HAL
open science

# The influence of periodic edge conditions for the simulation of some quantities of interest for separative chemistry <br> Anne-Françoise De Guerny 

## - To cite this version:

Anne-Françoise De Guerny. The influence of periodic edge conditions for the simulation of some quantities of interest for separative chemistry. Analysis of PDEs [math.AP]. Sorbonne Université, 2021. English. NNT: 2021SORUS086 . tel-03469446

HAL Id: tel-03469446
https://theses.hal.science/tel-03469446
Submitted on 7 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Sorbonne Université

École doctorale Sciences Mathématiques de Paris Centre (ED 386)
Unité de recherche Laboratoire Jacques-Louis Lions
Thèse présentée par Anne-Françoise Lempereur de Guerny
Soutenue le 23 avril 2021
En vue de l'obtention du grade de docteur de Sorbonne Université
Discipline Mathématiques appliquées
Spécialité Analyse numérique et dynamique moléculaire

# De l'influence des conditions aux bords périodiques pour la simulation de quelques quantités d'intérêt pour la chimie séparative 

## Thèse dirigée par Yvon Maday(LJLL) et Jean-François Dufrêche(ICSM)

Composition du jury :

| Rapporteurs | Huajie Chen <br> Gabriel Stoltz | Professeur à Beijing Normal University <br> Professeur à l'Ecole des Ponts |
| ---: | :--- | :--- |
| Examinateurs | Virginie EhrLacher <br> Marie JARDAT | Chercheur à l'Ecole des Ponts <br> Professeur à Sorbonne Université <br> Maître de conférence à Sorbonne Université |
|  | Pierre Monmarché | Professeur à Sorbonne Université |
| Directeur de thèse | Yvon MADAY | Professeur à l'Université de Montpellier |

## Résumé

L'objectif de cette thèse est d'étudier l'influence des conditions périodiques et notamment les corrections à apporter, en fonction de la période considérée, dans le calcul de certaines quantités d'intérêt tirées de simulations de dynamique moléculaire. Ces dernières sont particulièrement profitables pour la compréhension des phénomènes de solvatation de molécules en solution et voient naturellement leur utilité pour l'étude de la gestion des déchets radioactifs. Nous nous intéressons notamment à l'étude du potentiel de Force moyenne, décrit dans le formalisme de McMillan et Mayer entre deux solutés chargés en solution. On commence par calculer analytiquement le potentiel d'un tel système en considérant des conditions aux bords périodiques de période $L$. Le calcul se base sur les forces agissant sur l'une des particules et sur la réunion astucieuse des termes de la somme obtenue. On peut finalement vérifier que, à grande distance, le potentiel converge vers un potentiel coulombien, et on obtient un terme correctif en $L^{-5}$. A partir de simulations à partir de la méthode du Umbrella Sampling combinée à la méthode WHAM, on corrige le potentiel de McMillan et Mayer de chlorure de sodium, et de lanthanides, à partir du terme obtenu afin d'observer la constante d'association qui en résulte. Par ailleurs, on étudie le coefficient de diffusion d'une particule en milieu confiné. Notre calcul repose sur le passage de l'équation de Stokes en Fourier, ce qui nous donne des EDO avec distributions que l'on résout pour obtenir la vitesse de la particule. Ensuite, des développements limités aboutissent au coefficient de diffusion comprenant un terme correctif en $L^{-1}$.


#### Abstract

The objective of this thesis is to study the influence of periodic conditions and in particular the corrections to be made, depending on the period considered, in the calculation of certain quantities of interest from molecular dynamics simulations. The latter are particularly useful for the understanding of solvation phenomena of molecules in solution and are naturally useful for the study of radioactive waste management. We are particularly interested in the study of the potential of Mean Force, described in the McMillan and Mayer formalism between two charged solutes in solution. We start by calculating analytically the potential of such a system by considering periodic edge conditions of period $L$. The calculation is based on the forces acting on one of the particles and on the clever joining of the terms of the obtained sum. We can finally verify that, at large distances, the potential converges to a coulombic potential, and we obtain a corrective term in $L^{-5}$. From simulations using the Umbrella Sampling method combined with the WHAM method, we correct the McMillan and Mayer potential of sodium chloride, and lanthanides, from the term obtained in order to observe the resulting association constant. Moreover, we study the diffusion coefficient of a particle in a confined medium. Our calculation is based on the passage of the Stokes equation in Fourier, which gives us ODEs with distributions that we solve to obtain the velocity of the particle. Then, limited developments lead to the diffusion coefficient including a corrective term in $L^{-1}$.


## Remerciements

Pour commencer, je remercie mes directeurs Yvon Maday et Jean-François Dufrêche qui m'ont permis de faire cette thèse, et pour leurs aide et conseils au cours de celle-ci.
Je tiens également à remercier les membres du jury, et en premier lieu Gabriel Stoltz et Huajie Chen d'avoir accepté d'être les rapporteurs de ma thèse et pour leurs suggestions mises en évidence. Je remercie d'autre part Pierre Monmarché, Virginie Ehrlacher et Marie Jardat d'avoir accepté de constituer, avec ces derniers, mon jury de thèse.
Je remercie l'ISCD ainsi que l'erc EMC2 qui m'ont apporté des financements.
Je remercie sincèrement Louis Lagardère et Magali Duvail pour leur coaching pour les codes Tinker et WHAM ainsi que pour la création de boîte d'eau avec Packmol.
Pendant ma thèse, j'ai eu la chance de passer un séjour à Amsterdam dans le cadre d'un workshop de simulations moléculaires organiser par le CECAM, et également à l'ICSM à Marcoule. Je tiens à remercier toutes les personnes rencontrées là-bas et avec lesquels j'ai pu avoir des échanges fructueux notamment en chimie.
Un très grand merci par ailleurs aux professeurs que j'ai pu rencontrer à Dauphine, et notamment Julien Salomon, Guillaume Legendre et Pierre Lissy pour leurs nombreux conseils et aiguillages au cours de ma scolarité.
Je remercie l'équipe du secrétariat, Catherine Drouet, Malika Larcher et Salima Lounici, pour leur gentillesse et efficacité ; mais également Khashayar Dadras pour l'informatique.
Je tiens également à remercier l'ensemble des doctorants que j'ai pu côtoyer tout au long de ma thèse et notamment Jean-François, Pierre, Jean et Lise pour les nombreuses discussions, les fou rires, la PPG et leurs conseils et boost dans les moments de doute. Merci aux membres du LJLL qui ont partagé mon bureau : Anouk, Etienne, Geneviève, Gong, Hélin, Houssam, Jules, Lilian, Lucille, Valentin, Virgile. Merci également aux autres membres pour les pauses-déjeuner ou autre : Alexandre, Amaury, Ana, Bertrand, Cécile, Christophe, David, Elise, Fatima, Gabriela, Gontran, Guillaume, Idriss, Ludovic, Marc, Matthieu, Nicolas, Olivier, Teddy, Yipeng.
Je remercie mes amis pour leurs soutien et encouragements tout au long de cette aventure. Je remercie plus particulièrement Simon pour son aide précieuse, pour ses nombreuses relectures et ses conseils avisés.
Un immense merci à l'ensemble de ma famille et notamment mes parents, mes soeurs et mes tantes d'avoir été à mes côtés, pour leur écoute, et pour leurs encouragements jusqu'au bout. Merci aussi pour leurs relectures, et plus particulièrement mon père pour ses conseils mathématiques. Merci également à ma belle famille pour son soutien.
Last but not least, je souhaite adresser de vives remerciements à mon cher et génial mari qui a toujours cru en moi et m'a été d'un immense soutien. Je le remercie pour sa patience et d'avoir supporté ces moments coïncidant avec notre préparation au mariage (et son report suite au covid!) et ses débuts. Je tiens à le remercier aussi pour l'aide qu'il m'a apportée mathématiquement et informatiquement.

## Table des matières

Résumé ..... 3
Remerciements ..... 5
1 Introduction générale ..... 9
2 General introduction ..... 13
3 From interactions of matter to numerical simulations ..... 17
3.1 Motivation of this thesis ..... 17
3.1.1 Context of radioactive waste storage ..... 19
3.1.2 Context of extraction and recycling of rare earths (lanthanides) ..... 24
3.2 Description of matter and equilibrium models ..... 26
3.2.1 Description of the interactions of a system ..... 26
3.2.2 Statistical thermodynamics ..... 29
3.2.3 Distribution functions ..... 34
3.3 Simulation methods ..... 36
3.3.1 Molecular Dynamics ..... 36
3.3.2 Periodic boundary conditions ..... 41
3.3.3 Ewald ..... 42
4 Calculation of free energy differences ..... 49
4.1 Reaction coordinate ..... 49
4.2 Free energy ..... 49
4.3 Potential of Mean Force ..... 50
4.3.1 The Potential of Mean Force ..... 50
4.3.2 The Potential of McMillan and Mayer ..... 50
4.3.3 Practical calculation of McMillan and Mayer's potential ..... 52
4.4 The Problem of Barriers for the Calculation of the Potential of Mean Force ..... 52
4.5 Umbrella Sampling Method ..... 53
4.6 WHAM Method ..... 55
4.7 Analysis of a spring problem, period and stiffness constant ..... 60
4.7.1 Analysis with Newton's principles ..... 61
4.7.2 Analysis with Hamiltonian formulation ..... 62
4.7.3 Stiffness constant, umbrella amplitude and period for our simulations ..... 64
4.8 Calculation of coefficients of interest ..... 64
4.8.1 The association constant ..... 64
4.8.2 The osmotic coefficient of activity of the solvent ..... 65
5 Study of the Potential of McMillan and Mayer at long distance ..... 67
5.1 Mathematical problem ..... 68
5.2 Numerical results ..... 82
5.2.1 Size of a simulation box ..... 84
5.2.2 Description of the AMOEBA model ..... 84
5.2.3 Study of the potential of McMillan and Mayer for $\mathrm{Na}-\mathrm{Cl}$ in aqueous phase ..... 85
5.2.4 Macroscopic study for $\mathrm{Na}-\mathrm{Cl}$ in aqueous phase ..... 89
5.2.5 Comparison of our expansion with lanthanide salt potentials ..... 91
5.3 Conclusion ..... 92
6 Study of the diffusion constant in confined conditions ..... 101
6.1 Introduction ..... 101
6.2 Method of calculating the diffusion constant ..... 104
6.3 Study in the non-periodic case ..... 106
6.4 Study in the case with periodic boundary conditions ..... 118
6.5 Conclusion ..... 132
7 Conclusion and perspectives ..... 133
Bibliographie ..... 135

## Chapitre 1

## Introduction générale

Durant ces dernières décennies, les progrès des outils informatiques ont permis aux méthodes numériques de particulièrement se développer. Ces méthodes permettent la modélisation de systèmes complexes et d'analyser des phénomènes parfois difficilement identifiables expérimentalement car apparaissant à des échelles très fines. Dans ce contexte, la dynamique moléculaire cherche à étudier l'évolution de systèmes formés de particules fluctuant dans un milieu soumis à des contraintes thermodynamiques (température ou pression par exemple). Ces dernières sont particulièrement profitables pour la compréhension des phénomènes de solvatation de molécules en solution. Ces procédés voient naturellement leur utilité pour l'étude de réactions chimiques, et plus spécifiquement pour celle de la gestion des déchets radioactifs. En effet, la quantité de ces derniers a beaucoup augmenté depuis les années 40, d'où la nécessité d'élaborer des stratégies pour les traiter. Le but est de les détruire (dans des réacteurs) ou bien de garantir leur stockage.

Les méthodes de dynamique moléculaire se basent sur la thermodynamique statistique. Les quantités d'intérêt macroscopique étudiées apparaissent comme des moyennes sur des ensembles thermodynamiques. Il convient de décrire le système d'intérêt selon les interactions en jeu d'une part, les équations d'évolution en temps d'autre part, et, enfin, de déterminer l'ensemble thermodynamique, dont la mesure de probabilité, pour le calcul des moyennes, va dépendre. Il va notamment être possible d'obtenir des informations sur la différence d'énergie libre, et plus spécifiquement sur la différence de Potentiel de Force Moyenne entre deux états du système. Cela constitue des informations précieuses qui vont permettre de déduire les propriétés thermodynamiques du système. Dans ce cadre, McMillan et Mayer ont développé un formalismes pour des systèmes de multi-composants, adapté aux électrolytes. Ils ont ainsi pu définir un potentiel effectif (potentiel de McMillan Mayer)traduisant l'interaction entre solutés. Celui-ci permet ensuite de calculer les constantes reliées aux réactions chimiques (constante d'équilibre et coefficient d'activité).

Par ailleurs, dans le contexte de la gestion des déchets radioactifs, il a été envisagé un confinement implanté dans la couche d'argile du Callovo-Oxfordien pour le stockage de ceux-ci. Pour les argilites de cette zone, le transport d'eau et de solutés est essentiellement diffusif. Analyser le coefficient de diffusion, pour quantifier le transport des différentes espèces, présente donc un intérêt. En effet, cela permet d'obtenir des informations sur les radioéléments relâchés dans le milieu géologique puis dans la biosphère. Ce coefficient, dans le cas simplifié d'une particule se diffusant dans un solvant confiné, qui peut être étudié par dynamique moléculaire, peut être calculé analytiquement à partir de modèles hydrodynamiques.

Lors des simulations moléculaires, un artifice de calculs courant est d'imposer au système étu-
dié des conditions périodiques aux bords de la boite de simulation. Cela permet notamment de limiter les effets de surfaces et de mimer un système physique infini. Dans ces conditions, une particule interagit non seulement avec les proches voisines, mais également avec leurs images dans les autres boites pour les interactions à longue portée.

Cette thèse a pour objectif d'étudier les conséquences engendrées par les calculs pour les systèmes en conditions périodiques et notamment les corrections à apporter, en fonction de la période considérée, dans le calcul de certaines quantités d'intérêt. Tout d'abord le comportement du potentiel de McMillan et Mayer, d'après simulations numériques, semble, à grande distance, se rapprocher de celui d'un potentiel Coulombien. Nous souhaitons vérifier cette hypothèse théoriquement, tout en analysant comment les conditions périodiques modifient ce comportement. Ensuite, le coefficient de diffusion en milieu confiné est étudié et nous souhaitons observer comment les conditions imposées influent sur son calcul.

Pour présenter ces travaux, le manuscrit proposé s'organise comme suit.
Le chapitre 3 s'attache, après une brève mise en contexte, à définir les diverses interactions agissant dans la matière ainsi que les outils permettant l'analyse de celle-ci, puis à introduire les notions de simulations numériques en dynamique moléculaire. Une preuve mathématique de la formule d'Ewald est par ailleurs revisitée en fin de chapitre.

Dans le chapitre 4, la notion de différence énergie libre est plus particulièrement étudiée, et notamment la notion de Potentiel de Force Moyenne (PMF). Les méthodes, spécifiques à la détermination de ce dernier par simulations numériques, utilisées dans cette thèse sont ici introduites : il s'agit de la méthode "Umbrella Sampling", couplée à la méthode "Weighted Histogram Analysis Method" (WHAM). Pour cette dernière, une étude mathématique est redonnée pour aboutir à la méthode. Ensuite, est expliqué comment choisir divers paramètres utiles pour les simulations (quelle est la période du ressort introduit dans le Umbrella Sampling ainsi que l'amplitude des parapluies, en fonction de la constante de raideur choisie). Pour finir, les coefficients d'intérêts sont définis (constante d'association et coefficient osmotique).

Le chapitre 5 débute par une analyse mathématique liée au calcul du potentiel pour deux ions dans une boite constituée, par ailleurs, de molécules d'eau et avec conditions périodiques aux bords de la boite. Les deux ions sont supposés être assez éloignés, et donc seules les interactions à longue portée (Coulombiennes) sont prises en compte. Un développement, qui tient compte de la périodicité introduite dans les simulations, est alors obtenu. Pour se faire, l'idée mathématique est tout d'abord d'étudier les forces agissant sur l'une des particules, puis de réunir de façon astucieuse les termes de la somme obtenue. Cela permet, dans le contexte du problème, d'aboutir à une somme qui converge. La somme des forces calculée permet ensuite de remonter au potentiel du système étudié. Ensuite, une étude numérique, basée sur des simulations de boites d'eau salée à partir de trois tailles différentes $\left(L_{i}\right)_{i=1,2,3}$ de boite, permet d'observer l'évolution du potentiel de McMillan et Mayer en fonction de $L$ (où $L$ désigne successivement $\left(L_{1}\right),\left(L_{2}\right),\left(L_{3}\right)$ ), et d'ajuster la courbe de celui-ci (défini à une constante près) à celle issue de notre formule obtenue. Une étude macroscopique à partir des simulations s'ensuit également et permet d'observer les ajustements qui découlent de notre correction. Pour finir, la courbe tirée de notre formule est également utilisée afin d'ajuster la courbe de potentiel de McMillan et Mayer de différents chlorures de lanthanides.

Le but de cette partie est de permettre de calculer de façon plus précise le potentiel de McMilan et Mayer entre deux solutés chargés en solution en tenant compte rigoureusement des conditions aux limites périodiques.

Dans le chapitre 6, le coefficient de diffusion, pour une particule se déplaçant dans un fluide confiné entre deux murs, est étudié en fonction de la taille considérée du système et selon également l'influence des conditions aux limites appliquées. Tout d'abord, une méthode est introduite et fait intervenir des équations différentielles ordinaires (EDO) avec distributions, pour le calcul en condition non-périodique. Une comparaison de notre développement obtenu, en fonction de la distance entre les deux murs, avec celui obtenu par la méthode dans 155 permet de valider les calculs. Puis, une adaptation de la méthode, dans le cas de conditions périodiques, aboutit au calcul de la vitesse de la particule ; un calcul de type Ewald, avec une double et non triple somme, permet ensuite un développement du coefficient de diffusion dans ces conditions qui tient compte de la période appliquée au système.
Le but de cette seconde partie est ici de permettre de calculer de façon plus précise le coefficient de diffusion d'espèces chimiques confinées en tenant compte rigoureusement des conditions aux limites périodiques.

Pour finir, des conclusions générales sur ce travail de thèse sont proposées et des perspectives de poursuites de ces travaux sont introduites et détaillées.

## Chapitre 2

## General introduction

Over the last few decades, advances in computer tools have enabled numerical methods to particularly develop. These methods allow the modeling of complex systems and the analysis of phenomena that are sometimes difficult to experimentally identify because they appear at very fine scales. In this context, molecular dynamics seeks to study the evolution of systems made up of particles fluctuating in a medium subject to thermodynamic constraints (temperature or pressure for example). The latter are particularly beneficial for the understanding of solvation phenomena of molecules in solution. These processes are naturally useful for the study of chemical reactions, and more specifically for the study of radioactive waste management. Indeed, the quantity of radioactive waste has considerably increased since the 1940s, hence the need to develop strategies for its treatment. The goal is to destroy them (in reactors) or to guarantee their storage.

Molecular dynamics methods are based on statistical thermodynamics. The quantities of macroscopic interest studied appear as averages over thermodynamic sets. It is necessary to describe the system of interest according to the interactions at stake on the one hand, the equations of evolution in time on the other hand, and, finally to determine the thermodynamic set, on which the measure of probability for the calculation of the averages, will depend. In particular, it will be possible to obtain information on the difference in free energy, and more specifically on the difference in Mean Force Potential between two states of the system. This constitutes valuable information that will allow the thermodynamic properties of the system to be deduced. Within this framework, McMillan and Mayer have developed a formalisms for multi-component systems, adapted to electrolytes. They have thus been able to define an effective potential (McMillan Mayer potential) reflecting the interaction between solutes. This then allows them to calculate the constants related to chemical reactions (equilibrium constant and activity coefficient).

In addition, in the context of radioactive waste management, a confinement implanted in the Callovo-Oxfordian clay layer has been envisaged for the storage of radioactive waste. For the clays in this zone, the transport of water and solutes is essentially diffusive. Analysing the diffusion coefficient, to quantify the transport of the different species, is therefore of interest. Indeed, it allows to obtain information on the radioelements released in the geological environment and then in the biosphere. This coefficient, in the simplified case of a particle diffusing in a confined solvent, which can be studied by molecular dynamics, can be calculated analytically from hydrodynamic models.

During molecular simulations, a common calculation trick is to impose periodic conditions on the edges of the simulation box on the system under study. In particular, this makes it possible to
limit surface effects and to mimic an infinite physical system. Under these conditions, a particle interacts not only with its close neighbors, but also with their images in the other boxes for long-range interactions.

The objective of this thesis is to study the consequences generated by the calculations for the systems in periodic conditions and in particular the corrections to be made, according to the considered period, in the calculation of certain quantities of interest. First of all, the behaviour of McMillan and Mayer's potential, according to numerical simulations, seems at a great distance to be close to that of a Coulombian potential. We wish to theoretically verify this hypothesis, while analyzing how periodic conditions modify this behavior. Then, the confined diffusion coefficient is studied and we wish to observe how the imposed conditions influence its calculation.

To present this work, the proposed manuscript is organized as follows.
Chapter 3, after a brief background, defines the various interactions acting in matter as well as the tools for its analysis, and then introduces the concepts of numerical simulations in molecular dynamics. A mathematical proof of Ewald's formula is also revisited at the end of the chapter.

In chapter 4, the notion of free energy difference is more specifically studied, and in particular the notion of Mean Force Potential (PMF). The methods, specific to the determination of the latter by numerical simulations, used in this thesis are introduced : the "Umbrella Sampling" method, coupled with the "Weighted Histogram Analysis Method" (WHAM). For the latter, a mathematical study is given again to lead to the method. Then, is explained how to choose various useful parameters for the simulations (what is the period of the spring introduced in the Umbrella Sampling as well as the amplitude of the umbrellas, according to the chosen stiffness constant). Finally, the coefficients of interest are defined (association constant and osmotic coefficient).

Chapter 5 begins with a mathematical analysis related to the calculation of the potential for two ions in a box made of water molecules and with periodic boundary conditions. The two ions are assumed to be quite far apart, and thus only long range interactions (Coulombic) are taken into account. An expansion, which takes into account the periodicity introduced in the simulations, is then obtained. To do this, the mathematical idea is first of all to study the forces acting on one of the particles, and then to cleverly combine the terms of the sum obtained. This allows, in the context of the problem, to come to a converging sum. The sum of the forces calculated then makes it possible to go back to the potential of the studied system. Next, a numerical study, based on simulations of salt water boxes from three different sizes $\left(L_{i}\right)_{i=1,2,3}$ of box, allows us to observe the evolution of McMillan and Mayer's potential as a function of $L$ (where $L$ stands successively for $\left.\left(L_{1}\right),\left(L_{2}\right),\left(L_{3}\right)\right)$, and to fit the curve of this one (defined to a constant) to the curve obtained from our formula. A macroscopic study based on the simulations also follows and allows us to observe the adjustments resulting from our correction. Finally, the curve from our formula is also used to fit the McMillan and Mayer potential curve of different lanthanide chlorides.
The purpose of this part is to allow a more accurate calculation of the potential of McMilan and Mayer between two solution-charged solutes under strict consideration of periodic boundary conditions.

In chapter 6, the diffusion coefficient, for a particle moving in a fluid confined between two
walls, is studied as a function of the considered size of the system and also as a function of the influence of the boundary conditions applied. First of all, a method is introduced using Ordinary Differential Equations (ODE) with distributions for the calculation in non-periodic conditions. A comparison of our expansion obtained, as a function of the distance between the two walls, with that obtained by the method in [155] allows to validate the calculations. Then, an adaptation of the method, in the case of periodic conditions, leads to the calculation of the velocity of the particle ; an Ewald type calculation, with a double and not triple sum, then allows an expansion of the diffusion coefficient under these conditions which takes into account the period applied to the system.
The purpose of this second part is to allow a more precise calculation of the diffusion coefficient of confined chemical species, taking into account strictly the periodic boundary conditions.

Finally, general conclusions on this thesis work are proposed and perspectives for the continuation of this work are introduced and detailed.

## Chapitre 3

## From interactions of matter to numerical simulations

### 3.1 Motivation of this thesis

This thesis finds its motivation in the recycling and the nuclear fuel cycle as well as in the extraction of rare earths. For radioactive elements, article L. 542-1-1 10 of the environmental code specifies that "A radioactive substance is a substance that contains radionuclides, natural or artificial, whose activity or concentration justifies a radiation protection control" A distinction is made between radioactive materials "for which a subsequent use is planned or envisaged", and on the contrary, radioactive waste "requalified as such by the administrative authority in application of article L. 542-13-2.". It is also explained that the management of the latter "includes all activities related to the handling, pre-treatment, treatment, disposal, storage and disposal of radioactive waste". conditioning, storage and disposal of waste radioactive materials, excluding off-site transport."

The national inventory [2] lists the origin of waste essentially "according to five economic sectors : the nuclear power sector (which includes in particular nuclear power plants for electricity production and plants dedicated to the manufacture and reprocessing of nuclear fuel and to the recycling of part of the materials extracted from it), the research sector (particularly in the field of civil nuclear energy and nuclear and particle physics), the defense sector (deterrence force and activities related to the army), the non-nuclear industry sector (including the extraction of rare earths), and the medical sector (diagnostic and therapeutic activities)". Figure 1 shows the distribution of radioactive waste according to these five sectors. Among these radioactive wastes are the radioactive isotopes of long-lived actinides, which are known (provided they have a high atomic number and a main oxidation state of +3 ) to have a chemical behaviour similar to that of the lanthanides, for which specific potentials have been developed in modelling 55,60 .

The development of computer calculations tends to allow the prediction of the behavior of chemical systems. These calculations are of interest because of their low cost and because experiments on radioelements are particularly cumbersome. The use of mathematical models and numerical simulation is thus a way for the National Agency for Radioactive Waste Management to study the phenomena that exist or will exist in the storage facilities and their natural environments, especially since it must ensure that the solutions it adopts will be safe in the very long term [3].

The study by simulation of these materials is carried out by means of statistical thermodynamics. This uses statistical mathematical laws, such as the law of large numbers, to calculate the macroscopic thermodynamic quantities of interest from a representation of the system on a

## - RÉPARTITION dES dÉCHETS RADIOACTIFS À FIN 2016 PAR SECTEUR <br> économiaue



Figure 1 - Breakdown of sectors from which radioactive waste comes, end 2016 (figure from 2])
microscopic scale. In chemistry, the most accurate way to describe a system is to use quantum mechanics 41 (which takes into account the electronic cloud of particles). But if we want to describe larger systems, we rather use the so-called classical (or molecular) level, for two main reasons. The first is the cumbersome nature of quantum simulations, which cannot describe large systems. The second comes from the fact that recycling and extraction are mainly driven by weak, non-covalent interactions, for which a simple classical model is justified. In order to take advantage of these two levels of description, the QM/MM method [158, 181 has been developed; it is based on the description of part of the system at the quantum level and the rest at the classical level. In order to study in a simple way our systems of interest in the framework of this thesis, we have described them at the classical molecular scale.

Based on Newton's second law, molecular dynamics makes it possible to explore the movements of particles, described according to the previously mentioned scales, in order to deduce average properties of the system.

In numerical simulations, in order to reduce surface effects, it is often necessary to impose periodical conditions ${ }^{1}$ on the edges of the simulation boxes 29 . However, these can lead to problems of anisotropy, including in the case of short-range interactions $92,113,143,144$. Long-range interactions may be particularly affected depending on the size of the periodic system considered [6, 89]. Hence the importance of trying to correct, according to the period considered, the calculation of macroscopic properties obtained by this bias. In 185], Yeh and Hummer (as we will see specifically in chapter 6) have for example attempted to make a correction to the calculation of the diffusion coefficient for a particle in a free fluid, a correction which is a function of the spatial period considered. Through this thesis, we wish to focus on the theoretical research of the influence of periodic conditions on the calculation of quantities of interest : the Mean Force Potential (which leads notably to equilibrium constants and activity coefficients) on the one hand, and the diffusion coefficient in confined media on the other hand. Our studies thus lead us to try to make a correction, according to the given period, for these quantities of interest.

[^0]
### 3.1.1 Context of radioactive waste storage

In order to manage radioactive waste, the National Agency for Radioactive Waste Management (ANDRA), a French public institution under the supervision of the Ministries of Research, Industry and the Environment, independent of the producers of radioactive waste, classifies it according to its radioactivity and its lifespan. A distinction is made between high level waste, long-lived medium-level waste, low-level waste, short-lived low- and medium-level waste and, finally, very low-level waste.
Figure 2 shows their volume content at the end of 2016. It can be seen that high level waste accounts for only a small part of the volume ( $0.2 \%$ ), but that it contains $94.9 \%$ of the radioactivity.


Figure 2 - Volume of waste as a function of its level of radioactivity, end 2016 (figure derived from 2 )

Each category of waste has its own specific management method. Figure 3 shows these.

CLASSIFICATION DES DÉCHETS RADIOACTIFS ET FILIÈRES DE GESTION ASSOCIÉES

| Catégorie | Déchets dits à vie très courte | Déchets dits à vie courte | Déchets dits à vie longue |  |
| :---: | :---: | :---: | :---: | :---: |
| Très faible activité (TFA) | Gestion par décroissance radioactive | Stockage de surface <br> (Centre industriel de regroupement, d'entreposage et de stockage) |  |  |
| Faible activité (FA) |  | Stockage de surface (Centres de stockage de l'Aube et de la Manche) | FA-VL | Stockage à faible profondeur à l'étude |
| Moyenne activité (MA) |  |  |  | Stockage profond en projet |
| Haute activité (HA) | Non applicable |  |  |  |

Figure 3 - Radioactivity of radioactive waste and methods of management (figure taken from 2)

On December 30, 1991, the law $n^{\circ}$ 91-1381 108 on research on radioactive waste management states that "The management of high level and long life radioactive waste must be ensured in respect of the protection of nature, environment and health, taking into consideration the rights of future generations". (Article 1)

Then, on June 28, 2006, the law $n^{\circ}$ 2006-739 [109] on the program for the sustainable management of radioactive materials and waste specifies that concerning "the management of long-lived radioactive waste of high or medium activity, research (...) shall be pursued along the following three complementary lines : separation and transmutation of long-lived radioactive elements, reversible storage in deep geological strata, and, finally, disposal". (Article 3)

In order to implement the second axis of the law of June 28, 2006, the project for an Industrial Center for Deep Geological Disposal (Cigeo) [3], in Bure, is planned to store the highly radioactive and long-lived waste produced by all current nuclear facilities, until their dismantling, and by the treatment of spent fuel used in nuclear power plants.

It was necessary to find a stable geological layer, little exposed to earthquakes and erosion, and impermeable. Researchers looked at Callovo-Oxfordian (COx) clay sites. The site is expected to be used for more than a century (the duration of reversibility), for storage over 10,000 years.

The project provides for the digging of $15 \mathrm{~km}^{2}$ of galleries 490 m underground, in order to store $85000 \mathrm{~m}^{3}$ of radioactive waste by 2100 , for a bill estimated in 2016 at 25 billion euros by the State ( 34.5 billion by ANDRA) and financed according to law by the producers of radioactive waste (EDF, CEA, Areva).
Figure 4 presents a scheme of the installations planned for the project.
While in June 2018 ANDRA begins work to clear certain parts of the Lejuc woods to allow for the installation of Cigéo's aeration chimneys, in September 2018 the State announces the launch of a new public debate on the management of all of the country's radioactive waste, between December 2018 and March 2019, which will include the Bure site. The submission of the project, its application for authorization for its creation, is therefore postponed to 2019, which should push back the start of construction to 2022. Thereafter, the launch of the pilot phase is planned for 2025 : an industrial phase that should be implemented for 10 years. It should allow the storage of dummy then real packages to confirm the choices made in terms of storage and security, the type of site ventilation, storage, etc. The first packages should be transported between 2030 and 2033. In 2035, routine operations are scheduled to start with the filling of the site, which will last a century (at a rate of 5 to 10 packages per day). Finally, in 2150 , the storage facility is scheduled to close and the start of monitoring the site after closure.

Numerous projects have been initiated to study the behavior and properties of the 150 argillites present on the site that the project plans to use for the storage of radioactive waste. These come from the deposition of sedimentary particles resulting from the destructuring of rocks of the continental crust. The spatial organization of the minerals in a rock controls the geometry of the pores and thus the geometry of fluid circulation within a 50 rock. The argillites of COx are characterized by a clayey matrix consisting mainly of a mixture of illite and illite/smectite interlayers ${ }^{2}$ (72]. The arrangement of these minerals form a sheet-like structure. A multi-scale

[^1]

Schéma des installations de surface et souterraines du centre en projet Cigéo

Figure 4 - Scheme of the installations of the Cigeo project (scheme resulting from [3])
modeling makes it possible to study the physico-chemical properties of these structures. At the microscopic scale, the pores are thus described at the interpolar, interparticle and intergranular scales $44,49,154$ (cf figure5).


Figure 5 - Representation of the different porosity scales (figure taken from 150])
Porosity is a factor influencing the macroscopic transfer properties of particles within the clay medium. It is necessary to understand the transport phenomena and the containment capacity of radionuclides in order to prevent their return to the biosphere for as long as possible ${ }^{3}$. The pores of argillites are very small (of the order of nanometer), which gives this medium a low permeability. Therefore, the transport of ionic solutes is mainly done by diffusion ${ }^{4}$.

At the pore scale, the sorption phenomenon implies a (non-uniform) compensation of the negative charges of the sheets by cations. A diffuse layer is then formed from the surface to the liquid. This leads to the phenomenon of anionic exclusion : the porosity is accessible to cations and neutral species, while the diffuse layer prevents the passage of anions ${ }^{5}$
At this level of modeling, ab initio calculations 28 or by means of classical molecular dynamics 91,112 allow to account for the diffusion, within this geometry, of ions and solvent, the latter having to be considered as confined between the layers. Other studies are also carried out by Brownian dynamics, a description where the solvent is considered as a continuous medium, which allows a gain in the degrees of freedom 12,116 .

[^2]On the macroscopic scale ${ }^{6}$, porosity is considered to be uniformly distributed and averaged. For a confined medium, interactions with the solid surface modify the mechanics and dynamics, including diffusion-related properties 77, 157. This is described at this scale by an effective diffusion coefficient. The latter can be obtained, for example, using the "though-diffusion" technique 20 121 124], where the diffusion of an element (the "tracer") is established by measuring the concentration gradient between two reservoirs (one upstream which contains the tracer, and the second downstream which does not ; and the sample being placed between these two reservoirs). Other methods of measuring the liquid phase diffusion coefficient in the laboratory consist for example in measuring a flow at the terminals of the sample under consideration or a concentration profile 159 .

In an unconfined (free) fluid, the diffusion coefficient $D$ is defined by the Fick law :

$$
\begin{equation*}
\mathbf{j}=-D \nabla C \tag{3.1}
\end{equation*}
$$

where $\mathbf{j}$ is the molar flux of the diffusing species and $\nabla C$ is the local gradient of molar concentration.

In a saturated porous medium, such as compacted clay, this law is written for the effective diffusion coefficient $D_{e}{ }^{7}$ :

$$
\begin{equation*}
\mathbf{j}=-D_{e} \nabla C \tag{3.2}
\end{equation*}
$$

where $C$ concentrations here are macroscopic quantities at the ends of the sample.

In addition, the hydrodynamic models 27] established with the Stokes equations (equations on which we based our studies in chapter 6) can be used to model the transport of a particle in the solvent :

$$
\left\{\begin{array}{l}
\eta \Delta \mathbf{u}(x, y, z)=\nabla p(x, y, z)  \tag{3.3}\\
\nabla \cdot \mathbf{u}(x, y, z)=0
\end{array}\right.
$$

The resolution of these equations relates the speed $\mathbf{u}$ of the particle with the force it undergoes. This results in the relation between the mobility $\boldsymbol{\mu}$ of the particle and $\mathbf{u}$ by the formula:

$$
\begin{equation*}
\mathbf{u}=\boldsymbol{\mu} \mathbf{F} \tag{3.4}
\end{equation*}
$$

where $\mathbf{F}$ is the external force applied to the particle.
The diffusion coefficient can then be calculated from Einstein's relation 62 :

$$
\begin{equation*}
D=\boldsymbol{\mu} k_{B} T \tag{3.5}
\end{equation*}
$$

[^3]where $k_{B}$ is the Boltzmann constant and $T$ is the temperature.

Multi-scale modeling allows the link between the microscopic and macroscopic scales, in particular by using relevant information at various levels. For example, we can cite the coarse-grained models 53 as well as other techniques based on homogenization methods 131$]^{8}$.

As we have seen above, a common computational trick is to impose periodic conditions on the edges of simulation boxes, conditions that can lead to biases in the computation of macroscopic quantities. The phenomenon of diffusion being particularly important to quantify, the study of the diffusion coefficient, in the simplified case of a particle diffusing in a confined solvent under non-periodic and then periodic conditions, was the subject of chapter 6 of this thesis. It was here calculated analytically from hydrodynamic models, taking into account the periodic boundary conditions.

### 3.1.2 Context of extraction and recycling of rare earths (lanthanides)

Rare earths include 17 metals, including 15 elements in the lanthanides family (see figure 6). They have very interesting properties mainly due to f electrons [84, 133, especially optical and magnetic, particularly useful in the manufacture of permanent magnets, phosphors for the manufacture of light-emitting diodes, or in medicine for Magnetic Resonance Imaging, for example. The family of actinides, which is composed of 15 elements (see figure 6), have physico-chemical properties similar to lanthanides, particularly the oxidation degree +3 in aqueous phase $94,138,183$, which is why studies conducted on these two families can be compared.

Because of their growing need for the development of new technologies today, and because they are inhomogeneously distributed around the globe, component separation techniques present a significant challenge in order to exploit these resources contained in existing technologies.

Among the methods used in industry, we can mention hydrometallurgy, which consists in dissolving the material to be recycled in an acidic aqueous medium, but also pyrometallurgy, where the material is notably melted before proceeding to the extraction of the elements, for example by a liquid-liquid extraction process (cf figure 7). The latter, also called solvent extraction, is specifically exploited in the PUREX process (Plutonium-Uranium Refining by Extraction) $102,118,133,177$ for the recycling of used fuel (which contains uranium (U) and plutonium $(\mathrm{Pu})$ in particular). This process consists beforehand in a "shearing" that allows contact between the fuel and a nitric solution. Next, a key stage aims at a dissolution of the fuel. Uranium dioxide dissolves rapidly in hot nitric acid, unlike plutonium dioxide, which is why it is generally mixed solid solutions of uranium and plutonium (with a lower content than uranium) that are dissolved. Consequently, another important step is the separation and purification of uranium and plutonium by extraction, with Tributyl Phosphate (TBP) as the extractant ${ }^{9}$ (which is effective only in very acidic solution), diluted in an organic solvent the TetraPropylene-Hydrogen (TPH) ${ }^{10}$

[^4]

Figure 6 - Periodic Table of the Elements, showing in particular the lanthanide and actinide families (figure from [177)

This stage consists on the one hand in the co-extraction in the organic phase of the metallic elements of interest (uranium and plutonium, which are precipitated in the form of oxides), while maintaining the impurities in the aqueous phase. On the other hand, a second sub-step allows the desired elements to be de-extracted in another aqueous phase. The plutonium is reduced to the oxidation state +3 (instead of +4 ), with uranium as the reducing agent in the oxidation state +4 , which makes TBP ineffective for plutonium. To de-extract the uranium, the solvent phase is brought into contact with a slightly acidic aqueous phase at high temperature. In addition, the other minor actinides $(\mathrm{Am}, \mathrm{Cu}, \mathrm{Np})$ and the fission products ( $\mathrm{Cs}, \mathrm{Tc}$ ) that remain in the aqueous solution must be separated in order to reduce the concentration of the wastes.

In order to optimize these industrial processes, it is necessary to understand the structural and thermodynamic properties of the elements involved in the various stages of the adopted process. The structure of Lanthanides in solution has already been the subject of numerous studies 21 39, $78,82,114$, 184 , such as to provide information on water ions-molecule distances or the nature of ion-solvent and ion-ion interactions. Experimentally, this can be done using the EXAFS (Extended X-Ray Absorption Fine Structure) method [40, $93,139,175$ based on X-ray spectrum analysis. Although actinides are more difficult to analyze, as these elements are particularly oxidizable, studies conducted with the XAS (X-ray Absorption Spectroscopy) method 5.32 can be cited.

In addition to experiments, numerical studies such as by the Monte Carlo method 70.96 and by Molecular Dynamics methods are a good way to obtain additional information. The latter can be established at the classical level 36,123 , but other researches are carried out at the quantum level for example with the Car-Parinello method $90{ }^{11}$. In order to achieve these methods, sufficiently precise interaction potentials must be established. Thus, for example, in a study on Lanthanides in aqueous solution, one can note the important character of taking into account

[^5]the polarization ${ }^{[2]}$ to obtain the $L a-O$ distance 60 .
From the simulations, we will be able to calculate quantities of thermodynamic properties of interest such as the osmotic coefficient, activity coefficients or association constants $22,23,134$. In the PUREX process, for example, for extraction with TBP in organic phase, these last ones allow to obtain, thanks to the law of mass action, the extraction equilibrium constant. One way to obtain these coefficients is to calculate the McMillan and Mayer potential, which corresponds to an ion-ion potential averaged over the solvent configuration at infinite dilution. The interest of McMillan and Mayer's approach, compared for example to the Kirkwood-Buff theory, comes from the gain in simulation time, in particular because the degrees of freedom are smaller.

Chapter 5 of this thesis is devoted to the study of McMillan and Mayer's potential for a box composed of two ions surrounded by a solvent, when considering periodic conditions at the edges of the simulation box. Our study aims at giving a correction to the calculation of the McMillan and Mayer potential, a correction which takes into account the period considered. This will allow us to adjust the ensuing calculations. In addition, studies carried out on the one hand with NaCl in aqueous phase, and on the other hand on Lanthanide salts will make it possible to observe the adaptation of our calculations with the curves obtained by molecular simulations.


Figure 7 - Illustration of the liquid-liquid extraction technique (figure from 177)

### 3.2 Description of matter and equilibrium models

### 3.2.1 Description of the interactions of a system

In the following, in accordance with the choice of the General Conference on Weights and Measures of 2018 1] $e=1.602176634 .10^{-19} \mathrm{C}$ is the value of the elementary charge, $\epsilon_{0} \approx$ 8.854.10 ${ }^{-12} \mathrm{C}^{2} . \mathrm{J}^{-1} \mathrm{~m}^{-1}$ the permittivity of the vacuum, $\epsilon_{r}$ la permittivité relative du milieu,

[^6]$k_{B}=1.380649 .10^{-23} \mathrm{~J} . \mathrm{K}^{-1}$ Boltzmann's constant, $T$ the temperature, $h=6.62607015 .10^{-34} \mathrm{~m}^{2} \mathrm{~kg} \cdot \mathrm{~s}^{-1}$ Planck's constant.

We consider a system consisting of $N$ particles, defined by their positions and impulses ( $\mathbf{r}, \mathbf{p}$ ) where $\mathbf{r}=\left(\mathbf{r}_{1}, \ldots, \mathbf{r}_{N}\right) \in \mathbb{R}^{3 N}$ and $\mathbf{p}=\left(\mathbf{p}_{1}, \ldots, \mathbf{p}_{N}\right) \in \mathbb{R}^{3 N}$. The interactions of this system are described by the total energy of the system 105 167, 172 :

$$
\begin{equation*}
H(\mathbf{r}, \mathbf{p})=E_{c}(\mathbf{p})+\mathcal{V}(\mathbf{r}) \tag{3.6}
\end{equation*}
$$

where $H$ is the Hamiltonian of the system, with $E_{c}$ its kinetic energy and $\mathcal{V}$ its potential energy.
We have :

$$
\begin{equation*}
E_{c}(\mathbf{p})=\frac{1}{2} \mathbf{p}^{T} \mathbf{M}^{-1} \mathbf{p} \tag{3.7}
\end{equation*}
$$

where $\mathbf{M}$ is the mass matrix of the particles in the system.
Potential energy is defined from physical bonds on the one hand, which correspond to intermolecular forces, and chemical bonds on the other hand, which refer to intramolecular forces 9, $55,73,133$. These forces are described according to their origin, intensity, direction and range. The potential energy can then be written as a sum of $n$-body potentials $\mathcal{V}_{n}$ :

$$
\begin{equation*}
\mathcal{V}\left(\mathbf{r}_{1}, . ., \mathbf{r}_{N}\right)=\sum_{i=1}^{N} \mathcal{V}_{1}\left(\mathbf{r}_{i}\right)+\sum_{i, j=1, i<j}^{N} \mathcal{V}_{2}\left(\mathbf{r}_{i}, \mathbf{r}_{j}\right)+\ldots+\sum_{i, j, \ldots, z=1, i<j<\ldots<z}^{N} \mathcal{V}_{n}\left(\mathbf{r}_{i}, \mathbf{r}_{j}, \ldots, \mathbf{r}_{z}\right) \tag{3.8}
\end{equation*}
$$

$\mathcal{V}_{1}$ corresponds to the interaction potential with an external field (e.g. due to the volume of the box) and $\mathcal{V}_{2}$ to the additive pair interaction potential. The other terms are called $n$-body potentials [48, 85 and are associated with the interaction potential between $n$ (with $n>2$ ) particles. The latter, in the case of molecular systems, are generally of lower intensity than those of pairs (except for intramolecular terms), but they are nevertheless crucial to understand certain properties of a system such as polarisability. In practice, the effects of these interactions between $n$ particles are effectively included in the effective pair potential $\mathcal{V}_{2}^{\text {eff }}$. We then have the following approximation :

$$
\begin{equation*}
\mathcal{V}\left(\mathbf{r}_{1}, \ldots, \mathbf{r}_{N}\right) \simeq \sum_{i=1}^{N} \mathcal{V}_{1}\left(\mathbf{r}_{i}\right)+\sum_{i, j=1, i<j}^{N} \mathcal{V}_{2}^{e f f}\left(\mathbf{r}_{i}, \mathbf{r}_{j}\right) \tag{3.9}
\end{equation*}
$$

Intramolecular interactions (see figure 8) describe forces within molecules of which they ensure in particular their stability. The most common are those involving distances (binding energy), angles (bending energy) and dihedrals (torsion energy). In our simulations, we used the AMOEBA model [141, which describes intramolecular interactions by a sum of anharmonic potentials to represent binding, angle, cross-binding angle and out-of-plane bending energies, to which a Fourier series is added to express torsional rotation.

Intermolecular bonds, as for them, correspond to the interactions of unbound atoms. These are, on the one hand, interactions of atoms of the same molecule separated by more than two chemical bonds, and on the other hand, those existing between the different molecules of the system. We differentiate the attractive forces, which ensure the cohesions of the molecules with respect to


Figure 8 - Scheme of the main contributions to intramolecular interactions (taken from 55)
each other in the condensed phases, from the repulsive forces, forces generally at short distance which impose a stacking structure respecting their shapes (in fact, they ensure the Pauli principle, which prevents two particles from being in the same place at the same time).

The interactions described in 3.8 are of two kinds.
First of all, we distinguish electrostatic energies $\mathcal{V}_{\text {elec }}$, which are long-range interactions and which are decomposed into a multipolar series taking into account charge-charge (Columbian energy), charge-dipole, and dipole-dipole interactions on the one hand, and into a induced polarization energy for an instantaneous and fluctuating dipole on the other hand. For the latter, polarization translates the distortion of the electronic cloud of a molecule under the effect of an electric field created by the surrounding molecules.

Several force field writings exist in the literature and are used in modeling. Here is a possible example (cf [55]) to describe lanthanides, which are widely used in solution chemistry.

The Coulombic energy potential $\mathcal{V}_{\text {Coul }}$ is associated with an intense, long-range force. It is expressed as follows :

$$
\begin{equation*}
\mathcal{V}_{\text {Coul }}=\frac{1}{2} \sum_{i=1, i \neq j}^{N} \frac{z_{i} z_{j} e^{2}}{4 \pi \epsilon_{0} r_{i j}} \tag{3.10}
\end{equation*}
$$

where, for $i, j=1, \ldots, N, z_{i}$ is the charge number of the particle $i$ and $r_{i j}\left(=\left\|\mathbf{r}_{i}-\mathbf{r}_{j}\right\|\right)$ is the distance between the two particles $i$ and $j$.

The induced polarization energy potential $\mathcal{V}_{p o l}$ is written as follows :

$$
\begin{equation*}
\mathcal{V}_{\text {pol }}=-\frac{1}{2} \sum_{i=1}^{N} \mu_{i} E_{i}^{0} \tag{3.11}
\end{equation*}
$$

with, for $i=1, \ldots, N, \mu_{i}=\alpha_{i} E_{i}$ the induced moment of the particle $i$, where $\alpha_{i}$ is the atomic polarization and $E_{i}$ is the local electric field generated on the particle $i$, and where $E_{i}^{0}$ is the total electric field.

The interactions given in (3.8) also consist of short-range energy, including repulsive and other energy terms. An important interaction is the van der Waals interaction $\mathcal{V}_{v d W}$. It is an interaction in $r^{-6}$, where $r$ is the distance between two particles, and thus at short range. The dipole moment of the particle $i$ is designated by $\mu_{i}$. The potential $\mathcal{V}_{v d W}$ is composed of three terms :

- the Keesom term : $-\frac{\mu_{1}^{2} \mu_{2}^{2}}{3\left(4 \pi \epsilon_{0} \epsilon_{r}\right)^{2} k_{b} T r^{6}}$, which translates a dipolar force between two permanent dipoles whose rotations are thermally averaged ${ }^{13}$,
- the Debye term : $-\frac{\mu_{1}^{2} \alpha}{\left(4 \pi \epsilon_{0} \epsilon_{r}\right)^{2} r^{6}}$, which reflects an interaction between a permanent dipole and an induced dipole. ${ }^{14}$,
- the London term : $-\frac{3}{4} \frac{h \nu \alpha^{2}}{\left(4 \pi \epsilon_{0} \epsilon_{r}\right)^{2} r^{6}}$, which represents the force of dispersion; it is a force of quantum origin, and is the most important contribution of attractive forces. It is the interaction force between induced dipoles.
(In these three terms, $\alpha$ refers to electronic polarisability and $\nu$ refers to the frequency of fluctuation.)

In molecular simulation software, van der Waals energy is often taken into account using, for example, a Lennard-Jones potential $V_{L J}$, which is written as follows $\left(\epsilon_{i j}\right.$ and $\sigma_{i j}$ being the Lennard-Jones parameters 106) :

$$
\begin{equation*}
V_{L J}=\sum_{i, j=1, i \neq j}^{N} 4 \epsilon_{i j}\left(\left(\frac{\sigma_{i j}}{r_{i j}}\right)^{12}-\left(\frac{\sigma_{i j}}{r_{i j}}\right)^{6}\right) \tag{3.12}
\end{equation*}
$$

Here, the term in $r_{i j}^{-6}$ represents the Van der Waals forces (which are attractive), and the term in $r_{i j}^{-12}$ describes the repulsive forces between atoms at short distance, these being due to Pauli's principle, which forbids electrons to occupy the same region of space.

### 3.2.2 Statistical thermodynamics

## a. Reminders on the principles of thermodynamics

Let's first recall the fundamental principles of classical thermodynamics 67, 172] :
We consider an energy system $E_{\text {syst }}$.
First Principle of Thermodynamics (Conservation of Energy) : For any thermodynamic transformation, if the system absorbs an amount $Q$ of heat and produces an amount of work $W$, then its energy changes by an amount $\Delta E_{\text {syst }}=Q-W$. On the other hand, if we consider the external energy $E_{\text {ext }}$ and the total energy (of the universe) $E_{t o t}$ then :

$$
\begin{equation*}
\Delta E_{t o t}=\Delta E_{\text {syst }}+\Delta E_{e x t}=0 \tag{3.13}
\end{equation*}
$$

(i.e. any change in the energy of the system is exactly compensated by a change in the surrounding energy). For any system, we thus define a quantity that is conserved, i.e. it does not change by visible exchanges at the macroscopic scale (work) as well as at the microscopic scale (heat).

[^7]Second Principle of Thermodynamics (Irreversibility of physical phenomena) : We add another quantity that allows us to predict thermodynamics. Let $S_{\text {syst }}$ be the entropy of the system, $S_{\text {ext }}$ the external entropy, and $S_{t o t}$ the total entropy. So, for any thermodynamic transformation, we have :

$$
\begin{equation*}
d S_{t o t}=d S_{s y s t}+d S_{e x t} \geq 0 \tag{3.14}
\end{equation*}
$$

This reflects the fact that, for an isolated system, entropy increases 52 .
For a reversible transformation, $S_{t o t}$ is such that $d S_{t o t}=\frac{d Q_{r e v}}{T}$, where $d Q_{\text {rev }}$ is the amount of heat needed to change the temperature $T$ by an amount $d T$.

Any system described in this framework will therefore have to verify these principles. Let us now look more precisely at the systems studied in the framework of statistical physics.

## b. Thermodynamic ensembles

We consider a microscopic system composed of $N$ particles, described by their position and pulse, as defined in section 2.2.1. The pair $(\mathbf{r}, \mathbf{p})$ is called the microscopic state of the system, also called the system configuration. The possible ensemble of these pairs is called the phase space, the latter being of dimension $6 N$. It is used to describe the trajectories described in time.

In statistical physics, the macroscopic state of the system is described by a measure of probability $\phi$ on the phase space. The quantities of macroscopic interest appear as averages over thermodynamic ensembles, ensembles which represent these measurements :

$$
\begin{equation*}
E_{\phi}(A)=\int_{\mathbb{R}^{6 N}} A(\mathbf{r}, \mathbf{p}) d \phi(\mathbf{r}, \mathbf{p}) \tag{3.15}
\end{equation*}
$$

where $A$ is the observable.

In practice, in the simulations, the space of the positions is most often reduced on a range of values $D \subset \mathbb{R}^{3}$ corresponding to the space accessible by the particles and then we calculate :

$$
\begin{equation*}
E_{\phi}(A)=\int_{D^{N} \times \mathbb{R}^{3 N}} A(\mathbf{r}, \mathbf{p}) d \phi(\mathbf{r}, \mathbf{p}) \tag{3.16}
\end{equation*}
$$

The different ensembles of thermodynamics $35,67,80,172$ each represent specific experimental conditions. According to these conditions, thanks to the principles of thermodynamics and to statistical considerations, it will be possible to obtain the variables that are not fixed (depending on the case, the temperature ${ }^{15}$, the chemical potential, ...)

The microcanonics ensemble ( $N V E$ ) : ${ }^{16}$ We consider a closed and insulated system composed of $N$ particles, having a volume of $V$, and an energy $E{ }^{[17}$

[^8]The $\phi$ measure associated with this ensemble is the uniform probability measure normalized over the $\Gamma(E)$ configuration set at the given $E$ energy level, which ensemble is defined by :

$$
\Gamma(E)=\left\{(\mathbf{r}, \mathbf{p}) \in D^{N} \times \mathbb{R}^{3 N} \mid H(\mathbf{r}, \mathbf{p})=E\right\}
$$

$\phi$ being thus given : $d \phi(\mathbf{r}, \mathbf{p})=\delta_{H(\mathbf{r}, \mathbf{p})-E}$.
The associated partition function $\Psi$ is ${ }^{18]}$ :

$$
\begin{equation*}
\Psi=\frac{1}{N!h^{3 N}} \int_{\Gamma(E)} \delta_{H(\mathbf{r}, \mathbf{p})-E} d \mathbf{r} d \mathbf{p} \tag{3.17}
\end{equation*}
$$

where $h$ is Planck's constant. $h^{3 N}$ is a measure of the "volume" of the particular state, and the factor $N$ ! is needed to correct the state count $17,121{ }^{19}$,

The $S$ entropy of the system is defined according to the partition function by the Boltzmann formula :

$$
\begin{equation*}
S=k_{B} \ln (\Psi) \tag{3.18}
\end{equation*}
$$

where $k_{B}$ is Boltzmann's constant. The other thermodynamic quantities, in particular temperature $T$, pressure $P$ and chemical potential $\mu$, can be obtained from $S$. Indeed, we have the relation :

$$
\begin{equation*}
d S=\frac{1}{T} d E+\frac{P}{T} d V-\frac{\mu}{T} d N \tag{3.19}
\end{equation*}
$$

This leads us to obtain :

$$
\begin{equation*}
\frac{1}{T}=\left(\frac{\partial S}{\partial E}\right)_{V, N}, \frac{P}{T}=\left(\frac{\partial S}{\partial V}\right)_{E, N}, \frac{\mu}{T}=\left(\frac{\partial S}{\partial N}\right)_{E, V} \tag{3.20}
\end{equation*}
$$

The canonical ensemble ( $N V T$ ) : This time, the system is considered to be surrounded by a thermostat (which imposes a $T$ temperature on the system). Here, the number $N$ of particles and the volume $V$ of the system are also fixed, but the energy fluctuates.

The probability measure $\phi$ of the canonical ensemble is defined by the relation :

$$
\begin{equation*}
d \phi(\mathbf{r}, \mathbf{p})=Z^{-1} \exp (-\beta H(\mathbf{r}, \mathbf{p})) d \mathbf{r} d \mathbf{p} \tag{3.21}
\end{equation*}
$$

where $\beta=\frac{1}{k_{B} T}, H$ is the Hamiltonian of the system and $Z$ is the partition function of the canonical ensemble and has the form

$$
\begin{equation*}
Z=\frac{1}{N!h^{3 N}} \int_{D^{N} \times \mathbb{R}^{3 N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} d \mathbf{r} d \mathbf{p} \tag{3.22}
\end{equation*}
$$

18. In fact, physically, $\psi$ is defined as :

$$
\Psi=\frac{1}{N!h^{3 N}} \int_{E<H<E+\Delta E} d \mathbf{r} d \mathbf{p}
$$

where the energy variation $\Delta E$ is small, corresponding to the number of accessible states, i.e. compatible with the macroscopic variables. These two formulations are equivalent within the limits of large systems
19. Some authors disagree with this argument in the case of some systems although showing that it does not affect the study of its thermodynamics 66

Helmholtz free energy is defined as follows $F$ :

$$
\begin{equation*}
F=U-T S \tag{3.23}
\end{equation*}
$$

where $U$ is the internal energy of the system. We can show that :

$$
\begin{equation*}
F(N, V, T)=-k_{B} T \ln (Z(N, V, T)) \tag{3.24}
\end{equation*}
$$

From $F$, one can, again, deduce the macroscopic quantities of interest, thanks to the relation :

$$
\begin{equation*}
d F=-S d T-P d V+\mu d N \tag{3.25}
\end{equation*}
$$

which leads us to obtain :

$$
\begin{equation*}
\mu=\left(\frac{\partial F}{\partial N}\right)_{V, T}, P=-\left(\frac{\partial F}{\partial V}\right)_{N, T}, S=-\left(\frac{\partial F}{\partial T}\right)_{N, V} . \tag{3.26}
\end{equation*}
$$

The isothermal-isobaric ensemble ( $N P T$ ) : We consider here a system surrounded by a thermostat imposing a temperature $T$, and also subjected to a barostat that imposes a pressure $P$. The number of particles $N$ is fixed. But the energy $E$ and the volume $V$ vary.

The $\Delta$ partition function is defined by 172 :

$$
\begin{equation*}
\Delta=\frac{\beta P}{h^{3 N} N!} \int e^{-\beta P V} d V \int_{D^{N} \times \mathbb{R}^{3 N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} d \mathbf{r} d \mathbf{p} \tag{3.27}
\end{equation*}
$$

Gibbs free energy $G$ is defined as :

$$
\begin{equation*}
G=U+P V-T S \tag{3.28}
\end{equation*}
$$

We can show that :

$$
\begin{equation*}
G=-k_{b} T \ln (\Delta) . \tag{3.29}
\end{equation*}
$$

From relationships :

$$
\begin{equation*}
d G=-S d T+V d P+\mu d N \tag{3.30}
\end{equation*}
$$

we can deduce from this :

$$
\begin{equation*}
\mu=\left(\frac{\partial G}{\partial N}\right)_{T, P}, V=\left(\frac{\partial G}{\partial P}\right)_{N, T}, S=-G-\left(\frac{\partial G}{\partial T}\right)_{N, P} \tag{3.31}
\end{equation*}
$$

The Grand Canonical ensemble ( $\mu V T$ ) : We consider a system surrounded by a reservoir of particles (and thus here the number of particles $N$ varies), whose chemical potential $\mu$ and temperature $T$ are imposed. The volume $V$ of the system is also fixed.

We consider :

$$
\begin{equation*}
Z_{N}=\int_{D^{N}} e^{-\beta \mathcal{V}(\mathbf{r})} d \mathbf{r} \tag{3.32}
\end{equation*}
$$

The partition function $Q$ is defined by :

$$
\begin{align*}
Q(\mu, V, T) & =\sum_{N=1}^{\infty} \frac{e^{\beta \mu N}}{h^{3 N} N!} \int_{D^{N} \times \mathbb{R}^{3 N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} d \mathbf{r} d \mathbf{p}  \tag{3.33}\\
& =\sum_{N=1}^{\infty} \frac{z^{N}}{N!} Z_{N} \tag{3.34}
\end{align*}
$$

Here we have defined the $z$ fugacity of the system by the following relation :

$$
\begin{equation*}
z=\frac{e^{\beta \mu}}{\Lambda^{3}} \tag{3.35}
\end{equation*}
$$

where $\Lambda=\frac{h}{\left(2 \pi m k_{b} T\right)^{1 / 2}}$ is the Broglie wavelength of a particle ${ }^{20}$
We define the grand potential $\Xi$ :

$$
\begin{equation*}
\Xi=U-T S-\mu N . \tag{3.36}
\end{equation*}
$$

We can show that :

$$
\begin{equation*}
\Xi=-k_{b} T \ln (Q) . \tag{3.37}
\end{equation*}
$$

From the relationship :

$$
\begin{equation*}
d \Xi=-S d T-N d \mu-P d V \tag{3.38}
\end{equation*}
$$

macroscopic quantities can be obtained :

$$
\begin{equation*}
S=-\left(\frac{\partial \Xi}{\partial T}\right)_{V, \mu}, N=-\left(\frac{\partial \Xi}{\partial \mu}\right)_{V, T}, P=-\left(\frac{\partial \Xi}{\partial V}\right)_{V, T} . \tag{3.39}
\end{equation*}
$$

(N.B. : the $\mu P T$ ensemble does not exist, since the three control variables are intensive, and such an ensemble has no size, which makes no physical sense.)

## Case of mixtures :

Until now, we have evoked the case of a system formed by a single chemical species. When there are several chemical species, we define as many chemical potentials $\mu_{i}$ as there are species. The preceding formulas must then be adapted.

[^9]In the canonical ensemble, the $Z$ partition function in $(3.22)$ is expressed, in the case of $M$ species each formed of $N_{i}$ particles, defined on $D_{i}$ :
with (3.24) and :

$$
\begin{equation*}
d F=-S d T-P d V+\sum_{i} \mu_{i} d N_{i} \tag{3.41}
\end{equation*}
$$

In the canonical grand ensemble, the $Q$ partition function of 3.34 is written as follows:

$$
\begin{equation*}
Q\left(\left(\mu_{i}\right)_{i}, V, T\right)=\sum_{i} \sum_{N_{i}=1}^{\infty} \frac{z^{N_{i}}}{N_{i}!} Z_{N_{i}} \tag{3.42}
\end{equation*}
$$

where $Z_{N_{i}}$ is given in 3.32) and $z^{N_{i}}$ in 3.35).
$\Xi$ given in (3.37) verifies here:

$$
\begin{equation*}
d \Xi=-S d T-\sum_{i} N_{i} d \mu_{i}-P d V \tag{3.43}
\end{equation*}
$$

Another space, related to the work of McMillan and Mayer, is the semi-large canonical space which allows to treat the case of mixing. We will come back to it in more detail in Chapter 4.

### 3.2.3 Distribution functions

Spatial distribution functions provide information on the local structure as well as on the fluctuations of a fluid $127,133,172$.

To begin, we place ourselves in the conditions of the canonical ensemble and consider a system composed of $N$ particles and volume $V$, and the temperature $T$ is fixed.

## Correlation function :

We define the density of $n$ indistinguishable particles as a function of $Z_{N}$ defined in (3.32):

$$
\begin{equation*}
\rho_{N V T}^{(n)}\left(\mathbf{r}_{1}, . ., \mathbf{r}_{n}\right)=\frac{N!}{(N-n)!Z_{N}} \int_{D^{N-n}} e^{-\beta \mathcal{V}\left(\mathbf{r}_{1}, . ., \mathbf{r}_{n}\right)} d \mathbf{r}_{n+1} . . d \mathbf{r}_{N} \tag{3.44}
\end{equation*}
$$

The correlation function is then defined according to $\rho^{(n)}$ and the density $\rho=\frac{N}{V}$ :

$$
\begin{equation*}
g^{(n)}\left(\mathbf{r}_{1}, . ., \mathbf{r}_{n}\right)=\frac{\rho^{(n)}\left(\mathbf{r}_{1}, . ., \mathbf{r}_{n}\right)}{\rho^{n}} \tag{3.45}
\end{equation*}
$$

## Radial distribution function :

In case $n=2, g^{(2)}$ is called the pair correlation function. It represents the probability of finding an atom 1 at the $\mathbf{r}_{1}$ position and an atom 2 at the $\mathbf{r}_{2}$ position, normalized to 1 at long distance (i.e. when $\left\|\mathbf{r}_{1}-\mathbf{r}_{2}\right\| \rightarrow \infty$ ).

We have :

$$
\begin{aligned}
g^{(2)}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) & =\frac{N(N-1)}{\rho^{2} Z_{N}} \int_{D^{N-2}} e^{-\beta \mathcal{V}\left(\mathbf{r}_{1}, ., \mathbf{r}_{n}\right)} d \mathbf{r}_{3} . . d \mathbf{r}_{N} \\
& =\frac{N(N-1)}{\rho^{2}}\left\langle\delta\left(\mathbf{r}_{1}-\mathbf{r}_{1}^{\prime}\right) \delta\left(\mathbf{r}_{2}-\mathbf{r}_{2}{ }_{2}\right)\right\rangle_{\mathbf{r}_{1}, \ldots, \mathbf{r}^{\prime}{ }_{N}}
\end{aligned}
$$

where $\langle$.$\rangle indicates an average value.$
If the system is homogeneous and isotropic, $g$ depends only on $r_{12}$, i.e. it is a radial function, called a radial distribution function.

In the large canonical ensemble, that is a system with a fixed chemical potential $\mu$, volume $V$ and temperature $T$. The density at $n$-body is defined here as follows :

$$
\begin{equation*}
\rho_{\mu V T}^{(n)}=\frac{1}{Q(\mu, V, T)} \sum_{N=n}^{\infty} \frac{z^{N}}{(N-n)!} \int_{D^{N-n}} e^{-\beta \mathcal{V}\left(\mathbf{r}_{1}, . ., \mathbf{r}_{n}\right)} d \mathbf{r}_{n+1} . . d \mathbf{r}_{N} \tag{3.46}
\end{equation*}
$$

where $z$ is the fugacity of the system given in (3.35).
The correlation function is then given by (3.45).

## Case of mixtures :

We consider a multisystem formed of $N_{i}$ particles of species $i$ with density $\rho_{i}$ and of $N_{j}$ particles of type $j$ with density $\rho_{j}$.

The correlation function is then given by :

$$
\begin{equation*}
g^{(n)}\left(\mathbf{r}_{1}, . ., \mathbf{r}_{n}\right)=\frac{\rho^{(n)}\left(\mathbf{r}_{1}, . ., \mathbf{r}_{n}\right)}{\prod_{i=1}^{n} \rho_{i}} \tag{3.47}
\end{equation*}
$$

The radial distribution function verifies :

$$
\begin{equation*}
g^{(2)}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=\frac{N_{i}\left(N_{j}-\delta_{i j}\right)}{\rho_{i} \rho_{j}}\left\langle\delta\left(\mathbf{r}_{1}-\mathbf{r}_{1}\right) \delta\left(\mathbf{r}_{2}-\mathbf{r}^{\prime}{ }_{2}\right)\right\rangle_{\mathbf{r}_{1}, \ldots, \mathbf{r}^{\prime}{ }_{N}} . \tag{3.48}
\end{equation*}
$$

To each well defined (minimum) well of the radial distribution function $g^{(2)}$ corresponds a coordination sphere (see figure 9 ). We call coordination number $C_{N}$ the number of particles of species
$i$ around particles of type $j$ up to a distance $L$, which is obtained by the formula :

$$
\begin{equation*}
C_{N}(L)=4 \pi \rho_{j} \int_{0}^{L} g^{(2)}\left(r_{i j}\right) r_{i j}^{2} d r_{i j} \tag{3.49}
\end{equation*}
$$

On the figure 9 are represented the radial distribution function and the coordination number of the oxygen of the water around an ion $\mathrm{Na}^{+}$in solution.


Figure 9 - Illustration of the determination of the average number of coordinations around the ion $\mathrm{Na}^{+}$for the first sphere in a cubic side box $53,000 A$ containing 4998 molecules of water and 1 ion $\mathrm{Na}^{+}$and 1 ion $\mathrm{Cl}^{-}$: we observe a first minimum of the function $g_{N a-O}$ (black curve) at about 3.2 A , which corresponds to about 6 molecules of water around $\mathrm{Na}^{+}$(red curve)

### 3.3 Simulation methods

### 3.3.1 Molecular Dynamics

We recall Newton's second principle concerning, in a Galilean reference frame, the sum of forces $\mathbf{F}^{21}$ exerted on a particle of position $\mathbf{r}$, of mass $m$ :

$$
\begin{equation*}
\mathbf{F}=m \frac{d^{2} \mathbf{r}}{d t^{2}} \tag{3.50}
\end{equation*}
$$

This law allows, from the force fields that describe the system of interest, to know the trajectory of the particles of the system over time and is at the origin of molecular dynamics. The idea is, from the initial configuration of a $N$ particle system, to determine the forces of the system and then to perform the displacements of the particles from equations of motion established by Newton's second principle; at this stage one can calculate the static properties of the system (such as energy or temperature), and then pursue the dynamics iteratively.

[^10]
## - Verlet's integrator :

We begin by recalling that the law 3.50 can be found in Hamilton's relationship ${ }^{22}$ for every $i$ th coordinate at time $t$ with :

$$
\left\{\begin{array}{l}
\dot{\mathbf{r}_{i}}(t)=\frac{\partial H}{\partial \mathbf{p}_{i}}(\mathbf{r}(t), \mathbf{p}(t))  \tag{3.51}\\
\dot{\mathbf{p}_{i}}(t)=-\frac{\partial H}{\partial \mathbf{r}_{i}}(\mathbf{r}(t), \mathbf{p}(t))
\end{array}\right.
$$

Indeed $\frac{\partial H}{\partial \mathbf{p}_{i}}=\frac{\mathbf{p}_{i}}{m}$ so that $\ddot{\mathbf{r}}_{i}=\frac{\dot{\mathbf{p}}_{i}}{m}$. In addition $\frac{\partial H}{\partial \mathbf{r}_{i}}=\frac{\partial \mathcal{V}}{\partial \mathbf{r}_{i}}=-\mathbf{F}_{i}$.
(3.51) is in fact equivalent to the following system :

$$
\left\{\begin{array}{l}
\dot{\mathbf{r}}_{i}(t)=\frac{\mathbf{p}_{i}(t)}{m}  \tag{3.52}\\
\dot{\mathbf{p}}_{i}(t)=-\frac{\partial \mathcal{V}(\mathbf{r}(t))}{\partial \mathbf{r}_{i}}=\mathbf{F}_{i}(t)
\end{array}\right.
$$

(3.52) is an ordinary differential equation that can be classically integrated by means of the Verlet integrator for speed 168 : one notes $\left(r^{n}, p^{n}\right)$ an approximation of $\left(\mathbf{r}\left(t_{n}\right), \mathbf{p}\left(t_{n}\right)\right)$ for $t_{n}=n \Delta t$, then it comes :

```
\(p^{n+1 / 2}=p^{n}+0.5 * \Delta t * F^{n}\)
\(r^{n+1}=x^{n}+\Delta t * \frac{p^{n+1 / 2}}{m}\)
Calcul de \(F^{n+1}\)
\(p^{n+1}=p^{n+1 / 2}+0.5 * \Delta t * F^{n+1}\)
```

Note that this algorithm can also easily be find by means of Taylor-Young development of the position and retrogressive Taylor-Young development of the velocity of the considered system 55, 133$]^{23}$

## - RESPA Algorithm :

In order to accelerate the calculation of the dynamics, we used the algorithm RESPA. (REference System Propogator Algorithm [173]), which allows the forces to be processed according to their intensity and speed of evolution.

The Hamiltonian $H$ of a system consisting of a particle with coordinates $(x, p)$ in phase space and mass $m$, given by the formula (3.6) :

$$
H(x, p)=\frac{p^{2}}{2 m}+\mathcal{V}(x)
$$

[^11]The Liouville operator is introduced ${ }^{24}$ :

$$
\begin{equation*}
i L=\frac{\partial H}{\partial p} \frac{\partial}{\partial x}-\frac{\partial H}{\partial x} \frac{\partial}{\partial p} \tag{3.53}
\end{equation*}
$$

So we have (since $F=-\nabla \mathcal{V}): i L=\frac{p}{m} \frac{\partial}{\partial x}+F(x) \frac{\partial}{\partial p}$.
We know that $(x, p)$ verifies Hamilton's equations:

$$
\left\{\begin{array}{l}
\dot{x}=\frac{\partial H}{\partial p}  \tag{3.54}\\
\dot{p}=-\frac{\partial H}{\partial x}
\end{array}\right.
$$

On the other hand, for any function $f=f(x(),. p()$.$) we have :$

$$
\begin{equation*}
\frac{d f}{d t}=\frac{\partial f}{\partial x} \dot{x}+\frac{\partial f}{\partial p} \dot{p} . \tag{3.55}
\end{equation*}
$$

Thus, using (3.54) and (3.55), we have the equation:

$$
\begin{equation*}
\frac{d f}{d t}=i L f \tag{3.56}
\end{equation*}
$$

The solution to this equation is : $f(t)=e^{i L t} f(0)$.

Here, after having talked about the notion of semigroup, we will recall Trotter's theorem 33,47 , 171.

Definition 1. Let $E$ be a normed vector space, with the associated norm $\|$.$\| . For an application$ $\mathcal{A} \in \mathcal{L}(E, E)$ (where we note $\mathcal{L}(E, E)$ the set of continuous linear applications from $E$ to $E$ ), we define the norm :

$$
\|\mathcal{A}\|=\sup _{x \in E \backslash\{0\}} \frac{\|\mathcal{A} x\|}{\|x\|}
$$

Definition 2. Let $\mathcal{H}$ be an Hilbert space. A semigroup of operator is an operator family $\mathcal{U}=$ $\left\{\mathcal{U}_{t} \in \mathcal{L}(\mathcal{H}, \mathcal{H}), t \in \mathbb{R}^{+}\right\}$which satisfies the following properties :
i) $\forall t, s \in \mathbb{R}^{+}: \mathcal{U}_{t} \circ \mathcal{U}_{s}=\mathcal{U}_{t+s}$
ii) $\mathcal{U}_{0}=I d$ (where $\operatorname{Id}(x)=x$ for all $x \in \mathcal{H}$ )
iii) $\forall x \in \mathcal{H}, t \mapsto \mathcal{U}_{t} x$ is continuous from $\mathbb{R}^{+}$in $\mathcal{H}$.

Its semigroup is bounded if $\left\|\mathcal{U}_{t}\right\| \leq 1$ for all $t \geq 0$.
For a semigroup $\mathcal{U}$ bounded on $\mathcal{H}$, we note :

$$
D(\mathcal{G})=\left\{x \in \mathcal{H} \left\lvert\, \lim _{t \rightarrow 0, t>0} \frac{\mathcal{U}_{t} x-x}{t}\right. \text { exists }\right\}
$$

For all semigroup $\mathcal{U}$ is associated a generator $-\mathcal{G}$, which is an application $D(\mathcal{G}) \rightarrow \mathcal{H}$ defined such as :

$$
-\mathcal{G} x=\lim _{t \rightarrow 0, t>0} \frac{\mathcal{U}_{t} x-x}{t} .
$$

This generator is an operator.
We recall that saying that two operators $A_{1}, A_{2}$ commute means that $A_{1} \circ A_{2}=A_{2} \circ A_{1}$.

[^12]Theorem 1 (Trotter's Theorem). Let $\mathcal{A}$ and $\mathcal{B}$ be two generators of semigroups that do not necessarily commute. We suppose that $e^{\mathcal{A}}$ and $e^{\mathcal{B}}$ are bounded on $\mathcal{C}^{0}\left(\mathbb{R}^{N}\right)$. Then we have :

$$
\begin{equation*}
e^{\mathcal{A}+\mathcal{B}}=\lim _{n \rightarrow \infty}\left(e^{\frac{\mathcal{B}}{2 n}} \circ e^{\frac{\mathcal{A}}{n}} \circ e^{\frac{\mathcal{B}}{2 n}}\right)^{n} . \tag{3.57}
\end{equation*}
$$

As seen in 172 , since $i L=\frac{\partial}{\partial x} \frac{p}{m}+\frac{\partial}{\partial p} F(x)$, we can then decompose the propagator $e^{i L \Delta t}$ in the following way :

$$
\begin{equation*}
e^{i L \Delta t} \simeq\left(e^{\frac{F(x) \Delta t \frac{\partial}{\partial p}}{2}} \circ e^{\frac{p}{m} \Delta t \frac{\partial}{\partial x}} \circ e^{\frac{F(x) \Delta t \frac{\partial}{\partial p}}{2}}\right) \tag{3.58}
\end{equation*}
$$

Lemma 1. We consider the differential operator $c \frac{\partial}{\partial x}$ (where $c$ is a constant) and a function $g \in C^{\infty}(\mathbb{R})$. We can verify that :

$$
\begin{equation*}
e^{c \frac{\partial}{\partial x}} g(x)=g(x+c) \tag{3.59}
\end{equation*}
$$

Proof. We start by expressing the exponential of the differential operator $c \frac{\partial}{\partial x}$ in a Taylor series and we have :

$$
\begin{align*}
e^{c \frac{\partial}{\partial x}} g(x) & =\sum_{k=0}^{\infty} \frac{1}{k!}\left(c \frac{\partial}{\partial x}\right)^{k} g(x)  \tag{3.60}\\
& =\sum_{k=0}^{\infty} \frac{1}{k!} c^{k} \frac{\partial^{k} g}{\partial x^{k}}(x) \tag{3.61}
\end{align*}
$$

which corresponds to Taylor's development of $g(x+c)$ for $c$ in 0 .

One notes $\left(x^{n}, p^{n}\right)$ an approximation of $\left(x\left(t_{n}\right), p\left(t_{n}\right)\right)$ for $t_{n}=n \Delta t$. The approximation (3.58), the lemma 1 and the propagator $e^{i L t}$ applied to $(x, p)$, lead to the following algorithm :

$$
\begin{aligned}
& p^{n+1 / 2}=p^{n}+0.5 * \Delta t * F^{n} \\
& x^{n+1}=x^{n}+\Delta t * \frac{p^{n+1 / 2}}{m} \\
& \text { Calcul de } F^{n+1} \\
& p^{n+1}=p^{n+1 / 2}+0.5 * \Delta t * F^{n+1}
\end{aligned}
$$

It corresponds to the Velocity Verlet algorithm.
It is now considered that the $F$ forces of the system can be decomposed into those of short range $F_{s r}$ and those of long range $F_{l r}: F=F_{s r}+F_{l r}$. The first ones will be evaluated every $\delta t$ time steps, while the second ones will be calculated every $n$ time steps, i.e. $\Delta t=n \delta t$.

The Liouville operator is separated as follows : $i L=i L_{s r}+i L_{l r}$, with $i L_{l r}=F_{l r}(x) \frac{\partial}{\partial p}$ et $i L_{s r}=\frac{p}{m} \frac{\partial}{\partial x}+F_{s r}(x) \frac{\partial}{\partial p}$. We can decompose the propagator $e^{i L \Delta t}$ in the following way :

$$
\begin{equation*}
e^{i L \Delta t} \simeq e^{\frac{\Delta t}{2} F_{l r} \frac{\partial}{\partial p}} \circ\left(e^{\frac{\delta t}{2} F_{s r} \frac{\partial}{\partial p}} \circ e^{\delta t \frac{p}{m} \frac{\partial}{\partial x}} \circ e^{\frac{\delta t}{2} F_{s r} \frac{\partial}{\partial p}}\right)^{n} \circ e^{\frac{\Delta t}{2} F_{l r} \frac{\partial}{\partial p}} . \tag{3.62}
\end{equation*}
$$

This then leads to algorithms of the "multiple time step" type, where we will treat, here, the long-range forces once, then the short-range forces $n$ times, then again the long-range forces once :

```
\(p^{k+1 / 2}=p^{k}+0.5 * \Delta t * F_{l r}^{k}\)
for \(i=1\) à \(n\) do
    \(p^{k+i}=p^{k+i-1 / 2}+0.5 * \delta t * F_{s r}^{k+(i-1)}\)
    \(x^{k+i}=x^{k+(i-1)}+\delta t * \frac{p^{k+i}}{m}\)
    Calcul de \(F_{s r}^{k+i}\)
    \(p^{k+i+1 / 2}=p^{k+i}+0.5 * \delta t * F_{s r}^{k+i}\)
end
Calcul de \(F_{l r}^{k+1}\)
\(p^{k+n+1}=p^{k+n+1 / 2}+0.5 * \Delta t * F_{l r}^{k+1}\)
```

The interest is that long-range forces, which vary little with time, because little with distance, are going to be calculated more rarely, which is beneficial since the calculation costs to evaluate them are heavy. On the other hand, the establishment of the algorithm indicates that it is better to divide the effect of these long-range forces in two, and put the first part before calculating the effect of short-range forces, and then the other half afterwards. For short-range forces, a smaller time step is taken since they vary a lot with time.

## - Berendsen's thermostat :

In order to take into account the dependent conditions of the thermodynamic ensemble in which the simulations are carried out, different methods imposing "coupled" external stresses on the equations of motion have been proposed. In our case, having carried out our simulations in the $N P T$ ensemble, we used the Berendsen's thermostat 18 to treat temperature and pressure ${ }^{25}$ Contrary to methods such as the one proposed by Nosé $132{ }^{26}$. where the Hamiltonian of the system is modified to account for "outside agents", the idea is to scale up speed and positions.

For speed $v$, rescaling $v \rightarrow \lambda v$ is expressed as a function of temperature $T$ :

$$
\begin{equation*}
\lambda_{T}=\left(1+\frac{\Delta t}{\tau_{T}}\left(\frac{T_{0}}{T(t)}-1\right)\right)^{1 / 2} \tag{3.63}
\end{equation*}
$$

where $\tau_{T}$ is a relaxation parameter, $\Delta t$ is the time step, and $T_{0}$ is the reference temperature. Thus, when the temperature $T$ is higher than the reference temperature $T(0)$, the velocities decrease, which decreases the temperature. The time to return to $T(0)$, if the potential energy of the system does not change (which is guaranteed in the case of a perfect gas), is of the order of $\tau_{T}$.

For the positions $x$ and size of the simulation box (side length $l$ and volume $V$ ), the rescaling is expressed as a function of the pressure $P$ :

$$
\begin{equation*}
\lambda_{P}=\left(1+\frac{\Delta t}{\tau_{P}} \gamma\left(P(t)-P_{0}\right)\right)^{1 / 3} \tag{3.64}
\end{equation*}
$$

where $\tau_{P}$ is a relaxation parameter, $\Delta t$ is the time step, $P_{0}$ is the reference pressure and $\gamma$ is an isothermal compressibility term. Thus, when the pressure is higher than the reference pressure, the system expands. Isothermal compressibility ensures that the equation is homogeneous, and that the time $\tau_{P}$ is the time to return to the reference pressure at a fixed temperature.

[^13]
### 3.3.2 Periodic boundary conditions

In order to simulate an infinite physical system, a computational trick is to add periodic conditions to the edges of the (necessarily finite) simulation box under consideration. This allows, moreover, to avoid surface effects (the number of particles "stuck" to the surface being proportional to $N^{-1 / 3}$, where $N$ is the number of particles of the considered system) 73,150 .

Schematically, it is "as if" we surrounded the simulation box with strictly exact copies of it, i.e. the particles of the image boxes move exactly the same way as those of the "main" box. This ensures that if a particle leaves the simulation box, its exact copy enters through the opposite side simultaneously. (cf Figure 10)


Figure $10-2 \mathrm{D}$ scheme of a simulation box with periodic boundary conditions (from 145 )

Under these conditions, a particle interacts not only with the particles in the same simulation box, but also with those in the image boxes (including its own copies).

For short-range interactions, to limit the effects of periodization on computation times, we will impose a cutoff radius $r_{c}$ such that $0<r_{c}<\frac{L}{2}$ (where $L$ is the length of one side of the main box, which is considered cubic here) and we compute the interactions only between particles that are at most $r_{c}$ away from them.

For the calculation of energy and pressure, in order to correct the bias introduced by this truncation, one must add an analytically evaluated term (assuming that the correlations between atoms have disappeared beyond the cut-off radius).

For long-range interactions (typically electrostatic interactions), Ewald's summation technique exploits the periodization of the system.

### 3.3.3 Ewald

## Principle of Ewald's summation

We consider a system consisting of $N$ particles, each of which is of charge $q_{i}=z_{i} e$ (with $i=1, \ldots, N)$ and described by its position $\mathbf{r}_{i}(i=1, \ldots, N)$.

Periodic conditions at the edges of the box are considered.
Let $U_{P B C}$ be the energy potential of the periodic system. We have :

$$
\begin{equation*}
U_{P B C}=\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\mathbf{n} \neq(0,0,0)}^{\prime} \frac{q_{i} q_{j}}{\left\|\mathbf{r}_{i}-\mathbf{r}_{j}+\mathbf{n} L\right\|} \tag{3.65}
\end{equation*}
$$

where the ' in the last sum means that one takes $\mathbf{n} \neq(0,0,0)$ if $i=j$.
We observe that the sum in $\mathbf{n}$ in $U_{P B C}$ converges only conditionally. To arrive at Ewald's method, the electrostatic potential will be defined as the solution of the Poisson's equation in the simulation box with periodic boundary conditions.

Then, the physical idea will be to screen the load points by a Gaussian, these screened loads can then be calculated in real space. In order to correct this screener, one compensates each time by a Gaussian of opposite total charge, which is smooth enough to be evaluated in Fourier space (reciprocal) $13,45,46,64,67,88,165,170$. (illustration of the strategy on the figure 11).


Figure 11 - Scheme illustrating the strategy for Ewald's method (from 133)
$U_{P B C}$ verifies :

$$
\begin{equation*}
U_{P B C}(\mathbf{r}, L)=\frac{1}{2} \sum_{i=1}^{N} q_{i} \phi\left(\mathbf{r}_{i}\right) \tag{3.66}
\end{equation*}
$$

where $\phi$ corresponds to a solution of Poisson's equation

$$
\begin{equation*}
\Delta \phi(\mathbf{r})=-4 \pi \sum_{i=1}^{N} q_{i} \delta\left(\mathbf{r}-\mathbf{r}_{i}\right) \tag{3.67}
\end{equation*}
$$

with periodic conditions at the edges (of the simulation box).

## Poisson's equation in periodic conditions

For a simple charge particle $z$ at position $\mathbf{r}_{0}$, the Poisson's equation satisfied by the electrostatic potential $\phi$ is written :

$$
\begin{equation*}
\Delta \phi(\mathbf{r})=-4 \pi z \delta\left(\mathbf{r}-\mathbf{r}_{0}\right) \tag{3.68}
\end{equation*}
$$

where we impose that $\phi$ satisfies the periodicity conditions on the faces of the simulation box (i.e. $\phi\left(\mathbf{r}+L \mathbf{e}_{i}\right)=\phi(\mathbf{r})$, where $\left(\mathbf{e}_{1}, \mathbf{e}_{2}, \mathbf{e}_{3}\right)$ is the canonical basis of $\mathbb{R}^{3}$ ).

The system being invariant by translation, we set $\mathbf{r}_{0}=0$ without loss of generality.
The equation with the periodic boundary conditions defines $\phi$ completely to within one additive constant. This is not a physical problem since the energy is itself defined to within one additive constant. This constant is fixed as :

$$
\begin{equation*}
\int_{V} \phi(r) d r=0 \tag{3.69}
\end{equation*}
$$

where $V$ is the volume of the simulation box.
To obtain a finite solution for the electrostatic field, the equation is corrected by adding a uniform neutralizing background :

$$
\begin{equation*}
\Delta \phi(\mathbf{r})=-4 \pi\left(z \delta(\mathbf{r})-\frac{z}{V}\right) \tag{3.70}
\end{equation*}
$$

(We can verify : $\int_{V} \Delta \phi(\mathbf{r}) d \mathbf{r}=-4 \pi \int_{V}\left(z \delta(\mathbf{r})-\frac{z}{V}\right) d \mathbf{r}=-4 \pi\left(z-\frac{z V}{V}\right)=0$ ).
If the system is globally neutral (i.e. $\sum q_{i}=0$ ), we observe that the sum of the neutralizing funds is zero.

We will, in what follows, establish considerations of a mathematical nature; the reader interested in the physical aspect of the problem will be able, if he wishes, to refer directly to theorem 2 (which corresponds to Ewald's formula) and then to its interpretation, which follows the demonstration.

## Series and Fourier transforms in a cube

We begin with a brief reminder about the distributions [63, 76, 86, 119, 146.
Definition 3. We consider $T \in \boldsymbol{S}^{\prime}\left(\mathbb{R}^{3}\right)$ (where $\boldsymbol{S}$ is the space of Schwartz), i.e. a temperate distribution. We call Fourier transform of $T$ the distribution $\hat{T}=F T$, defined by the relation :

$$
\begin{equation*}
\forall \phi \in \boldsymbol{S}\left(\mathbb{R}^{3}\right),\langle F T, \phi\rangle=\langle T, F \phi\rangle \tag{3.71}
\end{equation*}
$$

If $f \in L^{1}\left(\mathbb{R}^{3}\right): F T_{f}=T_{\hat{f}}$, where for $\boldsymbol{k} \in \mathbb{R}^{3}:$

$$
\begin{equation*}
\hat{f}(\boldsymbol{k})=\int_{\mathbb{R}^{3}} f(\boldsymbol{x}) e^{i \boldsymbol{k} \boldsymbol{x}} d x_{1} d x_{2} d x_{3} . \tag{3.72}
\end{equation*}
$$

Let $f$ be a periodic distribution of $\mathbb{R}^{3}$, period $L$ in the three directions. We can decompose $f$ into a Fourier series (in the sense of distributions) :

$$
\begin{equation*}
f(\mathbf{r})=\frac{1}{V} \sum_{\mathbf{k}} c_{f}(\mathbf{k}) e^{i \mathbf{k} . \mathbf{r}} \tag{3.73}
\end{equation*}
$$

with $\mathbf{k}=\frac{2 \pi}{L} \mathbf{m}$ where $\mathbf{m} \in \mathbb{Z}^{3}, V=L^{3}$ and where $c_{f}(\mathbf{k})=\int_{V} f(\mathbf{r}) e^{-i \mathbf{k} . \mathbf{r}} d r$.
It is replaced in case there is only one $z$ charge point. (we set $z=1$ in order not to make the calculations more complicated). Since $\phi$ and $\delta$ are defined as being periodic, we can associate them a Fourier series and we have : $\phi(\mathbf{r})=\frac{1}{V} \sum_{k} c_{\phi}(\mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}}$ and $g(\mathbf{r})=\frac{1}{V} \sum_{\mathbf{k}} c_{g}(\mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}}$ where $g(\mathbf{r})=\delta(\mathbf{r})-\frac{1}{V}\left(\right.$ here, $\delta$ istaken for $N=1$ and $\left.q_{1}=z=1\right)$.

The Poisson equation associated with $\phi$ gives us :

$$
\begin{align*}
\Delta \phi(\mathbf{r}) & =-4 \pi\left(\delta(\mathbf{r})-\frac{1}{V}\right)  \tag{3.74}\\
\Leftrightarrow \Delta\left(\frac{1}{V} \sum_{\mathbf{k}} c_{\phi}(\mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}}\right) & =-4 \pi \frac{1}{V} \sum_{\mathbf{k}} c_{g}(\mathbf{k}) e^{i \mathbf{k} . \mathbf{r}}  \tag{3.75}\\
\Leftrightarrow \frac{1}{V} \sum_{\mathbf{k}} c_{\phi}(\mathbf{k}) \Delta e^{i \mathbf{k} . \mathbf{r}} & =\frac{1}{V} \sum_{\mathbf{k}}-4 \pi c_{g}(\mathbf{k}) e^{i \mathbf{k} . \mathbf{r}}  \tag{3.76}\\
\Leftrightarrow \frac{1}{V} \sum_{\mathbf{k}} c_{\phi}(\mathbf{k}) i^{2} \mathbf{k}^{2} e^{i \mathbf{k} . \mathbf{r}} & =\frac{1}{V} \sum_{\mathbf{k}}-4 \pi c_{g}(\mathbf{k}) e^{i \mathbf{k} . \mathbf{r}} \tag{3.77}
\end{align*}
$$

which expresses the equality of two series of Fourier.
By uniqueness of the Fourier coefficients, we obtain the following equations $\forall \mathbf{k} \neq(0,0,0)$ :

$$
\begin{equation*}
-k^{2} c_{\phi}(\mathbf{k})=-4 \pi c_{g}(\mathbf{k}) \Leftrightarrow c_{\phi}(\mathbf{k})=\frac{4 \pi}{k^{2}} c_{g}(\mathbf{k}) \tag{3.78}
\end{equation*}
$$

with $c_{g}(\mathbf{k})=\int_{V}\left(\delta(r)-\frac{1}{V}\right) e^{-i \mathbf{k} \cdot \mathbf{r}} d \mathbf{r}=1($ since $\mathbf{k} \neq(0,0,0))$.
To find the coefficient $c_{\phi}(0)$, we use the condition for the additivity constant :

$$
\begin{equation*}
\int_{V} \phi(\mathbf{r}) e^{i(0,0,0) \cdot \mathbf{r}} d r=\int_{V} \phi(\mathbf{r}) d r=0 \text { i.e. } c_{\phi}(0)=0 . \tag{3.79}
\end{equation*}
$$

Thus:

$$
\begin{equation*}
\phi(\mathbf{r})=\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{i \mathbf{k} \cdot \mathbf{r}} \tag{3.80}
\end{equation*}
$$

$\frac{4 \pi}{k^{2}}$ being the Fourier transform associated with $\frac{1}{\|\mathbf{r}\|}$ (Coulomb's potential).
(Given this way, $\phi$ converges only conditionally (remember that $\mathbf{k}=\left(k_{1}, k_{2}, k_{3}\right)$ et $k^{2}=k_{1}^{2}+$ $k_{2}^{2}+k_{3}^{2}$ ). Ewald's idea will be to introduce a cut-off function to overcome this problem).

By the principle of superposition for $i \neq j$, and by introducing the constant $\xi$ (which removes the interaction of a particle with itself introduced) defined as follows :

$$
\begin{equation*}
\xi=\lim _{\|\mathbf{r}\| \rightarrow 0}\left(\phi(\mathbf{r})-\frac{1}{\|\mathbf{r}\|}\right) \tag{3.81}
\end{equation*}
$$

in order to take into account the interactions between the particle $i$ and its own images, $U_{P B C}$ is written :

$$
\begin{equation*}
U_{P B C}=\frac{1}{2} \sum_{i=1}^{N} q_{i} \sum_{j \neq i, j=1}^{N} q_{j} \phi\left(\mathbf{r}_{i}-\mathbf{r}_{j}\right)+\frac{\xi}{2} \sum_{i=1}^{N} q_{i}^{2} \tag{3.82}
\end{equation*}
$$

## Demonstration of Ewald's formula

Theorem 2. We can rewrite $U_{P B C}$ and get :

$$
\begin{equation*}
U_{P B C}=U_{P B C}^{(r)}+U_{P B C}^{(k)}+U_{P B C}^{(s)}+U_{P B C}^{(n)} \tag{3.83}
\end{equation*}
$$

where :

$$
\begin{align*}
U_{P B C}^{(r)} & =\frac{1}{2} \sum_{i, j} \sum_{n}^{\prime} q_{i} q_{j} \frac{1-\operatorname{erf}\left(\alpha\left\|\boldsymbol{r}_{i}-\boldsymbol{r}_{j}+\boldsymbol{n} L\right\|\right)}{\left\|\boldsymbol{r}_{i}-\boldsymbol{r}_{j}+\boldsymbol{n} L\right\|}  \tag{3.84}\\
U_{P B C}^{(k)} & =\frac{1}{2} \sum_{i, j} q_{i} q_{j} \frac{1}{V} \sum_{k \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{-\frac{k^{2}}{4 \alpha^{2}}} e^{i \boldsymbol{k} \cdot\left(\boldsymbol{r}_{i}-\boldsymbol{r}_{j}\right)}  \tag{3.85}\\
U_{P B C}^{(s)} & =-\frac{\alpha}{\sqrt{\pi}} \sum_{i} q_{i}^{2}  \tag{3.86}\\
U_{P B C}^{(n)} & =-\frac{\pi}{2 \alpha^{2} V} Q_{t o t}^{2} \tag{3.87}
\end{align*}
$$

où $Q_{t o t}=\sum_{i} q_{i}$, and with $\alpha \in \mathbb{R}$.
Proof. We replace ourselves in the case of a particle as in 3.2. and we have seen that when we want to resolve

$$
\begin{equation*}
\Delta \phi(\mathbf{r})=-4 \pi\left(z \delta(\mathbf{r})-\frac{z}{V}\right) \tag{3.88}
\end{equation*}
$$

with periodic boudary conditions. (we will take, as before, $z=1$ ) we obtain :

$$
\phi(\mathbf{r})=\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{i \mathbf{k} \cdot \mathbf{r}}
$$

We are going to introduce a $f$ function so that, by adding and subtracting this function, we will obtain two sums that converge exponentially.

We are looking for $f$ such as :

$$
\begin{align*}
\phi(\mathbf{r}) & =\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{i \mathbf{k} \cdot \mathbf{r}}  \tag{3.89}\\
& =\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}}(1-f(\mathbf{k})+f(\mathbf{k})) e^{i \mathbf{k} \cdot \mathbf{r}}  \tag{3.90}\\
& =\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}}(1-f(\mathbf{k})) e^{i \mathbf{k} \cdot \mathbf{r}}+\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} f(\mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}} \tag{3.91}
\end{align*}
$$

(provided that the sums converge, for the passage to the third equality).
Let the Gaussian function $g: \mathbf{x} \mapsto \frac{\alpha^{3}}{\pi^{3 / 2}} e^{-\alpha^{2}\|\mathbf{x}\|^{2}}$, where $\alpha \in \mathbb{R}$.
We know that the Fourier transform of a Gaussian $X=\left(X_{1}, X_{2}, X_{3}\right) \sim N\left(\mathbf{O}, \frac{1}{2 \alpha^{2}} \mathbf{I}_{3}\right)$ corresponds to its characteristic function $E\left(e^{i X \mathbf{k}}\right)$, from which we derive $: \hat{g}(\mathbf{k})=e^{-\frac{\mathbf{k}^{2}}{4 \alpha^{2}}}$. We consider $f=\hat{g}$. We have then : $\phi(\mathbf{r})=\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{\mathbf{k}^{2}}\left(1-e^{-\frac{\mathbf{k}^{2}}{4 \alpha^{2}}}\right) e^{i \mathbf{k} \cdot \mathbf{r}}+\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{\mathbf{k}^{2}} e^{-\frac{\mathbf{k}^{2}}{4 \alpha^{2}}} e^{i \mathbf{k} \cdot \mathbf{r}}$.
We observe that the second sum in $\phi$ converges rapidly, which is not the case for the first one. In order to deal with the latter, we will use the Poisson's formula recalled hereafter 8 :

## Lemma 2. Poisson's Summing Formula

Let $h$ continue admitting a Fourier transform. Then, by posing $V=L^{3}$, when these sums make sense, we have :

$$
\begin{equation*}
\sum_{n} h(\boldsymbol{x}+\boldsymbol{n} L)=\frac{1}{V} \sum_{k} \hat{h}(\boldsymbol{k}) e^{i \boldsymbol{k} \cdot \boldsymbol{x}} \tag{3.92}
\end{equation*}
$$

with $\boldsymbol{k}=\frac{2 \pi}{L} \boldsymbol{m}$ where $\boldsymbol{m} \in \mathbb{Z}^{3}$.
(In particular, with $\boldsymbol{x}=(0,0,0)$, we get $: \sum_{n} h(\boldsymbol{n})=\sum_{k} \hat{h}(\boldsymbol{k})$ ).
Here, we have $\hat{h}: \mathbf{k} \mapsto \frac{4 \pi}{k^{2}}\left(1-e^{-\frac{\mathbf{k}^{2}}{4 \alpha^{2}}}\right)$. One observes that the formula of Poisson requires to have the term with the Fourier transform for $\mathbf{k}=(0,0,0)$, but it does not appear in the sum $\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}}\left(1-e^{-\frac{k^{2}}{4 \alpha^{2}}}\right) e^{i \mathbf{k} \cdot \mathbf{r}}$. We will make a 0 equivalent of $\frac{4 \pi}{k^{2}}\left(1-e^{-\frac{k^{2}}{4 \alpha^{2}}}\right)$ then add it and subtract it from the sum.

We have : $e^{-\frac{k^{2}}{4 \alpha^{2}}} \sim 1-\frac{k^{2}}{4 \alpha^{2}}$, so that $1-e^{-\frac{k^{2}}{4 \alpha^{2}}} \sim \frac{k^{2}}{4 \alpha^{2}}$, so that $\frac{4 \pi}{k^{2}}\left(1-e^{-\frac{k^{2}}{4 \alpha^{2}}}\right) \sim \frac{4 \pi k^{2}}{4 k^{2} \alpha^{2}} \sim \frac{\pi}{\alpha^{2}}$.
We thus set $\hat{h}(0,0,0)=\frac{\pi}{\alpha^{2}}$ and then we have :

$$
\begin{align*}
A & =\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}}\left(1-e^{-\frac{k^{2}}{4 \alpha^{2}}}\right) e^{i \mathbf{k} \cdot \mathbf{r}}  \tag{3.93}\\
& =\frac{1}{V} \sum_{\mathbf{k}} \hat{h}(\mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}}-\frac{\pi}{V \alpha^{2}} \tag{3.94}
\end{align*}
$$

We would like, in order to use the Poisson formula, to know the function which has for Fourier transform $\frac{4 \pi}{k^{2}} e^{-\frac{k^{2}}{4 \alpha^{2}}}$. We know that $\frac{4 \pi}{k^{2}}$ is the Fourier transform of $\frac{1}{\|\mathbf{x}\|}$ and that $e^{-\frac{k^{2}}{4 \alpha^{2}}}$ is that of $g$. Now, we know that a Fourier transform product corresponds to the Fourier transform of the convolution of the functions which have for Fourier transform the two factors of this product (i.e. : we consider $f_{1}$ and $f_{2}$ which Fourier transform is respectively $\hat{f}_{1}$ and $\hat{f}_{2}$, then $\widehat{f_{1} * f_{2}}=\hat{f}_{1} \cdot \hat{f}_{2}$ ). So that : $\hat{h}$ is the Fourier transform of $\frac{4 \pi}{k^{2}} * g$.

Lemma 3. We consider erf : $r \mapsto \frac{2}{\sqrt{\pi}} \int_{0}^{r} e^{-y^{2}} d y$. We have :

$$
\begin{equation*}
\Delta\left(\frac{1}{\|\boldsymbol{x}\|} \operatorname{erf}(\alpha\|\boldsymbol{x}\|)\right)=-\frac{4 \alpha^{3}}{\sqrt{\pi}} e^{-\alpha^{2}\|\boldsymbol{x}\|^{2}} \tag{3.95}
\end{equation*}
$$

Proof. We set $g: \mathbf{x} \mapsto \frac{1}{\|\mathbf{x}\|} \operatorname{erf}(\alpha\|\mathbf{x}\|)$. We have (considering the spherical coordinates $\left.(r, \phi, \theta)\right)$ :

$$
\begin{align*}
\Delta g(r) & =\frac{1}{r^{2}} \frac{\partial}{\partial r}\left(r^{2} \frac{\partial}{\partial r} g(r)\right)  \tag{3.96}\\
& =\frac{1}{r^{2}} \frac{\partial}{\partial r}\left(r^{2}\left(-\frac{1}{r^{2}} \operatorname{erf}(\alpha r)+\frac{1}{r} \frac{2}{\sqrt{\pi}} \alpha e^{-\alpha^{2} r^{2}}\right)\right)  \tag{3.97}\\
& =\frac{1}{r^{2}}\left(-\frac{2}{\sqrt{\pi}} \alpha e^{-\alpha^{2} r^{2}}-\frac{4 \alpha^{3}}{\sqrt{\pi}} r^{2} e^{-\alpha^{2} r^{2}}+\frac{2}{\sqrt{\pi}} \alpha e^{-\alpha^{2} r^{2}}\right)  \tag{3.98}\\
& =-\frac{4 \alpha^{3}}{\sqrt{\pi}} e^{-\alpha^{2} r^{2}} . \tag{3.99}
\end{align*}
$$

Lemma 4. For $\boldsymbol{x} \in \mathbb{R}^{3} \backslash(0,0,0)$, we can get :

$$
\begin{equation*}
\frac{1}{\|\boldsymbol{x}\|} *\left(\frac{4 \alpha^{3}}{\sqrt{\pi}} e^{-\alpha^{2}\|\boldsymbol{x}\|^{2}}\right)=\frac{1}{\|\boldsymbol{x}\|} \operatorname{erf}(\alpha\|\boldsymbol{x}\|) . \tag{3.100}
\end{equation*}
$$

Proof. Using previous lemma and by working in the sense of distributions, we have :

$$
\begin{align*}
\frac{1}{\|\mathbf{x}\|} \operatorname{erf}(\alpha\|\mathbf{x}\|) & =\Delta^{-1}\left(-\frac{4 \alpha^{3}}{\sqrt{\pi}} e^{-\alpha^{2}\|\mathbf{x}\|^{2}}\right)  \tag{3.101}\\
& =\delta_{0} *\left(\Delta^{-1}\right)\left(-\frac{4 \alpha^{3}}{\sqrt{\pi}} e^{-\alpha^{2}\|\mathbf{x}\|^{2}}\right)  \tag{3.102}\\
& =\left(\Delta^{-1} \delta_{0}\right) * \frac{4 \alpha^{3}}{\sqrt{\pi}} e^{-\alpha^{2}\|\mathbf{x}\|^{2}}  \tag{3.103}\\
& =\frac{1}{\|\mathbf{x}\|} * \frac{4 \alpha^{3}}{\sqrt{\pi}} e^{-\alpha^{2}\|\mathbf{x}\|^{2}} \tag{3.104}
\end{align*}
$$

Thus, thanks to Poisson's suming formula, one obtains :

$$
\begin{equation*}
A=\sum_{n} \frac{1-\operatorname{erf}(\alpha\|r+n L\|)}{\|r+n L\|}-\frac{\pi}{\alpha^{2} V} \tag{3.105}
\end{equation*}
$$

We reinject $A$ in $\phi$ and we get : $\phi(\mathbf{r})=\sum_{\mathbf{n}} \frac{1-\operatorname{erf}(\alpha\|\mathbf{r} \mathbf{r} L\|)}{\|\mathbf{r}+\mathbf{n} L\|}+\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{-\frac{k^{2}}{4 \alpha^{2}}} e^{i \mathbf{k} \cdot \mathbf{r}}-\frac{\pi}{\alpha^{2} V}$.
All that remains to be done is to calculate the constant $\xi$ to get the total energy $U_{P B C}$ :

$$
\begin{align*}
\xi & =\lim _{\|\mathbf{r}\| \rightarrow 0}\left(\phi(\mathbf{r})-\frac{1}{\|\mathbf{r}\|}\right)  \tag{3.106}\\
& =\lim _{\|\mathbf{r}\| \rightarrow 0}\left(\sum_{\mathbf{n}} \frac{1-\operatorname{erf}(\alpha\|\mathbf{r}+\mathbf{n} L\|)}{\|\mathbf{r}+\mathbf{n} L\|}+\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{-\frac{k^{2}}{4 \alpha^{2}}} e^{i \mathbf{k} \cdot \mathbf{r}}-\frac{\pi}{\alpha^{2} V}-\frac{1}{\|\mathbf{r}\|}\right)  \tag{3.107}\\
& =\sum_{\mathbf{n} \neq(0,0,0)} \frac{1-\operatorname{erf}(\alpha\|\mathbf{n} L\|)}{\|\mathbf{n} L\|}+\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{-\frac{k^{2}}{4 \alpha^{2}}}-\frac{\pi}{\alpha^{2} V}+\lim _{\|\mathbf{r}\| \rightarrow 0} \frac{(1-\operatorname{erf}(\alpha\|\mathbf{r}\|)-1)}{\|\mathbf{r}\|}  \tag{3.108}\\
& =\sum_{\mathbf{n} \neq(0,0,0)} \frac{1-\operatorname{erf}(\alpha\|\mathbf{n} L\|)}{\|\mathbf{n} L\|}+\frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{-\frac{k^{2}}{4 \alpha^{2}}}-\frac{\pi}{\alpha^{2} V}-\lim _{\|\mathbf{r}\| \rightarrow 0} \frac{\operatorname{erf}(\alpha\|\mathbf{r}\|)}{\|\mathbf{r}\|} . \tag{3.109}
\end{align*}
$$

We have $: \frac{\operatorname{erf}(\alpha\|\mathbf{r}\|)}{\|\mathbf{r}\|}=\frac{\operatorname{erf}(\alpha\|\mathbf{r}\|)-0}{\|\mathbf{r}\|}=\frac{\operatorname{erf}(\alpha\|\mathbf{r}\|)-\operatorname{erf}(\alpha\|0\|)}{\|\mathbf{r}\|}$.
But erf is derivable on $\mathbb{R} \backslash\{0\}$ and composing it with the function derivable on $\mathbb{R}, x \mapsto \alpha x$, we have:

$$
\operatorname{erf}^{\prime}(\alpha x)= \begin{cases}\frac{2}{\sqrt{\pi}} \alpha e^{-(\alpha x)^{2}} & x>0  \tag{3.110}\\ -\frac{2}{\sqrt{\pi}} \alpha e^{-(\alpha x)^{2}} & x<0\end{cases}
$$

As here we have $\|\mathbf{r}\|>0$, we have, by definition of the right-hand derivative : $\lim _{\|\mathbf{r}\| \rightarrow 0} \frac{\operatorname{erf}(\alpha\|\mathbf{r}\|)-\operatorname{erf}(\alpha\|0\|)}{\|\mathbf{r}\|}=$ $\frac{2 \alpha}{\sqrt{\pi}}$.

By reinjecting the value obtained for $\xi$ and that obtained for $\phi$, we obtain :

$$
\begin{equation*}
U_{P B C}=U_{P B C}^{(r)}+U_{P B C}^{(k)}+U_{P B C}^{(s)}+U_{P B C}^{(n)} \tag{3.111}
\end{equation*}
$$

where $U_{P B C}^{(r)}=\frac{1}{2} \sum_{i, j} \sum_{\mathbf{n}}^{\prime} q_{i} q_{j} \frac{1-\operatorname{erf}\left(\alpha\left\|\mathbf{r}_{i}-\mathbf{r}_{j}+\mathbf{n} L\right\|\right)}{\left\|\mathbf{r}_{i}-\mathbf{r}_{j}+\mathbf{n} L\right\|}$,
$U_{P B C}^{(k)}=\frac{1}{2} \sum_{i, j} q_{i} q_{j} \frac{1}{V} \sum_{\mathbf{k} \neq(0,0,0)} \frac{4 \pi}{k^{2}} e^{-\frac{k^{2}}{4 \alpha^{2}}} e^{i \mathbf{k} .\left(\mathbf{r}_{i}-\mathbf{r}_{j}\right)}$,
$U_{P B C}^{(s)}=-\frac{\alpha}{\sqrt{\pi}} \sum_{i} q_{i}^{2}$
and $U_{P B C}^{(n)}=-\frac{\pi}{2 \alpha^{2} V} Q_{t o t}^{2}$ where $Q_{t o t}=\sum_{i} q_{i}$, with $\alpha \in \mathbb{R}$.
$\alpha$ must be chosen in such a way that the two sums containing it converge quickly, and that a reasonable truncation can be performed in both cases (a small $\alpha$ favors convergence in real space, a large $\alpha$ favors convergence in Fourier space).

Note that $U_{P B C}^{(r)}$ corresponds to the sum of the interactions between not only the particles of the system, but also the image particles introduced by the periodicity, at which sum the same interactions have been removed, but which are screened. This sum is computed in real space (as indicated by the "r") because it converges rapidly. $U_{P B C}^{(k)}$ refers to the sum of the screened interactions (removed in the previous sum) and is computed in Fourier space. $U_{P B C}^{(s)}$ is a term that refers to the interactions between the particles themselves, a term that is removed as indicated by the " - " sign. Finally, $U_{P B C}^{(n)}$ indicates the neutrality of the system (if the system is electrically neutral, which translates into $\sum_{i} q_{i}=0$, this term is null).

## Chapitre 4

## Calculation of free energy differences

This chapter defines the notion of free energy, depending on a reaction coordinate, a notion already mentioned in the paragraph on thermodynamic ensembles. The free energy allows to have access to all the thermodynamic quantities associated to a system. More specifically, the notion of Potential of Mean Force is defined as well as the numerical methods used in the thesis to calculate this quantity. At the end, it is also explained how to optimally choose some parameters for our methods.

### 4.1 Reaction coordinate

A reaction coordinate allows to follow, in the space of the phases, the paths corresponding to the reactive trajectories followed to go from the region corresponding to the "reagents" (initial state) to that corresponding to the "products" (final state) 105, 150.

A reaction coordinate is a function of the form :

$$
\begin{equation*}
\xi: \Omega \rightarrow \mathbb{R}^{m} \tag{4.1}
\end{equation*}
$$

where $\Omega$ is the configuration space and $m \leq 3 N$ ( $\xi$ can correspond for example to a distance between two sets of molecules).

A $\xi$ is associated with a division of the phase space into sub-varieties (these are in fact the $\xi$ level lines) :

$$
\Sigma(z)=\{\mathbf{r} \in \Omega \mid \xi(\mathbf{r})=z\}
$$

so that :

$$
\Omega=\cup_{z \in \mathbb{R}^{m}} \Sigma(z)
$$

Simply related $\Sigma$ (i.e. arc related and homotopic) are assumed to ensure ergodicity.

### 4.2 Free energy

The absolute free energy $105,167 \mathrm{~F}$ of a system is defined by :

$$
\begin{equation*}
-\beta F=\ln (Z) \tag{4.2}
\end{equation*}
$$

where $Z$ is the partition function associated with the canonical bar, whose definition is given in (3.22) for a system defined by its positions and impulses. ( $\mathbf{r}, \mathbf{p}$ ) :

$$
Z=\int_{D^{N} \times \mathbb{R}^{3 N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} d \mathbf{r} d \mathbf{p}
$$

This quantity is very important in thermodynamics because it allows, as we have seen previously, to obtain all the macroscopic quantities of interest of a system (energy, temperature etc.) However, in practice, it is very difficult to determine the absolute free energy associated with a system.

Fortunately, we are rather interested in calculating the free energy difference $\Delta F$, in order to observe the difference between the initial state (numbered 0) of a system and its final state (indexed 1). In our studies, we have considered that the transition is indexed by a reaction coordinate, supposedly known, $\xi$. We then have :

$$
\begin{equation*}
\Delta F=F(1)-F(0)=-k_{b} T \ln \left(\frac{\int_{D^{N} \times \mathbb{R}^{3 N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} \delta_{\xi-x_{1}} d \mathbf{r} d \mathbf{p}}{\int_{D^{N} \times \mathbb{R}^{3 N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} \delta_{\xi-x_{0}} d \mathbf{r} d \mathbf{p}}\right) \tag{4.3}
\end{equation*}
$$

where $x_{i}$ is the value of the state reaction coordinate $i$. (It can be observed that the value of the free energy difference depends strongly on the reaction coordinate chosen to describe the path followed by the chemical reaction).

## $4.3 \quad$ Potential of Mean Force

### 4.3.1 The Potential of Mean Force

The Potential of Mean Force (PMF) corresponds to the free energy of a system according to its reaction coordinate. The PMF $F$ is a function of the probability $P$ of finding a system at a state (the chosen reaction coordinate, averaged over all other degrees of freedom of the system) $105,150,167 . F$ is given by :

$$
\begin{equation*}
-\beta F(x)=\ln (P(x))-\beta F_{0} \tag{4.4}
\end{equation*}
$$

where $F_{0}$ is a constant normalizing the probability $P$.
This is the function $x \mapsto F(x)$ given by :

$$
\begin{equation*}
F(x)=-k_{b} T \ln \left(\int_{D^{N} \times \mathbb{R}^{3 N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} \delta_{\xi-x} d \mathbf{r} d \mathbf{p}\right) . \tag{4.5}
\end{equation*}
$$

Its derivative, $F^{\prime}(z)$, is the mean force. It is the mean force exerted on the system when the reaction coordinate is kept constant and which drives the system to its final state.

### 4.3.2 The Potential of McMillan and Mayer

McMillan and Mayer's potential $31,56,120,174$ is the potential of mean force between solutes as a function of their distance when infinitely diluted. McMillan and Mayer showed that with this term, one can then easily calculate the thermodynamic quantities of the solution.

We consider the simplified case of a system composed of a solute formed of $N$ particles and a solvent of $M$ particles; the volume of the system, $V$, and the temperature $T$ are also fixed.

We place ourselves beforehand in the framework of the grand canonical set for mixtures, and thus, here, the chemical potentials of each species, respectively $\mu_{1}$ for the solute and $\mu_{2}$ for the solvent, are fixed, in addition to $V$ and $T$ (but not the number of particles). Let $\mathcal{V}_{\text {syst }}$ be the potential of the system. We also give $z_{1}$ the fugacity of the solute and $z_{2}$ that of the solvent. The partition function $Q$ is then given by (cf (3.42) ) :

$$
\begin{align*}
Q\left(\mu_{1}, \mu_{2}, V, T\right) & =\sum_{N, M=1}^{\infty} \frac{z_{1}^{N} z_{2}^{M}}{N!M!} \int_{D_{1}^{N} \times D_{2}^{M}} e^{-\beta \nu_{s y s t}\left(\mathbf{r}^{N}, \mathbf{R}^{M}\right)} d \mathbf{r}^{N} d \mathbf{R}^{M}  \tag{4.6}\\
& =\sum_{N=1}^{\infty} \frac{z_{1}^{N}}{N!} \int_{D_{1}^{N}} \sum_{M=1}^{\infty} \frac{z_{2}^{M}}{M!} \int_{D_{2}^{M}} e^{-\beta \nu_{s y s t}\left(\mathbf{r}^{N}, \mathbf{R}^{M}\right)} d \mathbf{R}^{M} d \mathbf{r}^{N} . \tag{4.7}
\end{align*}
$$

On the other hand, we consider the $n$-body $g^{(n)}$ correlation function, in the grand canonical set, of this two-component system :

$$
\begin{align*}
g^{(n)}\left(\mathbf{r}_{1}, \ldots, \mathbf{r}_{n}\right) & =\frac{1}{\rho^{n} Q\left(\mu_{1}, \mu_{2}, V, T\right)} \sum_{N=n+1}^{\infty} \frac{z_{1}^{N}}{(N-n)!} \int_{D_{1}^{N}} \sum_{M=1}^{\infty} \frac{z_{2}^{M}}{M!} \int_{D_{2}^{M}} e^{-\beta \mathcal{V}_{s y s t}\left(\mathbf{r}^{N}, \mathbf{R}^{M}\right)} d \mathbf{R}^{M} d \mathbf{r}^{N-n}  \tag{4.8}\\
& =\left(\frac{z_{1}}{\rho}\right)^{n} \frac{1}{Q\left(\mu_{1}, \mu_{2}, V, T\right)} \sum_{N=1}^{\infty} \frac{z_{1}^{N}}{N!} \int_{D_{1}^{N}} \sum_{M=1}^{\infty} \frac{z_{2}^{M}}{M!} \int_{D_{2}^{M}} e^{-\beta \mathcal{V}_{s y s t}\left(\mathbf{r}^{N+n}, \mathbf{R}^{M}\right)} d \mathbf{R}^{M} d \mathbf{r}^{N} \tag{4.9}
\end{align*}
$$

where $\rho$ is the solute density (re-indexing was done to move to the second tie).
If the solute is diluted, i.e. $z_{1} \rightarrow 0$ (i.e. $\mu_{1} \rightarrow-\infty$ ). We then have :

$$
\begin{equation*}
g^{(n)}\left(\mathbf{r}_{1}, \ldots, \mathbf{r}_{n}\right)_{\mid z_{1} \rightarrow 0}=\frac{\gamma^{n}}{Q\left(\mu_{1} \rightarrow-\infty, \mu_{2}, V, T\right)} \sum_{M=1}^{\infty} \frac{z_{2}^{M}}{M!} \int_{D_{2}^{M}} e^{-\beta \mathcal{V}_{s y s t}\left(\mathbf{r}^{n}, \mathbf{R}^{M}\right)} d \mathbf{R}^{M} \tag{4.10}
\end{equation*}
$$

where we set : $\gamma=\left(\frac{z_{1}}{\rho}\right)_{\mid z_{1} \rightarrow 0}$.
We replace in 4.7) and we get :

$$
\begin{equation*}
Q\left(\mu_{1}, \mu_{2}, V, T\right)=Q\left(\mu_{1} \rightarrow-\infty, \mu_{2}, V, T\right) \sum_{N=1}^{\infty} \frac{a^{N}}{N!} \int_{D_{1}^{N}} g^{(N)}\left(\mathbf{r}_{1}, \ldots, \mathbf{r}_{N}\right) d \mathbf{r}^{N} \tag{4.11}
\end{equation*}
$$

where the activity has been defined as $a=\frac{z_{1}}{\gamma}=z_{1}\left(\frac{\rho}{z_{1}}\right)_{\mid z_{1} \rightarrow 0}$.
This expression is used to factorize the $Q$ partition function in two terms. The first term corresponds to the case where there is no solute, when the solvent has the same chemical potential as in solution : it is therefore the great potential of the pure solvent when it has the same chemical potential as in solution. The second term (i.e. the sum) is formally equivalent to the great potential of a system where there are only solutes ${ }^{17}$. McMillan and Mayer's theory simplifies the

[^14]calculations of statistical thermodynamics : one replaces a calculation of a partition function on a solvent/solute mixture by the calculation of two simpler partition functions, as they are calculated for pure solvent and pure solute. All the difficulty consists in calculating the Potential of mean force at infinite dilution of the solute $W^{N}$, also called McMillan's and Mayer's Potential.
$W^{N}$ is related to the distribution function at $N$-infinitely diluted bodies by the expression :
\[

$$
\begin{equation*}
g^{(N)}\left(\mathbf{r}_{1}, \ldots, \mathbf{r}_{N}\right)=e^{-\beta W^{N}\left(\mathbf{r}_{1}, \ldots, \mathbf{r}_{N}\right)} \tag{4.12}
\end{equation*}
$$

\]

According to its definition, $W^{N}$ is calculated as free energy depending on the positions of the solute. The only difference is the scale of the activities which must be renormalized (from $z$ to a) and the potential $W^{N}$ reflecting the interaction between the solutes averaged over the solvent configurations.

We replace $(4.12)$ in 4.11 and we get :

$$
\begin{equation*}
Q\left(\mu_{1}, \mu_{2}, V, T\right)=Q\left(\mu_{1} \rightarrow-\infty, \mu_{2}, V, T\right) Q_{M M}(a, V, T) \tag{4.13}
\end{equation*}
$$

where $Q_{M M}$ is the McMillan and Mayer's partition function which is formally written as that of a simple fluid (without the solvent) ${ }^{2}$

### 4.3.3 Practical calculation of McMillan and Mayer's potential

McMillan and Mayer's potential is generally calculated by considering only 2-body potentials, an approximation valid only for a sufficiently diluted solution. Let a system with two particles (i.e. $N=2$ ) and surrounded by a solvent, the distance between the two particles being the reaction coordinate. $W^{(2)}$ is related to the mean force potential $F$ via the following expression :

$$
\begin{align*}
e^{-\beta F(r)} d r & =e^{-\beta W^{(2)}(r)} 4 \pi r^{2} d r  \tag{4.14}\\
\Leftrightarrow-\beta F(x) & =-\beta W^{(2)}(r)+\ln (4 \pi)+\ln \left(r^{2}\right)  \tag{4.15}\\
\Leftrightarrow \beta W^{(2)}(r) & =\beta F(r)+2 \ln (r)+c s t e . \tag{4.16}
\end{align*}
$$

Thus, McMillan and Mayer's potential takes this entropic correction into account in the calculation of the mean force potential.

### 4.4 The Problem of Barriers for the Calculation of the Potential of Mean Force

As shown in figure 12 , free energy plotted against a reaction coordinate $q$ is often made difficult by the existence of a barrier separating two stable states A and B. The transition from A to B, in simulation, is in this case a rare event. In order to calculate the free energy on either side of the barrier, the system must be biased to increase the statistics of these unlikely states.

Various techniques are used to overcome these barriers. They generally consist of biasing the system by modifying the Hamiltonian in order to achieve the passage of the barrier. We will then present a widely used method, that of Umbrella Sampling, which is often associated with the Weighted Histograms Analysis Method (WHAM).

[^15]

Figure 12 - Illustration of the phenomenon of balance barriers

### 4.5 Umbrella Sampling Method

In order to ensure that points on the trajectory followed by a system are sampled for all possible values of a reaction coordinate, one idea is to constrain the system by means of a biased potential.

We take the following case from the case of calculating the Mean Force Potential between two solutes, e.g. an ion $\mathrm{Na}^{+}$and an ion $\mathrm{Cl}^{-}$, expressed as a function of their relative distance $r$ and averaged over solvent configurations, e.g. water. The system is contained in a cubic box with side $L$ and periodic conditions at the edges.

The distance between the ion $\mathrm{Na}^{+}$and the ion $\mathrm{Cl}^{-}$is controlled by adding a harmonic force (spring) between these two ions. This is equivalent to adding to the energy $\mathcal{V}$ a harmonic potential $\mathcal{V}_{\text {harm }}^{r^{*}}$. The biased potential $\mathcal{V}_{\text {bias }}^{r^{*}}$ is like this :

$$
\begin{equation*}
\mathcal{V}_{\text {bias }}^{r^{*}}:=\mathcal{V}+\mathcal{V}_{\text {harm }}^{r^{*}} \tag{4.17}
\end{equation*}
$$

where :

$$
\begin{equation*}
\mathcal{V}_{h a r m}^{r^{*}}(r)=\frac{1}{2} k\left(r-r^{*}\right)^{2} \tag{4.18}
\end{equation*}
$$

with $k$ the spring stiffness constant and $r^{*}:=\left\|\mathbf{r}_{N a^{+}}-\mathbf{r}_{C l^{-}}\right\|$is the equilibrium distance of the spring holding the two ions. It is important to choose $r^{*} \leq \frac{L}{2}$, because of the periodicity of the box, otherwise the selected interaction would be the one with the closest image particle.

We vary $r^{*}$ between 2 A and up to $\frac{L}{2}$. We then draw the histograms of the distances between $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$for each $r^{*}$. Each histogram has roughly a Gaussian shape similar to an umbrella. In order to apply the method, each umbrella has to cover distances with its neighbors, as shown in figure 13. Umbrella sampling is indeed valid if the distances have been continuously explored. This is the method of Umbrella Sampling [71, 169 .

The probabilities obtained should be de-biased in order to obtain the free energy of the real system (without the spring energy).

Let $P_{b}$ be the probability (the index " $b$ " indicates that the function is biased ; since here we have added a potential that biases the original) that the chosen reaction coordinate $\xi$ will satisfy the


Figure 13 - Umbrella Sampling for a 36.342 A side water box with one ion $\mathrm{Na}^{+}$and an ion $\mathrm{Cl}^{-}$, with as reaction coordinate the distance between the two ions $r^{*}$, where $r^{*}=2,2.5, \ldots, 12$
given constraint $q$ :

$$
\begin{equation*}
P_{b}\left(q, r^{*}\right)=\frac{\int e^{-\beta\left(\mathcal{V}(r)+\mathcal{V}_{\text {harm }}^{r^{*}}(\xi(r))\right)} \delta(\xi(r)-q) d^{N} r}{\int e^{-\beta\left(\mathcal{V}(r)+\mathcal{V}_{\text {harm }}^{r^{*}}(\xi(r))\right)} d^{N} r} \tag{4.19}
\end{equation*}
$$

We know that the probability without the biased potential $P$ is :

$$
\begin{equation*}
P(q)=\frac{\int e^{-\beta \mathcal{V}(r)} \delta(\xi(r)-q) d^{N} r}{\int e^{-\beta \mathcal{V}(r)} d^{N} r} . \tag{4.20}
\end{equation*}
$$

We have :

$$
\begin{align*}
& P_{b}\left(q, r^{*}\right)=\frac{\int e^{-\beta\left(\mathcal{V}(r)+\nu_{\text {harm }}^{*}(\xi(r))\right)} \delta(\xi(r)-q) d^{N} r}{\int e^{-\beta\left(\mathcal{V}(r)+\mathcal{V}_{\text {harm }}^{* *}(\xi(r))\right)} d^{N} r}  \tag{4.21}\\
& =\frac{\int e^{-\beta\left(\mathcal{V}(r)+\mathcal{V}_{h a r m}^{r^{*}}(\xi(r))\right)} \delta(\xi(r)-q) d^{N} r}{\int e^{-\beta\left(\mathcal{V}(r)+V_{\text {harm }}^{*}(\xi(r))\right)} d^{N} r} \frac{\int e^{-\beta \mathcal{V}(r)} d^{N} r}{\int e^{-\beta \mathcal{V}(r)} d^{N} r}  \tag{4.22}\\
& =e^{-\beta \mathcal{V}_{\text {harm }}^{\nu^{*}}(q)} \frac{\int e^{-\beta \mathcal{V}(r)} \delta(\xi(r)-q) d^{N} r}{\int e^{-\beta \mathcal{V}(r)} d^{N} r} \frac{\int e^{-\beta \mathcal{V}(r)} d^{N} r}{\int e^{-\beta\left(\mathcal{V}(r)+\mathcal{V}_{\text {harm }}^{r *}(\xi(r))\right)} d^{N} r}  \tag{4.23}\\
& =e^{-\beta \mathcal{V}_{\text {harm }}^{r^{*}}(q)} P(q) \frac{\int e^{-\beta \mathcal{V}(r)} d^{N} r}{\int e^{-\beta\left(\mathcal{V}(r)+\mathcal{V}_{\text {harm }}^{*}(\xi(r))\right)} d^{N} r} \tag{4.24}
\end{align*}
$$

where for the second equality we have multiplied and divided by the same term $\int e^{-\beta \mathcal{V}(r)} d^{N} r$, which is strictly positive as an integral of a positive function and which is not zero everywhere.

We introduce : $\left\langle e^{-\beta V_{\text {harm }}^{* *}(\xi(.))}\right\rangle=\frac{\int e^{-\beta\left(\mathcal{V}(r)+\nu_{h a r m}^{\nu_{n}^{*}}(\xi(r))\right)} d^{N} r}{\int e^{-\beta \mathcal{V}(r) d^{N} r}}$, which is the average of $e^{-\beta V_{\text {harm }}^{* *}(\xi(r))}$ calculated in the unbiased system.

Thus, for the chosen reaction coordinate $\xi$ and the reference value $r^{*}$ in the harmonic potential, $P$ is expressed as :

$$
\begin{equation*}
P(q)=e^{\beta \mathcal{V}_{h a r m}^{r^{*}}(q)} P_{b}\left(q, r^{*}\right)\left\langle e^{-\beta \mathcal{V}_{\text {harm }}^{r^{*}}(\xi(.))}\right\rangle \tag{4.25}
\end{equation*}
$$

This relation allows directly to obtain the free energy as a function of the reaction coordinate with the relation (4.4), according to the biased probabilities $P_{b}\left(q, r^{*}\right)$. Each simulation thus gives a part of the free energy curve around its $r^{*}$ to within one constant. We then have to glue all these small pieces of curves together in a clever way to obtain the free energy as a function of the reaction coordinate. This is the purpose of the WHAM method ${ }^{3}$.

### 4.6 WHAM Method

The method chosen, in this thesis, to "reglue" the umbrellas sampled from the Umbrella Sampling (cf figure 14) in an optimal way, in order to estimate the (unbiased) probability of finding a system satisfying a given state (according to the chosen reaction coordinate), is the Wheighed Histograms Analysis Method (WHAM) 7, 100, 151, 163).

The idea, illustrated by the figure, is that each umbrella that is untied (represented by dotted lines) allows the average force potential to be found to within one constant. By the fact that these umbrellas overlap, we will be able to adjust the appropriate constant to obtain the full mean force potential (solid line). The constants will be chosen so that the PMF tends towards 0 at long distance. ${ }^{4}$

[^16]

Figure 14 - Illustration of umbrellas re-gluing from the Umbrella Sampling. Each umbrella gives an end of curve and we try to glue these ends together in the best way (figure from 150)

In what follows, we will explain the mathematical reasoning that leads to the method. To do so, we will discretize the problem introduced in the previous section.

We assume $N$ simulations, assumed independent, by the Umbrella Sampling method, where the $i$ th simulation was performed for a distance $r_{i}^{*}$ between the two ions. Each simulation has respectively generated, for $i=1, \ldots, N$, a sample of size $n_{i}$, these samples having been extracted over a sufficiently long time for them to be considered independent.

We suppose an orthonormal marker that we divide into $M$ subdivisions (]$a_{j}, a_{j+1}[)_{j=1, \ldots, M}$, these corresponding to the subdivisions used to draw the histograms of the Umbrella Sampling method.

Let $\left(P_{i, j}\right)_{i=1, \ldots, N, j=1, \ldots, M}$ be the matrix representing the biased probability in the $t h$ simulation and $j$ th subdivision, which is such that :

$$
\begin{equation*}
P_{i, j}=P_{b}\left(q(j), r_{i}^{*}\right) \tag{4.26}
\end{equation*}
$$

where $q(j)=\left(j-\frac{1}{2}\right)\left(a_{j+1}-a_{j}\right)$.
Similarly, we define $\left(P_{j}^{0}\right)_{j=1, \ldots, M}$ the vector representing the (unbiased) probability in the $j$ th subdivision, $\left(C_{i, j}\right)_{i=1, \ldots, N, j=1, \ldots, M}$ the matrix of biased factors, and $\left(f_{i}\right)_{i=1, \ldots, N}$ the vector of normalization constants, which are such that :

$$
\begin{align*}
P_{j}^{0} & =P(q(j))  \tag{4.27}\\
C_{i, j} & =e^{\beta \mathcal{V}_{\text {harm }}^{r_{j}^{*}}(q(j))}  \tag{4.28}\\
f_{i} & =\left\langle e^{-\beta \mathcal{V}_{\text {harm }}^{r_{i}^{*}}}(\xi(.))\right. \tag{4.29}
\end{align*}
$$

We deduce from 4.25 the following relation $\forall i=1, \ldots N$ :

$$
\begin{equation*}
P_{i, j}=f_{i} C_{i, j} P_{j}^{0} . \tag{4.30}
\end{equation*}
$$

We are looking for an optimal estimator for $\left(P_{j}^{0}\right)_{j=1, \ldots, M}$, that we will note $\left(\widehat{P_{j}^{0}}\right)_{j=1, \ldots, M}$.
Let $\left(n_{i, j}\right)_{i=1, \ldots, N, j=1, \ldots, M}$ be the matrix of the number of counts of the histogram for the simulation $i$ in the $j$ th subdivision. An estimator of $P_{i, j}$ is then :

$$
\begin{equation*}
\widehat{P_{i, j}}=\frac{n_{i, j}}{n_{i}} \tag{4.31}
\end{equation*}
$$

And we make sure that $\forall i=1, \ldots, N$ :

$$
\begin{equation*}
\sum_{j=1}^{M} \widehat{P_{i, j}}=1 \tag{4.32}
\end{equation*}
$$

Theorem 3. An optimal estimator for $\left(P_{j}^{0}\right)_{j=1, \ldots, M}$ is then given for $j=1, \ldots, M$ by :

$$
\begin{equation*}
\widehat{P_{j}^{0}}=\frac{\sum_{i=1}^{N} n_{i, j}}{\sum_{i=1}^{N} n_{i} f_{i} C_{i, j}} \tag{4.33}
\end{equation*}
$$

Here we will give two proofs corresponding to two approaches to the problem, and then we will give the WHAM algorithm that we derive from them.

## Proof. Approach by an optimization problem

We begin by recalling a method to solve a constrained optimization problem using a Lagrangien (not to be confused with the Lagrangian defined in analytical mechanics, which we will see in 3.8.2).

We consider the following problem for $J: \Omega \subset \mathbb{R}^{n} \rightarrow \mathbb{R}\left(n \in \mathbb{N}^{*}\right.$, and $\Omega$ is an open of $\left.\mathbb{R}^{n}\right)$ :

$$
\begin{equation*}
\min _{\mathbf{x} \in E} J(\mathbf{x}) \tag{4.34}
\end{equation*}
$$

where $E=\left\{\mathbf{x} \in \mathbb{R}^{N} \mid g(\mathbf{x})=0\right\}$ avec $g: \mathbb{R}^{n} \rightarrow \mathbb{R}^{m}\left(m \in \mathbb{N}^{*}\right) . E$ is the space of constraints.
Definition 4 (Lagrangian (in the sense of optimization)). Assumes $J, g$ of class $C^{1}$. The Lagrangian $L$ is the function defined on $\Omega \times \mathbb{R}^{m}$ by :

$$
\begin{equation*}
L\left(\boldsymbol{x}, \lambda_{1}, \ldots, \lambda_{m}\right)=J(x)-\sum_{i=1}^{m} \lambda_{i} g_{i}(x) \tag{4.35}
\end{equation*}
$$

The coefficients $\left(\lambda_{i}\right)_{i=1, \ldots, m}$ are called Lagrange multipliers.
Theorem 4. It is assumed that $E$ is a convex set and $J$ is a convex function. Then the problem (4.34) has a solution.

By using 4.30 and 4.31, a probability estimate (unbiased) in the $i$ th simulation and $j$ th subdivision is :

$$
\begin{equation*}
\Omega_{i, j}=\frac{n_{i, j}}{n_{i} C_{i, j} f_{i}} \tag{4.36}
\end{equation*}
$$

The idea is to make a most optimal convex combination with the $N$ estimators $\Omega_{i, j}(i=1, \ldots, N)$ to estimate $P_{j}^{0}$, i.e. we want to find $\left(\omega_{1}, \ldots, \omega_{N}\right)$ such that $\sum_{i=1}^{N} \omega_{i}=1$ and

$$
\begin{equation*}
\widehat{P_{j}^{0}}=\sum_{i=1}^{N} \omega_{i} \Omega_{i, j} \tag{4.37}
\end{equation*}
$$

has as little variance as possible.
The optimization problem is therefore the following :

$$
\begin{equation*}
\min _{\substack{N \\ \text { t.q. } \sum_{i=1} \omega_{i}=1}} \operatorname{var}\left(\widehat{P_{j}^{0}}\right) . \tag{4.38}
\end{equation*}
$$

It is easy to verify first of all that the set of constraints $C=\left\{\omega \in \mathbb{R}^{N} \mid \sum_{i=1}^{N} \omega_{i}=1\right\}$ is convex. Indeed : let $\mathbf{x}, \mathbf{y} \in C$, and let $\lambda \in(0,1)$. So then :

$$
\begin{equation*}
\sum_{i=1}^{N}\left(\lambda x_{i}+(1-\lambda) y_{i}\right)=\lambda \sum_{i=1}^{N} x_{i}+(1-\lambda) \sum_{i=1}^{N} y_{i}=\lambda+(1-\lambda)=1 \tag{4.39}
\end{equation*}
$$

where the penultimate tie comes from the fact that $\mathbf{x}$ and $\mathbf{y}$ belong to $C$. Thus, $(\lambda x+(1-\lambda) y) \in C$, and thus $C$ is quite convex.

We recall the following theorem :
Theorem 5. Let $\left(X_{k}\right)_{k}$ be a sequence of random variables following a binomial law $\mathcal{B}\left(k, p_{k}\right)$. We suppose that $k p_{k} \rightarrow \lambda>0$. Then $\left(X_{k}\right)_{k}$ converges in law to a Poisson random variable of parameter $\lambda$. In other words, for all $l \in \mathbb{N}$, we have :

$$
\begin{equation*}
\mathbb{P}\left(X_{k}=l\right) \rightarrow \frac{e^{-\lambda} \lambda^{l}}{l!} \tag{4.40}
\end{equation*}
$$

of expectation and variance $\lambda$.
This leads us to the following lemma:
Lemma 5. With the conditions of the problem, we have :

$$
\begin{equation*}
\operatorname{var}\left(\widehat{P_{j}^{0}}\right)=\sum_{i=1}^{N} \frac{\omega_{i}^{2} P_{j}^{0}}{n_{i} C_{i, j} f_{i}} . \tag{4.41}
\end{equation*}
$$

Proof. We have, by independence of the simulations :

$$
\begin{equation*}
\operatorname{var}\left(\widehat{P_{j}^{0}}\right)=\sum_{i=1}^{N} \frac{\omega_{i}^{2} \operatorname{var}\left(n_{i, j}\right)}{n_{i}^{2} C_{i, j}^{2} f_{i}^{2}} \tag{4.42}
\end{equation*}
$$

Since $n_{i, j}$ follows a binomial law, we have, for $n_{i}$ large, thanks to theorem 5 the result.

We set $J:\left(x_{1}, \ldots, x_{N}\right) \mapsto \sum_{i=1}^{N} \frac{x_{i}^{2} P_{j}^{0}}{n_{i} C_{i, j} f_{i}}, J$ is convex as the sum of convex functions. Thus, 4.38) does have a solution.

We put the lagrangian :

$$
\begin{equation*}
L\left(\omega_{1}, \ldots, \omega_{N}, \lambda\right)=\sum_{i=1}^{N} \frac{\omega_{i}^{2} P_{j}^{0}}{n_{i} C_{i, j} f_{i}}+\lambda\left(\sum_{i=1}^{N} \omega_{i}-1\right) . \tag{4.43}
\end{equation*}
$$

First-order conditions

- $\forall i: \frac{\partial L}{\partial \omega_{i}}=0 \Leftrightarrow \omega_{i}=\frac{-n_{i} C_{i, j} f_{i} \lambda}{2 P_{j}^{0}}$
- $\frac{\partial L}{\partial \lambda}=0 \Leftrightarrow \sum_{i=1}^{N} \omega_{i}=1$, from which we derive $\frac{-\lambda}{2 P_{j}^{0}} \sum_{i=1}^{N} n_{i} C_{i j} f_{i}=1$ and therefore $\lambda=\frac{-2 P_{j}^{0}}{\sum_{i=1}^{N} n_{i} C_{i, j} f_{i}}$,
which allows us to obtain : $\omega_{i}=\frac{n_{i} C_{i, j} f_{i}}{\sum_{k=1}^{N} n_{k} C_{k, j} f_{k}}$.
And then, in the end we have, for $j=1, \ldots, M$ :
$\widehat{P_{j}^{0}}=\frac{\sum_{i=1}^{N} n_{i, j}}{\sum_{i=1}^{N} n_{i} f_{i} C_{i, j}}$.


## Proof. Likelihood Maximization Approach

We have, for $i=1, \ldots, N$, that $\left(n_{i, 1}, \ldots, n_{i, M}\right)$ follows a multinomial law (since it is a $M$ i.i.d. sample of binomial law).

Since the $N$ simulations are independent, the likelihood of the model is therefore :

$$
L\left(f_{1}, \ldots, f_{N}, P_{1}^{0}, \ldots, P_{M}^{0}\right)=\prod_{i=1}^{N} f(i)
$$

where $f(i)=\frac{n_{i}!}{\prod_{k=1}^{M} n_{i, k}!} \prod_{j=1}^{M}\left(P_{i, j}\right)^{n_{i, j}}$ is the mass function of the simulation $i$ (and where $P_{i, j}=$
$f_{i} C_{i, j} P_{j}^{0}$ as a reminder). It is known that a good estimator can be obtained by maximizing the likelihood, which is equivalent to maximizing the log of the likelihood (and even the log of the likelihood deprived of the addition of the terms not containing $f_{i}(i=1, \ldots, N)$ ni $P_{j}^{0}$ $(j=1, \ldots, M)$, what will be noted $\mathcal{L})$.
We have : $\mathcal{L}\left(f_{1}, \ldots, f_{N}, P_{1}^{0}, \ldots, P_{M}^{0}\right)=\sum_{i=1}^{N} \sum_{j=1}^{M} n_{i, j} \ln \left(f_{i} C_{i, j} P_{j}^{0}\right)$.
Knowing the constraints $\sum_{j=1}^{M} f_{i} C_{i, j} P_{j}^{0}=1$ for $i=1, \ldots, N$ we then set the log of the Lagrangian
$\mathcal{M}:$

$$
\mathcal{M}\left(f_{1}, \ldots, f_{N}, P_{1}^{0}, \ldots, P_{M}^{0}, \lambda_{1}, . ., \lambda_{N}\right)=\sum_{i=1}^{N}\left(\sum_{j=1}^{M} n_{i, j} \ln \left(f_{i} C_{i, j} P_{j}^{0}\right)+\lambda_{i}\left(\sum_{j=1}^{M} f_{i} C_{i, j} P_{j}^{0}-1\right)\right)
$$

where the $\lambda_{i}(i=1, \ldots, N)$ are the Lagrange multipliers associated with the respective constraints.
First-order conditions :

- for $i=1, \ldots, N: 0=\frac{\partial \mathcal{M}}{\partial f_{i}}=\sum_{j=1}^{M}\left(\frac{n_{i, j}}{f_{i}}+\lambda_{i} C_{i, j} P_{j}^{0}\right)=\frac{n_{i}}{f_{i}}+\lambda_{i} \sum_{j=1}^{M} c_{i, j} P_{j}^{0}$
- for $j=1, \ldots, M: 0=\frac{\partial \mathcal{M}}{\partial P_{j}^{0}}=\sum_{i=1}^{N}\left(\frac{n_{i, j}}{P_{j}^{0}}+\lambda_{i} f_{i} C_{i, j}\right)$
- for $i=1, \ldots, N: 0=\frac{\partial \mathcal{M}}{\partial \lambda_{i}}=\sum_{j=1}^{M} f_{i} C_{i, j} P_{j}^{0}-1$

We then have, for $i=1, \ldots, N: \lambda_{i}=\frac{-n_{i}}{\sum_{j=1}^{M} f_{i} C_{i, j} P_{j}^{0}}=-n_{i}$,
so that, for $j=1, \ldots, M: \frac{\sum_{i=1}^{N} n_{i, j}}{P_{j}^{0}}=\sum_{i=1}^{N} n_{i} f_{i} C_{i, j}$
From where one obtain, for $j=1, \ldots, M: \widehat{P_{j}^{0}}=\frac{\sum_{i=1}^{N} n_{i, j}}{\sum_{i=1}^{N} n_{i} f_{i} C_{i, j}}$.

Thanks to the theorem and 4.30 and 4.32 we derive the following algorithm, which corresponds to the WHAM algorithm :

```
\(s 1^{0}=0\)
\(s 3^{0}=0\) for \(i=1 \grave{a} N\) do
    \(s 1^{i}=s 1^{i-1}+n_{i, j}\)
end
while \(\left\|f_{i}-f_{i-1}\right\|>\delta\) do
    for \(i=1 \grave{a} N\) do
        \(s 2^{j}=n_{i} f_{i} C_{i, j}\)
    end
    \(P^{j}=\frac{s 1^{N}}{s 2^{N}}\)
    for \(j=1 \grave{a} M\) do
        \(s 3^{j}=s 3^{j-1}+C_{i, j} P_{j}^{0}\)
    end
    \(f_{i+1}=s 3^{-1}\)
end
```


### 4.7 Analysis of a spring problem, period and stiffness constant

We are interested here in the analysis of a simple spring problem, which allows the recall of two different and interesting approaches in mechanics. By obtaining the period of the spring as a
function of its stiffness constant, we will then be able to deduce the choice of parameters that we will use in our simulations by Umbrella Sampling.

The following $(P)$ problem is considered in $\mathbb{R}$ :
Let two particles $M_{1}$ and $M_{2}$ with coordinates $x_{1}$ and $x_{2}$, with $x_{1}<x_{2}$, and respective mass $m_{1}$ and $m_{2}$. It is assumed that $M_{1}$ and $M_{2}$ are connected by a spring of stiffness constant $k$ (see figure 15 . We wish to determine the relations verified by their respective strength $F_{1}$ et $F_{2}$.


Figure 15 - Scheme representing the two particles M1 and M2, located at positions x1 and x2 respectively and connected by a spring of stiffness constant k

### 4.7.1 Analysis with Newton's principles

Let $U$ be the potential of the system. We have : $U=\frac{1}{2} k\left(\left(x_{2}-x_{1}\right)-d\right)^{2}$.
For $i=1,2$, let $F_{i}$ be the force of $p_{i}$ applied on $p_{j}$, with $j \neq i$. By Newton's second principle, we have :

$$
\begin{equation*}
F_{i}=m_{i} \ddot{x}_{i} . \tag{4.44}
\end{equation*}
$$

We know that, for $i=1,2$, we have : $F_{i}=-\frac{d U\left(x_{i}\right)}{d x_{i}}$, so that:

$$
\begin{equation*}
F_{1}=k\left(x_{2}-x_{1}-d\right)=-F_{2} . \tag{4.45}
\end{equation*}
$$

With 4.44 and 4.45, we thus obtain the following system of linear equations of order 2 :

$$
(S)\left\{\begin{array}{l}
k\left(x_{2}-x_{1}-d\right)=m_{1} \ddot{x}_{1}  \tag{4.46}\\
-k\left(x_{2}-x_{1}-d\right)=m_{2} \ddot{x_{2}}
\end{array}\right.
$$

Let $x_{G}$ be the position of the abscissa of the system's center of gravity, i.e. $x_{G}=\frac{m_{1} x_{1}+m_{2} x_{2}}{m_{1}+m_{2}}$. We verify that its second derivative with respect to time is zero, i.e.

$$
\begin{equation*}
\ddot{x_{G}}=\frac{m_{1} \ddot{x_{1}}+m_{2} \ddot{x_{2}}}{m_{1}+m_{2}}=0 \tag{4.47}
\end{equation*}
$$

which means, integrating with respect to time, that $m_{1} \dot{x_{1}}+m_{2} \dot{x_{2}}=C$ where $C$ is a constant.
We introduce $y$ tel que $x_{1}=x_{G}+y$; and therefore, after calculations :

$$
\begin{equation*}
y=\frac{m_{2}}{m_{1}+m_{2}}\left(x_{1}-x_{2}\right) . \tag{4.48}
\end{equation*}
$$

We then obtain for the first equation of the system $(S)$, thanks to 4.47) :

$$
\begin{equation*}
k\left(-\frac{m_{1}+m_{2}}{m_{2}} y-d\right)=m_{1} \ddot{y} . \tag{4.49}
\end{equation*}
$$

We set (all the terms under the root are positive) :

$$
\begin{equation*}
\omega=\sqrt{k \frac{m_{1}+m_{2}}{m_{1} m_{2}}} . \tag{4.50}
\end{equation*}
$$

The solutions of 4.49 are $\forall t$ of the form :

$$
\begin{equation*}
y(t)=r \cos (\omega t+\Phi)-\frac{m_{2} d}{m_{1}+m_{2}} \tag{4.51}
\end{equation*}
$$

with $r, \Phi \in \mathbb{R}$, i.e. it is a harmonic oscillator of frequency $\omega$, and its period $T$ is therefore :

$$
\begin{equation*}
T=\frac{2 \pi}{\omega}=2 \pi \sqrt{\frac{m_{1} m_{2}}{k\left(m_{1}+m_{2}\right)}} \tag{4.52}
\end{equation*}
$$

### 4.7.2 Analysis with Hamiltonian formulation

One introduces the Lagrangian (in the sense of analytical mechanics) $L$ associated with $(P)$ :

$$
\begin{equation*}
L=E_{c}-U . \tag{4.53}
\end{equation*}
$$

Here we have :

$$
\begin{equation*}
L\left(x_{1}, x_{2}, \dot{x_{1}}, \dot{x_{2}}\right)=\frac{1}{2}\left(m_{1}{\dot{x_{1}}}^{2}+m_{2}{\dot{x_{2}}}^{2}\right)-\frac{1}{2} k\left(x_{2}-x_{1}-d\right)^{2} . \tag{4.54}
\end{equation*}
$$

We introduce $a=x_{G}=\frac{m_{1} x_{1}+m_{2} x_{2}}{m_{1}+m_{2}}$ and $a^{\prime}=x_{2}-x_{1}$. We have then :

$$
\left\{\begin{array} { l } 
{ \dot { a } = \frac { m _ { 1 } \dot { x _ { 1 } } + m _ { 2 } \dot { x _ { 2 } } } { m _ { 1 } + m _ { 2 } } }  \tag{4.55}\\
{ \dot { a } ^ { \prime } = \dot { x _ { 2 } } - \dot { x _ { 1 } } }
\end{array} \Rightarrow \left\{\begin{array} { l } 
{ \dot { a } = \frac { m _ { 1 } \dot { x _ { 1 } } + m _ { 2 } \dot { x _ { 2 } } } { m _ { 1 } + m _ { 2 } } } \\
{ \frac { \sqrt { m _ { 1 } m _ { 2 } } } { m _ { 1 } + m _ { 2 } } \dot { a } ^ { \prime } = \frac { \sqrt { m _ { 1 } m _ { 2 } } } { m _ { 1 } + m _ { 2 } } ( \dot { x _ { 2 } } - \dot { x _ { 1 } } ) }
\end{array} \Rightarrow \left\{\begin{array}{l}
\dot{a}^{2}=\frac{m_{1}^{2} \dot{x}_{1}^{2}+m_{2}^{2} \dot{x}_{2}{ }^{2}+2 m_{1} m_{2} \dot{x_{1} \dot{x_{2}}}}{\left(m_{1}+m_{2}\right)^{2}} \\
\frac{m_{1} m_{2}}{\left(m_{1}+m_{2}\right)^{2}} \dot{a}^{\prime 2}=\frac{m_{1} m_{2}}{\left(m_{1}+m_{2}\right)^{2}}\left(\dot{x_{2}}{ }^{2}+\dot{x_{1}}{ }^{2}-2 \dot{x_{1}} \dot{x_{2}}\right)
\end{array}\right.\right.\right.
$$

By summing the two equations of the final system, we obtain :

$$
\begin{align*}
& \dot{a}^{2}+\frac{m_{1} m_{2}}{\left(m_{1}+m_{2}\right)^{2}} \dot{a}^{\prime 2}=\frac{m_{1}^{2}{\dot{x_{1}}}^{2}+m_{2}^{2}{\dot{x_{2}}}^{2}+2 m_{1} m_{2} \dot{x_{1}} \dot{x_{2}}}{\left(m_{1}+m_{2}\right)^{2}}+\frac{m_{1} m_{2}}{\left(m_{1}+m_{2}\right)^{2}}\left(\dot{x_{2}}\right. \\
& 2 \\
&=\frac{m_{1}\left(m_{1}+m_{2}\right)}{\left(m_{1}+m_{2}\right)^{2}}{\dot{x_{1}}}^{2}+\frac{m_{2}\left(m_{1}+m_{2}\right)}{\left(m_{1}+m_{2}\right)^{2}} \dot{x_{2}} \dot{x}^{2}  \tag{4.56}\\
&=\frac{m_{1}}{m_{1}+m_{2}}{\dot{x_{1}}}^{2}+\frac{m_{2}}{m_{1}+m_{2}}{\dot{x_{2}}}^{2}
\end{align*}
$$

$$
\Leftrightarrow\left(m_{1}+m_{2}\right) \dot{a}^{2}+\frac{m_{1} m_{2}}{m_{1}+m_{2}} a^{\prime 2}=m_{1}{\dot{x_{1}}}^{2}+m_{2}{\dot{x_{2}}}^{2}
$$

Let's start again 4.54 and you get :

$$
\begin{equation*}
L\left(a, a^{\prime}, \dot{a}, \dot{a^{\prime}}\right)=\frac{1}{2}\left(\left(m_{1}+m_{2}\right) \dot{a}^{2}+\frac{m_{1} m_{2}}{m_{1}+m_{2}} \dot{a}^{\prime 2}\right)-\frac{1}{2} k\left(a^{\prime}-d\right)^{2} . \tag{4.57}
\end{equation*}
$$

The Hamiltonian $H$ associated with $(P)$ is then :

$$
\begin{equation*}
H\left(a, a^{\prime}, b, b^{\prime}\right)=p \dot{a}+p^{\prime} \dot{a}^{\prime}-L\left(a, a^{\prime}, \dot{x_{1}}(b), \dot{x_{2}}\left(b^{\prime}\right)\right) \tag{4.58}
\end{equation*}
$$

where $b$ and $b^{\prime}$ are associated with a transformation of Legrendre of the Lagrangian.
We take $b=\frac{\partial L}{\partial \dot{a}}=\left(m_{1}+m_{2}\right) \dot{a}$ et $b^{\prime}=\frac{\partial L}{\partial \dot{a}^{\prime}}=\frac{m_{1} m_{2}}{m_{1}+m_{2}} \dot{a}^{\prime}$. So that:

$$
\begin{align*}
H\left(a, a^{\prime}, b, b^{\prime}\right) & =\frac{b^{2}}{m_{1}+m_{2}}+\frac{m_{1}+m_{2}}{m_{1} m_{2}} b^{\prime 2}-\left(\frac{1}{2}\left(\frac{b^{2}}{m_{1}+m_{2}}+\frac{m_{1}+m_{2}}{m_{1} m_{2}} b^{\prime}\right)-\frac{1}{2} k\left(a^{\prime}-d\right)^{2}\right)  \tag{4.59}\\
& =\frac{1}{2}\left(\frac{b^{2}}{m_{1}+m_{2}}+\frac{m_{1}+m_{2}}{m_{1} m_{2}} b^{\prime}\right)+\frac{1}{2} k\left(a^{\prime}-d\right)^{2} \tag{4.60}
\end{align*}
$$

We have :

$$
\begin{equation*}
\frac{\partial H}{\partial b}=\frac{b}{m_{1}+m_{2}}, \frac{\partial H}{\partial b^{\prime}}=\frac{m_{1}+m_{2}}{m_{1} m_{2}} b^{\prime}, \frac{\partial H}{\partial a}=0, \frac{\partial H}{\partial a^{\prime}}=k\left(a^{\prime}-d\right) \tag{4.61}
\end{equation*}
$$

Hamilton's equations of motion give us the following system of equations:

$$
\left\{\begin{array} { l } 
{ \dot { a } = \frac { \partial H } { \partial b } }  \tag{4.62}\\
{ \dot { a ^ { \prime } } = \frac { \partial H } { \partial b ^ { \prime } } } \\
{ \dot { b } = - \frac { \partial ^ { \prime } } { \partial a } } \\
{ \dot { b ^ { \prime } } = - \frac { \partial H } { \partial a ^ { \prime } } }
\end{array} \Leftrightarrow \left\{\begin{array}{l}
\dot{a}=\frac{b}{m_{1}+m_{2}} \\
\dot{a^{\prime}}=\frac{m_{1}+m_{2}}{m_{1} m_{2}} b^{\prime} \\
\dot{b}=0 \\
\dot{b^{\prime}}=-k\left(a^{\prime}-d\right)
\end{array}\right.\right.
$$

So that:

$$
\left\{\begin{array}{l}
\dot{x}_{G}=C  \tag{4.63}\\
\frac{m_{1} m_{2}}{m_{1}+m_{2}} \ddot{a}^{\prime}=-k\left(a^{\prime}-d\right)
\end{array}\right.
$$

The movement of the system therefore consists of a constant velocity for the center of gravity and a vibration for $a^{\prime}=x_{2}-x_{1}$ of period $2 \pi \sqrt{\frac{m_{1} m_{2}}{k\left(m_{1}+m_{2}\right.}}$ around the equilibrium position $a^{\prime}=d$.

On the other hand, the system writes in the form of 4.60) allows to decouple the vibration term $\left(a^{\prime}, b^{\prime}\right)$ from the translation term $(a, b)$ in the canonical set. It can therefore be factorized. Since we are dealing with quadratic degrees of freedom, we obtain according to the equirepartition energy distribution theorem :

$$
\begin{equation*}
\left\langle\frac{1}{2} k\left(a^{\prime}-d\right)^{2}\right\rangle=\frac{1}{2} k_{B} T \tag{4.64}
\end{equation*}
$$

So this gives an idea of the amplitude of the umbrella:

$$
\begin{equation*}
\sigma=\sqrt{\frac{k_{B} T}{k}} \tag{4.65}
\end{equation*}
$$

### 4.7.3 Stiffness constant, umbrella amplitude and period for our simulations

According to the calculations of the previous problem, the period $\Theta$ of the spring is related to the stiffness constant $k$ of the spring by the formula :

$$
\begin{equation*}
\Theta=2 \pi \sqrt{\frac{m_{1} m_{2}}{k\left(m_{1}+m_{2}\right)}} \tag{4.66}
\end{equation*}
$$

where $m_{i}$ is the mass of the particle $p_{i}$.
In the case where $p_{1}=N a^{+}$and $p_{2}=C l^{-}$we have : $m_{1}=23 \mathrm{~g} . \mathrm{mol}^{-1}$ and $m_{2}=35.5 \mathrm{~g} . \mathrm{mol}^{-1}$.
As the ideal stiffness constant to be applied to the spring force between the two ions, one wishes to choose $k=10 \mathrm{kcal} . \mathrm{mol}^{-1} . \mathrm{A}^{-2}$ (units corresponding to those of Tinker). We recall the following conversions of measures :

$$
\begin{align*}
1 \mathrm{kcal} & =4,184 \mathrm{~kJ}  \tag{4.67}\\
1 \mathrm{~J} & =1 \mathrm{~kg} \cdot \mathrm{~m}^{2} \cdot \mathrm{~s}^{-2}  \tag{4.68}\\
1 \mathrm{~A} & =10^{-10} \mathrm{~m} \tag{4.69}
\end{align*}
$$

Thus, we obtain that the period of the corresponding spring is $\Theta \simeq 0.3629$; ps. Thus, collecting the positions, in order to make the histograms by Umbrella Sampling, every $p s$ ensures that the spring has acted well to maintain the ions at the desired distance.

Moreover, the amplitude of the umbrella is then $\sigma=0.2433 \mathrm{~A}$.

### 4.8 Calculation of coefficients of interest

### 4.8.1 The association constant

Consider the chemical reaction in a surrounding solvent :

$$
\begin{equation*}
C^{c+}+A^{a-} \leftrightarrow C A^{(c-a)+} \tag{4.70}
\end{equation*}
$$

where $C^{c+}$ corresponds to the cation, $A^{a-}$ to the anion and $C A^{(c-a)+}$ to the ion pair.
At equilibrium, this reaction verifies the law of mass action which allows the concentration of the different species to be calculated.

The equilibrium constant $K$ quantifies the formation of the ion pair 14115 . Knowing the activity coefficients (equal to 1 if the solution is diluted), it allows to calculate the proportion of the pair by the law of mass action, which is written here :

$$
\begin{equation*}
K=\frac{1-\alpha}{\alpha^{2} c}=K^{(c)}\left(\frac{y_{ \pm}^{\prime 2}}{y_{I P}}\right) \tag{4.71}
\end{equation*}
$$

where $\alpha$ is the degree of dissociation of the pair, $c=\frac{\rho}{2 N_{A}}$ is the electrolyte concentration, $K^{(c)}$ is the association constant, and $y_{ \pm}^{\prime}$ et $y_{I P}$ are respectively the average activity coefficient of the free ions in solution and that of the ion pair.

The ion pair association constant $K^{(c)}$ can be calculated by integrating the McMillan and Mayer potential via the generalized Bjerrum equation, shown in 127, 128:

$$
\begin{equation*}
K^{(c)}=4 \pi N_{A} \int_{0}^{R} r^{2} e^{\frac{-V_{M M}(r)}{k_{B} T}} d r \tag{4.72}
\end{equation*}
$$

where $R$ is a distance to distinguish the ion pair from free ions in solution. $R$ is generally chosen so that the activity coefficients are close to 1 .

### 4.8.2 The osmotic coefficient of activity of the solvent

We consider a system described within the framework of McMillan and Mayer's theory, i.e. the chemical potential of the solvent $\mu_{w}$ and that of the solution $\mu_{s}$ are fixed, and the temperature $T$ and the volume $V$ are also fixed. We have the relation between the thermodynamic quantities and the partition function $\Omega$ 127, 133 :

$$
\begin{equation*}
d \Omega=-S d T-N_{w} d \mu_{w}-N_{s} d \mu_{s}-P d V \tag{4.73}
\end{equation*}
$$

where $S$ is the entropy, $N_{w}$ and $N_{s}$ are respectively the number of particles of the pure solvent and of the solute, and $P$ is the pressure of the solution. The latter verifies the formula :

$$
\begin{equation*}
P=P_{w}+P_{o s m} \tag{4.74}
\end{equation*}
$$

where $P_{w}$ is the pressure of the pure solvent and $P_{o s m}$ is the osmotic pressure, so called because it is the difference between the pressure of the solution and that of the pure solvent.

The relationship between the grand canonical partition function $Q$, expressed as a function of McMillan and Mayer's potential function $W$ (see section 4.3.2), and the osmotic pressure is as follows:

$$
\begin{equation*}
Q(W)=e^{\beta P_{o s m} V} \tag{4.75}
\end{equation*}
$$

The osmotic coefficient 69133 of the electrolyte solution at the McMillan and Mayer scale $\Phi^{M M}$ can be defined by the formula :

$$
\begin{equation*}
\Phi^{M M}=\frac{P_{o s m}}{\rho k_{B} T} \tag{4.76}
\end{equation*}
$$

where $\rho$ is the solute density. The osmotic coefficient tends towards 1 for an ideal solution, which is the case for a very dilute solution (indeed, the denominator $\rho k_{B} T$ corresponds to the osmotic coefficient in the ideal case, this is obtained with the Gibbs-Duhem relation). This coefficient is important because it then allows us to deduce the activity of the solvent. Using the Gibbs-Duhem relation, one can deduce the activity coefficients of the solutes.

The calculation of the activity coefficients is carried out by simulating the solute gas made up of ions and pairs interacting by the McMillan and Mayer potential. Using Monte Carlo simulations or Brownian dynamics, these activity coefficients can then be computed numerically. Analytically, another strategy using the MSA (Mean Spherical Approximation) integrals equations [19, 25, 26, 127, 179, 180 (whose applications can be seen in 83, 111, 152, 153) can also be calculated analytically and approximately, but can only be applied if the McMillan and Mayer potential has a hard core.

## Chapitre 5

## Study of the Potential of McMillan and Mayer at long distance

In this chapter, we are interested in the behavior of the McMillan and Mayer potential at large distances. During simulations, as seen for example on figure 16 , it seems that the latter approaches that of a coulombic potential. The McMillan and Mayer potential being defined to a constant, an important issue is to adjust this constant in order to approximate the macroscopic quantities of interest (such as the association constant). One idea seems to be to choose this constant such that the McMillan and Mayer potential fits the coulombic potential curve at large distances.


Figure 16 - Curves of various McMillan and Mayer potentials fitted to the coulombic potential curve (from 130])

Here we wish to study the influence of the periodicity introduced in the simulations in the calculation of the potential of the considered system, and from there, we will then adjust the McMillan and Mayer potential of our simulations in such a way that the long distance curve approaches the obtained development.

We will first study the problem from a mathematical point of view for a system formed by two particles surrounded by a solvent. We will then obtain a development of the potential of this system as a function of the period chosen for the sides of the simulation box. Then, we will carry out simulations for three systems of different size, formed by an ion $\mathrm{Na}^{+}$, an ion $t e x t C l^{-}$and $N$ water molecules ( $N$ depending on the size of the system). We will then study the consistency of the result that we obtained mathematically with the McMillan and Mayer potential curve of each system. By fitting, at a large distance, the latter to our development, we will also study some macroscopic properties associated with these systems. Furthermore, we will also evaluate the validity of our development from McMillan and Mayer potentials obtained for lanthanide salts.

### 5.1 Mathematical problem

We consider a system consisting of a ion $p_{1}$ of charge $q_{1}$, a ion $p_{2}$ of charge $q_{2}$ and surrounded by a solvent of dielectric constant $\epsilon_{r}$ (we can easily verify that the system is electrically neutral).

Each particle is described by its position, which is noted as $\mathbf{r}_{1}^{000}$ for $p_{1}$ and $\mathbf{r}_{2}^{000}$ for $p_{2}$.
We consider that the particles are in a cubic box of side $L$. Periodic conditions are considered at the edges of the box.

We call $\left(p_{1}^{i j k}\right)_{i, j, k \in \mathbb{Z}^{*}}$ and $\left(p_{2}^{i j k}\right)_{i, j, k \in \mathbb{Z}^{*}}$ the images of $p_{1}$ and $p_{2}$ by periodicity, which are described by their position $\mathbf{r}_{1}^{i j k}$ and $\mathbf{r}_{2}^{i j k}$ respectively.

We note $\|\mathbf{r}\|=\min _{i, j, k \in \mathbb{Z}}\left\|\overrightarrow{\mathbf{r}_{1}^{i j k} \mathbf{r}_{2}^{i j k}}\right\|$ the distance between ion $p_{1}$ and $p_{2} \underbrace{1}$
$L$ has been choosen so that $L \gg\|\mathbf{r}\|$ (that corresponds to a system in a large box with $N$ water molecules, where $N$ is large, which represents a diluted medium).

Let $U_{P B C}$ be the energy potential of the periodic system. We are interested in the behaviour of $U_{P B C}$ as a function of $\mathbf{r}$ and $L$.

For the two ions in infinite conditions or in a vacuum, we know that, at long distances ( $\|\mathbf{r}\|$ being large) the associated potential behaves like a Coulomb potential (i.e. there are only long range interactions that prevail) and thus decreases with a factor $\frac{1}{\|\mathbf{r}\|}$.

Here, we are going to prove the following theorem :
Theorem 6. Under the previous conditions, $U_{P B C}$ verifies :

$$
\begin{equation*}
U_{P B C}(\boldsymbol{r}, L)=\frac{q_{1} q_{2}}{4 \pi \epsilon_{0} \epsilon_{r}\|\boldsymbol{r}\|}\left(1+C\left(\frac{\|\boldsymbol{r}\|}{L}\right)^{5}\right)+\frac{q_{1} q_{2}}{4 \pi \epsilon_{0} \epsilon_{r}} \int_{S(r)}\left(\sum_{\boldsymbol{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{35}{2} \frac{(\boldsymbol{l} . \boldsymbol{n})^{3} \boldsymbol{n}}{\|\boldsymbol{n}\|^{9} L^{5}}\right) d \boldsymbol{l}+o\left(\frac{\|\boldsymbol{r}\|^{4}}{L^{5}}\right) \tag{5.1}
\end{equation*}
$$

[^17]with $C=-\left(21 \sum_{i>0, j \geq i, k \geq i+1} \frac{1}{\left\|(i, j, k)^{t}\right\|^{5}}+\left(\frac{21}{4}+\frac{7}{3^{5 / 2}}\right) \zeta(5)+\frac{21}{2} \sum_{i, j>0} \frac{1}{\left\|(i, j)^{t}\right\|^{5}}\right) \quad$ (so that $C \simeq-9.079945024529188$ ),
$\zeta$ being the zeta function. For $\boldsymbol{r}=(x, y, z), S(\boldsymbol{r})=\left[a_{1}, x\right] \times\left[a_{2}, y\right] \times\left[a_{3}, z\right]\left(a_{1}, a_{2}, a_{3}\right.$ being choosen such that the constant of that primitive is null).
The reader interested in the physical meaning of the theorem may skip the mathematical proof which follows.

The proof of the theorem being based on clever combinations of nodes in a triple sum, we first begin with the following definition that we will need later :
Definition 5. We define the circular permutation $\sigma$, of order 3, which is such that :

$$
\sigma=\left(\begin{array}{lll}
i & j & k \\
j & k & i
\end{array}\right)
$$

i.e. $\sigma(i)=j, \sigma(j)=k$ and $\sigma(k)=i$.

Before begining the theorem's proof, we concentrate attention of the lector to note that we choose in advance to study forces acting on a particle of the considered system, instead of the potential itself. This choice is explained by the fact that we know that opposing forces cancel each other out, so that clever combinations of forces may simplify the calculus and allow to eliminate the non-converging terms.

Proof. We begin by considering all the forces acting on $p_{1}$, and we note $\mathbf{F}_{1}(\mathbf{r}, L)$ the resulting sum. Knowing the periodical conditions, $p_{1}$ not only suffers the $p_{2}$ force but also those from the images of $p_{2}$, and so does that of its own images. In the end, for

$$
\mathbf{r}_{1 l}=\left\{\begin{array}{l}
0 \text { if } l=1 \\
\mathbf{r} \text { if } l=2
\end{array}\right.
$$

we have :

$$
\begin{align*}
\mathbf{F}_{1}(\mathbf{r}, L) & =\frac{q_{1}}{4 \pi \epsilon_{0} \epsilon_{r}} \sum_{l=1}^{2} \sum_{\mathbf{n} \in \mathbb{Z}^{3}}^{\prime} \frac{q_{l}}{\left\|\mathbf{r}_{1 l}+\mathbf{n} L\right\|^{3}}\left(\mathbf{r}_{1 l}+\mathbf{n} L\right)  \tag{5.2}\\
& =\frac{q_{1} q_{2} \mathbf{r}}{4 \pi \epsilon_{0} \epsilon_{r}\|\mathbf{r}\|^{3}}+\frac{q_{1}^{2}}{4 \pi \epsilon_{0} \epsilon_{r}} \sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{1}{\|\mathbf{n} L\|^{3}} \mathbf{n} L+\frac{q_{1} q_{2}}{4 \pi \epsilon_{0} \epsilon_{r}} \sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{1}{\|\mathbf{r}+\mathbf{n} L\|^{3}}(\mathbf{r}+\mathbf{n} L) \tag{5.3}
\end{align*}
$$

where, in the firt equality, the ' in the triple sum signifies that we take $\mathbf{n} \neq(0,0,0)$ if $l=1$.
Lemma 6. In the relation (5.3), the first triple sum is zero for each coordinates of $\boldsymbol{n}$.
Proof. For each coordinates of $\mathbf{n}$, we use the parity of the square function and the imparity of the identity function, and the fact that quotient of an odd and even function gives an odd function.

Physically, we can reason by observing that this term refers to the sum of the electric field created by the images of $p_{1}$. The latter satisfy a cubic symmetry for $p_{1}$, so that the electric field at zero according to $x$ created by the images, with $x>0$, is compensated by the one created by the images with $x<0$, and the same according to $y$ and $z$. At last, we can conclude that this term is null. (N.B. : regarding the images of $p_{2}$, they don't satistfy a cubic symmetry for $p_{1}$, so that the electric field created by the images of $p_{2}$, which corresponds to the last term in (5.3), has no reason to be null.)

We note :

$$
\begin{equation*}
A(\mathbf{r}, \mathbf{n}, L):=\frac{1}{\|\mathbf{r}+\mathbf{n} L\|^{3}}(\mathbf{r}+\mathbf{n} L) \tag{5.4}
\end{equation*}
$$

We have :

$$
\begin{align*}
A(\mathbf{r}, \mathbf{n}, L) & =(\mathbf{r}+\mathbf{n} L)\left(\|\mathbf{r}\|^{2}+2 \mathbf{r} \cdot \mathbf{n} L+\mathbf{n}^{2} L^{2}\right)^{-3 / 2} \\
& =(\mathbf{r}+\mathbf{n} L) \frac{1}{\|\mathbf{n}\|^{3} L^{3}}\left(1+2 \frac{\mathbf{r} . \mathbf{n}}{\|\mathbf{n}\|^{2} L}+\frac{\|\mathbf{r}\|^{2}}{\|\mathbf{n}\|^{2} L^{2}}\right)^{-3 / 2} . \tag{5.5}
\end{align*}
$$

We recall the expansion for small $u$ :

$$
\begin{equation*}
(1+u)^{-3 / 2}=1-\frac{3}{2} u+\frac{15}{8} u^{2}-\frac{35}{16} u^{3}+o\left(u^{3}\right) . \tag{5.6}
\end{equation*}
$$

So that for $L \gg\|\mathbf{r}\|$ :

$$
\begin{align*}
A(\mathbf{r}, \mathbf{n}, L) & =\left(\frac{\mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}+\frac{\mathbf{n}}{\|\mathbf{n}\|^{3} L^{2}}\right)\left(1-\frac{3}{2} \frac{2 \mathbf{r} . \mathbf{n}}{\|\mathbf{n}\|^{2} L}-\frac{3}{2} \frac{\|\mathbf{r}\|^{2}}{\|\mathbf{n}\|^{2} L^{2}}+\frac{15}{8} \frac{4(\mathbf{r} . \mathbf{n})^{2}}{\|\mathbf{n}\|^{4} L^{2}}\right. \\
& \left.+\frac{15}{8} \frac{4(\mathbf{r} . \mathbf{n})\|\mathbf{r}\|^{2}}{\|\mathbf{n}\|^{4} L^{3}}-\frac{35}{16} \frac{8(\mathbf{r} . \mathbf{n})^{3}}{\|\mathbf{n}\|^{6} L^{3}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{3}}\right)\right)  \tag{5.7}\\
& =\frac{A_{1}(\mathbf{r}, \mathbf{n})}{L^{2}}+\frac{A_{2}(\mathbf{r}, \mathbf{n})}{L^{3}}+\frac{A_{3}(\mathbf{r}, \mathbf{n})}{L^{4}}+\frac{A_{4}(\mathbf{r}, \mathbf{n})}{L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.8}
\end{align*}
$$

with :

$$
\begin{gather*}
A_{1}(\mathbf{r}, \mathbf{n})=\frac{\mathbf{n}}{\|\mathbf{n}\|^{3}}  \tag{5.9}\\
A_{2}(\mathbf{r}, \mathbf{n})=\left(\frac{\mathbf{r}}{\|\mathbf{n}\|^{3}}-\frac{3(\mathbf{r} . \mathbf{n}) \mathbf{n}}{\|\mathbf{n}\|^{5}}\right)  \tag{5.10}\\
A_{3}(\mathbf{r}, \mathbf{n})=\left(\frac{-3(\mathbf{r} . \mathbf{n}) \mathbf{r}}{\|\mathbf{n}\|^{5}}-\frac{3}{2} \frac{\|\mathbf{r}\|^{2} \mathbf{n}}{\|\mathbf{n}\|^{5}}+\frac{15}{2} \frac{(\mathbf{r} \mathbf{n})^{2} \mathbf{n}}{\|\mathbf{n}\|^{7}}\right)  \tag{5.11}\\
A_{4}(\mathbf{r}, \mathbf{n})=\left(\frac{-3}{2} \frac{\|\mathbf{r}\|^{2} \mathbf{r}}{\|\mathbf{n}\|^{5}}+\frac{15}{2} \frac{(\mathbf{r} . \mathbf{n})^{2} \mathbf{r}}{\|\mathbf{n}\|^{7}}+\frac{15}{2} \frac{(\mathbf{r} . \mathbf{n})\|\mathbf{r}\|^{2} \mathbf{n}}{\|\mathbf{n}\|^{7}}-\frac{35}{2} \frac{(\mathbf{r} . \mathbf{n})^{3} \mathbf{n}}{\|\mathbf{n}\|^{9}}\right) \tag{5.12}
\end{gather*}
$$

For the term or order 2 (in $\|\mathbf{n}\|$; i.e. $\left.\sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{A_{1}(\mathbf{r}, \mathbf{n})}{L^{2}}\right)$, the reader can refer to lemma (6). Same arguments can be used for the term of order 4 in $\|\mathbf{n}\|$. For the convergence of a triple sum, we can see that the major problem is the term or order 3 (in $\|\mathbf{n}\|$ ). In the following, we will treat the terms according to their order (in $\|\mathbf{n}\|$ ). To do so, we want to do clever combinations with nodes of the sums. We will consider three steps.

Step 1: We first define the quantity $B(\mathbf{r}, \mathbf{n}, L)$ such that:

$$
\begin{align*}
B(\mathbf{r}, \mathbf{n}, L) & :=A(\mathbf{r}, \mathbf{n}, L)+A(\mathbf{r},-\mathbf{n}, L)  \tag{5.13}\\
& =\frac{\mathbf{r}+\mathbf{n} L}{\|\mathbf{r}+\mathbf{n} L\|^{3}}+\frac{\mathbf{r}-\mathbf{n} L}{\|\mathbf{r}-\mathbf{n} L\|^{3}} \tag{5.14}
\end{align*}
$$

We note :

$$
\mathbf{n}=(i, j, k)
$$

In general case (conditions that we will give in the next lemma), we will associate the following nodes (remembering that each node is combined with its opposite in $B(\mathbf{r}, \mathbf{n}, L)$ ) :

1) ( $a, b, c$ ) and $(a,-b,-c)$ on the one hand
2) ( $a,-b, c)$ and $(a, b,-c)$ on the other hand.
for $a=i, b=j$ and $c=k$ and the same for the circular permutations (defined in the definition 3) of $(i, j, k)$.

To avoid duplication of nodes, we have to consider the three following special cases :
Case 1: if $i=k=0$ and $j>0$
In this case, we only have to consider the node $(0, j, 0)$ and its permutations, which corresponds, with their opposite of course, to only 6 different nodes. Indeed, we see that the nodes $(i,-j,-k)=(0,-j, 0)=(i,-j, k)$ and $(i, j,-k)=(0, j, 0)$ are already processed in the 6 previous terms. This cases refers to the 3 symmetry axis passing through centers of two opposite faces of a cube.

Case 2: if $i=j=k$
Here, we see that permutting the coordinates of the node $(i, j, k)=(i, i, i)$ wive give the same one. So that, we only have to consider 4 nodes : $(i, i, i),(i,-i,-i),(i,-i, i)$ and $(i, i,-i)$, and their opposite, i.e. it refers to 8 different nodes. This cases refers to the 4 symmetry axis passing through opposite tops of a cube.

Case 3: if $k=0$ and $i, j>0$
We see here that $(i,-j, k)=(i,-j, 0)=(i,-j,-k)$ and $(i, j,-k)=(i, j, 0)=(i, j, k)$, so that we dont have to proceed with this nodes and their permutations. Finally, it results in considering only 6 nodes : $(i, j, k)$ and $(i,-j,-k)$ and the same with the permutations of $(i, j, 0)$; which refers to 12 nodes, by taking their opposite ones. This cases refers to the 6 symmetry axis passing through middles of the edges of a cube.

Conditions in the general case will result on the following lemma:
Lemma 7. To make sure to consider all nodes while avoiding duplicates, $i, j, k$ will verify :

- $i, j, k>0$
- $j \geq i$ and $k \geq i+1$

Proof. To begin, as $\mathbf{n} \neq 0$ and because of the first and third special cases already processed, we easily see that $i, j, k \neq 0$. Moreover, because of the second special case, we will have at least $i, j$ or $k$ not equal to the two others.

Condition 1: To see that $i, j, k>0$ is a sufficient condition, four other configurations have to be examined.
a) The simplier case is when $i, j, k<0$. Only taking the opposite of $(i, j, k)$ will give a node $\left(i^{\prime}, j^{\prime}, k^{\prime}\right)=(-i,-j,-k)$ where $i^{\prime}, j^{\prime}, k^{\prime}>0$, so that this case is already solved.

It means that at least one of the coordinate is a non-negative one. This leads to the three other cases :
b) When $i>0$ and $j, k<0$
c) When $i, j>0$ and $k<0$
d) When $i, k>0$ and $j<0$.

For the sake of simplicity, we define $S_{a b c}$, which is such as :

$$
\begin{equation*}
S_{a b c}=B(\mathbf{r},(a, b, c), L)+B(\mathbf{r},(a,(-b),(-c)), L)+B(\mathbf{r},(a,(-b), c), L)+B(\mathbf{r},(a, b,(-c)), L) \tag{5.15}
\end{equation*}
$$

which corresponds to the sum of the four terms we want to associate.

We easily see that :

$$
\begin{equation*}
S_{i j k}=S_{i(-j)(-k)}=S_{i(-j) k}=S_{i j(-k)} \tag{5.16}
\end{equation*}
$$

so that working only with the case of the condition is sufficient and avoid treating two time the same node.

The three other final configurations that should occur (respectively when $i<0$ and $j, k>0$, $i, j<0$ and $k>0$, and when $i, k<0$ and $j>0$ ) are solved by taking the opposite of the node and by considering one of the three cases from above.

## Condition 2 :

Here, we will see that considering $j \geq i$ and $k \geq i+1$ is a sufficient condition.
a) We assume that $j \geq i$. We first suppose that $j=i$. By the absurd, we assume that $k \leq i-1$ (the case where $k=i$ is impossible as we saw at the begining of the proof). By taking the second permutation in the node $(i, j, k)$, we obtain a node $\left(i^{\prime}, j^{\prime}, k^{\prime}\right)=(k, i, j)$ which is such that $j^{\prime}=i$, $k^{\prime} \geq i$ and $i^{\prime} \leq i-1$, so that $j^{\prime} \geq i^{\prime}$ and $k^{\prime} \geq i^{\prime}+1$. This case is already treated.

Then, we consider $j>i$. The case when $k \leq i-1$ can be treated as the previous ones. It remains to study the case when $k=i$ (which is possible here seens $j \neq i$ ). By the same arguments as earlier we can prove that this case is already solved.
b) We suppose that $k \geq i+1$. By the absurd, we consider that $j<i$. We take the first permutation of the node $(i, j, k)$ and we obtain the node $\left(i^{\prime}, j^{\prime}, k^{\prime}\right)=(j, k, i)$, with $k^{\prime}=i, i^{\prime}<i$ and $j^{\prime} \geq i+1$, so that $j^{\prime} \geq i^{\prime}+1$ and $k^{\prime}>i^{\prime}$ i.e. $k^{\prime} \geq i^{\prime}+1$. This is the case of the condition.

Finally, we should consider this four cases which have just been described, and therefore, for each order in (5.8), we will decompose the triple sum into four terms.

## Step 2 :

Lemma 8. The term of order 3 (in $\|\boldsymbol{n}\|$ ) in $\sum_{n \in \mathbb{Z}^{3} \backslash\{0\}} A(\boldsymbol{r}, \boldsymbol{n}, L)$ (i.e. $\left.\sum_{n \in \mathbb{Z}^{3} \backslash\{0\}} \frac{A_{2}(r, n)}{L^{3}}\right)$ can be eliminated by means of our combinations.

Proof. We have :

$$
\begin{equation*}
B(\mathbf{r}, \mathbf{n}, L)=\frac{2 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}-\frac{6(\mathbf{r} . \mathbf{n}) \mathbf{n}}{\|\mathbf{n}\|^{5} L^{3}}+f(\mathbf{r}, \mathbf{n}, L)+o\left(L^{-6}\right) \tag{5.17}
\end{equation*}
$$

where $f$ is a function whose term in $\mathbf{n}$ is of order greater than 3 .
case 1 : We combine nodes $(0, j, 0)$ and its permutations. We first remark that :

$$
\begin{equation*}
\|\mathbf{n}\|=|j| \tag{5.18}
\end{equation*}
$$

so that, by additionning the three terms, we obtain :

$$
\begin{equation*}
\frac{6 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}-\frac{6 j^{2} \mathbf{r}}{\|\mathbf{n}\|^{5} L^{3}}=\frac{6 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}-\frac{6 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}=0 . \tag{5.19}
\end{equation*}
$$

case $2:$ We combine nodes $(i, i, i),(i,-i,-i),(i,-i, i)$ and $(i, i,-i)$. We have :

$$
\begin{equation*}
\|\mathbf{n}\|=3^{1 / 2}|i| \tag{5.20}
\end{equation*}
$$

so that we obtain, by additionning the four terms (by noting $\mathbf{r}=(x, y, z)$ ):

$$
\begin{align*}
\frac{8 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}- & \frac{6\left((x i+y i+z i)\left(\begin{array}{c}
i \\
i \\
i
\end{array}\right)+(x i-y i-z i)\left(\begin{array}{c}
i \\
-i \\
-i
\end{array}\right)+(x i-y i+z i)\left(\begin{array}{c}
i \\
-i \\
i
\end{array}\right)+(x i+y i-z i)\left(\begin{array}{c}
i \\
i \\
-i
\end{array}\right)\right)}{\|\mathbf{n}\|^{5} L^{3}} \\
& =\frac{8 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}-\frac{24 i^{2} \mathbf{r}}{3^{5 / 2}|i|^{5} L^{3}}=0 . \tag{5.21}
\end{align*}
$$

case 3 : We combine nodes $(i, j, 0)$ and $(i,-j, 0)$ and the same with the permutations of $(i, j, 0)$. We have :

$$
\begin{equation*}
\|\mathbf{n}\|=\|(i, j)\| \tag{5.22}
\end{equation*}
$$

so that we obtain, by additionning the six terms (by noting $\mathbf{r}=(x, y, z))$ :

$$
\begin{align*}
& \frac{12 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}-\frac{6\left((x i+y j)\left(\begin{array}{l}
i \\
j \\
0
\end{array}\right)+(x i-y j)\left(\begin{array}{c}
i \\
-j \\
0
\end{array}\right)+(x j+z i)\left(\begin{array}{l}
j \\
0 \\
i
\end{array}\right)+(x j-z i)\left(\begin{array}{c}
j \\
0 \\
-i
\end{array}\right)\right)}{\|\mathbf{n}\|^{5} L^{3}} \\
&-\frac{6\left((y i+z j)\left(\begin{array}{c}
0 \\
i \\
j
\end{array}\right)+(y i-z j)\left(\begin{array}{c}
0 \\
i \\
-j
\end{array}\right)\right)}{\|\mathbf{n}\|^{5} L^{3}}  \tag{5.23}\\
&=\frac{12 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}-\frac{12\left(i^{2}+j 2\right) \mathbf{r}}{\|\mathbf{n}\|^{5} L^{3}}=0 . \tag{5.24}
\end{align*}
$$

General case : We combine nodes $(a, b, c)=(i, j, k),(a, b, c)=(i,-j,-k),(a, b, c)=(i,-j, k)$, $(a, b, c)=(i, j,-k)$, and the same by taking the permutation of $(i, j, k)$ and the four terms each time and we obtain, by a similar thing that in the case 3 (by noting $\mathbf{r}=(x, y, z)$ ):

$$
\begin{equation*}
\frac{12 \mathbf{r}}{\|\mathbf{n}\|^{3} L^{3}}-\frac{12\left(i^{2}+j^{2}+z^{2}\right) \mathbf{r}}{\|\mathbf{n}\|^{5} L^{3}}=0 \tag{5.25}
\end{equation*}
$$

Lemma 9. By combining terms of order more than 4 (in $\|\boldsymbol{n}\|)$ in $\sum_{n \in \mathbb{Z}^{3} \backslash\{0\}} A(\boldsymbol{r}, \boldsymbol{n}, L)$ we get :

$$
\begin{align*}
\sum_{n \in \mathbb{Z}^{3} \backslash\{0\}} A(\boldsymbol{r}, \boldsymbol{n}, L) & =\sum_{i>0, j \geq i, k \geq i+1} 84 \frac{\|\boldsymbol{r}\|^{2}}{\|(i, j, k)\|^{5} L^{5}} \boldsymbol{r}+\sum_{i>0}\left(21+\frac{28}{3^{5 / 2}}\right) \frac{\|\boldsymbol{r}\|^{2}}{|i|^{5} L^{5}} \boldsymbol{r} \\
& +\sum_{i, j>0} 42 \frac{\|\boldsymbol{r}\|^{2}}{\left\|(i, j)^{t}\right\|^{5} L^{5}} \boldsymbol{r}-\sum_{n \in \mathbb{Z}^{3} \backslash\{0\}} \frac{35}{2} \frac{(\boldsymbol{r} \cdot \boldsymbol{n})^{3} \boldsymbol{n}}{\|\boldsymbol{n}\|^{9} L^{5}}+o\left(\frac{\|\boldsymbol{r}\|^{3}}{L^{5}}\right) . \tag{5.26}
\end{align*}
$$

Proof. Here, we are going to study each coordinates, distinguishing each of the four cases we described in step 1. Each time, we will just give details for the general case (the others resulting from the same calculations).

Let $\mathbf{r}=(x, y, z)$.

## A. Calculus for the first coordinate :

a) Case 1 :

We combine nodes $(0, j, 0)$ and its permutations and we obtain :

$$
\begin{equation*}
B(\mathbf{r},(0, j, 0), L)[x]+B(\mathbf{r},(j, 0,0), L)[x]+B(\mathbf{r},(0,0, j), L)[x]=21 \frac{\|\mathbf{r}\|^{2} x}{|j|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.27}
\end{equation*}
$$

b) Case 2 :

We combine nodes $(i, i, i),(i,-i,-i),(i,-i, i)$ and $(i, i,-i)$ and we obtain :
$B(\mathbf{r},(i, i, i), L)[x]+B(\mathbf{r},(i,-i,-i), L)[x]+B(\mathbf{r},(i,-i, i), L)[x]+B(\mathbf{r},(i, i,-i), L)[x]=28 \frac{\|\mathbf{r}\|^{2} x}{3^{5 / 2}|i|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right)$.
c) Case 3 :

We combine nodes $(i, j, 0)$ and $(i,-j, 0)$ and the same with the permutations of $(i, j, 0)$ and we obtain :

$$
\begin{align*}
B(\mathbf{r},(i, j, 0), L)[x] & +B(\mathbf{r},(i,-j, 0), L)[x]+B(\mathbf{r},(j, 0, i), L)[x] \\
& +B(\mathbf{r},(j, 0,-i), L)[x]+B(\mathbf{r},(0, i, j), L)[x]+B(\mathbf{r},(0, i,-j), L)[x]=42 \frac{\|\mathbf{r}\|^{2} x}{\left\|(i, j)^{t}\right\|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.29}
\end{align*}
$$

d) General case :

We combine nodes $(a, b, c)=(i, j, k)$ and $(a, b, c)=(i,-j,-k)$ and we obtain :

$$
\begin{align*}
B(\mathbf{r},(i, j, k), L)[x]+B(\mathbf{r},(i,-j,-k), L)[x] & =\frac{4 x}{A_{i j k}^{3} L^{3}}-6 \frac{\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+\frac{30 x}{A_{i j k}^{7} L^{5}}\left(x^{2} i^{2}+y^{2} j^{2}+z^{2} k^{2}+2 y z j k\right) \\
& -\frac{12 x i^{2}}{A_{i j k}^{5} L^{3}}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} x i^{2}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.30}
\end{align*}
$$

The same applies to $(a, b, c)=(j, k, i)$ and $(a, b, c)=(j,-k,-i)$ gives :

$$
\begin{align*}
B(\mathbf{r},(j, k, i), L)[x]+B(\mathbf{r},(j,-k,-i), L)[x] & =\frac{4 x}{A_{i j k}^{3} L^{3}}-6 \frac{\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+\frac{30 x}{A_{i j k}^{7} L^{5}}\left(x^{2} j^{2}+y^{2} k^{2}+z^{2} i^{2}+2 y z k i\right) \\
& -\frac{12 x j^{2}}{A_{i j k}^{5} L^{3}}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} x j^{2}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.31}
\end{align*}
$$

To finish, for $(a, b, c)=(k, i, j)$ and $(a, b, c)=(k,-i,-j)$, we get :

$$
\begin{align*}
B(\mathbf{r},(k, i, j), L)[x]+B(\mathbf{r},(k,-i,-j), L)[x] & =\frac{4 x}{A_{i j k}^{3} L^{3}}-6 \frac{\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+\frac{30 x}{A_{i j k}^{7} L^{5}}\left(x^{2} k^{2}+y^{2} i^{2}+z^{2} j^{2}+2 y z i j\right) \\
& -\frac{12 x k^{2}}{A_{i j k}^{5} L^{3}}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} x k^{2}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.32}
\end{align*}
$$

The three previous factors are added together, which gives

$$
\begin{align*}
B_{1}^{i j k, x}(L):= & B(\mathbf{r},(i, j, k), L)[x]+B(\mathbf{r},(i,-j,-k), L)[x]+B(\mathbf{r},(j, k, i), L)[x] \\
& +B(\mathbf{r},(j,-k,-i), L)[x]+B(\mathbf{r},(k, i, j), L)[x]+B(\mathbf{r},(k,-i,-j), L)[x]  \tag{5.33}\\
& =\frac{12 x}{A_{i j k}^{3} L^{3}}-18 \frac{\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+\frac{30 x}{A_{i j k}^{7} L^{5}}\left(x^{2}\left(A_{i j k}^{2}\right)+y^{2}\left(A_{i j k}^{2}\right)+z^{2}\left(A_{i j k}^{2}\right)+2 y z(j k+i k+i j)\right)  \tag{5.34}\\
& -\frac{12 x}{A_{i j k}^{3} L^{3}}+\frac{30\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right)  \tag{5.35}\\
& =-18 \frac{\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+\frac{30\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+\frac{60 x}{A_{i j k}^{7} L^{5}} y z(j k+i k+i j)+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{5} L^{5}} x+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right)  \tag{5.36}\\
& =42 \frac{\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+\frac{60 x}{A_{i j k}^{7} L^{5}} y z(j k+i k+i j)+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.37}
\end{align*}
$$

In order to take into account the last nodes, we repeat the same steps of the previous calculus, and this corresponds to calculate $B(\mathbf{r},(a, b, c), L)[x]+B\left(\mathbf{r},\left(a^{\prime}, b^{\prime}, c^{\prime}\right), L\right)[x]$ for $(a, b, c)=(i,-j, k)$ and $\left(a^{\prime}, b^{\prime}, c^{\prime}\right)=(i, j,-k)$ and the same with the permutations of $(i, j, k)$. We then get :

$$
\begin{align*}
B_{2}^{i j k, x}(L):= & B(\mathbf{r},(i,-j, k), L)[x]+B(\mathbf{r},(i, j,-k), L)[x]+B(\mathbf{r},(j,-k, i), L)[x] \\
& +B(\mathbf{r},(j, k,-i), L)[x]+B(\mathbf{r},(k,-i, j), L)[x]+B(\mathbf{r},(k, i,-j), L)[x]  \tag{5.38}\\
& =42 \frac{\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}-\frac{60 x}{A_{i j k}^{7} L^{5}} y z(j k+i k+i j)+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.39}
\end{align*}
$$

Finally :

$$
\begin{equation*}
B_{1}^{i j k, x}(L)+B_{2}^{i j k, x}(L)=84 \frac{\|\mathbf{r}\|^{2} x}{A_{i j k}^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.40}
\end{equation*}
$$

## B. Calculus for the second coordinate :

a) Case 1 :

We combine nodes $(0, j, 0)$ and its permutations and we obtain :

$$
\begin{equation*}
B(\mathbf{r},(0, j, 0), L)[y]+B(\mathbf{r},(j, 0,0), L)[y]+B(\mathbf{r},(0,0, j), L)[y]=21 \frac{\|\mathbf{r}\|^{2} y}{|j|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.41}
\end{equation*}
$$

b) Case 2 :

We combine nodes $(i, i, i),(i,-i,-i),(i,-i, i)$ and $(i, i,-i)$ and we obtain :
$B(\mathbf{r},(i, i, i), L)[y]+B(\mathbf{r},(i,-i,-i), L)[y]+B(\mathbf{r},(i,-i, i), L)[y]+B(\mathbf{r},(i, i,-i), L)[y]=28 \frac{\|\mathbf{r}\|^{2} y}{3^{5 / 2}|i|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right)$

## c) Case 3 :

We combine nodes $(i, j, 0)$ and $(i,-j, 0)$ and the same with the permutations of $(i, j, 0)$ and we obtain :

$$
\begin{align*}
B(\mathbf{r},(i, j, 0), L)[y]+ & B(\mathbf{r},(i,-j, 0), L)[y]+B(\mathbf{r},(j, 0, i), L)[y]+B(\mathbf{r},(j, 0,-i), L)[y] \\
& +B(\mathbf{r},(0, i, j), L)[y]+B(\mathbf{r},(0, i,-j), L)[y]=42 \frac{\|\mathbf{r}\|^{2} y}{\left\|(i, j)^{t}\right\|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.43}
\end{align*}
$$

## d) General case :

We combine nodes $(a, b, c)=(i, j, k)$ and $(a, b, c)=(i,-j,-k)$ and we obtain :

$$
\begin{align*}
B(\mathbf{r},(i, j, k), L)[y]+B(\mathbf{r},(i,-j,-k), L)[y] & =\frac{4 y}{A_{i j k}^{3} L^{3}}-6 \frac{\|\mathbf{r}\|^{2} y}{A_{i j k}^{5} L^{5}}+\frac{30 y}{A_{i j k}^{7} L^{5}}\left(x^{2} i^{2}+y^{2} j^{2}+z^{2} k^{2}+2 y z j k\right) \\
& -\frac{12 y j^{2}}{A_{i j k}^{5} L^{3}}-\frac{12 z j k}{A_{i j k}^{5} L^{3}}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} y j^{2}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} z j k+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.44}
\end{align*}
$$

The same applies to $(a, b, c)=(j, k, i)$ and $(a, b, c)=(j,-k,-i)$ gives :

$$
\begin{align*}
B(\mathbf{r},(j, k, i), L)[y]+B(\mathbf{r},(j,-k,-i), L)[y] & =\frac{4 y}{A_{i j k}^{3} L^{3}}-6 \frac{\|\mathbf{r}\|^{2} y}{A_{i j k}^{5} L^{5}}+\frac{30 y}{A_{i j k}^{7} L^{5}}\left(x^{2} j^{2}+y^{2} k^{2}+z^{2} i^{2}+2 y z k i\right) \\
& -\frac{12 y k^{2}}{A_{i j k}^{5} L^{3}}-\frac{12 z i k}{A_{i j k}^{5} L^{3}}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} y k^{2}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} z i k+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.45}
\end{align*}
$$

To finish, for $(a, b, c)=(k, i, j)$ and $(a, b, c)=(k,-i,-j)$, we get :

$$
\begin{align*}
B(\mathbf{r},(k, i, j), L)[y]+B(\mathbf{r},(k,-i,-j), L)[y] & =\frac{4 y}{A_{i j k}^{3} L^{3}}-6 \frac{\|\mathbf{r}\|^{2} y}{A_{i j k}^{5} L^{5}}+\frac{30 y}{A_{i j k}^{7} L^{5}}\left(x^{2} k^{2}+y^{2} i^{2}+z^{2} j^{2}+2 y z i j\right) \\
& -\frac{12 y i^{2}}{A_{i j k}^{5} L^{3}}-\frac{12 z i j}{A_{i j k}^{5} L^{3}}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} y i^{2}+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} z i j+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.46}
\end{align*}
$$

The three previous factors are added together, which gives

$$
\begin{align*}
B_{1}^{i j k, y}(L):= & B(\mathbf{r},(i, j, k), L)[y]+B(\mathbf{r},(i,-j,-k), L)[y]+B(\mathbf{r},(j, k, i), L)[y] \\
& +B(\mathbf{r},(j,-k,-i), L)[y]+B(\mathbf{r},(k, i, j), L)[y]+B(\mathbf{r},(k,-i,-j), L)[y]  \tag{5.47}\\
& =\frac{12 y}{A_{i j k}^{3} L^{3}}-18 \frac{\|\mathbf{r}\|^{2} y}{A_{i j k}^{5} L^{5}}+\frac{30 y}{A_{i j k}^{7} L^{5}}\left(x^{2}\left(A_{i j k}^{2}\right)+y^{2}\left(A_{i j k}^{2}\right)+z^{2}\left(A_{i j k}^{2}\right)+2 y z(j k+i k+i j)\right)  \tag{5.48}\\
& -\frac{12 y}{A_{i j k}^{3} L^{3}}-\frac{12 z}{A_{i j k}^{5} L^{3}}(i j+i k+j k)+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{5} L^{5}} y+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} z(i j+i k+j k)+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right)  \tag{5.49}\\
& =42 \frac{\|\mathbf{r}\|^{2} y}{A_{i j k}^{5} L^{5}}+\frac{60}{A_{i j k}^{7} L^{5}} y^{2} z(j k+i k+i j)-\frac{12 z}{A_{i j k}^{5} L^{3}}(i j+i k+j k) \\
& +\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} z(i j+i k+j k)+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.50}
\end{align*}
$$

In order to take into account the last nodes, we repeat the same steps of the previous calculus, and this corresponds to calculate $B(\mathbf{r},(a, b, c), L)[y]+B\left(\mathbf{r},\left(a^{\prime}, b^{\prime}, c^{\prime}\right), L\right)[y]$ for $(a, b, c)=(i,-j, k)$ and $\left(a^{\prime}, b^{\prime}, c^{\prime}\right)=(i, j,-k)$ and the same with the permutations of $(i, j, k)$. We then get :

$$
\begin{align*}
B_{2}^{i j k, y}(L):= & B(\mathbf{r},(i,-j, k), L)[y]+B(\mathbf{r},(i, j,-k), L)[y]+B(\mathbf{r},(j,-k, i), L)[y] \\
& +B(\mathbf{r},(j, k,-i), L)[y]+B(\mathbf{r},(k,-i, j), L)[y]+B(\mathbf{r},(k, i,-j), L)[y]  \tag{5.51}\\
= & 42 \frac{\|\mathbf{r}\|^{2} y}{A_{i j k}^{5} L^{5}}-\frac{60}{A_{i j k}^{7} L^{5}} y^{2} z(j k+i k+i j)+\frac{12 z}{A_{i j k}^{5} L^{3}}(i j+i k+j k) \\
& -\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} z(i j+i k+j k)+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.52}
\end{align*}
$$

Finally :

$$
\begin{equation*}
B_{1}^{i j k, y}(L)+B_{2}^{i j k, y}(L)=84 \frac{\|\mathbf{r}\|^{2} y}{A_{i j k}^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.53}
\end{equation*}
$$

## C. Calculus for the third coordinate :

By similar calculations as those for the second coordinate, we get :

## a) Case 1 :

For node $(0, j, 0)$ and its permutations :

$$
\begin{equation*}
B(\mathbf{r},(0, j, 0), L)[z]+B(\mathbf{r},(j, 0,0), L)[z]+B(\mathbf{r},(0,0, j), L)[z]=21 \frac{\|\mathbf{r}\|^{2} z}{|j|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.54}
\end{equation*}
$$

## b) Case 2 :

For nodes $(i, i, i),(i,-i,-i),(i,-i, i)$ and $(i, i,-i)$ :
$B(\mathbf{r},(i, i, i), L)[z]+B(\mathbf{r},(i,-i,-i), L)[z]+B(\mathbf{r},(i,-i, i), L)[z]+B(\mathbf{r},(i, i,-i), L)[z]=28 \frac{\|\mathbf{r}\|^{2} z}{3^{5 / 2}|i|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right)$.

## c) Case 3 :

For nodes $(i, j, 0)$ and $(i,-j, 0)$ and the same with the permutations of $(i, j, 0)$ :

$$
\begin{align*}
B(\mathbf{r},(i, j, 0), L)[z]+ & B(\mathbf{r},(i,-j, 0), L)[z]+B(\mathbf{r},(j, 0, i), L)[z]+B(\mathbf{r},(j, 0,-i), L)[z] \\
& +B(\mathbf{r},(0, i, j), L)[z]+B(\mathbf{r},(0, i,-j), L)[z]=42 \frac{\|\mathbf{r}\|^{2} z}{\left\|(i, j)^{t}\right\|^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.56}
\end{align*}
$$

## d) General case :

For nodes $(i, j, k)$ and $(i,-j,-k)$ and the same with the permutations of $(i, j, k)$ :

$$
\begin{align*}
B_{1}^{i j k, z}(L):= & B(\mathbf{r},(i, j, k), L)[z]+B(\mathbf{r},(i,-j,-k), L)[z]+B_{j k i}^{z}(L)+B(\mathbf{r},(j,-k,-i), L)[z] \\
& +B(\mathbf{r},(k, i, j), L)[z]+B(\mathbf{r},(k,-i,-j), L)[z] \\
& =\frac{12 z}{A_{i j k}^{3} L^{3}}-18 \frac{\|\mathbf{r}\|^{2} z}{A_{i j k}^{5} L^{5}}+\frac{30 z}{A_{i j k}^{7} L^{5}}\left(x^{2}\left(A_{i j k}^{2}\right)+y^{2}\left(A_{i j k}^{2}\right)+z^{2}\left(A_{i j k}^{2}\right)+2 r_{2} z(j k+i k+i j)\right) \\
& -\frac{12 z}{A_{i j k}^{3} L^{3}}-\frac{12 y}{A_{i j k}^{5} L^{3}}(i j+i k+j k)+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{5} L^{5}} z+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} y(i j+i k+j k)+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \\
& =42 \frac{\|\mathbf{r}\|^{2} z}{A_{i j k}^{5} L^{5}}+\frac{60}{A_{i j k}^{7} L^{5}} y z^{2}(j k+i k+i j)-\frac{12 y}{A_{i j k}^{5} L^{3}}(i j+i k+j k)+\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} y(i j+i k+j k)+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) . \tag{5.59}
\end{align*}
$$

For nodes $(i,-j, k)$ and $(i, j,-k)$ and the same with the permutations of $(i, j, k)$ :

$$
\begin{align*}
B_{2}^{i j k, z}(L):= & B(\mathbf{r},(i,-j, k), L)[z]+B(\mathbf{r},(i, j,-k), L)[z]+B(\mathbf{r},(j,-k, i), L)[z]+B(\mathbf{r},(j, k,-i), L)[z] \\
& +B(\mathbf{r},(k,-i, j), L)[z]+B(\mathbf{r},(k, i,-j), L)[z]  \tag{5.60}\\
& =42 \frac{\|\mathbf{r}\|^{2} z}{A_{i j k}^{5} L^{5}}-\frac{60}{A_{i j k}^{7} L^{5}} y z^{2}(j k+i k+i j)+\frac{12 y}{A_{i j k}^{5} L^{3}}(i j+i k+j k)-\frac{30\|\mathbf{r}\|^{2}}{A_{i j k}^{7} L^{5}} y(i j+i k+j k)+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.61}
\end{align*}
$$

So that finally :

$$
\begin{equation*}
B_{1}^{i j k, z}(L)+B_{2}^{i j k, z}(L)=84 \frac{\|\mathbf{r}\|^{2} z}{A_{i j k}^{5} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right) \tag{5.62}
\end{equation*}
$$

Step 3: In order to finish the proof, we remember that the potentiel of the system satisfies :

$$
\begin{align*}
\nabla_{1} U_{P B C}(\mathbf{r}, L) & =-\mathbf{F}_{1}(\mathbf{r}, L)  \tag{5.63}\\
& =-\frac{q_{1} q_{2} \mathbf{r}}{4 \pi \epsilon_{0} \epsilon_{r}\|\mathbf{r}\|^{3}}-\frac{q_{1} q_{2}}{4 \pi \epsilon_{0} \epsilon_{r}}\left(\left(\sum_{i>0, j \geq i, k \geq i+1} \frac{84}{\|(i, j, k)\|^{5} L^{5}}+\sum_{i>0}\left(21+\frac{28}{3^{5 / 2}}\right) \frac{1}{|i|^{5} L^{5}}\right.\right. \\
& \left.\left.+\sum_{i, j>0} \frac{42}{\left\|(i, j)^{t}\right\|^{5} L^{5}}\right)\|\mathbf{r}\|^{2} \mathbf{r}-\sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{35}{2} \frac{(\mathbf{r} . \mathbf{n})^{3} \mathbf{n}}{\|\mathbf{n}\|^{9} L^{5}}+o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right)\right) \tag{5.64}
\end{align*}
$$

so that we get (by symmetry of the potential to determine the constante) the result :
$U_{P B C}(\mathbf{r}, L)=\frac{q_{1} q_{2}}{4 \pi \epsilon_{0} \epsilon_{r}\|\mathbf{r}\|}\left(1+C\left(\frac{\|\mathbf{r}\|}{L}\right)^{5}\right)+\frac{q_{1} q_{2}}{4 \pi \epsilon_{0} \epsilon_{r}} \int_{S(\mathbf{r})}\left(\sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{35}{2} \frac{(\mathbf{l} . \mathbf{n})^{3} \mathbf{n}}{\|\mathbf{n}\|^{9} L^{5}}\right) d \mathbf{l}+o\left(\frac{\|\mathbf{r}\|^{4}}{L^{5}}\right)$
with $C=-\left(21 \sum_{i>0, j \geq i, k \geq i+1} \frac{1}{\left\|(i, j, k)^{t}\right\|^{5}}+\left(\frac{21}{4}+\frac{7}{3^{5 / 2}}\right) \zeta(5)+\frac{21}{2} \sum_{i, j>0} \frac{1}{\left\|(i, j)^{t}\right\|^{5}}\right)$ (so that $C \simeq-9.079945024529188), \zeta$ being the zeta function. $S(\mathbf{r})=\left[a_{1}, x\right] \times\left[a_{2}, y\right] \times\left[a_{3}, z\right]\left(\left(a_{1}, a_{2}, a_{3}\right)\right.$ being choosen such that the constant of that primitive is null).

First of all, we can note that the fist term of the expansion that we have obtain is one of a Coulomb potential, which makes sense with the conjecture that we can see for example in 129 . The second term takes into account the periodicity, and we can see that the larger $L$ is the smaller this term is, so that in fact the potential tends to the first term. This fact is in good agreement with the case of an infinite system that we told in the beginning of that part. This is difficult to interpret this term in a physical meaning. However, we will observ that it doesn't match to a dipole term as we could suppose. Indeed, we have $\frac{q_{1} q_{2}}{4 \pi \epsilon_{0} \epsilon_{r}} \frac{\|\mathbf{r}\|^{4}}{L^{5}}=\frac{-1}{4 \pi \epsilon_{0} \epsilon_{r}}\left(q_{1}\|\mathbf{r}\|\right)^{2} \frac{\|\mathbf{r}\|^{2}}{L^{5}}$ (because $q_{1}$ and $q_{2}$ are opposite charges) so that the term in parenthesis is a dipolar term, but the term tends to 0 when $\|\mathbf{r}\| \rightarrow 0$, instead of $\infty$.

On top of that, we can observ that the larger $L$ is the more the second term decreases towards 0 , so that our formula converges to the fisrt Coulomb term. We will verify this fact in our numerical simulations.

In order to estimate the last term, we will place ourselves in the case where $\mathbf{r}$ is located on one side of the box, then in the case where $\mathbf{r}$ is located on the small diagonal of the box, and to finish in the case where $\mathbf{r}$ is located on the large diagonal of the box. In all three cases, we will have $\mathbf{r}$ of the form $\mathbf{r}=\|\mathbf{r}\| \mathbf{u}$ where $\mathbf{u}$ is a unit vector. So that:

$$
\begin{equation*}
\sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{-35}{2} \frac{(\mathbf{r} . \mathbf{n})^{3} \mathbf{n}}{\|\mathbf{n}\|^{9} L^{5}}=\sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{-35}{2} \frac{\|\mathbf{r}\|^{3}(\mathbf{u} . \mathbf{n})^{3} \mathbf{n}}{\|\mathbf{n}\|^{9} L^{5}} \tag{5.66}
\end{equation*}
$$

$\mathbf{u}=(1,0,0)$ or $(0,1,0)$ or $(0,0,1)$ in the first case (we will analyze only the first vector, as the study of the two others can be made in the same way), $\mathbf{u}=\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)$ or $\left(0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right)$ or $\left(\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right)$ in the second case (we will also analyze only the first vector), and $\mathbf{u}=\left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)$ in the third case.

We will first estimate the term $\sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{-35}{2} \frac{(\mathbf{u} \cdot \mathbf{n})^{3} \mathbf{n}}{\|\boldsymbol{n}\|^{9}}$ numerically in all three cases. The results are shown in table 1

| unit vector $\mathbf{u}$ | term $\sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{-35}{2} \frac{\left(\frac{(r . n)^{3}}{\\| n} \\|^{\mathbf{n}}\right.}{\\| n}$ |
| :---: | :---: |
| $(1,0,0)$ | $(-48.8,0,0)$ |
| $\left.\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)\right)$ | $(-23.5,-23.5,0)$ |
| $\left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)$ | $(-16.2,-16.2,-16.2)$ |

Table 1 - Estimation of the term $\sum_{\left.\mathbf{n} \in \mathbb{Z}^{3}\right\}\{0\}} \frac{-35}{2} \frac{(\mathbf{u} \cdot \mathbf{n})^{3} \mathbf{n}}{\|\mathbf{n}\|^{9}}$ for three different unit vectors
Thus, in all three cases we obtain a result of the type $a \mathbf{u}$ where $a \in \mathbb{R}$, which is due to the situation on a symmetrical plane of the analyzed vectors.

In polar coordinates $(r, \theta, \phi)$, we know that the force on a symmetrical plane is as per :

$$
\left(\begin{array}{c}
\frac{-\partial U(r, \theta, \phi)}{\partial r}  \tag{5.67}\\
0 \\
0
\end{array}\right) .
$$

So that we can get here :

$$
\begin{equation*}
\int_{S(\mathbf{r})}\left(\sum_{\mathbf{n} \in \mathbb{Z}^{3} \backslash\{0\}} \frac{35}{2} \frac{(\mathbf{l} . \mathbf{n})^{3} \mathbf{n}}{\|\mathbf{n}\|^{9} L^{5}}\right) d \mathbf{l}=\frac{a\|\mathbf{r}\|^{4}}{4 L^{5}} \tag{5.68}
\end{equation*}
$$

where $a=48.8$ on the first case, $a=23.5$ on the second case, and $a=16.2$ on the third case.
In the end we have the following expansion depending on the geometrical constant $C_{1}$ :

$$
\begin{equation*}
U_{P B C}(\mathbf{r}, L)=\frac{q_{1} q_{2}}{4 \pi \epsilon_{0} \epsilon_{r}\|\mathbf{r}\|}\left(1+C_{1}\left(\frac{\|\mathbf{r}\|}{L}\right)^{5}\right)+o\left(\frac{\|\mathbf{r}\|^{4}}{L^{5}}\right) \tag{5.69}
\end{equation*}
$$

$C_{1}$ depends on the position of the two charges in the box :

- in the case where $\mathbf{r}$ is located on one side of the box : $C_{1}=3.12005497547$
- in the case where $\mathbf{r}$ is located on the small diagonal of the box : $C_{1}=-3.20494502453$
- in the case where $\mathbf{r}$ is located on the large diagonal of the box : $C_{1}=-5.02994502453$

This first term of developpement with even power function can be explained by the symmetry of the problem. Moreover, the difference in the sign of $C_{1}$ can be explained in a geometrical way as seen in figure 17. In fact, in diagonal cases, when the ions are far enough apart, each one tends to be closer to its images (of the same sign therefore) more than with the other one located in the same box which generates a repulsion. That is not the case in the parallel case where each ion is always further away from its own images than from the other ion and its images.


Figure 17 - Illustration in 2D of two opposite charges which tends to be far enough apart, in the parallel case and in small diagonal case (the third case, for large diagonal, being similar of the second case) : the blue segment tends to be larger of the red one in the second case, whereas in the first case it is always smaller

### 5.2 Numerical results

Since our goal was to test the influence of the simulation box size with periodic edge conditions for the calculation of the Potential of Mean Force at long distance, three box sizes were used. A first system consists of 498 water molecules and an ion $\mathrm{Na}^{+}$and an ion $\mathrm{Cl}^{-}$contained in a 24,662 A side cube box. A second one consists of 1598 water molecules and the 2 ions, in a 36,342 A cubic side box. A last system consists of 4998 water molecules and the 2 ions, contained in a cubic box with 53.000 A side (cf figure 18). The reaction coordinate chosen for the calculation of the Pmf being the distance between the two ions, for each box the two ions are initially placed at a distance $l \leq \frac{L}{2}$, where $L$ is the size of one side of the simulation box. The polarizable force field of each particle comes from the AMOEBABIO09 model [186 (Atomic multipole optimized energetics for biomolecular simulation). And given the chosen reaction coordinate, a spring force is added to keep the two ions at a chosen $l^{*}$ distance (illustration figure 19). The simulations were performed with the Tinker-hp code 101 (Parallel version of the Tinker Molecular Dynamics Code 140 ).

Each system is first balanced by a L-BFGS minimization of the Cartesian set, then a simulation of 10 ps in the isobaric-isothermal set $(N P T)$ where $N$ is the number of particles according to the box, $P=1$ bar and $T=298 \mathrm{~K}$ with a Berendsen thermostat. A dynamic is then carried out with the RESPA integrator on 2 ns with a time step of 2 fs . The positions of the particles are stored every ps, i.e. 1000 times during the 2 ns .

The electrostatic interactions are evaluated with the Ewald method, with a cut-off of 7 A . A cut-off of 9 A is also imposed for Van der Waals rays.

We run simulations with a spring of stiffness constant $10 \times 2 \mathrm{kcal} . \mathrm{mol}^{-1} . \mathrm{A}^{-2}$ for $l^{*}=2,2.5, \ldots, 10$ A (it is important that $l^{*} \leq \frac{L_{\min }}{2}$ where $L_{\min }=24.662 \mathrm{~A}$ ), that is 17 simulations for each system.

We then use Alan Grossfield's code 182 to plot the Pmf associated with the system (be careful that the Tinker code does not take into account the " $1 / 2$ " for added spring force). Then the McMillan and Mayer Potential (pmf with entropy correction) is plotted, correcting the Pmf, which


Figure 18 - Representations of box made up of water molecules (thus formed of ions $H^{+}$and ions $\mathrm{OH}^{-}$, represented "in the background" in white) and an ion $\mathrm{Na}^{+}$(dark blue) and an ion $\mathrm{Cl}^{-}$(cyan) according to the size L of the box
is expressed in kcal. $\mathrm{mol}^{-1}$, by expressing it in units of $k_{b} T$ (where $k_{b}$ is Boltzmann's constant).
Finally, the Coulombic potential is plotted, then the Coulombic potential to which the correction for $L$ has been added, in order to compare it, at great distance, to the McMillan and Mayer Potential.

In what follows, in the legends, "Coulomb" corresponds to the Coulomb potential curve between two ions in infinite medium, and "development" corresponds to our previous calculation for two ions under periodic conditions.


Figure 19 - Illustration (zoomed in) of two ions to which a spring force is applied to keep them at a distance of 5 A during a simulation with a 36.342 A side box, here the ions are at this stage of the simulation at a distance of 4.85 A

### 5.2.1 Size of a simulation box

We want to know the approximate number $N$ of water molecules contained in a box of volume $V=1 \mathrm{~nm}^{3}$. We know that $N$ is related to $V$ by the formula $N=n_{V} V$, where $n_{V}$ is the number of particles per unit of volume, i.e. $n_{V}=\frac{n N_{A}}{V}(n$ being the number of moles and $N_{A}=6.022 .10^{23} \mathrm{~mol}^{-1}$ the amount of matter per mole).

Remember the density $\mu$ of a molecule : $\mu=\frac{m}{V}$, where $m$ is the mass of a particle; and the molar mass $M$ of a particle : $M=\frac{m}{n}$. Thus we have :

$$
\begin{equation*}
n_{V}=\frac{n N_{A}}{V}=\frac{\mu}{m} n N_{A}=\frac{\mu N_{A}}{M} . \tag{5.70}
\end{equation*}
$$

Hence :

$$
\begin{equation*}
N=\frac{V \mu N_{A}}{M} \tag{5.71}
\end{equation*}
$$

We have : $1 \mathrm{~nm}^{3}=10^{-27} \mathrm{~m}^{3}, \mu=10^{3} \mathrm{~kg} \cdot \mathrm{~m}^{-3}$ et $M=18 \cdot 10^{-3} \mathrm{~kg} . \mathrm{mol}^{-1}$. Thus : $N=\frac{100}{3} \sim 33$.
This allowed us to approximate the number of water molecules needed to create a water box with Packmol 136].

### 5.2.2 Description of the AMOEBA model

The Atomic Multipole Optimized Energetics for Biomolecular Applications (AMOEBA) model [141, 160,186 is a polarizable force field model. Interactions are decomposed between valence and non-valence links. The $U$ potential of an atom is thus expressed in the following form :

$$
\begin{equation*}
U=U_{\text {bond }}+U_{\text {angle }}+U_{b-a}+U_{o o p}+U_{\text {torsion }}+U_{v d W}+U_{\text {ele }}^{\text {perm }}+U_{\text {ele }}^{i n d} \tag{5.72}
\end{equation*}
$$

where the first five terms refer to short-range valence interactions (respectively binding term, angle, cross-bond angle, out-of-plane bending and torsional rotation), the other three terms refer to non-valence interactions, respectively van der Waals term, and permanent and induced electrostatic contributions.

## Parameter Details :

Hereafter, the parameters (cf table 2) of the AMOEBA model to describe the force field for molecules $\mathrm{H}_{2} \mathrm{O}$ are presented 147]. The dielectric constant of water in this model, when considering periodic edge conditions, is $82 \pm 13$.

| O-H bond | $b_{0}(\mathrm{~A})$ <br> 0.9572 | $K_{b}\left(\mathrm{kcal} \cdot \mathrm{A}^{-2} \cdot \mathrm{~mol}^{-1}\right)$ |
| :---: | :---: | :---: |
|  | 529.6 |  |
| H-O-H angle | $\theta_{0}(\mathrm{deg})$ | $K_{\theta}\left(\mathrm{kcal} \cdot d e g^{-2} \cdot \mathrm{~mol}^{-1}\right)$ |
|  | 108.50 | 34.05 |
| Urey-Bradley | $l_{0}(\mathrm{~A})$ | $K_{l}\left(\mathrm{kcal} . \mathrm{A}^{-2} \cdot \mathrm{~mol}^{-1}\right)$ |
|  | 1.5537 | 38.25 |
| van der Waals | $R^{0}(\mathrm{~A})$ | $\epsilon\left(\mathrm{kcal} . \mathrm{mol}^{-1}\right)$ |
| O | 3.405 | 0.110 |
| H | 2.655 | 0.0135 |
| $H_{\text {reduction }}$ | 0.91 |  |
| polarizability | $\alpha\left(\mathrm{A}^{3}\right)$ |  |
| O | 0.837 |  |
| H | 0.496 |  |


| O multipoles | (a.u.) |
| :---: | :---: |
| Q | -0.51966 |
| $d_{z}$ | 0.14279 |
| $Q_{x x}$ | 0.37928 |
| $Q_{y y}$ | -0.41809 |
| $Q_{z z}$ | 0.03881 |
| H multipoles | (a.u.) |
| Q | 0.25983 |
| $d_{x}$ | -0.03859 |
| $d_{y}$ | -0.05818 |
| $Q_{x x}$ | -0.03673 |
| $Q_{y y}$ | -0.10739 |
| $Q_{x z}$ | -0.00203 |
| $Q_{z z}$ | 0.14412 |

TABLE 2 - Parameters of the AMOEBA model for water

The ions $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$have been described with the parameters described in table 3 .

| van der Waals | $R^{0}(\mathrm{~A})$ | $\epsilon\left(\mathrm{kcal} . \mathrm{mol}^{-1}\right)$ |
| :---: | :---: | :---: |
| $N_{a}^{+}$ | 3.020 | 0.2600 |
| $\mathrm{Cl}^{-}$ | 4.130 | 0.3400 |
| polarizability | $\alpha\left(\mathrm{A}^{3}\right)$ |  |
| $N_{a}^{+}$ | 0.120 |  |
| $\mathrm{Cl}^{-}$ | 4.000 |  |
| charge Q | $($ a.u. $)$ |  |
| $N_{a}^{+}$ | 1.00000 |  |
| $\mathrm{Cl}^{-}$ | -1.00000 |  |

TABLE 3 - Parameters of ions

### 5.2.3 Study of the potential of McMillan and Mayer for $\mathrm{Na}-\mathrm{Cl}$ in aqueous phase

## McMillan and Mayer potential and simulation box size

Our study being on the influence of the size of the simulation box on the calculation of the potential of mean force, hereafter, figure 20 shows the McMillan and Mayer potential for each system composed of water molecules and a $\mathrm{Na}^{+}$ion and a $\mathrm{Cl}^{-}$ion, the number of water molecules depending on the size of the simulation box.


Figure 20 - Comparison of the potential of McMillan and Mayer as a function of the size of the simulation box

To begin with, we observe, for the three curves, that the first minimum is around 3 A (which corresponds to the CIP (Contact Ion Pair 651 ), and the second minimum is around 5 A (this is the SIP (Solvent-shared Ion Pair 65]), the first maximum (which corresponds approximately to the center of the whole transition state between the CIP and SIP states [65]) is around 4 A ; which is in good agreement with the literature (cf for example the thesis of John Jairo Molina 127 page 105, as well as $38,83,111,129$ ).

It can be observed that the behaviour of the curve corresponding to the $24,662 \mathrm{~A}$ side box differs from that of the other two curves from a distance of about 7 A in both cases. In fact, it can be seen that, for the 24.662 A side box, there is a very marked maximum around 8 A , in contrast to the curves for the 36.342 A side box and the 53 . A side box which begin to increase more slightly towards 8 A ; whereas up to about 7 A , the behaviour of the three curves merges. One explanation could be that from a certain distance, depending on the size of the box, the presence of the images influences the behaviour of the potential.

As explained in the introduction to this chapter, McMillan and Mayer's potential is defined by one constant, and one of the major challenges is to choose this constant wisely. Here, we have defined it so that the first minimum of each curve corresponds, and those, in order to be able to compare the behaviours of these curves.

In order to calculate the macroscopic quantities of interest, McMillan and Mayer's potential is generally adjusted to a Coulombic potential. In what follows, we will first present the curves resulting from our expansion, for different sizes of boxes. We wish that this expansion will serve as a basis for us to adjust the constant of McMillan and Mayer's potential more precisely, so that at a great distance, it corresponds to our expansion.

## Evolution of the curve resulting from our expansion in relation to $L$

In this subsection, the idea was to observe the behavior of the potential expansion from our calculations as a function of the $L$ period, and then to compare these curves to the Coulomb potential between the two ions (see figure 21).


Figure 21 - Comparison of the curves resulting from our expansion as a function of the size of the box, and with the Coulomb potential curve, for each case

It is clear, for each case, that the larger $L$ is, the closer the associated curve is to the Coulomb curve (which was to be expected since the obtained expansion is inversely proportional to $L$ ).

For the first case, it can be noted that the curve for $L=15$ tends to look like that of a power function $a$ (where $0<a<1$ ) from about 6 A upwards. For the last two cases, it can be noted that the curve for $L=15$ tends to look like that of a power function $a$ (where $a>1$ ) from about 6 A upwards. This is because for such a $L$, the corrective term of our expansion is not weak enough from this distance (knowing that in our calculations we have considered $\|\mathbf{r}\| / L$ rather low, i.e. $L$ rather large compared to the distances studied). Then, we observe that the curves are approaching very quickly the Coulomb curve (this is due to a high power of $L$ to the denominator in our correction). Thus, very quickly it approaches the behavior of two ions in an
infinite medium (and not with periodic conditions at the edge.)
In fact, for too small box sizes (typically for $\mathrm{L}=15$ ), the behavior of our expansion deviates too much from that of a Coulombian potential, on the other hand for large box sizes (typically $\mathrm{L}=50$ ), it is very similar. Since we want to adjust McMillan and Mayer's potential to our expansion, it seems useful for intermediate box sizes.

In addition, we compared the evolution of our expansion with that of Ewald's potential, another way of obtaining the sum of the contributions of long-range interactions for a periodic system as seen in chapter 3 (see on figure 22).


Figure 22 - Comparison of the curves resulting from Ewald as a function of the size of the box, and with the Coulomb potential curve, for each case

Here, we can observe that the behavior of Ewald curve is not the same as that of our deveveloppement, in particular from 5 A for $\mathrm{L}=15$. We sought to understand this difference in behaviour. To do so, we performed a fit of the (Ewald- Coulomb) curve with a function of type $\alpha x^{\beta}$ (seen on figure 23).

We can note that the fit is for $\beta$ near 2 in each case. That differs from our result as the first term of our developpement is of power 4. This term of power 2 seems in fact to be the term of spherical surface area [13, which is added when Ewald's potential is calculated for an infinitely extended crystal with spherical form and surrounded by a continuous medium of the dielectric constant $\epsilon^{\prime}$. This one repesents the energy of surface charges at the boundaries of the crystal. It is given by the following expression :

$$
\begin{equation*}
\frac{2 \pi}{\left(1+2 \epsilon^{\prime}\right)} \frac{\mathbf{M}^{2}}{V_{\text {cell }}} \tag{5.73}
\end{equation*}
$$

where $\mathbf{M}=\sum_{i} q_{i} \mathbf{r}_{i}$ is the dipolar moment, and $V_{\text {cell }}$ is the volume of an elementary cell. In order to verify this fact, we plotted curves for $\mathrm{L}=10$ ans $\mathrm{L}=100$ and we observe, in the case when the vector is parallel to the box, that $\alpha$ is inversely proportional to $L^{3}$, i.e. the volume of a box (cf figure 24. Moreover, the approximate factor we found is around $2.1 \simeq \frac{2 \pi}{3}$ so that this correction is consisted with 5.73 (as $\epsilon^{\prime}$ is being taken equal to 1 in vacuum condition).

## McMillan and Mayer Potential and expansion fit

We plotted the curve obtained from the formula found for the Potential that we developed from the force field, for $L=24,662 \mathrm{~A}$ on the one hand, $L=36,342 \mathrm{~A}$ on the other hand, and, finally, for $L=53,000 \mathrm{~A}$. We then fitted each respective McMillan and Mayer potential curve (see figure 25) so that it approximates the long-distance expansion, and not the Coulomb potential curve.

It can be noted that the behaviour of McMillan and Mayer's potential is all the more similar to the potential curve resulting from our expansion as the $L$ is higher. For the size $L=24,662 \mathrm{~A}$, the behaviour between these two curves is close between 8.2 and 9.1 A , then the McMillan and Mayer potential curve tends to sag. The behaviour between the McMillan and Mayer potential curve is similar to that of the curve in our expansion especially near 8 A for the $36,342 \mathrm{~A}$ side box, with a slightly less marked sagging of the McMillan and Mayer potential from 9.2 A onwards. Both curves have a similar behaviour from about 7.5 A for the $53,000 \mathrm{~A}$ side box.
We can also see that at great distance, these curves are all the more "straightened" and close to the behaviour of the curve resulting from our expansion and Coulomb potential (including these latter approaches) the larger the size of the box. We can again suppose that this behavior is due to a box size too small compared to the tracing distance (given the hypothesis of the $\|\mathbf{r}\| \ll L$ theorem) and that from a certain distance, depending on the box size, the presence of the images influences the behavior of the potential.

We can therefore conclude, on the one hand, the interest of fitting the curve for large distances (similarity of behaviour with our expansion). On the other hand, the effect of the size of the simulation box proves to be important for small sizes. Thus, for example, for the side box $L=24,662$ A, we observe a shift in the curve of our expansion of about 0.03 kT with the Coulomb potential curve. This will result in a bigger deviation for the calculation of the association constant, because of the switch to the exponential function.

### 5.2.4 Macroscopic study for $\mathrm{Na}-\mathrm{Cl}$ in aqueous phase

## Calculation of coordination spheres

Below, figure 26 shows the radial distribution functions between $\mathrm{Na}^{+}$ions and water molecules, function $g_{N a-O}$, on the one hand, and between $\mathrm{Cl}^{-}$ions and water molecules, function $g_{C l-O}$, on
the other hand, these functions being represented when the $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$ions are at a distance $d$. Radial distribution functions represent the probability that a water molecule is at a distance of $r$ from the ion of interest. The curves in figure 26 were taken from simulations with the 53,000 A side box, and when the two ions are constrained at a distance $d=3,4,5,10 \mathrm{~A}$ by the force of the spring (between 5 and 10 A , the curves are very similar).

We see that $g_{N a-O}$ and $g_{C l-O}$ each have two clearly defined peaks, corresponding respectively to the first and second hydration sphere. The maxima and minima are presented in the following table 4 and are in good agreement with the literature 71, 162 :

| ion | $r_{\max }^{1}($ en A) | $r_{\min }^{1}($ en A) | $r_{\max }^{2}($ en A) | $r_{\min }^{2}($ en A) |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Na}^{+}$ | 2.5 | 3.2 | 4.5 | 5.6 |
| $\mathrm{Cl}^{-}$ | 3.4 | 4. | 5.2 | 6. |

TABLE 4 - Minima and maxima of the radial distribution function $g_{\mathrm{Na-O}}$ and $g_{C l-O}$

One observes, on the other hand, a peak of $g_{N a-O}$ which is lower than the others towards 2.5 A for $d=3 \mathrm{~A}$ (fushia curve) because the presence of chloride leaves less room for the water molecules, and for the second peak towards 4.5 A , it is lower because there again chloride prevents the water molecules from approaching for $d=3,4,5$. ( As explained in [71], the impact of the distance between $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$occurs only on the "weight" of the peaks (their height), and not on the distances corresponding to the maxima and minima).

For the $g_{C l-O}$ curve, there is an offset of the minimizer after the first peak, located around 4.8 A and not 4 A . This is due to the small size of the $\mathrm{Na}^{+}$ion, which does not prevent, at 4 A , that there is a water molecule at this distance from the $\mathrm{Cl}^{-}$ion. On top of that, we will notice that $\mathrm{Cl}^{-}$is an anion, contrary to $\mathrm{Na}^{+}$which is a cation, so that the force that binds $\mathrm{H}_{2} \mathrm{O}$ molecules to $\mathrm{Cl}^{-}$is weaker : $\mathrm{H}_{2} \mathrm{O}$ has to "invert" itself to present hydrogen ions to $\mathrm{Cl}^{-}$, which hinders the presence of oxygen. This explains why $g_{C l-O}$ peaks are lower than $g_{N a-O}$ peaks.

From the peaks of $g_{N a-O}$ and $g_{C l-O}$, we can deduce the average coordination number around each ion (cf figure 27 ). For $\mathrm{Na}^{+}$, it is about 6 for the first sphere and about 12 for the second, and for $\mathrm{Cl}^{-}$it is about 6 for the first sphere and about 16 for the second. One can note the absence of box effect here in the curves obtained.

Note that each peak of the radial distribution function corresponds to one of McMillan and Mayer's potential (figure 20) ; they correspond to the CIP, SIP and SSIP configurations.

On the other hand, with respect to the hydration spheres, the McMillan and Mayer potential also represents the energy of the movement of ions between the hydration spheres. Thus, to switch from CIP to SIP, an ion must pass an energy barrier of 1.9 kT and from SIP to SSIP about 0.6 kT . On the other hand, the reverse transition (from the third to the second coordination sphere) shows that an ion needs only about 0.2 kT to enter its second sphere of hydration.

## Calculation of the association constant

From the ion-ion potentials calculated in the aqueous phase, we were able to evaluate the association constant $K$ of the ion pairs, from the Bjerrum equation (described in Chapter 4 (4.72)). The figure 28 presents this constant associated with the simulations with the side box respectively $24.662 \mathrm{~A}, 36.342 \mathrm{~A}$ and 53 . A. It also shows, as a comparison, the Bjerrum constant plotted, for each box, when the McMillan and Mayer potential is corrected by the factor found in 5.1.

As seen in 127 on page 102, the cutoff distance can be defined as the inflection point in the built-in function $K$. Here, this distance corresponds to about 4.3 A . We then find $K$ when the potential is corrected or not with our expansion. The result is given in the following table 5 in addition of the percentage difference in each cases. It is of the same order of magnitude as the value calculated in 127 page 110 where $K=0.48 \mathrm{~L} . \mathrm{mol}^{-1}$.

| $\mathrm{L}(\mathrm{en} \mathrm{A})$ | $K$ (non corrected) (en L. $\left.\mathrm{mol}^{-1}\right)$ | $K\left(\mathrm{en} \mathrm{L}. \mathrm{~mol}^{-1}\right)$ | difference percentage |
| :---: | :---: | :---: | :---: |
| 24.662 | 3.8 | 4.1 | $7 \%$ |
| 36.342 | 3.95 | 4.1 | $4 \%$ |
| 53.000 | 4.1 | 4.1 | $0 \%$ |

TABLE 5 - Association constant $K$, corrected or not, as a function of $L$

On another note, we can see that the three curves obtained with the correction are merged. This is good news because our goal is to calculate the constant in the non-periodic case, but the correction allows us to remove the term of periodicity.

### 5.2.5 Comparison of our expansion with lanthanide salt potentials

In the context of this thesis, we saw that it was particularly interesting to study the Lanthanides family. To do so, we looked at the McMillan and Mayer potentials obtained for two types of lanthanide salts in [127, these potentials being calculated from a cubic box formed of 27 lanthanides $\mathrm{Ln}^{R}, 81$ anions $\mathrm{Cl}^{-}$and 1498 water molecules, and for distances between an ion $\mathrm{Ln}^{3+}$ and an ion $\mathrm{Cl}^{-}$of up to 12 A . In the first case, the lanthanides corresponded to Neodymium ions $\mathrm{Nd}^{3+}$, and in the second to Dysprosium ions $\mathrm{Dy}^{3+}$. In both cases, the parameters of the potentials were from 59,130 . The parameters of the $\mathrm{Cl}^{-}$ions corresponded to those of 162 , while the water molecules had been described with the POL3 model 34, 125, where the dielectric constant is $\epsilon_{r}=106$. MD simulations where perform with $T=300 \mathrm{~K}$.

We then wished to compare these curves with those coming from our expansion, as well as with the curve of the Coulomb potential between the two types of respective ions of the boxes, i.e. between $\mathrm{Nd}^{3+}$ and $\mathrm{Cl}^{-}$for the first one, and $\mathrm{Dy}^{3+}$ and $\mathrm{Cl}^{-}$for the second one (cf figure 29 ). We observe that the behavior of McMillan and Mayer's potential is close to the potential resulting from our expansion from 9.2 A in the first case, and from 8.7 A in the second case. On top of that, we can observ a deviation ok about 0.01 KT bewteen our developpement and the Coulomb curve from a great distance.
Moreover, we plotted the corrected or uncorrected association constant from our expansion. For the $\mathrm{Dy}^{3+}$ ion, the association constant is obtained for a distance of about 6.5 A at $5.9 \mathrm{~L} . \mathrm{mol}^{-1}$ in the uncorrected case and $5.85 \mathrm{~L} . \mathrm{mol}^{-1}$ when it is corrected by our expansion. For the $\mathrm{Nd}^{3+}$ ion, the association constant is obtained for a distance of about 6.9 A at $8.8 \mathrm{~L} . \mathrm{mol}^{-1}$ in the
uncorrected case and $8.7 \mathrm{~L} . \mathrm{mol}^{-1}$ when it is corrected by our expansion. Adjusting the accuracy leads to a deviation of $1 \%$ in the first case and $2 \%$ in the second.

### 5.3 Conclusion

In this chapter, we have studied the theoretical behaviour of McMillan and Mayer's potential for two ions quite distant from each other and surrounded by a solvent, this system being contained in a $L$ sidebox and with periodic edge conditions. We were able to establish, under these conditions, a fairly large expansion of this potential for $L$, this expansion converging towards the Coulomb potential especially since $L$ is important. We then performed molecular simulations using the Tinker-hp software for different sizes of boxes containing two ions and $N$ water molecules ( $N$ depending on the size of the box). One of the difficulties in exploiting the potential of McMillan and Mayer was to fit the constant, and since the simulations were performed under periodic conditions, we were able to fit the curves from our simulations with those from our previous expansion. A numerical comparison with a correction based on Ewald's formula allowed us to compare our result with another approach. Then we evaluated the association constant, in the uncorrected case on the one hand, and corrected from the end of our expansion on the other hand. In the end, the corrected curves for the three box sizes were merged, while a deviation between the two types of curves (corrected or not), the smaller L is, is observed. The corrective term resulting from our expansion would thus make it possible to obtain more precisely the association constant in the non-periodic case, from the periodic simulations. In addition, deviations in the behaviour of the corrected or uncorrected association constant could also be seen for lanthanide salts. Nevertheless, considering the relatively high order of the correction term $\frac{1}{L^{5}}$, the correction is relatively weak and it can be practically neglected for large simulation boxes.

(a) case parallel to the box

(b) case of the small diagonal of the box

(c) case of the large diagonal of the box

Figure 23 - Fit of the (Ewald - Coulomb) curve, for each case


Figure 24 - Fit of the (Ewald - Coulomb) curve, in the parallel case, for $\mathrm{L}=10$ and $\mathrm{L}=100$


Figure 25 - Comparison of the potential of McMillan and Mayer curves and ones resulting from our expansion


Figure 26 - O-ion radial distribution function curve


Figure 27 - Curves of radial distribution functions (continuous lines) and number of coordination spheres (dot lines)


Figure 28 - Comparison of the curves of the association constant, plotting according to the distance, as a function of the size of the simulation box


Figure 29 - Comparison of MM potential curves and curves resulting from our expansion, based on simulations with lanthanides


Figure 30 - Comparison of the curves of the association constant, plotting according to the distance, as a function of the size of the simulation box

## Chapitre 6

## Study of the diffusion constant in confined conditions

### 6.1 Introduction

In this chapter we are interested in the study of the dependence of the system size and hence the influence of boundary conditions on the diffusion coefficient. We consider a particle, represented by $B(0, a)$, the closed ball centered at the origin and of radius $a$, moving in a fluid of viscosity $\eta$.

We begin by recalling notions of statistical thermodynamics. Let a particle undergoing an external force $\mathbf{F}$. Then it has a mean velocity $\mathbf{u}$ such that :

$$
\begin{equation*}
\mathbf{u}=\mu \mathbf{F} \tag{6.1}
\end{equation*}
$$

where $\boldsymbol{\mu}$ is the mobility tensor of the particle. We can calculate the diffusion coefficient $D$ with Einstein's relation 62] :

$$
\begin{equation*}
D=\mu k_{B} T \tag{6.2}
\end{equation*}
$$

The case of a particle moving in an unconfined fluid and with non-periodic conditions has been solved by Stokes $15,75,81,87,122,166$ for the velocity calculation, and 6.2 gives a diffusion constant $D_{0}$ which verifies :

$$
\begin{equation*}
D_{0}=\frac{k_{B} T}{6 \pi \eta a} \tag{6.3}
\end{equation*}
$$

We are interested in the correction of the diffusion constant with respect to $D_{0}$ in a few special cases.

We place ourselves in non-periodic conditions and consider that the fluid is confined between two parallel walls spaced at a distance $H$ from each other. We consider here a partial sliding condition on the walls, by means of a sliding coefficient $\gamma$. This coefficient is defined such that $\gamma \rightarrow 0$ corresponds to non-slip conditions, and on the contrary $\gamma \rightarrow \infty$ stands for total slip conditions. Moreover, the center of the particle is located at a distance $z \leq H$ from one of the walls and the particle moves parallel to the walls (cf figure 31).


Figure 31 - Illustration of a particle modeled by a ball of radius $a$ and moving in a fluid confined between two parallel walls that are at a distance $H$ from each other. The center of the ball is located at a distance $z$ from the bottom wall and the particle is moving parallel to it at a velocity $U$.

An approach using the method of reflections $103,104,110$ (reflections made in the case of one wall at a time, and assuming that each wall acts independently of the other) leads to a correction of the diffusion constant $D_{\|}$taking into account the distance between the two walls 155 H :

$$
\begin{align*}
D_{\|} & =\frac{k_{B} T}{6 \pi \eta a} \frac{1}{\frac{1}{1-\frac{a}{z} C\left(\frac{z}{\gamma}\right)}+\frac{1}{1-\frac{a}{H-z} C\left(\frac{H-z}{\gamma}\right)}-1}  \tag{6.4}\\
& =D_{0} \frac{1}{\frac{1}{1-\frac{a}{z} C\left(\frac{z}{\gamma}\right)}+\frac{1}{1-\frac{a}{H-z} C\left(\frac{H-z}{\gamma}\right)}-1} \tag{6.5}
\end{align*}
$$

where $C$ is defined as $\left.C(y)=\frac{-3}{32} y^{2}-\frac{9}{32} y-\frac{3}{8}+\left(\frac{3}{32} y^{3}+\frac{3}{8} y^{2}+\frac{3}{8} y\right)\right) E(y)+\frac{3}{2} y E(2 y)$, with $E(y)=e^{y} \int_{y}^{\infty} \frac{e^{-t}}{t} d t$. As seen in 155, in the case where $\gamma \rightarrow 0$ (non-slip case), we have $C\left(\frac{l}{\gamma}\right) \rightarrow \frac{9}{16}, l$ being the distance of the ball to one of the walls. The non-slip case is the one we are interested in, so that we consider $\gamma \rightarrow 0$.

When $a / H$ is very small and $z=\alpha H(0<\alpha<1)$ we have :

$$
\begin{align*}
\frac{1}{\frac{1}{1-\frac{9 a}{16 z}}+\frac{1}{1-\frac{9 a}{16(H-z)}}-1} & =\frac{1}{1+\left(\frac{9 a}{16 z}+\frac{9 a}{16(H-z)}\right)+o(a / H)}  \tag{6.6}\\
& =1-\frac{9}{16} \frac{a H}{z(H-z)}+o(a / H) . \tag{6.7}
\end{align*}
$$

Then when $a / H$ is very small and $z=\alpha H(0<\alpha<1)$ we have :

$$
\begin{equation*}
D_{\|}=\frac{k_{B} T}{6 \pi \eta a}\left(1-\frac{9}{16} \frac{a H}{z(H-z)}+o(a / H)\right) . \tag{6.8}
\end{equation*}
$$

If we suppose $H$ large, $D_{\|}$can be written as :

$$
\begin{equation*}
D_{\|}=D_{0}-\frac{k_{B} T}{\pi \eta} \frac{3}{32} \frac{H}{z(H-z)}+o(1 / H) \tag{6.9}
\end{equation*}
$$

It can be seen here that the first expansion term does not depend on $a$.
When considering periodic boundary conditions (in the three directions of space), an approximation of the Oseen type [176] coupled with Kirkwood and Riseman theory 97 leads to the correction of a diffusion coefficient $D_{P B C}$ as a function of the period considered $L$ 185 :

$$
\begin{equation*}
D_{P B C}=D_{0}-\frac{k_{B} T \xi}{6 \pi \eta L}+o\left(L^{-1}\right) \tag{6.10}
\end{equation*}
$$

where $D_{0}$ is given in 6.3 and $\xi \approx 2.837297$. (To do this, the authors considered an incompressible fluid perturbed by a force point acting at the center of the periodic cell. The observation in (6.9), where the first expansion term does not depend on the radius $a$ of the ball that modeled the particle, gives coherence to this approach. Moreover, the authors made sure, knowing the periodicity, that the mean of the forces acting on the cell is null, i.e. they applied a correction equivalent to a pressure gradient, of the type addition analogous to the neutralizing background seen for Ewald in chapter 3).

Here, we will resume the study of the second case, when the particle is located at equal distance from the two walls and with the condition of non-slip on the walls. We will adapt an approach of the Oseen type coupled to the theory of Kirkwood and Riseman, and not assuming that each wall acts independently of the other. We will first study the case of non-periodic conditions. We will calculate the velocity of the particle, which moves parallel to the walls, and then the diffusion coefficient when the walls are assumed to be quite distant from each other. We will thus see a coherence in the expansion of this coefficient by our method, as a function of the distance between the two walls, and the one obtained by the approach of the previous case ( $\sqrt{6.4}$ ) taken for $z=\frac{H}{2}$ ). Finally, we will look at this problem when considering periodic conditions.

Let us reshape the domain and consider here the domain $\Omega=\mathbb{R}^{2} \times\left[-\frac{H}{2}, \frac{H}{2}\right]$ (where $H>0$ ). Let $\mathbf{u}$ be the velocity vector of the particle and $p$ the fluid pressure.

On $\Omega \backslash B(0, a)$ the previously described problem is rewritten as the following Stokes problem : find $\mathbf{u}, p$ such that

$$
\left\{\begin{array}{l}
\eta \Delta \mathbf{u}(x, y, z)=\nabla p(x, y, z)  \tag{6.11}\\
\nabla \cdot \mathbf{u}(x, y, z)=0
\end{array}\right.
$$

On the edge of the ball, i.e. for $(x, y, z) \in \partial B(0, a)$, we consider :

$$
\begin{equation*}
\mathbf{u}(x, y, z)=\mathbf{U} \tag{6.12}
\end{equation*}
$$

with $\mathbf{U}$ constant vector.

The conditions of non-slip on the two walls are then written :

$$
\begin{equation*}
\mathbf{u}\left(x, y, \pm \frac{H}{2}\right)=(0,0,0) \tag{6.13}
\end{equation*}
$$

for $(x, y) \in \mathbb{R}^{2}$.
We will consider that we are far from the particle, and therefore we will be led to solve a Stokes equation where the fluid is subjected to a point of force.

### 6.2 Method of calculating the diffusion constant

In the below, we will give an idea of the method as used in 185 to calculate the diffusion coefficient, adapted to our study with a particle confined between two walls, a method we will use in sections 5.3 and 5.4.

Starting from the statement that the first correction does not involve the radius $a$ of the ball, we introduce two intermediate problems with point charges :

- for a fluid subjected to a point of force $\mathbf{F}$, on $\mathbb{R}^{3}$, the following Stokes problem : find $\mathbf{u}_{\text {oseen }}, p$ such that

$$
\left\{\begin{array}{l}
\eta \Delta \mathbf{u}_{\text {oseen }}(x, y, z)=\nabla p_{\text {oseen }}(x, y, z)-\mathbf{F} \delta(x, y, z)  \tag{6.14}\\
\nabla \cdot \mathbf{u}_{\text {oseen }}(x, y, z)=0
\end{array}\right.
$$

where $\delta$ is the Dirac distribution centered in zero and with :

$$
\begin{equation*}
\lim _{\|(x, y, z)\| \rightarrow \infty} \mathbf{u}_{\text {oseen }}=(0,0,0) . \tag{6.15}
\end{equation*}
$$

We introduce :

$$
\begin{equation*}
\mathbf{T}_{\text {Oseen }}(x, y, z)=\frac{1}{8 \pi \eta\|(x, y, z)\|}\left(\mathbf{I}_{3}+\frac{(x, y, z) \otimes(x, y, z)}{\|(x, y, z)\|^{2}}\right) \tag{6.16}
\end{equation*}
$$

the Oseen tensor in $\mathbb{R}^{3}$ for a non-periodic system ${ }^{1}$
We have then 107 :

$$
\begin{equation*}
\mathbf{u}_{\text {oseen }}(x, y, z)=\mathbf{T}_{\text {Oseen }}(x, y, z) . \mathbf{F} \tag{6.18}
\end{equation*}
$$

- for a fluid subjected to a point of force $\mathbf{F}$, on $\mathbb{R}^{2}\left[-\frac{H}{2}, \frac{H}{2}\right]$, the following Stokes' problem : find $\mathbf{u}_{\text {confine }}, p$ such that

$$
\left\{\begin{array}{l}
\eta \Delta \mathbf{u}_{\text {confine }}(x, y, z)=\nabla p_{\text {confine }}(x, y, z)-\mathbf{F} \delta(x, y, z)  \tag{6.19}\\
\nabla \cdot \mathbf{u}_{\text {confine }}(x, y, z)=0
\end{array}\right.
$$

1. $\otimes$ corresponds to the tensor product : for two vectors $\left(x_{1}, y_{1}, z_{1}\right)$ and $\left(x_{2}, y_{2}, z_{2}\right)$, we have :

$$
\left(x_{1}, y_{1}, z_{1}\right) \otimes\left(x_{2}, y_{2}, z_{2}\right)=\left(\begin{array}{lll}
x_{1} x_{2} & x_{1} y_{2} & x_{1} z_{2}  \tag{6.17}\\
y_{1} x_{2} & y_{1} y_{2} & y_{1} z_{2} \\
z_{1} x_{2} & z_{1} y_{2} & z_{1} z_{2}
\end{array}\right)
$$

with the non-slip conditions on the walls :

$$
\begin{equation*}
\mathbf{u}_{\text {confine }}\left(x, y, \pm \frac{H}{2}\right)=(0,0,0) \tag{6.20}
\end{equation*}
$$

We add to this, for $z \in\left[-\frac{H}{2}, \frac{H}{2}\right]$, boundary conditions : typically periodic conditions, or a far-field condition in the layer plane:

$$
\begin{equation*}
\lim _{\|(x, y)\| \rightarrow \infty} \mathbf{u}_{\text {confine }}(x, y, z)=(0,0,0) \tag{6.21}
\end{equation*}
$$

Let us suppose we can express $\mathbf{u}_{\text {confine }}$ as :

$$
\begin{equation*}
\mathbf{u}_{\text {confine }}(x, y, z)=\mathbf{T}(x, y, z) . \mathbf{F} \tag{6.22}
\end{equation*}
$$

where $\mathbf{T}$ is a tensor.
Ansatz : place ourselves in the case where $a / H$ is sufficiently small (i.e. we consider that the radius a of the sphere is very small compared to the distance $H$ between the two walls). $D$ verifies the following relation :

$$
\begin{equation*}
D=D_{0}+\frac{k_{B} T}{3} \lim _{\|(x, y, z)\| \rightarrow 0} \operatorname{Tr}\left(\boldsymbol{T}(x, y, z)-\boldsymbol{T}_{O s e e n}(x, y, z)\right) \tag{6.23}
\end{equation*}
$$

where $D_{0}=\frac{k_{B} T}{6 \pi \eta a}$ is given in (6.3)

## Idea :

Stokes' equation 6.11 is here linear and so :

$$
\begin{equation*}
\mathbf{u}(x, y, z)=\mathbf{u}_{\text {sph }}(x, y, z)+\mathbf{u}_{\text {walls }}(x, y, z) \tag{6.24}
\end{equation*}
$$

where $\mathbf{u}_{s p h}$ is the velocity due to the force of the particle on the fluid, and $\mathbf{u}_{\text {walls }}$ is the velocity created by the force of the walls.

Since $a / H$ is small enough, $\mathbf{u}_{\text {sph }}$ is assimilated to the solution of the classical Stokes problem 166 in the domain $\mathbb{R}^{3} \backslash B(0, a)$ and we obtain at the surface of the sphere, i.e. for $(x, y, z) \in \partial B(0, a)$ :

$$
\begin{equation*}
\mathbf{u}_{s p h}(x, y, z)=\frac{1}{6 \pi \eta a} \mathbf{F} . \tag{6.25}
\end{equation*}
$$

On the other hand, in their work, Kirkwood and Riseman 97 use the fact that $\mathbf{u}_{\text {walls }}$ varies little at the scale of the sphere if it is small. We can therefore assume that $\mathbf{u}_{\text {walls }}=\mathbf{C}$ where $\mathbf{C}$ is a constant vector. This term is calculated by assimilating the force of the particle on the fluid (force that is applied to its surface) to a dirac at its center.

We have :

$$
\begin{equation*}
\mathbf{u}_{\text {walls }}(x, y, z)=\mathbf{u}_{\text {confine }}(x, y, z)-\mathbf{u}_{\text {Oseen }}(x, y, z) \tag{6.26}
\end{equation*}
$$

where $\mathbf{u}_{\text {confine }}$ is given in 6.19) (case of a particle in a fluid confined between two walls) and $\mathbf{u}_{\text {Oseen }}$ is given in 6.14 (case of a particle in an unconfined fluid).

Hence, in $(x, y, z)=(0,0,0)$ (point where the dirac acts, i.e. the point where the force of the particle acts on the fluid) :

$$
\begin{equation*}
\mathbf{u}_{\text {wall } \mid(x, y, z)=(0,0,0)}=\lim _{\|(x, y, z)\| \rightarrow 0}\left(\mathbf{T}(x, y, z) . \mathbf{F}-\mathbf{T}_{\text {Oseen }}(x, y, z) . \mathbf{F}\right) . \tag{6.27}
\end{equation*}
$$

And then finally, for $(x, y, z) \in \partial B(0, a)$ :

$$
\begin{equation*}
\mathbf{u}(x, y, z)=\frac{1}{6 \pi \eta a} \mathbf{F}+\lim _{\|(x, y, z)\| \rightarrow 0}\left(\mathbf{T}(x, y, z)-\mathbf{T}_{O \text { seen }}(x, y, z)\right) \cdot \mathbf{F} \tag{6.28}
\end{equation*}
$$

i.e. $\mathbf{u}$ is of the form $\mathbf{u}=\boldsymbol{\mu} . \mathbf{F}$, where $\boldsymbol{\mu}$ is the mobility tensor. According to $\sqrt{6.2}$, the diffusion tensor $\mathbf{D}$ is obtained by the following :

$$
\begin{align*}
\mathbf{D} & =\boldsymbol{\mu} k_{B} T \\
& =\frac{k_{B} T}{6 \pi \eta a}+k_{B} T \lim _{\|(x, y, z)\| \rightarrow 0}\left(\mathbf{T}(x, y, z)-\mathbf{T}_{\text {Oseen }}(x, y, z)\right) . \tag{6.29}
\end{align*}
$$

The diffusion coefficient $D$ is then obtained by taking $\frac{1}{3} \operatorname{Tr}(\mathbf{D})$ and finally we get 6.23).

### 6.3 Study in the non-periodic case

As explained in the introduction, we assume that we are at a large distance, so we consider the following problem on $\Omega$, find $\mathbf{u}, p$ which verifies 6.19 with the boundary conditions 6.20 and the condition 6.21.

Theorem 7. Under the conditions of the problem, $\boldsymbol{u}$ is of the form:

$$
\begin{align*}
\boldsymbol{u}(x, y, z) & =\boldsymbol{T}_{1}(x, y, z) \cdot \boldsymbol{F} \\
& =\int_{\mathbb{R}^{2}} d \boldsymbol{k}\left(\left(A_{2}(\boldsymbol{k})(z)\left(\begin{array}{ccc}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0
\end{array}\right)+A_{3}(\boldsymbol{k})(z)\left(\begin{array}{ccc}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 1
\end{array}\right)+A_{4}(\boldsymbol{k})(z) \boldsymbol{k}^{*} \otimes \boldsymbol{k}^{*}\right)\right. \\
& \left.+i\left(A_{5}(\boldsymbol{k})(z)\left(\begin{array}{lll}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 1
\end{array}\right)+A_{6}(\boldsymbol{k})(z)\left(\begin{array}{ccc}
0 & 0 & k_{1} \\
0 & 0 & k_{2} \\
0 & 0 & 0
\end{array}\right)+A_{7}(\boldsymbol{k})(z)\left(\begin{array}{ccc}
0 & 0 & 0 \\
0 & 0 & 0 \\
k_{1} & k_{2} & 0
\end{array}\right)\right)\right) e^{i \boldsymbol{k} \cdot(x, y)} \cdot \boldsymbol{F} \tag{6.30}
\end{align*}
$$

where $\boldsymbol{k}^{*}=\binom{\boldsymbol{k}}{0}$ and with

$$
\begin{equation*}
A_{2}(\boldsymbol{k})(z)=\frac{1}{2\|\boldsymbol{k}\| \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right) \eta}\left(\operatorname{sh}\left(\|\boldsymbol{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{sh}\left(\|\boldsymbol{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \tag{6.31}
\end{equation*}
$$

$$
\begin{align*}
& A_{3}(\boldsymbol{k})(z)=-\frac{1}{4 \operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right) \eta}\left(\left(z+\frac{H}{2}\right) \operatorname{sh}\left(\|\boldsymbol{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+\left(z-\frac{H}{2}\right) \operatorname{sh}\left(\|\boldsymbol{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\left(\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)+\frac{H\|\boldsymbol{k}\| \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{2}\right)\left(\frac { 1 } { 4 \| \boldsymbol { k } \| \operatorname { s h } ( \| \boldsymbol { k } \| \frac { H } { 2 } ) ^ { 2 } \eta } \left(\operatorname{ch}\left(\|\boldsymbol{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}\right.\right. \\
& \left.+\operatorname{ch}\left(\|\boldsymbol{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right)-\left(e^{\|\boldsymbol{k}\| z}+e^{-\|\boldsymbol{k}\| z}\right)\left(\frac{1}{8\|\boldsymbol{k}\| \operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2} \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right) \eta}\right. \\
& \left.+\frac{\frac{H}{64 s h\left(\|k\| \frac{H}{2}\right) c h\left(\|k\| \frac{H}{2}\right)^{2} \eta}\left(1+\frac{H\|k\|}{2}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|k\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|k\| \frac{H}{2}\right)}\right)\right)}{\frac{1}{4}-\frac{\|k\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|k\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|k\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|k\| \frac{H}{2}\right)}\right)^{2}}\right) \\
& \left.-\frac{\left(e^{\|\boldsymbol{k}\| z}-e^{-\|\boldsymbol{k}\| z}\right)}{2 \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right) \eta} \frac{z}{16 \operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2}} \frac{\left(1+\frac{\|\boldsymbol{k}\| H}{2}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right)\right)}{\frac{1}{4}-\frac{\| \boldsymbol{k} \boldsymbol{N}^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\| k \boldsymbol{H} \frac{H}{2}\right)}{\operatorname{ch}\left(\|k\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|k\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|k\| \frac{H}{2}\right)}\right)^{2}}\right)  \tag{6.32}\\
& A_{4}(\boldsymbol{k})(z)=\left(\frac{z}{4 \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)\|\boldsymbol{k}\|^{2} \eta}\left(\operatorname{ch}\left(\|\boldsymbol{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{ch}\left(\|\boldsymbol{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right)\right. \\
& \left.+\frac{H}{16\|\boldsymbol{k}\|^{2} c h\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2} \eta}\left(e^{\|\boldsymbol{k}\| z}+e^{-\|\boldsymbol{k}\| z}\right)\right)-\left(e^{\|\boldsymbol{k}\| z}+e^{-\|\boldsymbol{k}\| z}\right)\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\|\boldsymbol{k}\| \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right. \\
& \left.-\frac{H}{2}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2}}{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2}}-1\right)\right)\left(\frac{H^{2}}{128 c h\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2} \eta}\left(\frac{\sin }{4}-\frac{\|\boldsymbol{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}-\frac{c h\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right)^{2}\right)\right.
\end{align*}
$$

$$
\begin{align*}
& -\frac{1}{4\|\boldsymbol{k}\|^{3} \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right) \eta}\left(\operatorname{sh}\left(\|\boldsymbol{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{sh}\left(\|\boldsymbol{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right)  \tag{6.33}\\
& A_{5}(\boldsymbol{k})(z)=\left(\frac{-1}{4\|\boldsymbol{k}\| \operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right) \eta}\left(\left(z+\frac{H}{2}\right) \operatorname{ch}\left(\|\boldsymbol{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+\left(z-\frac{H}{2}\right) \operatorname{ch}\left(\|\boldsymbol{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right)\right) \\
& +\left(\frac{H \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{8\|\boldsymbol{k}\| \operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2} \eta}\left(\operatorname{sh}\left(\|\boldsymbol{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+\operatorname{sh}\left(\|\boldsymbol{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right)\right) \\
& +\left(e^{\|\boldsymbol{k}\| z}-e^{-\|\boldsymbol{k}\| z}\right)\left(\frac{H}{64 \operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2} \eta}\right) \frac{\left(\frac{1}{\operatorname{sh}\left(\|k\| \frac{H}{2}\right)\|\boldsymbol{k}\|}+\frac{H}{4}\left(1-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2}}{\operatorname{sh}\left(\|\boldsymbol{H}\| \frac{H}{2}\right)^{2}}\right)\right)}{\frac{1}{4}-\frac{\|\boldsymbol{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right)^{2}}\left(\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)\right. \\
& \left.+\frac{H\|\boldsymbol{k}\| \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{2}\right)-\frac{\left(e^{\|\boldsymbol{k}\| z}+e^{-\|\boldsymbol{k}\| z}\right)}{32\|\boldsymbol{k}\| \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right) \operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2} \eta}\left(1+\frac{\|\boldsymbol{k}\| H}{2}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right)\right) \\
& \left(\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)+\frac{H\|\boldsymbol{k}\| \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{2}\right) \frac{z}{\frac{1}{4}-\frac{\|\boldsymbol{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right)^{2}} \tag{6.34}
\end{align*}
$$

$$
\begin{align*}
A_{6}(\boldsymbol{k})(z) & =-\frac{\left(e^{\|\boldsymbol{k}\| z}+e^{-\|\boldsymbol{k}\| z}\right) z}{2 \eta} \frac{\frac{H}{32 \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2}}\left(1-\frac{H\|\boldsymbol{k}\|^{2}}{2}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right)\right)}{\frac{1}{4}-\frac{\|\boldsymbol{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right)^{2}} \\
& -\frac{z}{4\|\boldsymbol{k}\| \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right) \eta}\left(\operatorname{sh}\left(\|\boldsymbol{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{sh}\left(\|\boldsymbol{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& -\left(e^{\|\boldsymbol{k}\| z}-e^{-\|\boldsymbol{k}\| z}\right) \frac{\frac{H^{2}}{128 \operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2} \eta}\left(\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}-\frac{\|\boldsymbol{k}\| H}{2}\left(1-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2}}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)^{2}}\right)\right)}{\frac{1}{4}-\frac{\|\boldsymbol{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{ch(\| \boldsymbol {H}\| \frac {H}{2})}}-\frac{\operatorname{ch}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\boldsymbol{k}\| \frac{H}{2}\right)}\right)^{2}} \tag{6.35}
\end{align*}
$$

The reader interested in the physical aspects of the problem may skip the mathematical proof of the theorem. In what follows, $\mathbf{1}_{z>0}$ corresponds to the usual Heaviside function.

## Proof. Step 1 :

Soit $\mathbf{h}=\left(\begin{array}{l}h_{1} \\ h_{2} \\ h_{3}\end{array}\right)$ such as :

$$
\begin{equation*}
\mathbf{h}(x, y, z)=\eta \Delta \mathbf{u}(x, y, z)-\nabla p(x, y, z)+\delta(x, y, z) \mathbf{F} \tag{6.36}
\end{equation*}
$$

Going to the Fourier transform in dimension two, we have for $\mathbf{k} \in \mathbb{R}^{2}$ :

$$
\begin{align*}
\widehat{h_{1}}(\mathbf{k})(z) & =\int_{\mathbb{R}^{2}} h_{1}(x, y, z) e^{-i \mathbf{k} \cdot(x, y)} d x d y  \tag{6.37}\\
& =\int_{\mathbb{R}^{2}}\left(\eta \Delta u_{1}(x, y, z)-\frac{\partial}{\partial x} p(x, y, z)+\delta(x, y, z) F_{1}\right) e^{-i \mathbf{k} \cdot(x, y)} d x d y  \tag{6.38}\\
& =\int_{\mathbb{R}^{2}}\left(\eta\left(\frac{\partial^{2}}{\partial z^{2}} u_{1}(x, y, z)-u_{1}(x, y, z)\left(k_{1}^{2}+k_{2}^{2}\right)\right)-i k_{1} p(x, y, z)+\delta(x, y, z) F_{1}\right) e^{-i \mathbf{k} \cdot(x, y)} d x d y  \tag{6.39}\\
& =\eta\left(\widehat{u_{1}}(\mathbf{k})^{\prime \prime}(z)-\|\mathbf{k}\|^{2} \widehat{u_{1}}(\mathbf{k})(z)\right)-i k_{1} \widehat{p}(\mathbf{k})(z)+\widehat{\delta}(\mathbf{k})(z) F_{1} \tag{6.40}
\end{align*}
$$

where we integrated by part for the third equality and used the condition 6.21, and with :

$$
\begin{equation*}
\widehat{\delta}(\mathbf{k})(z)=\delta(z) \tag{6.41}
\end{equation*}
$$

Likewise :

$$
\begin{equation*}
\widehat{h_{2}}(\mathbf{k})(z)=\eta\left(\widehat{u_{2}}(\mathbf{k})^{\prime \prime}(z)-\|\mathbf{k}\|^{2} \widehat{u_{2}}(\mathbf{k})(z)\right)-i k_{2} \widehat{p}(\mathbf{k})(z)+\delta(z) F_{2} \tag{6.42}
\end{equation*}
$$

And to finish :

$$
\begin{equation*}
\widehat{h_{3}}(\mathbf{k})(z)=\eta\left(\widehat{u_{3}}(\mathbf{k})^{\prime \prime}(z)-\|\mathbf{k}\|^{2} \widehat{u_{3}}(\mathbf{k})(z)\right)-\widehat{p}(\mathbf{k})^{\prime}(z)+\delta(z) F_{3} . \tag{6.43}
\end{equation*}
$$

We inject 6.40, 6.42) and 6.43) into the first equation of 6.19), which gives us the following system of equations :

$$
\left\{\begin{array}{l}
\eta\left(\widehat{u_{1}}(\mathbf{k})^{\prime \prime}(z)-\|\mathbf{k}\|^{2} \widehat{u_{1}}(\mathbf{k})(z)\right)=i k_{1} \widehat{p}(\mathbf{k})(z)-\delta(z) F_{1}  \tag{6.44}\\
\eta\left(\widehat{u_{2}}(\mathbf{k})^{\prime \prime}(z)-\|\mathbf{k}\|^{2} \widehat{u_{2}}(\mathbf{k})(z)\right)=i k_{2} \widehat{p}(\mathbf{k})(z)-\delta(z) F_{2} \\
\eta\left(\widehat{u_{3}}(\mathbf{k})^{\prime \prime}(z)-\|\mathbf{k}\|^{2} \widehat{u_{3}}(\mathbf{k})(z)\right)=\widehat{p}(\mathbf{k})^{\prime}(z)-\delta(z) F_{3}
\end{array}\right.
$$

On the other hand, the second equation of (6.19) translates as equality $\forall z \in\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
i k_{1} \widehat{u_{1}}(\mathbf{k})(z)+i k_{2} \widehat{u_{2}}(\mathbf{k})(z)+\widehat{u_{3}}(\mathbf{k})^{\prime}(z)=0 \tag{6.45}
\end{equation*}
$$

## Step 2 :

We take the divergence of the first equation of (6.19) and we get :

$$
\begin{align*}
\nabla \cdot(\eta \Delta \mathbf{u}) & =\nabla \cdot(\nabla p-\delta \mathbf{F})  \tag{6.46}\\
& =\Delta p-\mathbf{F} \cdot \nabla(\delta) . \tag{6.47}
\end{align*}
$$

And then we have the equation :

$$
\begin{equation*}
\Delta p=\mathbf{F} \cdot \nabla \delta \tag{6.48}
\end{equation*}
$$

(since $\nabla . \mathbf{u}=0$. )
As a result:

$$
\begin{equation*}
\widehat{p}(\mathbf{k})^{\prime \prime}(z)-\|\mathbf{k}\|^{2} \widehat{p}(\mathbf{k})(z)=i\left(k_{1} F_{1}+k_{2} F_{2}\right) \widehat{\delta}(\mathbf{k})(z)+F_{3} \delta^{\prime}(z) . \tag{6.49}
\end{equation*}
$$

The idea will next be to solve the equation for $\widehat{p}(\mathbf{k})$ then to inject the solution obtained into the equation for $\widehat{u_{i}}(\mathbf{k})(i=1,2,3)$ and next to calculate the solution of the equation obtained then.

## Step 3 :

Here we will give a brief review of the computation of derivatives of distributions 30], and then deduce a succession of lemmas on various ODE solutions that we will need later on.

Let $f$ piecewise $C^{1}$ in $[a, b]$, and which admits, at any point where it is not continuous, a right and a left limit.
There is thus a subdivision $a=a_{0}<a_{1}<\ldots<a_{i}<\ldots<b=a_{n+1}$ such that for $i=0, \ldots, n$ the restriction of $f$ on the interval $] a_{i}, a_{i+1}$ [ can be extended into a class function $C^{1}$ on $\left[a_{i}, a_{i+1}\right]$. We note $f\left(a_{i}^{+}\right)$and $f\left(a_{i}^{-}\right)$the respective limits on the right and on the left at the point $a_{i}$. Let $T_{f}$ be the distribution associated with $f$. We can calculate its derivative, which we note $\left(T_{f}\right)^{\prime}$.

We remember the jump formula :
Theorem 8. The distribution $\left(T_{f}\right)^{\prime}$ is given, starting from $T_{f^{\prime}}$ and jumping $f$ in each $a_{i}$, by :

$$
\begin{equation*}
\left(T_{f}\right)^{\prime}=T_{f^{\prime}}+\sum_{i=0}^{n+1}\left(f\left(a_{i}^{+}\right)-f\left(a_{i}^{-}\right)\right) \delta a_{i} . \tag{6.50}
\end{equation*}
$$

This result extends to the successive derivatives in the case where $f$ is piecewise $C^{N}$ on $[a, b]$, such as notably for the second derivative, considering the jumps of $f$ and those of its derivative :

$$
\begin{equation*}
\left(T_{f}\right)^{\prime \prime}=T_{f^{\prime \prime}}+\sum_{i=0}^{n+1}\left(f\left(a_{i}^{+}\right)-f\left(a_{i}^{-}\right)\right) \delta_{a i}^{\prime}+\sum_{i=0}^{n+1}\left(f^{\prime}\left(a_{i}^{+}\right)-f^{\prime}\left(a_{i}^{-}\right)\right) \delta a_{i} \tag{6.51}
\end{equation*}
$$

Beforehand we have the following lemma:
Lemma 10. Let be the following differential equation :

$$
\begin{equation*}
y^{\prime \prime}(t)-A y(t)=g(t) \tag{6.52}
\end{equation*}
$$

with $A>0$ and $g$ is a function. The solution is of the form :

$$
\begin{equation*}
y(t)=y_{P}(t)+y_{H}(t) \tag{6.53}
\end{equation*}
$$

where $y_{P}$ is a particular solution and $y_{H}$ is the solution of the homogeneous equation associated with it :

$$
\begin{equation*}
y_{H}(t)=\alpha e^{\sqrt{A} t}+\beta e^{-\sqrt{A} t} \tag{6.54}
\end{equation*}
$$

with $\alpha, \beta \in \mathbb{C}$.
The first 5 following lemmas will be established for equations in the form of lemma 10.
Lemma 11. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
y^{\prime \prime}(t)-A y(t)=B e^{\sqrt{A} t}+B^{\prime} e^{-\sqrt{A} t}+C t+D \tag{6.55}
\end{equation*}
$$

with $A>0, B, B^{\prime}, C, D \in \mathbb{C}$. The solution is in the form :

$$
\begin{equation*}
y(t)=y_{P}(t)+y_{H}(t) \tag{6.56}
\end{equation*}
$$

where $y_{H}$ is defined in lemma 10 and $y_{P}$ is a particular solution :

$$
\begin{equation*}
y_{P}(t)=\frac{t}{2 \sqrt{A}}\left(B e^{\sqrt{A} t}-B^{\prime} e^{-\sqrt{A} t}\right)-\frac{1}{A}(C t+D) \tag{6.57}
\end{equation*}
$$

with $\alpha, \beta \in \mathbb{C}$.
We remind that :

$$
\begin{equation*}
\operatorname{ch}(\sqrt{A} t)=\frac{e^{\sqrt{A} t}+e^{-\sqrt{A} t}}{2}, \operatorname{sh}(\sqrt{A} t)=\frac{e^{\sqrt{A} t}-e^{-\sqrt{A} t}}{2} . \tag{6.58}
\end{equation*}
$$

Lemma 12. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
y^{\prime \prime}(t)-A y(t)=B \delta(t) \tag{6.59}
\end{equation*}
$$

with $A>0, B \in \mathbb{C}$. The solution is in the form:

$$
\begin{equation*}
y(t)=y_{P}(t)+y_{H}(t) \tag{6.60}
\end{equation*}
$$

where $y_{H}$ is defined in lemma 10 and $y_{P}$ is a particular solution:

Two choices of particular solutions $y_{P, 1}$ and $y_{P, 2}$ are :

$$
\begin{align*}
& y_{P, 1}(t)=\frac{-B \operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right)}{2 \sqrt{A} \operatorname{ch}\left(\sqrt{A} \frac{H}{2}\right)} \mathbf{1}_{t \leq 0}+\frac{B \operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right)}{2 \sqrt{A} \operatorname{ch}\left(\sqrt{A} \frac{H}{2}\right)} \mathbf{1}_{t>0}  \tag{6.61}\\
& y_{P, 2}(t)=\frac{-B}{2 \sqrt{A} \operatorname{sh}\left(\sqrt{A} \frac{H}{2}\right)}\left(\operatorname{ch}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right) \mathbf{1}_{t \leq 0}+\operatorname{ch}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right) \mathbf{1}_{t>0}\right) \tag{6.62}
\end{align*}
$$

(N.B. : $y_{P, 1}$ can be cancelled in $\pm \frac{H}{2}$ )

Proof. The homogeneous solution is shown in a classical way. Let us determine a particular solution of 6.59. Let us look for a solution of the form :
$y(t)=\left(\alpha_{-} \operatorname{ch}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right)+\beta_{-} \operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right)\right) \mathbf{1}_{t \leq 0}+\left(\alpha_{+} \operatorname{ch}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right)+\beta_{+} \operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right)\right) \mathbf{1}_{t>0}$.

We determine the second derivative of $y$ with theorem 8 and we find :

$$
\begin{align*}
y^{\prime \prime}(t) & =A\left(\alpha_{-} \operatorname{ch}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right)+\beta_{-} \operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right)\right) \mathbf{1}_{t \leq 0} \\
& +A\left(\alpha_{+} \operatorname{ch}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right)+\beta_{+} \operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right)\right) \mathbf{1}_{t>0} \\
& +\left(\left(\alpha_{+}-\alpha_{-}\right) \operatorname{ch}\left(\sqrt{A}\left(\frac{H}{2}\right)\right)+\left(-\beta_{+}-\beta_{-}\right) \operatorname{sh}\left(\sqrt{A}\left(\frac{H}{2}\right)\right)\right) \delta^{\prime}(t) \\
& +\sqrt{A}\left(\left(-\alpha_{+}-\alpha_{-}\right) \operatorname{sh}\left(\sqrt{A}\left(\frac{H}{2}\right)\right)+\left(\beta_{+}-\beta_{+}\right) \operatorname{ch}\left(\sqrt{A}\left(\frac{H}{2}\right)\right)\right) \delta(t) \tag{6.64}
\end{align*}
$$

Case 1: We take $\alpha_{-}=\alpha_{+}=0$ and we obtain by identification in the equation 6.59) :

$$
\left\{\begin{array}{l}
\sqrt{A}\left(\beta_{+}-\beta_{-}\right) \operatorname{ch}\left(\sqrt{A}\left(\frac{H}{2}\right)\right)=B  \tag{6.65}\\
\left(-\beta_{+}-\beta_{-}\right) \operatorname{sh}\left(\sqrt{A}\left(\frac{H}{2}\right)\right)=0
\end{array}\right.
$$

what gives us 6.61.
Case 2: We find 6.62 in a similar way, taking $\beta_{-}=\beta_{+}=0$.
Lemma 13. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
y^{\prime \prime}(t)-A y(t)=B \delta^{\prime}(t) \tag{6.66}
\end{equation*}
$$

with $A>0, B \in \mathbb{C}$. A family of solutions is of the form :

$$
\begin{equation*}
y(t)=y_{P}(t)+y_{H}(t) \tag{6.67}
\end{equation*}
$$

where $y_{H}$ is defined in lemma 10 and $y_{P}$ is a particular solution:

$$
\begin{equation*}
y_{P}(t)=\frac{-B \operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right)}{2 \operatorname{sh}\left(\sqrt{A} \frac{H}{2}\right)} \mathbf{1}_{t \leq 0}-\frac{B \operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right)}{2 \operatorname{sh}\left(\sqrt{A} \frac{H}{2}\right)} \mathbf{1}_{t>0} . \tag{6.68}
\end{equation*}
$$

Lemma 14. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
y^{\prime \prime}(t)-A y(t)=B \operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right) \mathbf{1}_{t \leq 0}+B^{\prime} \operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right) \mathbf{1}_{t>0} \tag{6.69}
\end{equation*}
$$

with $A>0, B, B^{\prime} \in \mathbb{C}$. The solution is in the form:

$$
\begin{equation*}
y(t)=y_{P}(t)+y_{H}(t) \tag{6.70}
\end{equation*}
$$

where $y_{H}$ is defined in lemma 10 and $y_{P}$ is a particular solution ${ }^{2}$ :

$$
\begin{align*}
y_{P}(t) & =\frac{B\left(t+\frac{H}{2}\right) \operatorname{ch}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right)}{2 \sqrt{A}} \mathbf{1}_{t \leq 0}+\frac{B^{\prime}\left(t-\frac{H}{2}\right) \operatorname{ch}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right)}{2 \sqrt{A}} \mathbf{1}_{t>0} \\
& -\left(B+B^{\prime}\right) \frac{H \operatorname{ch}\left(\sqrt{A} \frac{H}{2}\right)}{8 \sqrt{A} \operatorname{sh}\left(\sqrt{A} \frac{H}{2}\right)}\left(\operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right) \mathbf{1}_{t \leq 0}+\operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right) \mathbf{1}_{t>0}\right) \\
& +\left(B^{\prime}-B\right) \frac{1}{4 A}\left(\operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right) \mathbf{1}_{t \leq 0}-\operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right) \mathbf{1}_{t>0}\right) \\
& +\left(B^{\prime}-B\right) \frac{H}{8 \sqrt{A}}\left(\operatorname{ch}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right) \mathbf{1}_{t \leq 0}+\operatorname{ch}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right) \mathbf{1}_{t>0}\right) . \tag{6.71}
\end{align*}
$$

Lemma 15. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
y^{\prime \prime}(t)-A y(t)=B \operatorname{ch}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right) \mathbf{1}_{t \leq 0}+B^{\prime} \operatorname{ch}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right) \mathbf{1}_{t>0} \tag{6.72}
\end{equation*}
$$

with $A>0, B, B^{\prime} \in \mathbb{C}$. A family of solutions is of the form :

$$
\begin{equation*}
y(t)=y_{P}(t)+y_{H}(t) \tag{6.73}
\end{equation*}
$$

where $y_{H}$ is defined in lemma 10 and $y_{P}$ is a particular solution :

$$
\begin{align*}
y_{P}(t) & =\frac{B\left(t+\frac{H}{2}\right) \operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right)}{2 \sqrt{A}} \mathbf{1}_{t \leq 0}+\frac{B^{\prime}\left(t-\frac{H}{2}\right) \operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right)}{2 \sqrt{A}} \mathbf{1}_{t>0} \\
& +\left(B^{\prime}-B\right) \frac{H}{8 \sqrt{A}}\left(\operatorname{sh}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right) \mathbf{1}_{t \leq 0}+\operatorname{sh}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right) \mathbf{1}_{t>0}\right) \\
& -\left(B+B^{\prime}\right)\left(\frac{1}{4 A}+\frac{H \operatorname{ch}\left(\sqrt{A} \frac{H}{2}\right)}{4 \sqrt{A} \operatorname{sh}\left(\sqrt{A} \frac{H}{2}\right)}\right)\left(\operatorname{ch}\left(\sqrt{A}\left(t+\frac{H}{2}\right)\right) \mathbf{1}_{t \leq 0}+\operatorname{ch}\left(\sqrt{A}\left(t-\frac{H}{2}\right)\right) \mathbf{1}_{t>0}\right) . \tag{6.74}
\end{align*}
$$

Finally, the following lemma is established :
Lemma 16. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
y^{\prime \prime}(t)=A+B \delta(t)+C \delta^{\prime}(t) \tag{6.75}
\end{equation*}
$$

with $A, B, C \in \mathbb{C}$. The solution is in the form :

$$
\begin{equation*}
y(t)=\frac{A}{2} t^{2}+\alpha t+\beta+(B t+C) \mathbf{1}_{t>0} \tag{6.76}
\end{equation*}
$$

[^18]
## Step 4:

Here we will use the solutions of the equations defined in step 3 first to solve the equation (6.49) and then for 6.44.

We set beforehand :

$$
\begin{equation*}
A=\frac{F_{3}}{2 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}, B=\frac{\mathbf{k}^{*} \cdot \mathbf{F}}{2\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)} \tag{6.77}
\end{equation*}
$$

where $\mathbf{k}^{*}=\binom{\mathbf{k}}{0}$. We then find for 6.49 using lemmas 12 and 13 :
$\widehat{p}(\mathbf{k})(z)=\alpha e^{\|\mathbf{k}\| z}+\beta e^{-\|\mathbf{k}\| z}+(-A-i B) \operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+(-A+i B) \operatorname{sh}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}$.

So that :

$$
\begin{align*}
\widehat{p}(\mathbf{k})^{\prime}(z) & =\|\mathbf{k}\|\left((-A-i B) \operatorname{ch}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+(-A+i B) \operatorname{ch}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\|\mathbf{k}\|\left(\alpha e^{\|\mathbf{k}\| t}-\beta e^{-\|\mathbf{k}\| t}\right)+2 A \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \delta(z) \tag{6.79}
\end{align*}
$$

What gives us for (6.44) using the lemmas 12, 13, 14, and 15 :

## Step 5 :

Here we will use the conditions (6.20) over the "upper" and "lower" walls (i.e. level line respectively $z=\frac{H}{2}$ et $\left.z=\frac{-H}{2}\right)$.

We deduce from 6.20 :

$$
\begin{equation*}
\widehat{\mathbf{u}}(\mathbf{k})\left( \pm \frac{H}{2}\right)=(0,0,0) \tag{6.81}
\end{equation*}
$$

We then obtain after resolution of the systems :

Then :

$$
\left\{\begin{array}{l}
\alpha_{2}=\frac{B H k_{2}}{8\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}-\frac{i k_{2} H}{8\|\mathbf{k}\| \eta}\left((\alpha+\beta) \frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}+(\alpha-\beta) \frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{H}\right)}\right)  \tag{6.83}\\
\beta_{2}=\frac{B H k_{2}}{8\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}-\frac{i k_{2} H}{8\|\mathbf{k}\| \eta}\left((\alpha+\beta) \frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-(\alpha-\beta) \frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)
\end{array}\right.
$$

And to finish :

$$
\left\{\begin{array}{l}
\alpha_{3}=\frac{-A}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\left(\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)+\frac{H\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{2}\right)  \tag{6.84}\\
-\frac{H}{8 \eta}\left(\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)(\alpha-\beta)+\left(\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)(\alpha+\beta)\right) \\
\beta_{3}=\frac{-A}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\left(\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)+\frac{H\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{2}\right) \\
-\frac{H}{8 \eta}\left(\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)(\alpha-\beta)-\left(\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)(\alpha+\beta)\right)
\end{array}\right.
$$

## Step 6 :

Let us start again (6.45) and we then seek to identify $\alpha=\alpha(\mathbf{k})$ and $\beta=\beta(\mathbf{k})$ such that this identity is verified. We obtain, after simplifications :

$$
\begin{equation*}
i k_{1}\left(\alpha_{1} e^{\|\mathbf{k}\| z}+\beta_{1} e^{-\|\mathbf{k}\| z}\right)+i k_{2}\left(\alpha_{2} e^{\|\mathbf{k}\| z}+\beta_{2} e^{-\|\mathbf{k}\| z}\right)+\|\mathbf{k}\|\left(\alpha_{3} e^{\|\mathbf{k}\| z}-\beta_{3} e^{-\|\mathbf{k}\| z}\right)+\frac{1}{2 \eta}\left(\alpha e^{\|\mathbf{k}\| z}+\beta e^{-\|\mathbf{k}\| z}\right)=0 \tag{6.85}
\end{equation*}
$$

We deduce from 6.85 (this identity being true for any $z \in\left[\frac{-H}{2}, \frac{H}{2}\right]$ ) a system by identifying the parts in $e^{\|\mathbf{k}\| z}$ and in $e^{-\|\mathbf{k}\| z}$. We then find, by posing $c=\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)$ and $s=\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)$ :

$$
\left\{\begin{array}{l}
\alpha=\frac{\frac{-A}{8 s c}\left(s+\frac{H\|\mathbf{k}\| c}{2}\right)-\frac{i H\|\mathbf{k}\| B}{16 c}+\left(\frac{-A}{4 s c}\left(s+\frac{H\|k\| c}{2}\right)+\frac{i H\|\mathbf{k}\| B}{8 c}\right) \frac{\|\mathbf{k}\| H}{4}\left(\frac{s}{c}-\frac{c}{s}\right)}{\frac{1}{4}-\frac{\|k\|^{2} H^{2}}{16}\left(\frac{s}{c}-\frac{c}{s}\right)^{2}}  \tag{6.86}\\
\beta=\frac{\frac{A}{8 s c}\left(s+\frac{H\|k\| c}{2}\right)-\frac{i H \| \mathbf{k}}{16 c}-\left(\frac{-A}{s c c}\left(s+\frac{H\|k\| c}{2}\right)-\frac{i H\|\mathbf{k}\| B}{8 c}\right) \frac{\|k\| H}{4}\left(\frac{s}{c}-\frac{c}{s}\right)}{\frac{1}{4}-\frac{\|k\|^{2} H^{2}}{16}\left(\frac{s}{c}-\frac{c}{s}\right)^{2}}
\end{array}\right.
$$

## Step 7 :

Using $\sqrt{6.80},(6.82),(6.83),(6.84)$ and (6.86) gives the result.

Here we wish to evaluate the diffusion constant $D$ in the case of the problem in section 3 . We will then be able to compare our result with the one obtained in [155].

Theorem 9. We have for large $H$ :

$$
\begin{align*}
D & =D_{0}+\frac{k_{B} T}{3} \lim _{\|(x, y)\| \rightarrow 0} \operatorname{Tr}\left(\frac{1}{2 \pi\|(x, y)\| \eta}-\frac{H^{2}\left(2 H^{2}-\|(x, y)\|^{2}\right)}{4 \pi H^{5}\left(\frac{\|(x, y)\|^{2}}{H^{2}}+1\right)^{5 / 2} \eta}\right. \\
& \left.+\frac{H^{2}\left(8 H^{2}-\|(x, y)\|^{2}\right)}{64 \pi H^{5}\left(\frac{\|(x, y)\|^{2}}{4 H^{2}}+1\right)^{5 / 2}}-\frac{1}{2 \pi \eta\|(x, y)\|}+o\left(\frac{1}{H}\right)\right)  \tag{6.87}\\
& =D_{0}-\frac{3 k_{B} T}{16 \pi H \eta}+o\left(\frac{1}{H}\right) . \tag{6.88}
\end{align*}
$$

Proof. To begin we have :

$$
\begin{equation*}
\operatorname{Tr}\left(T_{\text {Oseen }}(x, y, z)\right)=\frac{1}{2 \pi \eta\|(x, y, z)\|} \tag{6.89}
\end{equation*}
$$

On the other hand, by taking $z=0$ we have :

$$
\begin{align*}
\operatorname{Tr}\left(\mathbf{T}_{1}(x, y, 0)\right)= & \int d \mathbf{k}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}-\frac{H}{8 \eta}+\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}+\frac{H \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{8 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}\right. \\
- & \left(\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)+\frac{H\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{2}\right)\left(\frac{1}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\right. \\
& \left.+\frac{\frac{H}{32 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}\left(1+\frac{H\|\mathbf{k}\|}{2}\left(\frac{\operatorname{sh}\left(\| \mathbf{k} \boldsymbol{H} \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)\right)}{\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}}\right) \\
+ & \frac{H}{8 \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}-\left(\frac{\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{H\|\mathbf{k}\| \|^{2}}{2}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}-1\right)\right) \\
& \left.\left(\frac{\frac{H^{2}}{64 \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}}{\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}}\right)-\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\right) e^{i \mathbf{k} \cdot(x, y)} \tag{6.90}
\end{align*}
$$

$$
=\int d \mathbf{k} C(\mathbf{k}, H) e^{i \mathbf{k} \cdot(x, y)}
$$

Let us analyze more precisely the term $C(\mathbf{k}, H)$.

## Terms in $\frac{1}{\|\mathbf{k}\|}$ :

Note that :

$$
\begin{align*}
\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}-\frac{1}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta} & =\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}-1}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta} \\
& =\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta} \\
& =\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta} \tag{6.91}
\end{align*}
$$

So we have :

$$
\begin{align*}
\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}+\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta} & -\frac{1}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta} \\
& -\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}=\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta} \tag{6.92}
\end{align*}
$$

We have :

$$
\begin{equation*}
\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-1=\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)-\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}=\frac{-2}{e^{\|\mathbf{k}\| H}+1} \tag{6.93}
\end{equation*}
$$

And so, for large $H$, we have :

$$
\begin{equation*}
\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}=1+o\left(\frac{1}{H}\right) \tag{6.94}
\end{equation*}
$$

Finally, we have :

$$
\begin{equation*}
\int \frac{1}{\|\mathbf{k}\|} e^{i \mathbf{k} \cdot(x, y)} d \mathbf{k}=\frac{1}{2 \pi\|(x, y)\|} \tag{6.95}
\end{equation*}
$$

## Terms in $" \frac{H}{8} "$ :

We have :

$$
\begin{equation*}
\frac{H \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{8 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}-\frac{H}{8 \eta}=\frac{H\left(\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}-\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}\right)}{8 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}=\frac{H}{8 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta} \tag{6.96}
\end{equation*}
$$

So that :

$$
\begin{equation*}
\frac{H \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{8 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}-\frac{H}{8 \eta}-\frac{H}{8 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}=0 \tag{6.97}
\end{equation*}
$$

## Other terms :

First of all, let us note that :

$$
\begin{equation*}
\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}=\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}-\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}=\frac{-1}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}=\frac{-2}{\operatorname{sh}(\|\mathbf{k}\| H)} . \tag{6.98}
\end{equation*}
$$

Thus, for large $H$ we have :

$$
\begin{array}{r}
1+\frac{H\|\mathbf{k}\|}{2}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)=1+o\left(\frac{1}{H}\right) \\
\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}=\frac{1}{4}+o\left(\frac{1}{H}\right) . \tag{6.100}
\end{array}
$$

On the other hand, we note that for large $H$ we have $\forall \mathbf{k} \neq(0,0)$ :

$$
\begin{align*}
& \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)=\frac{e^{\|\mathbf{k}\| \frac{H}{2}}}{2}+\frac{1}{2 \frac{e^{\|\mathbf{k}\| \frac{H}{2}}}{2}}=\frac{e^{\|\mathbf{k}\| \frac{H}{2}}}{2}+o\left(e^{\|\mathbf{k}\| \frac{H}{2}}\right)  \tag{6.101}\\
& \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)=\frac{e^{\|\mathbf{k}\| \frac{H}{2}}}{2}-\frac{1}{2 \frac{e^{\|\mathbf{k}\| \frac{H}{2}}}{2}}=\frac{e^{\|\mathbf{k}\| \frac{H}{2}}}{2}+o\left(e^{\|\mathbf{k}\| \frac{H}{2}}\right) . \tag{6.102}
\end{align*}
$$

Therefore, for large $H$, there are terms such as :

$$
\begin{align*}
\int \frac{H^{2}\|\mathbf{k}\| C}{e^{\|\mathbf{k}\| H}} e^{i \mathbf{k} \cdot(x, y)} d \mathbf{k} & =\frac{C H^{2}\left(2 H^{2}-\|(x, y)\|^{2}\right)}{2 \pi H^{5}\left(\frac{\|(x, y)\|^{2}}{H^{2}}+1\right)^{5 / 2}}  \tag{6.103}\\
\int \frac{H^{2}\|\mathbf{k}\| C}{e^{\|\mathbf{k}\| 2 H}} e^{i \mathbf{k} \cdot(x, y)} d \mathbf{k} & =\frac{C H^{2}\left(8 H^{2}-\|(x, y)\|^{2}\right)}{64 \pi H^{5}\left(\frac{\|(x, y)\|^{2}}{4 H^{2}}+1\right)^{5 / 2}} . \tag{6.104}
\end{align*}
$$

## Back to the calculation of $D$ :

Using the ansatz (see paragraph 6.2), we have for $z=0$ and large $H$ :

$$
\begin{align*}
D= & D_{0}+\frac{k_{B} T}{3} \lim _{\|(x, y)\| \rightarrow 0} \operatorname{Tr}\left(\frac{1}{2 \pi\|(x, y)\| \eta}-\frac{H^{2}\left(2 H^{2}-\|(x, y)\|^{2}\right)}{4 \pi H^{5}\left(\frac{\|(x, y)\|^{2}}{H^{2}}+1\right)^{5 / 2} \eta}\right. \\
- & \left.\frac{H^{2}\left(8 H^{2}-\|(x, y)\|^{2}\right)}{128 \pi H^{5}\left(\frac{\|(x, y)\|^{2}}{4 H^{2}}+1\right)^{5 / 2}}-\frac{1}{2 \pi \eta\|(x, y)\|}+o\left(\frac{1}{H}\right)\right)  \tag{6.105}\\
= & D_{0}-\frac{3 k_{B} T}{16 \pi H \eta}+o\left(\frac{1}{H}\right) \tag{6.106}
\end{align*}
$$

To place ourselves in our case for the diffusion constant calculated in the paper 155, we take $\delta \rightarrow 0$ and $z=\frac{H}{2}$ and we obtain for large $H$ :

$$
\begin{equation*}
D=\frac{k_{B} T}{6 \pi \eta a} \frac{1}{\frac{2}{1-\frac{9 a}{8 H}}-1}=\frac{k_{B} T}{6 \pi \eta a} \frac{1-\frac{9 a}{8 H}}{1+\frac{9 a}{8 H}}=D_{0}-\frac{3 k T}{16 \pi \eta H}+o\left(\frac{1}{H}\right) \tag{6.107}
\end{equation*}
$$

which is in line with our result 3
We observe that the expansion of the diffusion constant $D$, constant obtained by the method of the paper 155 or by our method, tends towards the diffusion constant $D_{0}$ when $H$ tends towards infinity. This is interpreted by the fact that the farthest the walls are from the particle, the less influence they have, i.e. the closer we get to the configuration of the Stokes problem for an unconfined sphere ( cf 6.3 ).

[^19]On the below graph (figure 32, we can observe the behavior of $D_{0}-\frac{3 k T}{16 \pi \eta H}$, i.e. the diffusion constant $D$ that we have developed in (6.106), with respect to $D_{0}$, according to the $H / a$ ratio, i.e. the distance between the two walls and the radius of the sphere that represents the particle. It is noted that this ratio evolves while increasing, the greater the ratio $H / a$ is large, i.e. the greater the distance between the two walls in relation to the radius of the sphere, and it tends towards 1 at great distance. That is to say that when the walls are quite far enough, for the same $a$ radius, the sphere tends to act "as if" it was not confined between two walls. A suggestion of interpretation of this result is that the proximity of the particle to the walls influences the friction of the particle, which interferes with diffusion; therefore, if the sphere is strongly confined, it rubs more, which slows it down. Its diffusion is then less.


Figure 32 - Curve representing the ratio $\frac{\left(D_{0}-\frac{3 k T}{16 \pi \eta H}\right)}{D_{0}}$ as a function of the ratio of the distance between the two walls and the size of the particle

### 6.4 Study in the case with periodic boundary conditions

Let us consider the following problem on $\Omega$ : find $\mathbf{u}, p$, periodicals in $x$ and $y$, of period $L$, which verify 6.19 with the condition at the edges of the walls 6.20.

Theorem 10. Under the conditions of the problem, we have $\boldsymbol{u}$ of the form:

$$
\begin{align*}
\boldsymbol{u}(x, y, z) & =\boldsymbol{T}_{2}(x, y, z) \cdot \boldsymbol{F} \\
& =\frac{1}{L^{2}} A_{1}(0,0)(z)\left(\begin{array}{ccc}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0
\end{array}\right) \cdot \boldsymbol{F}+\frac{1}{L^{2}} \sum_{k \neq 0}\left(\left(A_{2}(\boldsymbol{k})(z)\left(\begin{array}{ccc}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0
\end{array}\right)+A_{3}(\boldsymbol{k})(z)\left(\begin{array}{ccc}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 1
\end{array}\right)\right.\right. \\
& \left.\left.+A_{4}(\boldsymbol{k})(z) \boldsymbol{k}^{*} \otimes \boldsymbol{k}^{*}\right)+i\left(A_{5}(\boldsymbol{k})(z)\left(\begin{array}{ccc}
0 & 0 & k_{1} \\
0 & 0 & k_{2} \\
0 & 0 & 0
\end{array}\right)+A_{6}(\boldsymbol{k})(z)\left(\begin{array}{ccc}
0 & 0 & 0 \\
0 & 0 & 0 \\
k_{1} & k_{2} & 0
\end{array}\right)\right)\right) e^{i \boldsymbol{k} \cdot(x, y)} \cdot \boldsymbol{F} \tag{6.108}
\end{align*}
$$

where $\boldsymbol{k}=2 \pi\left(\frac{m_{1}}{L}, \frac{m_{2}}{L}\right)$ with $\left(m_{1}, m_{2}\right) \in \mathbb{Z}^{2}$, and where, for $\boldsymbol{k}=\left(k_{1}, k_{2}\right)$ we have $\boldsymbol{k}^{*}=\left(k_{1}, k_{2}, 0\right)$ and $\boldsymbol{k}^{*} \otimes \boldsymbol{k}^{*}=\left(\begin{array}{cc}\boldsymbol{k} \otimes \boldsymbol{k} & \binom{0}{0} \\ \left(\begin{array}{ll}0 & 0\end{array}\right) & 0\end{array}\right)$, and with

$$
\begin{equation*}
A_{1}(0,0)(z)=\left(\frac{1}{2 \eta} z-\frac{z}{\eta} \mathbf{1}_{z \geq 0}+\frac{H}{4 \eta}\right) \tag{6.109}
\end{equation*}
$$

where the $A_{i}(i=2, \ldots, 7)$ are given in theorem 7.
Here, we observe that the symmetry of the problem is ensured (with respect to the $z=0$ axis). On the other hand, we can note that (we only look at the case where $z<0$, given the symmetry) if we take the term $A_{2}$ and we make expansions in order 1 for small $\|\mathbf{k}\|$ in its terms, we get :

$$
\begin{align*}
& \lim _{\|\mathbf{k}\| \rightarrow 0} \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)=1  \tag{6.110}\\
& \operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right)=\|\mathbf{k}\|\left(z+\frac{H}{2}\right)+o\left(\|\mathbf{k}\|^{2}\right) \tag{6.111}
\end{align*}
$$

So that for small $\|\mathbf{k}\|$ :

$$
\begin{equation*}
A_{2}(\mathbf{k})(z)=\frac{-z}{2 \eta}+\frac{H}{4 \eta}+o\left(\|\mathbf{k}\|^{2}\right) \tag{6.112}
\end{equation*}
$$

We then find $A_{1}(0,0)(z)$ !
Again, the reader interested in the physical aspect of the problem, not the mathematical one, may skip the following proof.
Proof. To begin with, since $\mathbf{u}, p$ and $\delta$ (in the distribution space) are periodic in $x$ and $y$, we can decompose them into Fourier series :
$\mathbf{u}(x, y, z)=\frac{1}{L^{2}} \sum_{\mathbf{k}} \mathbf{u}_{\mathbf{k}}(z) e^{i \mathbf{k} \cdot(x, y)}, p(x, y, z)=\frac{1}{L^{2}} \sum_{\mathbf{k}} p_{\mathbf{k}}(z) e^{i \mathbf{k} \cdot(x, y)}, \delta(x, y, z)=\frac{1}{L^{2}} \sum_{\mathbf{k}} \delta_{\mathbf{k}}(z) e^{i \mathbf{k} \cdot(x, y)}$
with $\mathbf{k}=2 \pi\left(\frac{m_{1}}{L}, \frac{m_{2}}{L}\right)$ où $\left(m_{1}, m_{2}\right) \in \mathbb{Z}^{2}$, and where $\mathbf{u}_{\mathbf{k}}(z), p_{\mathbf{k}}(z)$ and $\delta_{\mathbf{k}}(z)$ are the $k$ th Fourier coefficients of $\mathbf{u}, p$ and $\delta$ respectively.

## Step 1 :

Using the first equation of (6.19) and invoking the uniqueness of the coefficients of a Fourier series, we obtain the following equations for $\mathbf{k}=2 \pi\left(\frac{m_{1}}{L}, \frac{m_{2}}{L}\right)$ :

$$
\left\{\begin{array}{l}
\eta\left(\left(u_{\mathbf{k}}^{1}\right)^{\prime \prime}(z)-u_{\mathbf{k}}^{1}(z)\left(k_{1}^{2}+k_{2}^{2}\right)\right)=i k_{1} p_{\mathbf{k}}(z)-\delta_{\mathbf{k}}(z) F_{1}  \tag{6.114}\\
\eta\left(\left(u_{\mathbf{k}}^{2}{ }^{\prime \prime}(z)-u_{\mathbf{k}}^{2}(z)\left(k_{1}^{2}+k_{2}^{2}\right)\right)=i k_{2} p_{\mathbf{k}}(z)-\delta_{\mathbf{k}}(z) F_{2}\right. \\
\eta\left(\left(u_{\mathbf{k}}^{3}\right)^{\prime \prime}(z)-u_{\mathbf{k}}^{3}(z)\left(k_{1}^{2}+k_{2}^{2}\right)\right)=\left(p_{\mathbf{k}}\right)^{\prime}(z)-\delta_{\mathbf{k}}(z) F_{3}
\end{array}\right.
$$

where $\delta_{\mathbf{k}}(z)=\delta(z)$.
(For $\mathbf{k} \neq(0,0)$, we find the system of equations 6.44).

Using the second equation of (6.19), we have $\forall z \in\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
i k_{1} u_{\mathbf{k}}^{1}(z)+i k_{2} u_{\mathbf{k}}^{2}(z)+\left(u_{\mathbf{k}}^{3}\right)^{\prime}(z)=0 \tag{6.115}
\end{equation*}
$$

## Step 2 :

We take the divergence of the first equation of 6.19) and we obtain (similar calculations to step 2 of the proof of theorem 7) :

$$
\begin{equation*}
\Delta p=\mathbf{F} . \nabla \delta \tag{6.116}
\end{equation*}
$$

(since $\nabla \cdot \mathbf{u}=0$.

We then obtain :

$$
\begin{equation*}
\left(p_{\mathbf{k}}\right)^{\prime \prime}(z)-p_{\mathbf{k}}(z)\left(k_{1}^{2}+k_{2}^{2}\right)=i\left(k_{1} F_{1}+k_{2} F_{2}\right) g_{\mathbf{k}}(z)+F_{3} \delta_{\mathbf{k}}^{\prime}(z) \tag{6.117}
\end{equation*}
$$

For $\mathbf{k} \neq(0,0)$, we find the equation 6.49$)$.

The idea will then be to solve the equation for $p_{\mathbf{k}}$ then to inject the solution obtained into the equation of $u_{\mathbf{k}}^{i}(i=1,2,3)$ then to calculate the solution of the equation then obtained.

## Step 3 :

We are interested here in the case where $\mathbf{k} \neq(0,0)$. We set beforehand :

$$
\begin{equation*}
A=\frac{F_{3}}{2 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}, B=\frac{\mathbf{k}^{*} \cdot \mathbf{F}}{2\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)} \tag{6.118}
\end{equation*}
$$

where $\mathbf{k}^{*}=\binom{\mathbf{k}}{0}$. Proceeding in the same way as in step 4 of the proof of theorem 7 , we find :

$$
\begin{equation*}
p_{k}(z)=\alpha e^{\|\mathbf{k}\| z}+\beta e^{-\|\mathbf{k}\| z}+(-A-i B) \operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+(-A+i B) \operatorname{sh}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0} . \tag{6.119}
\end{equation*}
$$

And then :

$$
\begin{align*}
p_{k}^{\prime}(z) & =\|\mathbf{k}\|\left((-A-i B) \operatorname{ch}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+(-A+i B) \operatorname{ch}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\|\mathbf{k}\|\left(\alpha e^{\|\mathbf{k}\| z}-\beta e^{-\|\mathbf{k}\| z}\right)+2 A \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \delta(z) . \tag{6.120}
\end{align*}
$$

Then :

$$
\begin{align*}
& \left\{\begin{array}{c}
u_{\mathbf{k}}^{1}(z)=\alpha_{1} e^{\|\mathbf{k}\| z}+\beta_{1} e^{-\|\mathbf{k}\| z}-\frac{i k_{1}}{\eta} \frac{A}{2\|\mathbf{k}\|}\left(\left(t+\frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+\left(z-\frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
+\frac{k_{1}}{\eta} \frac{B z}{2 z \| \mathbf{k}}\left(\operatorname{ch}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z<0}-\operatorname{ch}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right)
\end{array}\right. \\
& +\frac{k_{1}}{\eta} \frac{B z}{2\|\mathbf{k}\|}\left(\operatorname{ch}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{ch}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& -\frac{k_{1} B}{2\|\mathbf{k}\|^{2} \eta}\left(\operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{sh}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\left(\frac{F_{1}}{2\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}+\frac{i k_{1} A H \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\right) \operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0} \\
& \left.+\left(\frac{-F_{1}}{2\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}+\frac{i k_{1} A H \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\right) \operatorname{sh}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\frac{i k_{1} z}{2\|\mathbf{k}\| \eta}\left(\alpha e^{\|\mathbf{k}\| z}-\beta e^{-\|\mathbf{k}\| z}\right) \\
& u_{\mathbf{k}}^{2}(z)=\alpha_{2} e^{\|\mathbf{k}\| z}+\beta_{2} e^{-\|\mathbf{k}\| z}-\frac{i k_{2}}{\eta} \frac{A}{2\|\mathbf{k}\|}\left(\left(z+\frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+\left(z-\frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\frac{k_{2}}{\eta} \frac{B z}{2\|\mathbf{k}\|}\left(\operatorname{ch}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{ch}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& -\frac{k_{2} B}{2\|\mathbf{k}\|^{2} \eta}\left(\operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{sh}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\left(\frac{F_{2}}{2\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}+\frac{i k_{2} A H \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\right) \operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0} \\
& \left.+\left(\frac{-F_{2}}{2\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}+\frac{i k_{2} A H \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\right) \operatorname{sh}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\frac{i k_{2} z}{2\|\mathbf{k}\| \eta}\left(\alpha e^{\|\mathbf{k}\| z}-\beta e^{-\|\mathbf{k}\| z}\right) \\
& u_{\mathbf{k}}^{3}(z)=\alpha_{3} e^{\|\mathbf{k}\| z}+\beta_{3} e^{-\|\mathbf{k}\| z}-\frac{A}{2 \eta}\left(\left(z+\frac{H}{2}\right) \operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+\left(z-\frac{H}{2}\right) \operatorname{sh}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& -\frac{i B z}{2 \eta}\left(\operatorname{sh}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}-\operatorname{sh}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\frac{A}{2\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\left(\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)+\frac{H\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{2}\right)\left(\operatorname{ch}\left(\|\mathbf{k}\|\left(z+\frac{H}{2}\right)\right) \mathbf{1}_{z \leq 0}+\operatorname{ch}\left(\|\mathbf{k}\|\left(z-\frac{H}{2}\right)\right) \mathbf{1}_{z>0}\right) \\
& +\frac{z}{2 \eta}\left(\alpha e^{\|\mathbf{k}\| z}+\beta e^{-\|\mathbf{k}\| z}\right) \tag{6.121}
\end{align*}
$$

## Step 4 :

The condition 6.20 gives us, by invoking the uniqueness of the coefficients of a Fourier series :

$$
\begin{equation*}
\mathbf{u}_{\mathbf{k}}\left( \pm \frac{H}{2}\right)=0 \tag{6.122}
\end{equation*}
$$

and then the $\alpha_{i}, \beta_{i}(i=1,2,3)$ are given in (6.82), 6.83) and 6.84.

## Step 5 :

We go back to 6.115 and then $\alpha$ and $\beta$ are given by 6.86.

## Step 6 :

Steps 3, 4 and 5 are repeated here when $\mathbf{k}=(0,0)$.
First of all we have :

$$
\begin{equation*}
\left(p_{(0,0)}\right)^{\prime \prime}(z)=F_{3} \delta^{\prime}(z) \tag{6.123}
\end{equation*}
$$

We then find with the lemma 14 :

$$
\begin{equation*}
p_{(0,0)}(z)=\alpha z+\beta+F_{3} \mathbf{1}_{z \geq 0} \tag{6.124}
\end{equation*}
$$

with $\alpha, \beta \in \mathbb{C}$. We replace in 6.114 , and then we get thanks to the lemma 10 :

$$
\left\{\begin{array}{l}
u_{(0,0)}^{1}(z)=\frac{-F_{1}}{\eta} z \mathbf{1}_{z \geq 0}+\alpha_{1} z+\beta_{1}  \tag{6.125}\\
u_{(0,0)}^{2}(z)=\frac{-F_{2}}{\eta} z \mathbf{1}_{z \geq 0}+\alpha_{2} z+\beta_{2} \\
u_{(0,0)}^{3}(z)=\frac{\alpha_{2}}{2 \eta} z^{2}+\alpha_{3} z+\beta_{3}
\end{array}\right.
$$

Using the conditions 6.122, we have :

$$
\left\{\begin{array} { l } 
{ \alpha _ { 1 } = \frac { F _ { 1 } } { 4 \eta } }  \tag{6.126}\\
{ \beta _ { 1 } = \frac { F _ { 1 } H } { 4 \eta } }
\end{array} \quad \left\{\begin{array} { l } 
{ \alpha _ { 2 } = \frac { F _ { 2 } } { 4 \eta } } \\
{ \beta _ { 2 } = \frac { F _ { 2 } H } { 4 \eta } }
\end{array} \quad \left\{\begin{array}{l}
\alpha_{3}=0 \\
\beta_{3}=\frac{-\alpha H^{2}}{8 \eta}
\end{array}\right.\right.\right.
$$

We now use the equation 6.115) and we get for $z \in\left[\frac{-H}{2}, \frac{H}{2}\right]$ :

$$
\begin{equation*}
0=\left(u_{\mathbf{k}}^{3}\right)^{\prime}(z)=\frac{\alpha}{\eta} z \tag{6.127}
\end{equation*}
$$

And then :

$$
\begin{equation*}
\alpha=0 . \tag{6.128}
\end{equation*}
$$

And since the pressure is defined to one constant, we can take $\beta=0$.

## Step 8 :

Using (6.82), 6.83, (6.84), (6.86), 6.121, 6.126 and 6.128), we have the final result.

Let $D_{\text {per }}$ be the diffusion coefficient in the case of a particle confined between two walls and when considering periodic boundary conditions. We try to calculate :

$$
\begin{equation*}
D_{p e r}=D_{0}+\frac{k_{B} T}{3} \lim _{\|(x, y, z)\| \rightarrow 0} \operatorname{Tr}\left(\mathbf{T}_{2}(x, y, z)-\mathbf{T}_{\text {Oseen }}(x, y, z)\right) \tag{6.129}
\end{equation*}
$$

We set :

$$
\begin{equation*}
C_{1}=\sum_{\mathbf{n} \neq(0,0)} \int_{\mathbb{R}^{2}} e^{-\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m . \tag{6.130}
\end{equation*}
$$

In order to verify the convergence of the series in 6.130, in what follows, we are interested in the behavior of $\int_{\mathbb{R}^{2}} e^{-\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m$ when $\|\mathbf{n}\|$ is large. We have the following lemma:

Lemma 17. When $\|\boldsymbol{n}\|$ is large :

$$
\begin{equation*}
\int_{\mathbb{R}^{2}} e^{-\|(l, m)\|^{2}}\left(\frac{1}{\|\boldsymbol{n}\|}-\frac{1}{\|-(l, m)+\boldsymbol{n}\|}\right) d l d m \sim \frac{C s t}{\|\boldsymbol{n}\|^{3}} \tag{6.131}
\end{equation*}
$$

which is a term associated with a convergent series, where :

$$
\begin{equation*}
C s t=\int_{0}^{\infty} \int_{0}^{2 \pi} e^{-s^{2}} s^{3}\left(1+4 \cos (\phi-\theta)^{2}\right) d s d \phi \tag{6.132}
\end{equation*}
$$

is a constant which is independant of $r$.

Proof. In polar coordinates, we have :

$$
\begin{align*}
\mathbf{n} & =r e^{i \theta}  \tag{6.133}\\
(l, m) & =s e^{i \phi} \tag{6.134}
\end{align*}
$$

where $r, s$ and $\theta, \phi$ are respectively the module and the argument of $\mathbf{n}$ and $(l, m)$. So that we get :

$$
\begin{align*}
\frac{1}{\|\mathbf{n}\|} & =\frac{1}{r}  \tag{6.135}\\
\frac{1}{\|-(l, m)+\mathbf{n}\|} & =\frac{1}{r e^{i \theta}-s e^{i \phi}}=\frac{1}{r\left\|1-\frac{s}{r} e^{\phi-\theta}\right\|} . \tag{6.136}
\end{align*}
$$

We have:

$$
\begin{equation*}
\left\|1-\frac{s}{r} e^{\phi-\theta}\right\|=\left(1-\frac{s}{r} \cos (\phi-\theta)\right)^{2}+\left(\frac{s}{r} \sin (\phi-\theta)\right)^{2}=1-\frac{2 s}{r} \cos (\phi-\theta)+\left(\frac{s}{r}\right)^{2} \tag{6.137}
\end{equation*}
$$

Since $\|\mathbf{n}\|$ is large, $r$ is large, so that $\frac{s}{r}$ is small. We then have :

$$
\begin{equation*}
\frac{1}{1-\frac{2 s}{r} \cos (\phi-\theta)+\left(\frac{s}{r}\right)^{2}}=1+\frac{2 s}{r} \cos (\phi-\theta)-\left(\frac{s}{r}\right)^{2}\left(1+4 \cos (\phi-\theta)^{2}\right)+o\left(\left(\frac{s}{r}\right)^{2}\right) \tag{6.138}
\end{equation*}
$$

So that we have :

$$
\begin{align*}
\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|} & =\frac{1}{r}-\frac{1}{r}\left(1+\frac{2 s}{r} \cos (\phi-\theta)-\left(\frac{s}{r}\right)^{2}\left(1+4 \cos (\phi-\theta)^{2}\right)+o\left(\left(\frac{s}{r}\right)^{2}\right)\right)  \tag{6.139}\\
& =\left(\frac{-2 s}{r^{2}} \cos (\phi-\theta)+\left(\frac{s^{2}}{r^{3}}\right)\left(1+4 \cos (\phi-\theta)^{2}\right)+o\left(\frac{s^{2}}{r^{3}}\right)\right) \tag{6.140}
\end{align*}
$$

and then :

$$
\begin{align*}
\int_{\mathbb{R}^{2}} & e^{-\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m \\
& =\int_{0}^{\infty} \int_{0}^{2 \pi} e^{-s^{2}}\left(\frac{-2 s}{r^{2}} \cos (\phi-\theta)+\left(\frac{s^{2}}{r^{3}}\right)\left(1+4 \cos (\phi-\theta)^{2}\right)+o\left(\frac{s^{2}}{r^{3}}\right)\right) s d s d \phi \tag{6.141}
\end{align*}
$$

The integrale of the first term is null by periodicity of the cosinus function. For the second term we have :

$$
\begin{equation*}
\int_{0}^{\infty} \int_{0}^{2 \pi} e^{-s^{2}}\left(\frac{s^{3}}{r^{3}}\right)\left(1+4 \cos (\phi-\theta)^{2}\right) d s d \phi=\frac{C s t}{r^{3}} \tag{6.142}
\end{equation*}
$$

where Cst is a constant which is independant of $r$.

Theorem 11. For $h=\frac{\pi H}{L}$, we have :

$$
\begin{align*}
D_{p e r} & =D_{0}+\frac{k_{B} T}{3}\left(\frac{H}{8 L^{2} \eta}+\frac{1}{2 \pi^{2} L \eta} C_{1}+\frac{1}{\eta 2 \pi L} \sum_{\left(m_{1}, m_{2}\right) \neq 0} \frac{1}{\left\|\left(m_{1}, m_{2}\right)\right\|} e^{-\pi^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}-\frac{1}{2 \pi^{1 / 2} L \eta}\right. \\
& \left.+\frac{1}{8 \pi^{2} H \eta} \sum_{\left(m_{1}, m_{2}\right) \neq 0} f\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right) h^{2}\right) \tag{6.143}
\end{align*}
$$

where

$$
\begin{align*}
f: x \mapsto- & \frac{(\operatorname{sh}(x)+x \operatorname{ch}(x))}{\operatorname{ch}(x)}\left(\frac{1}{\operatorname{sh}(x) \operatorname{ch}(x)+x}\right)+\frac{1}{\operatorname{ch}(x)^{2} \eta} \\
& -\left(\frac{x \operatorname{sh}(x)}{\operatorname{ch}(x)}+\frac{x^{2}}{\operatorname{ch}(x)^{2}}\right)\left(\frac{\operatorname{sh}(x)^{2}}{\operatorname{sh}(x)^{2} \operatorname{ch}(x)^{2}-x^{2}}\right) . \tag{6.144}
\end{align*}
$$

Proof. Let us take $z=0$ and look at $\operatorname{Tr}\left(\mathbf{T}_{2}(x, y, 0)\right)$. We have :

$$
\begin{aligned}
\operatorname{Tr}\left(\mathbf{T}_{2}(x, y, 0)\right)= & \frac{H}{8 L^{2} \eta}+\frac{1}{L^{2}} \sum_{\mathbf{k} \neq 0}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}-\frac{H}{8 \eta}+\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\| \| \mathbf{k} \| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}+\frac{H \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{8 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}\right. \\
& -\left(\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)+\frac{H\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{2}\right)\left(\frac{1}{4\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\right. \\
& \left.+\frac{\frac{H}{32 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}\left(1+\frac{H\|\mathbf{k}\|}{2}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)\right)}{\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}}\right) \\
+ & \frac{H}{8 \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}-\left(\frac{\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{H\|\mathbf{k}\|^{2}}{2}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}-1\right)\right) \\
& \left.\left(\frac{\frac{H^{2}}{64 \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}}{\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}}\right)-\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{4\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}\right) e^{i \mathbf{k} \cdot(x, y)}
\end{aligned}
$$

$$
\begin{equation*}
=\frac{H}{8 L^{2} \eta}+\frac{1}{L^{2}} \sum_{\mathbf{k} \neq 0}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right) \eta}-\left(\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)+\frac{H\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{2}\right)\right. \tag{6.145}
\end{equation*}
$$

$$
\left(\frac{\frac{H}{32 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}\left(1+\frac{H\|\mathbf{k}\|}{2}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)\right)}{\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}}\right)
$$

$$
+\frac{H}{8 \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}-\left(\frac{\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{H\|\mathbf{k}\|^{2}}{2}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}-1\right)\right)
$$

$$
\begin{equation*}
\left.\left(\frac{\frac{H^{2}}{64 \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}}{\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}}\right)\right) e^{i \mathbf{k} \cdot(x, y)} \tag{6.146}
\end{equation*}
$$

where the second equality derives from the remarks in the proof of theorem 9 .
With (6.93), we have:

$$
\begin{equation*}
\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{1}{\|\mathbf{k}\|}=\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)-\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}=\frac{-2}{\left(e^{\|\mathbf{k}\| H}+1\right)\|\mathbf{k}\|} \tag{6.147}
\end{equation*}
$$

So that :

$$
\begin{equation*}
\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}=\frac{1}{\|\mathbf{k}\|}-\frac{2}{\left(e^{\|\mathbf{k}\| H}+1\right)\|\mathbf{k}\|} \tag{6.148}
\end{equation*}
$$

The double series in 6.146) then converges absolutely for all terms, except the term in $\frac{1}{\|\mathbf{k}\|}$ which remains in 6.148.
In order to calculate $\frac{1}{\eta L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} e^{i \mathbf{k} .(x, y)}$, in what follows, we will apply an Ewald-type method, adapted to the double (and not triple) sum.

If we go back to Ewald's method (see Chapter 3, section 3.3.3), the physical idea here is to compensate the load points by a two-dimensional Gaussian. Let the Gaussian function $g:(x, y) \mapsto$ $\frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)\|^{2}}$, where $\alpha \in \mathbb{R}$.

We know that the Fourier transform of a Gaussian $X=\left(X_{1}, X_{2}\right) \sim N\left(O, \frac{1}{2 \alpha^{2}} I_{2}\right)$ corresponds to its characteristic function $E\left(e^{i X \mathbf{k}}\right)$, from where we get : $\hat{g}(\mathbf{k})=e^{-\frac{\mathbf{k}^{2}}{4 \alpha^{2}}}$.

We have :

$$
\frac{1}{L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\| \eta} e^{i \mathbf{k} \cdot(x, y)}=\frac{1}{\eta L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|}\left(1-e^{-\frac{\|\mathbf{k}\|^{2}}{4 \alpha^{2}}}\right) e^{i \mathbf{k} \cdot(x, y)}+\frac{1}{\eta L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\left.\|\mathbf{k}\|^{-\frac{\|\mathbf{k}\|^{2}}{4 \alpha^{2}}} e^{i \mathbf{k} \cdot(x, y)} . . . \begin{array}{ll} \tag{6.149}
\end{array}\right]}
$$

For the first sum, we wish to use the formula of Poisson. We consider $\widehat{h}:\left(k_{1}, k_{2}\right) \mapsto \frac{1}{\|\mathbf{k}\|}\left(1-e^{-\frac{\|\mathbf{k}\|^{2}}{4 \alpha^{2}}}\right)$ for $\left(k_{1}, k_{2}\right) \neq(0,0)$. Poisson's formula requires to have the term of Fourier transform for $\left(k_{1}, k_{2}\right)=$ $(0,0)$, that is why, by extension by continuity, we set $\widehat{h}(0,0)=0$ (which does not add or subtract a term in the end).

Since $\widehat{h}$ is of type $\widehat{h}=\widehat{f} \cdot \widehat{g}$, then $h$ is of type $h=f * g$ (where $*$ is the convolution product). Thus, we get :
$\frac{1}{\eta L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|}\left(1-e^{-\frac{\|\mathbf{k}\|^{2}}{4 \alpha^{2}}}\right) e^{i \mathbf{k} \cdot(x, y)}=\frac{1}{\eta} \sum_{\mathbf{n}}\left(\frac{1}{2 \pi\|(x, y)+\mathbf{n} L\|}-\frac{1}{2 \pi\|(x, y)+\mathbf{n} L\|} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)+\mathbf{n} L\|^{2}}\right)$.

## Back to the calculation of $D_{p e r}$ :

By injecting 6.150 into 6.149) and subtracting by 6.89 and then taking the limits when $\|(x, y)\| \rightarrow 0$ it is still to be calculated :

$$
\begin{align*}
\xi & :=\lim _{\|(x, y)\| \rightarrow 0}\left(\frac{1}{\eta} \sum_{\mathbf{n}}\left(\frac{1}{2 \pi\|(x, y)+\mathbf{n} L\|}-\frac{1}{2 \pi\|(x, y)+\mathbf{n} L\|} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)+\mathbf{n} L\|^{2}}\right)\right. \\
& \left.+\frac{1}{\eta L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} e^{-\frac{\|\mathbf{k}\|^{2}}{4 \alpha^{2}}} e^{i \mathbf{k} \cdot(x, y)}-\frac{1}{2 \pi\|(x, y)\| \eta}\right) . \tag{6.151}
\end{align*}
$$

We have :

$$
\begin{align*}
\xi & =\frac{1}{\eta} \sum_{\mathbf{n} \neq(0,0)}\left(\frac{1}{2 \pi\|\mathbf{n} L\|}-\lim _{\|(x, y)\| \rightarrow 0} \frac{1}{2 \pi\|(x, y)+\mathbf{n} L\|} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)+\mathbf{n} L\|^{2}}\right) \\
& +\frac{1}{\eta L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} e^{-\frac{\| \mathbf{k} \mathbf{N}^{2}}{4 \alpha^{2}}}-\lim _{\|(x, y)\| \rightarrow 0} \frac{1}{2 \pi\|(x, y)\| \eta} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)\|^{2}} . \tag{6.152}
\end{align*}
$$

Step 1 : We have :

$$
\begin{equation*}
\frac{1}{2 \pi\|(x, y)\|} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)\|^{2}}=\int_{\mathbb{R}^{2}} \frac{1}{2 \pi\|(x-l, y-m)\|} \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(l, m)\|^{2}} d l d m . \tag{6.153}
\end{equation*}
$$

Using the Lebesgue dominated convergence theorem and then switching to polar variable we obtain :

$$
\begin{align*}
\lim _{\|(x, y)\| \rightarrow 0} \frac{1}{2 \pi\|(x, y)\|} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)\|^{2}} & =\int_{\mathbb{R}^{2}} \frac{1}{2 \pi\|(l, m)\|} \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(l, m)\|^{2}} d l d m \\
& =\int_{0}^{\infty} \int_{0}^{2 \pi} \frac{\alpha^{2}}{2 \pi^{2}} e^{-\alpha^{2} r^{2}} d \theta d r \\
& =\frac{\alpha}{2 \pi^{1 / 2}} \tag{6.154}
\end{align*}
$$

after recognizing the integral of a Gaussian in the second tie.
Step 2: We have :

$$
\begin{equation*}
\frac{1}{2 \pi\|(x, y)+\mathbf{n} L\|} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)+\mathbf{n} L\|^{2}}=\int_{\mathbb{R}^{2}} \frac{1}{2 \pi\|(x-l, y-m)+\mathbf{n} L\|} \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(l, m)\|^{2}} d l d m . \tag{6.155}
\end{equation*}
$$

So that using the Lebesgue dominated convergence theorem we have :

$$
\begin{equation*}
\lim _{\|(x, y)\| \rightarrow 0} \frac{1}{2 \pi\|(x, y)+\mathbf{n} L\|} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)+\mathbf{n} L\|^{2}}=\int_{\mathbb{R}^{2}} \frac{1}{2 \pi\|-(l, m)+\mathbf{n} L\|} \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(l, m)\|^{2}} d l d m \tag{6.156}
\end{equation*}
$$

We make the change of variable $(l, m) \rightarrow(l L, m L)$ and we get :

$$
\begin{equation*}
\lim _{\|(x, y)\| \rightarrow 0} \frac{1}{2 \pi\|(x, y)+\mathbf{n} L\|} * \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(x, y)+\mathbf{n} L\|^{2}}=\int_{\mathbb{R}^{2}} \frac{L}{2 \pi\|-(l, m)+\mathbf{n}\|} \frac{\alpha^{2}}{\pi} e^{-\alpha^{2} L^{2}\|(l, m)\|^{2}} d l d m . \tag{6.157}
\end{equation*}
$$

Step 3: For the first term of the series, the integral of a centered Gaussian and of variance $\sigma=\frac{1}{2 \alpha^{2}} \mathbf{I}_{2}$ is introduced (this integral is therefore worth 1) :

$$
\begin{equation*}
\frac{1}{2 \pi\|\mathbf{n} L\|}=\int_{\mathbb{R}^{2}} \frac{1}{2 \pi\|\mathbf{n} L\|} \frac{\alpha^{2}}{\pi} e^{-\alpha^{2}\|(l, m)\|^{2}} d l d m \tag{6.158}
\end{equation*}
$$

We make the change of variable $(l, m) \rightarrow(l L, m L)$ and we get :

$$
\begin{equation*}
\frac{1}{2 \pi\|\mathbf{n} L\|}=\int_{\mathbb{R}^{2}} \frac{L}{2 \pi\|\mathbf{n}\|} \frac{\alpha^{2}}{\pi} e^{-\alpha^{2} L^{2}\|(l, m)\|^{2}} d l d m \tag{6.159}
\end{equation*}
$$

Step 4: Differentiating the results of steps 2 and 3, and using step 1 and applying the ansatz
(see paragraph 6.2), we then find :

$$
\begin{align*}
& D_{p e r}= D_{0}+\frac{k_{B} T}{3}\left(\frac{H}{8 L^{2} \eta}+\frac{L}{\eta} \frac{\alpha^{2}}{2 \pi^{2}} \sum_{\mathbf{n} \neq(0,0)}\left(\int_{\mathbb{R}^{2}} e^{-\alpha^{2} L^{2}\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m\right)\right. \\
&+ \frac{1}{\eta L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} e^{-\frac{\|\mathbf{k}\|^{2}}{4 \alpha^{2}}}-\frac{\alpha}{2 \pi^{1 / 2} \eta}+\frac{1}{L^{2}} \sum_{\mathbf{k} \neq 0}\left(-\left(\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)+\frac{H\|\mathbf{k}\| \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{2}\right)\right. \\
&\left(\frac{\frac{H}{32 \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right) \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}\left(1+\frac{H\|\mathbf{k}\|}{2}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \| \frac{H}{2}\right)}\right)\right)}{\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}}\right) \\
&+\frac{H}{8 \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}-\left(\frac{\|\mathbf{k}\| \operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{H\|\mathbf{k}\|^{2}}{2}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2}}-1\right)\right) \\
&\left.\left.\left(\frac{\frac{H^{2}}{64 \operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)^{2} \eta}}{\frac{1}{4}-\frac{\|\mathbf{k}\|^{2} H^{2}}{16}\left(\frac{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}-\frac{\operatorname{ch}\left(\|\mathbf{k}\| \frac{H}{2}\right)}{\operatorname{sh}\left(\|\mathbf{k}\| \frac{H}{2}\right)}\right)^{2}}\right)\right)\right) . \tag{6.160}
\end{align*}
$$

We recall that $\mathbf{k}=\frac{2 \pi}{L}\left(m_{1}, m_{2}\right)$ with $m_{i} \in \mathbb{N}(i=1,2)$. Doing the indexing change $\mathbf{k} \rightarrow\left(m_{1}, m_{2}\right)$ for the series, we get :

$$
\begin{aligned}
& D_{\text {per }}=D_{0}+\frac{k_{B} T}{3}\left(\frac{H}{8 L^{2} \eta}+\frac{L}{\eta} \frac{\alpha^{2}}{2 \pi^{2}} \sum_{\mathbf{n} \neq(0,0)}\left(\int_{\mathbb{R}^{2}} e^{-\alpha^{2} L^{2}\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m\right)\right. \\
& +\frac{1}{\eta 2 \pi L} \sum_{\left(m_{1}, m_{2}\right) \neq(0,0)} \frac{1}{\left\|\left(m_{1}, m_{2}\right)\right\|} e^{-\frac{\pi^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}{L^{2} \alpha^{2}}}-\frac{\alpha}{2 \pi^{1 / 2} \eta} \\
& +\frac{1}{L^{2}} \sum_{\left(m_{1}, m_{2}\right) \neq 0}\left(-\left(\operatorname{sh}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)+\frac{\pi H\left\|\left(m_{1}, m_{2}\right)\right\| \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)}{L}\right)\right.
\end{aligned}
$$

$$
\begin{align*}
& +\frac{H}{8 \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)^{2} \eta} \\
& -\left(\frac{\pi H\left\|\left(m_{1}, m_{2}\right)\right\| \operatorname{sh}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)}{L \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)}-\frac{\pi^{2} H^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}{L^{2}}\left(\frac{\operatorname{sh}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)^{2}}{\operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)^{2}}-1\right)\right) \\
& \left.\left(\frac{\frac{H}{32 \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)^{2} \eta}}{\frac{\frac{1}{4}-\frac{\left\|\left(m_{1}, m_{2}\right)\right\|^{2} \pi^{2} H^{2}}{4 L^{2}}\left(\frac{\operatorname{sh}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{H}\right)}{\operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)}-\frac{\operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)}{\operatorname{sh} \|\left(\left\|\left(m_{1}, m_{2}\right)\right\| \frac{\pi H}{L}\right)}\right)^{2}}{L}}\right)\right) . \tag{6.161}
\end{align*}
$$

By taking $h=\frac{\pi H}{L}$ and by using hyperbolic trigonometry formulas, we finally get :

$$
\left.\left.\begin{array}{rl}
D_{p e r} & =D_{0}+\frac{k_{B} T}{3}\left(\frac{H}{8 L^{2} \eta}+\frac{L}{\eta} \frac{\alpha^{2}}{2 \pi^{2}} \sum_{\mathbf{n} \neq(0,0)}\left(\int_{\mathbb{R}^{2}} e^{-\alpha^{2} L^{2}\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m\right)\right. \\
& +\frac{1}{\eta 2 \pi L} \sum_{\left(m_{1}, m_{2}\right) \neq(0,0)} \frac{1}{\left\|\left(m_{1}, m_{2}\right)\right\|} e^{-\frac{\pi^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}{L^{2} \alpha^{2}}}-\frac{\alpha}{2 \pi^{1 / 2} \eta} \\
& +\frac{1}{L^{2}} \sum_{\left(m_{1}, m_{2}\right) \neq 0}\left(-\left(\operatorname{sh}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)+h\left\|\left(m_{1}, m_{2}\right)\right\| \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)\right)\right. \\
& \left.+\frac{\frac{H}{8 \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right) \eta}}{8 \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)^{2} \eta}\right) \\
& -\left(\frac{h\left\|\left(m_{1}, m_{2}\right)\right\| \operatorname{sh}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)}{\operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)}+\frac{h^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}{\operatorname{sh}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right) \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)+\left\|\left(m_{1}, m_{2}\right)\right\| h}\right) \\
\quad\left(\frac{H \operatorname{sh}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)^{2}}{8 \eta}\right) \\
& \left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)^{2} \operatorname{ch}\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)^{2}-\left\|\left(m_{1}, m_{2}\right)\right\|^{2} h^{2} \tag{6.162}
\end{array}\right)\right) .
$$

We define :

$$
\begin{align*}
f: x \mapsto- & \frac{(\operatorname{sh}(x)+x \operatorname{ch}(x))}{\operatorname{ch}(x)}\left(\frac{1}{\operatorname{sh}(x) \operatorname{ch}(x)+x}\right)+\frac{1}{\operatorname{ch}(x)^{2} \eta} \\
& -\left(\frac{x \operatorname{sh}(x)}{\operatorname{ch}(x)}+\frac{x^{2}}{\operatorname{ch}(x)^{2}}\right)\left(\frac{\operatorname{sh}(x)^{2}}{\operatorname{sh}(x)^{2} \operatorname{ch}(x)^{2}-x^{2}}\right) . \tag{6.163}
\end{align*}
$$

So that:

$$
\begin{align*}
D_{p e r} & =D_{0}+\frac{k_{B} T}{3}\left(\frac{H}{8 L^{2} \eta}+\frac{L}{\eta} \frac{\alpha^{2}}{2 \pi^{2}} \sum_{\mathbf{n} \neq(0,0)}\left(\int_{\mathbb{R}^{2}} e^{-\alpha^{2} L^{2}\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m\right)\right. \\
& \left.+\frac{1}{\eta 2 \pi L} \sum_{\left(m_{1}, m_{2}\right) \neq(0,0)} \frac{1}{\left\|\left(m_{1}, m_{2}\right)\right\|} e^{-\frac{\pi^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}{L^{2} \alpha^{2}}}-\frac{\alpha}{2 \pi^{1 / 2} \eta}+\frac{H}{8 L^{2} \eta} \sum_{\left(m_{1}, m_{2}\right) \neq 0} f\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right)\right) . \tag{6.164}
\end{align*}
$$

In order to obtain a Riemann'series for the last series, we have to multiply $f$ by $h^{2}$ so that we get :

$$
\begin{align*}
D_{\text {per }} & =D_{0}+\frac{k_{B} T}{3}\left(\frac{H}{8 L^{2} \eta}+\frac{L}{\eta} \frac{\alpha^{2}}{2 \pi^{2}} \sum_{\mathbf{n} \neq(0,0)}\left(\int_{\mathbb{R}^{2}} e^{-\alpha^{2} L^{2}\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m\right)\right. \\
& \left.+\frac{1}{\eta 2 \pi L} \sum_{\left(m_{1}, m_{2}\right) \neq(0,0)} \frac{1}{\left\|\left(m_{1}, m_{2}\right)\right\|} e^{-\frac{\pi^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}{L^{2} \alpha^{2}}}-\frac{\alpha}{2 \pi^{1 / 2} \eta}+\frac{H}{8 L^{2} \eta} \frac{1}{h^{2}} \sum_{\left(m_{1}, m_{2}\right) \neq 0} f\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right) h^{2}\right) . \tag{6.165}
\end{align*}
$$

This being valid $\forall \alpha>0$, it is true in particular for $\alpha=\frac{1}{L}(>0)$ and we then obtain, recalling
also that $h=\frac{\pi H}{L}$ :

$$
\begin{align*}
D_{p e r} & =D_{0}+\frac{k_{B} T}{3}\left(\frac{H}{8 L^{2} \eta}+\frac{1}{2 \pi^{2} L \eta} \sum_{\mathbf{n} \neq(0,0)}\left(\int_{\mathbb{R}^{2}} e^{-\|(l, m)\|^{2}}\left(\frac{1}{\|\mathbf{n}\|}-\frac{1}{\|-(l, m)+\mathbf{n}\|}\right) d l d m\right)\right. \\
& \left.+\frac{1}{\eta 2 \pi L} \sum_{\left(m_{1}, m_{2}\right) \neq(0,0)} \frac{1}{\left\|\left(m_{1}, m_{2}\right)\right\|} e^{-\pi^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}-\frac{1}{2 \pi^{1 / 2} L \eta}+\frac{1}{8 \pi^{2} H \eta} \sum_{\left(m_{1}, m_{2}\right) \neq 0} f\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right) h^{2}\right) . \tag{6.166}
\end{align*}
$$

Let interest us to the case where $H / L$ is small. For the first four terms of 6.143), when we multiply each term by $H$, we can easily see that they converges towards 0 in that case, as it corresponds respectively to a constant multiplies by $(H / L)^{2}$ and to a constant multiplies by $H / L$. The term in $\frac{H}{L^{2}}$ seems to show an attenuation of the effect of walls on the diffusion of the particle by periodicity.

The last series being a Riemann's series, we have for $H / L \rightarrow 0$ :

$$
\begin{equation*}
\sum_{\left(m_{1}, m_{2}\right) \neq 0} f\left(\left\|\left(m_{1}, m_{2}\right)\right\| h\right) h^{2} \rightarrow \int_{\mathbb{R}^{2}} f(\mathbf{x}) d \mathbf{x}:=I \tag{6.167}
\end{equation*}
$$

We then have :

$$
\begin{equation*}
D_{p e r}=D_{0}+\frac{k_{B} T}{3} \frac{I}{8 \pi^{2} H \eta}\left(1+o\left(\frac{H}{L}\right)\right) . \tag{6.168}
\end{equation*}
$$

For large $L$, we know with theorem 9 that the first term of expansion in $H$ is :

$$
\begin{equation*}
\frac{-3 k_{b} T}{16 \pi H \eta} \tag{6.169}
\end{equation*}
$$

so that it can be conjecture that ${ }^{4}$ :

$$
\begin{equation*}
I=\frac{-9 \pi}{2} \tag{6.170}
\end{equation*}
$$

If we want to obtain the second order for the expansion of $D_{p e r}$, we have on the one hand the three terms in the begining of $\sqrt{6.143}$ ( $n o t$ the first one, but the three after it). On the other hand, for $\int_{\mathbb{R}^{2}} f(\mathbf{x}) d \mathbf{x}$, we can observe the last series and decompose the integral on square $P_{m_{1}, m_{2}}=\left[m_{1} h-\frac{h}{2}, m_{1} h+\frac{h}{2}\right] \times\left[m_{2} h-\frac{h}{2}, m_{2} h+\frac{h}{2}\right]$ of size $h^{2}$ and centered on point $\left(x_{m 1}, x_{m 2}\right)$ with $x_{m i}=m_{i} h$ (for $i=1,2$ ), and we can consider a Taylor expansion of the order 2 of $f$ on each $P_{m_{1}, m_{2}}$ i.e. :

$$
\begin{equation*}
\int_{\mathbb{R}^{2}} f(\mathbf{x}) d \mathbf{x}=\sum_{\left(m_{1}, m_{2}\right)} \int_{P_{m_{1}, m_{2}}} f(\mathbf{x}) d \mathbf{x} \tag{6.171}
\end{equation*}
$$

with

$$
\begin{align*}
f(\mathbf{x})= & f\left(x_{m 1}, x_{m 2}\right)+\left(x-x_{m 1}\right) \frac{\partial f}{\partial x}\left(x_{m 1}, x_{m 2}\right)+\left(y-x_{m 2}\right) \frac{\partial f}{\partial y}\left(x_{m 1}, x_{m 2}\right)+\frac{1}{2}\left(x-x_{m 1}\right)^{2} \frac{\partial^{2} f}{\partial x^{2}}\left(x_{m 1}, x_{m 2}\right) \\
& +\frac{1}{2}\left(y-x_{m 2}\right)^{2} \frac{\partial^{2} f}{\partial y^{2}}\left(x_{m 1}, x_{m 2}\right)+\left(x-x_{m 1}\right)\left(y-x_{m 2}\right) \frac{\partial^{2} f}{\partial x \partial y}\left(x_{m 1}, x_{m 2}\right)+o\left(h^{2}\right) . \tag{6.172}
\end{align*}
$$

4. To calculate that integral, an idea might be to use a numerical integration of Gauss-Laguerre

The integral of the second, the third and the last term of 6.172 on $P_{m_{1}, m_{2}}$ is null by parity on the square. For the fourth and fifth terms, we have :

$$
\begin{equation*}
\int_{P_{m_{1}, m_{2}}} \frac{1}{2}\left(x-x_{m 1}\right)^{2} \frac{\partial^{2} f}{\partial x^{2}}\left(x_{m 1}, x_{m 2}\right) d x d y=\frac{h^{4}}{24} \frac{\partial^{2} f}{\partial x^{2}}\left(m_{1} h, m_{2} h\right) \tag{6.173}
\end{equation*}
$$

and

$$
\begin{equation*}
\int_{P_{m_{1}, m_{2}}} \frac{1}{2}\left(y-x_{m 2}\right)^{2} \frac{\partial^{2} f}{\partial y^{2}}\left(x_{m 1}, x_{m 2}\right) d x d y=\frac{h^{4}}{24} \frac{\partial^{2} f}{\partial y^{2}}\left(m_{1} h, m_{2} h\right) . \tag{6.174}
\end{equation*}
$$

We then have:

$$
\begin{equation*}
\sum_{\left(m_{1}, m_{2}\right)} \int_{P_{m_{1}, m_{2}}} f(\mathbf{x}) d \mathbf{x}=\sum_{\left(m_{1}, m_{2}\right)}\left(f\left(x_{m 1}, x_{m 2}\right) h^{2}+\frac{h^{4}}{24} \frac{\partial^{2} f}{\partial x^{2}}\left(m_{1} h, m_{2} h\right)+\frac{h^{4}}{24} \frac{\partial^{2} f}{\partial y^{2}}\left(m_{1} h, m_{2} h\right)\right) \tag{6.175}
\end{equation*}
$$

For the last two terms, we have :

$$
\begin{align*}
\sum_{\left(m_{1}, m_{2}\right)} \frac{h^{4}}{24} \frac{\partial^{2} f}{\partial x^{2}}\left(m_{1} h, m_{2} h\right) & =\frac{h^{2}}{24} \sum_{\left(m_{1}, m_{2}\right)} \frac{\partial^{2} f}{\partial x^{2}}\left(m_{1} h, m_{2} h\right) h^{2}  \tag{6.176}\\
\sum_{\left(m_{1}, m_{2}\right)} \frac{h^{4}}{24} \frac{\partial^{2} f}{\partial y^{2}}\left(m_{1} h, m_{2} h\right) & =\frac{h^{2}}{24} \sum_{\left(m_{1}, m_{2}\right)} \frac{\partial^{2} f}{\partial y^{2}}\left(m_{1} h, m_{2} h\right) h^{2} \tag{6.177}
\end{align*}
$$

where, for $h \rightarrow 0$, we have, as Riemann's series :

$$
\begin{align*}
\sum_{\left(m_{1}, m_{2}\right)} \frac{\partial^{2} f}{\partial x^{2}}\left(m_{1} h, m_{2} h\right) h^{2} & \rightarrow \int_{\mathbb{R}^{2}} \frac{\partial^{2} f}{\partial x^{2}}(x, y) d x d y  \tag{6.178}\\
\sum_{\left(m_{1}, m_{2}\right)} \frac{\partial^{2} f}{\partial y^{2}}\left(m_{1} h, m_{2} h\right) h^{2} & \rightarrow \int_{\mathbb{R}^{2}} \frac{\partial^{2} f}{\partial y^{2}}(x, y) d x d y \tag{6.179}
\end{align*}
$$

We recall that $h=\frac{\pi H}{L}$ so that $h^{2}=\pi^{2}\left(\frac{H}{L}\right)^{2}$.
If we take a Taylor expansion of highter order for $f$ on each $P_{m_{1}, m_{2}}$, they should be on $o\left(\left(\frac{H}{L}\right)^{2}\right)$.
At the end, we can rewrite $D_{\text {per }}$ as :

$$
\begin{equation*}
D_{p e r}=D_{0}-\frac{3 k_{B} T}{16 \pi H \eta}\left(1-\frac{8}{9} C_{2} \frac{H}{L}+o\left(\left(\frac{H}{L}\right)\right)\right) \tag{6.180}
\end{equation*}
$$

with :

$$
\begin{equation*}
C_{2}=\frac{1}{\pi} C_{1}+\sum_{\left(m_{1}, m_{2}\right) \neq(0,0)} \frac{1}{\left\|\left(m_{1}, m_{2}\right)\right\|} e^{-\pi^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}}-\pi^{1 / 2} \tag{6.181}
\end{equation*}
$$

where we recall that $C_{1}$ is defined in 6.130.

We numerically have

$$
\begin{equation*}
C_{1} \simeq-6.2387 \quad \text { and } \sum_{\left(m_{1}, m_{2}\right) \neq(0,0)} \frac{1}{\left\|\left(m_{1}, m_{2}\right)\right\|} e^{-\pi^{2}\left\|\left(m_{1}, m_{2}\right)\right\|^{2}} \simeq 2.06910^{-4} \tag{6.182}
\end{equation*}
$$

so that

$$
\begin{equation*}
C_{2} \simeq-3.7579 \tag{6.183}
\end{equation*}
$$

Finally, we get :

$$
\begin{equation*}
D_{p e r} \simeq D_{0}-\frac{3 k_{B} T}{16 \pi H \eta}\left(1+3.3403 \frac{H}{L}+o\left(\left(\frac{H}{L}\right)\right)\right) \tag{6.184}
\end{equation*}
$$

With that expansion, we can easily see that when $H \rightarrow \infty$ and $H / L \rightarrow 0$ we have $D_{\text {per }} \rightarrow D_{0}$, i.e. it corresponds to the non-periodic and non-confined case. Moreover, here we can see that the correction due to the ratio between the two walls $H$ and the period $L$ is not negligible, so that this is important to take into accompt that correction in order to find the diffusion coefficient in the non-periodic and non-confined case.


Figure 33 - Curve representing the ratio $\frac{\left(D_{0}-\frac{3 k T}{16 \pi \eta H}\left(1+3.3403 \frac{H}{L}\right)\right)}{D_{0}}$ as a function of the ratio of the distance between the two walls $H$ and the size of the particle $a$ and for different ratio of $H$ and the period $L$. These curves are compared to the ratio $\frac{\left(D_{0}-\frac{3 k T}{16 \pi \eta H}\right)}{D_{0}}$ found in the previous section in the non-periodic case

On the graph (figure 33), we can observe the behavior of $\frac{\left(D_{0}-\frac{3 k T}{16 \pi \eta H}\left(1+3.3403 \frac{H}{L}\right)\right)}{D_{0}}$, i.e. the diffusion constant $D$ that we have developed in 6.184, with respect to $D_{0}$, according to the $H / a$ ratio, i.e. the distance between the two walls and the radius of the sphere that represents
the particle, and for different $H / L$ ratios. These behaviors are compared to that of $\frac{\left(D_{0}-\frac{3 k T}{16 \pi \eta H}\right)}{D_{0}}$ found in the previous section in the non-periodic case. We can see that the curves in the periodic case are below those in the non-periodic case, i.e. the diffusion is less in that case. That fact can be compared to that of 6.10 which similarly shows that the diffusion in unconfined and periodic case is less than those in non-periodic case.

### 6.5 Conclusion

In this chapter, we first determined the velocity of a particle evolving in a fluid confined between two parallel walls, this particle being placed at equal distance from these two walls. We have considered an Oseen-type approximation, where the fluid is subjected to a point of force $\mathbf{F}$. Our calculations then led us to express the velocity as a tensor $\mathbf{T}$ multiplied by the force $\mathbf{F}$. A Kirkwood-Riseman type approach then allowed us to establish the diffusion constant according to the considered boundary conditions. We then calculated an expansion of the constant obtained when the walls are quite far from each other. We first performed this method when considering non-periodic boundary conditions, and thus obtained an expansion in agreement with an expansion of the constant obtained by Saugey and al. We then adapted our calculations when considering periodic boundary conditions and obtained an expansion of the diffusion constant under these conditions, an expansion which is a function of the distance between the two walls and the periodicity of the problem, and which is also a function of the diffusion constant for a particle evolving in an unconfined fluid and with non-periodic conditions. The expansion that we got has a simple expression which allows to see that for $H \rightarrow \infty$ and $H / L \rightarrow 0$ we have $D_{\text {per }} \rightarrow D_{0}$, i.e. we approximate the non-periodic and non-confined case.

Several perspectives could extend this work. First of all, it would be interesting to numerically calculate the ratio for different values of $H / L$ in order to determine the role of boundary conditions for all values of this geometric coefficient, and not only for those corresponding to large boxes compared to the lateral dimension. Thanks to the obtained expansion and to the limiting values, it should be possible to obtain by fitting a practical expression valid for any geometry. A second obvious generalisation would be to look at the case where the particle moves perpendicularly to the planes. The role of the hydrodynamic boundary conditions should also be analysed. We have considered a non-slip surface with sticky boundary conditions at the walls. However, in some porous media the fluid can slide on the surface and the boundary condition depends on a new parameter, the slip length. Diffusion should also be studied as a function of this parameter.

## Chapitre 7

## Conclusion and perspectives

## Conclusion :

In this thesis, we were particularly interested in the study of the influence of periodic edge conditions often introduced during molecular simulations, and thus to make corrections for the calculation of the quantity of interest by numerical experiments, corrections taking into account the periodicity.

On the one hand, we wanted to study the McMillan and Mayer potential of a system formed by two ions surrounded by $N$ water molecules for which we consider, as reaction coordinate, the distance between the two ions. From a theoretical point of view, we determined an expansion of the potential of a system made up of two ions rather distant from each other and surrounded by a solvent of dielectric constant $\epsilon_{r}$, expansion which is a function of the considered period $L$ and which approaches a Coulombic potential all the more as $L$ is large. From a numerical point of view, we have considered three cubic simulation boxes with respective sides $24,662 \mathrm{~A}, 36,342$ A and $53,000 \mathrm{~A}$, and containing a $\mathrm{Na}^{+}$, an ion $\mathrm{Cl}^{-}$and $N_{i}$ water molecules $(i=1,2,3$ referring to the $i$ th box). We used the Tinker-hp software to perform simulations of molecular dynamics. We wanted to use the Umbrella Sampling method, so for the chosen reaction coordinate (the distance between the two ions) we added a spring force to keep the two ions at a certain distance. We then obtained the Mean Force Potential from the WHAM method, and then calculated the McMillan and Mayer potential. Since one of the challenges was to fix the constant defining the McMillan and Mayer potential, our goal was to use our expansion to fit the potential curve with the McMillan and Mayer potential at a large distance. We also calculated the resulting association constants, corrected with our expansion or not, and thus were able to observe an effect due to our correction, the smaller the size of the box is, and also a result not depending on $L$ when we previously corrected the potential. We also studied the potential of McMillan and Mayer, obtained for lanthanide salts, using or not using the correction made by our expansion, in order to calculate again the association constant. With our tests, we have seen that the correction with the period that we have obtained here has in fact low influence in the calculations.

On the other hand, we sought to obtain an expansion of the diffusion constant for a particle moving in a fluid confined between two walls. To do so, we considered an Oseen-type approximation, i.e. we modelled the system by a fluid moving between two walls and subjected to a point of force $\mathbf{F}$. We have established an expansion according to the distance between the two walls when we consider the point of force at the same distance from the two walls. First of all, we placed ourselves in the case of non-periodic conditions and obtained an expansion in agreement
with the constant obtained by Saugey and al. This expansion is close to the diffusion constant in the case of a particle in an unconfined fluid with non-periodic conditions especially as the two walls are far from each other. In addition, we considered periodic boundary conditions and adapted our calculations, which allowed us to come to an expansion of the diffusion constant under these conditions, based on a mathematical hypothesis. This is a correction of the diffusion constant in the case of an unconfined particle with non-periodic conditions. This correction is a function of the distance between the two walls and the period of the problem. Here the correction that we obtained is not negligible in order to get the diffusion coefficient in the non-periodic case.

## Perspectives :

First of all, concerning the behavior of the Potential of Mean Force, it would be a question of deepening the study of cases of real interest, such as Lanthanids in the aqueous phase, since these components intervene in the processes of treatment of radioactive waste, and potentials have been specifically developed.
The study should also be continued in the case of more complex systems, and extended with a more detailed description of such systems using the QM/MM method which, it should be recalled, describes the system at the quantum level where the chemical reaction takes place, and the other part at the molecular level.

Concerning the study of the diffusion coefficient, this one having been limited in the case of a particle placed at equal distance from each wall, it would be judicious to analyze the more general case where the particle always moves parallel to the two walls but placed at a distance $z$ from the bottom wall. In addition, we carried out our study with non-slip conditions (stick) on the edges of the walls ; it would be necessary to observe the case of slip conditions, or partial slip. One idea would be to try to perform the "exact" calculations, i.e. to consider a Stokes equation with conditions at the edges of the sphere that describes the particle, and not using an Oseen equation. One idea, to do this, would be to use the method of reflections, considering on the one hand the case of a Stokes equation for a particle moving in a straight line in an unconfined fluid with periodic conditions (perhaps it would be necessary to adapt the calculations made by Stokes), and on the other hand the case of a fluid confined between two walls (see the calculations made by Saugey and al.).
From a numerical point of view, it would be interesting to carry out molecular dynamics simulations in order to observe the diffusion coefficient under our conditions and its evolution as a function of the size of the simulation boxes, and to compare it with the one we have obtained from our calculations.
It would also be interesting to make a comparison between the analytical results and those obtained with a fluid dynamics software, in order to interpret a possible discrepancy between molecular dynamics and the analytical calculations as being either hypotheses (fluid dynamics / molecular dynamics difference) or approximations for the analytical calculation (difference between the calculation we made and the fluid dynamics).

Finally, in order to improve the duration of simulations, it would be interesting to study the introduction of H-matrices [79] in molecular dynamics calculation algorithms. The H-matrices (H for Hierarchical), developed around 2000, are used to solve problems of the type $A x=b$ and have a complexity in $O\left(n \log _{2}^{\alpha}(n)\right)$ ( $n$ being the number of unknowns).

## Bibliographie

[1] 26è CGPM, Versailles, 13-16 novembre 2018
[2] Agence nationale pour la gestion des déchets radioactifs, Inventaire national des matières et déchets radioactifs, Rapport de Synthèse 2018
[3] Agence nationale pour la gestion des déchets radioactifs, Projet Cigeo
[4] G.Allaire, M.Briane, R.Brizzi, Y.Capdeboscq Two asymptotic models for arrays of underground waste containers, Applicable Analysis, 88 :10-11, 1445-1467, 2009
[5] P.G.Allen, J.J.Bucher, D.K.Shuh, N.M.Edelstein, T.Reich, Investigation of Aquo and Chloro Complexes of $\mathrm{UO}_{2}^{2+}, \mathrm{Np} \mathrm{O}_{2}^{+}, \mathrm{Np} p^{4+}$, and $\mathrm{Pu}^{3+}$ by X-ray Absorption Fine Structure Spectroscopy, Inorg. Chem. , 36, 21, 4676-4683, 1997
[6] M.P.Allen, D.J.Tildesley, Computer Simulations of Liquids, Clarendon Press-Oxford, 1991
[7] M.Andrec, The Weighted Histogram Analysis Method (WHAM), 2010
[8] W.Appel, Mathématiques pour la physique et les physiciens!, H and K Editions
[9] F.Archambault, Vers une modélisation plus réaliste des systèmes biologiques, Thèse de doctorat soutenue en 2011
[10] Article L542-1-1, du Code de l'Environnement, relatif aux déchets radioactifs et leur gestion
[11] R.Atta-Fynn, E.J.Bylaska, G.K.Schenter, W.A.deJong, Hydration Shell Structure and Dynamics of Curium (III) in Aqueous Solution First Principles and Empirical Studies, J. Phys. Chem. A, 115, 18, 4665-4677, 2011
[12] P.Bacle, J.-F.Dufrêche, B.Rotenberg, I.C.Bourg, V.Marry, Modeling the transport of water and ionic tracers in a micrometric clay sample, Appl. Clay Sci. 123, 18-28, 2016
[13] V.Ballenegger, Traitement exact de la longue portée des interactions coulombiennes dans les systèmes chargés : développements méthodologiques et applications, Habilitation à diriger des recherches soutenue en 2013
[14] J.Barthel, H.Krienke, M.F.Holovko, V.I.Kapko, I.A.Protsykevich, The application of the associative mean spherical approximation in the theory of nonaqueous electrolyte solutions, Condensed Matter Physics, 3, 657-674, 2000
[15] G.K.Batchelor, An Introduction to Fluid Dynamics, Cambridge University Press, 1973
[16] C.Bauer, P.Bauduin, J.-F.Dufrêche, T.Zemb, O.Diat, Liquid/liquid metal extraction : Phase diagram topology resulting from molecular interactions between extractant, ion, oil and water, Eur. Phys. J. Special Topics 213, 225-241, 2012
[17] P.Beale, R. Pathria, Statistical Mechanics, Academic Press, Boston, USA, 2011
[18] H.J.C.Berendsen, J.P.M.Postma, W.F.van Gunsteren, A.DiNola and J.R.Haak, Molecular dynamics with coupling to an external bath, J. Chem. Phys. 81, 3684, 1984
[19] O.Bernard, L.Blum, Binding mean spherical approximation for pairing ions : An exponential approximation and thermodynamics, J. Chem. Phys. 104, 4746, 1996
[20] G.Berthe, Évolution des propriétés de confinement des roches-couvertures type argilite soumises à des fluides enrichis en CO2 : impact des discontinuités naturelles et artificielles, thèse de doctorat soutenue en 2013
[21] C.Beuchat, D.Hagberg, R.Spezia, L.Gagliardi, Hydration of Lanthanide Chloride Salts : A Quantum Chemical and Classical Molecular Dynamics Simulation Study, J. Phys. Chem. B 114, 47, 15590-15597, 2010
[22] M.Bley, M.Duvail, P.Guilbaud, J.-F.Dufrêche, Activity Coefficients of Aqueous Sodium, Calcium, and Europium Nitrate Solutions from Osmotic Equilibrium MD Simulations, J. Phys. Chem. B 122, 31, 7726-7736, 2018
[23] M.Bley, M.Duvail, P.Guilbaud, J.-F.Dufrêche, Simulating Osmotic Equilibria : A New Tool for Calculating Activity Coefficients in Concentrated Aqueous Salt Solutions, J. Phys. Chem. B 121, 41, 9647-9658, 2017
[24] M.Bley, B.Siboulet, A.Karmakar, T.Zemb, J.-F.Dufrêche, A predictive model of reverse micelles solubilizing water for solvent extraction, J. Colloid Interface Sci. 479, 106-114, 2016
[25] L.Blum, O.Bernard, The general solution of the binding mean spherical approximation for pairing ions, Journal of Statistical Physics, 79, 569-583, 1995
[26] L.Blum, J.Hoye, Mean spherical model for asymmetric electrolytes. 2. Thermodynamic properties and the pair correlation function, J. Phys. Chem., 81, 13, 1311-1316, 1977
[27] L.Bocquet, J.-L.Barrat, Hydrodynamic boundary conditions, correlation functions, and Kubo relations for confined fluids, Phys. Rev. E 49, 3079, 1994
[28] E.S.Boek, M.Sprik, Ab initio molecular dynamics study of the hydration of a sodium smectite clay, J. Phys. Chem. B 107, 14, 3251-3256, 2003
[29] M.Born, T.von Karmann, Uber Schwingungen in Raumgittern, Physik. Z. 13, 1912
[30] H.Boumaza, Théorie des distributions, 2015-2016
[31] M.P.Breil, J.M.Mollerup, The McMillan-Mayer framework and the theory of electrolyte solutions, Fluid Phase Equilibria, 242, 129-135, 2006
[32] B.Brendebach, N.L.Banik, C.M.Marquardt, J.Rothe, M.Denecke, H.Geckeis, X-ray absorption spectroscopic study of trivalent and tetravalent actinides in solution at varying pH values Radiochim. Acta 97, 701-708, 2009
[33] V.Cachia, La formule de Trotter-Kato : approximation des semi-groupes en normes d'opérateur et de trace, thèse de doctorat soutenue en 2008
[34] J.W.Caldwell and P.A.Kollman, Structure and Properties of Neat Liquids Using Nonadditive Molecular Dynamics : Water, Methanol, and N-Methylacetamide, The Journal of Physical Chemistry, 99, 16, 6208-6219, 1995
[35] D.Chandler, Introduction to Modern Statistical Mechanics, Oxford University Press, 1987
[36] S.Chaussedent, A.Monteil, Molecular dynamics simulation of trivalent europium in aqueous solution : A study on the hydration shell structure, J. Chem. Phys. 105, 6532, 1996
[37] Y.S.Chen, M.Duvail, P.Guilbaud, J.-F.Dufrêche, Stability of reverse micelles in rare-earth separation : a chemical model based on a molecular approach, Phys. Chem. Chem. Phys. 19, 7094-7100, 2017
[38] A.A.Chialvo, P.T.Cummings, J.M.Simonson, R.E.Mesmer, Temperature and density effects on the high temperature ionic speciation in dilute $\mathrm{Na}^{+} / \mathrm{Cl}^{-}$aqueous solutions, J.Chem.Phys.105, 9248, 1996
[39] C.Clavaguera, F.Calvo, J.-P.Dognon, Theoretical study of the hydrated Gd ${ }^{3+}$ ion : Structure, dynamics, and charge transfer, J. Chem. Phys. 124, 074505, 2006
[40] P.D'Angelo, A Zitolo, V.Migliorati, G.Chillemi, M.Duvail, P.Vitorge, S.Abadie, R.Spezia, Revised Ionic Radii of Lanthanoid(III) Ions in Aqueous Solution , Inorg. Chem. 50, 10, 4572-4579, 2011
[41] M.Defranceschi, W.Kutzelnigg, C.Le Bris, Y.Maday, Computational Quantum Chemistry, Handbook of numerical analysis, P.G.Ciarlet Editor, Volume X, North-Holland, 2003
[42] C.Déjugnat, S.Dourdain, V.Dubois, L.Berthon, S.Pellet-Rostaing, J.-F.Dufrêche, T.Zemb, Reverse aggregate nucleation induced by acids in liquid-liquid extraction processes, Phys. Chem. Chem. Phys. 16, 7339-7349, 2014
[43] F.Delay, P.Sardini, G.Porel, Modelling diffusion in a heterogeneous matrix with a time domain Lagrangian method and an inversion procedure, Compte-Rendu Géosciences 334, 967973, 2002
[44] J.Delay, A.Trouiller, J.-M.Lavanchy, Hydrodynamic properties of the Callovo-Oxfordian formation in the East of the Paris Basin : comparison of results obtained through different approaches, Comptes Rendus Géoscience 338, 892-907, 2006
[45] S.W. Deleeuw, J.W. Perram, E.R. Smith, Simulation of electrostatic systems in periodic boundary conditions.1. lattice sums and dielectric-constants, Proc. R. Soc. Lond. A., 373, 1752, 1980
[46] S.W. Deleeuw, J.W. Perram, E.R. Smith, Simulation of electrostatic systems in periodic boundary conditions 2. equivalence of boundary-conditions, Proc. R. Soc. Lond. A., 373, 1752, 1980
[47] H.De Raedt,B.De Raedt, Applications of the generalized Trotter formula, Physical Review A 28, 3575, 1983
[48] E.Despiau-Pujo, Principes de la Dynamique Moléculaire, Atelier RPF MD, 28-30 octobre 2015
[49] D.N.Dewhurst, A.C.Aplin, J.P.Sarda, Y.Yang, Compaction driven evolution of porosity and permeability in natural mudstones : an experimental study Journal of Geophysical Research 103(B1), 651-661, 1998
[50] D.N.Dewhurst, Y.Yang, A.C.Aplin, Permability and fluid flow in natural mudstones, Geological Society of London, Special Publications, 158, 23-45, 1999
[51] N.Diaz, Modélisation prédictive de la migration des anions par description de la microstructure de la roche : application à l'argilite du Callovo-Oxfordien, thèse de doctorat soutenue en 2009
[52] J.-F.Dufreche, Les différentes versions du second principe comprises grâce à la formule de Boltzmann $S=k_{B} \ln W$ Ou comment la thermodynamique peut se ramener à une simple question de bon sens, exposé du vendredi 29 novembre 2019 à Marcoule
[53] J.-F.Dufrêche, B.Rotenberg, V.Marry, P.Turq, Bridging molecular and continuous descriptions : the case of dynamics in clays, Anais da Academia Brasileira de Ciencias, 2010
[54] J.-F.Dufrêche, T.Zemb, Effect of long-range interactions on ion equilibria in liquid-liquid extraction, Chem. Phys. Lett. 622, 45-49, 2015
[55] M.Duvail, Etude des trications lanthanide en solution aqueuse par dynamique moléculaire, Thèse de doctorat soutenue en 2007
[56] M.Duvail, Modélisation multi-échelle pour les phénomènes de transfert en chimie séparative : de l'atome au procédé, Habilitation à diriger des recherches
[57] M.Duvail, P.Guilbaud, Understanding the nitrate coordination to Eu3+ ions in solution by potential of mean force calculations, Phys. Chem. Chem. Phys. 13, 5840-5847, 2011
[58] M.Duvail, F.Martelli, P.Vitorge, R.Spezia, Polarizable interaction potential for molecular dynamics simulations of actinoids(III) in liquid water, J. Chem. Phys. 135, 044503, 2011
[59] M.Duvail, A.Ruas, L.Venault, P.Moisy, and P.Guilbaud, Molecular Dynamics Studies of Concentrated Binary Aqueous Solutions of Lanthanide Salts : Structures and Exchange Dynamics, Inorganic Chemistry, 49, 2, 519-530, 2010
[60] M.Duvail, M.Souaille, R.Spezia, T.Cartailler, P.Vitorge, Pair interaction potentials with explicit polarization for molecular dynamics simulations of La3+ in bulk water, J. Chem. Phys. 127, 034503, 2007
[61] M.Duvail, S.van Damme, P.Guilbaud, Y.Chen, T.Zemb, J.-F.Dufrêche, The role of curvature effects in liquid-liquid extraction : assessing organic phase mesoscopic properties from $M D$ simulations, Soft Matter 13, 5518-5526, 2017
[62] A.Einstein, Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen, Annalen der Physik 4, 549-560 1905
[63] L.C. Evans, Partial Differential Equations, Graduate Studies in Mathematics, ol.19, American Mathematical Society
[64] P.P.Ewald, Die Berechnung optischer und elektrostatischer Gitterpotentiale, Annalen der Physik 369, 3, 1921
[65] C.J.Fennell, A.Bizjak, V.Vlachy, K.A.Dill, Ion Pairing in Molecular Simulations of Aqueous Alkali Halide Solutions, J. Phys. Chem. 113, 19, 6782-6791, 2009
[66] D.Frenkel, Why colloidal systems can be described by statistical mechanics : some not very original comments on the Gibbs paradox, Molecular Physics, 112, 17, 2014
[67] D.Frankel and B.Smit, Understanding Molecular Simulation, From Algorithms to Applications, Second Edition, Academic Press, 2002
[68] D.Frenkel, P.B.Warren, Gibbs, Boltzmann, and negative temperatures, Am. J. Phys. 83, 163, 2015
[69] H.L.Friedman, Lewis-Randall to McMillan-Mayer conversion for the thermodynamic excess functions of solutions. Part I. Partial free energy coefficients, J. Sol. Chem. 1, 387-412, 1972
[70] S.Galera, J.-M.Lluch, A.OLiva, J.Bertram, E.Foglia, L.Helm, A.E.Marbach, Monte Carlo simulations of the tripositive lanthanide ions in aqueous solution, New. J. Chem. 17, 12, 773-779, 1993
[71] L.Garnier, J.Devémy, C.Bonnal, P.Malfreyt, Calculations of potential of mean force : application to ion-pairs and host-guest systems, Journal of Molecular Physics 116, 15-16, 2018
[72] E.Gaucher, C.Robelin, J.M. Matray, G. Négrel, Y.Gros, J.F. Heitz, A.Vinsot, H.Rebours, A.Cassagnabère, A.Bouchet, ANDRA underground research laboratory : interpretation of the mineralogical and geochemical data acquired in the Callovian-Oxfordian formation by investigative drilling, Physics and Chemistry of the Earth, Parts A/B/C 29, 1, 55-77, 2004
[73] A.Gerschel, Liaisons intermoleculaires, les forces en jeu dans la matière condensée, CNRS Editions, 1995
[74] A.Gloria, T.Goudon, S.Krell, Numerical homogenization of a nonlinearly coupled ellipticparabolic system, reduced basis method, and application to nuclear waste storage, Mathematical Models and Methods in Applied Sciences, World Scientific 23, 13, 2523-2560, 2013
[75] C.Glusa, G.Blanchard, S.Calisti, S.Calvet, P.Fourment, R.Leblanc, M.Quillas-Saavedra, Compréhension de la nage à faible nombre de Reynolds, Rapport final, 2010
[76] F.Golse, cours de Distributions, analyse de Fourier, équations aux dérivées partielles, 2012
[77] S.Granick, Motions and Relaxations of Confined Liquids, Science 253, 5026, 1374-1379, 1991
[78] A.Habenschuss, F.H.Spedding, The coordination (hydration) of rare earth ions in aqueous chloride solutions from $x$ ray diffraction. $I . T b C l_{3}, D y C l_{3}, E r C l_{3}, T m C l_{3}$, and $\mathrm{LuCl}_{3}$, J. Chem. Phys. 70, 2797, 1979
[79] W. Hackbusch, A Sparse Matrix Arithmetic Based on H-Matrices. Part I : Introduction to H-Matrices, Computing 62, 89-108, 1999
[80] J.P. Hansen, I.R. McDonald, Theory of simple liquids : with applications to soft matter, Fourth Edition, Academic Press, 2013
[81] J.Happel, H.Brenner, Low Reynolds Number Hydrodynamics, Springer Science and Business Media, 1973
[82] L.Helm, A.E.Merbach, Inorganic and Bioinorganic Solvent Exchange Mechanisms, Chem.Rev 105, 6, 1923-1960 2005
[83] B.Hess, C.Holm and N.van der Vegt, Osmotic coefficients of atomistic NaCl (aq) force fields, J. Chem. Phys. 124, 164509, 2006
[84] P.Hetzel, D.Bataille, Etude de la faisabilité de la saisine sur "les enjeux stratégiques des terres rares", par la Commission des affaires économiques du Sénat, 2014
[85] A.E.Howard, U.Chandra Singh,M.Billeter and P.A.Kollman, Many-Body Potential for Molecular Interactions, J.Am.Chem.Soc. 110, 21, 6984-6991, 1988
[86] G.C. Hsiao, W.L. Wendland, Boundary Integral Equations, Applied Mathematical Sciences 164, Springer
[87] D.Huilier, Ecoulement de Stokes - faible nombre de Reynolds, 2010
[88] G.Hummer, L.R.Pratt, A.E.García, Molecular Theories and Simulation of Ions and Polar Molecules in Water, J. Phys. Chem. A 102, 41, 7885-7895, 1998
[89] P.H.Hunenberger, J.A.Mc Cammon, Ewald artifacts in computer simulations of ionic solvation and ion-ion interaction : A continuum electrostatics study, J. Chem. Phys. 110, 1856, 1999
[90] T.Ikeda, M.Hireta, T.Kimura, Hydration structure of $Y^{3+}$ and $L a^{3+}$ compared : An application of metadynamics, J. Chem. Phys. 122, 244507, 2005
[91] R.W.Impey, P.A.Madden, I.R.McDonald, Spectroscopic and transport properties of water : Model calculations and the interpretation of experimental results, Molecular Physics 46, 513539, 1982
[92] R.W.Impey, P.A.Madden, D.J.Tildesley, On the calculation of the orientational correlation parameter $g_{2}$, Molecular Physics 44, 1319-1334, 1981
[93] J.Jiang, J.C.Renshaw, M.J.Sarsfield, F.R.Livens, D.Collison, J.M.Charnock, H.Eccles, Solution Chemistry of Uranyl Ion with Iminodiacetate and Oxydiacedate : A Combined NMR/EXAFS and Potentiometry/Calorimetry Study, Inorg. Chem. 42, 4, 1233-1240, 2003
[94] N.Kaltsoyannis, P.Scott, The f Elements, Oxford Chemistry Primers, Oxford University Press, Oxford, 1999
[95] A.Karmakar, M.Duvail, M.Bley, T.Zemb, J.-F.Dufrêche, Combined supramolecular and mesoscale modelling of liquid-liquid extraction of rare earth salts, Elsevier 555, 713-727, 2018
[96] H.-S.Kim, Solvent effect on $\mathrm{La}^{3+}$ to $\mathrm{Nd}^{3+}$ ion mutation : a Monte Carlo simulation study, Chem. Phys Lett. 330, 570-576, 2000
[97] J.G.Kirwood, J.Riseman, The Intrinsic Viscosities and Diffusion Constants of Flexible Macromolecules in Solution, J. Chem. Phys. 16, 565, 1948
[98] M.A.Koriche, Caractérisation du comportement couplé des argilites de Meuse/Haute-Marne aux états saturé et partiellement saturé, thèse de doctorat soutenue en 2004
[99] K.W.Kratky, W.Schreiner, Computational techniques for spherical boundary conditions, J.Compu.Phys. 47, 313-320, 1982
[100] S.Kumar, D.Bouzida, R.H.Swendsen, P.A.Kollman, J.M.Rosenberg, The weighted histogram analysis method for free-energy calculations on biomolecules. I : The method, Journal of Computational Chemistry 13, 1011-1021, 1992
[101] L.Lagardère, L-H.Jolly, F.Lipparini, F.Aviat, B.Stamm, Z.F.Jing, M.Harger, H.Torabifard, G.Andrés Cisneros, M.J. Schnieders, N.Gresh, Y.Maday, P.Y.Ren, J.W.Ponder, J-P.Piquemal, Tinker-HP : a massively parallel molecular dynamics package for multiscale simulations of large complex systems with advanced point dipole polarizable force fields, Chem. Sci. 9, 956972, 2018
[102] La radioactivité, déchet radioactif, Retraitement combustible, Procédé Purex, Institut National de Physique Nucléaire et de Physique des Particules
[103] P.Laurent, Méthodes d'accéleration pour la résolution numérique en électrolocation et en chimie quantique, Thèse de doctorat soutenue en 2015
[104] P.Laurent, G.Legendre, J.Salomon, On the method of reflections, hal-01439871v2, 2017
[105] T.Lelièvre, M.Rousset, G.Stoltz, Free Energy Computations, A Mathematical Perspective, Imperial College Press, 2010
[106] J.E.Lennard-Jones, On the Determination of Molecular Fields. II. From the Equation of State of a Gas, Proceedings of the Royal Society 106, 738, 1924
[107] M.Lisicki, Four approaches to hydrodynamic Green's functions - the Oseen tensors, arXiv :1312.6231 [physics.flu-dyn], 2013
[108] Loi du 30 décembre 1991 relative aux recherches sur la gestion des déchets radioactifs
[109] Loi du 28 juin 2006 de programme relative à la gestion durable des matières et déchets radioactifs
[110] J.H.C.Luke, Convergence of a multiple reflection method for calculating Stokes flow in a suspension, SIAM J. Appl. Math. 49, 1635-1651, 1989
[111] Y.Luo, W.Jiang, H.Yu, A.D.MacKerell, Jr., B.Roux, Simulation study of ion pairing in concentrated aqueous salt solutions with a polarizable force field, Faraday Discuss. 160, 135149, 2013
[112] N.Malikova, V.Marry, J.-F.Dufrêche, P.Turq, Temperature effect in a montmorillonite clay at low hydration-microscopic simulation, Mol. Phys. 102, 1965-1977, 2004
[113] M.J.Mandell, On the properties of a periodic fluid, J. Stat. Phys. 15, 299-305, 1976
[114] Y.Marcus, Ionic radii in aqueous solutions, Chem. Rev. 88, 8, 1475-1498, 1988
[115] Y.Marcus, G.Hefter, Ion Pairing, Chem. Rev. 106, 11, 4585-4621, 2006
[116] V.Marry, P.Turq, Microscopic simulations of interlayer structure and dynamics in bihydrated heteroionic montmorillonites, J. Phys. Chem. B 107, 8, 1832-1839, 2003
[117] J.-M.Matray, S.Savoye, J.Cabrera, Desaturation and structure relationships around drifts excavated in the well-compacted Tournemire's argillite (Aveyron, France), Engineering Geology 90, 1-16, 2007
[118] J.M.McKibben, Chemistry of the Purex Process, Radiochimica Acta 36, 3-15, 1984
[119] W. McLean, Strongly Elliptic Systems and Boundary Integral Equations, Cambridge University Press, 2000
[120] W.G.McMillan, J.E.Mayer, The Statistical Thermodynamics of Multicomponent Systems, The Journal of Chemical Physics 13, 276, 1945
[121] D.A.McQuarrie, Statistical mechanics, Harper and Row, New York, USA, 1975
[122] C.C.Mei, Notes on Advanced Environmental Fluid Mechanics, 2001
[123] W.Meier, P.Bopp, M.M.Probst, E.Spohr, J.L.Lin, Molecular dynamics studies of lanthanum chloride solutions, J. Phys. Chem. 94, 11, 4672-4682, 1990
[124] T. Melkior, S.Yahiaoui, D.Thoby, V.Barthèse, Diffusion coefficients of alkaline cations in Bure mudrock, Physics and Chemistry of the Earth, Parts A/B/C 32, 453-462, 2007
[125] E.C.Meng and P.A.Kollman, Molecular Dynamics Studies of the Properties of Water around Simple Organic Solutes, J. Phys. Chem. 100, 27, 11460-11470, 1996
[126] P.Moeyaert, T.Dumas, D.Guillaumont, K.Kvashnina, C.Sorel, M.Miguirditchian, P.Moisy, J.-F.Dufrêche, Modeling and Speciation Study of Uranium(VI) and Technetium(VII) Coextraction with DEHiBA, Inorg. Chem. 55, 13, 6511-6519, 2016
[127] J.J.Molina, Multi-scale modelling of ions in solution : from atomistic descriptions to chemical engineering, Thèse de doctorat soutenue en 2011
[128] J.J.Molina, J.-F.Dufrêche, M.Salanne, O.Bernard, M.Jardat, P.Turq, Models of electrolyte solutions from molecular descriptions : The example of NaCl solutions, Phys. Rev. E 80, 065103(R), 2009
[129] J.J.Molina, J-F.Dufrêche, M.Salanne, O.Bernard, P.Turq, Primitive models of ions in solution from molecular descriptions : A perturbation approach, J. Chem. Phys. 135, 234509, 2011
[130] J.J.Molina, M.Duvail, J-F.Dufrêche,and P.Guilbaud, Atomistic description of binary lanthanoid salt solutions : a coarse-graining approach, J. Phys. Chem. B 2011, 115, 15, 4329-4340, 2011
[131] C.Moyne, M.A.Murad, Electro-chemo-mechanical couplings in swelling clays derived from a micro/macro-homogenization procedure, Int. J. Solids Struct. 39, 6159-6190, 2002
[132] S.Nosé, A unified formulation of the constant temperature molecular dynamics methods, Journal of Chimical Physics 81, 511, 1984
[133] T.-N.Nguyen, Modélisation des solutions aqueuses concentrées d'éléments-f par une approche multi-échelle, Thèse de doctorat soutenue en 2015
[134] T.N.Nguyen, M.Duvail, A.Villard, J.J.Molina, P.Guilbaud, J.-F.Dufrêche, Multi-scale modelling of uranyl chloride solutions, J. Chem. Phys. 142, 024501, 2015
[135] S.O.Odoh, G.Schreckenbach, Theoretical Study of the Structural Properties of Plutonium(IV) and (VI) Complexes, J. Phys. Chem. A 115, 48, 14110-14119, 2011
[136] package de Packmol
[137] D.Patriarche, J.-L.Michelot, E.Ledoux, S.Savoye, Diffusion as the main process for mass transport in very low water content argillites : 1. Chloride as a natural tracer for mass transport-Diffusion coefficient and concentration measurements in interstitial water, Water.Resour. Res. 40, W01516, 2004
[138] D.F.Peppard, P.R.Gray, M.M.Markus, The Actinide—Lanthanide Analogy as Exemplified by Solvent Extraction Behavior, J. Am. Chem. Soc. 75, 23, 6063-6064, 1953
[139] I.Persson, P.D'Angelo, S.De Panfilis, M.Sandstrom, L.Eriksson, Hydration of Lanthanoid(III) Ions in Aqueous Solution and Crystalline Hydrates Studied by EXAFS Spectroscopy and Crystallography : The Myth of the "Gadolinium Break" Chem. -Eur. J. 14, 3056-3066, 2008
[140] J.W.Ponder, Tinker Molecular Modeling Pachage
[141] J.W.Ponder, C.Wu, V.S.Pande, J.D.Chodera, M.J.Schnieders, I.Haque, D.L.Mobley, D.S.Lambrecht, R.A.DiStasio, M.Head-Gordon, G.N.I.Clark, M.E.Johnson, T.Head-Gordon, Current Status of the AMOEBA Polarizable Force Field, J. Phys. Chem. B 114, 2549-2564, 2010
[142] S.Poulain, Caractérisation microbiologique de l'argile à Opalinus du Mont Terri et de l'argilite du Callovo-Oxfordien de Meuse/Haute-Marne, thèse de doctorat soutenue en 2008
[143] L.R.Pratt, S.W.Haan, Effects of periodic boundary-conditions on equilibrium properties of computer-simulated fluids. I. Theory, J. Chem. Phys. 74, 1864, 1981
[144] L.R.Pratt, S.W Haan, Effects of periodic boundary-conditions on equilibrium properties of computer-simulated fluids. II. Application to simple liquids, J. Chem. Phys. 74, 1873, 1981
[145] B.Radola, Modélisation à l'échelle moléculaire des aérosols carbonés dans la troposphère, Thèse de doctorat soutenu en 2017
[146] J.-L.Raimbault, cours d'Analyse de Fourier au sens des distributions, 2008
[147] P.Ren, J.W.Ponder, Polarizable Atomic Multipole Water Model for Molecular Mechanics Simulation, J. Phys. Chem. 107, 24, 5933-5947, 2003
[148] J.-C.Robinet, Minéralogie, porosité et diffusion des solutés dans l'argilite du CallovoOxfordien de Bure (Meuse, Haute-Marne, France) de l'échelle centimétrique à micrométrique, thèse de doctorat soutenue en 2008
[149] B.Rode, T.S.Hofer, How to access structure and dynamics of solutions : The capabilities of computational methods (Special Topic Article), Pure Appl. Chem. 78, 525-539, 2006
[150] B.Rotenberg, Modélisation multi-échelles du comportement de l'eau et des ions dans les argiles, Thèse de doctorat soutenue en 2007
[151] B.Roux, The calculation of the potential of mean force using computer simulations, Computer Physics Communications 91, 275-282, 1995
[152] A.Ruas, P.Guilbaud, C.Den Auwer, C.Moulin, J.-P.Simonin, P.Turq, P. Moisy, Experimental and Molecular Dynamics Studies of Dysprosium(III) Salt Solutions for a Better Representation of the Microscopic Features Used within the Binding Mean Spherical Approximation Theory, J. Phys. Chem. A 110, 41, 11770-11779, 2006
[153] A.Ruas, P.Moisy, J.-P.Simonin, O.Bernard, J.-F.Dufrêche, P.Turq, Lanthanide Salts Solutions : Representation of Osmotic Coefficients within the Binding Mean Spherical Approximation, J. Phys. Chem. B 109, 11, 5243-5248, 2005
[154] F.Salles, J.-M.Douillard, R.Denoyel, O.Bildstein, M.Jullien, I.Beurroies, H.Van Damme, Hydration sequence of swelling clays : Evolutions of specific surface area and hydration energy, Journal of Colloid and Interface Science 333, 510-522, 2009
[155] A.Saugey, L.Joly, C.Ybert, J-L.Barrat, L.Bocquet, Diffusion in pores and its dependence on boundary conditions, Journal Of Physics-Condensed Matter 17, S4075, 2005
[156] S.Savoye, J.Cabrera, J.-M.Matray, Different hydraulic properties of single fractures in argillaceous medium : the case of the IRSN Tournemire site (France), Groundwaters in Fractured Rocksn(France. In : Krasny, J.,Hrkal,Z., Bruthans J., Eds.), IHP-VI, series on groundwater, No.7, 383-384, 2003
[157] M.Schoen, J.H.Cushman, D.J.Diestler, C.L.Rhykerd Jr., Fluids in micropores. II. Selfdiffusion in a simple classical fluid in a slit pore, J. Chem. Phys. 88, 1394, 1988
[158] H.M.Senn, W.Thiel, QM/MM Methods for Biomolecular Systems, Angew. Chem. Int. Ed. 48, 1198-1229, 2009
[159] C.D.Shackelford, Laboratory diffusion testing for waste disposal - A review, Journal of Contaminant Hydrology 7, 177-217, 1991
[160] Y.Shi, Z.Xia, J.Zhang, R.Best, C.Wu, J.W.Ponder, P.Ren, Polarizable Atomic MultipoleBased AMOEBA Force Field for Proteins, J. Chem. Theory Comput. 9, 9, 4046-4063, 2013
[161] M.R.Shirts, J.D.Chodera, Statistically optimal analysis of samples from multiple equilibrium states, J. Chem. Phys. 129, 124105, 2008
[162] D.E.Smith and L.X.Dang, Computer simulations of NaCl association in polarizable water, J. Chem. Phys. 100, 3757-3766, 1994
[163] M.Souaille, B.Roux, Extension to the weighted histogram analysis method : combining umbrella sampling with free energy calculations, Computer Physics Communications 135, 40-57, 2001
[164] M.Špadina, K.Bohinc, T.Zemb, J.-F.Dufrêche, Multicomponent Model for the Prediction of Nuclear Waste/Rare-Earth Extraction Processes, Langmuir 34, 35, 10434-10447, 2018
[165] S.Stenberg, B.Stenqvist, An Exact Ewald Summation Method in Theory and Practice, J.Phys.Chem. A 124, 3943-3946, 2020
[166] Sir G.G.Stokes, On the effect of the internal friction of fluids on the motion of pendulums, Trans. Cambridge Philos. Soc. 9, 8-106, 1851
[167] G.Stoltz, Quelques méthodes mathématiques pour la simulation moléculaire et multiéchelle, Thèse de doctorat soutenue en 2007
[168] W.C. Swope, H.C. Andersen, P.H. Berens, K.R. Wilson, A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules : Application to small water clusters, J. Chem. Phys. 76, 637, 1982
[169] G.M.Torrie, J.P.Valleau, Nonphysical sampling distributions in Monte Carlo free-energy estimation : Umbrella sampling, Journal of Computational Physics 23, 187-199, 1977
[170] A.Y.Toukmaji, J.A.Board Jr., Ewald summation techniques in perspective : a survey, Computer Physics Communications 95, 73-92, 1996
[171] H.F.Trotter, On the product of semi-groups operators, Proc. Am. Math Soc. 10, 545-551, 1959
[172] M.E. Tuckerman, Statistical Mechanics : Theory and Molecular Simulations, Oxford Graduate texts, 2009
[173] M.Tuckerman, B.J.Berne and G.J.Martyna, Reversible multiple time scale molecular dynamics, J. Chem. Phys. 97, 1990, 1992
[174] S.Vafaei, B.Tomberli, C.G.Gray, McMillan-Mayer Theory of Solutions Revisited : Simplifications and Extensions, J. Chem. Phys. 141, 154501, 2014
[175] V.Vallet, U.Wahlgren, B.Schimmelpfennig, H.Moll, Z.Szabó, I.Grenthe, Solvent Effects on Uranium(VI) Fluoride and Hydroxide Complexes Studied by EXAFS and Quantum Chemistry, Inorg. Chem. 40, 14, 3516-3525, 2001
[176] C.Vanroyen, Interactions hydrodynamiques entre sphères dures en régime faiblement inertiel : modélisation et expérimentations à la sédimentation, Thèse de doctorat soutenue en 2004
[177] A.Vaudano, B.Dinh, P.Baron, J.Duhamet, Le procédé PUREX, CEA
[178] L.Verlet, Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules, Phys. Rev. 159, 98, 1967
[179] T.Vilarino, O.Bernard, J.-P.Simonin, Ionic solutions in the binding mean spherical approximation. Thermodynamics of associating electrolytes up to very high concentrations, J. Phys. Chem.B 108, 18, 5763-5770, 2004
[180] A.Villard, O.Bernard, J.-F.Dufrêche, Non-additivity of ionic radii in electrolyte solutions : Hofmeister effect on mixtures modeled by an Associated MSA model, Journal of Molecular Liquids 270, 30-39, 2018
[181] A.Warshel and M.Levitt, Theoretical studies of enzymic reactions : Dielectric, electrostatic and steric stabilization of the carbonium ion in the reaction of lysozyme, Journal of Molecular biology 103, 227-249, 1976
[182] WHAM code by Alan Grossfield
[183] R.Wietzke, M.Mazzanti, J.-M.Latour, J.Pecaut, P.-Y.Cordier, C.Madic, Lanthanide(III) Complexe of Tripodal N-Donor Ligands : Strutural Models for the Specie Involved in Solvent Extraction of Actinide (III), Inorg. Chem. 37, 26, 6690-6697, 1998
[184] T.Yamaguchi, M.Nomura, H.Wakita, H.Ohtaki, An extended x-ray absorption fine structure study of aqueous rare earth perchlorate solutions in liquid and glassy states, J. Chem. Phys. 89, 5153, 1988
[185] I-C.Yeh, G.Hummer, System-Size Dependence of Diffusion Coefficients and Viscosities from Molecular Dynamics Simulations with Periodic Boundary Conditions, J. Phys. Chem.B 108, 40, 15873-15879, 2004
[186] C.Zhang, C.Lu, Z.Jing, C.Wu, J-P.Piquemal, J.W.Ponder, P.Ren, AMOEBA Polarizable Atomic Multipole Force Field for Nucleic Acids, J. Chem. Theory Comput. 14, 4, 2084-2108, 2018


[^0]:    1. In the case of the simulation of an unconfined fluid, an alternative to the periodic boundary conditions can for example be to impose spherical boundary conditions 99
[^1]:    2. One can cite in particular the montmorillonites 98, which belong to the family of smectites and which are being studied as a barrier constituent for the storage of radioactive waste
[^2]:    3. In this context, microbiological studies are added to the factors likely to be involved in the transfer of radionuclides 142
    4. The presence of faults and overpressures exerted on the rock can also generate fluid movements : the transport is then convective 117,156
    5. In 150, a study by simulations of molecular dynamics at the quantum level leads to a precise description that confirms this phenomenon
[^3]:    6. In addition to studies conducted at the microscopic and macroscopic scales, the mesoscopic scale (intermediate to the two previous ones) also allows to improve the understanding of the diffusion phenomenon, for example with the Time Domain Diffusion method 43,148
    7. $D_{e}$ is lower than $D$, since "tracers" face obstacles, which are pores. These two coefficients can also be related by the relation :

    $$
    D_{e}=D \times\left(\frac{\omega \delta}{\tau^{2}}\right)
    $$

    where $\omega$ corresponds to porosity, $\delta$ to constrictivity, and $\tau$ to tortuosity.

[^4]:    8. Homogenization methods are particularly relevant for modeling the porous medium, which is very heterogeneous, for the storage of radioactive waste and for studying the behavior of radionuclides within this medium 474
    9. Other alternatives to TBP such as DEHiBA 126, as well as actinide extraction by DMDOHEMA 42 61, are also being studied
    10. Several recent studies focus specifically on the aggregates formed during extraction in an organic phase solvent, these aggregates can form reverse micelles and thus induce supramolecular organization at this phase | 16 | 24 | 37 | 54 | 95 | 164 |
    | :--- | :--- | :--- | :--- | :--- | :--- |
[^5]:    11. One can also note studies carried out in intermediate with these two levels of description through the QM/MM method 11, 149, or studies drawn from multi-scale modeling such as in 127 by a large-grain approach
[^6]:    12. Polarizable models have been specifically developed for the Lanthanides 55 as well as for the actinides [58. These molecular dynamics models have allowed for example to study the coordination of nitrates with 57 Lanthanides, as well as the properties of Uranyl chloride 134
[^7]:    13. This term is more precisely taken into account in Coulomb electronic interactions, reflecting the interactions with the partial charges of the particles
    14. This term is sometimes taken into account in polarizable forces
[^8]:    15. Negative temperatures that may be allowed 68
    16. This ensemble is fundamental to define thermodynamics, because it is the only one that accurately describes a system and it is from it that the other ensembles are built. However, mathematically, it is little used because the resulting calculations are analytically complicated, except for a perfect monoatomic gas.
    17. N.B. : it is the only ensemble where energy is fixed. Indeed, a system that can exchange work or matter without exchanging energy does not exist experimentally
[^9]:    20. To obtain the equality 3.34 we used the fact that the integral in $p$ corresponds to the integral of a Gaussian, hence the result
[^10]:    21. $\mathbf{F}$ is related to the $\mathcal{V}$ potential of the system by the relation for every $i$ th coordinate : $\mathbf{F}_{i}=-\nabla_{i} \mathcal{V}\left(\mathbf{r}_{1}, \ldots, \mathbf{r}_{N}\right)$
[^11]:    22. It is recalled 105 that Hamiltonian dynamics, which describe the trajectories of particles over time, have interesting properties such as energy conservation and symplecticity of the flow $g_{t}$ solution of the system in (3.51), i.e. it verifies $\left(\nabla g_{t}\right)^{t} J \nabla g_{t}=J$ où $J=\left(\begin{array}{cc}0 & I_{3 N} \\ -I_{3 N} & 0\end{array}\right)$. By this last property, it results the one of the preservation of volume
    23. In fact, originally, the more simple Verlet integrator 178 only involves Taylor-Young development of $\mathbf{r}$ in $t+\delta t$ and $t-\delta t$ at order 4. It allows to calculate the positions at time $t+\delta t$, knowing them at the two previous times $t$ and $t-\delta t$. The speed $\mathbf{v}$ can, in that case, be approximated by subtracting the same two previous quantities (taken at order 3).
[^12]:    24. Useful reminder in particular for $3.2 .3: i^{2}=-1$
[^13]:    25. In fact, this is equivalent to being in the modified $N V E$ ensemble such that it corresponds to being in NPT
    26. Contrary to Nosé type methods, in simulations with a Berendsen thermostat the fluctuations are not good, but this does not matter in our case since they are not taken into account in our studies.
[^14]:    1. In chemistry, we speak of osmotic equilibrium between the solution and the pure solvent
[^15]:    2. We are talking about solute gas
[^16]:    3. Other technics can be use, such as Multistate Bennett Acceptance Ratio (MBAR) 161. The latter can be seen as a WHAM method with bins of histogram of width zero (see next section about WHAM method). It has the advantage of not depending on the histogram, which avoids a bias.
    4. In 4.25,,$e^{\beta \mathcal{V}_{h a r m}^{r^{*}}{ }^{(q)}} P_{b}\left(q, r^{*}\right)$ corresponds to the debiated umbrella, and the term $\left\langle e^{-\beta \mathcal{V}_{h a r m}^{r^{*}}(\xi(.))}\right\rangle$, which is unknown, is constant within said umbrella. The goal of the method is to restick each portion of the curve obtained with each 4.25, adjusting the constant.
[^17]:    1. Taking this minimum on the images allow to avoid box effects
[^18]:    2. To come to this solution, one would be tempted at first to choose to keep only the first two terms. However, care must be taken to take into account the distribution derivative as seen in theorem 8 and the following remark for the second derivative. This remark and the lemmas 12 and 13 can be used to establish the given solution.
[^19]:    3. Pay attention that the expansion is in $a / H$, but because the first term of expansion is proportional to $1 / a$, "a" does not appear in $o\left(\frac{1}{H}\right)$
