \int_{\text{maille cubique}} e^{-2i\pi(hx+ky+lz)} dS$$

Ce calcul a été repris plus récemment par des méthodes numériques légèrement différentes, et les valeurs trouvées sont en bon accord.^{6,7} Les valeurs sont données dans le tableau ci-dessous. La normalisation des coefficients F_{hkl}^G est choisie par rapport au coefficient F_{000}^G qui est proportionnel à l'aire de la surface G dans une maille. Plus précisément, F_{000}^G est une quantité sans dimension, égale à A_c/a^2 , où A_c est l'aire de la surface G dans une maille cubique, et a le côté de cette maille cubique.

hkl	signe	F_{hkl}^G			
		surface G ⁴	surface G ⁶	surface G ⁷	surface nodale
000		3.091	3.0926	3.0967	3.0917
211	+	0.66	0.6607	0.6544	0.6612
220	+	0.451	0.4498	0.4306	0.4471
321	-	-0.092	-0.0922	-0.0971	-0.0936
400	-	-0.36	-0.3612	-0.3375	-0.3526
420	-	-0.338	-0.3382	-0.3309	-0.3355
332	+	0.467	0.4671	0.4751	0.4741
422	+	0.282	0.2812	0.2770	0.2818
431	+	0.209	0.2094	0.1898	0.2040
521	-	-0.077	-0.0776		-0.0753
440	-	-0.06	-0.0604	-0.0991	-0.0723
611	-	-0.245	-0.2451		-0.2401
532	-	-0.104	-0.1038		-0.1069
620	-	-0.06			-0.0572
541	-	-0.162			-0.1627
631	-	-0.199			-0.1989
444	+	0.395		0.4112	0.4044
543	+	0.302			0.3059

Facteur de structure de la surface G et facteur de structure de la surface nodale.

Ce calcul peut être considérablement simplifié en utilisant l'approximation par une surface nodale de la surface G. Cette approximation a été introduite par Von Schnering et Nesper⁸ et constitue une très bonne approximation de la surface G⁹. L'équation de cette surface nodale est :

$$\sin(2\pi x)\cos(2\pi y) + \sin(2\pi y)\cos(2\pi z) + \sin(2\pi z)\cos(2\pi x) = 0$$

Nous avons aussi calculé le facteur de structure de cette surface nodale. Les valeurs du facteur de structure sont données dans le tableau ci-dessus. Elles sont très proches de celle de la surface G, ce qui confirme que la surface nodale est une bonne approximation.

Contenu de la maille :

Une fois que l'on connaît le facteur de structure de la surface G, se pose la question de décrire au mieux le contenu de la maille en décorant cette surface. Il s'agit de donner une « épaisseur » L à cette surface, avec si possible un profil de densité électronique associé. Différentes méthodes ont été proposées (**Fig 16-4**). Les plus abouties permettent de remonter au profil complet de densité électronique.^{6,10,11}

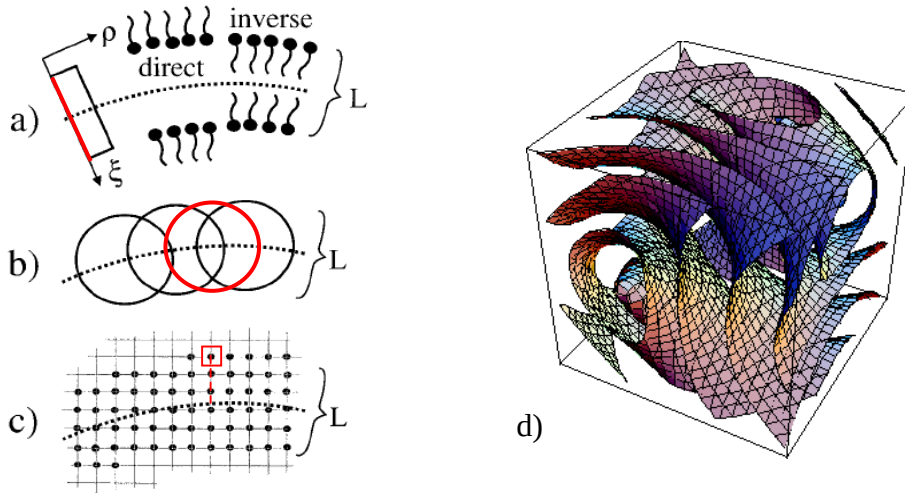


Figure 16-4. Les différentes méthodes pour décrire le profil de densité électronique⁷. (a) profil suivant la normale en chaque point de la surface G ; (b) profil reconstruit en convoluant chaque point par la surface d'une sphère⁴ ; (c) méthode point par point avec calcul de la distance à la surface ;¹¹ (d) surfaces iso-densité en utilisant les surfaces nodales.¹²

Nous avons pour notre part développé un modèle simplifié à deux niveaux de densité uniquement, et où l'épaisseur est introduite par convolution avec une sphère de densité constante en surface (**Fig 16-4b**).⁴ L'avantage de ce modèle est qu'il préserve une factorisation dans l'expression de l'intensité diffusée du facteur de structure (provenant de la surface G) et du facteur de forme (provenant de l'épaisseur L). Par contre, la densité électronique n'est pas rigoureusement constante dans l'épaisseur, et subit des variations liées à la courbure gaussienne en chaque point de la surface.

L'autre ingrédient de ce modèle est un terme de Debye-Waller, qui tient compte du fait que les interfaces fluctuent avec la température.

Finalement, l'intensité intégrée d'un pic de Bragg est modélisée par un produit de trois termes, avec seulement deux paramètres : l'épaisseur L et le coefficient α de l'exponentielle de Debye-Waller :

$$I_{\text{mon}}^{\text{int}}(k^*) \propto (F_{\text{coquille}}(k^*, L/2))^2 (F_{\text{hkl}}^G)^2 \exp(-\alpha(k^*)^2)$$

Ce modèle a été repris avec des améliorations par Garstecki et Holyst^{7,13-18} et les comparaisons avec des données expérimentales montrent que l'on peut tirer de ces modèles des grandeurs quantitatives pour L et α . Harper¹⁰ puis Enlow et MacGrowth¹¹ ont développés des méthodes encore plus raffinées, afin d'extraire le profil de densité électronique. Dans le cas des phases de tensioactifs, par rapport au modèle à deux niveaux où l'on décrit uniquement les chaînes et l'eau, ces modèles ont l'avantage de tenir compte de la densité électronique dans la région des têtes polaires. Ceci est important dans le cas des surfactants cationiques. Pour les phases de surfactants non-ioniques, ou les phases cubiques thermotropes, le modèle à deux niveaux est souvent suffisant.

Toutefois, pour que les raffinements mathématiques introduits soient véritablement pertinents dans l'analyse des intensités, il faut disposer de mesures d'intensité d'excellente qualité (précision des valeurs des intensités), et d'un nombre suffisant de raies distinctes.

Les modèles décrits jusqu'alors ont été développés essentiellement pour les phases cubiques de molécules de tensioactifs, de copolymères ou de molécules thermotropes. Et bien souvent, le nombre de raies observées est assez limité (moins de 10), ce qui fait que les modèles permettent tous de bien décrire les données, sans qu'il soit possible de trancher en faveur d'une modélisation particulière.

Cas des matériaux mésoporeux :

En parallèle, la même problématique s'est posée récemment pour des matériaux solides ayant la même structure cubique bicontinue (matériaux mésoporeux, voir chapitre 5).

Les modélisations précédentes s'appliquent toujours. On peut néanmoins remarquer que le terme en exponentielle Debye-Waller se justifie moins, dans la mesure où le matériau est solide, et que les interfaces ne fluctuent pas sous l'effet de la température. (la contribution du terme de Debye-Waller des atomes est négligeable aux petits angles de diffusion).

Solovyov¹² a ainsi pu mener une analyse poussée par diffusion des rayons X sur un nombre de raies suffisamment élevé (> 25), pour une réplique en silice de la surface G. La modélisation retenue utilise les surfaces iso-intensité de la surface nodale (**Fig 16-4d**), sans terme de Debye-Waller. On peut alors déduire précisément l'épaisseur de la réplique en silice à partir des intensités des pics de Bragg (**Fig 16-5**). Un affinement des fits indique que cette épaisseur est constante, avec une densité de la silice légèrement plus élevée (10%) au niveau des points plats de la surface.

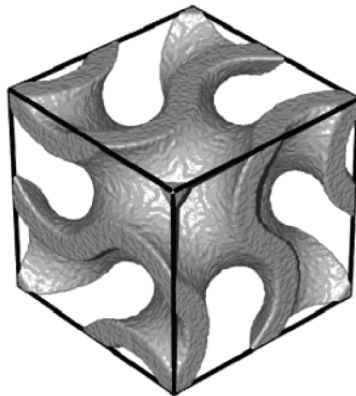


Figure 16-5. Réplique en silice de la surface G. Structure déduite des intensités diffusées en rayons X en utilisant les surfaces iso-densité de la surface nodale.¹²

Comme montré au chapitre 5, l'analyse de ces matériaux solides fait largement appel à la microscopie électronique. Aussi, les méthodes inverses sont plus facilement applicables que dans le cas des phases de tensioactifs ou de cristaux liquides.³ Le groupe de Terasaki¹⁹ a ainsi développé une méthode inverse de reconstruction à partir des amplitudes de diffusion mesurées en microscopie électronique. Le signe des amplitudes est déterminé expérimentalement (ce qui est un énorme avantage par rapport à la diffusion des rayons X).

Par contre, on a accès à la reconstruction du potentiel électrostatique, et pas directement à la densité (**Fig 16-6**).

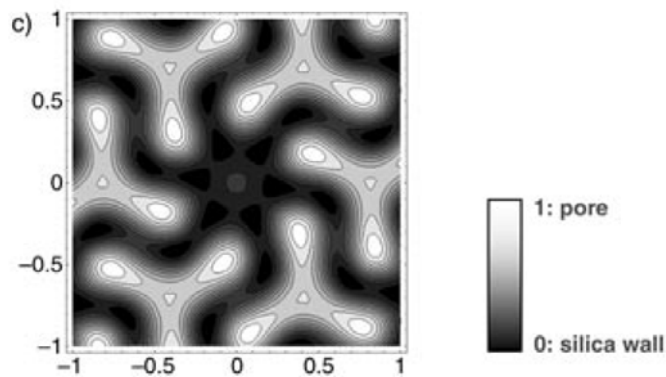


Figure 16-6. Reconstruction du potentiel électrostatique d'une réplique en silice de la surface G. Structure déduite des amplitudes diffusées en microscopie électronique par un monodomaine.¹⁹

En conclusion, ce chapitre montre que les méthodes inverses de reconstruction permettent d'établir la structure bicontinue de la phase $Ia\bar{3}d$.^{3,19} En ce qui concerne les méthodes directes, on a vu que plusieurs modélisations récentes basées sur la surface G ont été développées. Elles permettent toutes d'estimer l'épaisseur du milieu situé autour de la surface G. Il serait intéressant de les comparer entre elles, en utilisant les mêmes données expérimentales, mais actuellement, chaque méthode a été développée dans un contexte particulier (tensioactifs cationiques, mésoporeux ...). Néanmoins, les comparaisons déjà effectuées montrent que le point crucial reste la qualité des données expérimentales, pour vraiment pouvoir discriminer les modèles entre eux.

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X-ray scattering by bicontinuous cubic phases

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Abstract. — Ia3d bicontinuous cubic phases are interpreted as constituted of a fluid film of constant thickness supported by the gyroid minimal surface. We first compute the gyroid structure factor. Then we decorate the surface by the film. We compute the diffracted intensities and compare to X-ray intensities measured in some lipid systems.

1. Introduction.

Recently it has been shown that a large variety of cubic phases appearing in various biological or chemical systems can be described as triply-periodic bicontinuous phases. A panorama of all these systems is given in [1]. Such cubic phases appear for example in lyotropic compounds between the lamellar and the hexagonal phases [2-4]. They are different from the micellar cubic phases which exist in another part of the phase diagram and which are not bicontinuous. Following a similar scenario bicontinuous cubic phases with an analogous morphology appear in copolymer systems [1, p. 363] and phasmidic compounds [1, p. 229].

The common feature to all these phases is the importance of interfaces and the fact that mostly three space groups are observed : Ia3d, Pn3m and rarely the space group Im3m. It has been shown that these systems can be described in terms of a crystallography of films [1, p. 83, 5, 6] (or surfaces) and that good candidates for that were some infinite periodic minimal surfaces (I.P.M.S.) [7-9]. It also appeared that the structure of the two cubic blue phases of thermotropic liquid crystals could be described with use of the above I.P.M.S. [10]. The three cubic I.P.M.S. with the above space groups are the well-known gyroid G [11], F and P [12] I.P.M.S. They divide the space into two infinite, unconnected but mutually interwoven periodic labyrinths. Most of the experiments allowing the determination of the space groups are X-ray diffraction experiments or electron microscope image analysis. Then, to compare models linked to I.P.M.S. with experiments, we need to know the structure factor of these interfaces. The structure factors of the P and F surfaces are known [13] but not that of the G surface, which corresponds to the space group Ia3d commonly encountered in biologic

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systems [1, p. 35]. For lipid samples Luzzati and Spegt [14] proposed a structure with rods defining two infinite 3D-networks unconnected but mutually interwoven. These rods are somehow the cores of the minimal surface G. Both descriptions in terms of rods or I.P.M.S. appear to be complementary. The main conceptual difference between these two models is that interfaces built around I.P.M.S. are smooth curved surfaces, as is expected for fluid interfaces, contrary to cylindrical rods joining at vertices [15] which give curvature only on singularity lines. This point may be of importance if one considers the interfaces of the cubic phases as resulting from the release of a geometrical frustration in a curved space [5, 6].

The aim of this paper is to consider the G surface as the skeleton around which interfaces of Ia3d cubic structures organize themselves. Section 2 is devoted to the determination of the structure factor of the interface skeleton (G surface). In section 3 we give a simple model in order to compute the intensity scattered by a film of constant thickness supported by the minimal surface. We introduce a decoration of the surface with spheres and link the geometrical parameters of the model to those of the minimal surface. In section 4 we focus our attention to lyotropic systems. We examine the case of direct and inverse phases and compare the calculated diffracted intensities to those measured in X-ray experiments [15].

2. Structure factor of the gyroid surface.

Minimal surfaces can be generated by a set of equations giving their Cartesian coordinates $\mathbf{r} = (x, y, z)$ in terms of a complex variable ω as first given by Weierstrass

$$\mathbf{r}(\omega) = \mathbf{r}_0 + \text{Re} \left[\mu \int_{\omega_0}^{\omega} f(\omega) R(\omega) d\omega \right], \quad (1)$$

where $\mu = \gamma \exp[i\alpha]$, x, y, z are dimensionless coordinates ($\mathbf{r} = \mathbf{R}/a$, $\mathbf{R}$ defines the position of a point on the surface and a is the cubic cell parameter) and $f_x(\omega) = 1 - \omega^2$, $f_y(\omega) = i(1 + \omega^2)$, $f_z(\omega) = -2\omega$.

Each minimal surface is defined by the complex function $R(\omega) \exp(i\alpha)$. The function $R(\omega) = (1 + 14\omega^4 + \omega^8)^{-1/2}$ is the same [1, p. 237] [10] for the three surfaces P, G and F, which transform in one another by changing the value of α (Bonnet transformation) [16]. The P, G and F surfaces are obtained for $\alpha = 0$, $\alpha = 51.985^\circ$, $\alpha = 90^\circ$. It has been proved that these surfaces could be generated with a unique surface in $\mathbf{C}^3 \sim \mathbf{R}^6$ [17]. The three I.P.M.S. then correspond to a projection in $\mathbf{R}^3$, defined by the angle α .

For the G surface, the dimensionless number γ^{-1} equals 2.65624.

STRUCTURE FACTOR. — The dimensionless structure factor $F_{\mathbf{hkl}}^{\text{MS}}$ of the minimal surface reads

$$F_{\mathbf{hkl}}^{\text{MS}} = \int_{S_0} \exp^{2\pi i \mathbf{s} \cdot \mathbf{r}} d\sigma, \quad (2)$$

where $d\sigma$ is the surface element, $\mathbf{S}$ is the scattering vector, or in reduced units $d\sigma = d\Sigma/a^2$, $\mathbf{s} = \mathbf{S}/a$ with $s^2 = h^2 + k^2 + \ell^2$. Since the minimal surface is periodic the integral of equation (2) has to be performed on the surface S_0 of the minimal surface contained in the cubic unit cell. It may be expressed in terms of the two real coordinates $u = \text{Real}(\omega)$, $v = \text{Im}(\omega)$ in the Weierstrass plane. $\mathbf{r}$ is computed with use of equation (1) and the surface element $d\sigma = t^2(\omega) du dv$ is expressed with the Jacobian [10] $t(\omega) = \gamma |R(\omega)| (1 + \omega \bar{\omega})$.

Taking into account the symmetry operations of the space group we only perform the integration in the sector (Fig. 1) of the Weierstrass plane which generates the part of the surface

contained in the asymmetric unit. By definition the asymmetric unit allows us to rebuild the whole cubic cell by application of the 96 symmetry operations of the Ia3d group.

Let us point out that the symmetry operations defined in the crystallographic tables imply a well defined origin (point O in Fig. 1). We checked the program by performing a similar integration for the P surface for which results are known [13]. The precision of the calculus is estimated from the comparison between F_{000} and the theoretical value of the reduced surface $\sigma_c = A_c / \Omega_c^{2/3} = 3.091$ [12] where $\Omega_c = a^3$ and A_c is the surface contained in the cubic cell. Notice that $\sigma_c = 2^{1/3} \sigma_p$ where $\sigma_p = 2.453$ is the value for the primitive cell. We performed the integration with a mesh of the surface leading to a precision of 10^{-3} on the amplitudes. We give the results for the first 17 amplitudes in table I.

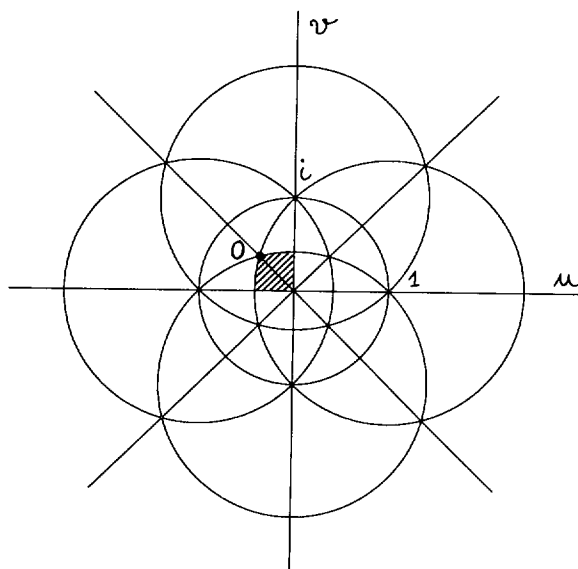


Fig. 1.

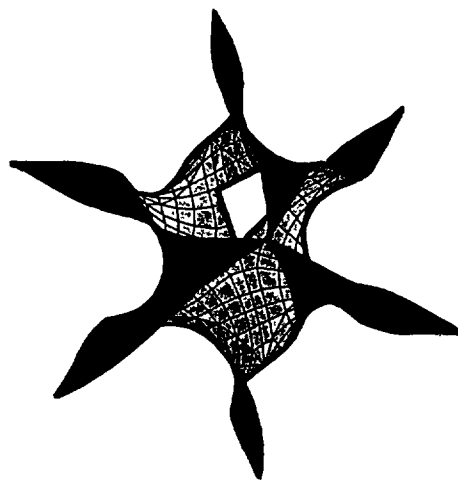


Fig. 2.

Fig. 1. — Weierstrass plane. The dashed region is the domain of integration corresponding to the asymmetric unit represented in figure 2.

Fig. 2. — Primitive cell with the asymmetric unit in white (with some hidden part). The origin of the cell corresponds to the (hidden) lower vertex of the asymmetric unit.

3 X-ray intensities diffracted by a film of constant thickness.

3.1 DECORATION OF THE MINIMAL SURFACE. — We decorate the skeleton of the minimal surface with a film of constant thickness and restrict the description to a model with two densities (ρ_1 and ρ_0 are the densities inside and outside of the film). An exact way to introduce the decoration of the minimal surface with a film of constant thickness 2ℓ and constant density takes into account the normal vector $\mathbf{N}$ at any point $\mathbf{R}_0$ of the minimal surface. The dimensionless diffracted amplitude F_{hkl} then is

$$F_{hkl} \approx \frac{1}{2\ell} \int_{-\ell}^{+\ell} \int_{S_0} e^{2\pi i S(\mathbf{R}_0 + \lambda \mathbf{N})} d\sigma d\lambda. \quad (3)$$

Table I. — *The computed G structure factor for the first 17 reflections. M is the multiplicity of the (hkl) reflection family. $M |F_{hkl}^{MS}|^2$ would correspond to a powder diagram intensity.*

G Surface

hkl	F_{hkl}^{MS}	M(hkl)	$M F_{hkl}^{MS} ^2$
211	+0.660	24	10.454
220	+0.451	12	2.441
321	-0.092	48	0.406
400	-0.360	6	0.778
420	-0.338	24	2.742
332	+0.467	24	5.234
422	+0.282	24	1.909
431	+0.209	48	2.097
521	-0.077	48	0.285
440	-0.060	12	0.043
611	-0.245	24	1.441
532	-0.104	48	0.519
620	-0.060	24	0.086
541	-0.162	48	1.26
631	-0.199	48	1.901
444	+0.395	8	1.248
543	+0.302	48	4.378

This description leads to tedious calculations since it does not lead, in the diffraction factor, to the factorization of the contributions coming from the skeleton (I.P.M.S.) and from the decoration (the film). In order to get a mathematical simplification (factorization) we perform the decoration in a simple manner which avoids a description including the normal vector at any point of the I.P.M.S. We introduce an isotropic decoration around each point $\mathbf{R}_0$ of the minimal surface with spheres of radius R_s and with a spherical distribution of the density $\rho_s(|\mathbf{R}|)$ at a point $\mathbf{R}$ of the sphere. This process describes a film of constant thickness $2R_s$. The density profile in the film depends (as we shall see later) on the overlap of the spheres and on the precise form of the density distribution $\rho_s(|\mathbf{R}|)$ for one sphere.

The density at a point $\mathbf{M}$ of the film is

$$\rho(\mathbf{OM}) = \int \int \rho_s(|\mathbf{R}|) \delta(\mathbf{OM} - (\mathbf{R}_0 + \mathbf{R})) d^3\mathbf{R} d^3\mathbf{R}_0 \quad (4)$$

where $\mathbf{R}$ is a point of the sphere. The dimensionless diffracted amplitude then is factorized as

$$F_{hkl} \approx \frac{1}{a^2} \int_{\text{Sphere}} \rho_s(|\mathbf{R}|) e^{2\pi i \mathbf{SR}} d^3\mathbf{R} \int_{S_0} e^{2\pi i \mathbf{SR}_0} d\Sigma$$

or with use of equation (2)

$$F_{hkl} \approx F_{hkl}^{\text{Sphere}} F_{hkl}^{\text{MS}}. \quad (5)$$

F_{hkl}^{Sphere} is the Fourier transform of a sphere with a density distribution $\rho_s(\mathbf{R})$. We have chosen a model with spheres with a constant surfacial density β_s . This simply leads to

$$F_{hkl}^{\text{Sphere}} = 4 \pi \beta_s R_s^2 \frac{\sin(2 \pi s r_s)}{(2 \pi s r_s)}, \quad r_s = \frac{R_s}{a} \quad (6)$$

which is the Fourier transform of a rectangular function of width $2 r_s$.

Let us now justify the choice of a constant surfacial density for the spheres. We show that, neglecting second-order terms in curvature, this distribution induces a constant density profile in the film of thickness $2 r_s$. At each point of the surface, we neglect the Gaussian curvature i.e. we approximate locally the surface to a plane portion. Then all the spheres give the same contribution to the density in a small layer of thickness dz at position z along the normal to the plane (Fig. 3). If n_s is the number of centers of spheres per unit area one obtains the density dm in the thickness dz as

$$dm = n_s \beta_s 2 \pi R_s \sin \theta R_s d\theta \quad \text{or} \quad dm = -2 \pi n_s \beta_s R_s dz.$$

This leads to a constant density profile in the film (in Fig. 4) [19]

$$\rho(z) = n_s \beta_s 2 \pi R_s = \rho_1 \quad \text{for} \quad |z| < R_s. \quad (7)$$

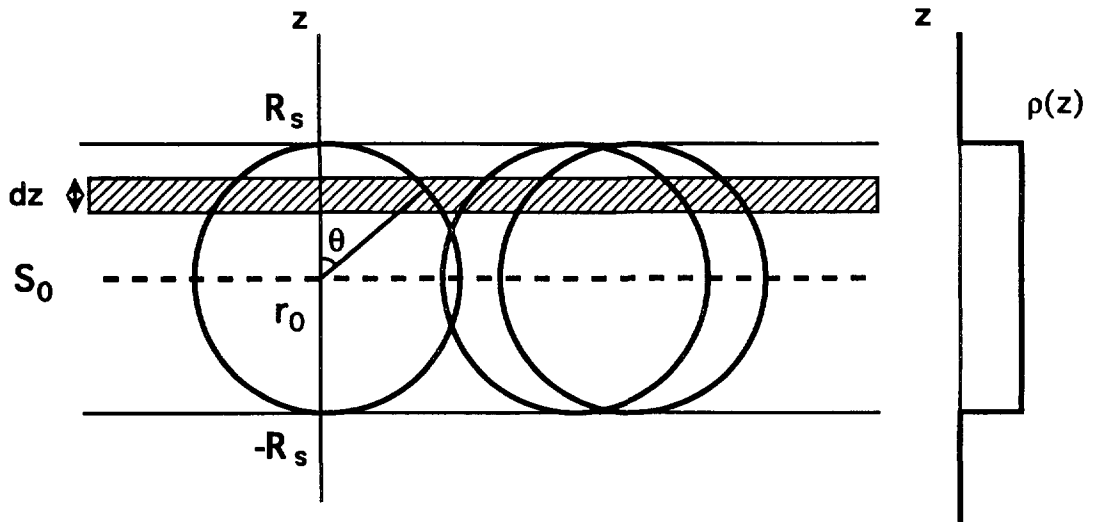


Fig. 3. — Density profile $\rho(z)$ induced by spheres with constant surfacial density β_s . All spheres give the same contribution in a small layer of thickness dz .

3.2 STRUCTURE FACTOR OF THE FILM. — We also introduce a Debye-Waller factor in order to take into account some thermic disorder characterized by the dimensionless displacement $u = \Delta U/a$ of the film. The total intensity for a powder diagram reads

$$I_{hkl}^{\text{tot}} = \lambda M(hkl) |F_{hkl}^{\text{MS}}|^2 |F_{hkl}^{\text{Sphere}}|^2 \exp^{-\alpha s^2}, \quad (8)$$

where $\alpha = \frac{2\pi^2}{3} \langle u^2 \rangle$, $M(hk\ell)$ is the multiplicity of the reflection $hk\ell$ and λ is a scaling factor.

3.3 GEOMETRICAL PARAMETERS OF THE FILM. — Let us now describe the geometrical parameters of a film of constant thickness 2ℓ supported by the minimal surface as seen in figure 4. We can express the volume V_p of the film and the surface $\Sigma_p = \Sigma_+ + \Sigma_-$ of the two interfaces in the primitive cell in terms of ℓ and of quantities linked to the minimal surface. Let us consider a surface element d^2A_0 at a point where the curvature radius is R_0 , we get easily for the minimal surface ($d^2\Sigma_- = d^2\Sigma_+$)

$$d^2\Sigma = d^2\Sigma_- + d^2\Sigma_+ = 2 d^2\Sigma_- = 2 \left(1 - \frac{\ell^2}{R_0^2} \right) d^2A_0 \quad (9)$$

$$d^3V = \int_0^\ell d^2\Sigma du = 2 \left(\ell - \frac{\ell^3}{3R_0^2} \right) d^2A_0 \quad (10)$$

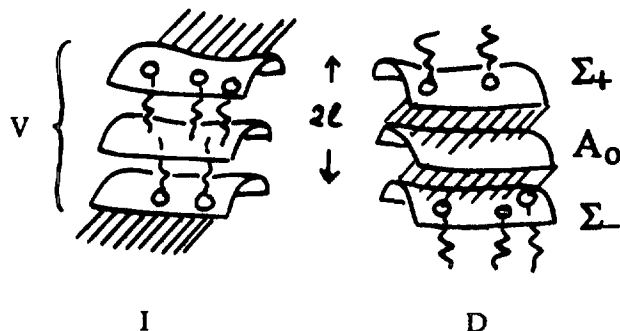


Fig. 4. — Film of direct (D) and inverse (I) phases. A_0 is the minimal surface. Σ_+ and Σ_- are surfaces parallel to A_0 at a distance ℓ . V is the volume enclosed by the film. The dashed regions correspond to the water.

V_p and Σ_p are obtained by integration of equations (9) and (10) over the primitive cell, with the use of the Gauss-Bonnet theorem :

$$\int_{\text{Primitive cell}} - \frac{d^2A_0}{R_0^2} = 4\pi(1-g) \quad (11)$$

where g is the genus of the minimal surface equal to 3 for the three surfaces P, G, F. This leads for reduced parameters for the cubic cell (twice the primitive cell) $s_c = \frac{\Sigma_c}{a^2} = \frac{2\Sigma_p}{a^2}$,

$$v_c = \frac{V_c}{a^3} = \frac{2V_p}{a^3}.$$

$$s_c = 2(\sigma_c - 16\pi p^2) \quad (12)$$

$$v_c = 2 \left(\sigma_c p - \frac{16\pi p^3}{3} \right). \quad (13)$$

Let us emphasize that the geometrical parameters of the film around the minimal surface only depend on one parameter, its reduced thickness $2p = 2\ell/a$. The model will be valid if the

radius of the sphere R_s is smaller than the curvature radius R_0 i.e. $p < r_0$. Minoration of $r_0 = \frac{\gamma}{2a} |R(\omega)| (1 + \omega \bar{\omega})^2$ in the Weierstrass plane gives $r_0 > 0.188$. Another estimate is obtained from the mean curvature radius calculated with the use of the Gauss-Bonnet theorem (Eq. (11))

$$\int_{\text{Primitive cell}} -\frac{d^2 A_0}{R_0^2} = 4 \pi (1 - g) = \left\langle \frac{1}{R_0^2} \right\rangle \int d^2 A_0 .$$

We obtain $\frac{\sqrt{\langle R_0^2 \rangle}}{a} = 0.25$. We shall then impose in the following fits $p < 0.25$.

4. X-ray intensities diffracted by Ia3d lipid cubic phases.

For lipids systems the film which decorates the minimal surface is a film of water (containing the polar heads) for direct phases and a film of paraffinic chains for inverse phases. The calculated intensities (Eq. (8)) depend on two parameters : the film thickness $2 r_s$ and the strength of the thermal disorder α . We shall now focus our discussion on the parameter p which can be deduced either from macroscopic measurements or from an estimate of the molecular parameters. For macroscopic criteria we use the relation

$$\Omega_c = V_w + V_{\text{part}} ,$$

where V_w and V_{part} are the volume respectively occupied by the water and by the paraffinic chains. The macroscopic measurement commonly given in the literature [15, 20] is the volume fraction $C_{v \text{ pol}} = V_w / \Omega_c$ occupied by the water. The molecular parameters are the volume v_0 occupied by one paraffinic chain and the surface s_0 occupied by one polar head.

4.1 DIRECT PHASE. — $V_c = V_w$ and equation (13) is simply

$$C_{v \text{ pol}} = v_c = 2 \left(\sigma_c p - \frac{16 \pi p^3}{3} \right) . \quad (14)$$

To relate p to the molecular parameters we use $V_{\text{part}} = N v_0$ where $N = \Sigma_c / s_0$ is the number of paraffinic molecules contained in the cubic cell. Simple algebra leads to the dimensionless equation for p

$$-\frac{16 \pi}{3} p^3 - 16 \pi m p^2 + \sigma_c p + m \sigma_c - \frac{1}{2} = 0 , \quad \text{with } m = v_0 / s_0 a . \quad (15)$$

4.2 INVERSE PHASE. — $V_{\text{part}} = V_c$ which leads, with use of equation (13) to

$$1 - C_{v \text{ pol}} = 2 \left(\sigma_c p - \frac{16 \pi p^3}{3} \right) . \quad (16)$$

Estimation of p in terms of the molecular parameter is straightforward as $\frac{v_c}{s_c} = m$. Combining equations (12) and (13) we obtain

$$\frac{16 \pi}{3} p^3 - 16 \pi m p^2 - \sigma_c p + m \sigma_c = 0 . \quad (17)$$

4.3 COMPARISON WITH EXPERIMENTS. — We now want to compare the above I.P.M.S. model with the experimental data of Ia3d structures, namely the two direct and three inverse lipid phases of references [14, 15]. Observations and results are summarized in tables II, III and IV. Let us first note that the I.P.M.S. model gives a prediction for the amplitude signs. This has to be compared with the signs deduced in very nice recent experiments [20] by confrontation of the electron density profile computed from X-ray diffraction analysis with freeze-feature electron micrographs. The F_{hkl}^{MS} signs and those selected in [20] are in complete agreement for the first 10 reflections. This is not the case for the complementary model with rods [14]. At first sight it seems to be in favour of the I.P.M.S. model. But one has to be aware of the decoration influence. A modification of r_s changes the signs *via* the oscillations of $\sin(2\pi r_s s)/(2\pi r_s s)$ (Eq. (6)). In our cases this occurs for $sr_s = 0.5$ this and affects the signs after the 10th peak, as can be seen in details in tables II, III and IV.

As we claimed earlier, the theoretical intensities depend on two parameter r_s , α and on an arbitrary scaling factor λ . Let us emphasize that $2r_s$ in the model with the above decoration is the film thickness. We have determined these factors in order to fit at best the data, using a least mean square fit criterion. In each case we have computed the factor

$$\Delta = \left[\sum_i \frac{(I_{i\text{ cal}} - I_{i\text{ obs}})^2}{N} \right]^{1/2}$$

where $I_{i\text{ cal}}$ and $I_{i\text{ obs}}$ are the theoretical and observed intensities of the i -th reflection. N is the total number of reflections.

For each compound we have verified (Tab. V) the agreement between the r_s value determined by the fit on intensities and the p value derived from macroscopic [15, 20] or microscopic data [21] using equations (14) to (17). The calculated intensities for the decorated I.P.M.S. fit quite well the data and the Δ values do not greatly exceed the uncertainty on the measured intensities. Δ values obtained for the rod model are much larger than that deduced from the I.P.M.S. model. However the rod model does not take the (211) reflection properly into account. On the contrary the I.P.M.S. model takes all the reflections into account and focus on the most intense ones. Nevertheless in order to perform the comparison between the two models we have also performed a fit excluding the (211) reflection and leading to different sets of intensities I_{ms}^* and Δ^* values. In order to lighten the presentation we only give in detail the resulting intensities for the Gal compound. The Δ^* values for the two models then become more comparable but nevertheless still with better values for the I.P.M.S. model. Let us note that results for the I.P.M.S. model are all the more satisfying since it only includes two parameters, contrary to three in the rod model. The radius of the cylinders r around the rod plays a role similar to that of the radius of the sphere r_s in the I.P.M.S. model. α is the same parameter in the two models. The extra parameter ε in the rod model is the gap of the cylinder length introduced at each end of the rods [15].

5. Conclusion.

In this paper we give an interpretation of the X-ray diffraction patterns observed in cubic phases with symmetry group Ia3d within the frame work of models linked to minimal surfaces. The governing idea is the organization of films around the gyroid minimal surface taking into account the curvature of the interfaces. In this spirit we have computed the structure factor of the G minimal surface. The result for the series of amplitude signs is note worthy. Indeed this series corresponds to a relevant density map selected in [20]. The simple sphere model is promising since the associated intensities fit the experimental data quite well. It would be of

Table II. — Inverse phases. I_{obs} : observed intensities reported from [15]. I_{rod} : fit by the rod model from [15]. I_{ms} : fit by the I.P.M.S. model. $\Delta = \left[\sum_i \frac{(I_{\text{cal}} - I_{\text{obs}})^2}{N} \right]^{1/2}$ where N is the total number of reflections. Δ^* corresponds to a fit for the I.P.M.S. model excluding the (211) reflection. r : (dimensionless quantity) is the sphere radius r_s in the I.P.M.S. model and a cylinder radius in the rod model. α : Coefficient in the exponential Debye-Waller term. D column : Amplitude sign derived from [20]. MS column : Amplitude sign for the I.P.M.S. model. $\Sigma_i I$ is the sum of the intensities.

SrC ₁₄					
hkl	I_{obs}	I_{rod}	I_{ms}	D	MS
211	12350	10000	12355	-	+
220	1020	975	922	-	+
321	48	43	17	+	+
400	145	333	88	+	+
420	794	1950	595	+	+
332	1205	2040	1216	-	-
422	333	470	432	-	-
431	208	110	431	-	-
521	<10	5	41	0	+
440	<10	5	5	0	+
611	{ 259	{ 376	50	-	+
532			18	-	+
620	<10	1	2	0	+
541	132	152	12	-	+
631	118	173	1	-	+
444	60	91	0	+	+
543	187	155	5	+	+
r		0	0.145		
Δ		672	110		
Δ^*		363	75		
$\Sigma_i I$	16859	16879	16190		
α		0.044	0.037		

Table III. — *Inverse phases. Notation is the same as in table II.*

Lecithin						Galactolipids						
hkl	I _{obs}	I _{rod}	I _{m s}	D	MS	hkl	I _{obs}	I _{rod}	I _{m s}	I _{ms} *	D	MS
211	12000	10000	12022	-	-	211	1800	10000	1830	3060	-	-
220	2080	520	1933	+	-	220	520	520	342	519	-	-
321	104	115	87	+	+	321	35	21	27	30	+	+
400	52	67	98	+	+	400	31	17	39	38	+	+
420	<20	26	89	0	+	420	40	24	72	52	+	+
332	<20	3	64	0	-	332	56	70	95	57	-	-
422	<20	2	5	0	-	422	7	22	23	11	-	-
431	<20	3	0	0	-	431	<7	9	15	5	0	-
521	<20	3	2	0	-	521	<7	2	0	0	0	+
440	<20	10	0	0	-	440	<10	9	0	0	0	+
611	{ 133	143	37	-	-	611	{ 24	127	1	3	+	-
532		1	13	-	-	532			0	1	-	-
620	<25	38	3	0	-	620	<12	0	0	0	0	-
541	48	21	40	+	-	541	20	34	3	4	+	-
631	78	49	64	-	-	631	20	28	10	9	-	-
444		42	42	-	+	444		21	8	6	+	+
543	81		142	+	+	543	30	22	35	22	+	+
r		0.129	0.098			r		0.14	0.085	0.09		
Δ		614	53			Δ		1987	46			
Δ*		390	26			Δ*		22		8		
Σ _i I	14576	11043	14641			Σ _i I	2604	10926	2500	3817		
α		0.036	0.03			α		0.038	0	0.032		

interest to describe more precisely a film of constant density around the minimal surface. This would lead to a more sophisticated model taking into account the local properties (normal and curvature) of the surface (Eq. 3) [22]. Details of the density profile (polar heads contribution...) could also be introduced. These refinements would be of interest only in comparison with precise intensity measurements on Ia3d structures for different compounds.

Table IV. — Direct phases. Notation is the same as in table II.

KC12						C16TAB					
hkl	I _{obs}	I _{rod}	I _{m s}	D	MS	hkl	I _{obs}	I _{rod}	I _{m s}	D	MS
211	7320	10000	7317	+	+	211	6000	10000	6035	+	+
220	980	980	1002	+	+	220	1280	1280	1051	+	+
321	12	6	30	-	-	321	14	13	65	-	-
400	16	7	31	-	-	400	10	6	85	-	-
420	31	27	28	-	-	420	30	31	124	-	-
332	85	117	24	+	+	332	59	120	138	+	+
422	25	70	4	+	+	422	11	51	26	+	+
431	14	30	1	+	+						
r		0.16 0.18	0.09			r		0.17 0.2	0.09		
Δ		948	25			Δ		1513	105		
Δ*		22	20			Δ*		30	19		
Σ _i I	8483	11237	8437			Σ _i I	7404	11501	7524		
α		0.047	0.14			α		0.104	0.019		

Table V. — Estimate of the parameter p . — p_1 is derived from equation (14) (respectively Eq. (16)). $C_{v\text{ pol}}$ values are taken from [15] and [20]. — p_2 is derived from equation (15) (respectively Eq. (17)). To calculate the parameter m , we take $v_0 = 27.4 + n 26.9 \text{ \AA}^3$, the volume occupied by one paraffinic chain of n carbon atoms, and we estimate the surface s_0 occupied by one polar head from [14] [15] and [21]. — r_s is the value used in the I.P.M.S. fit.

	Lec	Gal	C16TAB	KC12
p_1	0.12	0.10	0.05	0.07
p_2	0.13	0.10	0.05-0.1	0.04-0.1
r_s	0.098	0.085	0.09	0.09

Acknowledgments.

We thank C. Oguey and J. F. Sadoc for many fruitful discussions. We are also indebted to A. M. Levelut and B. Pansu for comments.

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Chapitre 17

Phase hexagonale 2D de matériaux mésoporeux

Concernant les matériaux mésoporeux (chapitre 5), nous nous sommes intéressés à la structure de la phase hexagonale 2D dites SBA-15, obtenue en utilisant le copolymère Pluronic P123 (chapitre 2) comme agent structurant de la silice. L'idée essentielle est de modéliser les intensités relatives des pics de Bragg de la phase hexagonale 2D afin de déterminer la taille des micelles cylindriques dans le matériau hybride, puis la taille des pores dans le matériau calciné. La méthode de modélisation est détaillée au chapitre 8. Aussi, ce chapitre est consacré uniquement à l'interprétation des résultats expérimentaux.

Auto-assemblage : suivi in-situ par SAXS

Publication [31]

Lors d'une synthèse de poudre par précipitation (voir le chapitre 5), il est possible de suivre en temps réel l'auto-assemblage du matériau hybride en utilisant la diffusion des rayons X aux petits angles (SAXS)^{1,2} ou des neutrons (SANS)³. Dans la solution de départ, le Pluronic P123 forme des micelles sphériques. L'analyse de l'évolution de ces micelles avant la précipitation du matériau hybride est en cours (chapitre 21), avec probablement une transition vers des micelles mixtes P123/espèces de silice de forme cylindrique (**Fig 17-1**).

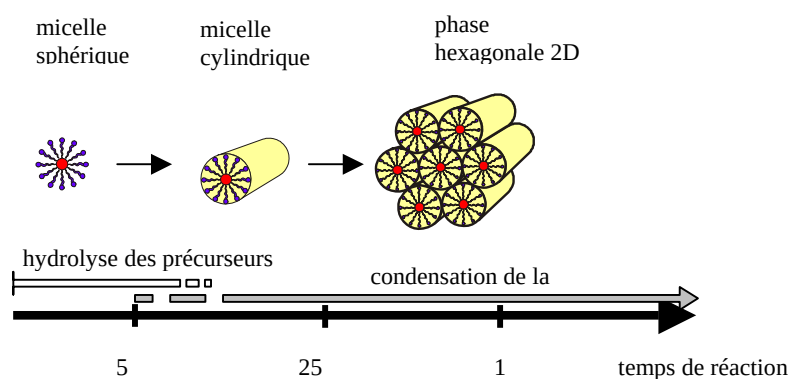


Figure 17-1. Etapes de la formation du matériau hybride SBA-15 déduites des expériences de SAXS/SANS.

Dès que le matériau hybride se forme, des pics de Bragg caractéristiques d'une phase hexagonale 2D apparaissent. Les intensités relatives des pics varient notablement au cours du temps durant la première heure de la synthèse (**Fig 17-2**).

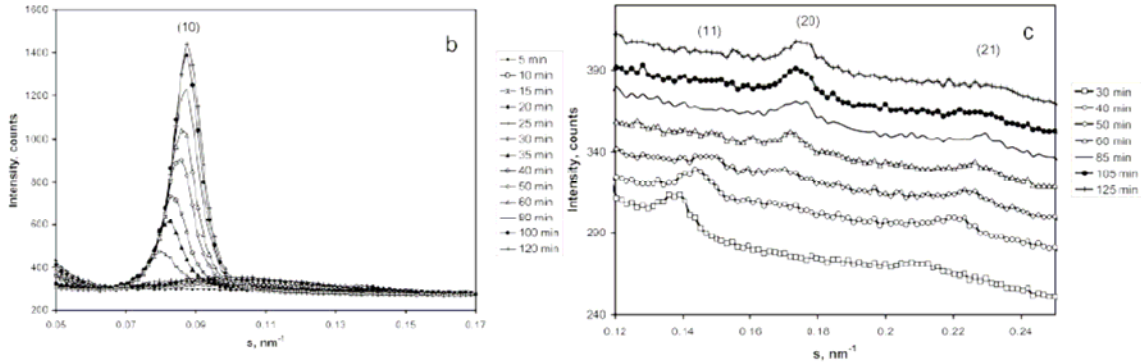


Figure 17-2. Evolution des pics (10), (11), (20) et (21) de la phase hexagonale 2D pendant la première heure suivant la précipitation (matériau SBA-15)².

On voit notamment que l'intensité du pic (11) diminue alors que celle du pic (20) augmente. Le nombre des pics de Bragg est relativement restreint (4), car les temps d'acquisition sont limités à moins de 5 minutes (rayonnement synchrotron, LURE). Néanmoins, une modélisation des intensités en utilisant un modèle cœur/couronne (voir le chapitre 8) met en évidence une évolution intéressante de la phase hexagonale (**Fig 17-3**).

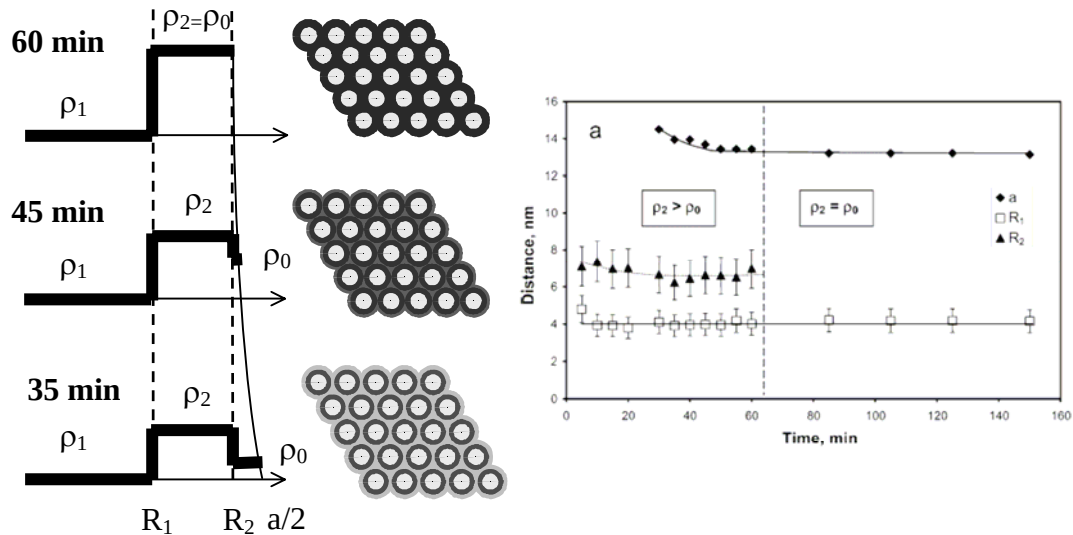


Figure 17-3. Modélisation par un modèle cœur/couronne.²Les couronnes des micelles cylindriques sont d'abord les régions les plus riches en silice, puis progressivement, des parois continues de silice se forment entre les micelles, c'est l'ébauche du matériau SBA-15 solide final.

On est sensible dans cette expérience essentiellement aux espèces de silice qui ont la densité électronique prépondérante. Juste après la formation du précipité, la densité électronique reste plus élevée dans la couronne qu'entre les micelles, ce qui signifie que les espèces de silice sont localisées principalement dans la couronne. Puis progressivement, la différence de densité électronique entre la couronne des micelles et le solvant s'estompe : des parois continues riches en silice entre les cœurs des micelles sont formées. L'obtention de telles informations en temps réel illustre bien l'intérêt des expériences de SAXS/SANS in-situ par rapport à des observations par microscopie électronique, réalisables uniquement en figeant la solution au cours du temps ce qui conduit souvent à des artefacts.

La modélisation des intensités des pics de Bragg se fait soit en utilisant une méthode directe comme nous l'avons fait (modèle cœur/couronne), soit par une méthode inverse de reconstruction de la densité électronique. C'est ce qui a été réalisé par une autre équipe.⁴ A partir de mesures similaires par SAXS, la méthode inverse conduit à une interprétation similaire de l'assemblage des micelles (**Fig 17-4**).

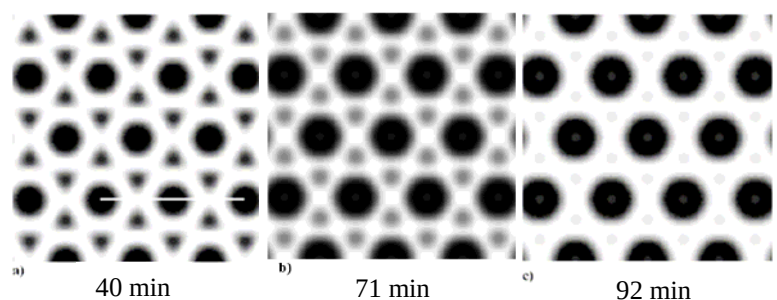


Figure 17-4. *Modélisation par la méthode inverse de reconstruction de la densité électronique.¹ Les régions en blancs sont les régions de fortes densité électronique (espèces de silice).*

Matériaux non-calcinés et calcinés : taille des pores

Publication [14]

Après précipitation du matériau hybride, la polymérisation de la silice est un phénomène relativement lent et, lors d'une synthèse, on attend généralement au moins une journée avant

de filtrer le matériau hybride, souvent en chauffant (traitement hydrothermal). Le matériau est ensuite calciné à haute température (de l'ordre de 400°C) afin d'éliminer la matière organique et de ne garder que la matrice de silice.

On a réalisé des modélisations des intensités des pics de Bragg de différents matériaux (non-calcinés ou calcinés), toujours dans le cadre de la synthèse SBA-15.⁵ Différents modèles ont été comparés : modèle à un niveau (pores parfaitement cylindriques pour un matériau calciné), modèle à deux niveaux (modèle cœur/couronne), modèle avec densité variant linéairement dans la couronne. Ces modèles sont introduits dans le chapitre 8. Ces modélisations montrent que le modèle à un niveau ne rend pas bien compte des intensités expérimentales et qu'un modèle cœur/couronne donne de bien meilleurs résultats.

En utilisant ce modèle, on met en évidence une couronne dans laquelle la densité des espèces de silice est plus faible que dans les parois proprement dites (**Fig 17-5**).

De plus, cette méthode donne une mesure du diamètre des pores. Elle présente l'avantage, par rapport aux méthodes d'adsorption/désorption d'azote couramment utilisées pour déterminer les tailles de pores, d'être une méthode d'analyse directe. Des analyses plus poussées pour comparer quantitativement les deux méthodes sont développées par un autre groupe.^{6,7}

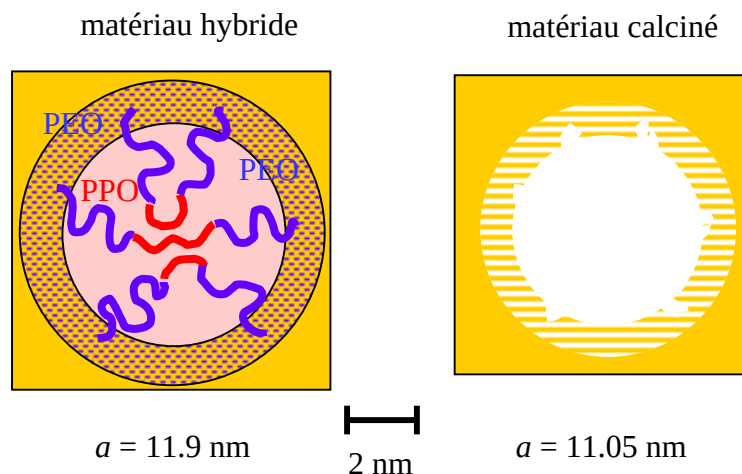


Figure 17-5. Modélisation du matériau SBA-15 non-calciné (hybride) et calciné par un modèle cœur/couronne.⁵ On détermine les rayons et les différents niveaux de densité électronique. Les espèces de silice sont représentées en jaune.

Actuellement, on cherche à généraliser cette approche dans le cas où la porosité du matériau calciné est remplie par une autre espèce (chapitre 21). Cela peut être par un fluide qui remplit entièrement la porosité,⁸ des espèces adsorbées en surface, ou encore des nano-particules d'oxydes métalliques synthétisées directement dans la porosité.^{9,10}

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Existence of a Microporous Corona around the Mesopores of Silica-Based SBA-15 Materials Templated by Triblock Copolymers

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Abstract: Materials showing long-range two-dimensional hexagonal order (called SBA-15 in the literature) were produced by templating a silica precursor (TEOS) with two Pluronic copolymers, $\text{EO}_x\text{PO}_y\text{EO}_x$, of nearly the same x/y (0.3) ratio but different y values ($x = 18$, $y = 60$ and $x = 20$, $y = 70$, respectively). These materials were hydrothermally treated to increase the condensation of silicate species around the Pluronic aggregates and calcined to liberate the hexagonal array of mesopores. All materials, i.e., before and after hydrothermal treatment and calcination, were investigated by X-ray diffraction (XRD), and all calcined samples were further characterized by transmission electron microscopy and N_2 sorption experiments. The large number and narrow width of the XRD powder diffraction lines demonstrate the good crystallographic quality of the materials. This allows us to quantitatively exploit the XRD reflection intensities and to show that simple structural models of the silica lattice cannot account for them. This means that SBA-15 materials cannot be regarded as an ideal hexagonal lattice of pores imbedded in a uniform silica matrix. The structure of the silica walls is more complex and shows a “corona” region of lower density around the cylindrical organic aggregates. This corona becomes microporous upon calcination, and we suggest that it arises from the partial occlusion of the PEO chains in the silica matrix. Modeling the XRD intensities allows us, for all the solids of this series, to derive estimates of pore diameters, corona, and wall thicknesses and to examine the influence on these structural parameters of the hydrothermal treatment.

Introduction

The field of ordered mesoporous materials obtained by solution templating with cationic surfactant molecules has sparked worldwide interest, owing to potential applications for shape-selective heterogeneous catalysis and separation techniques.^{1–4} In addition to cationic amphiphiles, neutral block copolymers can also be used as templating agents to produce materials such as the MSU series, which have well-defined pores that are not well-ordered,^{5,6} or as SBA-15 compounds, which possess a well-ordered hexagonal array of mesopores.^{7–11} This

latter development actually represents an important step because catalytic applications of mesoporous solids were somewhat restricted thus far by their low thermal stability in the presence of water due to the thin wall thicknesses (1–1.5 nm, without additional treatment).^{12,13} In contrast, the wall thickness of mesoporous solids obtained by block copolymer templating is larger (3–6 nm) and their pore diameter can be more widely varied (3–30 nm for SBA-15 materials compared to 2–10 nm for MCM41 materials).^{1,7,8} In this context, it is clear that both pore diameter and wall thickness are key features that need to be tuned in view of the particular application. These features are usually assessed by transmission electron microscopy (TEM) and nitrogen adsorption/desorption isotherms.^{1–4,7–11} In practice, both techniques have specific drawbacks. It was recently shown that TEM images depend on the amount of defocus so that the wall thickness estimated in this way can vary by a factor of 2.¹⁴ The results of N_2 sorption isotherms strongly depend on the model that is used to analyze them. The calculation methods based on the Kelvin equation, in particular the method developed by Barrett, Joyner, and Halenda (BJH method),¹⁵ systematically underestimate pore diameters by at least 10%.^{9,16–19} In this work,

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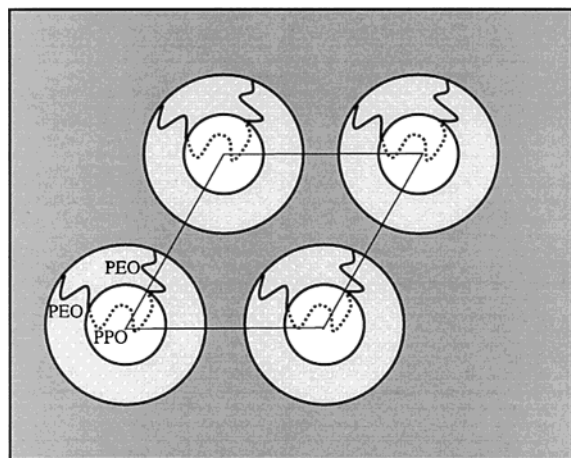


Figure 1. Schematic picture of the organization of uncalcined SBA-15 materials.

we show how X-ray diffraction powder patterns can be quantitatively modeled to obtain lattice parameters, pore diameters, and wall thicknesses. We thus give very detailed new information about the silica organization in the walls of SBA-15 materials.

The mesoporous solids considered here, labeled SBA-15, are synthesized with triblock copolymers and have two-dimensional hexagonal symmetry.^{7,8} We used two neutral triblock copolymers (Pluronic (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) EO₂₀PO₇₀EO₂₀ and EO₁₈PO₆₀EO₁₈, BASF[®], labeled P123 and P103, respectively) and tetraethyl orthosilicate (TEOS) as the silicate source. At room temperature, the poly(ethylene oxide) (PEO) chains are hydrophilic whereas the poly(propylene oxide) (PPO) chains tend to be hydrophobic, thus driving the formation of direct cylindrical micelles with the PEO chains on the outside. Consequently, a specific and interesting feature of the SBA-15 materials is that, as suggested by NMR,²⁰ the PEO chains of the Pluronics may be deeply occluded within the silica walls and therefore the density of the walls may not be uniform (Figure 1). Then, the solids obtained upon calcination should display not only the mesoporosity (pore diameter > 2 nm) due to the hexagonal arrangement of cylindrical aggregates but also the microporosity (pore diameter < 2 nm) liberated by the PEO moieties. This would result in a complex structure in which a microporous silica “corona” surrounds the mesopores. Furthermore, hydrothermal treatments of as-synthesized SBA-15 materials in the reaction solution at different temperatures (80–140 °C) and for different times (11–72 h) are known to increase pore sizes and to decrease wall thicknesses.^{7,8,11} Very little information about the evolution of the silica walls introduced by this postsynthesis treatment is currently available.

To our knowledge, previous attempts to model the structure of organized mesoporous solids have only dealt with the MCM-41 materials obtained by templating with cationic surfactants.^{14,21–26} The most comprehensive one is the neutron scattering study of White et al., which shows that the mesopores of these materials are not as well-defined as commonly assumed.²³ In contrast, there exists no detailed structural study of SBA-15 materials. We obtained here the dimensions and electron density contrasts of the different parts of the unit cell

Table 1. Main Characteristics of Pluronics and Synthesis Conditions

	Pluronic		synthesis	
	mol wt	formula	Pluronic (wt, g)	temp (°C)
P123	5838	EO ₂₀ PO ₇₀ EO ₂₀	4.0	30
P103	4994	EO ₁₇ PO ₆₀ EO ₁₇	4.4	35

Table 2. Main Characteristics of SBA-15 Materials^a

solid	<i>a</i> (nm)	Si/EO/Cl	<i>D</i> _{BH} (nm)	<i>V</i> _{mp} (cm ³ /g)	<i>V</i> _{MP} (cm ³ /g)
P123AU	11.85	1/0.5/0.3			
P123AC	9.6		4.0	0.10	0.60
P123BU	11.9	1/0.4/0.4			
P123BC	11.05		6.0	*	1.06
P103AU	11.0	1/0.5/0.6			
P103AC	8.8		3.8	0.12	0.52
P103BU	10.85	1/0.4/0.2			
P103BC	10.45		5.0	*	1.18

^aKey: *a*, unit cell parameter determined by XRD; Si/EO/Cl molar ratios, ±0.1 error bars; *D*_{BH}, pore diameter as obtained on the desorption branch of the isotherm by the BJH formula; *V*_{mp} and *V*_{MP}, microporous and mesoporous volumes, respectively; * undetected on β-plot.

of these materials by modeling the intensities of their X-ray diffraction powder lines. This information proves that these solids should not be regarded either as an ideal hexagonal lattice of mesopores imbedded in a silica matrix. In particular, we demonstrate here the existence of the microporous corona and we monitor how it is affected by hydrothermal treatments.

Experimental Section

Synthesis. The triblock copolymers were kindly donated by BASF and were used as received. In a typical synthesis, an aqueous solution of Pluronic, acidified to pH 1 by adding HCl, was mixed with TEOS under constant stirring.^{7,8} For given amounts of water (6.46 mol), TEOS (0.0409 mol), and HCl (0.24 mol), the amount of Pluronic (4–4.5 g) and the temperature of reaction (30–40 °C) required to obtain a well-ordered SBA-15 material vary, as described in ref 27 (Table 1). The mixture, initially homogeneous, became heterogeneous after less than 15 min of reaction. The heterogeneous mixture was maintained for 24 h at the reaction temperature and then divided into two parts. White solids (labeled A type hereafter) were recovered by filtration of the first part (no washing). The second part was submitted to hydrothermal treatment at 100 °C for 3 days before recovering by filtration other solids, labeled B type in the following. A- and B-type solids were both calcined in air at 400 °C (6 h) in order to remove the Pluronics. Hereafter, calcined solids are respectively labeled AC and BC whereas uncalcined ones are respectively labeled AU and BU. For instance, the material labeled P123BC was templated with the P123 Pluronic, submitted to hydrothermal treatment, and calcined. Uncalcined materials were submitted to chemical analysis at the CNRS Centre d'Analyse-Solaize to obtain the Si/EO/Cl ratios summarized in Table 2. To check for its stability upon air exposure, a given P123BC solid was characterized twice, before and after 6 months of storage in air. To check for its reproducibility, the synthesis at 30 °C of the P123BC solid was performed twice. To check for the effect of the temperature of the synthesis, another P123BC solid was prepared at 35 °C.

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Transmission Electron Microscopy. AC- and BC-type solids, as obtained after calcination, were examined by transmission electron microscopy (JEOL JEM-100 CX II microscope operating at 100 kV). The samples were prepared by dispersing the powders as a slurry of acetone which was then deposited and dried on copper grids covered with a holey carbon thin film.

Nitrogen Adsorption/Desorption Isotherms. Nitrogen sorption isotherms at $-196\text{ }^{\circ}\text{C}$ were measured on an ASAP 2010 apparatus (Micromeritics, Norcross, GA). Prior to the experiment, the samples were dehydrated at $50\text{ }^{\circ}\text{C}$ overnight and then at $\sim 120\text{ }^{\circ}\text{C}$ for at least 5 h under a vacuum better than 10^{-4} Torr.

A single-point total pore volume was measured at $P/P^0 = 0.974$. The average diameter of primary mesopores, labeled D_{BJH} , was obtained from the maximum of a pore size distribution calculated using the BJH formula applied to the desorption part of the isotherm for relative (P/P^0) pressures larger than 0.31.¹⁵ The pore size distribution curve exhibits sharp maximums for all samples (fwhm lower than 0.5 nm). Even if such an analysis underestimates pore size, relative variations among samples should be correct.^{9,16–19} To assess the possible existence of micropores (diameter $< 2\text{ nm}$) in our samples, we have used the β -plot method. As detailed in ref 17, in this method, the volume of nitrogen adsorbed at a given relative pressure P/P^0 is plotted as a function of a β parameter defined as $\beta = \ln(0.4/(P/P^0))^{1/2.7}$.

For clarity, we do not show the curved low-pressure part of the β plot, which is mainly due to adsorption within micropores ($\beta < 0.7$). Then, three different regions can be seen on these plots: (i) a linear region due to multilayer adsorption in mesopores; (ii) a steep region due to capillary condensation within these mesopores; (iii) a last linear region due to multilayer formation onto the external surface of the grains. Microporous, V_{mp} , and mesoporous, V_{Mp} , volumes can be obtained by determining the intercept between the adsorbed amount (y-axis) and the linear segments i and iii. These two extrapolations give V_{mp} and $(V_{\text{mp}} + V_{\text{Mp}})$, respectively. These volumes, expressed in amounts of nitrogen gas adsorbed at standard temperature and pressure, were multiplied by the coefficient 0.001 547 to be converted into liquid nitrogen volumes, as adsorbed at $-196\text{ }^{\circ}\text{C}$.

X-ray Diffraction. Compared to MCM-41 materials, the rather large values of the hexagonal lattice parameters ($\sim 10\text{ nm}$) of the materials investigated here make it necessary to record X-ray diffraction lines at rather low scattering angles, as described below. Such X-ray scattering experiments were performed first with an already described laboratory setup²⁸ and second at the D43 experimental station of the LURE synchrotron facility (Orsay, France).²⁹ In the following, we only show results obtained at LURE although similar results were obtained with the laboratory rotating anode setup, with a lower resolution. The D43 experimental station uses a single bent Ge monochromator (111 reflection) to select the wavelength ($\lambda = 0.145\text{ nm}$) and to focus the beam. The beam size was defined by a collimator of 0.5 mm diameter. Vacuum flight tubes were inserted between the sample and the detection in order to get rid of the parasitic air scattering. Powder samples were held in Lindemann glass capillaries usually of 1 mm diameter. Scattering patterns were recorded on phosphor image plates scanned with a pixel size of $0.1 \times 0.1\text{ mm}^2$. The sample–detection distance was precisely determined by calibration with silver behenate ($d_{001} = 5.838\text{ nm}$). The diffraction patterns consisted in several concentric circles so that the scattered intensity was azimuthally integrated and plotted as a function of the scattering angle 2θ . These curves are called “powder scans” in the following.

The scattering of the calcined samples, due to the large contrast between silica and the empty pores, is naturally much stronger than that of the uncalcined ones. Exposure times typically ranged from a few minutes for calcined samples up to 2 h for uncalcined ones.

Additional high-resolution experiments were performed at the H10 experimental station of LURE. This apparatus, already described in detail,³⁰ involves a diffractometer which allows one to perform scans of the powder diffraction lines with a resolution of $\Delta q \approx 0.014\text{ nm}^{-1}$, where q is the scattering vector modulus $q = (4\pi \sin \theta)/\lambda$. Thus, any line broadening due to grain size smaller than $\sim 900\text{ nm}$ can be detected.

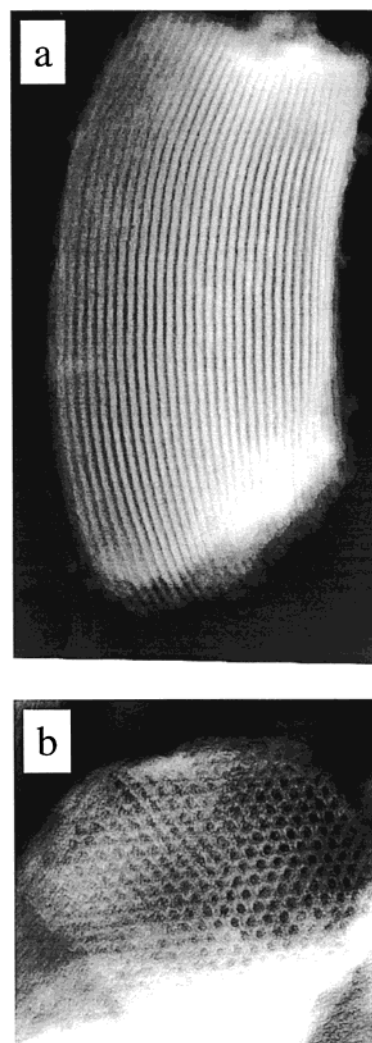


Figure 2. Transmission electron microscopy images of the P123BC solid. Electron beam perpendicular (a) and parallel (b) to the main axis of the pores (grain length $\sim 1\text{ }\mu\text{m}$).

Results

Electron Microscopy. SBA-15 powder grains are in the shape of curved cylinders of relatively uniform size (typically 200–400 nm diameter and 1–3 μm long). As illustrated in Figure 2 for the P123BC sample, a well-ordered hexagonal array of mesopores is observed for all calcined samples, when the electron beam is parallel to the main axis of these cylinders. When the electron beam is perpendicular to the main axis, the hexagonal arrays of cylindrical pores are viewed from the side, resulting in a striped image. The two-dimensional hexagonal structure (p6mm) is therefore confirmed. According to typical TEM images, one can roughly estimate the pore diameter to 3–6 nm and the lattice parameter to $\sim 10\text{ nm}$.

Nitrogen Adsorption/Desorption Isotherms. The nitrogen sorption isotherms of SBA-15 materials have been used to obtain information about their mesoporosity. These isotherms are of type IV, according to the IUPAC classification.¹⁹ As illustrated in Figure 3a for the P123AC and P123BC solids, a sharp increase of the adsorbed N_2 volume, characteristic of the capillary condensation within mesopores, occurs for a relative pressure P/P^0 larger than 0.4. This jump is irreversible: a hysteresis loop with parallel desorption and adsorption branches is observed (type H1). The sharpness of this jump indicates the

(28) Imp  rator-Clerc, M.; Davidson, P. *Eur. Phys. J. B* **1999**, 9, 93–104.

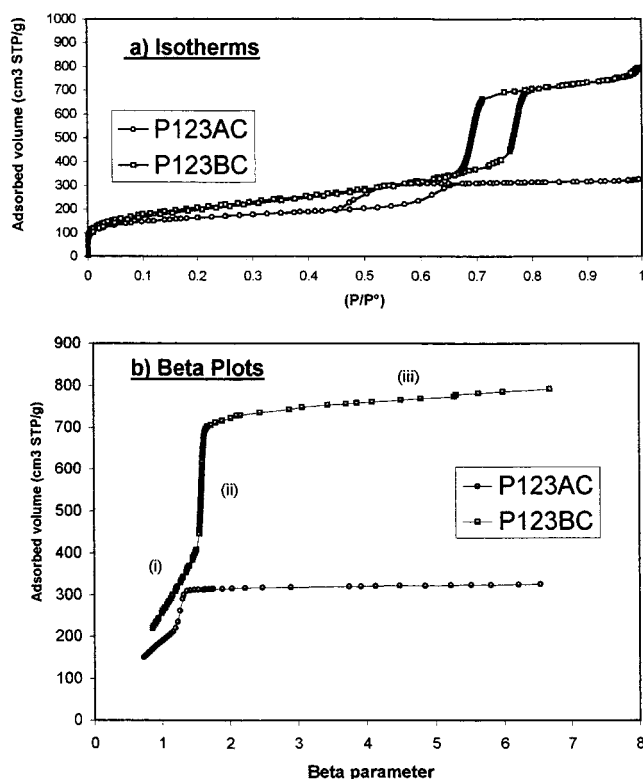


Figure 3. N_2 adsorption/desorption experiments with the P123AC and P123BC samples: (a) isotherms at 77 K; (b) β plots, $\beta = \ln(0.4/(P/P^0))^{1/2.7}$.

uniformity of mesopore sizes. Nitrogen condensation occurs at relative pressures much lower for the AC-type solids than for the BC-type ones. This indicates that the hydrothermal treatment induces a significant mesopore enlargement, as confirmed by BJH analysis (Table 2). Similarly, for BC-type solids, nitrogen condensation occurs at much higher relative pressure for the solids based on P123 than for the ones based on P103, thus suggesting that the solids templated with P123 have larger pores. Furthermore, the BC-type solids have Brunauer–Emmett–Teller (BET) surface areas and overall pore volumes similar to the values previously reported in the literature (for instance, $S_{BET} = 841 \text{ m}^2/\text{g}$ and $V_{0.974} = 1.11 \text{ mL/g}$).^{7–9}

These isotherms have been further used to evidence an additional microporosity. The β plots (Figure 3b) of AC-type solids systematically yield nonzero V_{mp} values, thus indicating the presence of micropores. In contrast, this microporosity could not be detected in the BC-type samples.

X-ray Diffraction. Powder X-ray diffraction patterns were obtained for all solids, calcined and uncalcined. The powder scans derived from the powder patterns are shown in Figure 4a,b. The first five diffraction lines (10), (11), (20), (21), and (30) are observed for most samples. Moreover, the patterns of the A-type solids also display weak (22) and (31) diffraction lines. The relatively large number of observable reflections and the fact that their widths remain limited by the resolution of the D43 experimental station demonstrate the good quality of the long-range order. In this respect, the solids described here compare favorably with the best ordered mesoporous materials of hexagonal symmetry reported in the literature.²³ Nevertheless,

the limited number of observable diffraction lines suggests that the two-dimensional (2-d) lattice is not perfect. More precisely, the intensities of the diffraction lines decrease rapidly with their order even though their widths are resolution limited. This situation often arises with lyotropic hexagonal mesophases.^{28,31} This is due both to the form factor of the cylinders and to the existence of an appreciable disorder similar to frozen thermal fluctuations,³² the effect of which may be described by a Debye–Waller factor. This point will be dealt with in more detail under Structural Models.

In addition, a continuous background, which slowly decreases with scattering angle, is also observed, especially for calcined samples, and hampers the measurement of weak diffraction lines. This background approximately follows a q^{-3} decay and might therefore be interpreted as the “Porod” regime of the small-angle scattering signal arising from rough interfaces.^{33,34} Due to a better contrast, this background would then be larger for calcined samples. In this work, we only focus on the diffraction line intensities and do not analyze this background any further since it is not relevant to our approach.

All the diffraction lines of the scattering patterns could be accurately indexed with a 2-d hexagonal lattice. The lattice constants a of each solid are given in Table 2. Error bars on these values are $\sim 0.5\%$. As already reported in the literature,^{7,8,11,27} calcination brings about a contraction of the 2-d lattice due to further condensation of the silica network. Moreover, it is clear that the A-type solids undergo a much larger contraction ($\sim 20\%$) than the B types ($\sim 3\text{--}8\%$).^{11,27}

Using the higher resolution H10 experimental station, the powder diffraction scan of the P103BC solid actually shows that the diffraction lines are not resolution limited (Figure 5). By applying Scherrer’s formula,³² a transverse grain size of 370 nm is obtained, in good agreement with the electron microscopy measurements. This proves that the hexagonal long-range order actually extends over the whole grain (~ 35 unit cells), which can be considered as a single domain, thus confirming the good crystallographic quality of the samples. Moreover, the domain size is large enough not to affect the diffraction lines of the powder scans performed at the D43 experimental station, which is a lower resolution setup. However, the limited domain size may bring about the continuous background mentioned above.²³

Close inspection of the powder scans reveals that, for all the A-type solids, the intensity of the (11) diffraction line is weaker than that of the (20). In contrast, none of the B-type solids display this intensity inversion. Structural information can be obtained from this intensity inversion by modeling the structure factor of the unit cell as described in the next section. The peak integrated intensities were measured from the powder scans by determining the area of each peak and subtracting the contribution due to the background. The intensities of the (hk) diffraction lines normalized to that of the (10) reflection are shown for each solid in Table 3. The (22) and (31) diffraction lines could not be fully resolved so their intensities were estimated together. The error bars on these values are $\sim 10\%$ and are essentially due to background subtraction. Less than 1% variation on the lattice constant a and less than 10% variation on the relative intensities of the (10) and (11) diffraction lines are obtained with the calcined P123BC solid after six months of air exposure.

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(34) Pauly, T. R.; Liu, Y.; Pinnavaia, T. J.; Billinge, S. J. L.; Rieker, T. P. *J. Am. Chem. Soc.* **1999**, *121*, 8835–8842.

(29) Pelta, J.; Durand, D.; Doucet, J.; Livolant, F. *Biophys. J.* **1996**, *71*, 48–63.

(30) Gailhanou, M.; Dubuisson, J. M.; Ribbens, M.; Roussier, L.; B  taille, D.; Cr  off, C.; Lemonnier, M.; Denoyer, J.; Jucha, A.; Lena, A.; Idir, M.; Bess  re, M.; Thiaud  re, D.; Hennet, L.; Landron, C.; Coutures, J. P. Submitted to *Nucl. Instrum. Methods Sect. A*.

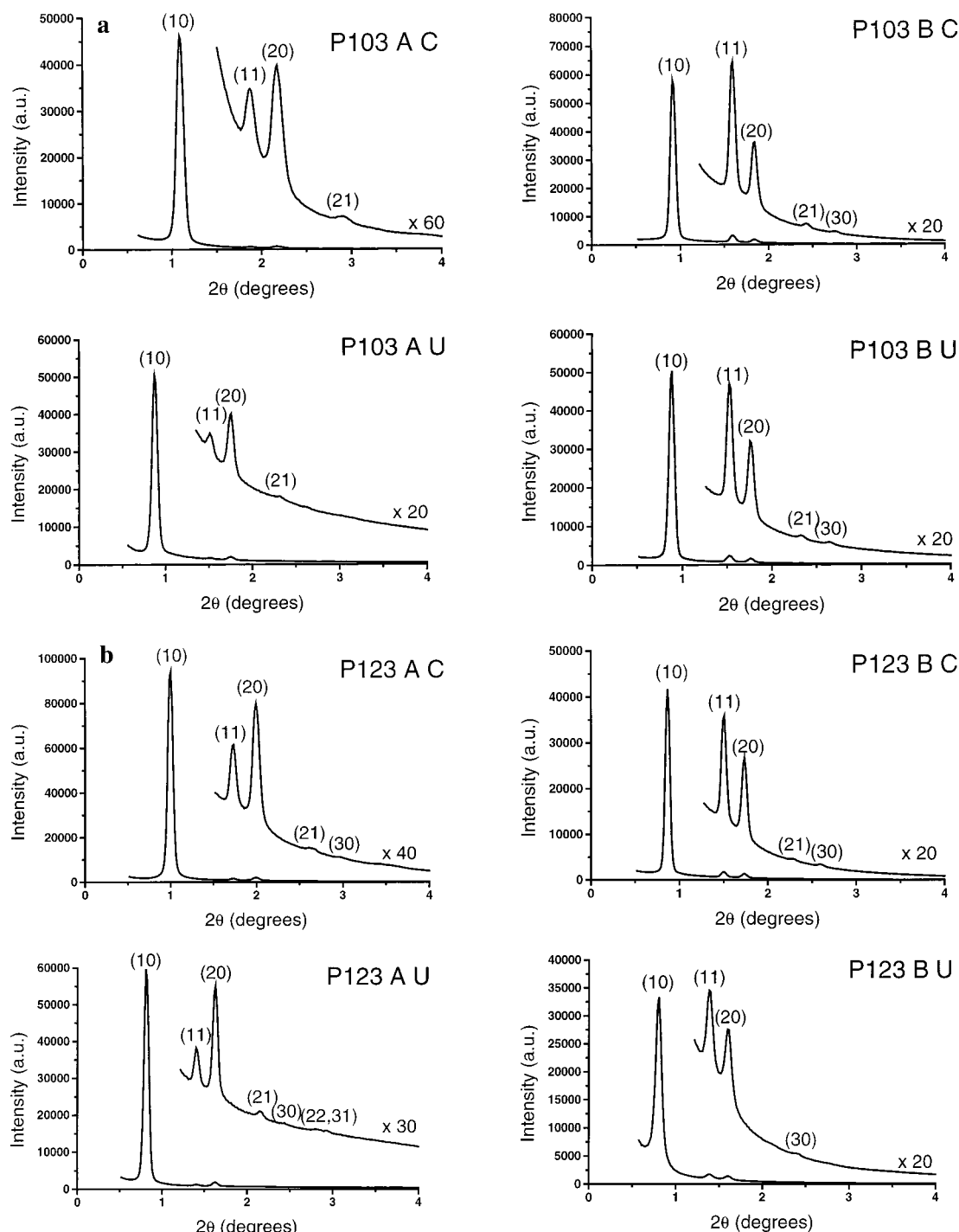


Figure 4. X-ray diffraction powder scans of the SBA-15 materials. (a) Templated with the P103 Pluronic. Uncalcined: P103AU and P103BU. Calcined: P103AC and P103BC. (b) Templated with the P123 Pluronic. Uncalcined: P123AU and P123BU. Calcined: P123AC and P123BC.

Similar results are obtained with two distinct P123BC samples synthesized at 30 °C (~2% variation on the lattice constant a and less than 10% variation on the relative intensities of the (10) and (11) diffraction lines). Finally, increasing the temperature of synthesis (35 °C) yields a significant decrease of the lattice constant a (~7%) and a more than 10% variation in the relative intensities of the (10) and (11) diffraction lines.

The comparison of Figure 4a and b shows that the materials based on P123 have powder scans quite similar to the respective ones of the materials based on P103. This remark suggests that the same description of the unit cell may apply quantitatively for both families of materials.

Structural Models

In this section, we try to analyze the diffraction intensities of all the A-type and B-type solids in the framework of various structural models of the hexagonal unit cell. The different parameters of these models are the dimensions and electron densities of each area (silica walls, Pluronic, mesopores) of the unit cell. Let us emphasize here two points. First, the scattering power only depends on the electron density contrast between the different moieties of the unit cell. This means that the electron density levels are only obtained up to an additive constant. However, for the calcined samples, we can set the electron density value of the mesopores to zero. Second, we

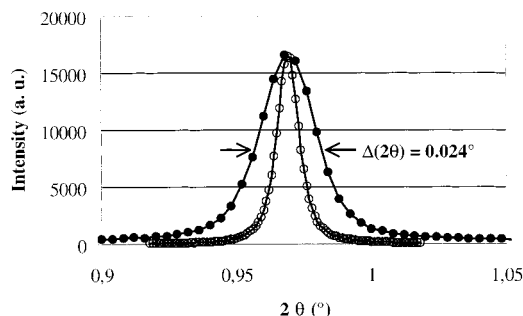


Figure 5. High-resolution profile of the (10) diffraction line of the P103BC solid. The thin line shows the direct beam profile, which determines the experimental resolution.

have not performed absolute measurements of the diffraction intensities so that, for any given solid, the intensities of the various (*hk*) diffraction lines are only given relative to that of the (10) line. This means that the electron density levels are only considered through their ratios. In the following subsections, we only illustrate the differences between various models on the structure of the P123 BC solid because all solids behave in the same way in this respect. However, in the end of this section, we show, for all solids, the results provided by the best models.

For all models, we calculate the diffraction intensities in the following form:

$$I(\bar{q}) = KM(h,k) \frac{|A(\bar{q})|^2}{\bar{q}^2}$$

where

$$\bar{q} = qa = \frac{4\pi}{\sqrt{3}} \sqrt{h^2 + k^2 + hk}$$

is the normalized scattering vector modulus, $M(h,k)$ is the line multiplicity, $1/\bar{q}^2$ represents the Lorentz factor for a powder, and $A(\bar{q})$ is the form factor introduced by each model (Fourier transform of the electron density distribution in the unit cell). K is a multiplicative constant adjusted to normalize the intensity of the (10) line to the arbitrary value of 10 000.

Model Based on Two Density Levels. The simplest model of a SBA-15 material is a 2-d hexagonal assembly of cylinders imbedded in a uniform silica matrix (Figure 6a). Let us call r the radius of the cylinders, d_1 their electron density, and d_2 the electron density of the silica matrix. We use a normalized radius defined by $\bar{r} = r/a$. In the frame of this model, the amplitudes of the diffraction lines are given by the formula

$$A(\bar{q}) = (d_2 - d_1)2\pi a^2 \bar{r}^2 \frac{J_1(\bar{q}\bar{r})}{\bar{q}\bar{r}}$$

where J_1 is the Bessel function of order 1.³⁵ The only fit parameter of this model is $\bar{r}$ because d_1 and d_2 only enter in the prefactor, which is normalized. The fit of the diffraction data by this model is shown in Table 4. It is obvious that this intuitive model does not describe the data properly and is therefore inadequate. It predicts much too large intensities for the higher order reflections (21) and (30). Moreover, it predicts intensity inversions between the (11) and (20) reflections for the P123BC and P123BU solids. This behavior strongly suggests the need to introduce more complicated models.

Model Based on Two Density Levels and a Debye–Waller Factor. We now consider that the positions of the cylinders may fluctuate in the unit cell, for instance, due to thermal fluctuations frozen in by silica polymerization (Figure 6b). This simply affects the diffraction intensities through a Debye–Waller exponential factor so that the diffraction amplitudes now read

$$A(\bar{q}) = (d_2 - d_1)2\pi a^2 \bar{r}^2 \frac{J_1(\bar{q}\bar{r})}{\bar{q}\bar{r}} \exp\left(-\frac{\langle \bar{u}^2 \rangle \bar{q}^2}{4}\right)$$

where $\langle \bar{u}^2 \rangle$ is the normalized mean-squared displacement of the cylinders. This model involves two fit parameters $\bar{r}$ and $\langle \bar{u}^2 \rangle$. As expected (see Table 4), the intensities of the higher order reflections are now greatly reduced and the description of the data looks much more satisfactory. The values of $\langle \bar{u}^2 \rangle$ obtained correspond to average displacements of the order of 1 nm, i.e., $\sim 10\%$ of the unit cell parameter. This model provides a better fit to the data (Table 4), but it predicts for all calcined samples, mesopore diameters that are much too large compared to the values derived from N_2 adsorption/desorption experiments and TEM. For the P123 BC solid for instance, N_2 adsorption gives a mesopore diameter of 6 nm, a value that is known to be underestimated by $\sim 10\%$.^{9,16–19} The model predicts a mesopore diameter of 8.2 nm, clearly conflicting with this estimate. Therefore, although this model is more efficient than the previous one, it is still not satisfactory.

Model Involving a Corona of Uniform Density. A more realistic model should distinguish the regions of dense silica from the regions (corona) where silica species and ethylene oxide segments are mixed in uncalcined materials (Figure 1). These latter regions are microporous in the calcined solids. In this section and the next one, we consider two variants of models that involve a corona. First, we consider a model (Figure 6c) in which the cylinders have an inner core of density d_1 and radius r_1 and are surrounded by a corona of uniform density d_2 and of radius r_2 . The density of the continuous silicate matrix is labeled d_3 . The densities affect the intensities only through the ratio $\alpha = (d_2 - d_1)/(d_3 - d_1)$ so that this model has three fit parameters (α , $\bar{r}_1$, $\bar{r}_2$). The diffraction amplitudes now read

$$A(\bar{q}) = (d_3 - d_1)2\pi a^2 \left[\alpha \bar{r}_1^2 \frac{J_1(\bar{q}\bar{r}_1)}{\bar{q}\bar{r}_1} + (1 - \alpha) \bar{r}_2^2 \frac{J_1(\bar{q}\bar{r}_2)}{\bar{q}\bar{r}_2} \right]$$

This model gives a quite satisfactory description of the diffraction data (see Table 4) with mesopore diameters in better agreement with the other characterization techniques. Including a Debye–Waller factor may result in an even better agreement but would unnecessarily increase the number of fit parameters.

Model Involving a Corona of Linearly Increasing Density. Another way of introducing a corona is to consider a constant gradient of silica density between the mesopores and the denser part of the walls (Figure 6d). The advantage of this model compared to the previous one, is that it only has two fit parameters ($\bar{r}_1$, $\bar{r}_2$). In this frame, the diffraction amplitudes can be expressed as

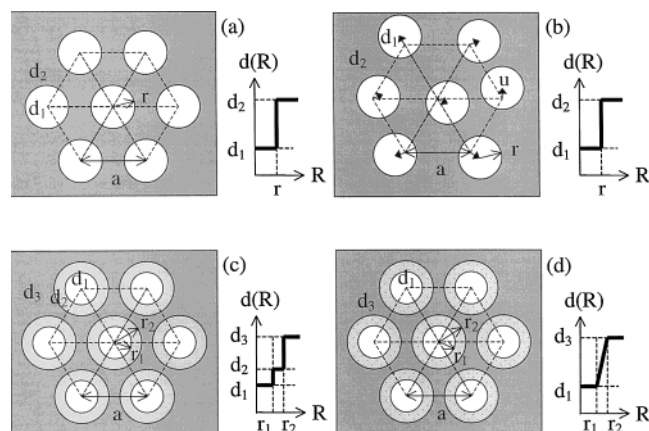
$$A(\bar{q}) = \frac{(d_3 - d_1)2\pi a^2}{\bar{r}_2 - \bar{r}_1} \left[\bar{r}_1^3 \left(\frac{J_1(\bar{q}\bar{r}_1)}{\bar{q}\bar{r}_1} - \text{int}(\bar{q}\bar{r}_1) \right) - \bar{r}_2^3 \left(\frac{J_1(\bar{q}\bar{r}_2)}{\bar{q}\bar{r}_2} - \text{int}(\bar{q}\bar{r}_2) \right) \right]$$

where

(35) Oster, G.; Riley, D. P. *Acta Crystallogr.* **1952**, *5*, 272–276.

Table 3. Intensities of the (*hk*) Diffraction Lines Normalized to That of the (10) Line for Each A-Type and B-Type Solid

	P103AC	P103BC	P103AU	P103BU	P123AC	P123BC	P123AU	P123BU
(10)	10000	10000	10000	10000	10000	10000	10000	10000
(11)	38	434	34	324	79	289	56	283
(20)	107	203	148	213	165	214	181	240
(21)	6	11	5	6	4	2	9	
(30)		5		6	1	5	1	2
(22)	1		0.5		3		6	
(31)								

**Figure 6.** Schematic representations of the structure in the frame of different models based on (a) two density levels and (b) two density levels and a Debye–Waller factor. Arrows indicate a random displacement of the pore centers. (c) A corona of uniform density. (d) A corona of linearly increasing density.

$$\text{int}(\bar{q}\bar{r}) = \frac{1}{3} {}_1F_2 \left[\begin{matrix} \{3\} \\ \{2\} \end{matrix} ; \begin{matrix} \{1, 5\} \\ \{1, 2\} \end{matrix} ; -\frac{(\bar{q}\bar{r})^2}{4} \right]$$

involves a hypergeometric function.^{36,37}

The results for the P123BC solid (Table 4) are almost as good as those of the previous one. Most importantly, this model, which has the same number of fit parameters as the model based on two density levels considered in the section Model Based on Two Density Levels and a Debye–Waller Factor, always provides better fits of the data and yields pore radii in much better agreement with the nitrogen sorption experiments.

Figure 7, which summarizes the density profiles of the different models for the P123BC solid, shows that this model and the previous one yield similar radii for the different parts of the unit cell. Therefore, both models are comparable and provide two limit descriptions of the corona density profiles. The results of these two models are discussed in more detail from the chemical point of view in the Discussion.

Discussion

Let us first analyze the information provided by the structural models. The failure of the simple model based on two density levels to properly describe the diffraction data of the SBA-15 materials shows that these solids cannot be regarded as an ideal array of mesopores. Considering a Debye–Waller factor does not really improve things since the pore diameters modeled in this way show too large discrepancies with estimates obtained from N₂ sorption experiments (Figure 3). This means that the structure of SBA-15 materials is more complex, which substantiates the assumption of the existence of two silica density

regions around the cylinders. A somewhat similar situation was pointed out by White et al. for MCM-41 materials.²³ However, for these latter materials, the wall region of lower silica density (called lining) arises from the meandering of smooth tubes. This explanation does not hold here because a microporosity is indeed observed for the AC-type solids and because the templating agents are very different from the cationic surfactants used in MCM41 syntheses. The corona region can be taken into account by introducing either a third level of silica density (Figure 6c) or a linear density variation between the mesopore and the wall (Figure 6d). Considering the different numbers of model parameters (respectively, 3 and 2) and experimental error bars, both models provide similarly good descriptions of the data. For all the solids synthesized, we detail in Table 5 the fits obtained with the two models involving a corona. These results suggest the following comments:

(i) For calcined samples, the uniform corona model directly gives the ratio of the corona silica density to that of the denser part of the walls, d_2/d_3 . For instance, for the P123 AC solid, the corona has a density of ~33% that of the denser part of the walls, which we may assume to be that of amorphous silica.²³ This implies that, at least in this case, the corona has a very large volume fraction of pores. Unfortunately, for uncalcined samples, we cannot set the electron density of the cylinders to zero, and since we did not perform diffraction intensity absolute measurements, estimating the silica density of the corona is awkward.

(ii) As expected, the solids based on P123 and the respective ones based on P103 have very similar organizations. Even though they have different lattice parameters a and pore sizes r_1 , the ratio r_1/a does not depend on the choice of one of these two Pluronics. This directly appears in their relative diffraction intensities (Table 3) and consequently also in their structures as obtained from the models. This obviously results from the fact that P123 and P103 have almost the same hydrophilic/hydrophobic ratio and in a way validates the idea that one can tune the organization of silica by tailoring this Pluronic specific feature.

(iii) Calcination has distinct effects depending on whether the solids have undergone thermal treatment (A or B type). The lattice parameter of A-type solids contract by a large extent (~20%). Moreover, while the r_2/a ratio remains almost constant, the r_1/a ratio strongly increases. In absolute values, the thickness ($r_2 - r_1$) actually decreases, demonstrating that the microporous corona of the A-type solids contracts upon calcination. In contrast, B-type solids contract slightly and uniformly upon calcination (3–8%), thus keeping their r_1/a and r_2/a ratios almost constant. Finally, it is important to stress that the presence of micropores in SBA-15 materials has been recently confirmed by platinum and carbon deposition followed by dissolution of the silica framework.^{38,39}

(36) *Handbook of Mathematical Functions*; Abramowitz, M.; Stegun, I. A., Eds.; Dover Publications Inc.: New York, 1972; Chapter 15.

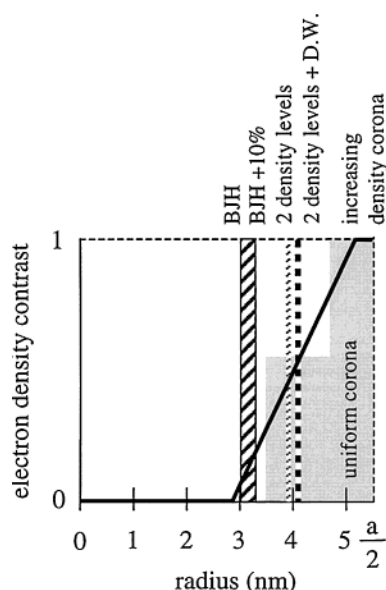
(37) All fitting procedures were performed with the Mathematica 4.0 software, Wolfram Research Inc. (<http://www.wolfram.com>).

(38) Kruk, M.; Jaroniec, M.; Ko, C. H.; Ryoo, R. *Chem. Mater.* **2000**, 12, 1961–1968.

(39) Jun, S.; Joo, S. H.; Ryoo, R.; Kruk, M.; Jaroniec, M.; Liu, Z.; Oshuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, 122, 10712–10713.

Table 4. Fits of the Experimental Diffraction Intensities for the P123 BC Solid from the Four Different Structural Models (Described in the Text)

(hk)	P123 BC type				
	<i>I</i> obsd	<i>I</i> 2-d levels	<i>I</i> 2-d levels + Debye–Waller	<i>I</i> uniform corona	<i>I</i> increasing density corona
<i>r</i> (nm)		3.9	4.1	3.5, 4.7	2.9, 5.2
$\bar{r} = r/a$		0.355	0.372	0.317, 0.429	0.266, 0.467
			$\sqrt{u^2} = 0.95$ nm	$d_2/d_3 = 0.55$	
χ^2		13753	11	0.6	4
(10)	10000	10000	10000	10000	10000
(11)	289	241	289	289	289
(20)	214	320	214	214	214
(21)	2	6	1	0	1
(30)	5	19	8	5	7
(22)	0	20	2	1	1
(31)		21	1	0	0

**Figure 7.** Electron density profiles provided by the different models.

Let us now analyze the results from a more chemical point of view. Our experiments clearly show that the most relevant feature of all these solids lies in whether they have undergone hydrothermal treatment. Thus, all A-type solids show the intensity inversion between the (11) and (20) powder diffraction lines whereas this inversion is not observed for any B-type solid. The polymerization degree of silica is obviously increased by the hydrothermal treatment, thus limiting the calcination-induced contraction of the unit cell. The comparison of the ratios d_2/d_3 (Table 5) shows that the coronas of the B-type solids also have larger densities than those of the A-type ones, which may explain why no microporosity could be detected with the B-type solids. In addition, as already concluded by Stucky et al.,^{7,8} the B-type solids have larger pore diameters than the respective A-type ones. These observed trends differ from those recently reported by Feng et al., which were obtained on SBA-15 materials templated by preformed lyotropic hexagonal liquid crystal phases at high surfactant concentrations (>20 wt %), without precipitation.¹¹

In our experimental conditions (low surfactant concentration, <4 wt %), SBA-15 materials form by precipitation. The mesomorphic order proceeds from the cooperative self-assembly of inorganic precursors with the amphiphilic block copolymers.^{7,8} At low pH, protonated PEO chains are associated with silica cationic molecular species through weak electrostatic

Table 5. Values of the Different Structural Parameters Obtained from the Two Models Involving a Corona (Figure 6c,d) for All the Solids of the Series^a

		A type		B type	
		calcined	uncalcined	calcined	uncalcined
P103					
uniform corona	r_{BJH} (nm)	1.9		2.5	
	<i>a</i> (nm)	8.80	11.00	10.45	10.85
	r_1 (nm)	2.2	1.6	3.3	3.3
	r_2 (nm)	3.3	3.7	4.6	4.6
	d_2/d_3	0.43		0.49	
increasing density corona	$(d_2 - d_1)/(d_3 - d_1)$		0.17		0.46
	r_1 (nm)	1.9	2.8	2.9	2.9
	r_2 (nm)	3.8	4.4	5.2	5.1
P123					
uniform corona	r_{BJH} (nm)	2		3	
	<i>a</i> (nm)	9.60	11.85	11.05	11.90
	r_1 (nm)	2.5	1.3	3.5	4.1
	r_2 (nm)	3.5	4.0	4.7	5.6
	d_2/d_3	0.33		0.55	
increasing density corona	$(d_2 - d_1)/(d_3 - d_1)$		0.14		0.78
	r_1 (nm)	2.4	3.2	2.9	3.3
	r_2 (nm)	4.0	4.6	5.2	5.4

^a For comparison, the values of r_{BJH} are also quoted.

interactions mediated by the negatively charged chloride ions. Support for such a mechanism, labeled $\text{S}^+\text{X}^-\text{I}^+$ in the literature,^{5,6,40} is obtained by chemical analysis. Indeed, A-type solids have large amounts of chlorine and their Cl/EO molar ratio is close to 1/1 for both P123 and P103. This mechanism explains why, by screening electrostatic repulsive interactions between PEO chains, the inorganic species induce the formation of cylindrical aggregates in a concentration range well below the critical micellization concentration of Pluronics. Figure 8 depicts this organization in which the silica precursors are located within the PEO chains to explain the structure of our AU-type samples.

The transformation of AU-type solids into BU ones is most probably correlated with the fact that the PEO chains become dehydrated with increasing temperature. Recent ESR experiments on another Pluronic (P85) in aqueous solutions at 100 °C have shown that this dehydration may not be uniform.⁴¹ In fact, it is progressive and principally affects the EO groups located in close vicinity of the hydrophobic/hydrophilic interface. In other words, the hydrophilic character increases along

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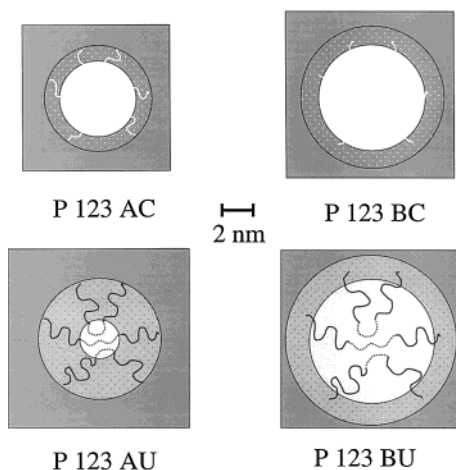


Figure 8. Influence of the hydrothermal treatment on the organization of SBA-15 materials. The shading involves gray levels that correspond to different levels of electron density (in increasing order): pores, PPO cores, corona, dense silica. (All the figures are drawn to scale.)

the PEO chain. If extrapolated in the presence of silica precursors, this behavior would nicely explain the validity of the increasing density corona model and the larger pore sizes detected after calcination. The model depicted in Figure 8 therefore provides insight into the complex structure of SBA-15 materials and into its modification by hydrothermal treatment.

Conclusions

X-ray diffraction quantitative measurements have been performed for the first time on hexagonally ordered mesoporous SBA-15 materials templated by Pluronic triblock copolymers. These measurements cannot be interpreted by considering these solids as ideal arrays of mesopores imbedded in a uniform silica matrix but can be accounted for by models involving a corona, which arises from the partial occlusion of the PEO chains into the silica matrix, and which becomes microporous upon calcination. In this way, quantitative information about pore size, wall thickness, and silica density distribution have been obtained. Moreover, our findings confirm previous ones showing that hydrothermal treatment is a convenient way to tune pore size and wall thickness of SBA-15 materials. In fact, this treatment also deeply modifies the corona by reducing its microporosity.

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Characterization of the Initial Stages of SBA-15 Synthesis by in Situ Time-Resolved Small-Angle X-ray Scattering

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The initial stages of SBA-15 synthesis have been studied by using in situ time-resolved small-angle X-ray scattering with a synchrotron radiation source. The quantitative analysis of X-ray scattering and diffraction intensities allows the structures of intermediates to be identified at the different stages of SBA-15 synthesis. Following tetraethylorthosilicate (TEOS) addition, an intense small-angle scattering and an associated secondary maximum are observed, which are attributed to non-interacting surfactant template micelles encrusted with silicate species. After 25–30 min of the reaction, the broad scattering disappears and narrow Bragg diffraction peaks typical of hexagonally ordered structure are observed. The cylindrical micelles identified from X-ray scattering data appear to be the direct precursors of 2D hexagonal SBA-15 structure. Just after the formation of the SBA-15 hexagonal phase, the cylindrical micelles are only weakly linked in the hexagonal structure. As the synthesis proceeds, the solvent in the void volume between the cylindrical micelles is gradually replaced by more dense silicate species. The unit cell parameter of SBA-15 is progressively decreasing during the SBA-15 synthesis, which can be related to the condensation and densification of silicate fragments in the spaces between the cylinders. The volume fraction of the 2D hexagonally ordered phase is sharply growing during the first 2 h of the reaction. The inner core radius of SBA-15 material remains almost constant during the whole synthesis and is principally affected by the size of the poly(propylene oxide) inner core in the original cylindrical micelles.

1. Introduction

Novel mesostructured materials with adjustable porous networks have shown a great deal of promise for the design of new heterogeneous catalysts,^{1–4} semiconductors, low dielectric devices,⁵ and new separation processes.⁶ Therefore, their potential applications, synthesis, and characterization have been extensively investigated and reported.^{7–13} The most common 2D hexagonal type involves MCM-41^{10,14–18} and SBA-15.^{19–21} The mechanism of synthesis of mesoporous materials has been recently reviewed by Patarin et al.²² Synthesis of these siliceous mesoporous materials is similar in some ways to the procedures available for zeolites, requiring a silica source and a templating agent.²² Isomorphously substituted and composite materials can also be prepared using appropriate additives. However, in the synthesis of mesoporous materials, supramolecular assemblies of surfactant species act as the structure-directing agents.²² The reaction temperature is usually lower than that required for zeolite syntheses with many preparations carried out at 25–100 °C. When the solid structure is formed, the template molecules present in the channels can be removed by calcining

the sample or via solvent extraction.^{8,9,17} The pore diameter of a periodic solid can be controlled to a certain degree by choosing appropriate template and synthesis conditions. For the original M41S syntheses, two reaction pathways involving liquid crystal templating (LCT) have been proposed.^{14,15} The true LCT mechanism is based on the premise that the surfactant molecules organize independently of the inorganic silicate into a liquid crystal phase and the siliceous framework polymerizes around the preformed surfactant aggregates. According to the self-assembly mechanism, silicate anions in solution, being negatively charged species, play an intimate role in directing the formation of the supramolecular surfactant arrays. In both cases, the inorganic components (usually negatively charged at the high pH used) preferentially interact with the positively charged ammonium headgroups of the surfactants and are condensed into a solid. The resulting organic/inorganic mesostructure can be viewed as an array (e.g., hexagonal) of surfactant micelle rods embedded in a silica matrix. It is thought that the first mechanism does not operate for cationic surfactants because the surfactant concentrations used are below the critical concentration required for the liquid crystal phase formation. The second mechanism allows cooperative self-assembly of surfactant micelles and silicate precursor at much lower concentrations, and therefore, no preformed liquid crystal phase is necessary for the generation of mesostructured materials. The interplay between the two pathways depends on the surfactant properties, its concentration, and the ionic makeup of the

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synthesis mixture.^{7,8,23,24} Further analysis of the self-assembly mechanism has been undertaken by Stucky and co-workers^{25–28} including the polydentate binding of silicate oligomeric species to the cationic surfactant, silicate polymerization in the interface region, and charge density matching between the silicate and the surfactant.

The important feature of the MCM-41 formation mechanisms is the interaction between cationic quaternary ammonium surfactants and anionic inorganic species ($S^{+}-I^{-}$) to produce two- or three-dimensional ordered structures. However, mesoporous materials can also be produced utilizing a range of electrostatic, covalent, van der Waals interaction, and hydrogen bonding (e.g., $S^{+}-X^{-}-I^{+}$, $S^{-}-M^{+}-I^{-}$, S^0-I^0 , etc.).^{19,20,26,29} In particular, the preparation of mesoporous silica employing nonionic surfactants has an advantage over the “electrostatic” route in the ease of surfactant removal by solvent extraction and the tendency to produce materials with thicker walls and a larger pore size. These materials of varying pore size can be synthesized from alkoxysilanes or from sodium silicate and a poly(ethylene glycol) ether neutral surfactant.^{19,20,30} For instance, SBA-15 type materials are synthesized in an acidic medium with poly(alkylene oxide) triblock copolymers such as Pluronic.^{19,20} The block copolymer molecules consist of hydrophobic and hydrophilic blocks.^{31–33} These molecules aggregate in aqueous solutions forming multimolecular aggregates having mostly spherical or cylindrical morphologies.³² In these aggregates, the hydrophobic blocks constitute the core and the hydrophilic blocks along with water compose the corona. Due to their larger pores (3–15 nm) and higher stability, SBA-15 materials are considered much more suitable than MCM-41 for a number of practical applications.^{4,19,20}

The pore diameter and the wall thickness are the major parameters, which influence possible utilization of mesoporous materials. Although it is known that the pore diameter in periodic mesoporous materials can vary from 2 to 30 nm, pore size tailoring of these materials appears to be a difficult task. Therefore, detailed information about the mechanism of the synthesis of mesoporous materials is indispensable for “tuning” the pore diameter and wall thickness in SBA-15 to the required values in a predefined range. Valuable structural information has been gained about ordered mesoporous materials using X-ray scattering, electron microscopy, and adsorption measurements, particularly from in situ investigation of the synthesis of mesoporous materials, including self-organization of organic and inorganic species, nucleation, and crystallization processes. Indeed, in situ X-ray diffraction (XRD) measurements have provided valuable insight into the formation of thin films of mesostructured materials,^{34–38} the transformation of hexagonal, lamellar, and cubic phases at elevated temperatures,^{39–45} and the development of periodic phases with d spacing values between 2 and 25 nm.^{46–50}

Small-angle X-ray scattering has been utilized as a powerful method for characterization of the structure of hexagonally ordered SBA-15 mesoporous materials.^{22,50–52} X-ray scattering could be very helpful in the identification of intermediates of SBA-15 synthesis present in the aqueous solutions and suspensions, while the position of Bragg diffraction peaks provides important information about the type of ordering and unit cell parameters in the ordered structures. The X-ray studies utilizing a synchrotron radiation source are well suited for in situ time-resolved measurements of the evolution of the ordered mesoporous phase in dilute synthesis mixtures, as the high brilliance of the synchrotron source allows fast acquisition of X-ray scattering patterns for the most demanding systems.

TABLE 1: Chemical Composition of Synthesis Mixtures

synthesis	concd HCl, g	TEOS, g	Pluronic, g	water, g
I	47.85	17.0	8.0	252.15
II	17.94	11.84	4	103.11

Our previous report⁵⁰ demonstrated the viability of the synchrotron based XRD method for characterization of synthesis mixtures for SBA-15 materials. It has been found that the unit cell of the forming SBA-15 materials is gradually contracting as the synthesis proceeds, which can be explained by the condensation reactions proceeding within the silicate walls of SBA-15. The XRD intensity values however are rather scattered, which has been attributed to the inhomogeneity of sampling from the reaction medium for XRD measurements. Since the XRD measurements have been delayed by the time required for sample collection and transfer from the synthesis mixture to the capillaries, very little information has been obtained about the first minutes of the SBA-15 synthesis. The initial stages of SBA-15 formation were also very recently studied by Flodström et al.⁵³ using in situ small-angle X-ray scattering. Flodström et al. suggested⁵³ that the formation of SBA-15 proceeded via clustering spherical P123 micelles. The cylindrical micelles were not detected in that work⁵³ at any stage of the synthesis. It appears, however, that some conclusions of their work regarding the structure of the intermediate species of SBA-15 synthesis may require further refinement.

The present work focuses on in situ characterization of the initial stages of SBA-15 synthesis by synchrotron based time-resolved X-ray scattering using a specially designed experimental setup. The detailed information about the intermediate structures was extracted from quantitative analysis of the small-angle scattering and diffraction intensities at different stages of SBA-15 synthesis. The results of this work are discussed together with the earlier data from the literature.

2. Experimental Section

The chemical composition of the two mixtures used for the synthesis of SBA-15 materials is shown in Table 1. In a typical SBA-15 synthesis,¹⁹ P123 block copolymer (poly(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol), average molecular mass 5800, Aldrich) was dissolved in a mixture of water and concentrated HCl under stirring. Tetraethylorthosilicate (TEOS) was the last component added to the synthesis mixture. The experimental setup used for the in situ X-ray scattering and XRD measurements is shown in Figure 1. The synthesis was carried out in a 250 mL glass flask, equipped with a magnetic stirrer, heated at 313 K. The synthesis mixture was circulating continuously through a 1.5 mm quartz capillary (wall thickness 0.01 mm). The circulation velocity was about 130 mL/min. To minimize any effects which might be due to possibly different flow characteristics during syntheses I and II, the diameter of the capillary, the geometry of the experimental cell, and the flow velocity were kept exactly the same during both syntheses.

The in situ small-angle X-ray scattering patterns were measured at the D43 experimental station at LURE, Orsay, France, using synchrotron radiation from the DCI storage ring running at 1.85 GeV with an average current of 250 mA. The D43 station utilized a single bent Ge monochromator (111) reflection, to select the wavelength and to focus the X-ray beam. The experimental setup was optimized for the measurements at small scattering angles bearing in mind large values of the

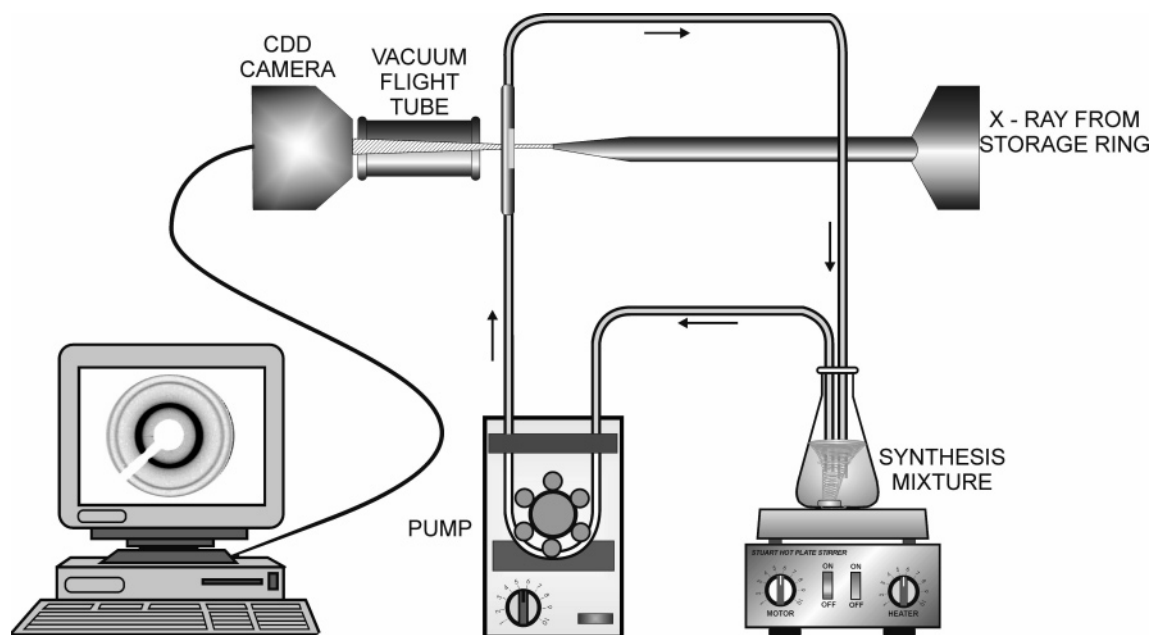


Figure 1. Experimental setup for in situ measurements of X-ray scattering and X-ray diffraction.

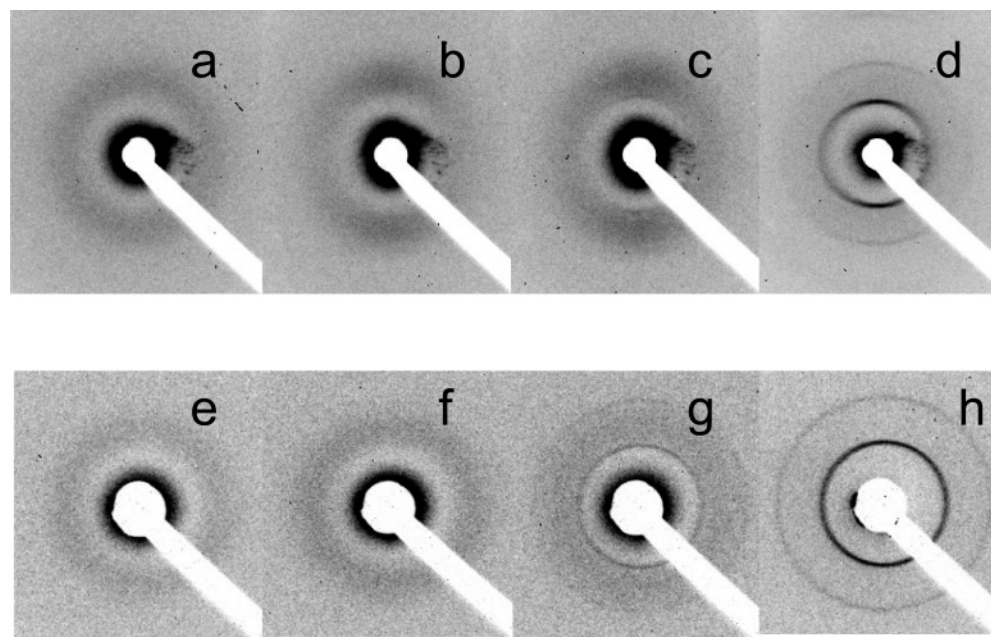


Figure 2. 2D X-ray scattering images measured after 15 (a), 20 (b), 25 (c), and 30 (d) min of synthesis I and after 15 (e), 20 (f), 25 (g), and 30 (h) min of synthesis II.

interplanar spacing in SBA-15 materials. The wavelength of the X-ray radiation was set to $\lambda = 0.1670$ (synthesis I) or 0.1449 nm (synthesis II), and the beam size was defined by a 0.5 mm diameter collimator. Vacuum flight tubes were placed between the sample and the detector to remove scattering and absorption of the X-ray beam by air.

The sample–detector distance was determined by calibration with silver behenate ($d_{001} = 5.838$ nm). The scattering patterns were recorded using the two-dimensional detector provided by the Laboratoire de Physique de Solides, Université Paris-Sud (CDD camera, Princeton Instruments). The spatial resolution (pixel size) of the detector was 0.054 mm. The scattering patterns were radially integrated, and the integrated intensity was plotted as a function of the scattering vector modulus $s = 2 \sin(\theta)/\lambda$, where 2θ is the scattering angle. The experimental

resolution was 0.0084 nm^{-1} (fwhm) for the s scale. The exposure times were typically 5 or 10 min for in situ measurements.

3. Results and Discussion

3.1. In Situ Time-Resolved X-ray Scattering Measurements. The in situ time-resolved 2D scattering image and integrated X-ray profiles of the synthesis mixtures I and II are presented in Figures 2–5. Very weak background X-ray scattering without any Bragg lines is observed prior to the addition of TEOS. After the addition of TEOS, an intense small-angle scattering along with an associated scattering ring are detected, with their intensity increasing during the first 20 min of the synthesis. The 2D X-ray scattering images (Figure 2b–d) measured at 20 – 25 min of synthesis I exhibit visible anisotropy, with the intensity of the scattering ring being higher

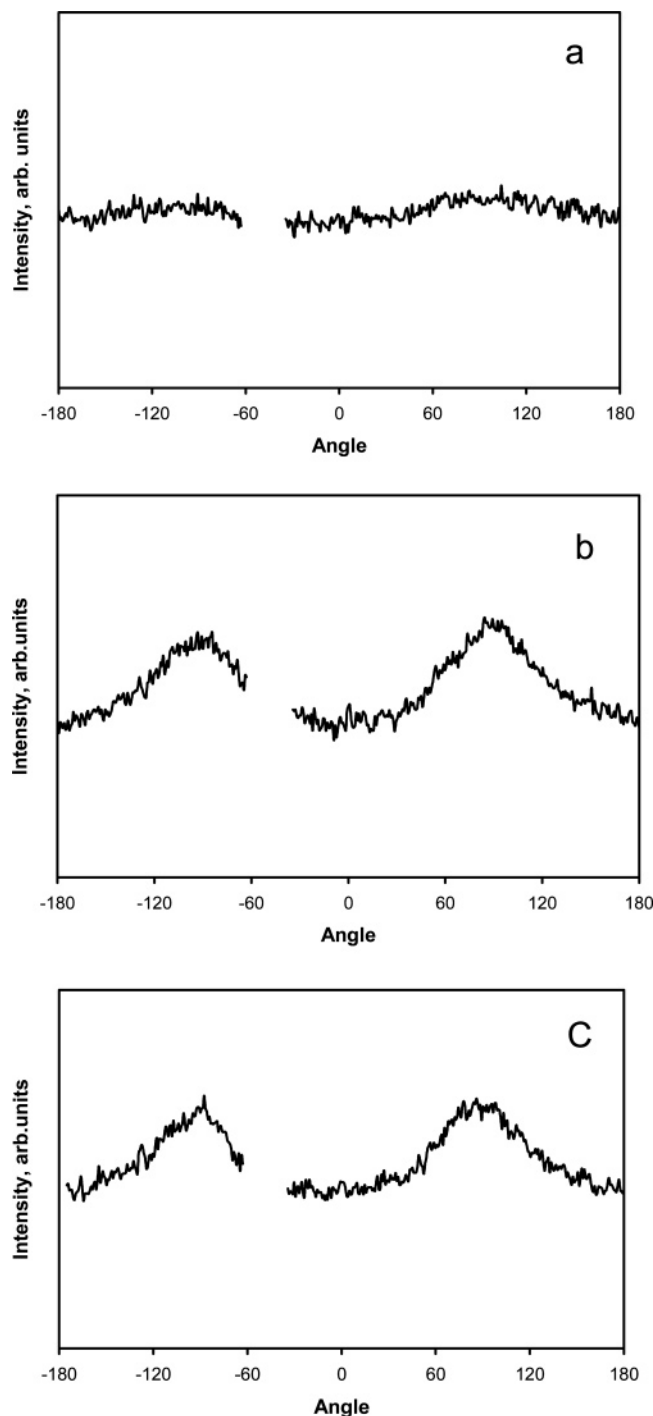


Figure 3. Profiles obtained by integrating the 2D scattering images measured after 15 (a), 20 (b), and 25 (c) min of synthesis I (Figure 2) along the scattering ring. The angles 0 and 90° correspond respectively to the equator and meridian of the scattering ring.

at the meridian than at the equator. The anisotropy is confirmed by the results of integration of the 2D images along the scattering ring (Figure 3). Taking into consideration the anisotropy of the 2D scattering images (Figures 2b–d and 3), the integration of scattering was carried out along a vertical line of 20 pixel width. Then the scattering profiles of the synthesis mixture prior to TEOS addition were subtracted from the patterns exhibiting broad scattering rings. The resulting scattering profiles for synthesis I are shown in Figure 4. No anisotropy in 2D scattering images was observed in synthesis II (Figure 2e–h). The scattering profiles (Figure 5) were obtained from the integration of full scattering images.

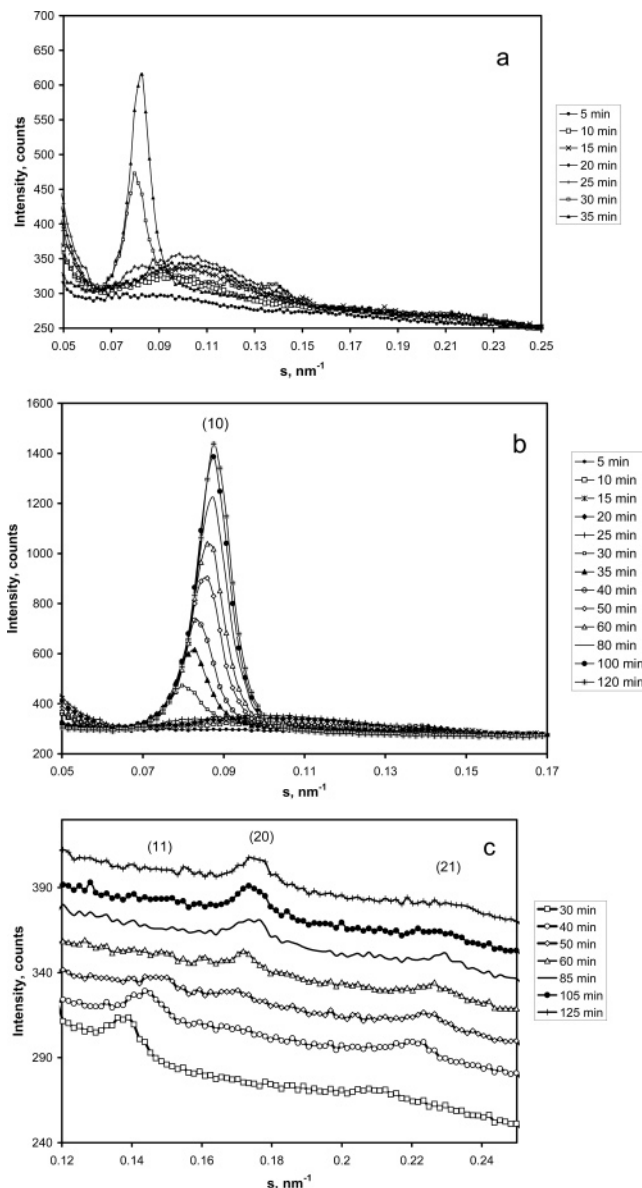


Figure 4. In situ time-resolved X-ray scattering profiles measured during synthesis I. The X-ray scattering profiles are offset in Figure 4c.

A similar broad scattering has been detected in previous reports^{47,53} during the initial stages of the formation of SBA-15 and MCM-41 materials and was attributed to the presence of micelles, which are supposed to be synthesis intermediates. The origin of the scattering observed at the initial stages of SBA-15 synthesis is discussed in more detail in section 3.2.

During the first 20 min, the solution has still been clear. After ~25 min of the synthesis, the solution becomes turbid; the solid precipitate is formed, and the X-ray patterns dramatically change (Figures 2, 4, and 5b,c). The intense small-angle scattering and broad scattering ring disappear, and the X-ray profiles characteristic of a 2D hexagonal structure are observed with up to four diffraction reflections, (10), (11), (20), and (21) detected for most samples. The width of the diffraction peaks is equal to the experimental resolution (0.0084 nm⁻¹). Therefore, the sizes of the 2D hexagonally ordered domains, which are produced in the early stages of the synthesis, are larger than 200 nm.

Figures 4 and 5 show that, as the reaction proceeds, the (10), (11), (20), and (21) diffraction peaks are shifting to higher s

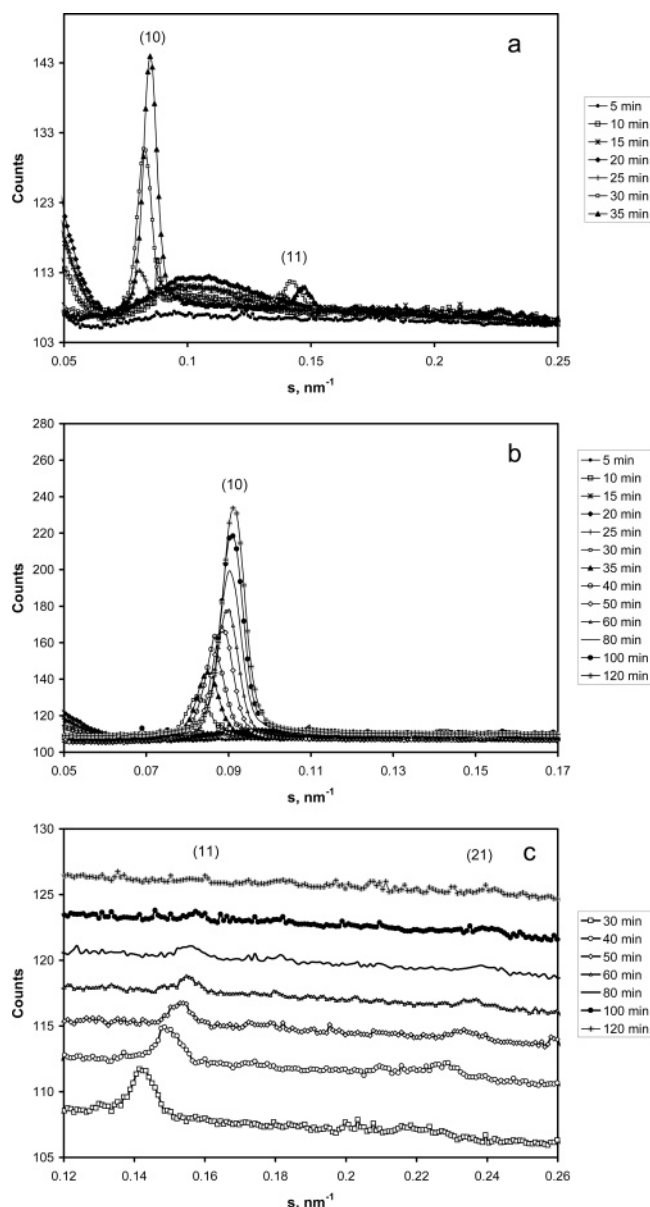


Figure 5. In situ time-resolved X-ray scattering profiles measured during synthesis II. The X-ray scattering profiles are offset in Figure 5c.

values. They indicate a decrease in the d_{10} , d_{11} , and d_{20} spacings and in the unit cell parameter, a , which can be calculated from the position of the (10) diffraction line using the equation

$$a = \frac{2}{\sqrt{3}}d_{10}$$

Our data show a steady decrease in the calculated unit cell parameter, a , of the hexagonal lattice for both preparations during the first 2 h of the synthesis. This observation is consistent with earlier reports,^{50,53} and such a decrease in the hexagonal unit cell parameter during SBA-15 synthesis can be explained by the condensation reactions within silicate walls.^{21,48,49}

For both syntheses, the intensity of the (10) reflection is increasing during the first hours of the reaction, while the intensities of the (11) and (21) reflections are decreasing. The behavior of the (20) reflection intensity is somewhat more complex. In the early stages of synthesis I, the (20) reflection is not observed; it can be seen only after 40 min of the reaction

(Figure 4c). During synthesis II (Figure 5c), the (20) diffraction reflection has not been detected.

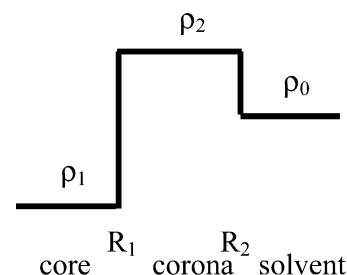
The obtained in situ X-ray time-resolved results reveal the presence of two different steps of SBA-15 synthesis: the first step is characterized by the broad X-ray scattering signals and the second by the Bragg diffraction peaks. The sections below address the determination of the structures of the synthesis intermediates associated with these two steps, using the original method of quantitative analysis of X-ray scattering and X-ray diffraction intensities.

3.2. Characterization of the Intermediates of SBA-15 Synthesis using X-ray Scattering. Before discussing X-ray scattering data, some basic equations should be briefly reviewed.^{54,55} The intensity of X-ray scattering over identical micelles in the solution is expressed by

$$I(s) = F(s) S(s) \quad (1)$$

where $F(s)$ is the form factor, $S(s)$ is the structure factor, and s is the modulus of scattering vector. The structure factor is due to the interactions between the micelles and could produce a peak of intermicelle correlation in the scattering patterns. If the interaction between the micelles is negligible, the scattering intensity, $I(s)$, is equal to the form factor, $F(s)$.

In agreement with previous reports,^{31–33} we suggest that, in the micelles originating from dissolution of P123 block polymer in aqueous solutions, the poly(propylene oxide) (PPO) hydrophobic block with electron density ρ_1 constitutes the inner core and the poly(ethylene oxide) (PEO) hydrophilic block along with water molecules and eventually silicate species (after TEOS addition) with electron density ρ_2 form the corona. These micelles are free to move inside the aqueous solution of hydrochloric acid with electron density ρ_0 .



The electron density was estimated from the known electronic structure and volumetric density of the substances considered in the present study. The electron densities of the aqueous solution of hydrochloric acid and the PPO core of micelles are respectively $\rho_0 \approx 0.35 \text{ e}/\text{\AA}^3$ and $\rho_1 \approx 0.33 \text{ e}/\text{\AA}^3$. The electron density of the PEO corona, ρ_2 , is about $0.36 \text{ e}/\text{\AA}^3$, taking into account its hydration (0.37 for pure PEO).³²

Previous reports^{32,53,56} suggest that the micelles forming from P123 Pluronic block polymer in aqueous solution might have spherical or cylindrical morphologies. Below are some equations describing X-ray scattering on spherical or cylindrical micelles.^{54,55}

Spherical Micelles. The intensity of scattering can be presented as

$$I(s) = n_s \left(\frac{4}{3}\pi \right)^2 [(\rho_2 - \rho_0)\Phi(2\pi s R_2)R_2^3 + (\rho_1 - \rho_2)\Phi(2\pi s R_1)R_1^3]^2 \quad (2)$$

where n_s is the number of the spherical micelles, R_2 is the external micelle radius, and R_1 is the radius of the PPO inner

core. The function Φ is given by

$$\Phi(2\pi sR) = 3 \frac{\sin(2\pi sR) - 2\pi sR \cos(2\pi sR)}{(2\pi sR)^3}$$

After denoting $\beta = (\rho_2 - \rho_1)/(\rho_2 - \rho_0)$, eq 1 can be rewritten in the form

$$I(s) = n_s \left(\frac{4}{3}\pi \right)^2 (\rho_2 - \rho_0)^2 R_2^6 \left[\Phi(2\pi sR_2) - \beta \frac{R_1^3}{R_2^3} \Phi(2\pi sR_1) \right]^2 \quad (3)$$

Cylindrical Micelles. Provided that the length of the cylindrical micelles is $L \gg 1/s$, the scattering intensity is defined by the following equation

$$I(s) = n_s \frac{1}{s} 4\pi (\rho_2 - \rho_0)^2 L R_2^4 \left[\frac{J_1(2\pi sR_2)}{2\pi sR_2} - \beta \frac{R_1^2}{R_2^2} \frac{J_1(2\pi sR_1)}{2\pi sR_1} \right]^2 \quad (4)$$

where n_s is the number of cylindrical micelles in the solution, R_1 and R_2 are respectively the radii of the inner core and micelle corona, and $J_1(2\pi sR)$ is the Bessel function of order 1.

The experimental in situ time-resolved X-ray scattering profiles of syntheses I and II are presented in Figures 4 and 5. First, we will discuss the data obtained for synthesis I.

A very weak and flat X-ray scattering without any Bragg lines is observed in synthesis I prior to the addition of TEOS. The very low intensity of X-ray scattering prior to the addition of TEOS is consistent with the presence in the solution of hydrochloric acid of either spherical or cylindrical micelles constituted by the PPO core and PEO corona. Indeed, whatever the shape of micelles, the scattering intensity (eqs 3 and 4) depends on the disparity of electron density between the micelle core, corona, and solvent. The corona and solvent are expected to have very similar electron densities ($\rho_0 \approx 0.35 \text{ e}/\text{\AA}^3$ and $\rho_2 \approx 0.36 \text{ e}/\text{\AA}^3$). The contrast with the core ($\rho_1 \approx 0.33 \text{ e}/\text{\AA}^3$) appears to also be too small to yield any detectable signal.

A broad scattering ring along with an intense small-angle scattering can be seen after 5, 10, 15, 20, and 25 min of synthesis I (Figures 2a–d and 4). This scattering disappears completely after 30 min of the reaction, and the Bragg reflections characteristic of the 2D hexagonal phase can be observed. After 25 min of synthesis I, the intense small-angle scattering and scattering ring coexist with the already generated Bragg diffraction reflections of the 2D hexagonal phase.

The presence of the broad scattering ring during the first minutes of synthesis I can be interpreted in two ways: First, this ring can be related to the correlation between scattering objects or, in other words, to a maximum of the structure factor, $S(s)$ (eq 1). Second, the broad scattering ring can be attributed to the first secondary maximum of the form factor, $F(s)$, for a system of identical spherical or cylindrical micelles without any correlation.

A more detailed analysis, however, suggests that the broad X-ray scattering ring observed at the early stages of synthesis I is more likely to be attributed to the X-ray scattering over independent identical particles rather than to the short-distance correlation. Indeed, if the broad peak located at $s_m \approx 0.1 \text{ nm}^{-1}$ were related to the short-distance correlation, this would give an average micelle–micelle distance $d \approx 1.23/s_m \approx 12\text{--}12.5 \text{ nm}$ shorter than the lattice parameter, a , in the 2D hexagonally ordered solid materials ($a \approx 14.3 \text{ nm}$ at 25 min synthesis time)

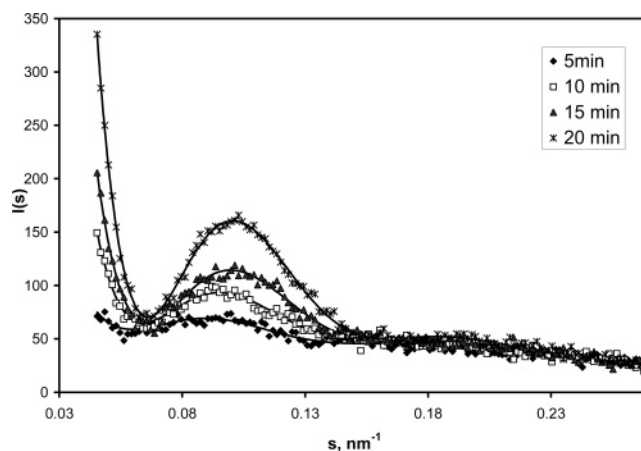


Figure 6. Fits of X-ray scattering profiles observed during the initial stages of synthesis I using the model of cylindrical micelles.

(Figure 4a,b). The appearance of a broad scattering peak at 0.1 nm^{-1} during the first minutes of synthesis I is accompanied by an increase in the intensity of X-ray scattering at very small angles ($<0.6 \text{ nm}^{-1}$). This observation seems to be in favor of attribution of the broad peak to the scattering from independent particles. Therefore, it is suggested that the broad peak at 0.1 nm^{-1} might be attributed to the first secondary maximum of X-ray scattering over non-interacting micelles.

The scattering images obtained after 20 and 25 min of synthesis I exhibit noticeable anisotropy (Figures 2b–d and 3). The anisotropy of 2D scattering images suggests the alignment of the micelles along the flow in the capillary used in the experimental setup (Figure 1) for measuring X-ray scattering. The anisotropy of the scattering also suggests that the micelles are nonspherical after the TEOS addition. This suggestion is consistent with earlier works. It was shown, for example,³² that the micelles of Pluronic polymers could be cylindrical or spherical in aqueous solutions. The observed X-ray scattering profiles after subtraction of the background were fitted using the model of cylindrical micelles (eq 4). The background scattering was approximated by a straight line. Figure 6 shows that the fits using eq 4 are all of excellent quality even at very low s . The results (Table 2) suggest, therefore, that the cylindrical micelles could form at the very beginning of synthesis I and their structure (β , R_1 , and R_2 parameters) evolves only very slightly with time.

Assuming the electron densities of the micelle core ($\rho_1 = \rho_{\text{PPO}} = 0.33 \text{ e}/\text{\AA}^3$) and the solvent ($\rho_0 = \rho_{\text{solvent}} = 0.35 \text{ e}/\text{\AA}^3$) are close to the known values, the value $\beta = 1.22$ evaluated from the fits corresponds to an electron density of the cylinder corona of $\rho_2 = 0.44 \text{ e}/\text{\AA}^3$. Thus, the electron density of the cylinder corona increases after the addition of TEOS from a value of $\rho_{\text{PEO}} = 0.36 \text{ e}/\text{\AA}^3$ in the initial PEO block to a value of $0.44 \text{ e}/\text{\AA}^3$ after TEOS addition. The increase in the electron density in the cylinder shell, ρ_2 , could be attributed to the diffusion of TEOS molecules from the solution of hydrochloric acid to the hydrophilic PEO layer and their subsequent hydrolysis. Thus, the silicate species released on TEOS hydrolysis densify the cylinder shells and, thus, increase the electron density. The densification of the micelle corona also increases the intensity of X-ray scattering after TEOS addition relative to the scattering on the original Pluronic PPO–PEO micelles. The radii of the inner core and whole micelle evaluated from eq 4 were respectively about 4 and 7 nm (Table 1). These values are close to the previously calculated dimensions of P123 Pluronic cylindrical micelles in aqueous solutions. The calculations³² using a simple molecular theory of solubilization yield

TABLE 2: Fits of the Experimental Scattering Profiles and Bragg Intensities Observed during Synthesis I^a

time, min	I_{10} , arb units	$(I_{11}/I_{10})10000$ (sign(F_{11}/F_{10}))		$(I_{20}/I_{10})10000$ (sign(F_{20}/F_{10}))		$(I_{21}/I_{10})10000$ (sign(F_{21}/F_{10}))		a , nm	R_1	R_2	β
		exptl	calcd	exptl	calcd	exptl	calcd				
5				cylindrical micelles					4.8	7.1	1.21
10				cylindrical micelles					3.94	7.37	1.19
15				cylindrical micelles					3.91	6.96	1.22
20				cylindrical micelles					3.79	7.01	1.22
30	1.84	1000	1000 (+)	0	1 (−)	818	819 (−)	14.49	4.1	6.66	1.927
35	3.62	650	650 (+)	0	0 (+)	575	574 (−)	13.94	3.9	6.23	2.679
40	5	327	327 (+)	10	0 (−)	389	389 (−)	13.94	3.96	6.44	3.38
45	6.04	147	147 (+)	53	54 (−)	279	281 (−)	13.68	3.98	6.63	3.777
50	6.98	99	99 (+)	71	71 (−)	247	246 (−)	13.43	3.95	6.6	4.04
55	7.76	57	57 (+)	155	155 (−)	274	273 (−)	13.43	4.18	6.51	2.89
60	8.41	21	21 (+)	106	106 (−)	150	151 (−)	13.43	4.02	6.97	5.711
85	10.6	0	16 (−)	159	145 (−)	123	91 (−)	13.20	4.2		
105	12.2	0	13 (−)	148	140 (−)	105	95 (−)	13.20	4.18		
125	13.05	0	13 (−)	146	141 (−)	83	94 (−)	13.20	4.18		
150	12.6	0	2 (−)	142	142 (−)	90	92 (−)	13.13	4.15		

^a For reaction times less than 25 min, the scattering profiles were fitted using the model of cylindrical micelles; fits of the Bragg peak intensities were performed using the model of a hexagonal phase. The signs of the calculated diffraction amplitudes are given, where $I_{hk} = |F_{hk}|^2$.

TABLE 3: Fits of the Experimental Scattering Profiles and Bragg Intensities Observed during Synthesis II (the Notation Is the Same as That in Table 2)

time, min	I_{10} , arb units	$I_{11}/I_{10}(10000)$ (sign(F_{11}/F_{10}))		$I_{20}/I_{10}(10000)$ (sign(F_{20}/F_{10}))		$I_{21}/I_{10}(10000)$ (sign(F_{21}/F_{10}))		a , nm	R_1 , nm	R_2 , nm	β
		exptl	calcd	exptl	calcd	exptl	calcd				
20				cylindrical micelles					3.26	7.0	1.10
30	1.89	1618		0		0		14.05			
35	2.76	871	871 (+)	0	4 (+)	1036	1038 (−)	13.62	4.22	5.32	1.65
40	3.73	575	574 (+)	0	3 (+)	514	517 (−)	13.33	3.73	5.69	3.03
45	3.76	360	360 (+)	0	2 (+)	303	305 (−)	13.20	3.59	5.57	5.18
50	4.05	280	280 (+)	0	0 (+)	168	168 (−)	12.97	3.37	6.43	9.04
55	4.51	229	229 (+)	0	0 (+)	150	150 (−)	12.93	3.37	6.55	12.16
60	5.05	145	145 (+)	0	0 (−)	141	136 (−)	12.83	3.4		
80	6.69	85	86 (+)	0	6 (−)	156	146 (−)	12.80	3.51		

for the cylindrical P123 micelles in aqueous solutions a radius of the inner PPO block of 4.2 nm and a radius of the whole micelles of 6.6 nm.

An attempt was also made to fit the scattering patterns obtained during the first 30 min of synthesis I using the model based on spherical micelles (eq 3). The fitting, however, produces incoherent parameters for the scattering profiles observed after 10, 15, and 20 min of the reaction. The values of R_1 obtained from the fit were between 2.39 and 4.3 nm, and the values of R_2 were 8.4–8.9 nm with $\beta = 2.15$ –8.44. A value of β higher than 2 gives the electron density of the micelle corona after the addition of TEOS, ρ_2 , close to that of initial PEO (0.353–0.367 e/Å³). Note that no X-ray scattering should be observed under these conditions, since the electron density of the micelle corona, ρ_2 , would be very close to the electron density of the HCl solution, ρ_0 (eq 3). Note, however, that the fitting of scattering patterns with spherical micelles at 5 min of synthesis I yields values of $\beta = 1.2$ with $R_1 = 6.5$ nm and $R_2 = 7.5$ nm. $\beta = 1.2$ corresponds to a value of $\rho_2 = 0.44$, that is, to the corona of spherical micelles containing dense silicate species. Therefore, the presence of spherical micelles cannot be ruled out prior to TEOS addition and after 5 min of synthesis I. The spherical shape of P123 micelles in aqueous solutions of hydrochloric acid prior to TEOS addition is consistent with previous neutron scattering data.⁵⁷ Our X-ray scattering data show however that if even the spherical micelles were present prior to TEOS addition and during the first 5 min of synthesis I, in the presence of TEOS after 10 min of the reaction, all of them would adopt a cylindrical shape.

For synthesis II, the data are qualitatively similar to those of synthesis I. No measurable X-ray scattering was observed prior

to TEOS addition. An intense central scattering spot together with first secondary maxima are detected during the first 25 min of the reaction (Figures 2e–h and 5). Then, the intensity of the broad scattering ring drops sharply and the Bragg diffraction lines of the 2D hexagonal phase are observed. In contrast to synthesis I, no anisotropy of the scattering image was observed during the first minutes of the reaction. For the scattering profile obtained after 20 min of synthesis II, the model of cylindrical micelles yields fitting of good quality with the parameters (Table 3), which only slightly differ from those of synthesis I (Table 2). A β value of 1.10 corresponds to an electron density in the micelle corona of $\rho_2 = 0.55$ e/Å³, which is a little higher than that in synthesis I and is consistent with the higher concentration of TEOS involved in synthesis II than in synthesis I. On the contrary, the fitting of scattering profiles with cylindrical micelles observed at 5, 10, and 15 min of synthesis II leads to a β parameter lower than 1. $\beta < 1$ corresponds to the situation where the electron density of the solvent is lower than the electron density of the micelle inner core ($\rho_0 < \rho_1$), which is incompatible with the known values of the electronic density of PPO (0.33 e/Å³) and solution of hydrochloric acid (0.35 e/Å³). This suggests that the model of cylindrical micelles does not provide an adequate representation of the X-ray scattering profiles at reaction times smaller than 20 min. That was the reason why the model of spherical micelles was also used to fit the scattering data obtained during synthesis II after 5–20 min of the reaction.

The results obtained for synthesis II using the model of spherical micelles are presented in Table 4. First, we tried to fit with spheres the scattering profiles obtained after 20 min of the reaction. For the data at 20 min, the fitting yields the

TABLE 4: Fits of Experimental Scattering Intensities at the Initial Stages of Synthesis II Using the Model of Spherical Micelles

time, min	R_1 , nm	R_2 , nm	β
5	6.3	7.0	1.10
10	4.7	8.18	1.32
15	4.59	8.24	1.31
20	2.36	8.46	5.8

parameter $\beta \approx 5.8$ which corresponds to an electron density in the micelle corona, ρ_2 , that is too close to the density of HCl solution, ρ_0 . When the electron density of the corona is very close to the density of the solution (eq 3), the intensity of X-ray scattering on the micelle corona should be very low. This seems to confirm the suggestion that after 20 min of the reaction just prior to the appearance of the 2D hexagonal phase, the synthesis mixture does not contain spherical micelles but consists of mostly cylindrical ones. Note, however, that, similar to synthesis I, the fit using the model of spherical micelles gives reasonable values of $\beta = 1.1$ and $R_1 = 6.3$ nm and $R_2 = 7.0$ nm after 5 min of the reaction. This suggests that, as it was with synthesis I, identical spherical micelles are present during the first 5 min of synthesis II. The model based on the assumption of identical spherical micelles does not provide, however, an adequate description of the micelles after 10 and 15 min of the synthesis. Table 4 shows that the parameter β slightly increases as the synthesis progresses. The increase in the β parameter is not consistent with an increase in the electron density in the corona and consequently with the suggested mechanism of the synthesis, which involves gradual enrichment of the PEO corona with silicate ions after TEOS addition.

Thus, both models based on the assumption of identical cylindrical or spherical micelles fail to provide the appropriate description of the micelle structure after 10–15 min of synthesis II. It can be suggested therefore that at this stage that the system appears to be much more complex than that of synthesis I. It may consist of spherical and cylindrical micelles of different sizes. The presence of micelles of different geometries during the first minutes of synthesis II could explain the absence of anisotropy in the 2D scattering images (Figure 2e–h). This would also certainly make it difficult to model the scattering profiles at this stage of the synthesis.

Interestingly, in syntheses I and II, the modeling strongly indicates that the cylindrical micelles precede the appearance of the 2D hexagonal phase. This suggests the crucial role that the cylindrical micelles could play in the mechanism of SBA-15 synthesis.

3.3. Analysis of Bragg Diffraction Intensities. The structure of the 2D hexagonal phase at the second stage of SBA-15 synthesis has been analyzed in a more quantitative manner using the intensities of the (10), (11), (20), and (21) Bragg diffraction lines. First, we will recall the model used for the analysis of XRD reflection intensities in our earlier work.⁵¹ For a 2D hexagonal structure,^{51,52} the diffraction intensity associated with the line of indexes (h, k) is given by

$$I(s) = KM(h, k) \frac{|A(s)|^2}{s^2} \phi \quad (5)$$

The scattering vector modulus, s , is a function of indexes (h, k)

$$s = \frac{2}{\sqrt{3}a} \sqrt{h^2 + k^2 + hk} \quad (6)$$

where a is the lattice parameter of the 2D hexagonal structure. $A(s)$ represents the structure factor that is the Fourier transform of the electronic density in the unit cell. $1/s^2$ is the Lorentz factor at small angles for powder,⁵⁸ and $M(h, k)$ is the line multiplicity; ϕ is the volume fraction of the hexagonal SBA-15 phase. The line multiplicities in the 2D hexagonal lattice were respectively 6 for the lines (10), (11), (20), and (30) and 12 for the line (21). K is a multiplicative constant related to the X-ray beam intensity and sample volume, assuming a constant absorption by the sample.

First, the simple model, which assumes the presence of a two-dimensional assembly of cylinders embedded in a uniform silica matrix was used to simulate the diffraction intensities.⁵¹ The two-level model suggests the presence of two regions of electron density, that is, a two-level approach. The electron density in the present model is described by a step change between the core and silica matrix. The intensity is calculated as

$$I(s) = \frac{R^4}{(sa)^2} KM(h, k) (\rho_2 - \rho_1)^2 \left[\frac{J_1(2\pi s R)}{2\pi s R} \right]^2 \phi \quad (7)$$

where R is the core radius, ρ_1 and ρ_2 are electronic densities in the cylinder core and silica matrix, and J_1 is the Bessel function of order 1.

At the very beginning, the observed intensities of the Bragg peaks cannot be described using the two-density-level model. In agreement with our previous work,⁵¹ a more realistic model, which takes into consideration the presence of three regions of electron density, was used for the quantitative description of XRD data. This model is consistent with the description of the first stage of the synthesis using the model of cylindrical micelles (section 3.2). In the three-level model, the first region of electron density represents the inner core of the cylinders filled by PPO species (electron density ρ_1), the second region corresponds to the cylinder corona formed by the mixture of silicate and PEO species with electron density ρ_2 , and the third region with electron density ρ_0 is constituted by the spaces between the cylinders. The intensity of the diffraction lines is given by the following formula:

$$I(s) = \frac{R_2^4}{(sa)^2} KM(h, k) (\rho_2 - \rho_0)^2 \left[\frac{J_1(2\pi s R_2)}{2\pi s R_2} - \beta \frac{R_1^2}{R_2^2} \frac{J_1(2\pi s R_1)}{2\pi s R_1} \right]^2 \phi \quad (8)$$

where R_1 and R_2 are respectively the radii of the inner core and the whole cylinder. The electron densities affect the XRD intensities through the ratio $\beta = (\rho_2 - \rho_1)/(\rho_2 - \rho_0)$. The fit parameters of this model are only R_1 , R_2 , and β . Note that ρ_2 , ρ_0 , and ϕ enter only in the prefactor, which is normalized during the fitting. From eq 8, one can also calculate the signs of the diffraction amplitudes, which are given by the sign of the expression in square brackets $[(J_1(2\pi s R_2)/2\pi s R_2) - (\beta R_1^2/R_2^2) \cdot (J_1(2\pi s R_1)/2\pi s R_1)]$, taking into account the values of the parameters (R_1 , R_2 , and β) determined by the fitting procedure.

The results of the fits along with the signs of the diffraction amplitudes for syntheses I and II are shown in Tables 2 and 3. The three-level model (eq 8) represents satisfactorily the XRD data obtained during the first hour of the synthesis. After 60 min of synthesis, this model transforms into the model based on the two density levels (eq 7). The model based on two density levels corresponds to the situation in the three-density-level model where ρ_2 is equal to ρ_0 . Consequently, eq 8 reduces to

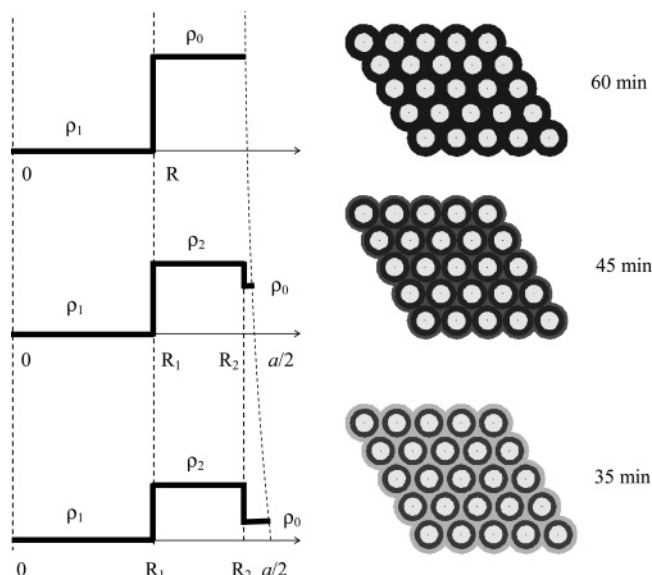


Figure 7. Formation of 2D hexagonal SBA-15 structure from cylindrical polymer-silicate micelles.

eq 7. It can be suggested, therefore, that, after 60 min of synthesis, the electron density of the cylinder corona becomes close to the electron density in the spaces between the cylinders. The observed phenomenon is likely to be attributed to the densification of the spaces between the cylinders due to silica condensation. Tables 2 and 3 display a monotonic increase in the β parameter during the first hour of the synthesis. Assuming an electron density in the inner core of the cylinders close to that in PPO ($\rho_1 = 0.33 \text{ e}/\text{\AA}^3$) and an electron density in the cylinder corona in hexagonal structure close to the value determined for cylindrical micelles from X-ray scattering ($\rho_2 = 0.44$ in synthesis I and $0.55 \text{ e}/\text{\AA}^3$ in synthesis II), the increase in the β parameter would correspond to the increase in the electron density in the intercylinder gaps, ρ_0 , from its initial value in the solution of hydrochloric acid ($0.35 \text{ e}/\text{\AA}^3$) up to the electron density in the corona. The mechanism of packing cylindrical micelles into 2D hexagonal structure is schematically presented in Figure 7. During the first 20 min after TEOS addition, the Pluronic micelles represent almost independent objects in the solution of hydrochloric acid. After 25 min, these micelles start packing into 2D hexagonal structure. At the beginning, the cylinders are only weakly linked via their coronas in the 2D hexagonal matrix. As the synthesis proceeds, the spaces between the cylinders are gradually filled by the silicate species. After 1 h of the reaction, the density in the spaces between the cylinders is getting very close to the electron density in the micelle corona.

The evolution of the hexagonal unit cell parameter, a , calculated radii of the inner core, R_1 , and whole cylinder, R_2 , during the second step of SBA-15 synthesis is shown in Figure 8. The hexagonal unit cell parameter, a , shows continuous decrease during the synthesis. Despite significant changes in the ratio of diffraction intensities, the radius of the cylinder inner core, R_1 , only slightly fluctuates during the SBA-15 synthesis. This observation is in accordance with the self-assembly mechanism, in which the formation of the ordered mesophase is initiated by the added silicate species. Moreover, the fact that the lattice parameter, a , is almost equal to $2R_2$ is also in agreement with this mechanism.

3.4. Initial Stages of SBA-15 Synthesis. In summary, the analysis of the X-ray scattering data suggests that, during the first 5 min of the reaction, the PPO-PEO micelles might have

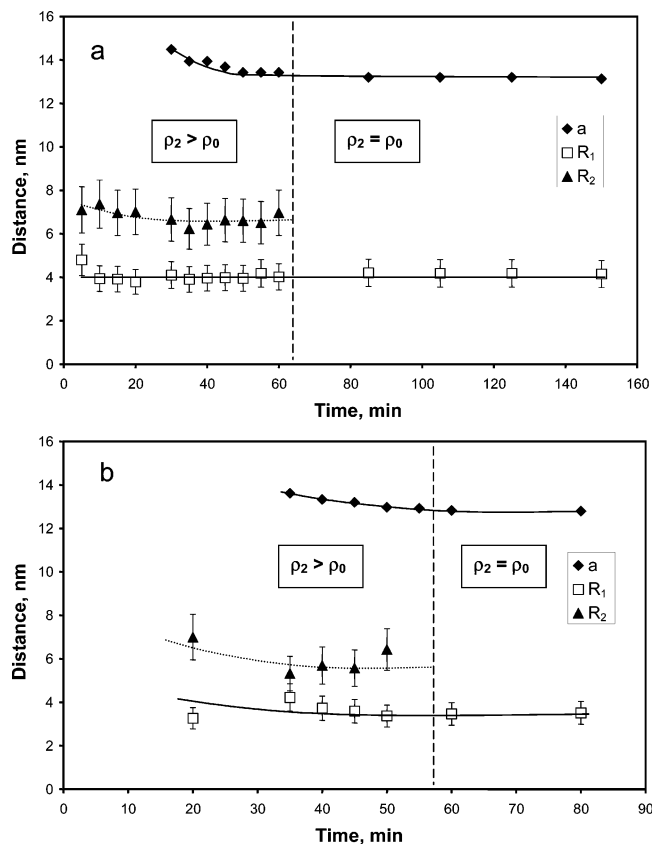


Figure 8. Evolution of the structural parameters of the 2D hexagonal phase during SBA-15 synthesis: (a) synthesis I; (b) synthesis II.

a spherical shape. In the presence of silicate species generated via TEOS hydrolysis in both synthesis I and synthesis II, most of micelles adopt the cylindrical shape. For synthesis I, the conversion to the cylindrical shape seems to proceed more swiftly than that for synthesis II. These cylindrically shaped micelles are then packing in 2D hexagonal structure yielding SBA-15 materials. Overall, within the accuracy of the model, the diameter of inner core of the SBA-15 mesoporous materials prepared at lower temperatures appears to be principally determined by the diameter of the PPO core in the surfactant-silicate cylindrical micelles. In the present work, the analysis of scattering patterns after 10–20 min of syntheses I and II clearly indicates that a solution of non-interacting cylindrical micelles precedes the appearance of the 2D hexagonal phase. The presence of cylindrical micelles is also proved by the anisotropy of scattering images observed after 20–25 min of synthesis I. The solution was limpid before the appearance of the 2D hexagonal phase, and no peak of intermicelle correlation was observed. This suggests that the micelles could be considered as non-interacting objects during 20–25 min of the synthesis and their aggregation immediately results in the formation of the 2D hexagonal phase detectable by intense XRD patterns.

In very recent papers by Flodström et al.,^{53,56} X-ray scattering and electron microscopy were used to study the different intermediates during the initial stages of SBA-15 synthesis. In contrast to the publication by Flodström et al.,⁵³ we propose a mechanism of formation of SBA-15 materials based on the non-interacting cylindrical micelles. In the previous report by Flodström et al.,⁵³ the synthesis of SBA-15 materials was suggested to proceed via spherical micelles. No cylindrical micelles were identified by Flodström et al.⁵³ from X-ray scattering data during SBA-15 synthesis. The suggestion about

the spherical shape of micelles in that paper⁵³ was partially based on the previously published transmission electron microscopy (TEM) data⁵⁶ showing the absence of elongated particles at the short reaction time. Note, however, that the TEM analysis was carried out under conditions very different from those employed in the paper of Flodström et al.⁵³ and in the present work. This suggests that the TEM data of the paper⁵⁶ could be hardly relevant to SBA-15 synthesis. Note that in our work the scattering patterns attributed to silica-polymer micelles after 15–25 min of syntheses I and II, which precede the appearance of the 2D hexagonal phase, cannot be fitted assuming the presence of identical spherical micelles. This discrepancy with the previous report seems to be attributed to the fact that the fitting in the paper of Flodström et al.⁵³ was limited only to the secondary scattering maxima and did not take into account the scattering behavior at very small angles near the central spot.

A more comprehensive analysis of X-ray scattering carried out in our work suggests that the cylindrical and not spherical micelles are the key intermediates of SBA-15 synthesis. The structure of cylindrical micelles has been extensively characterized in the present work during the SBA-15 synthesis using the in situ X-ray scattering data. For the 2D hexagonal phase, we have also developed the original procedure to analyze the Bragg peak intensities. This procedure allows estimation of the values of important structural parameters, the radii of the cylindrical micelles, R_1 and R_2 , and the electron densities.

A different mechanism of synthesis in a related system, a hexagonally ordered ZrO_2 /surfactant mesophase, has recently been proposed by Né et al.⁵⁹ In that case, the X-ray scattering data showed at the initial stages of the synthesis the presence of a broad “soft” peak at low q and a “sharp” Bragg peak resulting from hexagonal order. The soft peak remains in coexistence with the sharp peak and does not shift its position during the hexagonal crystallization. It was suggested⁵⁹ that the micelles act as surfactant monomer for feeding zirconia grains. The hexagonal organization proceeds on zirconia clusters which represent the nucleation sites. The mechanism proposed by Né et al.⁵⁹ is different from that observed in the present work, and the kinetic times are also much smaller (only a few seconds). Indeed, in the absence of nucleation sites introduced from the exterior (zirconia grains), the synthesis of hexagonally ordered SBA-15 appears to be initiated by packing the cylindrical surfactant template micelles coated with silica into large hexagonally ordered domains.

4. Conclusion

In situ time-resolved small-angle X-ray scattering and X-ray diffraction allow new information about the initial stages of SBA-15 synthesis to be obtained. Contrary to a previous report,⁵³ a comprehensive analysis of X-ray scattering suggests that, at the first stage of the synthesis, non-interacting cylindrical polymer-silicate micelles are formed, constituted by the poly(propylene oxide) inner core and the cylinder corona made up of a mixture of poly(ethylene oxide), water, and silicate species. At the second stage, these cylindrical micelles pack into larger domains of 2D hexagonal structure. As the synthesis proceeds, the electron density in the voids between the cylinders gradually increases as the solvent is replaced by silicate species. The volume fraction of the SBA-15 phase rapidly grows during the first 2 h of the reaction. Analysis of X-ray scattering and XRD intensities suggests that the diameters of the inner core of the cylindrical micelles and the 2D hexagonal structure do not vary much during the synthesis.

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Chapitre 18

Mono-domaine de phase hexagonale 2D

L'obtention d'un mono-domaine orienté d'une phase hexagonale 2D lyotrope est importante pour qu'un échantillon reflète macroscopiquement l'anisotropie de la phase. Une méthode simple a été élaborée pour obtenir de tels monodomains.^{1,2} L'instabilité inhérente à ces mono-domaines dites de zig-zag a été caractérisée à la fois par diffusion des rayons X et par microscopie optique en lumière polarisée.

Mono-domaine et instabilité en zig-zag

Publication [11]

Une phase hexagonale 2D lyotrope se présente macroscopiquement comme un gel visco-élastique. La méthode utilisée pour réaliser des mono-domaines orientés consiste à aspirer doucement une phase hexagonale à l'intérieur d'un capillaire plat optique. Le cisaillement mécanique de la phase entre les parois planes du capillaire induit une orientation macroscopique de la phase : le directeur hexagonal s'aligne suivant la direction d'écoulement et une famille de plans (10) se met parallèlement aux parois du capillaire. Cette orientation a été vérifiée par des mesures de diffusion des rayons X.¹

Les mono-domaines ainsi obtenus ne sont pas parfaits. Observés au microscope en lumière polarisée, ils présentent le plus souvent une texture optique caractéristique d'une instabilité d'ondulation/zig-zag du directeur hexagonal. Cette instabilité apparaît pour de très faibles variations de température et est donc en pratique impossible à éviter. Elle se produit lorsque le paramètre de maille diminue lors d'une variation de température. Pour une phase donnée, cela se produit soit au chauffage, soit au refroidissement, selon le signe de la variation en température du paramètre. Lorsque le paramètre diminue, le confinement entre les deux parois planes du capillaire de la phase hexagonale provoque une dilatation 2D du réseau hexagonal. Une façon de relaxer cette dilatation est d'incliner les colonnes dans le plan du capillaire plat

(ondulation ou zig-zag), ce qui augmente la section transverse offerte aux colonnes.³ Les expériences de diffusion des rayons X réalisées en variant la température ont permis de confirmer ce mécanisme. On a pu en particulier suivre l'établissement de la texture en zig-zag lorsque l'instabilité se produit, grâce au dédoublement progressif de certains pics de Bragg (10) de la phase hexagonale.

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An X-ray scattering study of flow-aligned samples of a lyotropic liquid-crystalline hexagonal phase

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Abstract. Large flow-aligned samples of the hexagonal mesophase of the (sodium dodecylsulfate, pentanol, water) ternary system were produced by merely sucking the material into flat glass capillaries. These samples were examined by polarized light microscopy and X-ray scattering. In the plane of the hexagonal lattice, the “ ϕ -mosaic” is only $\cong 0.1^\circ$ because the dense (10) hexagonal planes lie parallel to the flat glass plates of the capillaries. In contrast, the “ χ -mosaic” of the C_6 axis reaches $5\text{--}10^\circ$ because the samples undergo a thermomechanical instability of the columns already investigated by Oswald *et al.* in detail on the ($C_{12}EO_6$, H_2O) system. Anisotropic thermal diffuse scattering is observed around the Bragg peaks and its description in the frame of an elastic continuum model provides estimates of the elastic constants. On heating the samples, we observed a clear splitting of four of the (10) hexagonal lattice reflections. This splitting is the defining signature of the thermomechanical instability by which the columns form zig-zags. The fact that two of the (10) reflections are not affected by the instability demonstrates that it is confined to the plane of the capillary. The influence of temperature on the thermomechanical instability was also studied in detail.

PACS. 61.10.Eq X-ray scattering (including small-angle scattering) – 61.30.-v Liquid crystals – 61.30.Jf Defects in liquid crystals – 65.70.+y Thermal expansion and density changes; thermomechanical effects

1 Introduction

Mesophases of hexagonal symmetry are very often encountered in the field of complex fluids. A large number of molecular moieties or aggregates such as disc-like molecules [1], block-copolymers [2], rod-like polymers [3] and micelles of amphiphilic molecules [4] form a hexagonal mesophase in a given range of concentration and temperature. The hexagonal phase has long-range orientational order but only 2-dimensional long-range positional order [5]. Therefore, there are no long-range positional correlations along the C_6 axis so that the phase only shows a 2- d lattice of Bragg reflections by X-ray scattering. Although there have been numerous structural studies of hexagonal mesophases performed on “powder” samples, only very few aligned samples have been described in the literature. Some hexagonal mesophases spontaneously grow into single domains or may be oriented by a magnetic field [6] but these are rather exceptional cases. Sophisticated techniques such as “strand pulling” [7], the “X-ray Surface Force Apparatus” [8] or shear cells [9] have already been successfully applied to produce aligned samples but simpler methods are clearly needed in order to easily inves-

tigate a larger number of hexagonal mesophases. Single domains are very useful for structural studies since very valuable information is lost in the process of powder averaging and the signal-to-noise ratio of a single domain is always much larger than that of a powder. In addition, the study of the thermal diffuse scattering (TDS), which gives access to the elastic constants, requires the use of a single domain. Since the elastic constants are themselves derived from the free energy, the thermal diffuse scattering indirectly gives information on the thermodynamics of the phase [7c]. Direct mechanical measurements [10] of the elastic constants are often complicated by the presence of residual topological defects. In contrast, our approach provides more local estimates which agree well with the values obtained from the analysis of textures [11,12].

In this work, we describe how we produced highly aligned samples of a lyotropic hexagonal mesophase of amphiphilic molecules by merely sucking the material into flat glass capillaries. The molecules form very long cylindrical micelles which are aligned along the capillary main axis by the flow. We characterized these samples by polarized light optical microscopy and X-ray scattering. The TDS is essentially localized around the Bragg reflections and can be described in the frame of an elastic continuum model thus providing estimates of the elastic constants of

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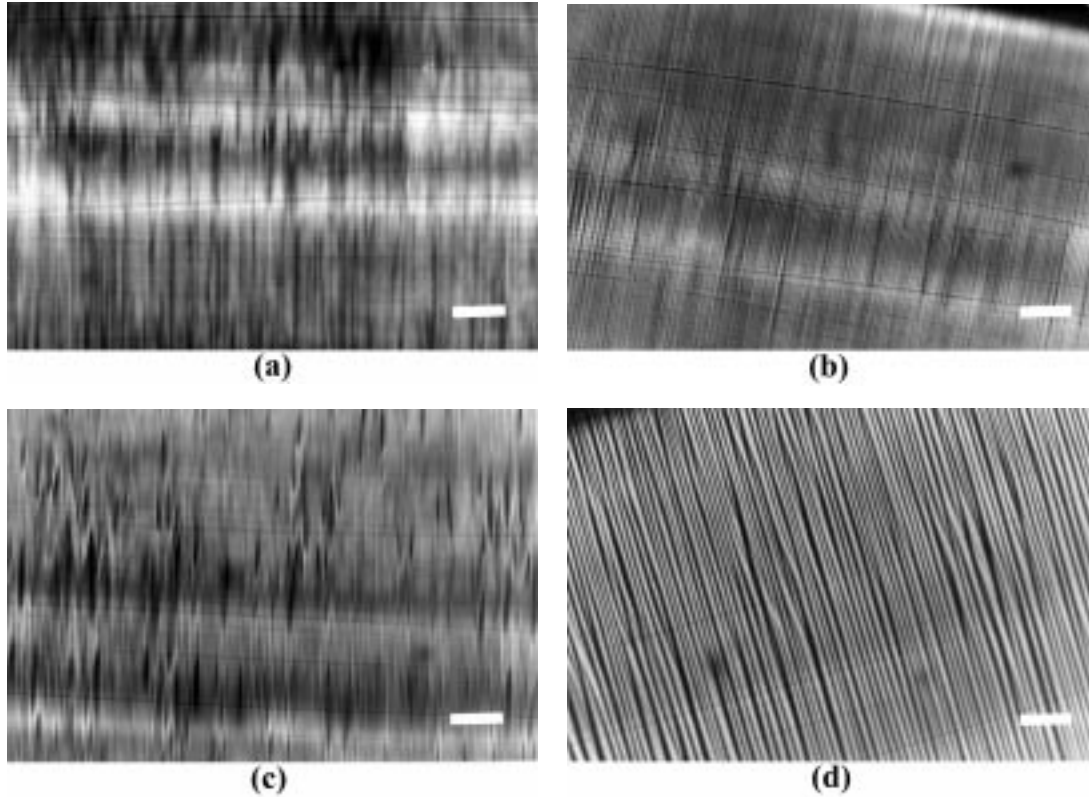


Fig. 1. Textures of the samples in polarized light microscopy (Sample thickness is $100\ \mu\text{m}$, the white bars are $100\ \mu\text{m}$ long. The crossed polarizers are parallel to the sides of the photographs.) (a) Room temperature, capillary axis parallel to the polarizer direction; (b) Room temperature, capillary axis at an angle $\theta = 5^\circ$ with the polarizer direction; (c) $T = 80^\circ\text{C}$, capillary axis parallel to the polarizer direction; (d) $T = 80^\circ\text{C}$, capillary axis at an angle $\theta = 15^\circ$ with the polarizer direction

the hexagonal phase. Besides, we found that the distribution of the TDS is very different from that observed in previous studies of thermotropic hexagonal phases [6a,7c]. Finally, we show that our samples undergo a thermomechanical instability already studied in detail by Oswald *et al.* [12]. This instability reveals itself on heating by the appearance of a striated texture indicative of undulations or zig-zag conformations of the micelles.

2 Experimental

We selected the lyotropic hexagonal phase already reported at room temperature in the ternary phase diagram of sodium dodecylsulfate (SDS), pentanol and water [13]. Homogeneous mixtures of 35.6 w% SDS, 9.2 w% pentanol and 55.2 w% water were prepared by weighing in test-tubes the appropriate amounts of chemicals and mixing them first with a spatula, then with a vortexer. Before use, the test-tubes were left to stand several weeks until the mixtures were completely transparent.

Aligned samples of the hexagonal phase were obtained in flat optical glass capillaries (Vitro Com Inc., Mountain Lakes, NJ, USA), of thicknesses 50 or $100\ \mu\text{m}$, according to a procedure described in the next section and observed in polarized light with an Olympus BH2 microscope. Textures were photographed using an Olympus

camera. The microscope was also equipped with a Mettler heating stage.

Preliminary X-ray scattering experiments were performed in our laboratory using a rotating anode setup ($\lambda\ \text{CuK}\alpha = 0.154\ \text{nm}$). The X-ray beam delivered by the anode is punctually focused by two perpendicular curved mirrors coated with a 60 nm nickel layer [14]. The mirrors cut the high energy radiations issued from the anode and a $20\ \mu\text{m}$ nickel foil filters the K_β emission line. The X-ray intensity at the sample level is about $10^7\ \text{photons/s.mm}^2$. The scattered X-rays were detected on imaging plates and the sample-detection distance was 50 cm. Exposure times were typically one hour.

Additional high resolution X-ray scattering experiments were performed at the synchrotron beamlines D23 at LURE in Orsay, France and D2AM at ESRF in Grenoble, France. Both beamlines have already been described in detail [15,16] and have very similar designs. The beam is first monochromatized by reflection on a flat Si (111) crystal and then focused in the horizontal plane by reflection on a curved Si (111) crystal. Moreover, the use of mirrors (one for D23 and two for D2AM) ensures the rejection of higher harmonics. On D23, the beam size was ($500\ \mu\text{m} \times 250\ \mu\text{m}$) at the sample level and a wavelength of $\lambda = 0.154\ \text{nm}$ was selected. The X-ray beam had a flux of a few $10^9\ \text{photons/s.mm}^2$. The sample was set at the center of a Huber diffractometer equipped with a crystal

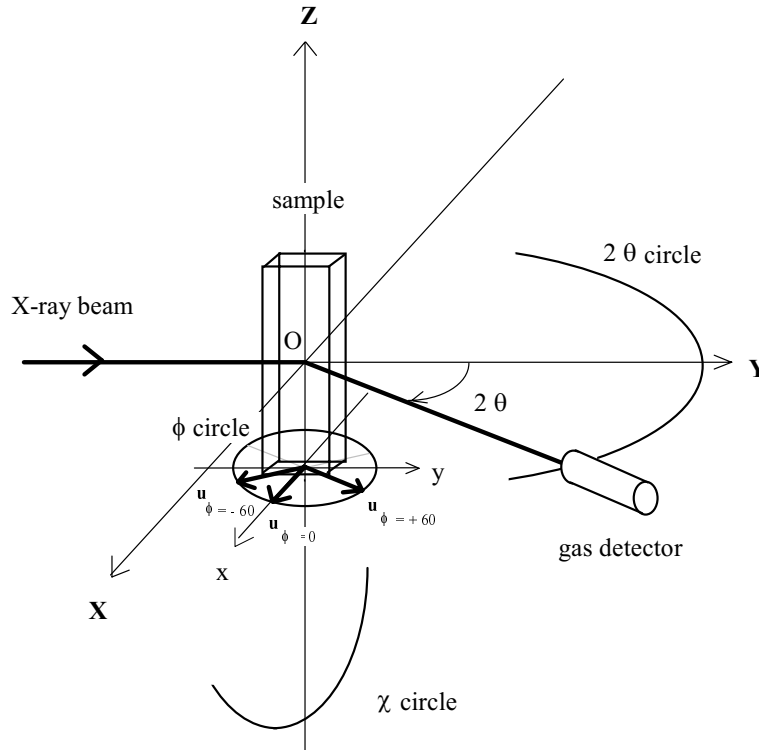


Fig. 2. Schematic drawing of the 4-circle X-ray scattering setup. The gas detector moves along the 2θ -circle in the OXY plane. Its position along the 2θ -circle selects the value of Q . The sample is oriented by using two circles: the χ -circle in the OXZ plane and the ϕ -circle in the OXY plane. The position $\chi = 0$ and $\phi = 0$ corresponds to: (i) The Oz axis of the capillary is parallel to the OZ axis of the diffractometer; (ii) The (10) reticular planes of the 2 - d hexagonal lattice lying parallel to the flat plates of the capillary are in reflection position.

analyzer. On D2AM, the beam size was $(250\ \mu\text{m})^2$ at the sample position and a wavelength $\lambda = 0.1549\ \text{nm}$ was selected. The X-ray beam in single bunch mode had a flux of a few 10^{10} photons/s.mm². This line is equipped with a “7-circles” diffractometer (Microcontrole, France) which we used in a conventional “4-circles” configuration. On both beamlines, the scattered X-rays were detected either with a Bicorn point-detector or using imaging plates fixed onto the analyzer arm. The resolution of the X-ray scans was $\delta Q \cong 7 \times 10^{-3}\ \text{nm}^{-1}$ (FWHM) with the D23 setup and $\delta Q \cong 1.4 \times 10^{-2}\ \text{nm}^{-1}$ with the D2AM setup (where Q is the scattering vector of modulus $Q = (4\pi \sin \theta / \lambda)$ and 2θ is the scattering angle). X-ray scans and imaging plate exposures typically required about ten minutes on D23 and two minutes on D2AM. For temperature control, we also used on D2AM a home-made oven and a computer-driven temperature controller.

3 Sample alignment and characterization

Aligned samples were prepared in a very straightforward and reproducible way according to the following procedure. The test tube is first mildly centrifuged upside-down so as to collect all the material at its neck. Meanwhile, the tip of a flat optical glass capillary, of thickness $100\ \mu\text{m}$, is connected to a small primary vacuum pump through a

rubber hose equipped with a valve. The other tip of the capillary is then dipped into the material and the vacuum pump turned on. The material is thus sucked into the capillary at a speed controlled by the valve. When there is enough material in the capillary, the tip is taken out of the test tube and the material is centered inside the capillary. Usually, the whole process only takes a few seconds. At this point, the vacuum pump can be disconnected and the capillary is flame-sealed at each end.

Immediate inspection of the capillaries by polarized light optical microscopy reveals that the hexagonal phase is highly aligned, in spite of a few defects distributed at random. The capillaries are uniformly bright when their main axis lies at an angle of 45° with respect to those of the polarizer-analyzer system and are dark when they lie parallel to the polarizer-analyzer directions. A more careful examination shows a system of stripes. This system becomes more regular whereas the random defects tend to disappear as the samples anneal over several days (Fig. 1). This procedure takes place at room temperature and obviously will require modifications to be applied to mesophases stable at higher temperatures only.

These samples have been characterized by X-ray diffraction on the LURE D23 beamline in order to fully determine the hexagonal lattice orientation with respect to the capillary axes and the mosaic distributions (Figs. 2 and 3). As inferred from the optical experiments, we

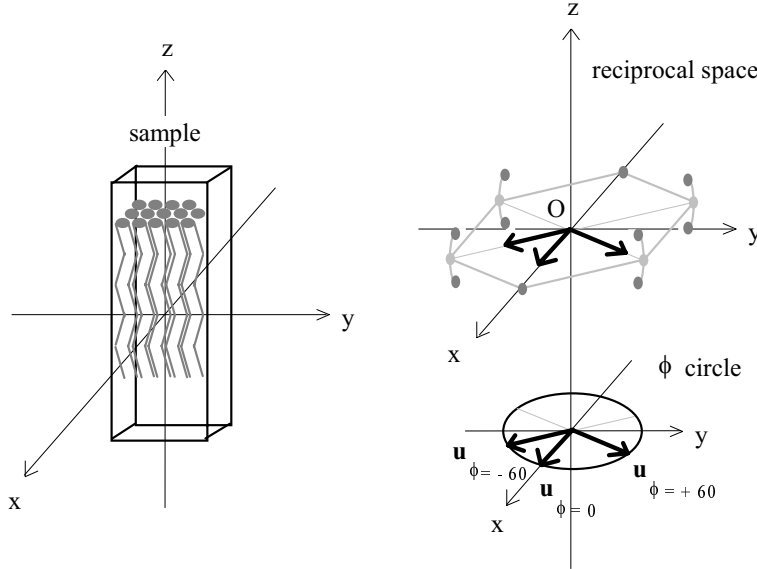


Fig. 3. Diffraction by an aligned sample. The average direction of the columns is along Oz , the direction of the capillary axis. Because of the strong anchoring of a family of (10) reticular planes on the flat walls of the capillary, the direction Ox ($\phi = 0$) corresponds to a Bragg reflection. Two other Bragg reflections are recorded for $\phi = 60^\circ$ and $\phi = -60^\circ$, as expected for a hexagonal C_6 axis along Oz . On heating, the thermomechanical instability is observed in the reciprocal space. Each Bragg spot at $\phi = 60^\circ$ and $\phi = -60^\circ$ splits into two spots, corresponding to the two types of domains of the zig-zag texture. The Bragg spot at $\phi = 0^\circ$ is not affected, showing that the zig-zag texture only develops within the Oyz plane.

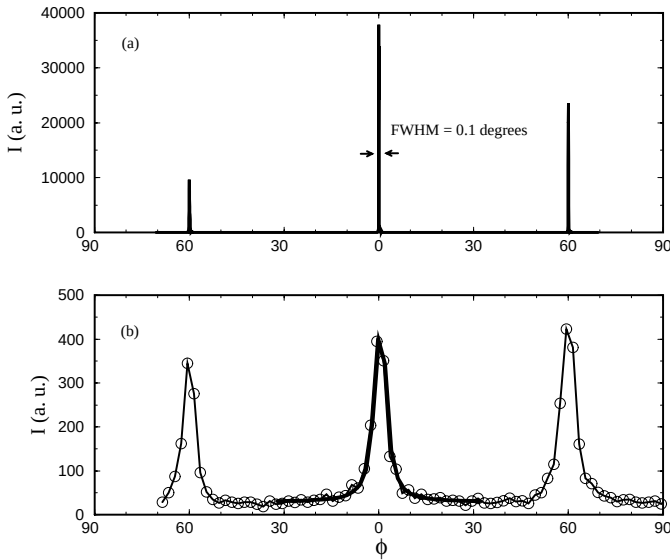


Fig. 4. ϕ -scans at room temperature of an aligned sample. (a) ϕ -scan at $Q = Q_{\text{Bragg}} = 1.542 \text{ nm}^{-1}$. Three Bragg peaks at $\phi = -60^\circ$, $\phi = 0^\circ$ and $\phi = 60^\circ$ with a FWHM of 0.1° are recorded. The three peaks have different intensities essentially because the OZ diffractometer axis and the Oz sample axis are not perfectly parallel. (b) ϕ -scan at $Q = Q_{\text{Bragg}} + \Delta Q$, with $\Delta Q/Q_{\text{Bragg}} = 2.4\%$. The thermal diffuse scattering signal (see Sect. 4) of each peak is only recorded in this case. The fitted intensity using the continuum elastic model with $\alpha = 2.94$ is shown (thick solid line) for one Bragg spot. Intensity units are the same in (a) and (b).

observe that the C_6 axis is oriented along the capillary main axis Oz . Moreover, we also observe that a family of dense planes (10) of the hexagonal lattice lie parallel to the capillary flat walls. The azimuthal “ ϕ -scan” shown in Figure 4a is a scan for which $\mathbf{Q}$ describes a circle, of constant modulus Q_{Bragg} , going through the (10) reflections of the 2- d hexagonal lattice. Three (10) reflections can be seen equally spaced by 60° as expected and no other hexagonal domain can be detected. A more detailed scan allows us to measure the “ ϕ -mosaic” (*i.e.* the width of the ϕ distribution for all the crystallites in the X-ray beam), which is found to be 0.1° full width at half maximum (FWHM). The scan presented in Figure 4a is a typical one for samples prepared by this method. Poor samples may show a worse ϕ -mosaic that may reach up to 0.25° or several domains in the beam. Outstanding samples may have a ϕ -mosaic as low as 0.03° , a value quite unusual in the field of liquid crystals. This high quality is obviously related to the anchoring of the dense planes of the hexagonal lattice onto the flat walls of the capillary. Indeed, this anchoring is observed all along the length of the capillary over several centimeters. Therefore, the hexagonal lattice does not twist and keeps its azimuthal ϕ orientation as the capillary is scanned. In contrast, the polar “ χ -scans” (Fig. 5) do not show such a good mosaic. Typical values of the χ -mosaic lie in the range $5\text{--}10^\circ$ (FWHM) which could indeed be expected from the observation of the striated texture. Though these χ -mosaic values still compare quite reasonably with those reported in other previous studies, they will hamper more demanding investigations such as that of the diffuse scattering (Sect. 4).

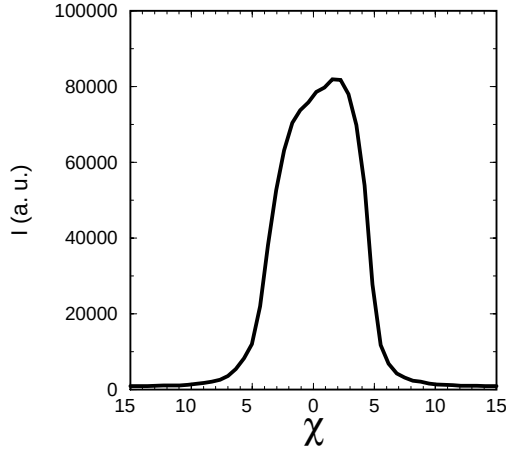


Fig. 5. X-ray scattered intensity along a χ -scan going through the (10) reflections at room temperature.

Finally, the 2θ -scans going through the (10) reflections of the 2- d hexagonal lattice show a resolution limited peak (Fig. 6). This observation proves that the hexagonal lattice has true long range order. The position of the peak at $Q_{\text{Bragg}} = 1.56 \text{ nm}^{-1}$ gives us the value of the hexagonal lattice parameter $a = 4.64 \text{ nm}$ at room temperature.

4 X-ray diffuse scattering

The good crystallographic quality of our samples allows us to perform more sophisticated studies such as that of the X-ray diffuse scattering. A cross section of the reciprocal space parallel to the C_6 axis (Fig. 7) shows a (10) Bragg spot in reflection condition on one side of the image and some additional diffuse scattering on the other side. Since the sample was held fixed during the experiment and its ϕ -mosaicity ($\cong 0.1^\circ$ FWHM) is much smaller than the scattering angle ($2\theta = 2.1^\circ$), the additional scattering cannot be due to another (10) reflection but must arise from fluctuations. This diffuse scattering is clearly anisotropic. In order to estimate this anisotropy, we show in Figure 8 the intensity profiles along the Q_z and Q_x directions, drawn from Figure 7, for the Bragg spot (Figs. 8b, 8d) and for the diffuse scattering (Figs. 8a, 8c). The distribution of diffuse scattering is wider along the Q_z direction (a) than along the Q_x direction (c). The widths of the corresponding profiles for the Bragg spot give the contributions of both the resolution and the mosaicity. When we take these effects into account, we estimate a factor of 10 for the anisotropy of the diffuse scattering in the Oxz plane. Since the sample mosaicity (“ χ -mosaic”) affects the intensity profile along Q_z , this measurement does not truly correspond to the case of a single domain. Therefore, this value of 10 should only be regarded as an order of magnitude.

In contrast, we consider that the diffuse scattering intensity measured in the Oxy plane is due to a single domain, because the value of the “ ϕ -mosaic” is very small and the 2θ -scans are resolution limited. Unfortunately, our sample geometry does not allow us to observe directly

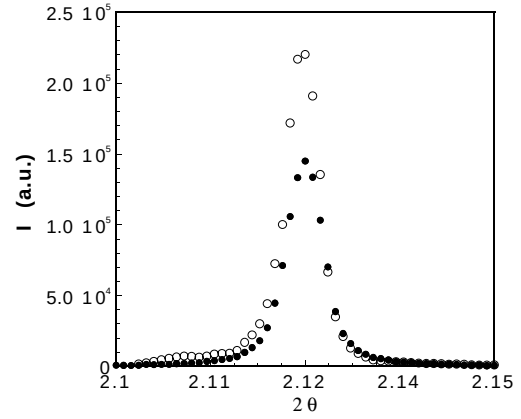


Fig. 6. X-ray scattered intensity along a 2θ -scan going through the (10) reflections (open circles) at room temperature compared to a scan of the direct beam (filled circles), which defines the experimental resolution.

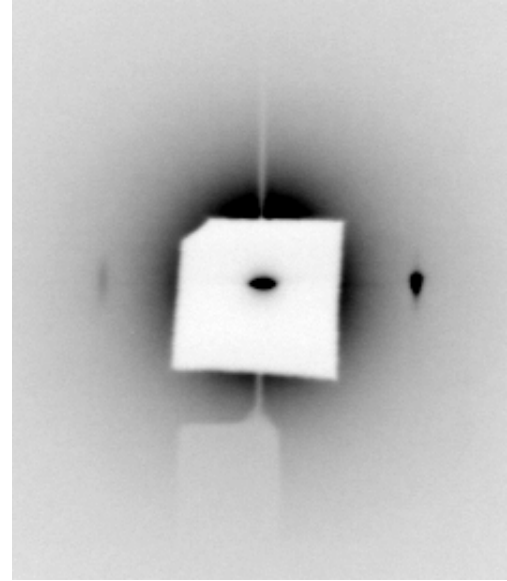


Fig. 7. 2- d image of the X-ray scattered intensity in the xOz plane. The Bragg reflection can be seen to the right of the beam-stop and the diffuse scattering signal to the left.

the Oxy reciprocal plane, because it is not possible to send the X-ray beam along the capillary axis. Nevertheless, we can perform, in this plane, different ϕ -scans at various scattering vector moduli Q (Fig. 4b) and build a complete intensity map at the vicinity of a Bragg spot (Fig. 9). The diffuse scattering intensity decreases quite rapidly as the scattering vector moves away from the Bragg condition.

In order to describe quantitatively these experimental results, we use an elastic continuum model detailed in [7c]. This model treats the fluctuations as elastic waves

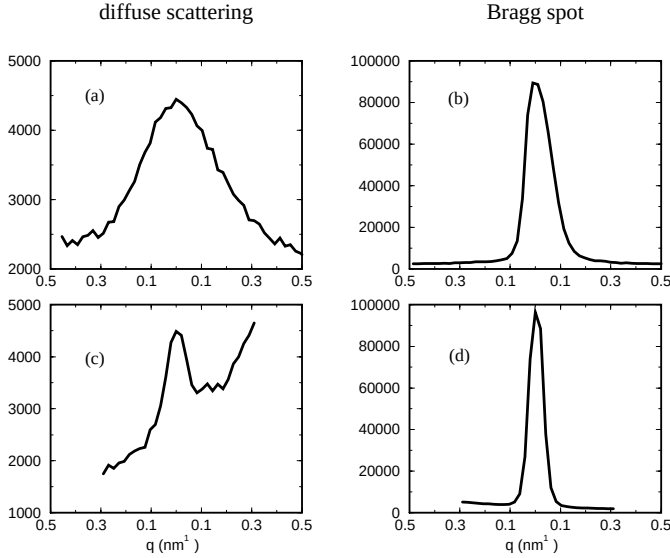


Fig. 8. Profiles derived from Figure 7 of the Bragg spot and the diffuse scattering. (a) Diffuse scattering along q_z . (b) Bragg spot along q_z . (c) Diffuse scattering along q_x . (d) Bragg spot along q_x .

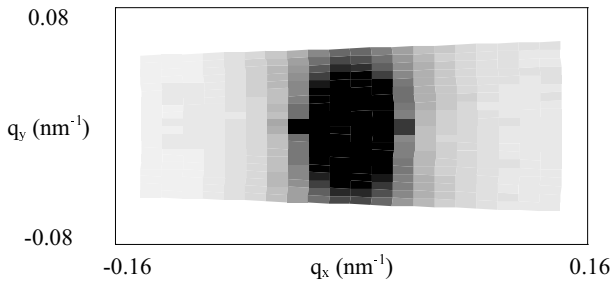


Fig. 9. Thermal diffuse scattering experimental map in the xOy plane. This map is obtained by varying the two angles 2θ and ϕ by constant increments. A linear gray scale is used to visualize clearly the distribution of the TDS.

governed by the following expression for the elastic energy density f [5, 12]:

$$f = \frac{1}{2}(\lambda + 2\mu) \left(\left(\frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial v}{\partial y} \right)^2 \right) + \lambda \frac{\partial u}{\partial x} \frac{\partial v}{\partial y} + \frac{1}{2}\mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)^2 + \frac{1}{2}k_3 \left(\left(\frac{\partial^2 u}{\partial z^2} \right)^2 + \left(\frac{\partial^2 v}{\partial z^2} \right)^2 \right)$$

where u and v are the two components of the displacement vector of an elastic wave along Ox and Oy respectively. k_3 is the Frank bend elastic constant of the columns. λ and μ are the Lamé elastic constants of the 2-dimensional hexagonal array, where $B = (\lambda + 2\mu)$ is the compressibility modulus and μ the shear modulus. It was shown [7c] that, for small $\mathbf{q}$ vectors, the diffuse scattering intensity

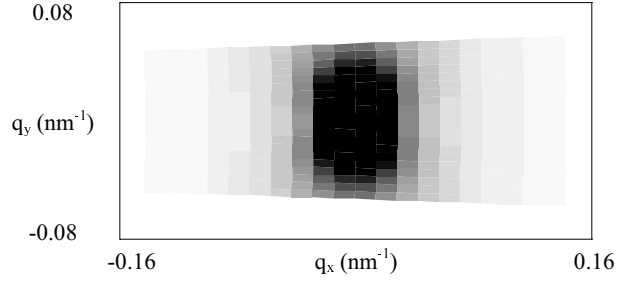


Fig. 10. Scattered intensities calculated using the elastic continuum model, with $\alpha = 3.01$, in order to fit the intensity map of Figure 9. The value of α is obtained from a linear fitting program, taking into account all the experimental points of Figure 9 (about 400 points), except a few points of very high intensities very close to the Bragg peak. The gray scales are the same in Figures 9 and 10.

at a vector $\mathbf{Q} = \mathbf{Q}_{\text{Bragg}} + \mathbf{q}$ reads:

$$I(Q) = \frac{A}{q_x^2 + q_y^2} \left(\frac{\alpha(Q_{\text{Bragg}}q_y)^2}{q_x^2 + q_y^2 + \alpha\Lambda_C^2 q_z^4} + \frac{(Q_{\text{Bragg}}q_x + q_x^2 + q_y^2)^2}{q_x^2 + q_y^2 + \Lambda_C^2 q_z^4} \right) + C$$

where $\Lambda_C = \sqrt{\frac{k_3}{\lambda + 2\mu}} = \sqrt{\frac{k_3}{B}}$ is a characteristic length of the hexagonal phase and $\alpha = \frac{\lambda + 2\mu}{\mu} = \frac{B}{\mu}$ ($2 \leq \alpha < +\infty$). A is a constant scaling factor and C is the background correction, supposed to be constant. In the Oxy plane, this formula simply reads:

$$I(Q) = \frac{A}{(q_x^2 + q_y^2)^2} (\alpha(Q_{\text{Bragg}}q_y)^2 + (Q_{\text{Bragg}}q_x + q_x^2 + q_y^2)^2) + C.$$

Using this expression for the intensity, we reach a very good description of our experimental results for a value of $\alpha = 3$ (Figs. 4 and 10). This value was obtained by calculating for each experimental point the values of q_x and q_y , and then using a linear curve fitting program to determine the values of A , α and C . Both for the ϕ -scan (Fig. 4b) and the intensity map (Fig. 10), the program gives for the best fit (least mean square criterion) the same value of $\alpha = 3$ with an error bar of a few percents. Therefore, by this method, we can give a measure of $\alpha = \frac{\lambda + 2\mu}{\mu} = \frac{B}{\mu}$, which characterizes the 2d elasticity of the hexagonal phase.

If we now come back to the diffuse scattering in the Oxz plane, the same model gives:

$$I(Q) = A \frac{(Q_{\text{Bragg}} + q_x)^2}{q_x^2 + \Lambda_C^2 q_z^4} + C$$

which shows that the length Λ_C is the only relevant parameter in this plane. We have explained above that the distribution of scattered intensity is anisotropic by about a factor 10 and oriented along Oz . A straightforward estimation then yields the value $\Lambda_C \cong 0.2$ nm.

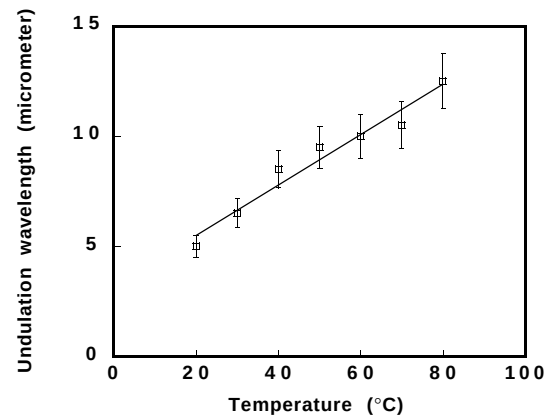
We have shown that the quality of our samples allows us to perform detailed diffuse scattering measurements, especially inside the *Oxy* plane. The continuum elastic model that we applied gives a very good description of the data and provides the value $\alpha = 3$. However, we can only estimate an order of magnitude of 0.2 nm for the characteristic length Λ_C . To conclude this section, we can compare these results to those obtained in similar previous studies of the hexagonal mesophase of thermotropic disk-like compounds [6a,7c]. Λ_C was of the same order of magnitude but the distributions of the TDS in the *Oxy* plane are quite different (compare for instance the ϕ -scans, Fig. 4 of [7c] to Fig. 4 in this paper). In the thermotropic hexagonal phase, the diffuse scattering extended far away from the Bragg peaks. In fact, the elastic continuum model only gives a good description of the scattering in this plane by the lyotropic hexagonal phase investigated in this paper.

5 Thermomechanical instability

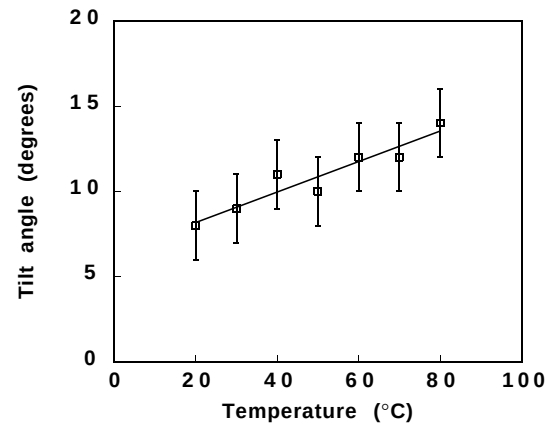
5.1 Optical microscopy experiments

As mentioned in Section 3, our samples present a striated texture when observed in polarized light microscopy. This striated texture occurs frequently in hexagonal mesophases and has already been reported by numerous authors [17]. Oswald *et al.* [12] have recently studied this texture in the lyotropic mixture ($C_{12}EO_6$, H_2O) and demonstrated that it results from a thermomechanical instability by which the columns show undulations or zig-zag conformations (Fig. 14). The mechanism of the instability is the following: on cooling, the hexagonal lattice parameter decreases and since the sample dimensions are kept constant, the hexagonal lattice is dilated. This dilation can relax either by climb of transverse edge dislocations or by tilting the columns so as to increase their transverse cross-section. The first mechanism does not seem to occur in lyotropic phases so that column undulations or zig-zags are readily seen. This phenomenon is very similar to the Helfrich-Hurault effect which takes place in smectics [5]. This instability was also recently detected by NMR experiments on sheared samples [17j].

In contrast to the samples studied by Oswald *et al.* [12], the instability in our samples appears on heating. This suggests that the hexagonal lattice thermal dilation coefficient of our samples is negative, a fact that we checked by X-ray diffraction (see below). Actually, even a very small temperature jump such as that achieved by merely breathing over the sample is enough to induce this instability. The sinusoidal undulations of the columns represent the linear regime of the instability whereas the zig-zag conformations represent the non-linear regime. Due to the small wavelength ($= 5 \mu m$ at room temperature) of the instability, it is difficult to differentiate these two regimes by optical microscopy. The only typical feature that we could detect is the appearance of a slight contrast in natural light in the zig-zag regime at high temperature. This contrast probably arises from the small den-



(a)



(b)

Fig. 11. (a) Wavelength Λ of the zig-zags *versus* temperature. (Error bars are estimated by taking into account the measurements dispersion over the particular sample shown in Fig. 1.) (b) Zig-zag angle θ *versus* temperature measured by the optical method developed in [12]. (Error bars essentially result from the accuracy of the determination of the maximum optical contrast.)

sity difference between the bulk material and that of the domain walls located between consecutive “zig” and “zag” domains. The maximum contrast of the texture (Fig. 1) in polarized light is obtained when the capillary main axis makes an angle $\pm \theta$ with the polarizer-analyzer system [12] where θ is either the undulation angular amplitude or the zig-zag angle.

Both the instability wavelength, Λ and θ depend on the dilation, γ , which in turn depends on the temperature. At room temperature, the values of Λ and θ measured on our samples show a rather large dispersion compared to those carefully grown by Oswald *et al.* This is not surprising because our samples are prepared in only a few seconds and probably have a much larger defect

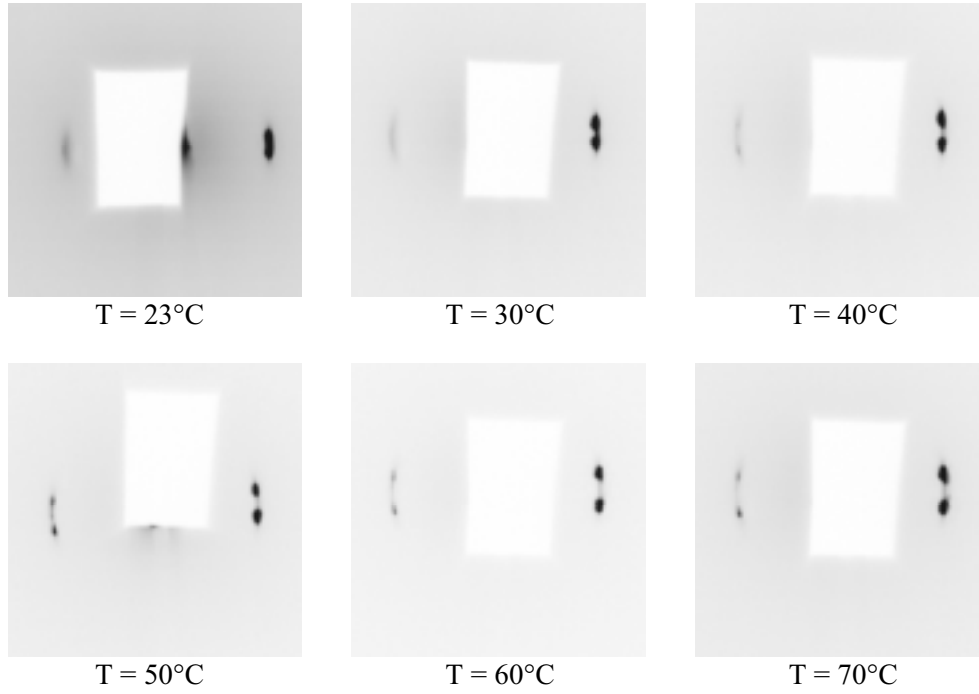


Fig. 12. Series of 2-d images of the X-ray scattered intensity in the xOz plane at different temperatures.

density. Typically, the values of θ range from 5° to 10° and those of Λ from 4 to $6\mu\text{m}$. These values vary from a sample to another. We measured Λ and θ as a function of temperature for a given sample using the optical methods developed by Oswald *et al.* [12] (Fig. 11). At each temperature, both Λ and θ reach their equilibrium value in a few minutes and do not evolve with time any further. θ increases regularly with temperature (heating rate: $\cong 1^\circ\text{C}/\text{min}$ from 20°C to 80°C) and therefore with dilation, in good agreement with the predictions of reference [12]. However, Λ increases by almost a factor of 3 in sharp contrast with the few % predicted by reference [12]. This discrepancy may be due to two reasons: firstly, we explore a quite larger temperature range and therefore we reach much larger dilation rates at which the model may not be valid any more. Secondly, it is possible that the behaviour of the elastic constant of compression, B , of our system differs from that of the system investigated in reference [12]. In fact, B can vary quite appreciably over the large temperature range of 50° that we have explored.

Besides, our samples are far from being defect-free. In particular, they show edge-dislocations in the system of stripes. As temperature increases and the wavelength Λ with it, these dislocations move as zippers across the sample width and suppress stripes. This phenomenon at the textural scale is similar to the climb of edge dislocations which is a classical plastic relaxation mechanism at the structural scale.

When the samples are cooled to room temperature, the optical contrast of the stripes gradually disappears, without any change of Λ until a completely aligned sample is obtained. This behaviour is observed for all cooling rates investigated, *i.e.* between 1 and $20^\circ/\text{min}$. However,

Table 1. Evolution with temperature of the sample of Figure 12. The hexagonal lattice parameter, a (nm), is measured from a 2θ -scan with the X-ray diffractometer. The zig-zag angle θ is measured from the image-plate recordings shown in Figure 12.

T ($^\circ\text{C}$)	23	30	40	50	60	70
a (nm)	4.640	4.605	4.591	4.576	4.565	4.543
θ ($^\circ$)	–	5.5	7	7.5	8.7	9

the completely aligned sample is very unstable, since any slight temperature increase brings about the instability again with the wavelength of $\cong 5\mu\text{m}$ usually measured at room temperature. Therefore, heating and cooling are not reversible processes but rather depend on the previous thermal history of the sample. This fact seriously hampers our quantitative analysis of this instability.

5.2 X-ray diffraction experiments

Table 1 clearly shows that the hexagonal lattice parameter decreases when the temperature increases, and this is the reason why the instability occurs in our samples on heating. The thermal expansion coefficient derived from Table 1 was found to be:

$$\frac{1}{a} \frac{da}{dT} = -3.3 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}.$$

This value is of the same order of magnitude as that measured on the $(\text{C}_{12}\text{EO}_6, \text{H}_2\text{O})$ system but it is of opposite sign.

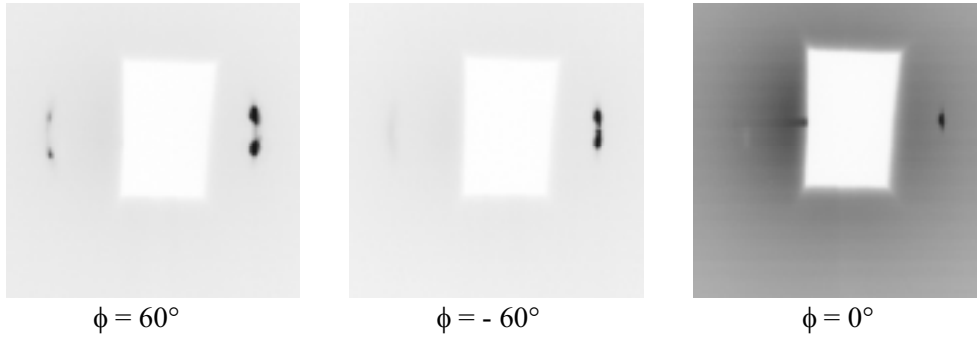


Fig. 13. 2-d images of the X-ray scattered intensity in planes parallel to Oz and: (a) at $\phi = +60^\circ$; (b) at $\phi = -60^\circ$; (c) at $\phi = 0^\circ$.

A temperature ramp from room temperature to 70°C is illustrated in Figure 12. At room temperature, one observes as expected the (10) hexagonal lattice reflection and its χ -mosaic which reaches a value of $\cong 8^\circ$ (FWHM) is affected by the column instability. This value is to be compared with the typical values of θ ($5\text{--}10^\circ$) measured by optical microscopy. As the temperature increases (heating rate $\cong 1^\circ/\text{min}$), the (10) reflection splits into two symmetrical spots. This splitting increases with temperature to reach a maximum value of $\cong 10^\circ$ at 70°C . Such a splitting can be interpreted as the superposition of the two (10) reflections of the two hexagonal lattices of the “zig” and “zag” domains. The splitting is therefore the defining X-ray scattering signature of the thermomechanical instability. We have checked (Figs. 3 and 13) that the (10) reflection at $\phi = 0$ is never affected by the instability. This means that, whatever the temperature and therefore the dilation of our samples, the columns remain parallel to the flat glass plates of the capillary. This is an important point put forward by Oswald *et al.* that is proved by our X-ray scattering experiments. On cooling (cooling rate $\cong 1^\circ/\text{min}$), the splitting decreases and finally vanishes so that the whole thermal behaviour seems qualitatively reversible, although a detailed comparison shows quantitative differences as discussed in the previous section.

At room temperature, when the tilt angle θ is small, it is actually as difficult to tell the difference between column undulations and zig-zags by X-ray scattering (see Appendix) as it is by optical microscopy. In ideal experimental conditions, (*i.e.* with no additional χ -mosaic, no instrumental broadening of any kind such as finite beam size, finite divergence, etc.) a zig-zag texture should show up on the X-ray scattering patterns by the appearance of two Bragg spots at $\chi = \pm\theta$. (A very similar phenomenon of electric-field-induced layer buckling in chiral smectic A liquid crystals was recently reported which also gave rise to a splitting of the smectic reflection observed by X-ray scattering [18].) In contrast, sinusoidal undulations should show up as a continuous distribution of scattering for $-\theta < \chi < \theta$, this distribution having peaks around $\pm\theta$. Non ideal experimental conditions will broaden the Bragg peaks of the zig-zags so that any tilt angle smaller than the angular broadening won’t be detected. Similarly, the continuous distribution of scattering of the undula-

tions will look like a broad featureless maximum of total width 2θ . Moreover, the columns being anchored along the z -axis ($\theta = 0$) at the glass surfaces, there are twist boundary layers in which the tilt varies regularly from 0 to θ [12]. The thickness of these layers decreases with increasing dilation so that at room temperature their contributions to the scattering at $\chi = 0$ may be important. Experimentally, at room temperature, we observe a broad reflection (Fig. 5) which therefore may be either due to zig-zags of small tilt angle or due to undulations. We tend to favour the undulation model for the following reasons. i) The undulations represent the linear regime valid at the onset of the instability, that is at small dilations γ . ii) The tilt angle measured optically at room temperature is at least 5° , a value that should induce a detectable splitting of the reflection in the case of zig-zags. iii) We have not observed any contrast due to domain walls in natural light by optical microscopy at room temperature. However, the quality of our samples does not really allow us to reach a definitive answer to this question. Nevertheless, at high temperature, the scattered intensity at $\chi = 0$ falls down to the background level which clearly indicates that the non-linear zig-zag regime prevails.

6 Conclusion

We have described a very simple, useful and cheap method for producing highly aligned samples of a hexagonal liquid-crystalline phase, suitable for detailed X-ray analysis. Preliminary experiments show that this method also efficiently applies to the hexagonal phase of other materials such as non-ionic surfactants (C_{12}EO_6 , H_2O) and diblock copolymers. We are therefore confident that this simple technique will prove useful to investigate very different systems. The production of a highly aligned sample allowed us to record the thermal diffuse scattering intensity. Its good description by a simple elastic continuum model provided estimates of the characteristic mechanical parameters of the mesophase ($\alpha = 3$ and $\Lambda_C \cong 0.2\text{ nm}$) in agreement with other estimates previously derived from X-ray scattering studies and analysis of textures. However, for this lyotropic phase, the distribution of the TDS in the hexagonal plane is highly localized close to the Bragg

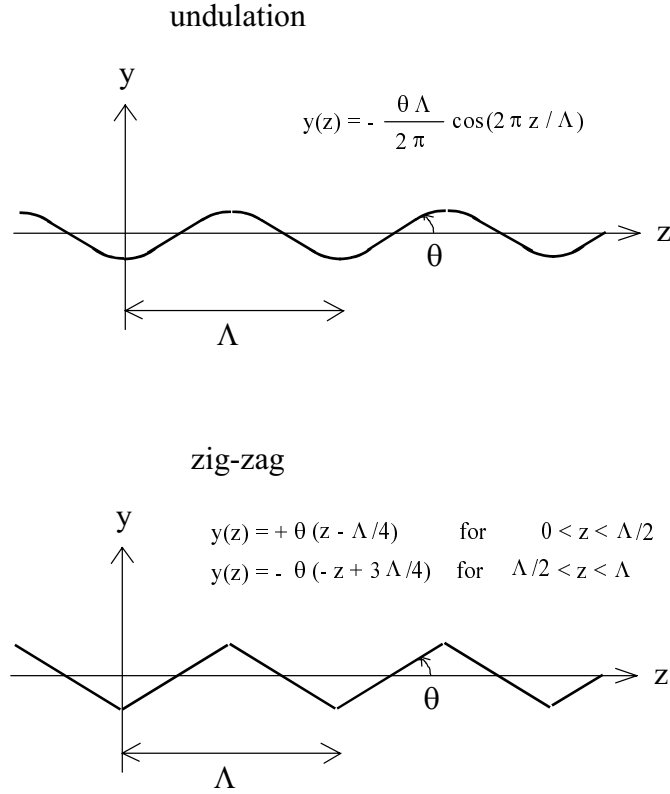


Fig. 14. Profiles $y(z)$ of the molecular columns for the two models. For the undulation model, the profile is taken as a cosine wave. The two parameters, Λ and θ define the amplitude along the Oy direction.

peaks, a result in sharp contrast to thermotropic hexagonal phases for which the TDS extended far away from the reflections. We presently do not understand the origin of such a variation between the two kinds of materials. Clearly, the study of other hexagonal mesophases is required to try to solve this question and we hope that this aligned domain growth technique will prove useful to achieve this task. Finally, we completely confirm the analysis of the thermomechanical instability presented by Oswald *et al.* [12]. Moreover, we have detected the X-ray signature of the instability in the fully developed, non-linear regime as a splitting of four of the six hexagonal Bragg peaks and demonstrated that the instability remains confined in the plane parallel to the flat glass plates of the capillary. It should be here noted that the appearance of this striated texture, when it is uniform over a large distance, indicates that the sample observed is highly aligned.

We are deeply indebted to J.C. Geminard, P. Oswald, J. Prost, L. Sallen and J. Selinger for pleasant and enlightening discussions. J.F. Berar, M. Gailhanou and S. Lefebvre are warmly thanked for taking part in the synchrotron X-ray scattering experiments at LURE and ESRF. We are also grateful to S.H.J. Idziak and C.R. Safinya for drawing our attention to this particularly interesting lyotropic system.

Appendix: Undulation or zigzag?

Two models are proposed for the striated texture (Fig. 14):

- Undulations of infinite columns following a sinusoidal profile, with a maximum angular amplitude θ .
- The so-called “zigzag” configuration resulting from the periodic stacking of tilted “zig” and “zag” domains, at the angles θ and $-\theta$, with walls between two adjacent domains.

A χ -scan of a Bragg peak (at $\phi = 60^\circ$ or $\phi = -60^\circ$) is directly related to the bulk distribution of the tilt-angle of the columns inside the sample. In order to try to discriminate between the undulation and the zigzag models, we will calculate in this appendix the intensity profile of a χ -scan for both models.

We assume that the undulation or the zigzag is located in the Oyz plane and we approximate a χ -scan to a scan along the Oz direction. For both models, all the columns have the same profile $y(z)$, which is periodic along z with a period Λ . Since the tilt angle is small, we can identify dy/dz to the tilt angle at a given point of the profile. The intensity of a χ -scan reads:

$$i(\chi) = (1/\Lambda) \int_0^\Lambda \delta(\chi - dy/dz) dz.$$

The expressions of $i(\chi)$ for the two models are:

- Zigzag model:

$$i^{z-z}(\chi) = \frac{1}{2}(\delta(\chi - \theta) + \delta(\chi + \theta)).$$

- Undulation model:

$$i^{\text{und}}(\chi) = \frac{1}{\pi \sqrt{\theta^2 - \chi^2}} \quad \text{for } |\chi| < \theta \quad \text{and}$$

$$i^{\text{und}}(\chi) = 0 \quad \text{for } |\chi| \geq \theta$$

$i^{z-z}(\chi)$ and $i^{\text{und}}(\chi)$ both have singularities at $\chi = \theta$ and $\chi = -\theta$. Since the experimental χ -scans show wide peaks of several degrees (FWHM), then we have to consider a superposition of undulations or zigzags rather than the ideal situation depicted in Figure 14. We can consider different origins for this superposition.

First, we consider the influence of the mosaicity, assuming that the sample is made of several domains, slightly disoriented around the z direction, and describing this disorientation by a Gaussian distribution $f(\chi)$: in this case, we assume that the maximum tilt angle θ is the same for all the domains.

The total intensity is the convolution product of $i(\chi)$ by the Gaussian distribution $f(\chi)$:

$$I_{\text{mos}}(\chi) = \int_{-\infty}^{+\infty} i(X) f(\chi - X) dX \quad \text{with}$$

$$f(\chi) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\chi^2}{2\sigma^2}\right).$$

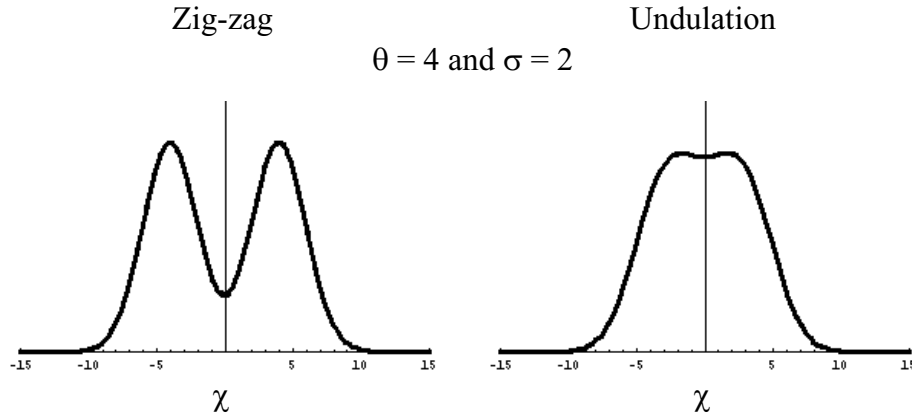


Fig. 15. Simulated χ -scans calculated in the frame of the zig-zag and undulation models for $\theta = 4$ and $\sigma = 2$. The undulation model is the only one able to reproduce the shape of the experimental χ -scan of Figure 5.

We could also consider the influence of other factors such as a distribution $P(\theta)$ of the maximum tilt angle θ around an average value for instance. In this case, the calculations lead to results that are quite similar to those derived above by studying the influence of mosaicity, so we will only take the mosaicity distribution into account.

We obtain the two following expressions:

– For the zig-zag model:

$$I^{z-z}(\chi) = \frac{1}{2\sqrt{2\pi}\sigma} \times \left(\exp\left(-\frac{(\chi - \theta)^2}{2\sigma^2}\right) + \exp\left(-\frac{(\chi + \theta)^2}{2\sigma^2}\right) \right).$$

– For the undulation model:

$$I^{\text{und}}(\chi) = \int_{-\theta}^{+\theta} \frac{1}{\pi\sqrt{\theta^2 - X^2}} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(\chi - X)^2}{2\sigma^2}\right) dX.$$

This last expression is numerically evaluated using the MATHEMATICA 3.0 software, for different combinations of the two parameters θ and σ .

Figure 15 shows numerical simulations using the above two expressions for the experimental χ -scan of Figure 5. The width of this experimental profile is 8° (FWHM). On the one hand, the value of θ cannot be larger than 4° because otherwise the total width of the profile would be larger than 8° . On the other hand, we never measured by optical microscopy a value of θ smaller than 4° . So we choose $\theta = 4^\circ$ for the simulation. Then, we examine the influence of the second parameter σ . For the zig-zag model, one obtains either a splitted profile (Fig. 15) or, by increasing the value of σ , a single large peak of width much larger than 8° however. For the undulation model, the value $\sigma = 2$ provides a good description of the experimental profile. Values of σ larger than 2 increase the total width of the profile without changing its shape. For values of σ smaller than 2, the shape of the profile is slightly modified, with a decrease of the intensity around $\chi = 0$.

To conclude, we see that the undulation model is the only one which can reproduce the global shape of the χ -scan of Figure 5. Although both models are strongly idealized, this nevertheless suggests that the instability is better described in terms of undulations at room temperature.

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Chapitre 19

Fluctuations en phase cubique bicontinue

L'étude des fluctuations structurales des phases cubiques est un sujet difficile, et peu de publications y sont consacrées, tant expérimentalement^{1,2} que théoriquement³. Notre contribution dans ce domaine a été de réaliser des expériences de dynamique d'une phase cubique bicontinue par diffusion quasi-élastique des neutrons (spin-écho) (publication [8] jointe).⁴ Les principaux résultats de cette étude sont rappelés ci-dessous.

Diffusion quasi-élastique des neutrons -spin-écho-

Publication [8]

collaboration avec Yolande Hendrikx (LPS) et Bela Farago (ILL)

La diffusion quasi-élastique des neutrons par la technique de spin-écho (NSE) permet de mesurer directement la fonction de diffusion $S(q,t)$ dépendante du temps, dans une gamme temporelle relativement étroite (quelques dizaines de ns).⁵ Afin de réaliser ces expériences, nous avons élaboré des mono-domaines de taille millimétrique de la phase bicontinue Ia3d du système binaire $C_{12}EO_6$ /eau.⁴ Grâce à l'obtention de mono-domaines, il est possible d'analyser séparément dans l'espace réciproque l'intensité diffusée entre des pics de Bragg (pics 211 et 220, voir les chapitres 9 et 16). L'intensité diffusée entre ces pics de Bragg est confinée dans des plans diffus, et est visible également en diffusion des rayons X. L'existence de ces plans diffus est reliée à des fluctuations structurales. La position de ces plans dans l'espace réciproque permet d'établir que ce sont des rangées périodiques de nœuds des labyrinthes (ou de manière équivalente de points plats de la surface G) le long des axes d'ordre 3 qui fluctuent en bloc, en se translatant principalement le long de ces axes 3.

Le résultat important obtenu par NSE est que ces fluctuations sont de nature dynamique. On a pu mesurer la fonction de diffusion $S(q,t)$ pour différents modules du vecteur q dans un plan diffus, et modéliser par une exponentielle la décroissance temporelle de $S(q,t)$. Le coefficient effectif de diffusion D_{eff} utilisé est de l'ordre de $3-5 \cdot 10^{-11} \text{ m}^2/\text{s}$. De plus, la variation de $1/D_{\text{eff}}$

en fonction de q présente un minimum au niveau de maximum de l'intensité diffusée. Ce comportement qualitatif (connu sous le nom de « De Gennes narrowing » dans les liquides) est en accord avec des modes de relaxation collectifs.

D'autre part, l'existence des plans diffus est une constante de la phase bi-continue Ia3d. En effet, les mono-domaines des différentes phases thermotropes que nous avons étudiés présentent tous ce phénomène. Les fluctuations sont donc probablement toujours du même type, et même si les expériences de NSE ont été réalisées sur un système lyotrope bien particulier ($C_{12}EO_6$ /eau), on peut raisonnablement généraliser le résultat de la nature dynamique des fluctuations aux phases thermotropes.

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Dynamics of a Lyotropic Cubic Phase

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Abstract. — We study the cubic phase made of the non-ionic surfactant $C_{12}(EO)_6$ in presence of water. The 3D periodic structure of this phase is characterized by the space group Ia3d. This structure corresponds to a centred cubic phase where the surfactant molecules build two identical 3D periodic interwoven labyrinths separated from each other by a continuous water medium. We present recent results obtained at I.L.L. on the Spin Echo spectrometer IN 11. Our experiments show for the first time, the dynamical character of the fluctuations observed in the investigated cubic phase. Therefore measurement have been performed on a single crystal ($\sim 0.1 \text{ cm}^3$). The time dependent diffusion function $S(\mathbf{q}, t)$ has been measured for different scattering vectors $\mathbf{q}$. For $\mathbf{q}$ vectors which do not correspond to Bragg peaks, the neutrons are scattered according to a quasi-elastic process and the associated $S(\mathbf{q}, t)$ function decreases with a characteristic time of about 20 ns. The dynamical fluctuations are most probably related to collective deformation modes of the labyrinths.

Résumé. — Nous étudions la phase cubique du système binaire $C_{12}(EO)_6$ /eau. La structure périodique tridimensionnelle de cette phase correspond au groupe d'espace Ia3d. Dans ce cas, la phase cubique est centrée et les molécules de surfactant s'organisent en deux labyrinthes tridimensionnels interpénétrés, séparés par un milieu continu d'eau. Nous présentons des résultats récents obtenus en utilisant le spectromètre spin-écho IN 11 à l'I.L.L. Nos expériences ont permis de mettre en évidence, pour la première fois, le caractère dynamique des fluctuations observées dans la phase cubique étudiée. Pour ce faire, des mesures ont été effectuées sur un monocristal ($\sim 0,1 \text{ cm}^3$). La fonction de diffusion $S(\mathbf{q}, t)$ a été mesurée pour différents vecteurs de diffusion $\mathbf{q}$. Pour des vecteurs $\mathbf{q}$ qui ne correspondent pas à des réflexions de Bragg, la diffusion des neutrons est quasi-élastique et la fonction associée, $S(\mathbf{q}, t)$, décroît avec un temps caractéristique d'environ 20 ns. Les fluctuations dynamiques sont probablement apparentées à des modes collectifs de déformation des labyrinthes.

This paper is the last contribution of Yolande Hendrikx, who departed from this life on March, the 28th 1997. We would like to dedicate this article to her memory.

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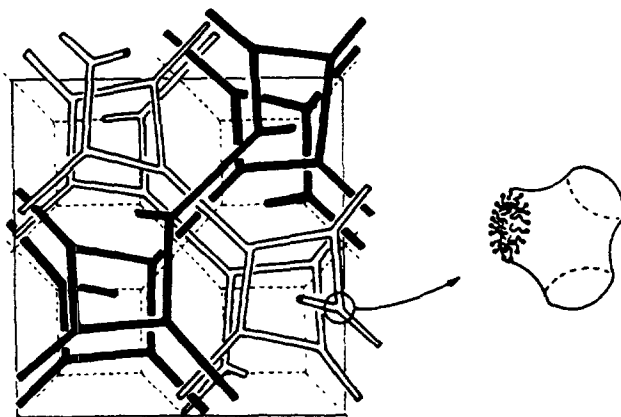


Fig. 1. — The direct bicontinuous cubic phase of space group $Ia3d$ [6]. The surfactant molecules are building two equivalent infinite periodic 3D-labyrinths, one drawn with black lines, the other with white lines. The surfactant rods meet three by three at the vertices of the labyrinths. The two labyrinths are separated by an infinite periodic water film, that can be described using the Schoen Gyroid I.P.M.S. (this water film is not represented here). Two cubic unit cells are drawn along the vertical axis. The unit cell parameter, a , equals $110 \text{ \AA}$ in the case of our $C_{12}EO_6$ /water sample.

1. Introduction

Bicontinuous cubic phases of surfactants or lipids in presence of water are now well-described [1–4]. They are direct or inverse and their extension domain (concentration and temperature ranges) as well as their location in phase diagrams depend on the involved surfactant molecules. At the macroscopic level, they are very viscous and optically isotropic. Their microscopic structure can be determined mainly using X-ray scattering or in some cases by image-filtering analyzes of freeze-fracture electron micrographs. A 3D-periodic order, characterized by a cubic unit cell, which results from the segregation of the surfactant molecules in water, is observed. In the case of a direct bicontinuous cubic phase, a water film separates two equivalent 3D-labyrinths formed by the so-called surfactant “rods” (see Fig. 1). In the symmetrical situation of an inverse bicontinuous cubic phase, the lipid molecules are building an infinite 3D-periodic fluid bilayer that separates two equivalent continuous water media. In both cases, the continuous medium (water film or surfactant bilayer) can be described using an infinite periodic minimal surface I.P.M.S. [3, 4]. Several cubic space groups are known ($Ia3d$, $Pn3m$, $Im3m$), corresponding to three different I.P.M.S. (the Schoen Gyroid, the Schwarz F surface, the Schwarz P surface); the respectively associated 3D-labyrinths are formed by rods with different connectivities (3, 4 and 6). In the case of the $Ia3d$ cubic phase, shown in Figure 1, the connectivity of each system of rods is 3.

These fascinating structures are of course not solid like, because both the water molecules and the surfactant molecules are in the liquid state. But they also exhibit a true 3D long range order at the mesoscopic scale. So one expects an unusual dynamical behaviour, as shown for instance by some theoretical predictions [5]. To our knowledge, we describe in this paper the first experiment that gives access to the dynamical fluctuations of a bicontinuous cubic phase.

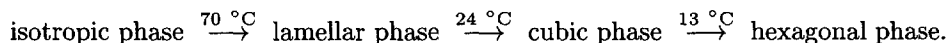
We used the binary mixture of the non-ionic surfactant $C_{12}EO_6$ with water, which exhibits a $Ia3d$ direct bicontinuous cubic phase (see Fig. 1). This system has been extensively studied

[6–8], because large single domains of the cubic phase can grow quite easily [8]. It is then possible to do an X-ray scattering experiment on a single cubic “crystal” [6, 7]. X-ray patterns reveal intense diffuse scattering streaks in-between some Bragg peaks, showing that fluctuations of the average structure take place. These fluctuations are inherent to the cubic phase as they are observed far from any phase transformation. In order to elucidate the nature of these fluctuations, static defects or dynamical deformations, we decided to realize a neutron scattering experiment using the Neutron Spin Echo spectrometer at I.L.L., Grenoble. First, we will describe how we obtained a sufficiently large single cubic domain. Then, we will give the analysis of the scatterings of this single domain thanks to the Neutron Spin Echo technique.

2. Experimental

2.1. SAMPLE PREPARATION. — In order to obtain the best signal to noise ratio required for our neutron experiments, $C_{12}EO_6$ molecules with perdeuterated alkyl chains are needed. Therefore such molecules were specially synthesized [9]. The deuteration of the alkyl chain appears to affect only very slightly the concentration range and the temperature range where the cubic phase is identified. The cubic phase has been prepared by mixing the $C_{12}EO_6$ molecules, either with D_2O , or a mixture of H_2O and D_2O which scattering length density matches that of the polar heads. The experiments which we are dealing with, concern the cubic phase prepared with such a water mixture. In order to match the scattering length density of the polar heads one must take into account the isotopic exchange between H and D which occurs for the terminal alcohol group of the polar heads and the isotopic purity of the deuterated water we used (99.98%). We thus prepared a water mixture of H_2O and D_2O , with a molar ratio $H_2O/D_2O = 4.42$. The calculated scattering length densities are then, $0.679 \times 10^{10} \text{ cm}^{-2}$ for water and $0.687 \times 10^{10} \text{ cm}^{-2}$ for the polar heads. That of the deuterated alkyl chains is equal to $7.02 \times 10^{10} \text{ cm}^{-2}$ and we may infer that when the perdeuterated $C_{12}EO_6$ molecules are mixed with the above water mixture only the alkyl chains are labelled for the neutron scattering. According to its composition, the molar ratio of our sample was, $(H_2O + D_2O)/C_{12}EO_6 = 14.60$. When equilibrium is achieved, the sample is homogeneous and forms a cubic phase at 20 °C.

At the above concentration, the following phase sequence *versus* temperature is observed [7]:



For our neutron experiments, we used a square quartz cell ($30 \times 30 \text{ mm}^2$) with a thickness of 1 mm. To fill it, the mixture was first heated in the isotropic phase and then rapidly introduced inside the cell. The cell was closed by Teflon plugs and sealed with glue. In order to allow the growth of large single cubic domains inside the cell, the sample was cooled very slowly (0.3°C per hour) from the isotropic phase (75°C) down to the cubic phase (21°C). During this controlled cooling process, the cell was observed between crossed polarizers [10].

As already mentioned, the cubic phase is optically isotropic and appears homogeneously black in polarized light (see Fig. 2). When it is cooled below 13°C , it transforms into an hexagonal phase, according the above phase sequence. The hexagonal phase is birefringent (uniaxial medium) and one can observe its texture which presents large homogeneous domains inside the cell (see Fig. 2). Our previous study of the cubic/hexagonal phase transition [7] together with this observation allowed us to infer precisely the location of cubic single domains.

The sample was finally kept in the cubic phase at 21°C during several weeks until the neutron experiment has been performed.

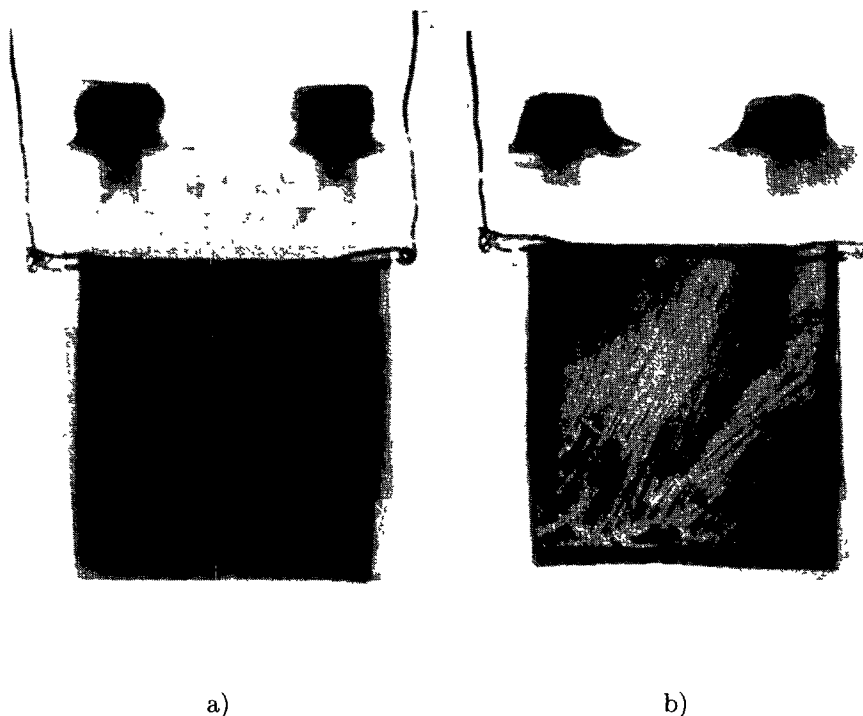


Fig. 2. — Photographs of the cell in-between crossed polarizers a) $T = 21\text{ }^{\circ}\text{C}$. One observes the cubic phase, which is optically isotropic. The cell appears homogeneously black. b) $T = 11\text{ }^{\circ}\text{C}$. One observes the hexagonal phase. The striated texture [7] allows to identify large homogeneous regions. The arrow indicates for instance the average orientation in the left upper part of the cell. In the lower part, small regions appear very dark, because their optical axes is almost perpendicular to the walls of the cell.

2.2. SMALL ANGLE NEUTRON SCATTERING. — The quality and the exact location of a single cubic domain was first checked by a small angle neutron scattering experiment (I.L.L., spectrometer D 17). The wavelength was equal to $\lambda = 8.5\text{ \AA}$ ($\Delta\lambda/\lambda = 10\%$) and the neutron beam cross-section to 0.2 cm^2 . The spectrometer is provided with a 2D-multidetector. The distance between the sample and the multidetector was 90 cm.

The sample holder, thermostated at $21\text{ }^{\circ}\text{C}$ using a water bath circulation, was mounted on a goniometric head. The latter could be translated and different regions of the cell could be explored. When a large homogeneous region was detected, different rotations of the sample allowed to identify different orientations of the single cubic domain with respect to the cell walls.

Figure 3a shows a diffraction pattern of the single cubic domain we studied. Several Bragg peaks are observed, and in-between, intense diffuse streaks, as expected from the previous X-ray scattering studies [6, 7]. Rocking-curves give an angular extension of 1.5° for the Bragg peaks. This corresponds to a value of residual mosaicity comparable to the experimental resolution. We have verified that the positions in the reciprocal space of the Bragg peaks correspond to the diffraction due to a unique cubic domain. The sample was then translated with steps of 5 mm and we measured a size of about 1 cm^2 for this domain, in agreement with our preliminary optical observations (see Sect. 2.1 or Fig. 2). This domain was then selected using

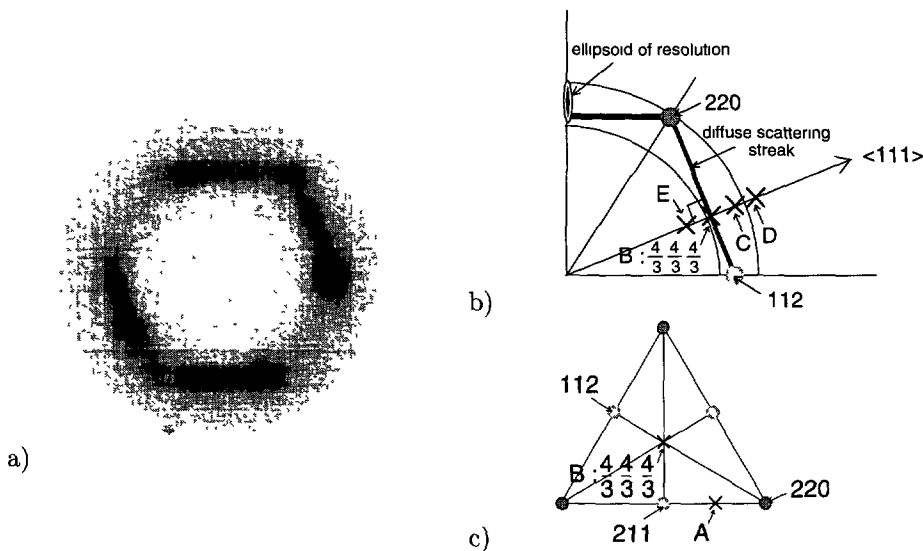


Fig. 3. — Small angle neutron scattering by the single cubic domain a) Pattern obtained on the 2D-multidetector at D 17 (I.L.L.). Single Bragg peaks are observed, all corresponding to (2 2 0) or (2 1 1) reticular planes of the cubic reciprocal lattice ($a = 110 \text{ \AA}$). In-between the 2 2 0 and 1 1 2 Bragg peaks, a diffuse scattering streak is observed. b) Part of the reciprocal space observed in 3ax. One can see that the size of the ellipsoid of resolution allows to detect for a same $|\mathbf{q}|$, Bragg peaks corresponding to (2 2 0) or (2 1 1) reticular planes. The vector $\mathbf{q} = \frac{2\pi}{a} \left(\frac{4}{3}, \frac{4}{3}, \frac{4}{3} \right) \text{ \AA}^{-1}$ corresponds to the maximum intensity, B, of the diffuse scattering along the $\langle 1 1 1 \rangle$ direction [6, 7]. The three crosses B, C, and D correspond to the three $\mathbf{q}$ vectors of Figures 5b, 5c and 5d. Point E was also investigated (see Tab. I). c) Reciprocal plane perpendicular to the $\langle 1 1 1 \rangle$ direction, where the diffuse scattering is located. Relative positions of A and B.

a cadmium mask so that the scattering area available for the neutron spin echo experiment was about 0.7 cm^2 .

2.3. THE NEUTRON SPIN ECHO EXPERIMENT. — Results of the study of the single cubic domain are given in Section 3. We will first summarize some experimental features of the neutron spin echo experiment. The method and the instrument are described in details elsewhere [11, 12].

A detector is movable in the horizontal plane in order to select the momentum transfer $|\mathbf{q}|$. From the small angle scattering experiment, we know the crystallographic orientation of the cubic single domain with respect to the quartz cell. Using the goniometric head, we can analyze the scattering at different $\mathbf{q}$ vectors of the reciprocal space.

We used polarized neutrons with $\lambda = 8.1 \text{ \AA}$ and $\Delta\lambda/\lambda = 18\%$ FWHM monochromatization. The angular divergence of the beam before the sample is about 0.5 degree and after the sample 1.0 degree, as determined by round diaphragms. This gives a relatively bad $|\mathbf{q}|$ resolution (18%) along the $\mathbf{q}$ scattering vector and a relatively good resolution in the perpendicular direction. This fact was taken into account by the so-called ellipsoid of resolution (see Fig. 3b). The energy resolution of the instrument was calibrated with a standard elastic scatterer.

In a neutron spin-echo experiment, the directly measured quantity is $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$, the normalized time dependent intermediate scattering function. The time t is varied by changing

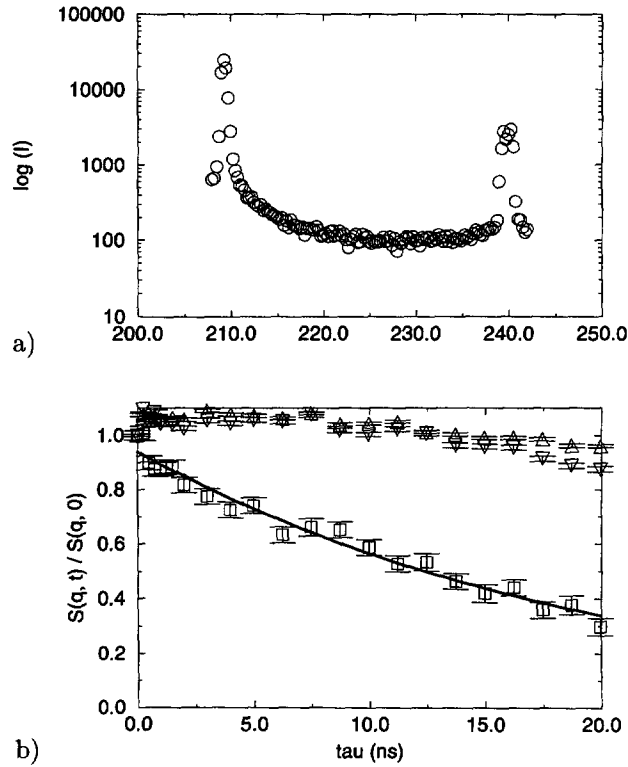


Fig. 4. — Comparison of the spin echo signal of a Bragg peak and of diffuse scattering. a) Intensity scan between the 2 1 1 and the 2 2 0 Bragg peaks (see Fig. 3c). As explained in Figure 3b, the size of the ellipsoid of resolution allows to detect these two Bragg peaks for a same $|\mathbf{q}|$ value. The X co-ordinate is the value of the angle of rotation of the cell around the vertical axis. In-between the two Bragg peaks, one measures the diffuse scattering contribution. b) $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ curves for the 2 1 1 Bragg peak, the 2 2 0 Bragg peak and point A. A mono-exponential decay time $\tau = 19.6 \pm 0.7$ ns is measured.

the field integral of the precession field [11,13]. In our case, the accessible time range was 0.25–20 ns. In the case of a pure elastic scattering, $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ does not decay but stays always equal to 1.0. If at least a fraction of the scattered intensity is quasi-elastic, with a time constant comparable to the instrumental window, this fraction of the observed signal will show some sort of decay.

3. Results

A suitable orientation of the cubic crystal was first checked performing an intensity scan by rotation of the sample around the vertical axis. The detector selects then a constant value of $|\mathbf{q}|$, chosen between $|\mathbf{q}_{211}|$ and $|\mathbf{q}_{220}|$. Indeed, the size of the ellipsoid of resolution (see Fig. 3b) allows to detect for this $|\mathbf{q}|$ value both Bragg peaks ($|\mathbf{q}_{220}| = \sqrt{\frac{8}{6}}|\mathbf{q}_{211}| \cong 1.155 |\mathbf{q}_{211}|$). Figure 4a shows the intensity scan at this $|\mathbf{q}|$ modulus and three $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ associated curves are shown in Figure 4b. The two sharp peaks of the intensity scan correspond to the

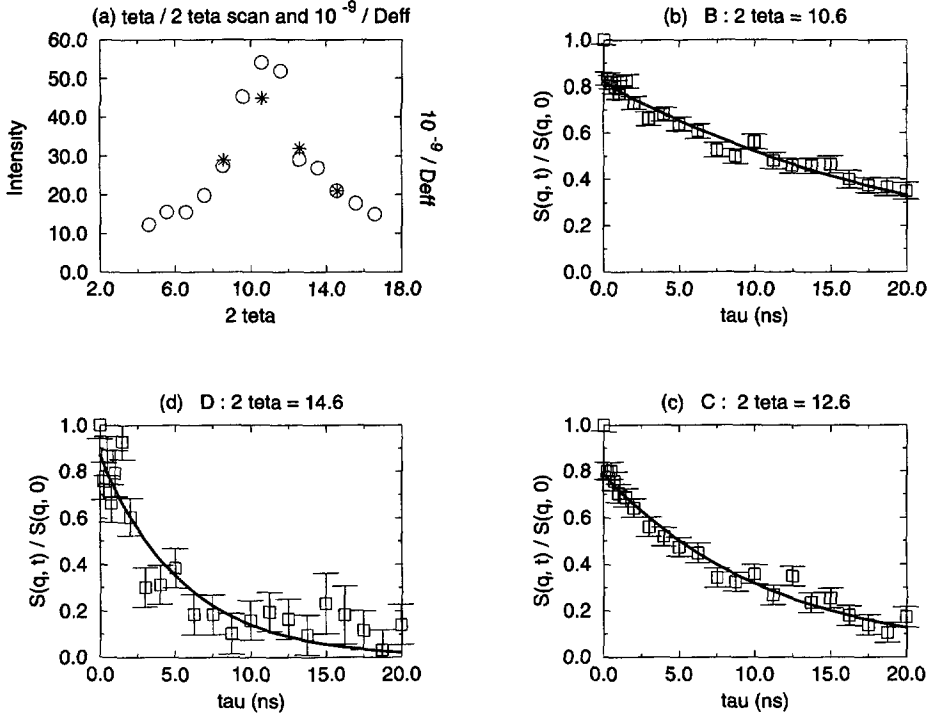


Fig. 5. — Spin echo signal along the $\langle 1\ 1\ 1 \rangle$ direction. a) $\theta/2\theta$ scan along the $\langle 1\ 1\ 1 \rangle$ direction. The maximum intensity of the diffuse scattering is measured for $2\theta = 10.6^\circ$, point B, corresponding to the vector $\mathbf{q} = \frac{2\pi}{a} \begin{pmatrix} 4 \\ 3 \end{pmatrix}, \begin{pmatrix} 4 \\ 3 \end{pmatrix}, \begin{pmatrix} 4 \\ 3 \end{pmatrix} \text{ \AA}^{-1}$. The stars correspond to $10^{-9}/D_{\text{eff}}$ ($\text{m}^{-2} \text{ s}$) ($D_{\text{eff}} = \frac{1}{\tau q^2}$, see Tab. I and Sect. 3). The intensity scale of the $\theta/2\theta$ scan has been adjusted in order to show its similar behaviour to the one of $1/D_{\text{eff}}$. b) $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ curve for $2\theta = 10.6^\circ$ (B). A mono-exponential decay time $\tau = 22.1 \pm 1.1$ ns is measured. c) $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ curve for $2\theta = 12.6^\circ$ (C). A mono-exponential decay time $\tau = 11.0 \pm 0.6$ ns is measured. d) $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ curve for $2\theta = 14.6^\circ$ (D). A mono-exponential decay time $\tau = 5.5 \pm 0.6$ ns is measured.

$2\ 1\ 1$ and the $2\ 2\ 0$ Bragg peaks. The $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ curves have been measured for $\mathbf{q}_{211}$, $\mathbf{q}_{220}$ and between both (point A in Fig. 4a), for $\frac{\mathbf{q}_{211} + \mathbf{q}_{220}}{2} = \frac{2\pi}{a} (2, 1.5, 0.5) \text{ \AA}^{-1}$. For the Bragg peaks, $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ is roughly equal to 1 at any time [14]. This means that the scattering originates from a purely elastic process. Contrariwise, the $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ curve at point A (Fig. 4a) decreases *versus* time. A quasi-elastic process is involved at this position, which corresponds to a diffuse scattering signal in-between the two Bragg peaks. Assuming a mono-exponential decay for $S(\mathbf{q}, t) = S(\mathbf{q}, 0) \exp(-t/\tau)$, we measure a decay time τ equal to 19.6 ± 0.7 ns.

We investigated a second direction of the reciprocal space, varying the value of the $|\mathbf{q}|$ modulus along the $\langle 1\ 1\ 1 \rangle$ axis (see Fig. 3b). No Bragg peak is crossed and only a diffuse scattering signal is measured. The $\theta/2\theta$ scan along the $\langle 1\ 1\ 1 \rangle$ axis is shown in Figure 5a. The maximum of intensity is obtained for $2\theta = 10.6^\circ$, at $\mathbf{q} = \frac{2\pi}{a} \begin{pmatrix} 4 \\ 3 \end{pmatrix}, \begin{pmatrix} 4 \\ 3 \end{pmatrix}, \begin{pmatrix} 4 \\ 3 \end{pmatrix} \text{ \AA}^{-1}$ [6, 7].

Table I. — *Spin echo measurements along the $\langle 1\ 1\ 1 \rangle$ direction. For the four points we investigated, τ is the time constant deduced from a mono-exponential fit. The quantity $D_{\text{eff}} = \frac{1}{\tau q^2}$ (Sect. 3) is calculated, in order to characterize furthermore the dependence of τ versus the $|\mathbf{q}|$ modulus.*

Echo points	E	B	C	D
2θ ($^\circ$)	8.6	10.6	12.6	14.6
$ \mathbf{q} $ ($\text{\AA}^{-1}$)	0.116	0.143	0.17	0.197
τ (ns)	21.5	22.1	11	5.5
$D_{\text{eff}} \times 10^{11} \text{ m}^2 \text{ s}^{-1}$	3.46	2.21	3.15	4.68
$10^{-9}/D_{\text{eff}} \text{ m}^{-2} \text{ s}$	29	45	32	21

Three $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ curves are shown in Figure 5. They correspond to three values of 2θ on the $\theta/2\theta$ scan (Fig. 5a): 10.6° (B), 12.6° (C) and 14.6° (D). The three curves are decreasing *versus* time. Again, we find that the scattering process is quasi-elastic when diffuse scattering is analyzed. Furthermore, the three curves do not extrapolate to 1 at $t = 0$ (Fig. 5). This means that about 20% of the intensity decreases with a time constant faster than our first point at 0.24 ns. This fast component can not be attributed to the scattering from the water. Indeed, solvent scattering is isotropic in this $|\mathbf{q}|$ range, while the diffuse scattering from the sample increases by a factor three between $2\theta = 14.6^\circ$ and $2\theta = 10.6^\circ$. This contribution can not come from the solvent, because its relative fraction would not remain always equal to about 20% for different $\mathbf{q}$ vectors.

The results concerning the slower decay are summarized in Table I, assuming again a mono-exponential decay for $S(\mathbf{q}, t)$. One observes a strong dependence of the time constant τ *versus* the $|\mathbf{q}|$ modulus. In order to analyse this dependence, the quantity $D_{\text{eff}} = \frac{1}{\tau q^2}$ is calculated [15]. In the case of a pure diffusive process, D_{eff} is a constant. Here, we observe that the variation of $1/D_{\text{eff}}$ *versus* the $|\mathbf{q}|$ modulus is similar to the intensity profile of the diffuse scattering, as shown in Figure 5a. It means that D_{eff} has a minimum at the maximum of the intensity profile. This looks similar to the de Gennes narrowing in liquids [16].

We have obtained two types of results: on one hand, the scattering process is purely elastic for a Bragg peak (Fig. 4), as expected for a true 3D long range order; on the other hand, the analysis of a diffuse scattering signal reveals always a slow quasi-elastic scattering process (Figs. 4 and 5), compatible with a single exponential decay. In addition to this slow decay, a fast component is involved within less than 0.24 ns, that can not be attributed to the solvent.

Finally, it is worthwhile to compare the diffuse scatterings in A and B. They correspond to the maximum intensity of diffuse scattering along two different directions and they have approximately the same $|\mathbf{q}|$ ($|\mathbf{q}_A| = \frac{2\pi}{a} |(2, 1.5, 0.5)| \text{\AA}^{-1} = \frac{2\pi}{a} 2.55 \text{\AA}^{-1}$ and $|\mathbf{q}_B| = \frac{2\pi}{a} \left| \left(\frac{4}{3}, \frac{4}{3}, \frac{4}{3} \right) \right| \text{\AA}^{-1} = \frac{2\pi}{a} 2.31 \text{\AA}^{-1}$). The measured τ values in A and in B are very close, *i.e.*, $\tau_A = 19.6 \pm 0.7$ ns, and $\tau_B = 22.1 \pm 1.1$ ns. We may conclude that for any q corresponding to the maximum intensity of a diffuse streak, the characteristic decay time is of the same order of magnitude, equal to 20 ns.

4. Conclusion

We succeeded to obtain a large enough single cubic domain essential for the spin echo experiment. Indeed, a large single domain reduces the count times and allows the analysis of weak scattering such as those of the diffuse scattering discussed in the present paper. All the $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ curves corresponding to diffuse scattering are decreasing *versus* time. This proves that dynamical fluctuations are at the origin of this diffuse scattering, observed before on the X-ray patterns [6, 7]. In addition, the neutron spin echo experiment gives access to quantitative results about this dynamic, for instance the value of the time decay τ for a selected $\mathbf{q}$ vector. In the future, we will explore furthermore the dependence of τ *versus* the $|\mathbf{q}|$ modulus.

So far, our results concern a mixture where only the paraffinic chains are labelled. It seems us important to investigate samples with other contrasts, in particular a mixture where only the polar heads are labelled. Comparing these different samples, we expect to be able to separate different contributions to the dynamics. The sample we have already studied probe essentially the fluctuations of the structure, while a sample with only the polar heads labelled might show dynamics of the building-blocks themselves [15].

Most probably, collective modes of the building-blocks inside the cubic unit cell are involved. As already proposed [6, 7], periodic rows of vertices of the surfactant rods, parallels to the $\langle 1\ 1\ 1 \rangle$ axes, should play a predominant role in the dynamics of a cubic Ia3d structure. Following this interpretation, each row (i) has an associated displacement $u_{(i)}$ along its direction. The displacements of the rows are assumed to be uncorrelated. From our N.S.E. experiment, we may conclude that the displacements are time-dependent — $u_{(i)}(t)$ — Then, it appears that $S(\mathbf{q}, t)/S(\mathbf{q}, 0)$ can be directly related to the correlation function *versus* time of the displacement of a row: $\langle u_{(i)}(0) u_{(i)}(t) \rangle_{(i)}$. The dependence of τ *versus* the $|\mathbf{q}|$ modulus could be then related to a correlation length for the displacement along a row.

Our experimental results should be interpreted in the frame of a complete dynamical model. However, the dynamics of a cubic phase is far to be entirely theoretically understood [5]. This study deserves being carried on, because the dynamical fluctuations we have studied are an inherent feature of the investigated cubic phase, and we may infer that they should play a role in the stability of this cubic phase.

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Chapitre 20

Facettage

Lors de la préparation de mono-domaines de phases cubiques, on a observé que des gouttelettes de telles phases présentent un facettage particulièrement riche de leur interface avec l'air. Ce phénomène existe aussi bien pour les phases lyotropes^{1,2} où les mono-domaines sont stabilisés en contrôlant l'humidité et la température, que pour les phases thermotropes,³⁻⁵ où le paramètre de contrôle est uniquement la température. Les phases cubiques constituent ainsi un système expérimental original pour des études sur le facettage et la transition rugueuse, habituellement réalisées avec des cristaux d'atomes ou de petites molécules. Les facettes des phases cubiques thermotropes sont observées à l'aide d'un microscope à force atomique (AFM), ce qui permet de visualiser aisément les marches moléculaires à la surface d'une goutte.⁵

Microscopie optique

Il a été montré que les phénomènes de facettage et de transition rugueuse se décrivent théoriquement pratiquement de la même manière pour les phases cubiques que pour les cristaux atomiques usuels.⁶ La richesse du facettage des phase cubiques peut ainsi s'expliquer dans le cadre théorique habituel, où les marches moléculaires jouent le rôle des marches atomiques.

Nous nous intéressons à des gouttes de phase cubique déposées sur un substrat dont la taille est d'une fraction de millimètre, et qui sont donc facilement observables au microscope optique. La nature fluide de la phase (diffusion des molécules) fait que la surface d'une telle goutte atteint rapidement (en quelques minutes) sa forme d'équilibre après que la goutte ait transité en phase cubique. On postule donc que le facettage observé correspond à une forme d'équilibre et pas à une forme de croissance. La forme d'équilibre est donnée par la construction de Wulff, basée sur l'anisotropie de la tension de surface. De plus, si la

température est plus élevée que la température de transition rugueuse T_R d'une facette, cette facette n'est pas observée et la surface est rugueuse à l'échelle moléculaire. Cette température est donnée dans la relation ci-dessous, où γ est la tension de surface, d_{hkl} la distance entre les plans parallèles au plan de la facette concernée, et C un facteur numérique de l'ordre de 1 :^{4,5}

$$k_B T_R \approx C \gamma d_{hkl}^2$$

La taille de la maille cubique est de l'ordre de 10 nm, ce qui est beaucoup plus grand que les périodes des cristaux atomiques. En conséquence, les températures de transition rugueuses sont nettement plus élevées dans le cas d'une phase cubique que dans le cas des cristaux atomiques et ainsi, à la température ambiante, un nombre beaucoup plus grand de facettes distinctes est observé pour une phase cubique (**fig 20-1**).

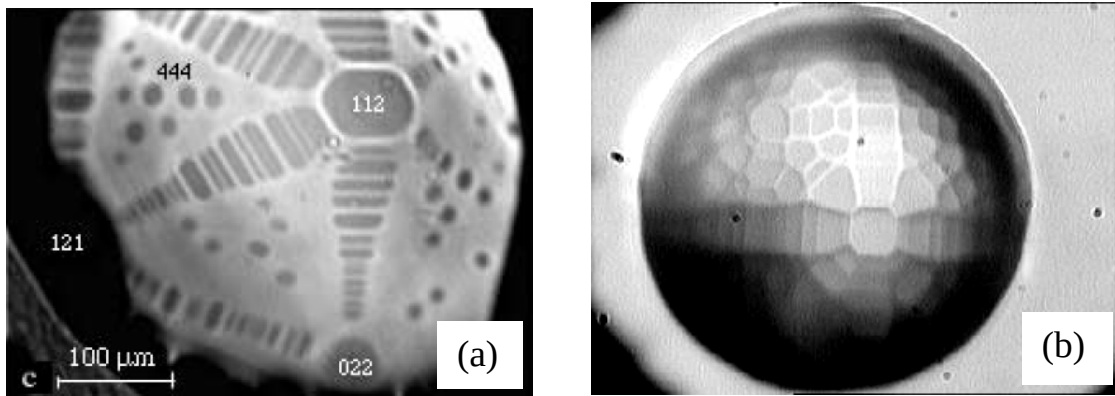


Figure 20-1. Goutte facettée de phases cubiques lyotropes (microscopie optique). (a) cubique bicontinue du système $C_{12}EO_6$ /eau.² (b) cubique micellaire du système DTACl/eau.

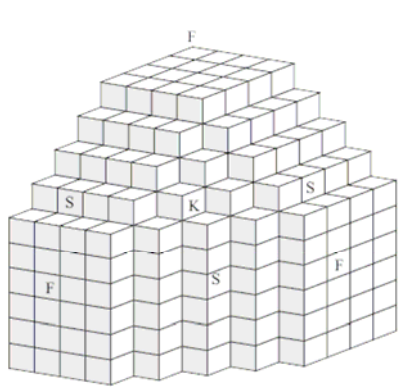


Figure 20-2. Schéma des trois types de facettes cristallines. Les facettes principales de type F (F = flat) planes à l'échelle moléculaire, les facettes de type S , constituées d'alignement de marches moléculaires régulièrement espacées (S = stepped) et les facettes de type K (K = kinked), formées de marches « obliques » composées de décrochements régulièrement espacés.⁵

Sur ces images (**Fig 20-1**), on distingue d'une part des facettes principales de type F, des facettes de type S (constituées par des alignements de marches moléculaires) et enfin des zones rugueuses. Les différents types de facettes sont schématisés sur la **figure 20-2**.

Les facettes principales de type F sont les facettes 211 et 220 pour la phase bicontinue Ia3d, et les facettes 200 et 211 pour la phase micellaire Pm3n. Les facettes de type S se succèdent en forme d'escaliers, et ont des indices de Miller relativement élevés, qui ne sont pas observée habituellement dans le cas des cristaux atomiques.

En conclusion, deux phénomènes peuvent expliquer la richesse du facettage des phases cubiques. D'une part, le caractère fluide permet d'atteindre rapidement une forme d'équilibre de la surface, sans que la cinétique de croissance privilégie certaines facettes. Et d'autre part, la taille de la maille (10 nm) fait que de nombreuses facettes d'indices de Miller élevés sont observées, car leur température de transition rugueuse est plus élevée que la température d'observation.

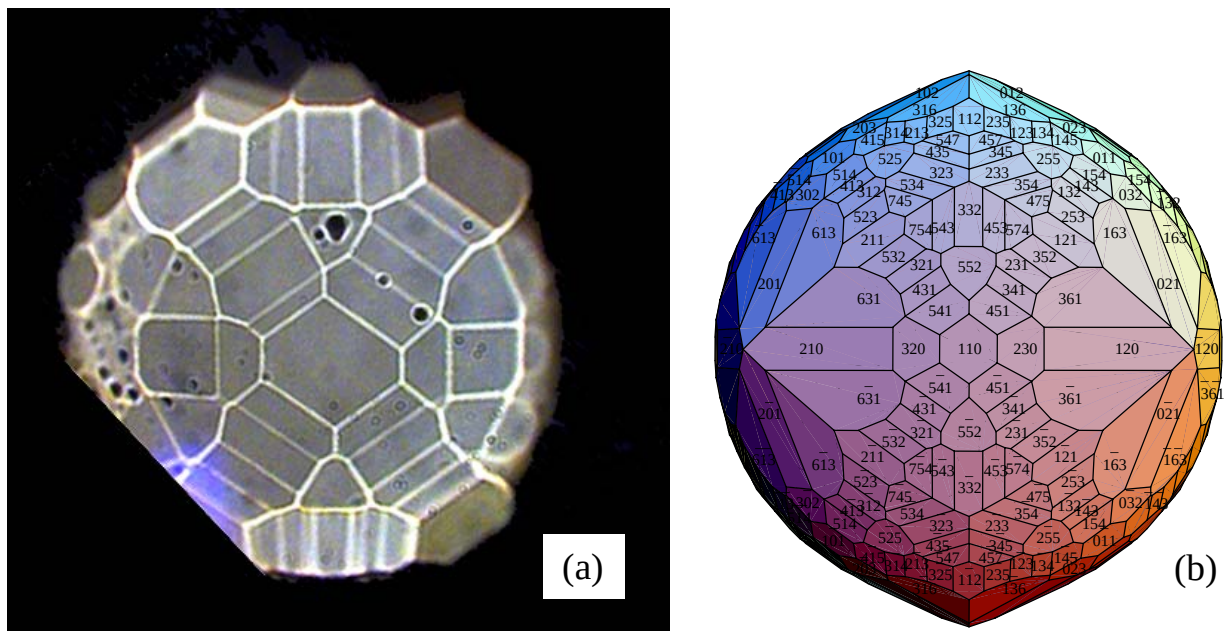


Figure 20-3. Goutte facettée d'une phase cubique thermotrope (bicontinue Ia3d) et indices de Miller des facettes correspondantes.⁷

Résultats d'AFM

Dans le cas des phases cubiques thermotropes, une goutte facettée (**Fig 20-3**) a un aspect similaire à celui de gouttes de phases lyotropes, les facettes de type S étant néanmoins sensiblement moins nombreuses. Il a été possible d'observer alors directement par AFM la surface de gouttes thermotropes (**Fig 20-4**), et de visualiser ainsi les marches moléculaires.

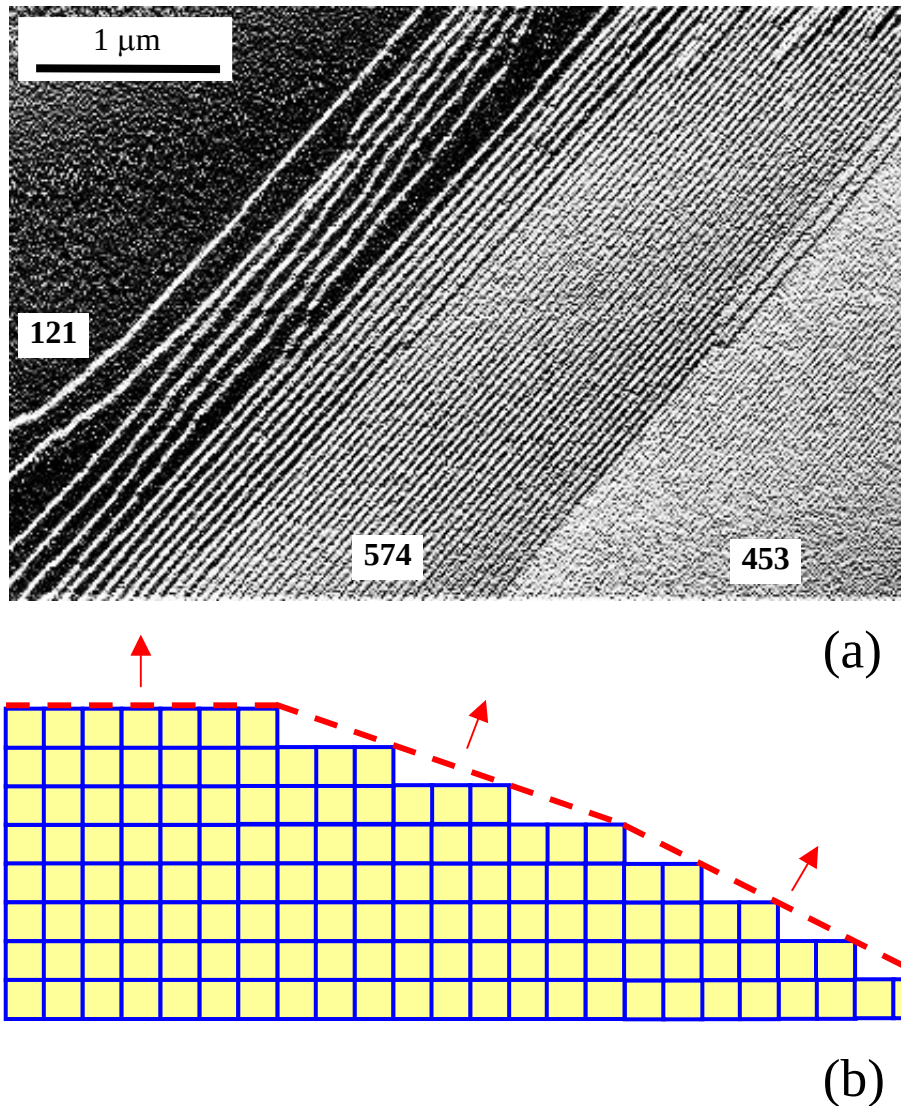


Figure 20-4. Marches moléculaires observées par AFM (image de phase).⁷ La facette principale 121 est essentiellement plane (type F) et les facettes 574 et 453 (type S) sont constituées de marches moléculaires parallèles, plus espacées sur la facette 574 que sur la facette 453.

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Chapitre 21

Perspectives

Actuellement, je travaille principalement sur deux projets, l'un sur les matériaux mésoporeux, l'autre sur les fluides complexes. Ils ont en commun de porter sur des systèmes mixtes, c'est-à-dire combinant des molécules de tensioactifs et une composante inorganique (silice amorphe, nano-particules), mais les aspects abordés sont différents dans chaque projet.

Les matériaux mésoporeux : diffusion in-situ

Il s'agit de réaliser des expériences de diffusion des rayons X ou des neutrons résolues en temps. Deux types d'expériences sont en développement.

- Tout d'abord, il s'agit de déterminer les étapes du mécanisme de formation d'un matériau mésoporeux, qui sont encore mal connues, grâce à des techniques de diffusion aux petits angles des rayons X (SAXS) et des neutrons (SANS), en réalisant des mesures in-situ résolues en temps de l'évolution de la solution de synthèse (chapitre 17). Les premiers résultats ont été obtenus par SAXS sur le matériau modèle hexagonal 2D dit SBA-15 [31, collaboration avec *Dominique Durand* à l'IBBMC, UPS, *Andrei Khodakov* à l'Université de Lille, *Vladimir Zholobenko* à l'Université de Keele, UK]. D'autres expériences sont prévues prochainement par SANS [34, collaboration avec *Isabelle Grillo* à l'ILL, Grenoble]. Ces expériences permettent de suivre l'évolution des micelles de tensioactifs lors de la réaction de condensation des espèces de silice. On a pu montrer que, pour une phase hexagonale 2D, la forme des micelles évolue d'une forme sphérique vers une forme cylindrique avant que le matériau hybride (de structure hexagonale 2D) ne précipite. Le but de ce projet est de mieux comprendre comment la silice s'associe aux micelles en même temps qu'elle se condense à la surface des micelles, ceci afin de contrôler les propriétés du matériau hybride final. On cherchera aussi à corréler les caractéristiques des micelles hybrides à la structure du matériau final (phases ordonnées hexagonale ou cubique, ou au contraire phases désordonnées), en fonction de la température et de l'addition d'un agent gonflant (TMB, dodecane).

- Le second aspect consistera à étudier la cristallisation de nano-particules d'oxydes métalliques (oxydes de Co et mixte Mn/Co) dans des matrices mésoporeuses. Des résultats ont déjà été obtenus dans le cas des oxydes de Mn uniquement [21,28 collaboration avec *Anne Davidson* au LRS -Paris VI-]. Le but sera d'utiliser un effet de moulage pour obtenir des nano-fils de diamètre calibré, intéressants pour leurs propriétés électroniques. Un précurseur métallique dissous dans un milieu aqueux (généralement un sel) est introduit dans les pores avant d'être transformé en oxyde par des traitements thermiques. On peut ensuite éliminer la matrice de silice et obtenir une réplique de la porosité constituée de l'oxyde métallique. Les expériences de diffusion des rayons X permettront de suivre pendant les traitements thermiques l'évolution de la taille, de la forme, de la distribution spatiale des nanoparticules en croissance dans les mésopores. Ces résultats permettront d'optimiser les propriétés catalytiques de nanoparticules d'oxyde.

Les fluides complexes comme matrice de confinement de nano-particules :

En ce qui concerne les fluides complexes, je participe depuis un an au développement d'une nouvelle thématique au sein du pôle "fluides complexes" du LPS, intitulée nanoparticules confinées en mésophase (dans une phase lamellaire ou hexagonale 2D) [collaboration avec *Doru Constantin, Patrick Davidson, Catherine Even, Brigitte Pansu, Andreas Poulos* au LPS]. Le fil conducteur de cette nouvelle thématique "systèmes mixtes" est d'utiliser des mésophases pour y confiner des nanoparticules, de forme sphérique ou fortement anisotrope. Le but est d'étudier l'effet du confinement des nanoparticules sur leur dynamique et leurs interactions. Un des buts recherchés est de montrer comment le confinement engendre de l'ordre entre les nanoparticules (ordre nématique 2D pour des particules anisotropes ou réseaux ordonnés de nanoparticules sphériques). Les modifications des propriétés rhéologiques des mésophases par la présence des nanoparticules seront également abordées. L'accueil en séjour post-doctoral de *Rema Krishnaswamy* en 2004-2005 s'est fait dans ce cadre. Il a permis de commencer à explorer une méthode de synthèse par radiolyse de nanoparticules (métalliques) directement en mésophase. Nous avons déjà montré que des nanoparticules anisotropes de Pt peuvent être synthétisées par radiolyse en présence du tensioactif CTAB, et l'étude du mécanisme de cette synthèse est en cours [33, collaboration avec *Hynd Remita* au LCP, UPS]. Ce projet est pour moi l'occasion de participer au LPS au développement des possibilités expérimentales (diffusion des rayons X, AFM, rhéologie, microscopie électronique, diffusion de lumière ...), ceci autour d'une nouvelle thématique.

Conclusion

Un des objectifs principaux de ce manuscrit est de montrer l'intérêt des mesures quantitatives des intensités des pics de Bragg, afin de déterminer de la manière la plus quantitative possible les différentes structures auxquelles nous nous intéressons. Deux méthodes sont alors possibles. Tout d'abord, c'est la méthode inverse (chapitre 11) qui semble la plus appropriée dans le cas où l'on souhaite déterminer une nouvelle structure, comme dans le cas de la phase cubique tri-continue (chapitre 15). Cette méthode nécessite toutefois d'explorer un nombre important de combinaisons de phases. Une fois la structure connue (phase bi-continue, phases micellaires de sphères, phase hexagonale 2D), la méthode directe, s'appuyant sur un modèle structural prédéfini, est mieux adaptée afin d'extraire des informations quantitatives (modèle cœur/couronne de sphères ou de cylindres, chapitres 14, 16 et 17). Quelle que soit la méthode utilisée, la qualité des mesures expérimentales, et notamment le nombre de pics de Bragg mesurés, sont déterminants pour pouvoir raffiner les modèles structuraux. Dans le cas des matériaux mésoporeux, la microscopie électronique est certainement une technique complémentaire indispensable, notamment dans le cas de matériaux fonctionnalisés à l'intérieur de la porosité.

Il semble intéressant de continuer à appliquer ces méthodes, notamment aux différentes phases micellaires (chapitre 3, 14), empilements de sphères (bcc, fcp, hcp) et phases tcp (phase $Pm3n$...), ceci afin de mieux comprendre le lien entre la forme des micelles et le type d'ordre à grande distance.

Lors d'une transition de phase, les relations d'épitaixie (chapitre 13) permettent d'élaborer des mécanismes de transition, sous-tendus par des modifications de la forme des micelles. On retrouve finalement un peu cette problématique lors de l'auto-assemblage des micelles pour former un matériau mésoporeux (chapitres 17,21), avec probablement une transition sphère/cylindre de la forme des micelles. Les expériences de diffusion du rayonnement réalisée in-situ, grâce à l'utilisation des grands instruments, permettent de suivre en temps réel les modifications de structure. Ceci est un grand avantage par rapport aux observations par microscopie électronique, qui ne sont pas réalisables in-situ.

Enfin, des études structurales sous cisaillement des fluides complexes sont aussi en cours (cellule de Couette couplée à la diffusion des rayons X). Leur but est de permettre de faire le lien entre les propriétés macroscopiques (visco-élasticité) des phases et les fluctuations structurales.