

The influence of periodic edge conditions for the simulation of some quantities of interest for separative chemistry

Anne-Françoise De Guerny

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Sorbonne Université

École doctorale Sciences Mathématiques de Paris Centre (ED 386) Unité de recherche Laboratoire Jacques-Louis Lions

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

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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} .

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Table des matières

Ré	Résumé 3					
Re	merc	iements	5			
1	Introduction générale					
2	General introduction					
3	Fron	n interactions of matter to numerical simulations	17			
	3.1	3.1 Motivation of this thesis				
		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	4 Calculation of free energy differences					
	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		Umbrella Sampling Method	53			
		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 \ldots	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	Stu	ly of the Potential of McMillan and Mayer at long distance	67		
	5.1	Mathematical problem	68		
	5.2	5.2 Numerical results			
		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 Na-Cl in aqueous phase	85		
		5.2.4 Macroscopic study for Na-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				
	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	7 Conclusion and perspectives				
Bi	bliog	raphie	135		

Bibliographie

8

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 $(L_i)_{i=1,2,3}$ de boite, permet d'observer l'évolution du potentiel de McMillan et Mayer en fonction de L (où L désigne successivement $(L_1), (L_2), (L_3)$), 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 $(L_i)_{i=1,2,3}$ of box, allows us to observe the evolution of McMillan and Mayer's potential as a function of L (where L stands successively for (L_1) , (L_2) , (L_3)), 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





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.

^{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]

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 (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)			MA-VL				
Haute activité (HA)			HA				

FIGURE 3 – Radioactivity of radioactive waste and methods of management (figure taken from [2])

On December 30, 1991, the law n° 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° 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 km^2 of galleries 490 m underground, in order to store 85000 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

^{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



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 figure 5).



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 possible³. 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 anions⁵.

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].

^{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

On the macroscopic scale⁶, 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 [20,51,124,137], 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** :

$$\mathbf{j} = -D\nabla C \tag{3.1}$$

where **j** is the molar flux of the diffusing species and ∇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} :

$$\mathbf{j} = -D_e \nabla C \tag{3.2}$$

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 :

$$\begin{cases} \eta \Delta \mathbf{u}(x, y, z) = \nabla p(x, y, z) \\ \nabla . \mathbf{u}(x, y, z) = 0 \end{cases}$$
(3.3)

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 :

$$\mathbf{u} = \boldsymbol{\mu} \mathbf{F} \tag{3.4}$$

where \mathbf{F} is the external force applied to the particle.

The diffusion coefficient can then be calculated from Einstein's relation [62]:

$$D = \mu k_B T \tag{3.5}$$

$$D_e = D \times \left(\frac{\omega\delta}{\tau^2}\right)$$

where ω corresponds to porosity, δ to constrictivity, and τ to tortuosity.

^{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 :

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 (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.

^{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 [4,74] 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]



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 (Am, Cu, Np) and the fission products (Cs, 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

^{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

the polarization ¹² to obtain the La - 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], $e = 1.602176634.10^{-19}$ C is the value of the elementary charge, $\epsilon_0 \approx 8.854.10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \text{ m}^{-1}$ the permittivity of the vacuum, ϵ_r la permittivité relative du milieu,

^{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]

 $k_B = 1.380649.10^{-23}$ J.K⁻¹ Boltzmann's constant, T the temperature, $h = 6.62607015.10^{-34}$ m² kg s⁻¹ Planck's constant.

We consider a system consisting of N particles, defined by their positions and impulses (\mathbf{r}, \mathbf{p}) where $\mathbf{r} = (\mathbf{r}_1, ..., \mathbf{r}_N) \in \mathbb{R}^{3N}$ and $\mathbf{p} = (\mathbf{p}_1, ..., \mathbf{p}_N) \in \mathbb{R}^{3N}$. The interactions of this system are described by the total energy of the system [105, 167, 172] :

$$H(\mathbf{r}, \mathbf{p}) = E_c(\mathbf{p}) + \mathcal{V}(\mathbf{r}) \tag{3.6}$$

where H is the Hamiltonian of the system, with E_c its kinetic energy and \mathcal{V} its potential energy.

We have :

$$E_c(\mathbf{p}) = \frac{1}{2} \mathbf{p}^T \mathbf{M}^{-1} \mathbf{p}$$
(3.7)

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 :

$$\mathcal{V}(\mathbf{r}_1,..,\mathbf{r}_N) = \sum_{i=1}^N \mathcal{V}_1(\mathbf{r}_i) + \sum_{i,j=1,i< j}^N \mathcal{V}_2(\mathbf{r}_i,\mathbf{r}_j) + ... + \sum_{i,j,..,z=1,i< j<...< z}^N \mathcal{V}_n(\mathbf{r}_i,\mathbf{r}_j,...,\mathbf{r}_z)$$
(3.8)

 \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^{eff} . We then have the following approximation :

$$\mathcal{V}(\mathbf{r}_1, .., \mathbf{r}_N) \simeq \sum_{i=1}^N \mathcal{V}_1(\mathbf{r}_i) + \sum_{i,j=1, i < j}^N \mathcal{V}_2^{eff}(\mathbf{r}_i, \mathbf{r}_j).$$
(3.9)

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}_{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 po- larization 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}_{Coul} is associated with an intense, long-range force. It is expressed as follows :

$$\mathcal{V}_{Coul} = \frac{1}{2} \sum_{i=1, i \neq j}^{N} \frac{z_i z_j e^2}{4\pi \epsilon_0 r_{ij}}$$
(3.10)

where, for i, j = 1, ..., N, z_i is the charge number of the particle *i* and $r_{ij} (= ||\mathbf{r}_i - \mathbf{r}_j||)$ is the distance between the two particles *i* and *j*.

The induced polarization energy potential \mathcal{V}_{pol} is written as follows :

$$\mathcal{V}_{pol} = -\frac{1}{2} \sum_{i=1}^{N} \mu_i E_i^0 \tag{3.11}$$

with, for i = 1, ..., N, $\mu_i = \alpha_i E_i$ the induced moment of the particle *i*, where α_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}_{vdW} . 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 μ_i . The potential \mathcal{V}_{vdW} is composed of three terms :

- the Keesom term : $-\frac{\mu_1^2 \mu_2^2}{3(4\pi\epsilon_0\epsilon_r)^2 k_b T r^6}$, which translates a dipolar force between two permanent dipoles whose rotations are thermally averaged ¹³,
- the Debye term : $-\frac{\mu_1^2 \alpha}{(4\pi\epsilon_0 \epsilon_r)^2 r^6}$, which reflects an interaction between a permanent dipole and an induced dipole.¹⁴,
- the London term : $-\frac{3}{4} \frac{h\nu\alpha^2}{(4\pi\epsilon_0\epsilon_r)^2 r^6}$, 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, α refers to electronic polarisability and ν 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_{LJ} , which is written as follows (ϵ_{ij} and σ_{ij} being the Lennard-Jones parameters [106]) :

$$V_{LJ} = \sum_{i,j=1,i\neq j}^{N} 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right).$$
(3.12)

Here, the term in r_{ij}^{-6} represents the Van der Waals forces (which are attractive), and the term in r_{ij}^{-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_{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 $\Delta E_{syst} = Q - W$. On the other hand, if we consider the external energy E_{ext} and the total energy (of the universe) E_{tot} then :

$$\Delta E_{tot} = \Delta E_{syst} + \Delta E_{ext} = 0 \tag{3.13}$$

(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).

^{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

Second Principle of Thermodynamics (Irreversibility of physical phenomena): We add another quantity that allows us to predict thermodynamics. Let S_{syst} be the **entropy** of the system, S_{ext} the external entropy, and S_{tot} the total entropy. So, for any thermodynamic transformation, we have :

$$dS_{tot} = dS_{syst} + dS_{ext} \ge 0 \tag{3.14}$$

This reflects the fact that, for an isolated system, entropy increases [52].

For a reversible transformation, S_{tot} is such that $dS_{tot} = \frac{dQ_{rev}}{T}$, where dQ_{rev} is the amount of heat needed to change the temperature T by an amount dT.

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 6N. 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 ϕ on the phase space. The quantities of macroscopic interest appear as averages over **thermodynamic ensembles**, ensembles which represent these measurements :

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

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 :

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

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 temperature¹⁵, the chemical potential, ...)

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

^{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

The ϕ 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 :

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

 ϕ being thus given : $d\phi(\mathbf{r}, \mathbf{p}) = \delta_{H(\mathbf{r}, \mathbf{p}) - E}$.

The associated **partition function** Ψ is ¹⁸ :

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

where h is Planck's constant. h^{3N} 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 :

$$S = k_B \ln(\Psi) \tag{3.18}$$

where k_B is Boltzmann's constant. The other thermodynamic quantities, in particular temperature T, pressure P and chemical potential μ , can be obtained from S. Indeed, we have the relation :

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN.$$
(3.19)

This leads us to obtain :

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}, \frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}.$$
(3.20)

The canonical ensemble (NVT): 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 ϕ of the canonical ensemble is defined by the relation :

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

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

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

18. In fact, physically, ψ is defined as :

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

where the energy variation ΔE 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:

$$F = U - TS \tag{3.23}$$

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

$$F(N, V, T) = -k_B T \ln(Z(N, V, T)).$$
(3.24)

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

$$dF = -SdT - PdV + \mu dN \tag{3.25}$$

which leads us to obtain :

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

The isothermal-isobaric ensemble (NPT): 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 Δ partition function is defined by [172] :

$$\Delta = \frac{\beta P}{h^{3N} N!} \int e^{-\beta PV} dV \int_{D^N \times \mathbb{R}^{3N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} d\mathbf{r} d\mathbf{p}.$$
 (3.27)

Gibbs free energy G is defined as :

$$G = U + PV - TS. ag{3.28}$$

We can show that :

$$G = -k_b T \ln(\Delta). \tag{3.29}$$

From relationships :

$$dG = -SdT + VdP + \mu dN \tag{3.30}$$

we can deduce from this :

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}, V = \left(\frac{\partial G}{\partial P}\right)_{N,T}, S = -G - \left(\frac{\partial G}{\partial T}\right)_{N,P}.$$
(3.31)

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

We consider :

$$Z_N = \int_{D^N} e^{-\beta \mathcal{V}(\mathbf{r})} d\mathbf{r}.$$
(3.32)

The partition function Q is defined by :

$$Q(\mu, V, T) = \sum_{N=1}^{\infty} \frac{e^{\beta\mu N}}{h^{3N} N!} \int_{D^N \times \mathbb{R}^{3N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} d\mathbf{r} d\mathbf{p}$$
(3.33)

$$=\sum_{N=1}^{\infty} \frac{z^N}{N!} Z_N. \tag{3.34}$$

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

$$z = \frac{e^{\beta\mu}}{\Lambda^3} \tag{3.35}$$

where $\Lambda = \frac{h}{(2\pi m k_b T)^{1/2}}$ is the Broglie wavelength of a particle ²⁰.

We define the grand potential Ξ :

$$\Xi = U - TS - \mu N. \tag{3.36}$$

We can show that :

$$\Xi = -k_b T \ln(Q). \tag{3.37}$$

From the relationship :

$$d\Xi = -SdT - Nd\mu - PdV \tag{3.38}$$

macroscopic quantities can be obtained :

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

(N.B. : the μPT 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 μ_i as there are species. The preceding formulas must then be adapted.

^{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

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 :

$$Z = \frac{1}{\left(\prod_{i} N_{i}!\right) h^{3} \sum_{i} N_{i}} \int_{D_{1}^{N_{1}} \times \ldots \times D_{M}^{N_{M}} \times \mathbb{R}^{3} \sum_{i} N_{i}} e^{-\beta H(\mathbf{r}^{1}, \ldots, \mathbf{r}^{M}, \mathbf{p}^{1}, \ldots, \mathbf{p}^{M})} d\mathbf{r}^{1} \ldots d\mathbf{r}^{M} d\mathbf{p}^{1} \ldots d\mathbf{p}^{M}}$$

$$(3.40)$$

with (3.24) and :

$$dF = -SdT - PdV + \sum_{i} \mu_i dN_i \tag{3.41}$$

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

$$Q((\mu_i)_i, V, T) = \sum_i \sum_{N_i=1}^{\infty} \frac{z^{N_i}}{N_i!} Z_{N_i}$$
(3.42)

where Z_{N_i} is given in (3.32) and z^{N_i} in (3.35).

 Ξ given in (3.37) verifies here :

$$d\Xi = -SdT - \sum_{i} N_i d\mu_i - PdV.$$
(3.43)

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):

$$\rho_{NVT}^{(n)}(\mathbf{r}_1,..,\mathbf{r}_n) = \frac{N!}{(N-n)!Z_N} \int_{D^{N-n}} e^{-\beta \mathcal{V}(\mathbf{r}_1,..,\mathbf{r}_n)} d\mathbf{r}_{n+1}..d\mathbf{r}_N.$$
(3.44)

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

$$g^{(n)}(\mathbf{r}_1,..,\mathbf{r}_n) = \frac{\rho^{(n)}(\mathbf{r}_1,..,\mathbf{r}_n)}{\rho^n}.$$
(3.45)

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 $\|\mathbf{r}_1 - \mathbf{r}_2\| \to \infty$).

We have :

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{\rho^2 Z_N} \int_{D^{N-2}} e^{-\beta \mathcal{V}(\mathbf{r}_1, \dots, \mathbf{r}_n)} d\mathbf{r}_3 \dots d\mathbf{r}_N$$
$$= \frac{N(N-1)}{\rho^2} \langle \delta(\mathbf{r}_1 - \mathbf{r'}_1) \delta(\mathbf{r}_2 - \mathbf{r'}_2) \rangle_{\mathbf{r'}_1, \dots, \mathbf{r'}_N}$$

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 μ , volume V and temperature T. The density at n-body is defined here as follows :

$$\rho_{\mu VT}^{(n)} = \frac{1}{Q(\mu, V, T)} \sum_{N=n}^{\infty} \frac{z^N}{(N-n)!} \int_{D^{N-n}} e^{-\beta \mathcal{V}(\mathbf{r}_1, \dots, \mathbf{r}_n)} d\mathbf{r}_{n+1} ... d\mathbf{r}_N$$
(3.46)

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 ρ_i and of N_j particles of type *j* with density ρ_j .

The correlation function is then given by :

$$g^{(n)}(\mathbf{r}_1,..,\mathbf{r}_n) = \frac{\rho^{(n)}(\mathbf{r}_1,..,\mathbf{r}_n)}{\prod_{i=1}^n \rho_i}.$$
(3.47)

The radial distribution function verifies :

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N_i(N_j - \delta_{ij})}{\rho_i \rho_j} \langle \delta(\mathbf{r}_1 - \mathbf{r'}_1) \delta(\mathbf{r}_2 - \mathbf{r'}_2) \rangle_{\mathbf{r'}_1, \dots, \mathbf{r'}_N}.$$
(3.48)

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 :

$$C_N(L) = 4\pi\rho_j \int_0^L g^{(2)}(r_{ij})r_{ij}^2 dr_{ij}.$$
(3.49)

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



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

$$\mathbf{F} = m \frac{d^2 \mathbf{r}}{dt^2}.\tag{3.50}$$

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.

^{21.} **F** is related to the \mathcal{V} potential of the system by the relation for every *i*th coordinate : $\mathbf{F}_i = -\nabla_i \mathcal{V}(\mathbf{r}_1, ..., \mathbf{r}_N)$

- 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 :

$$\begin{cases} \dot{\mathbf{r}}_{i}(t) = \frac{\partial H}{\partial \mathbf{p}_{i}}(\mathbf{r}(t), \mathbf{p}(t)) \\ \dot{\mathbf{p}}_{i}(t) = -\frac{\partial H}{\partial \mathbf{r}_{i}}(\mathbf{r}(t), \mathbf{p}(t)) \end{cases}$$
(3.51)

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 :

$$\begin{cases} \dot{\mathbf{r}}_{i}(t) = \frac{\mathbf{p}_{i}(t)}{m} \\ \dot{\mathbf{p}}_{i}(t) = -\frac{\partial \mathcal{V}(\mathbf{r}(t))}{\partial \mathbf{r}_{i}} = \mathbf{F}_{i}(t) \end{cases}$$
(3.52)

(3.52) is an ordinary differential equation that can be classically integrated by means of the Verlet integrator for speed [168] : one notes (r^n, p^n) an approximation of $(\mathbf{r}(t_n), \mathbf{p}(t_n))$ 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):

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

^{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 $(\nabla g_t)^t J \nabla g_t = J$ où $J = \begin{pmatrix} 0 & I_{3N} \\ -I_{3N} & 0 \end{pmatrix}$. 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).

The **Liouville operator** is introduced 24 :

$$iL = \frac{\partial H}{\partial p} \frac{\partial}{\partial x} - \frac{\partial H}{\partial x} \frac{\partial}{\partial p}.$$
(3.53)

So we have (since $F = -\nabla \mathcal{V}$) : $iL = \frac{p}{m} \frac{\partial}{\partial x} + F(x) \frac{\partial}{\partial p}$.

We know that (x, p) verifies Hamilton's equations :

$$\begin{pmatrix}
\dot{x} = \frac{\partial H}{\partial p} \\
\dot{p} = -\frac{\partial H}{\partial x}
\end{cases}$$
(3.54)

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

$$\frac{df}{dt} = \frac{\partial f}{\partial x}\dot{x} + \frac{\partial f}{\partial p}\dot{p}.$$
(3.55)

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

$$\frac{df}{dt} = iLf. \tag{3.56}$$

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

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 :

$$\|\mathcal{A}\| = \sup_{x \in E \setminus \{0\}} \frac{\|\mathcal{A}x\|}{\|x\|}.$$

Definition 2. Let \mathcal{H} be an Hilbert space. A semigroup of operator is an operator family $\mathcal{U} = \{\mathcal{U}_t \in \mathcal{L}(\mathcal{H}, \mathcal{H}), t \in \mathbb{R}^+\}$ which satisfies the following properties : $i) \forall t, s \in \mathbb{R}^+ : \mathcal{U}_t \circ \mathcal{U}_s = \mathcal{U}_{t+s}$ $ii) \mathcal{U}_0 = Id \text{ (where } Id(x) = x \text{ for all } x \in \mathcal{H})$

iii) $\forall x \in \mathcal{H}, t \mapsto \mathcal{U}_t x \text{ is continuous from } \mathbb{R}^+ \text{ in } \mathcal{H}.$

Its semigroup is bounded if $\|\mathcal{U}_t\| \leq 1$ for all $t \geq 0$.

For a semigroup \mathcal{U} bounded on \mathcal{H} , we note :

$$D(\mathcal{G}) = \left\{ x \in \mathcal{H} \mid \lim_{t \to 0, t > 0} \frac{\mathcal{U}_t x - x}{t} exists \right\}$$

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

$$-\mathcal{G}x = \lim_{t \to 0, t > 0} \frac{\mathcal{U}_t x - x}{t}.$$

This generator is an operator.

We recall that saying that two operators A_1, A_2 commute means that $A_1 \circ A_2 = A_2 \circ A_1$.

^{24.} Useful reminder in particular for 3.2.3 : $i^2 = -1$

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 $\mathcal{C}^0(\mathbb{R}^N)$. Then we have :

$$e^{\mathcal{A}+\mathcal{B}} = \lim_{n \to \infty} \left(e^{\frac{\mathcal{B}}{2n}} \circ e^{\frac{\mathcal{A}}{n}} \circ e^{\frac{\mathcal{B}}{2n}} \right)^n.$$
(3.57)

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

$$e^{iL\Delta t} \simeq \left(e^{\frac{F(x)\Delta t}{2} \frac{\partial}{\partial p}} \circ e^{\frac{p}{m}\Delta t} \frac{\partial}{\partial x} \circ e^{\frac{F(x)\Delta t}{2} \frac{\partial}{\partial p}} \right).$$
(3.58)

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 :

$$e^{c\frac{\partial}{\partial x}}g(x) = g(x+c). \tag{3.59}$$

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

$$e^{c\frac{\partial}{\partial x}}g(x) = \sum_{k=0}^{\infty} \frac{1}{k!} \left(c\frac{\partial}{\partial x}\right)^k g(x)$$
(3.60)

$$=\sum_{k=0}^{\infty}\frac{1}{k!}c^{k}\frac{\partial^{k}g}{\partial x^{k}}(x).$$
(3.61)

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

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

$$p^{n+1/2} = p^n + 0.5 * \Delta t * F^n$$

$$x^{n+1} = x^n + \Delta t * \frac{p^{n+1/2}}{m}$$

Calcul de F^{n+1}

$$p^{n+1} = p^{n+1/2} + 0.5 * \Delta t * F^{n+1}$$

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_{sr} and those of long range $F_{lr}: F = F_{sr} + F_{lr}$. The first ones will be evaluated every δt 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 : $iL = iL_{sr} + iL_{lr}$, with $iL_{lr} = F_{lr}(x)\frac{\partial}{\partial p}$ et $iL_{sr} = \frac{p}{m}\frac{\partial}{\partial x} + F_{sr}(x)\frac{\partial}{\partial p}$. We can decompose the propagator $e^{iL\Delta t}$ in the following way :

$$e^{iL\Delta t} \simeq e^{\frac{\Delta t}{2}F_{lr}\frac{\partial}{\partial p}} \circ \left(e^{\frac{\delta t}{2}F_{sr}\frac{\partial}{\partial p}} \circ e^{\delta t\frac{p}{m}\frac{\partial}{\partial x}} \circ e^{\frac{\delta t}{2}F_{sr}\frac{\partial}{\partial p}}\right)^n \circ e^{\frac{\Delta t}{2}F_{lr}\frac{\partial}{\partial p}}.$$
(3.62)

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 :

 $\begin{array}{l} p^{k+1/2} = p^k + 0.5 * \Delta t * F_{lr}^k \\ \text{for } i=1 \ a \ n \ \text{do} \\ \\ \\ p^{k+i} = p^{k+i-1/2} + 0.5 * \delta t * F_{sr}^{k+(i-1)} \\ x^{k+i} = x^{k+(i-1)} + \delta t * \frac{p^{k+i}}{m} \\ \text{Calcul de } F_{sr}^{k+i} \\ p^{k+i+1/2} = p^{k+i} + 0.5 * \delta t * F_{sr}^{k+i} \\ \text{end} \\ \text{Calcul de } F_{lr}^{k+1} \\ p^{k+n+1} = p^{k+n+1/2} + 0.5 * \Delta t * F_{lr}^{k+1} \end{array}$

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 NPT ensemble, we used the **Berendsen's thermostat** [18] to treat temperature and pressure²⁵. 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 $v \to \lambda v$ is expressed as a function of temperature T :

$$\lambda_T = \left(1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T(t)} - 1\right)\right)^{1/2} \tag{3.63}$$

where τ_T is a relaxation parameter, Δt 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 τ_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:

$$\lambda_P = \left(1 + \frac{\Delta t}{\tau_P}\gamma(P(t) - P_0)\right)^{1/3} \tag{3.64}$$

where τ_P is a relaxation parameter, Δt is the time step, P_0 is the reference pressure and γ 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 τ_P is the time to return to the reference pressure at a fixed temperature.

^{25.} In fact, this is equivalent to being in the modified NVE ensemble such that it corresponds to being in NPT26. 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.

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 – 2D 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, ..., N) and described by its position \mathbf{r}_i (i = 1, ..., N).

Periodic conditions at the edges of the box are considered.

Let U_{PBC} be the energy potential of the periodic system. We have :

$$U_{PBC} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\mathbf{n} \neq (0,0,0)}^{\prime} \frac{q_i q_j}{\|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L\|}$$
(3.65)

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 **n** in U_{PBC} 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_{PBC} verifies :

$$U_{PBC}(\mathbf{r}, L) = \frac{1}{2} \sum_{i=1}^{N} q_i \phi(\mathbf{r}_i)$$
(3.66)

where ϕ corresponds to a solution of Poisson's equation

$$\Delta\phi(\mathbf{r}) = -4\pi \sum_{i=1}^{N} q_i \delta(\mathbf{r} - \mathbf{r}_i)$$
(3.67)

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 ϕ is written :

$$\Delta\phi(\mathbf{r}) = -4\pi z \delta(\mathbf{r} - \mathbf{r}_0) \tag{3.68}$$

where we impose that ϕ satisfies the periodicity conditions on the faces of the simulation box (i.e. $\phi(\mathbf{r} + L\mathbf{e}_i) = \phi(\mathbf{r})$, where $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ 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 ϕ 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 :

$$\int_{V} \phi(r)dr = 0 \tag{3.69}$$

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 :

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

(We can verify : $\int_V \Delta \phi(\mathbf{r}) d\mathbf{r} = -4\pi \int_V (z\delta(\mathbf{r}) - \frac{z}{V}) d\mathbf{r} = -4\pi (z - \frac{zV}{V}) = 0$).

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 $T \in \mathbf{S}'(\mathbb{R}^3)$ (where \mathbf{S} is the space of Schwartz), i.e. a temperate distribution. We call Fourier transform of T the distribution $\hat{T} = FT$, defined by the relation :

$$\forall \phi \in \boldsymbol{S}(\mathbb{R}^3), \langle FT, \phi \rangle = \langle T, F\phi \rangle. \tag{3.71}$$

If $f \in L^1(\mathbb{R}^3)$: $FT_f = T_{\hat{f}}$, where for $\mathbf{k} \in \mathbb{R}^3$:

$$\hat{f}(\boldsymbol{k}) = \int_{\mathbb{R}^3} f(\boldsymbol{x}) e^{i\boldsymbol{k}\cdot\boldsymbol{x}} dx_1 dx_2 dx_3.$$
(3.72)

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) :

$$f(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} c_f(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$
(3.73)

with $\mathbf{k} = \frac{2\pi}{L}\mathbf{m}$ where $\mathbf{m} \in \mathbb{Z}^3$, $V = L^3$ and where $c_f(\mathbf{k}) = \int_V f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} dr$.

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 ϕ and δ 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 $g(\mathbf{r}) = \delta(\mathbf{r}) - \frac{1}{V}$ (here, δ istaken for N = 1 and $q_{1} = z = 1$).

The Poisson equation associated with ϕ gives us :

$$\Delta\phi(\mathbf{r}) = -4\pi \left(\delta(\mathbf{r}) - \frac{1}{V}\right) \tag{3.74}$$

$$\Leftrightarrow \Delta\left(\frac{1}{V}\sum_{\mathbf{k}}c_{\phi}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}\right) = -4\pi\frac{1}{V}\sum_{\mathbf{k}}c_{g}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}$$
(3.75)

$$\Leftrightarrow \frac{1}{V} \sum_{\mathbf{k}} c_{\phi}(\mathbf{k}) \Delta e^{i\mathbf{k}.\mathbf{r}} = \frac{1}{V} \sum_{\mathbf{k}} -4\pi c_g(\mathbf{k}) e^{i\mathbf{k}.\mathbf{r}}$$
(3.76)

$$\Leftrightarrow \frac{1}{V} \sum_{\mathbf{k}} c_{\phi}(\mathbf{k}) i^{2} \mathbf{k}^{2} e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{V} \sum_{\mathbf{k}} -4\pi c_{g}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$
(3.77)

which expresses the equality of two series of Fourier.

By uniqueness of the Fourier coefficients, we obtain the following equations $\forall \mathbf{k} \neq (0,0,0)$:

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

with $c_g(\mathbf{k}) = \int_V (\delta(r) - \frac{1}{V}) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} = 1$ (since $\mathbf{k} \neq (0, 0, 0)$).

To find the coefficient $c_{\phi}(0)$, we use the condition for the additivity constant :

$$\int_{V} \phi(\mathbf{r}) e^{i(0,0,0)\cdot\mathbf{r}} dr = \int_{V} \phi(\mathbf{r}) dr = 0 \ i.e. \ c_{\phi}(0) = 0.$$
(3.79)

Thus :

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

 $\frac{4\pi}{k^2}$ being the Fourier transform associated with $\frac{1}{||\mathbf{r}||}$ (Coulomb's potential).

(Given this way, ϕ converges only conditionally (remember that $\mathbf{k} = (k_1, k_2, k_3)$ 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 ξ (which removes the interaction of a particle with itself introduced) defined as follows :

$$\xi = \lim_{\|\mathbf{r}\| \to 0} \left(\phi(\mathbf{r}) - \frac{1}{\|\mathbf{r}\|} \right)$$
(3.81)

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

$$U_{PBC} = \frac{1}{2} \sum_{i=1}^{N} q_i \sum_{j \neq i, j=1}^{N} q_j \phi(\mathbf{r}_i - \mathbf{r}_j) + \frac{\xi}{2} \sum_{i=1}^{N} q_i^2.$$
(3.82)

Demonstration of Ewald's formula

Theorem 2. We can rewrite U_{PBC} and get :

$$U_{PBC} = U_{PBC}^{(r)} + U_{PBC}^{(k)} + U_{PBC}^{(s)} + U_{PBC}^{(n)}$$
(3.83)

where :

$$U_{PBC}^{(r)} = \frac{1}{2} \sum_{i,j} \sum_{n}' q_i q_j \frac{1 - \operatorname{erf}(\alpha \| \boldsymbol{r}_i - \boldsymbol{r}_j + \boldsymbol{n}L \|)}{\| \boldsymbol{r}_i - \boldsymbol{r}_j + \boldsymbol{n}L \|}$$
(3.84)

$$U_{PBC}^{(k)} = \frac{1}{2} \sum_{i,j} q_i q_j \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} e^{-\frac{k^2}{4\alpha^2}} e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)}$$
(3.85)

$$U_{PBC}^{(s)} = -\frac{\alpha}{\sqrt{\pi}} \sum_{i} q_i^2 \tag{3.86}$$

$$U_{PBC}^{(n)} = -\frac{\pi}{2\alpha^2 V} Q_{tot}^2$$
(3.87)

où $Q_{tot} = \sum_{i} q_i$, 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

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

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

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

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 :

$$\phi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}}$$
(3.89)

$$= \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} (1 - f(\mathbf{k}) + f(\mathbf{k})) e^{i\mathbf{k} \cdot \mathbf{r}}$$
(3.90)

$$= \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} (1 - f(\mathbf{k})) e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} f(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$
(3.91)

(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 $X = (X_1, X_2, X_3) \sim N(\mathbf{0}, \frac{1}{2\alpha^2} \mathbf{I}_3)$ corresponds to its characteristic function $E(e^{iX\mathbf{k}})$, from which we derive : $\hat{g}(\mathbf{k}) = e^{-\frac{\mathbf{k}^2}{4\alpha^2}}$. We consider $f = \hat{g}$. We have then : $\phi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{\mathbf{k}^2} (1 - e^{-\frac{\mathbf{k}^2}{4\alpha^2}}) e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{\mathbf{k}^2} e^{-\frac{\mathbf{k}^2}{4\alpha^2}} e^{i\mathbf{k}\cdot\mathbf{r}}.$

We observe that the second sum in ϕ 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 :

$$\sum_{\boldsymbol{n}} h(\boldsymbol{x} + \boldsymbol{n}L) = \frac{1}{V} \sum_{\boldsymbol{k}} \hat{h}(\boldsymbol{k}) e^{i\boldsymbol{k}.\boldsymbol{x}}$$
(3.92)

with $\mathbf{k} = \frac{2\pi}{L} \mathbf{m}$ where $\mathbf{m} \in \mathbb{Z}^3$. (In particular, with $\mathbf{x} = (0, 0, 0)$, we get : $\sum_{\mathbf{n}} h(\mathbf{n}) = \sum_{\mathbf{k}} \hat{h}(\mathbf{k})$).

Here, we have $\hat{h} : \mathbf{k} \mapsto \frac{4\pi}{k^2} (1 - e^{-\frac{\mathbf{k}^2}{4\alpha^2}})$. 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 $\frac{1}{V} \sum_{\mathbf{k} \neq (0, 0, 0)} \frac{4\pi}{k^2} (1 - e^{-\frac{k^2}{4\alpha^2}}) e^{i\mathbf{k}\cdot\mathbf{r}}$. We will make a 0 equivalent of $\frac{4\pi}{k^2} (1 - e^{-\frac{k^2}{4\alpha^2}})$ then add it and we have the formula of $\frac{4\pi}{k^2} (1 - e^{-\frac{k^2}{4\alpha^2}}) e^{i\mathbf{k}\cdot\mathbf{r}}$. 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 $\frac{4\pi}{k^2} \left(1 - e^{-\frac{k^2}{4\alpha^2}}\right) \sim \frac{4\pi k^2}{4k^2\alpha^2} \sim \frac{\pi}{\alpha^2}$.

We thus set $\hat{h}(0,0,0) = \frac{\pi}{\alpha^2}$ and then we have :

$$A = \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} \left(1 - e^{-\frac{k^2}{4\alpha^2}} \right) e^{i\mathbf{k}.\mathbf{r}}$$
(3.93)

$$= \frac{1}{V} \sum_{\mathbf{k}} \hat{h}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\pi}{V\alpha^2}.$$
(3.94)

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 $\operatorname{erf} : r \mapsto \frac{2}{\sqrt{\pi}} \int_0^r e^{-y^2} dy$. We have :

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

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

$$\Delta g(r) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} g(r) \right)$$
(3.96)

$$=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left(-\frac{1}{r^2}\operatorname{erf}(\alpha r)+\frac{1}{r}\frac{2}{\sqrt{\pi}}\alpha e^{-\alpha^2 r^2}\right)\right)$$
(3.97)

$$=\frac{1}{r^2}\left(-\frac{2}{\sqrt{\pi}}\alpha e^{-\alpha^2 r^2} - \frac{4\alpha^3}{\sqrt{\pi}}r^2 e^{-\alpha^2 r^2} + \frac{2}{\sqrt{\pi}}\alpha e^{-\alpha^2 r^2}\right)$$
(3.98)

$$= -\frac{4\alpha^3}{\sqrt{\pi}}e^{-\alpha^2 r^2}.$$
 (3.99)

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

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

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

$$\frac{1}{\|\mathbf{x}\|}\operatorname{erf}(\alpha\|\mathbf{x}\|) = \Delta^{-1} \left(-\frac{4\alpha^3}{\sqrt{\pi}} e^{-\alpha^2 \|\mathbf{x}\|^2} \right)$$
(3.101)

$$= \delta_0 * (\Delta^{-1}) \left(-\frac{4\alpha^3}{\sqrt{\pi}} e^{-\alpha^2 \|\mathbf{x}\|^2} \right)$$
(3.102)

$$= (\Delta^{-1}\delta_0) * \frac{4\alpha^3}{\sqrt{\pi}} e^{-\alpha^2 \|\mathbf{x}\|^2}$$
(3.103)

$$= \frac{1}{\|\mathbf{x}\|} * \frac{4\alpha^3}{\sqrt{\pi}} e^{-\alpha^2 \|\mathbf{x}\|^2}.$$
 (3.104)

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

$$A = \sum_{n} \frac{1 - \operatorname{erf}(\alpha || r + nL ||)}{|| r + nL ||} - \frac{\pi}{\alpha^2 V}.$$
(3.105)

We reinject A in ϕ and we get : $\phi(\mathbf{r}) = \sum_{\mathbf{n}} \frac{1 - \operatorname{erf}(\alpha \|\mathbf{r} + \mathbf{n}L\|)}{\|\mathbf{r} + \mathbf{n}L\|} + \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} e^{-\frac{k^2}{4\alpha^2}} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\pi}{\alpha^2 V}.$

All that remains to be done is to calculate the constant ξ to get the total energy U_{PBC} :

$$\xi = \lim_{\|\mathbf{r}\| \to 0} \left(\phi(\mathbf{r}) - \frac{1}{\|\mathbf{r}\|} \right) \tag{3.106}$$

$$= \lim_{\|\mathbf{r}\|\to 0} \left(\sum_{\mathbf{n}} \frac{1 - \operatorname{erf}(\alpha \|\mathbf{r} + \mathbf{n}L\|)}{\|\mathbf{r} + \mathbf{n}L\|} + \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} e^{-\frac{k^2}{4\alpha^2}} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\pi}{\alpha^2 V} - \frac{1}{||\mathbf{r}||} \right)$$
(3.107)

$$=\sum_{\mathbf{n}\neq(0,0,0)}\frac{1-\operatorname{erf}(\alpha\|\mathbf{n}L\|)}{\|\mathbf{n}L\|} + \frac{1}{V}\sum_{\mathbf{k}\neq(0,0,0)}\frac{4\pi}{k^2}e^{-\frac{k^2}{4\alpha^2}} - \frac{\pi}{\alpha^2 V} + \lim_{\|\mathbf{r}\|\to 0}\frac{(1-\operatorname{erf}(\alpha\|\mathbf{r}\|)-1)}{\|\mathbf{r}\|}$$
(3.108)

$$=\sum_{\mathbf{n}\neq(0,0,0)}\frac{1-\operatorname{erf}(\alpha\|\mathbf{n}L\|)}{\|\mathbf{n}L\|} + \frac{1}{V}\sum_{\mathbf{k}\neq(0,0,0)}\frac{4\pi}{k^2}e^{-\frac{k^2}{4\alpha^2}} - \frac{\pi}{\alpha^2 V} - \lim_{\|\mathbf{r}\|\to 0}\frac{\operatorname{erf}(\alpha\|\mathbf{r}\|)}{\|\mathbf{r}\|}.$$
(3.109)

We have : $\frac{\operatorname{erf}(\alpha \|\mathbf{r}\|)}{\|\mathbf{r}\|} = \frac{\operatorname{erf}(\alpha \|\mathbf{r}\|) - 0}{\|\mathbf{r}\|} = \frac{\operatorname{erf}(\alpha \|\mathbf{r}\|) - \operatorname{erf}(\alpha \|\mathbf{0}\|)}{\|\mathbf{r}\|}.$

But erf is derivable on $\mathbb{R} \setminus \{0\}$ and composing it with the function derivable on $\mathbb{R}, x \mapsto \alpha x$, we have :

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

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

By reinjecting the value obtained for ξ and that obtained for ϕ , we obtain :

$$U_{PBC} = U_{PBC}^{(r)} + U_{PBC}^{(k)} + U_{PBC}^{(s)} + U_{PBC}^{(n)}$$
(3.111)

where $U_{PBC}^{(r)} = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{n}}' q_i q_j \frac{1 - \operatorname{erf}(\alpha \| \mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L \|)}{\| \mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L \|},$ $U_{PBC}^{(k)} = \frac{1}{2} \sum_{i,j} q_i q_j \frac{1}{V} \sum_{\mathbf{k} \neq (0,0,0)} \frac{4\pi}{k^2} e^{-\frac{k^2}{4\alpha^2}} e^{i\mathbf{k}.(\mathbf{r}_i - \mathbf{r}_j)},$ $U_{PBC}^{(s)} = -\frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2$ and $U_{PBC}^{(n)} = -\frac{\pi}{2\alpha^2 V} Q_{tot}^2$ where $Q_{tot} = \sum_i q_i$, with $\alpha \in \mathbb{R}.$

 α 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 α favors convergence in real space, a large α favors convergence in Fourier space).

Note that $U_{PBC}^{(r)}$ 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. $U_{PBC}^{(k)}$ refers to the sum of the screened interactions (removed in the previous sum) and is computed in Fourier space. $U_{PBC}^{(s)}$ is a term that refers to the interactions between the particles themselves, a term that is removed as indicated by the "-" sign. Finally, $U_{PBC}^{(n)}$ 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 :

$$\xi: \Omega \to \mathbb{R}^m \tag{4.1}$$

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

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

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

so that :

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

Simply related Σ (i.e. arc related and homotopic) are assumed to ensure ergodicity.

4.2 Free energy

The absolute free energy [105, 167] F of a system is defined by :

$$-\beta F = \ln(Z) \tag{4.2}$$

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}) :

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

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 ΔF , 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, ξ . We then have :

$$\Delta F = F(1) - F(0) = -k_b T \ln \left(\frac{\int_{D^N \times \mathbb{R}^{3N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} \delta_{\xi - x_1} d\mathbf{r} d\mathbf{p}}{\int_{D^N \times \mathbb{R}^{3N}} e^{-\beta H(\mathbf{r}, \mathbf{p})} \delta_{\xi - x_0} d\mathbf{r} d\mathbf{p}} \right)$$
(4.3)

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 **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 :

$$-\beta F(x) = \ln(P(x)) - \beta F_0 \tag{4.4}$$

where F_0 is a constant normalizing the probability P.

This is the function $x \mapsto F(x)$ given by :

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

Its derivative, F'(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 μ_1 for the solute and μ_2 for the solvent, are fixed, in addition to V and T (but not the number of particles). Let \mathcal{V}_{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)) :

$$Q(\mu_1, \mu_2, V, T) = \sum_{N,M=1}^{\infty} \frac{z_1^N z_2^M}{N!M!} \int_{D_1^N \times D_2^M} e^{-\beta \mathcal{V}_{syst}(\mathbf{r}^N, \mathbf{R}^M)} d\mathbf{r}^N d\mathbf{R}^M$$
(4.6)

$$=\sum_{N=1}^{\infty} \frac{z_1^N}{N!} \int_{D_1^N} \sum_{M=1}^{\infty} \frac{z_2^M}{M!} \int_{D_2^M} e^{-\beta \mathcal{V}_{syst}(\mathbf{r}^N, \mathbf{R}^M)} d\mathbf{R}^M d\mathbf{r}^N.$$
(4.7)

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

$$g^{(n)}(\mathbf{r}_{1},...,\mathbf{r}_{n}) = \frac{1}{\rho^{n}Q(\mu_{1},\mu_{2},V,T)} \sum_{N=n+1}^{\infty} \frac{z_{1}^{N}}{(N-n)!} \int_{D_{1}^{N}} \sum_{M=1}^{\infty} \frac{z_{2}^{M}}{M!} \int_{D_{2}^{M}} e^{-\beta \mathcal{V}_{syst}(\mathbf{r}^{N},\mathbf{R}^{M})} d\mathbf{R}^{M} d\mathbf{r}^{N-n}$$

$$(4.8)$$

$$= \left(\frac{z_1}{\rho}\right)^n \frac{1}{Q(\mu_1, \mu_2, V, T)} \sum_{N=1}^{\infty} \frac{z_1^N}{N!} \int_{D_1^N} \sum_{M=1}^{\infty} \frac{z_2^M}{M!} \int_{D_2^M} e^{-\beta \mathcal{V}_{syst}(\mathbf{r}^{N+n}, \mathbf{R}^M)} d\mathbf{R}^M d\mathbf{r}^N$$
(4.9)

where ρ is the solute density (re-indexing was done to move to the second tie).

If the solute is diluted, i.e. $z_1 \to 0$ (i.e. $\mu_1 \to -\infty$). We then have :

$$g^{(n)}(\mathbf{r}_{1},...,\mathbf{r}_{n})|_{z_{1}\to0} = \frac{\gamma^{n}}{Q(\mu_{1}\to-\infty,\mu_{2},V,T)} \sum_{M=1}^{\infty} \frac{z_{2}^{M}}{M!} \int_{D_{2}^{M}} e^{-\beta \mathcal{V}_{syst}(\mathbf{r}^{n},\mathbf{R}^{M})} d\mathbf{R}^{M}$$
(4.10)

where we set : $\gamma = \left(\frac{z_1}{\rho}\right)_{|z_1 \to 0}$.

We replace in (4.7) and we get :

$$Q(\mu_1, \mu_2, V, T) = Q(\mu_1 \to -\infty, \mu_2, V, T) \sum_{N=1}^{\infty} \frac{a^N}{N!} \int_{D_1^N} g^{(N)}(\mathbf{r}_1, ..., \mathbf{r}_N) d\mathbf{r}^N$$
(4.11)

where the activity has been defined as $a = \frac{z_1}{\gamma} = z_1 \left(\frac{\rho}{z_1}\right)_{|z_1 \to 0}$.

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 ¹. McMillan and Mayer's theory simplifies the

^{1.} In chemistry, we speak of osmotic equilibrium between the solution and the pure solvent

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 :

$$g^{(N)}(\mathbf{r}_1,...,\mathbf{r}_N) = e^{-\beta W^N(\mathbf{r}_1,...,\mathbf{r}_N)}.$$
(4.12)

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 :

$$Q(\mu_1, \mu_2, V, T) = Q(\mu_1 \to -\infty, \mu_2, V, T)Q_{MM}(a, V, T)$$
(4.13)

where Q_{MM} 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 :

$$e^{-\beta F(r)}dr = e^{-\beta W^{(2)}(r)} 4\pi r^2 dr$$
(4.14)

$$\Leftrightarrow -\beta F(x) = -\beta W^{(2)}(r) + \ln(4\pi) + \ln(r^2) \tag{4.15}$$

$$\Leftrightarrow \beta W^{(2)}(r) = \beta F(r) + 2\ln(r) + cste. \tag{4.16}$$

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).

^{2.} We are talking about solute gas



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 Na⁺ and an ion 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 Na⁺ and the ion 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 $\mathcal{V}_{harm}^{r^*}$. The biased potential $\mathcal{V}_{bias}^{r^*}$ is like this :

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

where :

$$\mathcal{V}_{harm}^{r^*}(r) = \frac{1}{2}k(r - r^*)^2 \tag{4.18}$$

with k the spring stiffness constant and $r^* := \|\mathbf{r}_{Na^+} - \mathbf{r}_{Cl^-}\|$ 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 Na⁺ and 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 ξ will satisfy the



FIGURE 13 – Umbrella Sampling for a 36.342 A side water box with one ion Na⁺ and an ion Cl⁻, with as reaction coordinate the distance between the two ions r^* , where $r^* = 2, 2.5, ..., 12$

given constraint q :

$$P_b(q, r^*) = \frac{\int e^{-\beta(\mathcal{V}(r) + \mathcal{V}_{harm}^{r^*}(\xi(r)))} \delta(\xi(r) - q) d^N r}{\int e^{-\beta(\mathcal{V}(r) + \mathcal{V}_{harm}^{r^*}(\xi(r)))} d^N r}.$$
(4.19)

We know that the probability without the biased potential ${\cal P}$ is :

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

We have :

$$P_b(q, r^*) = \frac{\int e^{-\beta(\mathcal{V}(r) + \mathcal{V}_{harm}^{r^*}(\xi(r)))} \delta(\xi(r) - q) d^N r}{\int e^{-\beta(\mathcal{V}(r) + \mathcal{V}_{harm}^{r^*}(\xi(r)))} d^N r}$$
(4.21)

$$=\frac{\int e^{-\beta(\mathcal{V}(r)+\mathcal{V}_{harm}^{r*}(\xi(r)))}\delta(\xi(r)-q)d^{N}r}{\int e^{-\beta(\mathcal{V}(r)+\mathcal{V}_{harm}^{r*}(\xi(r)))}d^{N}r}\frac{\int e^{-\beta\mathcal{V}(r)}d^{N}r}{\int e^{-\beta\mathcal{V}(r)}d^{N}r}$$
(4.22)

$$=e^{-\beta\mathcal{V}_{harm}^{r^{*}}(q)}\frac{\int e^{-\beta\mathcal{V}(r)}\delta(\xi(r)-q)d^{N}r}{\int e^{-\beta\mathcal{V}(r)}d^{N}r}\frac{\int e^{-\beta\mathcal{V}(r)}d^{N}r}{\int e^{-\beta(\mathcal{V}(r)+\mathcal{V}_{harm}^{r^{*}}(\xi(r)))}d^{N}r}$$
(4.23)

$$=e^{-\beta\mathcal{V}_{harm}^{r^*}(q)}P(q)\frac{\int e^{-\beta\mathcal{V}(r)}d^Nr}{\int e^{-\beta(\mathcal{V}(r)+\mathcal{V}_{harm}^{r^*}(\xi(r)))}d^Nr}$$
(4.24)

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 : $\langle e^{-\beta \mathcal{V}_{harm}^{r^*}(\xi(.))} \rangle = \frac{\int e^{-\beta(\mathcal{V}(r) + \mathcal{V}_{harm}^{r^*}(\xi(r)))} d^N r}{\int e^{-\beta \mathcal{V}(r)} d^N r}$, which is the average of $e^{-\beta \mathcal{V}_{harm}^{r^*}(\xi(r))}$ calculated in the unbiased system.

Thus, for the chosen reaction coordinate ξ and the reference value r^* in the harmonic potential, P is expressed as :

$$P(q) = e^{\beta \mathcal{V}_{harm}^{r^*}(q)} P_b(q, r^*) \langle e^{-\beta \mathcal{V}_{harm}^{r^*}(\xi(.))} \rangle.$$
(4.25)

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 $P_b(q, r^*)$. 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 method³.

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

^{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), $e^{\beta \mathcal{V}_{harm}^{r^*}(q)} P_b(q, r^*)$ corresponds to the debiated umbrella, and the term $\langle e^{-\beta \mathcal{V}_{harm}^{r^*}(\xi(.))} \rangle$, 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.



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, ..., 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 $(]a_j, a_{j+1}[)_{j=1,...,M}$, these corresponding to the subdivisions used to draw the histograms of the Umbrella Sampling method.

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

$$P_{i,j} = P_b(q(j), r_i^*)$$
(4.26)

where $q(j) = (j - \frac{1}{2})(a_{j+1} - a_j).$

Similarly, we define $(P_j^0)_{j=1,...,M}$ the vector representing the (unbiased) probability in the *j*th subdivision, $(C_{i,j})_{i=1,...,N,j=1,...,M}$ the matrix of biased factors, and $(f_i)_{i=1,...,N}$ the vector of normalization constants, which are such that :

$$P_{j}^{0} = P(q(j)) \tag{4.27}$$

$$C_{i,j} = e^{\beta \mathcal{V}_{harm}^{r_j^*}(q(j))} \tag{4.28}$$

$$f_i = \langle e^{-\beta \mathcal{V}_{harm}^{r_i^*}(\xi(.))} \rangle \tag{4.29}$$

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

$$P_{i,j} = f_i C_{i,j} P_j^0. (4.30)$$

We are looking for an optimal estimator for $(P_j^0)_{j=1,\ldots,M}$, that we will note $(\widehat{P_j^0})_{j=1,\ldots,M}$.

Let $(n_{i,j})_{i=1,\dots,N,j=1,\dots,M}$ be the matrix of the number of counts of the histogram for the simulation i in the jth subdivision. An estimator of $P_{i,j}$ is then :

$$\widehat{P_{i,j}} = \frac{n_{i,j}}{n_i}.$$
(4.31)

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

$$\sum_{j=1}^{M} \widehat{P_{i,j}} = 1.$$
(4.32)

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

$$\widehat{P_{j}^{0}} = \frac{\sum_{i=1}^{N} n_{i,j}}{\sum_{i=1}^{N} n_{i} f_{i} C_{i,j}}.$$
(4.33)

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 $J: \Omega \subset \mathbb{R}^n \to \mathbb{R}$ $(n \in \mathbb{N}^*, \text{ and } \Omega \text{ is an open of } \mathbb{R}^n)$:

$$\min_{\mathbf{x}\in E} J(\mathbf{x}) \tag{4.34}$$

where $E = \{ \mathbf{x} \in \mathbb{R}^N \mid g(\mathbf{x}) = 0 \}$ avec $g : \mathbb{R}^n \to \mathbb{R}^m \ (m \in \mathbb{N}^*)$. 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 :

$$L(\boldsymbol{x}, \lambda_1, ..., \lambda_m) = J(\boldsymbol{x}) - \sum_{i=1}^m \lambda_i g_i(\boldsymbol{x}).$$
(4.35)

The coefficients $(\lambda_i)_{i=1,...,m}$ 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 :

$$\Omega_{i,j} = \frac{n_{i,j}}{n_i C_{i,j} f_i}.$$
(4.36)

The idea is to make a most optimal convex combination with the N estimators $\Omega_{i,j}$ (i = 1, ..., N) to estimate P_j^0 , i.e. we want to find $(\omega_1, ..., \omega_N)$ such that $\sum_{i=1}^N \omega_i = 1$ and

$$\widehat{P_j^0} = \sum_{i=1}^N \omega_i \Omega_{i,j} \tag{4.37}$$

has as little variance as possible.

The optimization problem is therefore the following :

$$\min_{t.q.\sum_{i=1}^{N}\omega_i=1} var(P_j^0). \tag{4.38}$$

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 :

$$\sum_{i=1}^{N} (\lambda x_i + (1-\lambda)y_i) = \lambda \sum_{i=1}^{N} x_i + (1-\lambda) \sum_{i=1}^{N} y_i = \lambda + (1-\lambda) = 1$$
(4.39)

where the penultimate tie comes from the fact that **x** and **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 $(X_k)_k$ be a sequence of random variables following a binomial law $\mathcal{B}(k, p_k)$. We suppose that $kp_k \to \lambda > 0$. Then $(X_k)_k$ converges in law to a Poisson random variable of parameter λ . In other words, for all $l \in \mathbb{N}$, we have :

$$\mathbb{P}(X_k = l) \to \frac{e^{-\lambda}\lambda^l}{l!} \tag{4.40}$$

of expectation and variance λ .

This leads us to the following lemma :

Lemma 5. With the conditions of the problem, we have :

$$var(\widehat{P_{j}^{0}}) = \sum_{i=1}^{N} \frac{\omega_{i}^{2} P_{j}^{0}}{n_{i} C_{i,j} f_{i}}.$$
 (4.41)

Proof. We have, by independence of the simulations :

$$var(\widehat{P_{j}^{0}}) = \sum_{i=1}^{N} \frac{\omega_{i}^{2} var(n_{i,j})}{n_{i}^{2} C_{i,j}^{2} f_{i}^{2}}.$$
(4.42)

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

We set $J: (x_1, ..., x_N) \mapsto \sum_{i=1}^N \frac{x_i^2 P_j^0}{n_i C_{i,j} f_i}$, J is convex as the sum of convex functions. Thus, (4.38) does have a solution.

We put the lagrangian :

$$L(\omega_1, ..., \omega_N, \lambda) = \sum_{i=1}^N \frac{\omega_i^2 P_j^0}{n_i C_{i,j} f_i} + \lambda \left(\sum_{i=1}^N \omega_i - 1\right).$$
(4.43)

First-order conditions : $-n_i C_{i,j} f_i \lambda$

$$-\forall i: \frac{\partial L}{\partial \omega_i} = 0 \Leftrightarrow \omega_i = \frac{1}{2P_j^0}$$
$$-\frac{\partial L}{\partial \lambda} = 0 \Leftrightarrow \sum_{i=1}^N \omega_i = 1, \text{ from which we derive } \frac{-\lambda}{2P_j^0} \sum_{i=1}^N n_i C_{ij} f_i = 1 \text{ and therefore } \lambda = \frac{-2P_j^0}{\sum_{i=1}^N n_i C_{i,j} f_i}$$

which allows us to obtain : $\omega_i = \frac{n_i C_{i,j} f_i}{\sum\limits_{k=1}^{N} n_k C_{k,j} f_k}.$

And then, in the end we have, for j = 1, ..., M:

$$\widehat{P_j^0} = \frac{\sum\limits_{i=1}^{N} n_{i,j}}{\sum\limits_{i=1}^{N} n_i f_i C_{i,j}}.$$

Proof. Likelihood Maximization Approach

We have, for i = 1, ..., N, that $(n_{i,1}, ..., n_{i,M})$ 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 :

$$L(f_1, ..., f_N, P_1^0, ..., P_M^0) = \prod_{i=1}^N f(i)$$

where $f(i) = \frac{n_i!}{\prod_{i=1}^{M} n_{i,k}!} \prod_{j=1}^{M} (P_{i,j})^{n_{i,j}}$ 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, ..., N) ni P_j^0 (j = 1, ..., M), what will be noted \mathcal{L}).

We have : $\mathcal{L}(f_1, ..., f_N, P_1^0, ..., P_M^0) = \sum_{i=1}^N \sum_{j=1}^M n_{i,j} \ln(f_i C_{i,j} P_j^0).$

Knowing the constraints $\sum_{j=1}^{M} f_i C_{i,j} P_j^0 = 1$ for i = 1, ..., N we then set the log of the Lagrangian

 $\mathcal{M}:$

$$\mathcal{M}(f_1, ..., f_N, P_1^0, ..., P_M^0, \lambda_1, ..., \lambda_N) = \sum_{i=1}^N (\sum_{j=1}^M n_{i,j} \ln(f_i C_{i,j} P_j^0) + \lambda_i (\sum_{j=1}^M f_i C_{i,j} P_j^0 - 1))$$

where the λ_i (i = 1, ..., N) are the Lagrange multipliers associated with the respective constraints.

First-order conditions :
- for
$$i = 1, ..., N : 0 = \frac{\partial \mathcal{M}}{\partial f_i} = \sum_{j=1}^{M} \left(\frac{n_{i,j}}{f_i} + \lambda_i C_{i,j} P_j^0\right) = \frac{n_i}{f_i} + \lambda_i \sum_{j=1}^{M} c_{i,j} P_j^0$$

- for $j = 1, ..., M : 0 = \frac{\partial \mathcal{M}}{\partial P_j^0} = \sum_{i=1}^{N} \left(\frac{n_{i,j}}{P_j^0} + \lambda_i f_i C_{i,j}\right)$
- for $i = 1, ..., N : 0 = \frac{\partial \mathcal{M}}{\partial \lambda_i} = \sum_{j=1}^{M} f_i C_{i,j} P_j^0 - 1$
We then have, for $i = 1, ..., N : \lambda_i = \frac{-n_i}{\sum_{j=1}^{M} f_i C_{i,j} P_j^0} = -n_i$,
so that, for $j = 1, ..., M : \frac{\sum_{i=1}^{N} n_{i,j}}{P_j^0} = \sum_{i=1}^{N} n_i f_i C_{i,j}$
From where one obtain, for $j = 1, ..., M : \widehat{P_j^0} = \frac{\sum_{i=1}^{N} n_{i,j}}{\sum_{i=1}^{N} n_i f_i C_{i,j}}$.

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

$$\begin{split} s1^0 &= 0 \\ s3^0 &= 0 \text{ for } i = 1 \text{ à } N \text{ do} \\ \mid s1^i &= s1^{i-1} + n_{i,j} \\ \text{end} \\ \text{while } \|f_i - f_{i-1}\| > \delta \text{ do} \\ \mid s2^j &= n_i f_i C_{i,j} \\ \text{end} \\ P^j &= \frac{s1^N}{s2^N} \\ \text{for } j = 1 \text{ à } M \text{ do} \\ \mid s3^j &= s3^{j-1} + C_{i,j} P_j^0 \\ \text{end} \\ f_{i+1} &= s3^{-1} \\ \text{end} \\ \end{split}$$

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 : $U = \frac{1}{2}k((x_2 - x_1) - d)^2$.

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 :

$$F_i = m_i \ddot{x}_i. \tag{4.44}$$

We know that, for i = 1, 2, we have : $F_i = -\frac{dU(x_i)}{dx_i}$, so that :

$$F_1 = k(x_2 - x_1 - d) = -F_2. (4.45)$$

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

$$(S) \begin{cases} k(x_2 - x_1 - d) = m_1 \ddot{x_1} \\ -k(x_2 - x_1 - d) = m_2 \ddot{x_2} \end{cases}$$
(4.46)

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.

$$\ddot{x_G} = \frac{m_1 \ddot{x_1} + m_2 \ddot{x_2}}{m_1 + m_2} = 0 \tag{4.47}$$

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 :

$$y = \frac{m_2}{m_1 + m_2} (x_1 - x_2). \tag{4.48}$$

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

$$k(-\frac{m_1+m_2}{m_2}y-d) = m_1\ddot{y}.$$
(4.49)

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

$$\omega = \sqrt{k \frac{m_1 + m_2}{m_1 m_2}}.$$
(4.50)

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

$$y(t) = r\cos(\omega t + \Phi) - \frac{m_2 d}{m_1 + m_2}$$
(4.51)

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

$$T = \frac{2\pi}{\omega} = 2\pi \sqrt{\frac{m_1 m_2}{k(m_1 + m_2)}}.$$
(4.52)

4.7.2 Analysis with Hamiltonian formulation

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

$$L = E_c - U. \tag{4.53}$$

Here we have :

$$L(x_1, x_2, \dot{x_1}, \dot{x_2}) = \frac{1}{2}(m_1 \dot{x_1}^2 + m_2 \dot{x_2}^2) - \frac{1}{2}k(x_2 - x_1 - d)^2.$$
(4.54)

We introduce $a = x_G = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$ and $a' = x_2 - x_1$. We have then :

$$\begin{cases} \dot{a} = \frac{m_1 \dot{x}_1 + m_2 \dot{x}_2}{m_1 + m_2} \\ \dot{a}' = \dot{x}_2 - \dot{x}_1 \end{cases} \Rightarrow \begin{cases} \dot{a} = \frac{m_1 \dot{x}_1 + m_2 \dot{x}_2}{m_1 + m_2} \\ \frac{\sqrt{m_1 m_2}}{m_1 + m_2} \dot{a}' = \frac{\sqrt{m_1 m_2}}{m_1 + m_2} (\dot{x}_2 - \dot{x}_1) \end{cases} \Rightarrow \begin{cases} \dot{a}^2 = \frac{m_1^2 \dot{x}_1^2 + m_2^2 \dot{x}_2^2 + 2m_1 m_2 \dot{x}_1 \dot{x}_2}{(m_1 + m_2)^2} \\ \frac{m_1 m_2}{(m_1 + m_2)^2} \dot{a}'^2 = \frac{m_1 m_2}{(m_1 + m_2)^2} (\dot{x}_2^2 + \dot{x}_1^2 - 2\dot{x}_1 \dot{x}_2) \end{cases}$$

$$(4.55)$$

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

$$\dot{a}^{2} + \frac{m_{1}m_{2}}{(m_{1} + m_{2})^{2}}\dot{a}^{\prime 2} = \frac{m_{1}^{2}\dot{x_{1}}^{2} + m_{2}^{2}\dot{x_{2}}^{2} + 2m_{1}m_{2}\dot{x_{1}}\dot{x_{2}}}{(m_{1} + m_{2})^{2}} + \frac{m_{1}m_{2}}{(m_{1} + m_{2})^{2}}(\dot{x_{2}}^{2} + \dot{x_{1}}^{2} - 2\dot{x_{1}}\dot{x_{2}})$$
$$= \frac{m_{1}(m_{1} + m_{2})}{(m_{1} + m_{2})^{2}}\dot{x_{1}}^{2} + \frac{m_{2}(m_{1} + m_{2})}{(m_{1} + m_{2})^{2}}\dot{x_{2}}^{2}$$
$$= \frac{m_{1}}{m_{1} + m_{2}}\dot{x_{1}}^{2} + \frac{m_{2}}{m_{1} + m_{2}}\dot{x_{2}}^{2}$$
(4.56)

 $\Leftrightarrow (m_1 + m_2)\dot{a}^2 + \frac{m_1m_2}{m_1 + m_2}a'^2 = m_1\dot{x_1}^2 + m_2\dot{x_2}^2.$

Let's start again (4.54) and you get :

$$L(a, a', \dot{a}, \dot{a'}) = \frac{1}{2} \left((m_1 + m_2)\dot{a}^2 + \frac{m_1 m_2}{m_1 + m_2} \dot{a'}^2 \right) - \frac{1}{2}k(a' - d)^2.$$
(4.57)

The Hamiltonian H associated with (P) is then :

$$H(a, a', b, b') = p\dot{a} + p'\dot{a}' - L(a, a', \dot{x}_1(b), \dot{x}_2(b'))$$
(4.58)

where b and b' are associated with a transformation of Legrendre of the Lagrangian.

We take $b = \frac{\partial L}{\partial \dot{a}} = (m_1 + m_2)\dot{a}$ et $b' = \frac{\partial L}{\partial \dot{a}'} = \frac{m_1 m_2}{m_1 + m_2}\dot{a}'$. So that :

$$H(a,a',b,b') = \frac{b^2}{m_1 + m_2} + \frac{m_1 + m_2}{m_1 m_2} b'^2 - \left(\frac{1}{2}\left(\frac{b^2}{m_1 + m_2} + \frac{m_1 + m_2}{m_1 m_2}b'\right) - \frac{1}{2}k(a'-d)^2\right)$$
(4.59)

$$= \frac{1}{2} \left(\frac{b^2}{m_1 + m_2} + \frac{m_1 + m_2}{m_1 m_2} b' \right) + \frac{1}{2} k(a' - d)^2.$$
(4.60)

We have :

$$\frac{\partial H}{\partial b} = \frac{b}{m_1 + m_2} , \ \frac{\partial H}{\partial b'} = \frac{m_1 + m_2}{m_1 m_2} b' , \ \frac{\partial H}{\partial a} = 0 , \ \frac{\partial H}{\partial a'} = k(a' - d).$$
(4.61)

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

$$\begin{cases} \dot{a} = \frac{\partial H}{\partial b} \\ \dot{a}' = \frac{\partial H}{\partial b'} \\ \dot{b} = -\frac{\partial H}{\partial a} \\ \dot{b}' = -\frac{\partial H}{\partial a'} \end{cases} \Leftrightarrow \begin{cases} \dot{a} = \frac{b}{m_1 + m_2} \\ \dot{a}' = \frac{m_1 + m_2}{m_1 m_2} b' \\ \dot{b} = 0 \\ \dot{b}' = -k(a' - d) \end{cases}$$
(4.62)

So that :

$$\begin{cases} \dot{x}_G = C\\ \frac{m_1 m_2}{m_1 + m_2} \ddot{a'} = -k(a' - d) \end{cases}$$
(4.63)

The movement of the system therefore consists of a constant velocity for the center of gravity and a vibration for $a' = x_2 - x_1$ of period $2\pi \sqrt{\frac{m_1 m_2}{k(m_1 + m_2)}}$ around the equilibrium position a' = d.

On the other hand, the system writes in the form of (4.60) allows to decouple the vibration term (a', b') 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 :

$$\langle \frac{1}{2}k(a'-d)^2 \rangle = \frac{1}{2}k_BT.$$
 (4.64)

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

$$\sigma = \sqrt{\frac{k_B T}{k}}.\tag{4.65}$$

4.7.3 Stiffness constant, umbrella amplitude and period for our simulations

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

$$\Theta = 2\pi \sqrt{\frac{m_1 m_2}{k(m_1 + m_2)}} \tag{4.66}$$

where m_i is the mass of the particle p_i .

In the case where $p_1 = Na^+$ and $p_2 = Cl^-$ we have : $m_1 = 23 \text{ g} \cdot \text{mol}^{-1}$ and $m_2 = 35.5 \text{ g} \cdot \text{mol}^{-1}$.

As the ideal stiffness constant to be applied to the spring force between the two ions, one wishes to choose $k = 10 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{A}^{-2}$ (units corresponding to those of Tinker). We recall the following conversions of measures :

$$1 \text{ kcal} = 4,184 \text{ kJ}$$
 (4.67)

$$1 J = 1 kg.m^2.s^{-2}$$
(4.68)

$$1 A = 10^{-10} m (4.69)$$

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 ps ensures that the spring has acted well to maintain the ions at the desired distance.

Moreover, the amplitude of the umbrella is then $\sigma = 0.2433$ A.

4.8 Calculation of coefficients of interest

4.8.1 The association constant

Consider the chemical reaction in a surrounding solvent :

$$C^{c+} + A^{a-} \leftrightarrow CA^{(c-a)+} \tag{4.70}$$

where C^{c+} corresponds to the cation, A^{a-} to the anion and $CA^{(c-a)+}$ 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 [14,115]. 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 :

$$K = \frac{1 - \alpha}{\alpha^2 c} = K^{(c)} \left(\frac{y_{\pm}^{\prime 2}}{y_{IP}} \right)$$
(4.71)

where α is the degree of dissociation of the pair, $c = \frac{\rho}{2N_A}$ is the electrolyte concentration, $K^{(c)}$ is the **association constant**, and y'_{\pm} et y_{IP} 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] :

$$K^{(c)} = 4\pi N_A \int_0^R r^2 e^{\frac{-V_{MM}(r)}{k_B T}} dr$$
(4.72)

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 μ_w and that of the solution μ_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 Ω [127,133]:

$$d\Omega = -SdT - N_w d\mu_w - N_s d\mu_s - PdV \tag{4.73}$$

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 :

$$P = P_w + P_{osm} \tag{4.74}$$

where P_w is the pressure of the pure solvent and P_{osm} 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 :

$$Q(W) = e^{\beta P_{osm}V} \tag{4.75}$$

The **osmotic coefficient** [69,133] of the electrolyte solution at the McMillan and Mayer scale Φ^{MM} can be defined by the formula :

$$\Phi^{MM} = \frac{P_{osm}}{\rho k_B T} \tag{4.76}$$

where ρ 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 Na⁺, an ion $textCl^-$ 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 ϵ_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 $(p_1^{ijk})_{i,j,k\in\mathbb{Z}^*}$ and $(p_2^{ijk})_{i,j,k\in\mathbb{Z}^*}$ the images of p_1 and p_2 by periodicity, which are described by their position \mathbf{r}_1^{ijk} and \mathbf{r}_2^{ijk} respectively.

We note $\|\mathbf{r}\| = \min_{i,j,k \in \mathbb{Z}} \|\overrightarrow{\mathbf{r}_1^{ijk}\mathbf{r}_2^{ijk}}\|$ the distance between ion p_1 and p_2^{-1} .

L has been choosen so that $L >> ||\mathbf{r}||$ (that corresponds to a system in a large box with N water molecules, where N is large, which represents a diluted medium).

Let U_{PBC} be the energy potential of the periodic system. We are interested in the behaviour of U_{PBC} as a function of **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_{PBC} verifies :

$$U_{PBC}(\boldsymbol{r},L) = \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon_r \|\boldsymbol{r}\|} \left(1 + C\left(\frac{\|\boldsymbol{r}\|}{L}\right)^5 \right) + \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon_r} \int_{S(r)} \left(\sum_{\boldsymbol{n}\in\mathbb{Z}^3\setminus\{0\}} \frac{35}{2} \frac{(\boldsymbol{l}.\boldsymbol{n})^3 \boldsymbol{n}}{\|\boldsymbol{n}\|^9 L^5} \right) d\boldsymbol{l} + o\left(\frac{\|\boldsymbol{r}\|^4}{L^5}\right)$$
(5.1)

^{1.} Taking this minimum on the images allow to avoid box effects

69

with $C = -\left(21 \sum_{i>0, j \ge i, k \ge i+1} \frac{1}{\|(i,j,k)^t\|^5} + \left(\frac{21}{4} + \frac{7}{3^{5/2}}\right)\zeta(5) + \frac{21}{2} \sum_{i,j>0} \frac{1}{\|(i,j)^t\|^5}\right)$ (so that $C \simeq -9.079945024529188$), ζ being the zeta function. For $\mathbf{r} = (x, y, z)$, $S(\mathbf{r}) = [a_1, x] \times [a_2, y] \times [a_3, z]$ (a_1, a_2, a_3) 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 σ , of order 3, which is such that :

$$\sigma = \begin{pmatrix} i \ j \ k \\ j \ k \ i \end{pmatrix}$$

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

$$\mathbf{r}_{1l} = \begin{cases} 0 \ if \ l = 1 \\ \mathbf{r} \ if \ l = 2 \end{cases}$$

we have :

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

$$= \frac{q_1 q_2 \mathbf{r}}{4\pi\epsilon_0 \epsilon_r \|\mathbf{r}\|^3} + \frac{q_1^2}{4\pi\epsilon_0 \epsilon_r} \sum_{\mathbf{n} \in \mathbb{Z}^3 \setminus \{0\}} \frac{1}{\|\mathbf{n}L\|^3} \mathbf{n}L + \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon_r} \sum_{\mathbf{n} \in \mathbb{Z}^3 \setminus \{0\}} \frac{1}{\|\mathbf{r} + \mathbf{n}L\|^3} \left(\mathbf{r} + \mathbf{n}L\right) \quad (5.3)$$

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 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 satisfy 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 :

$$A(\mathbf{r}, \mathbf{n}, L) := \frac{1}{\|\mathbf{r} + \mathbf{n}L\|^3} \left(\mathbf{r} + \mathbf{n}L\right).$$
(5.4)

We have :

$$A(\mathbf{r}, \mathbf{n}, L) = (\mathbf{r} + \mathbf{n}L) \left(\|\mathbf{r}\|^2 + 2\mathbf{r} \cdot \mathbf{n}L + \mathbf{n}^2 L^2 \right)^{-3/2}$$

= $(\mathbf{r} + \mathbf{n}L) \frac{1}{\|\mathbf{n}\|^3 L^3} \left(1 + 2\frac{\mathbf{r} \cdot \mathbf{n}}{\|\mathbf{n}\|^2 L} + \frac{\|\mathbf{r}\|^2}{\|\mathbf{n}\|^2 L^2} \right)^{-3/2}.$ (5.5)

We recall the expansion for small \boldsymbol{u} :

1

$$(1+u)^{-3/2} = 1 - \frac{3}{2}u + \frac{15}{8}u^2 - \frac{35}{16}u^3 + o(u^3).$$
(5.6)

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

$$A(\mathbf{r}, \mathbf{n}, L) = \left(\frac{\mathbf{r}}{\|\mathbf{n}\|^{3}L^{3}} + \frac{\mathbf{n}}{\|\mathbf{n}\|^{3}L^{2}}\right) \left(1 - \frac{3}{2}\frac{2\mathbf{r}\cdot\mathbf{n}}{\|\mathbf{n}\|^{2}L} - \frac{3}{2}\frac{\|\mathbf{r}\|^{2}}{\|\mathbf{n}\|^{2}L^{2}} + \frac{15}{8}\frac{4(\mathbf{r}\cdot\mathbf{n})^{2}}{\|\mathbf{n}\|^{4}L^{2}} + \frac{15}{8}\frac{4(\mathbf{r}\cdot\mathbf{n})\|\mathbf{r}\|^{2}}{\|\mathbf{n}\|^{4}L^{3}} - \frac{35}{16}\frac{8(\mathbf{r}\cdot\mathbf{n})^{3}}{\|\mathbf{n}\|^{6}L^{3}} + o\left(\frac{\|\mathbf{r}\|^{3}}{L^{3}}\right)\right)$$
(5.7)

$$= \frac{A_1(\mathbf{r}, \mathbf{n})}{L^2} + \frac{A_2(\mathbf{r}, \mathbf{n})}{L^3} + \frac{A_3(\mathbf{r}, \mathbf{n})}{L^4} + \frac{A_4(\mathbf{r}, \mathbf{n})}{L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right)$$
(5.8)

with :

$$A_1(\mathbf{r}, \mathbf{n}) = \frac{\mathbf{n}}{\|\mathbf{n}\|^3} \tag{5.9}$$

$$A_2(\mathbf{r}, \mathbf{n}) = \left(\frac{\mathbf{r}}{\|\mathbf{n}\|^3} - \frac{3(\mathbf{r}, \mathbf{n})\mathbf{n}}{\|\mathbf{n}\|^5}\right)$$
(5.10)

$$A_{3}(\mathbf{r}, \mathbf{n}) = \left(\frac{-3(\mathbf{r}, \mathbf{n})\mathbf{r}}{\|\mathbf{n}\|^{5}} - \frac{3}{2}\frac{\|\mathbf{r}\|^{2}\mathbf{n}}{\|\mathbf{n}\|^{5}} + \frac{15}{2}\frac{(\mathbf{r}, \mathbf{n})^{2}\mathbf{n}}{\|\mathbf{n}\|^{7}}\right)$$
(5.11)

$$A_4(\mathbf{r}, \mathbf{n}) = \left(\frac{-3}{2} \frac{\|\mathbf{r}\|^2 \mathbf{r}}{\|\mathbf{n}\|^5} + \frac{15}{2} \frac{(\mathbf{r}, \mathbf{n})^2 \mathbf{r}}{\|\mathbf{n}\|^7} + \frac{15}{2} \frac{(\mathbf{r}, \mathbf{n}) \|\mathbf{r}\|^2 \mathbf{n}}{\|\mathbf{n}\|^7} - \frac{35}{2} \frac{(\mathbf{r}, \mathbf{n})^3 \mathbf{n}}{\|\mathbf{n}\|^9}\right)$$
(5.12)

For the term or order 2 (in $\|\mathbf{n}\|$; i.e. $\sum_{\mathbf{n}\in\mathbb{Z}^3\setminus\{0\}} \frac{A_1(\mathbf{r},\mathbf{n})}{L^2}$), 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 :

$$B(\mathbf{r}, \mathbf{n}, L) := A(\mathbf{r}, \mathbf{n}, L) + A(\mathbf{r}, -\mathbf{n}, L)$$
(5.13)

$$= \frac{\mathbf{r} + \mathbf{n}L}{\|\mathbf{r} + \mathbf{n}L\|^3} + \frac{\mathbf{r} - \mathbf{n}L}{\|\mathbf{r} - \mathbf{n}L\|^3}.$$
(5.14)

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
- $j \ge i$ and $k \ge i+1$

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 (i', j', k') = (-i, -j, -k) where i', j', k' > 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_{abc} , which is such as :

$$S_{abc} = B(\mathbf{r}, (a, b, c), L) + B(\mathbf{r}, (a, (-b), (-c)), L) + B(\mathbf{r}, (a, (-b), c), L) + B(\mathbf{r}, (a, b, (-c)), L)$$
(5.15)

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

We easily see that :

$$S_{ijk} = S_{i(-j)(-k)} = S_{i(-j)k} = S_{ij(-k)}$$
(5.16)

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 $j \ge i$ and $k \ge i + 1$ is a sufficient condition.

a) We assume that $j \ge i$. We first suppose that j = i. By the absurd, we assume that $k \le i - 1$ (the case where k = i is impossible as we saw at the beginning of the proof). By taking the second permutation in the node (i, j, k), we obtain a node (i', j', k') = (k, i, j) which is such that j' = i, $k' \ge i$ and $i' \le i - 1$, so that $j' \ge i'$ and $k' \ge i' + 1$. This case is already treated.

Then, we consider j > i. The case when $k \le i-1$ can be treated as the previous ones. It remains to study the case when k = i (which is possible here seens $j \ne i$). By the same arguments as earlier we can prove that this case is already solved.

b) We suppose that $k \ge i+1$. By the absurd, we consider that j < i. We take the first permutation of the node (i, j, k) and we obtain the node (i', j', k') = (j, k, i), with k' = i, i' < i and $j' \ge i+1$, so that $j' \ge i' + 1$ and k' > i' i.e. $k' \ge i' + 1$. 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 $||\mathbf{n}||$) in $\sum_{\mathbf{n}\in\mathbb{Z}^3\setminus\{0\}} A(\mathbf{r},\mathbf{n},L)$ (i.e. $\sum_{\mathbf{n}\in\mathbb{Z}^3\setminus\{0\}} \frac{A_2(\mathbf{r},\mathbf{n})}{L^3}$) can be eliminated by means of our combinations.

Proof. We have :

$$B(\mathbf{r}, \mathbf{n}, L) = \frac{2\mathbf{r}}{\|\mathbf{n}\|^3 L^3} - \frac{6(\mathbf{r}.\mathbf{n})\mathbf{n}}{\|\mathbf{n}\|^5 L^3} + f(\mathbf{r}, \mathbf{n}, L) + o(L^{-6})$$
(5.17)

where f is a function whose term in **n** is of order greater than 3.

case 1 : We combine nodes (0, j, 0) and its permutations. We first remark that :

$$\|\mathbf{n}\| = |j| \tag{5.18}$$

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

$$\frac{6\mathbf{r}}{\|\mathbf{n}\|^3 L^3} - \frac{6j^2 \mathbf{r}}{\|\mathbf{n}\|^5 L^3} = \frac{6\mathbf{r}}{\|\mathbf{n}\|^3 L^3} - \frac{6\mathbf{r}}{\|\mathbf{n}\|^3 L^3} = 0.$$
(5.19)

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

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

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

$$\frac{8\mathbf{r}}{\|\mathbf{n}\|^{3}L^{3}} - \frac{6\left((xi+yi+zi)\begin{pmatrix}i\\i\\i\end{pmatrix} + (xi-yi-zi)\begin{pmatrix}i\\-i\\-i\end{pmatrix} + (xi-yi+zi)\begin{pmatrix}i\\-i\\i\end{pmatrix} + (xi+yi-zi)\begin{pmatrix}i\\i\\-i\end{pmatrix}\right)}{\|\mathbf{n}\|^{5}L^{3}} = \frac{8\mathbf{r}}{\|\mathbf{n}\|^{3}L^{3}} - \frac{24i^{2}\mathbf{r}}{3^{5/2}|i|^{5}L^{3}} = 0.$$
(5.21)

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

$$\|\mathbf{n}\| = \|(i,j)\| \tag{5.22}$$

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

$$\frac{12\mathbf{r}}{\|\mathbf{n}\|^{3}L^{3}} - \frac{6\left((xi+yj)\begin{pmatrix}i\\j\\0\end{pmatrix} + (xi-yj)\begin{pmatrix}i\\-j\\0\end{pmatrix} + (xj+zi)\begin{pmatrix}j\\0\\i\end{pmatrix} + (xj-zi)\begin{pmatrix}j\\0\\-i\end{pmatrix}\right)}{\|\mathbf{n}\|^{5}L^{3}} - \frac{6\left((yi+zj)\begin{pmatrix}0\\i\\j\end{pmatrix} + (yi-zj)\begin{pmatrix}0\\i\\-j\end{pmatrix}\right)}{\|\mathbf{n}\|^{5}L^{3}}$$
(5.23)

$$= \frac{12\mathbf{r}}{\|\mathbf{n}\|^3 L^3} - \frac{12\left(i^2 + j^2\right)\mathbf{r}}{\|\mathbf{n}\|^5 L^3} = 0.$$
(5.24)

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

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

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

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

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 :

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

b) Case 2 :

We combine nodes (i, i, i), (i, -i, -i), (i, -i, i) and (i, i, -i) and we obtain :

$$B(\mathbf{r},(i,i,i),L)[x] + B(\mathbf{r},(i,-i,-i),L)[x] + B(\mathbf{r},(i,-i,i),L)[x] + B(\mathbf{r},(i,i,-i),L)[x] = 28 \frac{\|\mathbf{r}\|^2 x}{3^{5/2} |i|^5 L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right)$$
(5.28)

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 :

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

d) General case :

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

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

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

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

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

$$B(\mathbf{r},(k,i,j),L)[x] + B(\mathbf{r},(k,-i,-j),L)[x] = \frac{4x}{A_{ijk}^3 L^3} - 6\frac{\|\mathbf{r}\|^2 x}{A_{ijk}^5 L^5} + \frac{30x}{A_{ijk}^7 L^5} (x^2 k^2 + y^2 i^2 + z^2 j^2 + 2yzij) - \frac{12xk^2}{A_{ijk}^5 L^3} + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^7 L^5} xk^2 + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.32)

The three previous factors are added together, which gives

$$B_{1}^{ijk,x}(L) := B(\mathbf{r}, (i, j, k), L)[x] + B(\mathbf{r}, (i, -j, -k), L)[x] + B(\mathbf{r}, (j, k, i), L)[x] + B(\mathbf{r}, (j, -k, -i), L)[x] + B(\mathbf{r}, (k, i, j), L)[x] + B(\mathbf{r}, (k, -i, -j), L)[x]$$
(5.33)

$$=\frac{12x}{A_{ijk}^3L^3} - 18\frac{\|\mathbf{r}\|^2 x}{A_{ijk}^5L^5} + \frac{30x}{A_{ijk}^7L^5}(x^2(A_{ijk}^2) + y^2(A_{ijk}^2) + z^2(A_{ijk}^2) + 2yz(jk + ik + ij))$$
(5.34)

$$-\frac{12x}{A_{ijk}^3 L^3} + \frac{30 \|\mathbf{r}\|^2 x}{A_{ijk}^5 L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right)$$
(5.35)

$$= -18\frac{\|\mathbf{r}\|^2 x}{A_{ijk}^5 L^5} + \frac{30\|\mathbf{r}\|^2 x}{A_{ijk}^5 L^5} + \frac{60x}{A_{ijk}^7 L^5} yz(jk+ik+ij) + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^5 L^5} x + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right)$$
(5.36)

$$=42\frac{\|\mathbf{r}\|^2 x}{A_{ijk}^5 L^5} + \frac{60x}{A_{ijk}^7 L^5} yz(jk+ik+ij) + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.37)

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

$$B_{2}^{ijk,x}(L) := B(\mathbf{r}, (i, -j, k), L)[x] + B(\mathbf{r}, (i, j, -k), L)[x] + B(\mathbf{r}, (j, -k, i), L)[x] + B(\mathbf{r}, (j, k, -i), L)[x] + B(\mathbf{r}, (k, -i, j), L)[x] + B(\mathbf{r}, (k, i, -j), L)[x]$$
(5.38)

$$=42\frac{\|\mathbf{r}\|^2 x}{A_{ijk}^5 L^5} - \frac{60x}{A_{ijk}^7 L^5} yz(jk+ik+ij) + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.39)

Finally :

$$B_1^{ijk,x}(L) + B_2^{ijk,x}(L) = 84 \frac{\|\mathbf{r}\|^2 x}{A_{ijk}^5 L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.40)

B. Calculus for the second coordinate :

a) **Case 1 :**

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

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

b) Case 2 :

We combine nodes (i, i, i), (i, -i, -i), (i, -i, i) and (i, i, -i) and we obtain : $B(\mathbf{r}, (i, i, i), L)[y] + B(\mathbf{r}, (i, -i, -i), L)[y] + B(\mathbf{r}, (i, -i, i), L)[y] + B(\mathbf{r}, (i, i, -i), L)[y] = 28 \frac{\|\mathbf{r}\|^2 y}{3^{5/2} |i|^5 L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right)$ (5.42)

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 :

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

$\operatorname{d})$ General case :

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

$$B(\mathbf{r},(i,j,k),L)[y] + B(\mathbf{r},(i,-j,-k),L)[y] = \frac{4y}{A_{ijk}^3 L^3} - 6\frac{\|\mathbf{r}\|^2 y}{A_{ijk}^5 L^5} + \frac{30y}{A_{ijk}^7 L^5} (x^2 i^2 + y^2 j^2 + z^2 k^2 + 2yzjk) - \frac{12yj^2}{A_{ijk}^5 L^3} - \frac{12zjk}{A_{ijk}^5 L^3} + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^7 L^5} yj^2 + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^7 L^5} zjk + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$

$$(5.44)$$

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

$$B(\mathbf{r},(j,k,i),L)[y] + B(\mathbf{r},(j,-k,-i),L)[y] = \frac{4y}{A_{ijk}^3 L^3} - 6\frac{\|\mathbf{r}\|^2 y}{A_{ijk}^5 L^5} + \frac{30y}{A_{ijk}^7 L^5} (x^2 j^2 + y^2 k^2 + z^2 i^2 + 2yzki) - \frac{12yk^2}{A_{ijk}^5 L^3} - \frac{12zik}{A_{ijk}^5 L^3} + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^7 L^5} yk^2 + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^7 L^5} zik + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.45)

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

$$B(\mathbf{r},(k,i,j),L)[y] + B(\mathbf{r},(k,-i,-j),L)[y] = \frac{4y}{A_{ijk}^3 L^3} - 6\frac{\|\mathbf{r}\|^2 y}{A_{ijk}^5 L^5} + \frac{30y}{A_{ijk}^7 L^5} (x^2 k^2 + y^2 i^2 + z^2 j^2 + 2yzij) \\ - \frac{12yi^2}{A_{ijk}^5 L^3} - \frac{12zij}{A_{ijk}^5 L^3} + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^7 L^5} yi^2 + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^7 L^5} zij + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$

$$(5.46)$$

The three previous factors are added together, which gives

$$B_{1}^{ijk,y}(L) := B(\mathbf{r}, (i, j, k), L)[y] + B(\mathbf{r}, (i, -j, -k), L)[y] + B(\mathbf{r}, (j, k, i), L)[y] + B(\mathbf{r}, (j, -k, -i), L)[y] + B(\mathbf{r}, (k, i, j), L)[y] + B(\mathbf{r}, (k, -i, -j), L)[y]$$
(5.47)

$$=\frac{12y}{A_{ijk}^3L^3} - 18\frac{\|\mathbf{r}\|^2 y}{A_{ijk}^5L^5} + \frac{30y}{A_{ijk}^7L^5}(x^2(A_{ijk}^2) + y^2(A_{ijk}^2) + z^2(A_{ijk}^2) + 2yz(jk + ik + ij))$$
(5.48)

$$-\frac{12y}{A_{ijk}^3L^3} - \frac{12z}{A_{ijk}^5L^3}(ij+ik+jk) + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^5L^5}y + \frac{30\|\mathbf{r}\|^2}{A_{ijk}^7L^5}z(ij+ik+jk) + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right)$$
(5.49)

$$= 42 \frac{\|\mathbf{r}\|^2 y}{A_{ijk}^5 L^5} + \frac{60}{A_{ijk}^7 L^5} y^2 z(jk + ik + ij) - \frac{12z}{A_{ijk}^5 L^3} (ij + ik + jk) + \frac{30 \|\mathbf{r}\|^2}{A_{ijk}^7 L^5} z(ij + ik + jk) + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.50)

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

$$B_{2}^{ijk,y}(L) := B(\mathbf{r}, (i, -j, k), L)[y] + B(\mathbf{r}, (i, j, -k), L)[y] + B(\mathbf{r}, (j, -k, i), L)[y] + B(\mathbf{r}, (j, k, -i), L)[y] + B(\mathbf{r}, (k, -i, j), L)[y] + B(\mathbf{r}, (k, i, -j), L)[y]$$
(5.51)

$$= 42 \frac{\|\mathbf{r}\|^2 y}{A_{ijk}^5 L^5} - \frac{60}{A_{ijk}^7 L^5} y^2 z(jk + ik + ij) + \frac{12z}{A_{ijk}^5 L^3} (ij + ik + jk) - \frac{30 \|\mathbf{r}\|^2}{A_{ijk}^7 L^5} z(ij + ik + jk) + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.52)

Finally :

$$B_1^{ijk,y}(L) + B_2^{ijk,y}(L) = 84 \frac{\|\mathbf{r}\|^2 y}{A_{ijk}^5 L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.53)

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 :

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

b) Case 2 :

For nodes (i, i, i), (i, -i, -i), (i, -i, i) and (i, i, -i): $B(\mathbf{r}, (i, i, i), L)[z] + B(\mathbf{r}, (i, -i, -i), L)[z] + B(\mathbf{r}, (i, -i, i), L)[z] + B(\mathbf{r}, (i, i, -i), L)[z] = 28 \frac{\|\mathbf{r}\|^2 z}{3^{5/2} |i|^5 L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$ (5.55)

c) Case 3 :

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

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

d) General case :

 $\begin{aligned} \text{For nodes } (i, j, k) \text{ and } (i, -j, -k) \text{ and the same with the permutations of } (i, j, k) : \\ B_1^{ijk,z}(L) &:= B(\mathbf{r}, (i, j, k), L)[z] + B(\mathbf{r}, (i, -j, -k), L)[z] + B_{jki}^z(L) + B(\mathbf{r}, (j, -k, -i), L)[z] \\ &\quad + B(\mathbf{r}, (k, i, j), L)[z] + B(\mathbf{r}, (k, -i, -j), L)[z] \quad (5.57) \\ &= \frac{12z}{A_{ijk}^3 L^3} - 18 \frac{\|\mathbf{r}\|^2 z}{A_{ijk}^5 L^5} + \frac{30z}{A_{ijk}^7 L^5} (x^2 (A_{ijk}^2) + y^2 (A_{ijk}^2) + z^2 (A_{ijk}^2) + 2r_2 z (jk + ik + ij)) \\ &\quad - \frac{12z}{A_{ijk}^3 L^3} - \frac{12y}{A_{ijk}^5 L^3} (ij + ik + jk) + \frac{30 \|\mathbf{r}\|^2}{A_{ijk}^5 L^5} z + \frac{30 \|\mathbf{r}\|^2}{A_{ijk}^7 L^5} y(ij + ik + jk) + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right) \\ &\quad (5.58) \\ &= 42 \frac{\|\mathbf{r}\|^2 z}{A_{ijk}^5 L^5} + \frac{60}{A_{ijk}^7 L^5} yz^2 (jk + ik + ij) - \frac{12y}{A_{ijk}^5 L^3} (ij + ik + jk) + \frac{30 \|\mathbf{r}\|^2}{A_{ijk}^7 L^5} y(ij + ik + jk) + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right). \end{aligned}$

For nodes (i, -j, k) and (i, j, -k) and the same with the permutations of (i, j, k): $B_{2}^{ijk,z}(L) := B(\mathbf{r}, (i, -j, k), L)[z] + B(\mathbf{r}, (i, j, -k), L)[z] + B(\mathbf{r}, (j, -k, i), L)[z] + B(\mathbf{r}, (j, k, -i), L)[z] + B(\mathbf{r}, (k, i, -j), L)[z]$ $+ B(\mathbf{r}, (k, -i, j), L)[z] + B(\mathbf{r}, (k, i, -j), L)[z]$ $= 42 \frac{\|\mathbf{r}\|^{2}z}{A_{ijk}^{5}L^{5}} - \frac{60}{A_{ijk}^{7}L^{5}}yz^{2}(jk + ik + ij) + \frac{12y}{A_{ijk}^{5}L^{3}}(ij + ik + jk) - \frac{30\|\mathbf{r}\|^{2}}{A_{ijk}^{7}L^{5}}y(ij + ik + jk) + o\left(\frac{\|\mathbf{r}\|^{3}}{L^{5}}\right).$ (5.61)

So that finally :

$$B_1^{ijk,z}(L) + B_2^{ijk,z}(L) = 84 \frac{\|\mathbf{r}\|^2 z}{A_{ijk}^5 L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right).$$
(5.62)

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

$$\nabla_1 U_{PBC}(\mathbf{r}, L) = -\mathbf{F}_1(\mathbf{r}, L) \tag{5.63}$$

$$= -\frac{q_1 q_2 \mathbf{r}}{4\pi\epsilon_0 \epsilon_r \|\mathbf{r}\|^3} - \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon_r} \left(\left(\sum_{i>0,j\ge i,k\ge i+1} \frac{84}{\|(i,j,k)\|^5 L^5} + \sum_{i>0} \left(21 + \frac{28}{3^{5/2}} \right) \frac{1}{|i|^5 L^5} \right) \right)$$

$$+\sum_{i,j>0}\frac{42}{\|(i,j)^t\|^5 L^5}\bigg)\|\mathbf{r}\|^2\mathbf{r} - \sum_{\mathbf{n}\in\mathbb{Z}^3\setminus\{0\}}\frac{35}{2}\frac{(\mathbf{r}.\mathbf{n})^3\mathbf{n}}{\|\mathbf{n}\|^9 L^5} + o\left(\frac{\|\mathbf{r}\|^3}{L^5}\right)\bigg)$$
(5.64)

so that we get (by symmetry of the potential to determine the constante) the result :

$$U_{PBC}(\mathbf{r},L) = \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon_r \|\mathbf{r}\|} \left(1 + C\left(\frac{\|\mathbf{r}\|}{L}\right)^5 \right) + \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon_r} \int_{S(\mathbf{r})} \left(\sum_{\mathbf{n}\in\mathbb{Z}^3\setminus\{0\}} \frac{35}{2} \frac{(\mathbf{l}.\mathbf{n})^3 \mathbf{n}}{\|\mathbf{n}\|^9 L^5} \right) d\mathbf{l} + o\left(\frac{\|\mathbf{r}\|^4}{L^5}\right)$$
(5.65)

with $C = -\left(21 \sum_{i>0, j \ge i, k \ge i+1} \frac{1}{\|(i, j, k)^t\|^5} + \left(\frac{21}{4} + \frac{7}{3^{5/2}}\right) \zeta(5) + \frac{21}{2} \sum_{i, j>0} \frac{1}{\|(i, j)^t\|^5}\right)$ (so that $C \simeq -9.079945024529188$), ζ being the zeta function. $S(\mathbf{r}) = [a_1, x] \times [a_2, y] \times [a_3, z]$ ((a_1, a_2, a_3) being choosen such that the constant of that primitive is null).

First of all, we can note that the first 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 $\frac{q_1q_2}{4\pi\epsilon_0\epsilon_r} \frac{\|\mathbf{r}\|^4}{L^5} = \frac{-1}{4\pi\epsilon_0\epsilon_r} (q_1\|\mathbf{r}\|)^2 \frac{\|\mathbf{r}\|^2}{L^5}$ (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 $\|\mathbf{r}\| \to 0$, instead of ∞ .

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 first 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 :

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

 $\mathbf{u} = (1,0,0)$ 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), $\mathbf{u} = (\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0)$ or $(0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}})$ or $(\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}})$ in the second case (we will also analyze only the first vector), and $\mathbf{u} = (\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}})$ in the third case.

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

unit vector ${\bf u}$	term $\sum_{\mathbf{n}\in\mathbb{Z}^3\setminus\{0\}} \frac{-35}{2} \frac{(\mathbf{r}.\mathbf{n})^3\mathbf{n}}{\ \mathbf{n}\ ^9}$
(1, 0, 0)	(-48.8, 0, 0)
$\left(\frac{1}{\sqrt{2}},\frac{1}{\sqrt{2}},0\right)$	(-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 $\sum_{\mathbf{n}\in\mathbb{Z}^3\setminus\{0\}} \frac{-35}{2} \frac{(\mathbf{u}.\mathbf{n})^3\mathbf{n}}{\|\mathbf{n}\|^9}$ 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, θ, ϕ) , we know that the force on a symmetrical plane is as per :

$$\begin{pmatrix} \frac{-\partial U(r,\theta,\phi)}{\partial r} \\ 0 \\ 0 \end{pmatrix}.$$
 (5.67)

So that we can get here :

$$\int_{S(\mathbf{r})} \left(\sum_{\mathbf{n} \in \mathbb{Z}^3 \setminus \{0\}} \frac{35}{2} \frac{(\mathbf{l} \cdot \mathbf{n})^3 \mathbf{n}}{\|\mathbf{n}\|^9 L^5} \right) d\mathbf{l} = \frac{a \|\mathbf{r}\|^4}{4L^5}$$
(5.68)

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 :

$$U_{PBC}(\mathbf{r},L) = \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon_r \|\mathbf{r}\|} \left(1 + C_1 \left(\frac{\|\mathbf{r}\|}{L}\right)^5 \right) + o\left(\frac{\|\mathbf{r}\|^4}{L^5}\right)$$
(5.69)

 C_1 depends on the position of the two charges in the box :

- in the case where **r** is located on one side of the box : $C_1 = 3.12005497547$

- in the case where **r** is located on the small diagonal of the box : $C_1 = -3.20494502453$
- in the case where **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 Na⁺ and an ion 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 (NPT) where N is the number of particles according to the box, P = 1 bar and T = 298 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 $10 \times 2 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{A}^{-2}$ for $l^* = 2, 2.5, ..., 10$ A (it is important that $l^* \leq \frac{L_{min}}{2}$ where $L_{min} = 24.662$ 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 Mc-Millan 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 OH^- , represented "in the background" in white) and an ion Na⁺ (dark blue) and an ion Cl⁻ (cyan) according to the size L of the box

is expressed in kcal.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 $V = 1 \text{ nm}^3$. 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. $n_V = \frac{nN_A}{V}$ (n being the number of moles and $N_A = 6.022.10^{23} \text{ mol}^{-1}$ the amount of matter per mole).

Remember the density μ 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 :

$$n_V = \frac{nN_A}{V} = \frac{\mu}{m} nN_A = \frac{\mu N_A}{M}.$$
 (5.70)

Hence :

$$N = \frac{V\mu N_A}{M}.$$
(5.71)

We have : $1 \text{ nm}^3 = 10^{-27} \text{ m}^3$, $\mu = 10^3 \text{ kg} \cdot \text{m}^{-3}$ et $M = 18.10^{-3} \text{ kg} \cdot \text{mol}^{-1}$. 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 :

$$U = U_{bond} + U_{angle} + U_{b-a} + U_{oop} + U_{torsion} + U_{vdW} + U_{ele}^{perm} + U_{ele}^{ind}$$
(5.72)

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 H_2O are presented [147]. The dielectric constant of water in this model, when considering periodic edge conditions, is 82 ± 13 .

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	O-H bond	$h_0(\mathbf{A})$	$K_{\rm L}$ (kcal A ⁻² mol ⁻¹)	O multipoles	(a.u.)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	0 II boliu	0.0572	520.6	Q	-0.51966
H-O-H angle $\theta_0(\deg)$ K_{θ} (kcal. deg^{-2} . mol 1) 108.50 Q_{xx} 0.37928 0.37928Urey-Bradley $l_0(A)$ K_l (kcal. A^{-2} . mol 1) 1.5537 Q_{xx} 0.37928 Q_{yy} van der Waals $R^0(A)$ ϵ (kcal. M^{-2} . mol 1) 38.25 Q_{xx} 0.37928 Q_{yy} van der Waals $R^0(A)$ ϵ (kcal. M^{-1}) 0 Q_{zz} 0.03881H2.6550.0110 0.91 Q_{xx} -0.03859 d_{y} H2.6550.0135 d_{y} -0.05818 Q_{xx} Q_{yy} -0.05818 Q_{yy} Q_{xx} -0.03673 Q_{yy} O0.8377 H Q_{xz} -0.00203 Q_{xz}		0.9572	323.0	d _z	0.14279
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	H-O-H angle	$\theta_0(\text{deg})$	$K_{\theta} \; (\text{kcal} .deg^{-2} . \text{mol}^{-1})$		0.37028
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		108.50	34.05	Q_{xx}	0.01920
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Urev-Bradlev	$l_0(\mathbf{A})$	$K_l (\text{kcal} \cdot \text{A}^{-2} \cdot \text{mol}^{-1})$	Q_{yy}	-0.41809
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		1 5537	38.25	Q_{zz}	0.03881
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	1 117 1	$D^{0}(\Lambda)$	$(1, 1, 1^{-1})$	H multipoles	(a.u.)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	van der waals	$R^{\circ}(\mathbf{A})$	$\epsilon (\text{kcal.mol}^{-})$	Q	0.25983
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	0	3.405	0.110	d	-0.03859
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	H	2.655	0.0135	$\begin{bmatrix} a_x \\ d \end{bmatrix}$	0.05919
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Hraduction	0.91		u_y	-0.05616
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>reaaction</i>	α (Λ^3)		Q_{xx}	-0.03673
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	polarizability	α (A)		Q_{yy}	-0.10739
	0	0.837		Q_{xz}	-0.00203
0.450 0.14412	H	0.496		\dot{O}_{aa}	0.14412

TABLE 2 – Parameters of the AMOEBA model for water

The ions Na^+ and Cl^- have been described with the parameters described in table 3.

van der Waals	$R^0(A)$	$\epsilon \; (\text{kcal.mol}^{-1})$
N_a^+	3.020	0.2600
Cl ⁻	4.130	0.3400
polarizability	α (A ³)	
N_a^+	0.120	
Cl ⁻	4.000	
charge Q	(a.u.)	
N_a^+	1.00000	
Cl ⁻	-1.00000	

TABLE 3 - Parameters of ions

5.2.3 Study of the potential of McMillan and Mayer for Na-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 Na^+ ion and a 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 [65]), 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 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).



(c) case of the large diagonal of the box

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 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 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).



(c) case of the large diagonal of the box

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 developpement, in particular from 5 A for 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 αx^{β} (seen on figure 23). We can note that the fit is for β 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 ϵ' . This one repesents the energy of surface charges at the boundaries of the crystal. It is given by the following expression :

$$\frac{2\pi}{(1+2\epsilon')} \frac{\mathbf{M}^2}{V_{cell}} \tag{5.73}$$

where $\mathbf{M} = \sum_{i} q_i \mathbf{r}_i$ is the dipolar moment, and V_{cell} is the volume of an elementary cell. In order to verify this fact, we plotted curves for L=10 and L=100 and we observe, in the case when the vector is parallel to the box, that α 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 ϵ' 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 A on the one hand, L = 36,342 A on the other hand, and, finally, for L = 53,000 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 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 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 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 Na-Cl in aqueous phase

Calculation of coordination spheres

Below, figure 26 shows the radial distribution functions between Na⁺ ions and water molecules, function g_{Na-O} , on the one hand, and between Cl⁻ ions and water molecules, function g_{Cl-O} , on

the other hand, these functions being represented when the Na⁺ and 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 A by the force of the spring (between 5 and 10 A, the curves are very similar).

We see that g_{Na-O} and g_{Cl-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)
Na^+	2.5	3.2	4.5	5.6
Cl^{-}	3.4	4.	5.2	6.

TABLE 4 – Minima and maxima of the radial distribution function g_{Na-O} and g_{Cl-O}

One observes, on the other hand, a peak of g_{Na-O} which is lower than the others towards 2.5 A for d = 3 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 Na⁺ and 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_{Cl-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 Na⁺ ion, which does not prevent, at 4 A, that there is a water molecule at this distance from the Cl⁻ ion. On top of that, we will notice that Cl⁻ is an anion, contrary to Na⁺ which is a cation, so that the force that binds H_2O molecules to Cl⁻ is weaker : H_2O has to "invert" itself to present hydrogen ions to Cl⁻, which hinders the presence of oxygen. This explains why g_{Cl-O} peaks are lower than g_{Na-O} peaks.

From the peaks of g_{Na-O} and g_{Cl-O} , we can deduce the average coordination number around each ion (cf figure 27). For Na⁺, it is about 6 for the first sphere and about 12 for the second, and for 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 A, 36.342 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 $K = 0.48 \,\mathrm{L \cdot mol}^{-1}$.

L (en A)	$K \text{ (non corrected) (en L.mol}^{-1})$	$K (\text{en L}.\text{mol}^{-1})$	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	nt K , corrected	l or not, as a	function of .	L
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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 Ln^R , 81 anions Cl⁻ and 1498 water molecules, and for distances between an ion Ln³⁺ and an ion Cl⁻ of up to 12 A. In the first case, the lanthanides corresponded to Neodymium ions Nd³⁺, and in the second to Dysprosium ions Dy³⁺. In both cases, the parameters of the potentials were from [59, 130]. The parameters of the 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 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 Nd^{3+} and Cl^- for the first one, and Dy^{3+} and 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 Dy^{3+} ion, the association constant is obtained for a distance of about 6.5 A at 5.9 L.mol⁻¹ in the uncorrected case and 5.85 L.mol⁻¹ when it is corrected by our expansion. For the Nd³⁺ ion, the association constant is obtained for a distance of about 6.9 A at 8.8 L.mol⁻¹ in the

uncorrected case and $8.7 \text{ L} \cdot \text{mol}^{-1}$ 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 (Ndepending 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 L=10 and L=100 $\,$



 $\ensuremath{\mathsf{FIGURE}}\xspace 25$ – Comparison of the potential of McMillan and Mayer curves and ones resulting from our expansion



FIGURE 26 - O-ion radial distribution function curve



 $\ensuremath{\mathsf{Figure}}\xspace 27-\ensuremath{\mathsf{Curves}}\xspace$ of radial distribution functions (continuous lines) and number of coordination spheres (dot lines)



 ${\rm FIGURE}$ 28 – Comparison of the curves of the association constant, plotting according to the distance, as a function of the size of the simulation box



 $\ensuremath{\mathsf{FIGURE}}\xspace 29$ – 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 η .

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 :

$$\mathbf{u} = \boldsymbol{\mu} \mathbf{F} \tag{6.1}$$

where μ is the mobility tensor of the particle. We can calculate the diffusion coefficient D with Einstein's relation [62] :

$$D = \mu k_B T. \tag{6.2}$$

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 :

$$D_0 = \frac{k_B T}{6\pi\eta a}.\tag{6.3}$$

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 γ . This coefficient is defined such that $\gamma \to 0$ corresponds to non-slip conditions, and on the contrary $\gamma \to \infty$ 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_{\parallel} taking into account the distance between the two walls [155] H:

$$D_{\parallel} = \frac{k_B T}{6\pi\eta a} \frac{1}{\frac{1}{1 - \frac{a}{z}C(\frac{z}{\gamma})} + \frac{1}{1 - \frac{a}{H-z}C(\frac{H-z}{\gamma})} - 1}$$
(6.4)

$$= D_0 \frac{1}{\frac{1}{1 - \frac{a}{z}C(\frac{z}{\gamma})} + \frac{1}{1 - \frac{a}{H-z}C(\frac{H-z}{\gamma})} - 1}$$
(6.5)

where C is defined as $C(y) = \frac{-3}{32}y^2 - \frac{9}{32}y - \frac{3}{8} + \left(\frac{3}{32}y^3 + \frac{3}{8}y^2 + \frac{3}{8}y\right) E(y) + \frac{3}{2}yE(2y)$, with $E(y) = e^y \int_y^{\infty} \frac{e^{-t}}{t} dt$. As seen in [155], in the case where $\gamma \to 0$ (non-slip case), we have $C(\frac{l}{\gamma}) \to \frac{9}{16}$, 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 $\gamma \to 0$.

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

$$\frac{1}{\frac{1}{1-\frac{9a}{16z}} + \frac{1}{1-\frac{9a}{16(H-z)}} - 1} = \frac{1}{1 + \left(\frac{9a}{16z} + \frac{9a}{16(H-z)}\right) + o(a/H)}$$
(6.6)

$$= 1 - \frac{9}{16} \frac{aH}{z(H-z)} + o(a/H).$$
(6.7)

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

$$D_{\parallel} = \frac{k_B T}{6\pi\eta a} \left(1 - \frac{9}{16} \frac{aH}{z(H-z)} + o(a/H) \right).$$
(6.8)

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

$$D_{\parallel} = D_0 - \frac{k_B T}{\pi \eta} \frac{3}{32} \frac{H}{z(H-z)} + o(1/H).$$
(6.9)

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_{PBC} as a function of the period considered L [185] :

$$D_{PBC} = D_0 - \frac{k_B T \xi}{6\pi\eta L} + o(L^{-1})$$
(6.10)

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 ((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 **u** be the velocity vector of the particle and p the fluid pressure.

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

$$\begin{cases} \eta \Delta \mathbf{u}(x, y, z) = \nabla p(x, y, z) \\ \nabla . \mathbf{u}(x, y, z) = 0 \end{cases}$$
(6.11)

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

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

with U constant vector.

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

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

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 **F**, on \mathbb{R}^3 , the following Stokes problem : find \mathbf{u}_{oseen} , p such that

$$\begin{cases} \eta \Delta \mathbf{u}_{oseen}(x, y, z) = \nabla p_{oseen}(x, y, z) - \mathbf{F}\delta(x, y, z) \\ \nabla . \mathbf{u}_{oseen}(x, y, z) = 0 \end{cases}$$
(6.14)

where δ is the Dirac distribution centered in zero and with :

$$\lim_{\|(x,y,z)\| \to \infty} \mathbf{u}_{oseen} = (0,0,0).$$
(6.15)

We introduce :

$$\mathbf{T}_{Oseen}(x, y, z) = \frac{1}{8\pi\eta \| (x, y, z) \|} \left(\mathbf{I}_3 + \frac{(x, y, z) \otimes (x, y, z)}{\| (x, y, z) \|^2} \right)$$
(6.16)

the Oseen tensor in \mathbb{R}^3 for a non-periodic system¹.

We have then [107]:

$$\mathbf{u}_{oseen}(x, y, z) = \mathbf{T}_{Oseen}(x, y, z).\mathbf{F}$$
(6.18)

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

$$\eta \Delta \mathbf{u}_{confine}(x, y, z) = \nabla p_{confine}(x, y, z) - \mathbf{F}\delta(x, y, z)$$

$$\nabla \cdot \mathbf{u}_{confine}(x, y, z) = 0$$
(6.19)

1. \otimes corresponds to the tensor product : for two vectors (x_1, y_1, z_1) and (x_2, y_2, z_2) , we have :

$$(x_1, y_1, z_1) \otimes (x_2, y_2, z_2) = \begin{pmatrix} x_1 x_2 & x_1 y_2 & x_1 z_2 \\ y_1 x_2 & y_1 y_2 & y_1 z_2 \\ z_1 x_2 & z_1 y_2 & z_1 z_2 \end{pmatrix}$$
(6.17)

with the non-slip conditions on the walls :

$$\mathbf{u}_{confine}\left(x, y, \pm \frac{H}{2}\right) = (0, 0, 0). \tag{6.20}$$

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 :

$$\lim_{\|(x,y)\| \to \infty} \mathbf{u}_{confine}(x,y,z) = (0,0,0).$$
(6.21)

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

$$\mathbf{u}_{confine}(x, y, z) = \mathbf{T}(x, y, z).\mathbf{F}$$
(6.22)

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 :

$$D = D_0 + \frac{k_B T}{3} \lim_{\|(x,y,z)\| \to 0} Tr(\mathbf{T}(x,y,z) - \mathbf{T}_{Oseen}(x,y,z))$$
(6.23)

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 :

$$\mathbf{u}(x, y, z) = \mathbf{u}_{sph}(x, y, z) + \mathbf{u}_{walls}(x, y, z)$$
(6.24)

where \mathbf{u}_{sph} is the velocity due to the force of the particle on the fluid, and \mathbf{u}_{walls} is the velocity created by the force of the walls.

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

$$\mathbf{u}_{sph}(x,y,z) = \frac{1}{6\pi\eta a} \mathbf{F}.$$
(6.25)

On the other hand, in their work, Kirkwood and Riseman [97] use the fact that \mathbf{u}_{walls} varies little at the scale of the sphere if it is small. We can therefore assume that $\mathbf{u}_{walls} = \mathbf{C}$ 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 :

$$\mathbf{u}_{walls}(x, y, z) = \mathbf{u}_{confine}(x, y, z) - \mathbf{u}_{Oseen}(x, y, z)$$
(6.26)

where $\mathbf{u}_{confine}$ is given in (6.19) (case of a particle in a fluid confined between two walls) and \mathbf{u}_{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) :

$$\mathbf{u}_{wall|(x,y,z)=(0,0,0)} = \lim_{\|(x,y,z)\|\to 0} (\mathbf{T}(x,y,z).\mathbf{F} - \mathbf{T}_{Oseen}(x,y,z).\mathbf{F}).$$
(6.27)

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

$$\mathbf{u}(x,y,z) = \frac{1}{6\pi\eta a} \mathbf{F} + \lim_{\|(x,y,z)\|\to 0} (\mathbf{T}(x,y,z) - \mathbf{T}_{Oseen}(x,y,z)).\mathbf{F}$$
(6.28)

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

$$\mathbf{D} = \boldsymbol{\mu} k_B T$$

= $\frac{k_B T}{6\pi\eta a} + k_B T \lim_{\|(x,y,z)\|\to 0} (\mathbf{T}(x,y,z) - \mathbf{T}_{Oseen}(x,y,z)).$ (6.29)

The diffusion coefficient D is then obtained by taking $\frac{1}{3}Tr(\mathbf{D})$ 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 Ω , 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, u is of the form :

$$\begin{aligned} \boldsymbol{u}(x,y,z) &= \boldsymbol{T}_{1}(x,y,z).\boldsymbol{F} \\ &= \int_{\mathbb{R}^{2}} d\boldsymbol{k} \bigg(\left(A_{2}(\boldsymbol{k})(z) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + A_{3}(\boldsymbol{k})(z) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + A_{4}(\boldsymbol{k})(z)\boldsymbol{k}^{*} \otimes \boldsymbol{k}^{*} \bigg) \\ &+ i \bigg(A_{5}(\boldsymbol{k})(z) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + A_{6}(\boldsymbol{k})(z) \begin{pmatrix} 0 & 0 & k_{1} \\ 0 & 0 & k_{2} \\ 0 & 0 & 0 \end{pmatrix} + A_{7}(\boldsymbol{k})(z) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ k_{1} & k_{2} & 0 \end{pmatrix} \bigg) \bigg) e^{i\boldsymbol{k}.(x,y)}.\boldsymbol{F} \end{aligned}$$

$$(6.30)$$

where
$$\mathbf{k}^* = \begin{pmatrix} \mathbf{k} \\ 0 \end{pmatrix}$$
 and with

$$A_2(\mathbf{k})(z) = \frac{1}{2\|\mathbf{k}\| ch(\|\mathbf{k}\| \frac{H}{2})\eta} \left(sh(\|\mathbf{k}\|(z + \frac{H}{2})) \mathbf{1}_{z \le 0} - sh(\|\mathbf{k}\|(z - \frac{H}{2})) \mathbf{1}_{z > 0} \right)$$
(6.31)

$$A_{3}(\mathbf{k})(z) = -\frac{1}{4sh(\|\mathbf{k}\|_{\frac{H}{2}}^{2})\eta} \left((z + \frac{H}{2})sh(\|\mathbf{k}\|(z + \frac{H}{2}))\mathbf{1}_{z \le 0} + (z - \frac{H}{2})sh(\|\mathbf{k}\|(z - \frac{H}{2}))\mathbf{1}_{z > 0} \right) \\ + \left(sh(\|\mathbf{k}\|_{\frac{H}{2}}) + \frac{H\|\mathbf{k}\|ch(\|\mathbf{k}\|_{\frac{H}{2}})}{2} \right) \left(\frac{1}{4\|\mathbf{k}\|sh(\|\mathbf{k}\|_{\frac{H}{2}})^{2}\eta} \left(ch(\|\mathbf{k}\|(z + \frac{H}{2}))\mathbf{1}_{z \le 0} \right) \\ + ch(\|\mathbf{k}\|(z - \frac{H}{2}))\mathbf{1}_{z > 0} \right) - (e^{\|\mathbf{k}\|z} + e^{-\|\mathbf{k}\|z}) \left(\frac{1}{8\|\mathbf{k}\|sh(\|\mathbf{k}\|_{\frac{H}{2}})^{2}ch(\|\mathbf{k}\|_{\frac{H}{2}})\eta} \\ + \frac{\frac{64sh(\|\mathbf{k}\|_{\frac{H}{2}})ch(\|\mathbf{k}\|_{\frac{H}{2}})^{2}\eta}{14} \left(\frac{1}{2} \left(\frac{sh(\|\mathbf{k}\|_{\frac{H}{2}})}{ch(\|\mathbf{k}\|_{\frac{H}{2}})} - \frac{ch(\|\mathbf{k}\|_{\frac{H}{2}})}{sh(\|\mathbf{k}\|_{\frac{H}{2}})} \right) \right) \\ - \frac{(e^{\|\mathbf{k}\|z} - e^{-\|\mathbf{k}\|z})}{2ch(\|\mathbf{k}\|_{\frac{H}{2}})\eta} \frac{z}{16sh(\|\mathbf{k}\|_{\frac{H}{2}})^{2}} \frac{\left(1 + \frac{\|\mathbf{k}\|H}{2} \left(\frac{sh(\|\mathbf{k}\|_{\frac{H}{2}})}{ch(\|\mathbf{k}\|_{\frac{H}{2}})} - \frac{ch(\|\mathbf{k}\|_{\frac{H}{2}})}{sh(\|\mathbf{k}\|_{\frac{H}{2}})} \right) \right)}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}}{16sh(\|\mathbf{k}\|_{\frac{H}{2}})^{2}} \frac{\left(1 + \frac{\|\mathbf{k}\|H}{2} \left(\frac{sh(\|\mathbf{k}\|_{\frac{H}{2}})}{ch(\|\mathbf{k}\|_{\frac{H}{2}})} - \frac{ch(\|\mathbf{k}\|_{\frac{H}{2}})}{sh(\|\mathbf{k}\|_{\frac{H}{2}})} \right) \right)}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16sh(\|\mathbf{k}\|_{\frac{H}{2}})^{2}} \frac{\left(1 + \frac{\|\mathbf{k}\|H}{2} \left(\frac{sh(\|\mathbf{k}\|_{\frac{H}{2}})}{ch(\|\mathbf{k}\|_{\frac{H}{2}})} - \frac{ch(\|\mathbf{k}\|_{\frac{H}{2}})}{sh(\|\mathbf{k}\|_{\frac{H}{2}})} \right)}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{sh(\|\mathbf{k}\|_{\frac{H}{2}})}{ch(\|\mathbf{k}\|_{\frac{H}{2}})} - \frac{ch(\|\mathbf{k}\|_{\frac{H}{2}})}{sh(\|\mathbf{k}\|_{\frac{H}{2}})} \right)^{2}} \right)$$

$$(6.32)$$

$$\begin{aligned} A_{4}(\boldsymbol{k})(z) &= \left(\frac{z}{4ch(\|\boldsymbol{k}\|\|\frac{H}{2})\|\boldsymbol{k}\|^{2}\eta} \left(ch(\|\boldsymbol{k}\|(z+\frac{H}{2}))\mathbf{1}_{z\leq0} - ch(\|\boldsymbol{k}\|(z-\frac{H}{2}))\mathbf{1}_{z>0}\right) \\ &+ \frac{H}{16\|\boldsymbol{k}\|^{2}ch(\|\boldsymbol{k}\|\frac{H}{2})^{2}\eta} (e^{\|\boldsymbol{k}\|z} + e^{-\|\boldsymbol{k}\|z}) \right) - (e^{\|\boldsymbol{k}\|z} + e^{-\|\boldsymbol{k}\|z}) \left(\frac{sh(\|\boldsymbol{k}\|\frac{H}{2})}{\|\boldsymbol{k}\|ch(\|\boldsymbol{k}\|\frac{H}{2})} \\ &- \frac{H}{2} \left(\frac{sh(\|\boldsymbol{k}\|\frac{H}{2})^{2}}{ch(\|\boldsymbol{k}\|\frac{H}{2})^{2}} - 1\right) \right) \left(\frac{\frac{H^{2}}{128ch(\|\boldsymbol{k}\|\frac{H}{2})^{2}\eta}}{\frac{1}{4} - \frac{\|\boldsymbol{k}\|^{2}H^{2}}{16} \left(\frac{sh(\|\boldsymbol{k}\|\frac{H}{2})}{ch(\|\boldsymbol{k}\|\frac{H}{2})} - \frac{ch(\|\boldsymbol{k}\|\frac{H}{2})}{sh(\|\boldsymbol{k}\|\frac{H}{2})}\right)^{2}} \right) \\ &+ \frac{(e^{\|\boldsymbol{k}\|z} - e^{-\|\boldsymbol{k}\|z})}{2\|\boldsymbol{k}\|\eta} \frac{\frac{zH}{32ch(\|\boldsymbol{k}\|\frac{H}{2})^{2}} \left(1 - \frac{H\|\boldsymbol{k}\|}{2} \left(\frac{sh(\|\boldsymbol{k}\|\frac{H}{2})}{ch(\|\boldsymbol{k}\|\frac{H}{2})} - \frac{ch(\|\boldsymbol{k}\|\frac{H}{2})}{sh(\|\boldsymbol{k}\|\frac{H}{2})}\right)\right)}{\frac{1}{4} - \frac{\|\boldsymbol{k}\|^{2}H^{2}}{16} \left(\frac{sh(\|\boldsymbol{k}\|\frac{H}{2})}{ch(\|\boldsymbol{k}\|\frac{H}{2})} - \frac{ch(\|\boldsymbol{k}\|\frac{H}{2})}{sh(\|\boldsymbol{k}\|\frac{H}{2})}\right)^{2}}{sh(\|\boldsymbol{k}\|\frac{H}{2})} \\ &- \frac{1}{4\|\boldsymbol{k}\|^{3}ch(\|\boldsymbol{k}\|\frac{H}{2})\eta} \left(sh(\|\boldsymbol{k}\|(z+\frac{H}{2}))\mathbf{1}_{z\leq0} - sh(\|\boldsymbol{k}\|(z-\frac{H}{2}))\mathbf{1}_{z>0}\right) \tag{6.33} \end{aligned}$$

$$\begin{split} A_{5}(\mathbf{k})(z) &= \left(\frac{-1}{4\|\mathbf{k}\|sh(\|\mathbf{k}\|\frac{H}{2})\eta} \left((z+\frac{H}{2})ch(\|\mathbf{k}\|(z+\frac{H}{2}))\mathbf{1}_{z\leq 0} + (z-\frac{H}{2})ch(\|\mathbf{k}\|(z-\frac{H}{2}))\mathbf{1}_{z>0}\right)\right) \\ &+ \left(\frac{Hch(\|\mathbf{k}\|\frac{H}{2})}{8\|\mathbf{k}\|sh(\|\mathbf{k}\|\frac{H}{2})^{2}\eta} \left(sh(\|\mathbf{k}\|(z+\frac{H}{2}))\mathbf{1}_{z\leq 0} + sh(\|\mathbf{k}\|(z-\frac{H}{2}))\mathbf{1}_{z>0}\right)\right) \\ &+ (e^{\|\mathbf{k}\|z} - e^{-\|\mathbf{k}\|z}) \left(\frac{H}{64sh(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}\right) \frac{\left(\frac{1}{sh(\|\mathbf{k}\|\frac{H}{2})\|\mathbf{k}\|} + \frac{H}{4}\left(1 - \frac{ch(\|\mathbf{k}\|\frac{H}{2})^{2}}{sh(\|\mathbf{k}\|\frac{H}{2})^{2}}\right)\right)}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16}\left(\frac{sh(\|\mathbf{k}\|\frac{H}{2})}{ch(\|\mathbf{k}\|\frac{H}{2})} - \frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})}\right)^{2}} \left(sh(\|\mathbf{k}\|\frac{H}{2}) \\ &+ \frac{H\|\mathbf{k}\|ch(\|\mathbf{k}\|\frac{H}{2})}{2}\right) - \frac{(e^{\|\mathbf{k}\|z} + e^{-\|\mathbf{k}\|z})}{32\|\mathbf{k}\|ch(\|\mathbf{k}\|\frac{H}{2})sh(\|\mathbf{k}\|\frac{H}{2})^{2}\eta} \left(1 + \frac{\|\mathbf{k}\|H}{2}\left(\frac{sh(\|\mathbf{k}\|\frac{H}{2})}{ch(\|\mathbf{k}\|\frac{H}{2})} - \frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})}\right)\right) \\ &\left(sh(\|\mathbf{k}\|\frac{H}{2}) + \frac{H\|\mathbf{k}\|ch(\|\mathbf{k}\|\frac{H}{2})}{2}\right) \frac{z}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16}\left(\frac{sh(\|\mathbf{k}\|\frac{H}{2})}{ch(\|\mathbf{k}\|\frac{H}{2})} - \frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})}\right)^{2}} \end{aligned}$$
(6.34)
$$A_{6}(\mathbf{k})(z) = -\frac{\left(e^{\|\mathbf{k}\|z} + e^{-\|\mathbf{k}\|z}\right)z}{2\eta} \frac{\frac{H}{32ch(\|\mathbf{k}\|\frac{H}{2})^{2}} \left(1 - \frac{H\|\mathbf{k}\|^{2}}{2} \left(\frac{sh(\|\mathbf{k}\|\frac{H}{2})}{ch(\|\mathbf{k}\|\frac{H}{2})} - \frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})}\right)\right)}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{sh(\|\mathbf{k}\|\frac{H}{2})}{ch(\|\mathbf{k}\|\frac{H}{2})} - \frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})}\right)^{2}} - \frac{z}{4\|\mathbf{k}\|ch(\|\mathbf{k}\|\frac{H}{2})\eta} \left(sh(\|\mathbf{k}\|(z + \frac{H}{2}))\mathbf{1}_{z\leq 0} - sh(\|\mathbf{k}\|(z - \frac{H}{2}))\mathbf{1}_{z>0}\right) - \left(e^{\|\mathbf{k}\|z} - e^{-\|\mathbf{k}\|z}\right)\frac{H^{2}}{128ch(\|\mathbf{k}\|\frac{H}{2})^{2}\eta} \left(\frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})} - \frac{\|\mathbf{k}\|H}{2} \left(1 - \frac{ch(\|\mathbf{k}\|\frac{H}{2})^{2}}{sh(\|\mathbf{k}\|\frac{H}{2})^{2}}\right)\right)}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{sh(\|\mathbf{k}\|\frac{H}{2})}{ch(\|\mathbf{k}\|\frac{H}{2})} - \frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})}\right)^{2}}$$

$$(6.35)$$

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
$$\mathbf{h} = \begin{pmatrix} h_1 \\ h_2 \\ h_3 \end{pmatrix}$$
 such as :
 $\mathbf{h}(x, y, z) = \eta \Delta \mathbf{u}(x, y, z) - \nabla p(x, y, z) + \delta(x, y, z) \mathbf{F}$ (6.36)

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

$$\widehat{h_1}(\mathbf{k})(z) = \int_{\mathbb{R}^2} h_1(x, y, z) e^{-i\mathbf{k}.(x, y)} dx dy$$
(6.37)

$$= \int_{\mathbb{R}^2} \left(\eta \Delta u_1(x, y, z) - \frac{\partial}{\partial x} p(x, y, z) + \delta(x, y, z) F_1 \right) e^{-i\mathbf{k} \cdot (x, y)} dx dy$$
(6.38)

$$= \int_{\mathbb{R}^2} \left(\eta \left(\frac{\partial^2}{\partial z^2} u_1(x, y, z) - u_1(x, y, z) (k_1^2 + k_2^2) \right) - ik_1 p(x, y, z) + \delta(x, y, z) F_1 \right) e^{-i\mathbf{k}.(x, y)} dx dy$$
(6.39)

$$= \eta \left(\widehat{u_1}(\mathbf{k})''(z) - \|\mathbf{k}\|^2 \widehat{u_1}(\mathbf{k})(z) \right) - ik_1 \widehat{p}(\mathbf{k})(z) + \widehat{\delta}(\mathbf{k})(z) F_1$$
(6.40)

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

$$\widehat{\delta}(\mathbf{k})(z) = \delta(z). \tag{6.41}$$

 ${\it Likewise}:$

$$\widehat{h_2}(\mathbf{k})(z) = \eta \left(\widehat{u_2}(\mathbf{k})''(z) - \|\mathbf{k}\|^2 \widehat{u_2}(\mathbf{k})(z) \right) - ik_2 \widehat{p}(\mathbf{k})(z) + \delta(z) F_2.$$
(6.42)

And to finish :

$$\widehat{h_3}(\mathbf{k})(z) = \eta \left(\widehat{u_3}(\mathbf{k})''(z) - \|\mathbf{k}\|^2 \widehat{u_3}(\mathbf{k})(z)\right) - \widehat{p}(\mathbf{k})'(z) + \delta(z) F_3.$$
(6.43)

We inject (6.40), (6.42) and (6.43) into the first equation of (6.19), which gives us the following system of equations :

$$\begin{cases} \eta\left(\widehat{u_1}(\mathbf{k})''(z) - \|\mathbf{k}\|^2 \widehat{u_1}(\mathbf{k})(z)\right) = ik_1 \widehat{p}(\mathbf{k})(z) - \delta(z)F_1\\ \eta\left(\widehat{u_2}(\mathbf{k})''(z) - \|\mathbf{k}\|^2 \widehat{u_2}(\mathbf{k})(z)\right) = ik_2 \widehat{p}(\mathbf{k})(z) - \delta(z)F_2\\ \eta\left(\widehat{u_3}(\mathbf{k})''(z) - \|\mathbf{k}\|^2 \widehat{u_3}(\mathbf{k})(z)\right) = \widehat{p}(\mathbf{k})'(z) - \delta(z)F_3 \end{cases}$$
(6.44)

On the other hand, the second equation of (6.19) translates as equality $\forall z \in \left[\frac{-H}{2}, \frac{H}{2}\right]$:

$$ik_1\widehat{u_1}(\mathbf{k})(z) + ik_2\widehat{u_2}(\mathbf{k})(z) + \widehat{u_3}(\mathbf{k})'(z) = 0.$$

$$(6.45)$$

Step 2:

We take the divergence of the first equation of (6.19) and we get :

$$\nabla (\eta \Delta \mathbf{u}) = \nabla (\nabla p - \delta \mathbf{F}) \tag{6.46}$$

$$=\Delta p - \mathbf{F} \cdot \nabla \left(\delta\right). \tag{6.47}$$

And then we have the equation :

$$\Delta p = \mathbf{F}. \bigtriangledown \delta \tag{6.48}$$

(since $\nabla . \mathbf{u} = 0.$)

As a result :

$$\widehat{p}(\mathbf{k})''(z) - \|\mathbf{k}\|^2 \widehat{p}(\mathbf{k})(z) = i \left(k_1 F_1 + k_2 F_2\right) \widehat{\delta}(\mathbf{k})(z) + F_3 \delta'(z).$$
(6.49)

The idea will next be to solve the equation for $\hat{p}(\mathbf{k})$ then to inject the solution obtained into the equation for $\hat{u}_i(\mathbf{k})$ (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 $a = a_0 < a_1 < ... < a_i < ... < b = a_{n+1}$ such that for i = 0, ..., n the restriction of f on the interval $]a_i, a_{i+1}[$ can be extended into a class function C^1 on $[a_i, a_{i+1}]$. We note $f(a_i^+)$ and $f(a_i^-)$ 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 $(T_f)'$.

We remember the jump formula :

Theorem 8. The distribution $(T_f)'$ is given, starting from $T_{f'}$ and jumping f in each a_i , by :

$$(T_f)' = T_{f'} + \sum_{i=0}^{n+1} (f(a_i^+) - f(a_i^-))\delta a_i.$$
(6.50)

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 :

$$(T_f)'' = T_{f''} + \sum_{i=0}^{n+1} (f(a_i^+) - f(a_i^-))\delta'_{ai} + \sum_{i=0}^{n+1} (f'(a_i^+) - f'(a_i^-))\delta a_i.$$
(6.51)

Beforehand we have the following lemma :

Lemma 10. Let be the following differential equation :

$$y''(t) - Ay(t) = g(t)$$
(6.52)

with A > 0 and g is a function. The solution is of the form :

$$y(t) = y_P(t) + y_H(t)$$
(6.53)

where y_P is a particular solution and y_H is the solution of the homogeneous equation associated with it :

$$y_H(t) = \alpha e^{\sqrt{A}t} + \beta e^{-\sqrt{A}t} \tag{6.54}$$

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 $\left[\frac{-H}{2}, \frac{H}{2}\right]$:

$$y''(t) - Ay(t) = Be^{\sqrt{A}t} + B'e^{-\sqrt{A}t} + Ct + D$$
(6.55)

with $A > 0, B, B', C, D \in \mathbb{C}$. The solution is in the form :

$$y(t) = y_P(t) + y_H(t)$$
(6.56)

where y_H is defined in lemma 10 and y_P is a particular solution :

$$y_P(t) = \frac{t}{2\sqrt{A}} \left(Be^{\sqrt{A}t} - B'e^{-\sqrt{A}t} \right) - \frac{1}{A}(Ct + D)$$
(6.57)

with $\alpha, \beta \in \mathbb{C}$.

We remind that :

$$ch(\sqrt{A}t) = \frac{e^{\sqrt{A}t} + e^{-\sqrt{A}t}}{2}, \ sh(\sqrt{A}t) = \frac{e^{\sqrt{A}t} - e^{-\sqrt{A}t}}{2}.$$
 (6.58)

Lemma 12. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$:

$$y''(t) - Ay(t) = B\delta(t) \tag{6.59}$$

with $A > 0, B \in \mathbb{C}$. The solution is in the form :

$$y(t) = y_P(t) + y_H(t)$$
(6.60)

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 :

$$y_{P,1}(t) = \frac{-Bsh(\sqrt{A}(t+\frac{H}{2}))}{2\sqrt{A}ch(\sqrt{A}\frac{H}{2})} \mathbf{1}_{t \le 0} + \frac{Bsh(\sqrt{A}(t-\frac{H}{2}))}{2\sqrt{A}ch(\sqrt{A}\frac{H}{2})} \mathbf{1}_{t > 0}$$
(6.61)

$$y_{P,2}(t) = \frac{-B}{2\sqrt{A}sh(\sqrt{A}\frac{H}{2})} \left(ch(\sqrt{A}(t+\frac{H}{2}))\mathbf{1}_{t\leq 0} + ch(\sqrt{A}(t-\frac{H}{2}))\mathbf{1}_{t>0} \right)$$
(6.62)

(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 :

$$y(t) = \left(\alpha_{-} \operatorname{ch}(\sqrt{A}(t+\frac{H}{2})) + \beta_{-} \operatorname{sh}(\sqrt{A}(t+\frac{H}{2}))\right) \mathbf{1}_{t \le 0} + \left(\alpha_{+} \operatorname{ch}(\sqrt{A}(t-\frac{H}{2})) + \beta_{+} \operatorname{sh}(\sqrt{A}(t-\frac{H}{2}))\right) \mathbf{1}_{t > 0}$$
(6.63)

We determine the second derivative of y with theorem 8 and we find :

$$y''(t) = A\left(\alpha_{-}\operatorname{ch}(\sqrt{A}(t+\frac{H}{2})) + \beta_{-}\operatorname{sh}(\sqrt{A}(t+\frac{H}{2}))\right) \mathbf{1}_{t \leq 0}$$
$$+ A\left(\alpha_{+}\operatorname{ch}(\sqrt{A}(t-\frac{H}{2})) + \beta_{+}\operatorname{sh}(\sqrt{A}(t-\frac{H}{2}))\right) \mathbf{1}_{t > 0}$$
$$+ \left((\alpha_{+} - \alpha_{-})\operatorname{ch}(\sqrt{A}(\frac{H}{2})) + (-\beta_{+} - \beta_{-})\operatorname{sh}(\sqrt{A}(\frac{H}{2}))\right) \delta'(t)$$
$$+ \sqrt{A}\left((-\alpha_{+} - \alpha_{-})\operatorname{sh}(\sqrt{A}(\frac{H}{2})) + (\beta_{+} - \beta_{+})\operatorname{ch}(\sqrt{A}(\frac{H}{2}))\right) \delta(t)$$
(6.64)

Case 1: We take $\alpha_{-} = \alpha_{+} = 0$ and we obtain by identification in the equation (6.59):

$$\begin{cases} \sqrt{A}(\beta_+ - \beta_-)\operatorname{ch}(\sqrt{A}(\frac{H}{2})) = B\\ (-\beta_+ - \beta_-)\operatorname{sh}(\sqrt{A}(\frac{H}{2})) = 0 \end{cases}$$
(6.65)

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 $\left[\frac{-H}{2}, \frac{H}{2}\right]$:

$$y''(t) - Ay(t) = B\delta'(t)$$
(6.66)

with $A > 0, B \in \mathbb{C}$. A family of solutions is of the form :

$$y(t) = y_P(t) + y_H(t)$$
(6.67)

where y_H is defined in lemma 10 and y_P is a particular solution :

$$y_P(t) = \frac{-Bsh(\sqrt{A(t+\frac{H}{2})})}{2sh(\sqrt{A\frac{H}{2}})} \mathbf{1}_{t \le 0} - \frac{Bsh(\sqrt{A(t-\frac{H}{2})})}{2sh(\sqrt{A\frac{H}{2}})} \mathbf{1}_{t > 0}.$$
 (6.68)

Lemma 14. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$:

$$y''(t) - Ay(t) = Bsh(\sqrt{A}(t + \frac{H}{2}))\mathbf{1}_{t \le 0} + B'sh(\sqrt{A}(t - \frac{H}{2}))\mathbf{1}_{t > 0}$$
(6.69)

with $A > 0, B, B' \in \mathbb{C}$. The solution is in the form :

$$y(t) = y_P(t) + y_H(t)$$
(6.70)

where y_H is defined in lemma 10 and y_P is a particular solution² :

$$y_{P}(t) = \frac{B\left(t + \frac{H}{2}\right)ch(\sqrt{A}(t + \frac{H}{2}))}{2\sqrt{A}} \mathbf{1}_{t \leq 0} + \frac{B'\left(t - \frac{H}{2}\right)ch(\sqrt{A}(t - \frac{H}{2}))}{2\sqrt{A}} \mathbf{1}_{t > 0}$$
$$- (B + B')\frac{Hch\left(\sqrt{A}\frac{H}{2}\right)}{8\sqrt{A}sh\left(\sqrt{A}\frac{H}{2}\right)} \left(sh(\sqrt{A}(t + \frac{H}{2}))\mathbf{1}_{t \leq 0} + sh(\sqrt{A}(t - \frac{H}{2}))\mathbf{1}_{t > 0}\right)$$
$$+ (B' - B)\frac{1}{4A} \left(sh(\sqrt{A}(t + \frac{H}{2}))\mathbf{1}_{t \leq 0} - sh(\sqrt{A}(t - \frac{H}{2}))\mathbf{1}_{t > 0}\right)$$
$$+ (B' - B)\frac{H}{8\sqrt{A}} \left(ch(\sqrt{A}(t + \frac{H}{2}))\mathbf{1}_{t \leq 0} + ch(\sqrt{A}(t - \frac{H}{2}))\mathbf{1}_{t > 0}\right). \tag{6.71}$$

Lemma 15. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$:

$$y''(t) - Ay(t) = Bch(\sqrt{A}(t + \frac{H}{2}))\mathbf{1}_{t \le 0} + B'ch(\sqrt{A}(t - \frac{H}{2}))\mathbf{1}_{t > 0}$$
(6.72)

with $A > 0, B, B' \in \mathbb{C}$. A family of solutions is of the form :

$$y(t) = y_P(t) + y_H(t)$$
(6.73)

where y_H is defined in lemma 10 and y_P is a particular solution :

$$y_{P}(t) = \frac{B\left(t + \frac{H}{2}\right)sh(\sqrt{A}(t + \frac{H}{2}))}{2\sqrt{A}}\mathbf{1}_{t\leq 0} + \frac{B'\left(t - \frac{H}{2}\right)sh(\sqrt{A}(t - \frac{H}{2}))}{2\sqrt{A}}\mathbf{1}_{t>0} + (B' - B)\frac{H}{8\sqrt{A}}\left(sh(\sqrt{A}(t + \frac{H}{2}))\mathbf{1}_{t\leq 0} + sh(\sqrt{A}(t - \frac{H}{2}))\mathbf{1}_{t>0}\right) - (B + B')\left(\frac{1}{4A} + \frac{Hch\left(\sqrt{A}\frac{H}{2}\right)}{4\sqrt{A}sh\left(\sqrt{A}\frac{H}{2}\right)}\right)\left(ch(\sqrt{A}(t + \frac{H}{2}))\mathbf{1}_{t\leq 0} + ch(\sqrt{A}(t - \frac{H}{2}))\mathbf{1}_{t>0}\right).$$
(6.74)

Finally, the following lemma is established :

Lemma 16. Let the following differential equation on $\left[\frac{-H}{2}, \frac{H}{2}\right]$:

$$y''(t) = A + B\delta(t) + C\delta'(t) \tag{6.75}$$

with $A, B, C \in \mathbb{C}$. The solution is in the form :

$$\underline{y(t) = \frac{A}{2}t^2 + \alpha t + \beta + (Bt + C)\mathbf{1}_{t>0}.$$
(6.76)

^{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.

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 :

$$A = \frac{F_3}{2\mathrm{sh}(\|\mathbf{k}\|_2^{\underline{H}})}, \ B = \frac{\mathbf{k}^* \cdot \mathbf{F}}{2\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|_2^{\underline{H}})}$$
(6.77)

where $\mathbf{k}^* = \begin{pmatrix} \mathbf{k} \\ 0 \end{pmatrix}$. We then find for (6.49) using lemmas 12 and 13 :

$$\widehat{p}(\mathbf{k})(z) = \alpha e^{\|\mathbf{k}\|_{z}} + \beta e^{-\|\mathbf{k}\|_{z}} + (-A - iB)\operatorname{sh}(\|\mathbf{k}\|(z + \frac{H}{2}))\mathbf{1}_{z \le 0} + (-A + iB)\operatorname{sh}(\|\mathbf{k}\|(z - \frac{H}{2}))\mathbf{1}_{z > 0}.$$
(6.78)

So that :

$$\widehat{p}(\mathbf{k})'(z) = \|\mathbf{k}\| \left((-A - iB) \operatorname{ch}(\|\mathbf{k}\|(z + \frac{H}{2})) \mathbf{1}_{z \le 0} + (-A + iB) \operatorname{ch}(\|\mathbf{k}\|(z - \frac{H}{2})) \mathbf{1}_{z > 0} \right) \\ + \|\mathbf{k}\| \left(\alpha e^{\|\mathbf{k}\|t} - \beta e^{-\|\mathbf{k}\|t} \right) + 2A \operatorname{sh}(\|\mathbf{k}\|\frac{H}{2}) \delta(z).$$
(6.79)

What gives us for (6.44) using the lemmas 12, 13, 14, and 15 :

$$\begin{cases} \widehat{u_{1}}(\mathbf{k})(z) = \alpha_{1}e^{||\mathbf{k}||z} + \beta_{1}e^{-||\mathbf{k}||z} - \frac{ik_{1}}{\eta}\frac{2}{2||\mathbf{k}||}\left((z + \frac{H}{2})\operatorname{ch}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} + (z - \frac{H}{2})\operatorname{ch}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{k_{1}}{\eta}\frac{Bz}{2||\mathbf{k}||^{2}}\left(\operatorname{ch}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} - \operatorname{ch}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \left(\frac{E}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{sh}(||\mathbf{k}||\frac{H}{2})\eta + \frac{ik_{1}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\mathbf{sh}(||\mathbf{k}||\frac{H}{2})\eta}\right)\operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \geq 0} \\ + \left(\frac{-F_{1}}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{ce}^{||\mathbf{k}||^{2}\eta}\eta + \frac{ik_{1}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\mathbf{sh}(||\mathbf{k}||\frac{H}{2})\eta}\right)\operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0} \right) \\ + \frac{ik_{1}z}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{ce}^{||\mathbf{k}||^{2}\eta}\theta - \frac{ik_{2}}{\eta}\frac{A}{2||\mathbf{k}||}\left((z + \frac{H}{2})\operatorname{ch}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \geq 0}\right) \\ + \frac{ik_{1}z}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{ce}^{||\mathbf{k}||^{2}\eta}\theta - \frac{ik_{2}}{\eta}\frac{A}{2||\mathbf{k}||}\left((z + \frac{H}{2})\operatorname{ch}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \geq 0}\right) \\ + \frac{k_{2}z}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} - \operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{k_{2}z}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{sh}(||\mathbf{k}||^{2}\eta + \frac{ik_{2}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\mathbf{sh}(||\mathbf{k}||\frac{H}{2})\eta}\right)\operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \left(\frac{F_{2}}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{sh}(||\mathbf{k}||^{2}\eta + \frac{ik_{2}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\mathbf{sh}(||\mathbf{k}|||\frac{H}{2})\eta}\right)\operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \left(\frac{F_{2}}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{sh}(||\mathbf{k}||^{2}\eta + \frac{ik_{2}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\mathbf{sh}(||\mathbf{k}|||\frac{H}{2})\eta}\right)\operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{2}z}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{sh}(||\mathbf{k}||^{2}\eta + \frac{ik_{2}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\mathbf{sh}(||\mathbf{k}|||\frac{H}{2})\eta}\right)\operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{2}z}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{sh}(||\mathbf{k}||^{2}\eta - \frac{ik_{2}z}{4||\mathbf{k}||\mathbf{sh}(||\mathbf{k}|||\frac{H}{2})\eta}\right)\operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{2}z}{2||\mathbf{k}||^{2}\eta}\left(\operatorname{sh}(||\mathbf{k}||^{2}\eta - \frac{ik_{2}z}{4||\mathbf{k}||\mathbf{sh}(||\mathbf{k}|||\frac{H}{2})\eta}\right)\operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{2}z}{2||$$

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 $z = \frac{-H}{2}$).

We deduce from (6.20):

$$\widehat{\mathbf{u}}(\mathbf{k})\left(\pm\frac{H}{2}\right) = (0,0,0). \tag{6.81}$$

We then obtain after resolution of the systems :

$$\begin{cases} \alpha_{1} = \frac{BHk_{1}}{8\|\mathbf{k}\|ch(\|\mathbf{k}\|\frac{H}{2})\eta} - \frac{ik_{1}H}{8\|\mathbf{k}\|\eta} \left((\alpha + \beta) \frac{sh(\|\mathbf{k}\|\frac{H}{2})}{ch(\|\mathbf{k}\|\frac{H}{2})} + (\alpha - \beta) \frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})} \right) \\ \beta_{1} = \frac{BHk_{1}}{8\|\mathbf{k}\|ch(\|\mathbf{k}\|\frac{H}{2})\eta} - \frac{ik_{1}H}{8\|\mathbf{k}\|\eta} \left((\alpha + \beta) \frac{sh(\|\mathbf{k}\|\frac{H}{2})}{ch(\|\mathbf{k}\|\frac{H}{2})} - (\alpha - \beta) \frac{ch(\|\mathbf{k}\|\frac{H}{2})}{sh(\|\mathbf{k}\|\frac{H}{2})} \right) \end{cases}$$
(6.82)

Then :

$$\begin{cases} \alpha_{2} = \frac{BHk_{2}}{8\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})\eta} - \frac{ik_{2}H}{8\|\mathbf{k}\|\eta} \left((\alpha + \beta) \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} + (\alpha - \beta) \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})} \right) \\ \beta_{2} = \frac{BHk_{2}}{8\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})\eta} - \frac{ik_{2}H}{8\|\mathbf{k}\|\eta} \left((\alpha + \beta) \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} - (\alpha - \beta) \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})} \right)$$
(6.83)

And to finish :

$$\begin{cases} \alpha_{3} = \frac{-A}{4\|\mathbf{k}\| \operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})\eta} \left(\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2}) + \frac{H\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})}{2}\right) \\ -\frac{H}{8\eta} \left(\left(\frac{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})} \right) (\alpha - \beta) + \left(\frac{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})} \right) (\alpha + \beta) \right) \\ \beta_{3} = \frac{-A}{4\|\mathbf{k}\|\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})\eta} \left(\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2}) + \frac{H\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})}{2} \right) \\ -\frac{H}{8\eta} \left(\left(\frac{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})} \right) (\alpha - \beta) - \left(\frac{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})} \right) (\alpha + \beta) \right) \end{cases}$$
(6.84)

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 :

$$ik_1\left(\alpha_1 e^{\|\mathbf{k}\|_z} + \beta_1 e^{-\|\mathbf{k}\|_z}\right) + ik_2\left(\alpha_2 e^{\|\mathbf{k}\|_z} + \beta_2 e^{-\|\mathbf{k}\|_z}\right) + \|\mathbf{k}\|\left(\alpha_3 e^{\|\mathbf{k}\|_z} - \beta_3 e^{-\|\mathbf{k}\|_z}\right) + \frac{1}{2\eta}\left(\alpha e^{\|\mathbf{k}\|_z} + \beta e^{-\|\mathbf{k}\|_z}\right) = 0.$$
(6.85)

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 $c = \operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})$ and $s = \operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})$:

$$\begin{cases} \alpha = \frac{\frac{-A}{8sc} \left(s + \frac{H \|\mathbf{k}\|_{c}}{2}\right) - \frac{iH \|\mathbf{k}\|_{B}}{16c} + \left(\frac{-A}{4sc} \left(s + \frac{H \|\mathbf{k}\|_{c}}{2}\right) + \frac{iH \|\mathbf{k}\|_{B}}{8c}\right) \frac{\|\mathbf{k}\|_{H}}{4} \left(\frac{s}{c} - \frac{c}{s}\right)}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{s}{c} - \frac{c}{s}\right)^{2}}{\beta}} \\ \beta = \frac{\frac{A}{8sc} \left(s + \frac{H \|\mathbf{k}\|_{c}}{2}\right) - \frac{iH \|\mathbf{k}\|_{B}}{16c} - \left(\frac{-A}{4sc} \left(s + \frac{H \|\mathbf{k}\|_{c}}{2}\right) - \frac{iH \|\mathbf{k}\|_{B}}{8c}\right) \frac{\|\mathbf{k}\|_{H}}{4} \left(\frac{s}{c} - \frac{c}{s}\right)}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{s}{c} - \frac{c}{s}\right)^{2}} \end{cases}$$
(6.86)

Step 7 :

Using (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:

$$D = D_0 + \frac{k_B T}{3} \lim_{\|(x,y)\| \to 0} Tr\left(\frac{1}{2\pi \|(x,y)\|\eta} - \frac{H^2(2H^2 - \|(x,y)\|^2)}{4\pi H^5 \left(\frac{\|(x,y)\|^2}{H^2} + 1\right)^{5/2} \eta} + \frac{H^2(8H^2 - \|(x,y)\|^2)}{64\pi H^5 \left(\frac{\|(x,y)\|^2}{4H^2} + 1\right)^{5/2}} - \frac{1}{2\pi \eta \|(x,y)\|} + o\left(\frac{1}{H}\right)\right)$$
(6.87)

$$= D_0 - \frac{3k_BT}{16\pi H\eta} + o\left(\frac{1}{H}\right).$$
(6.88)

Proof. To begin we have :

$$Tr(T_{Oseen}(x, y, z)) = \frac{1}{2\pi\eta \|(x, y, z)\|}.$$
(6.89)

On the other hand, by taking z = 0 we have :

$$\begin{aligned} Tr(\mathbf{T}_{1}(x,y,0)) &= \int d\mathbf{k} \left(\frac{\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})}{\|\mathbf{k}\| \mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})\eta} - \frac{H}{8\eta} + \frac{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{4\|\mathbf{k}\| \mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})\eta} + \frac{\mathrm{Hch}(\|\mathbf{k}\| \frac{H}{2})^{2}}{8\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta} \right. \\ &- \left(\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2}) + \frac{H\|\mathbf{k}\| \mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{2} \right) \left(\frac{1}{4\|\mathbf{k}\| \mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})^{2} \mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})\eta} \right. \\ &+ \frac{\frac{32\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2}) \mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta}{14 - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})}{2} - \frac{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})} \right)^{2}} \right) \\ &+ \frac{H}{8\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta} - \left(\frac{\|\mathbf{k}\| \mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{2} - \frac{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})} \right) \\ &\left(\frac{\frac{\mathrm{d}}{\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta}{16 - \left(\frac{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}}{2} - 1 \right) \right) \\ &\left(\frac{\frac{\mathrm{d}}{\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right)^{2}} \right) - \frac{\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})\eta}{4\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})\eta} \right) e^{i\mathbf{k}.(x,y)} \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right)^{2}} \right) \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{\mathrm{sh}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right)^{2}} \right) \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2}) + \frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right) \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2}) + \frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right)^{2}} \right) \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2}) + \frac{\mathrm{d}\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right) \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2}) + \frac{\mathrm{d}\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right) \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2}) + \frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right) \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2}) + \frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2})} \right) \\ &\left(\frac{\mathrm{d}\mathrm{d}\mathrm{ch}(\|\mathbf{k}\| \frac{H}{2}) + \frac{\mathrm{d}\mathrm{ch}$$

Let us analyze more precisely the term $C(\mathbf{k}, H)$.

Terms in $\frac{1}{\|\mathbf{k}\|}$:

Note that :

$$\frac{\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{4\|\mathbf{k}\|\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta} - \frac{1}{4\|\mathbf{k}\|\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta} = \frac{\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2} - 1}{4\|\mathbf{k}\|\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta} = \frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2}}{4\|\mathbf{k}\|\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta} = \frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{4\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta}.$$
(6.91)

So we have :

$$\frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta} + \frac{\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta}{4\|\mathbf{k}\|\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta} - \frac{1}{4\|\mathbf{k}\|\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta} - \frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{4\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta} = \frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta}{\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})\eta}.$$
(6.92)

We have :

$$\frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})} - 1 = \frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H}) - \operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})} = \frac{-2}{e^{\|\mathbf{k}\|H} + 1}.$$
(6.93)

And so, for large H, we have :

$$\frac{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})} = 1 + o\left(\frac{1}{H}\right).$$
(6.94)

Finally, we have :

$$\int \frac{1}{\|\mathbf{k}\|} e^{i\mathbf{k}.(x,y)} d\mathbf{k} = \frac{1}{2\pi \|(x,y)\|}.$$
(6.95)

Terms in " $\frac{H}{8}$ ":

We have :

$$\frac{H\mathrm{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2}}{8\mathrm{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2}\eta} - \frac{H}{8\eta} = \frac{H(\mathrm{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2} - \mathrm{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2})}{8\mathrm{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2}\eta} = \frac{H}{8\mathrm{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2}\eta}.$$
(6.96)

So that :

$$\frac{H \operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2}}{8 \operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2} \eta} - \frac{H}{8\eta} - \frac{H}{8 \operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})^{2} \eta} = 0.$$
(6.97)

Other terms :

First of all, let us note that :

$$\frac{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})} = \frac{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})^2 - \operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})^2}{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})} = \frac{-1}{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})} = \frac{-2}{\operatorname{sh}(\|\mathbf{k}\|H)}.$$
(6.98)

Thus, for large H we have :

$$1 + \frac{H\|\mathbf{k}\|}{2} \left(\frac{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})} \right) = 1 + o\left(\frac{1}{H}\right)$$
(6.99)

$$\frac{1}{4} - \frac{\|\mathbf{k}\|^2 H^2}{16} \left(\frac{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\operatorname{ch}(\|\mathbf{k}\|\frac{H}{2})}{\operatorname{sh}(\|\mathbf{k}\|\frac{H}{2})} \right)^2 = \frac{1}{4} + o\left(\frac{1}{H}\right).$$
(6.100)

On the other hand, we note that for large H we have $\forall \mathbf{k} \neq (0,0)$:

$$\operatorname{ch}\left(\|\mathbf{k}\|\frac{H}{2}\right) = \frac{e^{\|\mathbf{k}\|\frac{H}{2}}}{2} + \frac{1}{2\frac{e^{\|\mathbf{k}\|\frac{H}{2}}}{2}} = \frac{e^{\|\mathbf{k}\|\frac{H}{2}}}{2} + o(e^{\|\mathbf{k}\|\frac{H}{2}})$$
(6.101)

$$\operatorname{sh}\left(\|\mathbf{k}\|\frac{H}{2}\right) = \frac{e^{\|\mathbf{k}\|\frac{H}{2}}}{2} - \frac{1}{2\frac{e^{\|\mathbf{k}\|\frac{H}{2}}}{2}} = \frac{e^{\|\mathbf{k}\|\frac{H}{2}}}{2} + o(e^{\|\mathbf{k}\|\frac{H}{2}}).$$
(6.102)

Therefore, for large H, there are terms such as :

$$\int \frac{H^2 \|\mathbf{k}\| C}{e^{\|\mathbf{k}\| H}} e^{i\mathbf{k}.(x,y)} d\mathbf{k} = \frac{CH^2 (2H^2 - \|(x,y)\|^2)}{2\pi H^5 \left(\frac{\|(x,y)\|^2}{H^2} + 1\right)^{5/2}}$$
(6.103)

$$\int \frac{H^2 \|\mathbf{k}\| C}{e^{\|\mathbf{k}\| 2H}} e^{i\mathbf{k}.(x,y)} d\mathbf{k} = \frac{CH^2 (8H^2 - \|(x,y)\|^2)}{64\pi H^5 \left(\frac{\|(x,y)\|^2}{4H^2} + 1\right)^{5/2}}.$$
(6.104)

Back to the calculation of D:

Using the ansatz (see paragraph 6.2), we have for z = 0 and large H:

$$D = D_0 + \frac{k_B T}{3} \lim_{\|(x,y)\| \to 0} Tr\left(\frac{1}{2\pi \|(x,y)\|\eta} - \frac{H^2(2H^2 - \|(x,y)\|^2)}{4\pi H^5 \left(\frac{\|(x,y)\|^2}{H^2} + 1\right)^{5/2} \eta} - \frac{H^2(8H^2 - \|(x,y)\|^2)}{128\pi H^5 \left(\frac{\|(x,y)\|^2}{4H^2} + 1\right)^{5/2}} - \frac{1}{2\pi \eta \|(x,y)\|} + o\left(\frac{1}{H}\right)\right)$$
(6.105)

$$= D_0 - \frac{3k_BT}{16\pi H\eta} + o\left(\frac{1}{H}\right). \tag{6.106}$$

To place ourselves in our case for the diffusion constant calculated in the paper [155], we take $\delta \to 0$ and $z = \frac{H}{2}$ and we obtain for large H:

$$D = \frac{k_B T}{6\pi\eta a} \frac{1}{\frac{2}{1 - \frac{9a}{8H}} - 1} = \frac{k_B T}{6\pi\eta a} \frac{1 - \frac{9a}{8H}}{1 + \frac{9a}{8H}} = D_0 - \frac{3kT}{16\pi\eta H} + o\left(\frac{1}{H}\right)$$
(6.107)

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).

^{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 $o\left(\frac{1}{H}\right)$

On the below graph (figure 32), we can observe the behavior of $D_0 - \frac{3kT}{16\pi\eta H}$, 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 $\frac{\left(D_0 - \frac{3kT}{DamH}\right)}{D_0}$ 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 Ω : 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 u of the form :

$$\begin{aligned} \boldsymbol{u}(x,y,z) &= \boldsymbol{T}_{2}(x,y,z).\boldsymbol{F} \\ &= \frac{1}{L^{2}}A_{1}(0,0)(z) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} .\boldsymbol{F} + \frac{1}{L^{2}}\sum_{\boldsymbol{k}\neq 0} \left(\left(A_{2}(\boldsymbol{k})(z) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + A_{3}(\boldsymbol{k})(z) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right. \\ &+ A_{4}(\boldsymbol{k})(z)\boldsymbol{k}^{*} \otimes \boldsymbol{k}^{*} \right) + i \left(A_{5}(\boldsymbol{k})(z) \begin{pmatrix} 0 & 0 & k_{1} \\ 0 & 0 & k_{2} \\ 0 & 0 & 0 \end{pmatrix} + A_{6}(\boldsymbol{k})(z) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ k_{1} & k_{2} & 0 \end{pmatrix} \right) \right) e^{i\boldsymbol{k}.(x,y)}.\boldsymbol{F} \end{aligned}$$

$$(6.108)$$

where $\mathbf{k} = 2\pi \left(\frac{m_1}{L}, \frac{m_2}{L}\right)$ with $(m_1, m_2) \in \mathbb{Z}^2$, and where, for $\mathbf{k} = (k_1, k_2)$ we have $\mathbf{k}^* = (k_1, k_2, 0)$ and $\mathbf{k}^* \otimes \mathbf{k}^* = \begin{pmatrix} \mathbf{k} \otimes \mathbf{k} & \begin{pmatrix} 0 \\ 0 \\ \begin{pmatrix} 0 & 0 \end{pmatrix} \end{pmatrix}$, and with $A_1(0,0)(z) = \left(\frac{1}{2\eta}z - \frac{z}{\eta}\mathbf{1}_{z\geq 0} + \frac{H}{4\eta}\right)$ (6.109)

where the A_i (i = 2, ..., 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 :

$$\lim_{\|\mathbf{k}\| \to 0} \operatorname{ch}(\|\mathbf{k}\| \frac{H}{2}) = 1$$
(6.110)

$$\operatorname{sh}(\|\mathbf{k}\|(z+\frac{H}{2})) = \|\mathbf{k}\|(z+\frac{H}{2}) + o(\|\mathbf{k}\|^2).$$
(6.111)

So that for small $\|\mathbf{k}\|$:

$$A_2(\mathbf{k})(z) = \frac{-z}{2\eta} + \frac{H}{4\eta} + o(\|\mathbf{k}\|^2).$$
(6.112)

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 δ (in the distribution space) are periodic in x and y, we can decompose them into Fourier series :

$$\mathbf{u}(x,y,z) = \frac{1}{L^2} \sum_{\mathbf{k}} \mathbf{u}_{\mathbf{k}}(z) e^{i\mathbf{k}.(x,y)}, \\ p(x,y,z) = \frac{1}{L^2} \sum_{\mathbf{k}} p_{\mathbf{k}}(z) e^{i\mathbf{k}.(x,y)}, \\ \delta(x,y,z) = \frac{1}{L^2} \sum_{\mathbf{k}} \delta_{\mathbf{k}}(z) e^{i\mathbf{k}.(x,y)}$$
(6.113)

with $\mathbf{k} = 2\pi(\frac{m_1}{L}, \frac{m_2}{L})$ où $(m_1, m_2) \in \mathbb{Z}^2$, and where $\mathbf{u}_{\mathbf{k}}(z)$, $p_{\mathbf{k}}(z)$ and $\delta_{\mathbf{k}}(z)$ are the kth Fourier coefficients of \mathbf{u} , p and δ 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 $\mathbf{k} = 2\pi (\frac{m_1}{L}, \frac{m_2}{L})$:

$$\begin{cases} \eta \left((u_{\mathbf{k}}^{1})''(z) - u_{\mathbf{k}}^{1}(z)(k_{1}^{2} + k_{2}^{2}) \right) = ik_{1}p_{\mathbf{k}}(z) - \delta_{\mathbf{k}}(z)F_{1} \\ \eta \left((u_{\mathbf{k}}^{2})''(z) - u_{\mathbf{k}}^{2}(z)(k_{1}^{2} + k_{2}^{2}) \right) = ik_{2}p_{\mathbf{k}}(z) - \delta_{\mathbf{k}}(z)F_{2} \\ \eta \left((u_{\mathbf{k}}^{3})''(z) - u_{\mathbf{k}}^{3}(z)(k_{1}^{2} + k_{2}^{2}) \right) = (p_{\mathbf{k}})'(z) - \delta_{\mathbf{k}}(z)F_{3} \end{cases}$$

$$(6.114)$$

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 $\forall z \in [\frac{-H}{2}, \frac{H}{2}]$:

$$ik_1 u_{\mathbf{k}}^1(z) + ik_2 u_{\mathbf{k}}^2(z) + (u_{\mathbf{k}}^3)'(z) = 0.$$
(6.115)

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) :

$$\Delta p = \mathbf{F} \cdot \nabla \delta \tag{6.116}$$

(since $\nabla . \mathbf{u} = 0.$)

We then obtain :

$$(p_{\mathbf{k}})''(z) - p_{\mathbf{k}}(z)(k_1^2 + k_2^2) = i(k_1F_1 + k_2F_2)g_{\mathbf{k}}(z) + F_3\delta'_{\mathbf{k}}(z).$$
(6.117)

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 :

$$A = \frac{F_3}{2\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}, \ B = \frac{\mathbf{k}^* \cdot \mathbf{F}}{2\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}$$
(6.118)

where $\mathbf{k}^* = \begin{pmatrix} \mathbf{k} \\ 0 \end{pmatrix}$. Proceeding in the same way as in step 4 of the proof of theorem 7, we find :

$$p_{k}(z) = \alpha e^{\|\mathbf{k}\|z} + \beta e^{-\|\mathbf{k}\|z} + (-A - iB)\operatorname{sh}(\|\mathbf{k}\|(z + \frac{H}{2}))\mathbf{1}_{z \le 0} + (-A + iB)\operatorname{sh}(\|\mathbf{k}\|(z - \frac{H}{2}))\mathbf{1}_{z > 0}.$$
(6.119)

And then :

$$p_{k}'(z) = \|\mathbf{k}\| \left((-A - iB) \operatorname{ch}(\|\mathbf{k}\|(z + \frac{H}{2})) \mathbf{1}_{z \leq 0} + (-A + iB) \operatorname{ch}(\|\mathbf{k}\|(z - \frac{H}{2})) \mathbf{1}_{z > 0} \right) \\ + \|\mathbf{k}\| \left(\alpha e^{\|\mathbf{k}\|z} - \beta e^{-\|\mathbf{k}\|z} \right) + 2A \operatorname{sh}(\|\mathbf{k}\|\frac{H}{2}) \delta(z).$$
(6.120)

Then:

$$\begin{cases} u_{\mathbf{k}}^{1}(z) = \alpha_{1} e^{||\mathbf{k}||z} + \beta_{1} e^{-||\mathbf{k}||z} - \frac{ik_{1}}{\eta} \frac{2}{\eta|\mathbf{k}||} \left(\left(t + \frac{H}{2}\right) \operatorname{ch}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} + \left(z - \frac{H}{2}\right) \operatorname{ch}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{k_{1}}{\eta} \frac{Bz}{2||\mathbf{k}||^{2}\eta} \left(\operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} - \operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ - \frac{k_{1}B}{2||\mathbf{k}||^{2}\eta} \left(\operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} - \operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \left(\frac{E}{2||\mathbf{k}||^{2}\eta} \left(\operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} - \operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \left(\frac{E}{2||\mathbf{k}||^{2}\eta} \left(\operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\right) \right) \operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{1}z}{2||\mathbf{k}||\eta} \left(\operatorname{ch}(||\mathbf{k}|||\frac{H}{2})\eta + \frac{ik_{1}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\mathbf{sh}||\mathbf{sh}||\frac{H}{2}|\eta}\right) \operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{1}z}{2||\mathbf{k}||\eta} \left(\operatorname{ch}(||\mathbf{k}||(z - \beta e^{-||\mathbf{k}||z}) + \frac{ik_{2}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{\eta}\right) \operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{k_{2}}{2||\mathbf{k}||\eta} \left(\operatorname{ch}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} - \operatorname{ch}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ - \frac{k_{2}B}{\eta} \frac{Bz}{2||\mathbf{k}||\eta} \left(\operatorname{ch}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \leq 0} - \operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \left(\frac{E}{2||\mathbf{k}||\operatorname{ch}(||\mathbf{k}|||\frac{H}{2})\eta} + \frac{ik_{2}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\operatorname{sh}(||\mathbf{k}||\frac{H}{2})\eta}\right) \operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \left(\frac{E}{2||\mathbf{k}||\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta} + \frac{ik_{2}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{4||\mathbf{k}||\operatorname{sh}(||\mathbf{k}||\frac{H}{2})\eta}\right) \operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z \geq 0} + \left(z - \frac{H}{2}\right)\operatorname{sh}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{2}z}{2||\mathbf{k}||\eta} \left(\operatorname{ch}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z < 0} - \operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{2}z}{2||\mathbf{k}||\eta} \left(\operatorname{ch}(||\mathbf{k}|||z - \beta - \frac{H}{2})\left(\frac{H}{2}\right) - \operatorname{sh}(||\mathbf{k}||(z + \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{2}z}{2||\mathbf{k}||\eta} \left(\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta - \frac{ik_{2}z}{2\eta} \left(\operatorname{ch}(||\mathbf{k}||\frac{H}{2}\right) + \frac{ik_{2}AH\operatorname{ch}(||\mathbf{k}||\frac{H}{2})\eta}{2\eta}\right) \left(\operatorname{ch}(||\mathbf{k}||(z - \frac{H}{2}))\mathbf{1}_{z > 0}\right) \\ + \frac{ik_{2}$$

Step 4 :

The condition (6.20) gives us, by invoking the uniqueness of the coefficients of a Fourier series :

$$\mathbf{u}_{\mathbf{k}}\left(\pm\frac{H}{2}\right) = 0\tag{6.122}$$

and then the α_i, β_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 α and β 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 :

$$(p_{(0,0)})''(z) = F_3 \delta'(z). \tag{6.123}$$

We then find with the lemma 14 :

$$p_{(0,0)}(z) = \alpha z + \beta + F_3 \mathbf{1}_{z \ge 0} \tag{6.124}$$

with $\alpha, \beta \in \mathbb{C}$. We replace in (6.114), and then we get thanks to the lemma 10 :

$$\begin{cases}
 u_{(0,0)}^{1}(z) = \frac{-F_{1}}{\eta} z \mathbf{1}_{z \ge 0} + \alpha_{1} z + \beta_{1} \\
 u_{(0,0)}^{2}(z) = \frac{-F_{2}}{\eta} z \mathbf{1}_{z \ge 0} + \alpha_{2} z + \beta_{2} \\
 u_{(0,0)}^{3}(z) = \frac{\alpha}{2\eta} z^{2} + \alpha_{3} z + \beta_{3}
\end{cases}$$
(6.125)

Using the conditions (6.122), we have :

$$\begin{cases} \alpha_1 = \frac{F_1}{4\eta} \\ \beta_1 = \frac{F_1H}{4\eta} \end{cases} \begin{cases} \alpha_2 = \frac{F_2}{4\eta} \\ \beta_2 = \frac{F_2H}{4\eta} \end{cases} \begin{cases} \alpha_3 = 0 \\ \beta_3 = \frac{-\alpha H^2}{8\eta} \end{cases}$$
(6.126)

We now use the equation (6.115) and we get for $z \in [\frac{-H}{2}, \frac{H}{2}]$:

$$0 = (u_{\mathbf{k}}^3)'(z) = \frac{\alpha}{\eta} z.$$
 (6.127)

And then :

$$\alpha = 0. \tag{6.128}$$

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_{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 :

$$D_{per} = D_0 + \frac{k_B T}{3} \lim_{\|(x,y,z)\| \to 0} Tr(\mathbf{T}_2(x,y,z) - \mathbf{T}_{Oseen}(x,y,z)).$$
(6.129)

We set :

$$C_1 = \sum_{\mathbf{n} \neq (0,0)} \int_{\mathbb{R}^2} e^{-\|(l,m)\|^2} \left(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m) + \mathbf{n}\|} \right) dl dm.$$
(6.130)

In order to verify the convergence of the series in (6.130), in what follows, we are interested in the behavior of $\int_{\mathbb{R}^2} e^{-\|(l,m)\|^2} \left(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m)+\mathbf{n}\|}\right) dl dm$ when $\|\mathbf{n}\|$ is large. We have the following lemma :

Lemma 17. When $||\mathbf{n}||$ is large :

$$\int_{\mathbb{R}^2} e^{-\|(l,m)\|^2} \left(\frac{1}{\|\boldsymbol{n}\|} - \frac{1}{\|-(l,m)+\boldsymbol{n}\|} \right) dl dm \sim \frac{Cst}{\|\boldsymbol{n}\|^3}$$
(6.131)

which is a term associated with a convergent series, where :

$$Cst = \int_0^\infty \int_0^{2\pi} e^{-s^2} s^3 (1 + 4\cos(\phi - \theta)^2) ds d\phi$$
 (6.132)

is a constant which is independent of r.

Proof. In polar coordinates, we have :

$$\mathbf{n} = r e^{i\theta} \tag{6.133}$$

$$(l,m) = se^{i\phi} \tag{6.134}$$

where r, s and θ, ϕ are respectively the module and the argument of **n** and (l, m). So that we get :

$$\frac{1}{\|\mathbf{n}\|} = \frac{1}{r} \tag{6.135}$$

$$\frac{1}{\|-(l,m)+\mathbf{n}\|} = \frac{1}{re^{i\theta} - se^{i\phi}} = \frac{1}{r\|1 - \frac{s}{r}e^{\phi-\theta}\|}.$$
(6.136)

We have :

$$\|1 - \frac{s}{r}e^{\phi - \theta}\| = \left(1 - \frac{s}{r}\cos(\phi - \theta)\right)^2 + \left(\frac{s}{r}\sin(\phi - \theta)\right)^2 = 1 - \frac{2s}{r}\cos(\phi - \theta) + \left(\frac{s}{r}\right)^2.$$
 (6.137)

Since $\|\mathbf{n}\|$ is large, r is large, so that $\frac{s}{r}$ is small. We then have :

$$\frac{1}{1 - \frac{2s}{r}\cos(\phi - \theta) + \left(\frac{s}{r}\right)^2} = 1 + \frac{2s}{r}\cos(\phi - \theta) - \left(\frac{s}{r}\right)^2 \left(1 + 4\cos(\phi - \theta)^2\right) + o\left(\left(\frac{s}{r}\right)^2\right).$$
 (6.138)

So that we have :

$$\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m) + \mathbf{n}\|} = \frac{1}{r} - \frac{1}{r} \left(1 + \frac{2s}{r} \cos(\phi - \theta) - \left(\frac{s}{r}\right)^2 (1 + 4\cos(\phi - \theta)^2) + o\left(\left(\frac{s}{r}\right)^2\right) \right)$$
(6.139)
$$= \left(\frac{-2s}{r^2} \cos(\phi - \theta) + \left(\frac{s^2}{r^3}\right) (1 + 4\cos(\phi - \theta)^2) + o\left(\frac{s^2}{r^3}\right) \right)$$
(6.140)

and then :

$$\begin{split} \int_{\mathbb{R}^2} e^{-\|(l,m)\|^2} \left(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m) + \mathbf{n}\|} \right) dl dm \\ &= \int_0^\infty \int_0^{2\pi} e^{-s^2} \left(\frac{-2s}{r^2} \cos(\phi - \theta) + \left(\frac{s^2}{r^3}\right) (1 + 4\cos(\phi - \theta)^2) + o\left(\frac{s^2}{r^3}\right) \right) s ds d\phi. \quad (6.141) \end{split}$$

The integrale of the first term is null by periodicity of the cosinus function. For the second term we have :

$$\int_{0}^{\infty} \int_{0}^{2\pi} e^{-s^{2}} \left(\frac{s^{3}}{r^{3}}\right) (1 + 4\cos(\phi - \theta)^{2}) ds d\phi = \frac{Cst}{r^{3}}$$
(6.142)

where Cst is a constant which is independent of r.

Theorem 11. For
$$h = \frac{\pi H}{L}$$
, we have :

$$D_{per} = D_0 + \frac{k_B T}{3} \left(\frac{H}{8L^2 \eta} + \frac{1}{2\pi^2 L \eta} C_1 + \frac{1}{\eta 2\pi L} \sum_{(m_1, m_2) \neq 0} \frac{1}{\|(m_1, m_2)\|} e^{-\pi^2 \|(m_1, m_2)\|^2} - \frac{1}{2\pi^{1/2} L \eta} + \frac{1}{8\pi^2 H \eta} \sum_{(m_1, m_2) \neq 0} f(\|(m_1, m_2)\|h)h^2 \right)$$

$$(6.143)$$

where

$$f: x \mapsto -\frac{(sh(x) + xch(x))}{ch(x)} \left(\frac{1}{sh(x)ch(x) + x}\right) + \frac{1}{ch(x)^2\eta} - \left(\frac{xsh(x)}{ch(x)} + \frac{x^2}{ch(x)^2}\right) \left(\frac{sh(x)^2}{sh(x)^2ch(x)^2 - x^2}\right).$$
(6.144)

Proof. Let us take z = 0 and look at $Tr(\mathbf{T}_2(x, y, 0))$. We have :

$$\begin{split} Tr(\mathbf{T}_{2}(x,y,0)) &= \frac{H}{8L^{2}\eta} + \frac{1}{L^{2}} \sum_{\mathbf{k}\neq 0} \left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})\eta} - \frac{H}{8\eta} + \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{4\|\mathbf{k}\|\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})\eta} + \frac{H\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}}{8\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta} \right. \\ &- \left(\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2}) + \frac{H\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{2} \right) \left(\frac{1}{4\|\mathbf{k}\|\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{6\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})} \right) \\ &+ \frac{\frac{H}{32\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})} \right) \\ &+ \frac{H}{8\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta} - \left(\frac{\|\mathbf{k}\|\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{2} \left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})^{2}} - 1 \right) \right) \\ &\left(\frac{\frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{(\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{2} \right) - \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})^{2}}{4\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}} - 1 \right) \right) \\ &\left(\frac{\frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{(\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{2} \right) - \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{4\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})\eta} \right) e^{\mathrm{i}\mathbf{k}.(x,y)} \\ &\left(\frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{(\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{2} \right)^{2} \right) - \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{4\|\mathbf{k}\|\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})\eta} \right) e^{\mathrm{i}\mathbf{k}.(x,y)} \\ &\left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}{4} - \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta} - \left(\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2}) - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{(\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} \right) \right) \\ &\left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}{4} - \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}{1} - \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} - \frac{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} \right) \right) \\ \\ &\left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})^{2}\eta}{1} - \left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2}) + \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{ch}(\|\mathbf{k}\|\frac{H}{2})} \right) \right) \\ \\ &\left(\frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{1} - \frac{\mathrm{sh}(\|\mathbf{k}\|\frac{H}{2})}{\mathrm{sh}(\|\mathbf{k}\|\frac{H$$

where the second equality derives from the remarks in the proof of theorem 9.

With (6.93), we have :

$$\frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})} - \frac{1}{\|\mathbf{k}\|} = \frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H}) - \operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})} = \frac{-2}{\left(e^{\|\mathbf{k}\|H} + 1\right)\|\mathbf{k}\|}.$$
(6.147)

So that :

$$\frac{\operatorname{sh}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})}{\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\|_{\frac{H}{2}}^{H})} = \frac{1}{\|\mathbf{k}\|} - \frac{2}{\left(e^{\|\mathbf{k}\|H} + 1\right)\|\mathbf{k}\|}.$$
(6.148)

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 $X = (X_1, X_2) \sim N(O, \frac{1}{2\alpha^2}I_2)$ corresponds to its characteristic function $E(e^{iX\mathbf{k}})$, from where we get $: \hat{g}(\mathbf{k}) = e^{-\frac{\mathbf{k}^2}{4\alpha^2}}$.

We have :

$$\frac{1}{L^2} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|\eta} e^{i\mathbf{k}.(x,y)} = \frac{1}{\eta L^2} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} \left(1 - e^{-\frac{\|\mathbf{k}\|^2}{4\alpha^2}}\right) e^{i\mathbf{k}.(x,y)} + \frac{1}{\eta L^2} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} e^{-\frac{\|\mathbf{k}\|^2}{4\alpha^2}} e^{i\mathbf{k}.(x,y)}.$$
(6.149)

For the first sum, we wish to use the formula of Poisson. We consider $\hat{h} : (k_1, k_2) \mapsto \frac{1}{\|\mathbf{k}\|} \left(1 - e^{-\frac{\|\mathbf{k}\|^2}{4\alpha^2}} \right)$ for $(k_1, k_2) \neq (0, 0)$. Poisson's formula requires to have the term of Fourier transform for $(k_1, k_2) = (0, 0)$, that is why, by extension by continuity, we set $\hat{h}(0, 0) = 0$ (which does not add or subtract a term in the end).

Since \hat{h} is of type $\hat{h} = \hat{f} \cdot \hat{g}$, then h is of type h = f * g (where * is the convolution product). Thus, we get :

$$\frac{1}{\eta L^2} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} \left(1 - e^{-\frac{\|\mathbf{k}\|^2}{4\alpha^2}} \right) e^{i\mathbf{k}.(x,y)} = \frac{1}{\eta} \sum_{\mathbf{n}} \left(\frac{1}{2\pi \|(x,y) + \mathbf{n}L\|} - \frac{1}{2\pi \|(x,y) + \mathbf{n}L\|} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y) + \mathbf{n}L\|^2} \right). \tag{6.150}$$

Back to the calculation of D_{per} :

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 :

$$\begin{split} \xi &:= \lim_{\|(x,y)\| \to 0} \left(\frac{1}{\eta} \sum_{\mathbf{n}} \left(\frac{1}{2\pi \|(x,y) + \mathbf{n}L\|} - \frac{1}{2\pi \|(x,y) + \mathbf{n}L\|} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y) + \mathbf{n}L\|^2} \right) \\ &+ \frac{1}{\eta L^2} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} e^{-\frac{\|\mathbf{k}\|^2}{4\alpha^2}} e^{i\mathbf{k}.(x,y)} - \frac{1}{2\pi \|(x,y)\|\eta} \right). \end{split}$$
(6.151)

We have :

$$\xi = \frac{1}{\eta} \sum_{\mathbf{n} \neq (0,0)} \left(\frac{1}{2\pi \|\mathbf{n}L\|} - \lim_{\|(x,y)\| \to 0} \frac{1}{2\pi \|(x,y) + \mathbf{n}L\|} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y) + \mathbf{n}L\|^2} \right) + \frac{1}{\eta L^2} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} e^{-\frac{\|\mathbf{k}\|^2}{4\alpha^2}} - \lim_{\|(x,y)\| \to 0} \frac{1}{2\pi \|(x,y)\|\eta} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y)\|^2}.$$
(6.152)

Step 1 : We have :

$$\frac{1}{2\pi \|(x,y)\|} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y)\|^2} = \int_{\mathbb{R}^2} \frac{1}{2\pi \|(x-l,y-m)\|} \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(l,m)\|^2} dl dm.$$
(6.153)

Using the Lebesgue dominated convergence theorem and then switching to polar variable we obtain :

$$\lim_{\|(x,y)\|\to 0} \frac{1}{2\pi \|(x,y)\|} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y)\|^2} = \int_{\mathbb{R}^2} \frac{1}{2\pi \|(l,m)\|} \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(l,m)\|^2} dl dm$$
$$= \int_0^\infty \int_0^{2\pi} \frac{\alpha^2}{2\pi^2} e^{-\alpha^2 r^2} d\theta dr$$
$$= \frac{\alpha}{2\pi^{1/2}}.$$
(6.154)

after recognizing the integral of a Gaussian in the second tie.

Step 2 : We have :

$$\frac{1}{2\pi \|(x,y) + \mathbf{n}L\|} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y) + \mathbf{n}L\|^2} = \int_{\mathbb{R}^2} \frac{1}{2\pi \|(x-l,y-m) + \mathbf{n}L\|} \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(l,m)\|^2} dl dm.$$
(6.155)

So that using the Lebesgue dominated convergence theorem we have :

$$\lim_{\|(x,y)\|\to 0} \frac{1}{2\pi \|(x,y) + \mathbf{n}L\|} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y) + \mathbf{n}L\|^2} = \int_{\mathbb{R}^2} \frac{1}{2\pi \|-(l,m) + \mathbf{n}L\|} \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(l,m)\|^2} dl dm.$$
(6.156)

We make the change of variable $(l,m) \to (lL,mL)$ and we get :

$$\lim_{\|(x,y)\|\to 0} \frac{1}{2\pi \|(x,y) + \mathbf{n}L\|} * \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(x,y) + \mathbf{n}L\|^2} = \int_{\mathbb{R}^2} \frac{L}{2\pi \| - (l,m) + \mathbf{n}\|} \frac{\alpha^2}{\pi} e^{-\alpha^2 L^2 \|(l,m)\|^2} dl dm.$$
(6.157)

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):

$$\frac{1}{2\pi \|\mathbf{n}L\|} = \int_{\mathbb{R}^2} \frac{1}{2\pi \|\mathbf{n}L\|} \frac{\alpha^2}{\pi} e^{-\alpha^2 \|(l,m)\|^2} dl dm.$$
(6.158)

We make the change of variable $(l,m) \rightarrow (lL,mL)$ and we get :

$$\frac{1}{2\pi \|\mathbf{n}L\|} = \int_{\mathbb{R}^2} \frac{L}{2\pi \|\mathbf{n}\|} \frac{\alpha^2}{\pi} e^{-\alpha^2 L^2 \|(l,m)\|^2} dl dm.$$
(6.159)

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 :

$$D_{per} = D_{0} + \frac{k_{B}T}{3} \left(\frac{H}{8L^{2}\eta} + \frac{L}{\eta} \frac{\alpha^{2}}{2\pi^{2}} \sum_{\mathbf{n} \neq (0,0)} \left(\int_{\mathbb{R}^{2}} e^{-\alpha^{2}L^{2} \|(l,m)\|^{2}} \left(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m)+\mathbf{n}\|} \right) dldm \right) \\ + \frac{1}{\eta L^{2}} \sum_{\mathbf{k} \neq 0} \frac{1}{\|\mathbf{k}\|} e^{-\frac{\|\mathbf{k}\|^{2}}{4\alpha^{2}}} - \frac{\alpha}{2\pi^{1/2}\eta} + \frac{1}{L^{2}} \sum_{\mathbf{k} \neq 0} \left(-\left(\operatorname{sh}(\|\mathbf{k}\| \frac{H}{2}) + \frac{H\|\mathbf{k}\|\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})}{2} \right) \right) \\ \left(\frac{\frac{32\operatorname{sh}(\|\mathbf{k}\| \frac{H}{2})\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta}{14} \left(\frac{1 + \frac{H\|\mathbf{k}\|}{2} \left(\frac{\operatorname{sh}(\|\mathbf{k}\| \frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})} - \frac{\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})}{\operatorname{sh}(\|\mathbf{k}\| \frac{H}{2})} \right) \right) \\ + \frac{H}{\operatorname{8ch}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta} - \left(\frac{\|\mathbf{k}\|\operatorname{sh}(\|\mathbf{k}\| \frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})} - \frac{H\|\mathbf{k}\|^{2}}{2} \left(\frac{\operatorname{sh}(\|\mathbf{k}\| \frac{H}{2})^{2}}{\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}} - 1 \right) \right) \\ \left(\frac{\frac{H}{64\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}\eta}}{\frac{1}{4} - \frac{\|\mathbf{k}\|^{2}H^{2}}{16} \left(\frac{\operatorname{sh}(\|\mathbf{k}\| \frac{H}{2})}{\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})} - \frac{\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}}{\operatorname{ch}(\|\mathbf{k}\| \frac{H}{2})^{2}} - 1 \right) \right) \right)$$

$$(6.160)$$

We recall that $\mathbf{k} = \frac{2\pi}{L}(m_1, m_2)$ with $m_i \in \mathbb{N}$ (i = 1, 2). Doing the indexing change $\mathbf{k} \to (m_1, m_2)$ for the series, we get :

$$\begin{split} D_{per} &= D_0 + \frac{k_B T}{3} \bigg(\frac{H}{8L^2 \eta} + \frac{L}{\eta} \frac{\alpha^2}{2\pi^2} \sum_{\mathbf{n} \neq (0,0)} \bigg(\int_{\mathbb{R}^2} e^{-\alpha^2 L^2 \|(l,m)\|^2} \bigg(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m) + \mathbf{n}\|} \bigg) \, dldm \bigg) \\ &+ \frac{1}{\eta 2\pi L} \sum_{(m_1,m_2) \neq (0,0)} \frac{1}{\|(m_1,m_2)\|} e^{-\frac{\pi^2 \|(m_1,m_2)\|^2}{L^2 \alpha^2}} - \frac{\alpha}{2\pi^{1/2} \eta} \\ &+ \frac{1}{L^2} \sum_{(m_1,m_2) \neq 0} \bigg(-\bigg(\mathrm{sh}(\|(m_1,m_2)\| \frac{\pi H}{L}) + \frac{\pi H \|(m_1,m_2)\| \mathrm{ch}(\|(m_1,m_2)\| \frac{\pi H}{L})}{L} \bigg) \\ & \bigg(\frac{\frac{32\mathrm{sh}(\|(m_1,m_2)\| \frac{\pi H}{L})\mathrm{ch}(\|(m_1,m_2)\| \frac{\pi H}{L})^2 \eta}{4L^2} \bigg(\frac{1 + \frac{\pi H \|(m_1,m_2)\|}{L} \bigg(\frac{\mathrm{sh}(\|(m_1,m_2)\| \frac{\pi H}{L})}{\mathrm{ch}(\|(m_1,m_2)\| \frac{\pi H}{L})} - \frac{\mathrm{ch}(\|(m_1,m_2)\| \frac{\pi H}{L})}{\mathrm{sh}(\|(m_1,m_2)\| \frac{\pi H}{L})} \bigg) \bigg) \\ &+ \frac{H}{\mathrm{sch}(\|(m_1,m_2)\| \frac{\pi H}{L})^2 \eta} \\ &- \bigg(\frac{\pi H \|(m_1,m_2)\| \mathrm{sh}(\|(m_1,m_2)\| \frac{\pi H}{L})}{L\mathrm{ch}(\|(m_1,m_2)\| \frac{\pi H}{L})} - \frac{\pi^2 H^2 \|(m_1,m_2)\|^2}{L^2} \bigg(\frac{\mathrm{sh}(\|(m_1,m_2)\| \frac{\pi H}{L})^2}{\mathrm{ch}(\|(m_1,m_2)\| \frac{\pi H}{L})^2} - 1 \bigg) \bigg) \\ & \bigg(\frac{\frac{32\mathrm{sh}(\|(m_1,m_2)\| \frac{\pi H}{L}) + 1}{4} - \frac{\|(m_1,m_2)\| \frac{\pi H}{L}}{\mathrm{sh}(\|(m_1,m_2)\| \frac{\pi H}{L})} \bigg) \bigg) \bigg) \bigg) \bigg) \bigg) . \quad (6.161) \end{aligned}$$

By taking $h = \frac{\pi H}{L}$ and by using hyperbolic trigonometry formulas, we finally get :

$$D_{per} = D_{0} + \frac{k_{B}T}{3} \left(\frac{H}{8L^{2}\eta} + \frac{L}{\eta} \frac{\alpha^{2}}{2\pi^{2}} \sum_{\mathbf{n} \neq (0,0)} \left(\int_{\mathbb{R}^{2}} e^{-\alpha^{2}L^{2} \|(l,m)\|^{2}} \left(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m) + \mathbf{n}\|} \right) dldm \right) \\ + \frac{1}{\eta 2\pi L} \sum_{(m_{1},m_{2}) \neq (0,0)} \frac{1}{\|(m_{1},m_{2})\|} e^{-\frac{\pi^{2} \|(m_{1},m_{2})\|^{2}}{L^{2}\alpha^{2}}} - \frac{\alpha}{2\pi^{1/2}\eta} \\ + \frac{1}{L^{2}} \sum_{(m_{1},m_{2}) \neq 0} \left(-\left(\operatorname{sh}(\|(m_{1},m_{2})\|h) + h\|(m_{1},m_{2})\|\operatorname{ch}(\|(m_{1},m_{2})\|h)\right) \\ \left(\frac{\frac{8\operatorname{ch}(\|(m_{1},m_{2})\|h)}{\operatorname{sh}(\|(m_{1},m_{2})\|h)} + \frac{h^{2}\|(m_{1},m_{2})\|^{2}}{\operatorname{ch}(\|(m_{1},m_{2})\|h)} \right) \\ + \frac{H}{8\operatorname{ch}(\|(m_{1},m_{2})\|h)^{2}\eta} \\ - \left(\frac{h\|(m_{1},m_{2})\|\operatorname{sh}(\|(m_{1},m_{2})\|h)}{\operatorname{ch}(\|(m_{1},m_{2})\|h)} + \frac{h^{2}\|(m_{1},m_{2})\|^{2}}{\operatorname{ch}(\|(m_{1},m_{2})\|h)^{2}} \right) \\ \left(\frac{\frac{H\operatorname{sh}(\|(m_{1},m_{2})\|h)^{2}}{\operatorname{sh}(\|(m_{1},m_{2})\|h)^{2}\operatorname{ch}(\|(m_{1},m_{2})\|h)^{2}} - \|(m_{1},m_{2})\|^{2}h^{2}} \right) \right) \right).$$
(6.162)

We define :

$$f: x \mapsto -\frac{(\operatorname{sh}(x) + x\operatorname{ch}(x))}{\operatorname{ch}(x)} \left(\frac{1}{\operatorname{sh}(x)\operatorname{ch}(x) + x}\right) + \frac{1}{\operatorname{ch}(x)^2 \eta} - \left(\frac{x\operatorname{sh}(x)}{\operatorname{ch}(x)} + \frac{x^2}{\operatorname{ch}(x)^2}\right) \left(\frac{\operatorname{sh}(x)^2}{\operatorname{sh}(x)^2\operatorname{ch}(x)^2 - x^2}\right).$$
(6.163)

So that :

$$D_{per} = D_0 + \frac{k_B T}{3} \left(\frac{H}{8L^2 \eta} + \frac{L}{\eta} \frac{\alpha^2}{2\pi^2} \sum_{\mathbf{n} \neq (0,0)} \left(\int_{\mathbb{R}^2} e^{-\alpha^2 L^2 \|(l,m)\|^2} \left(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m) + \mathbf{n}\|} \right) dl dm \right) \\ + \frac{1}{\eta 2\pi L} \sum_{(m_1,m_2) \neq (0,0)} \frac{1}{\|(m_1,m_2)\|} e^{-\frac{\pi^2 \|(m_1,m_2)\|^2}{L^2 \alpha^2}} - \frac{\alpha}{2\pi^{1/2} \eta} + \frac{H}{8L^2 \eta} \sum_{(m_1,m_2) \neq 0} f(\|(m_1,m_2)\|h) \right).$$

$$(6.164)$$

In order to obtain a Riemann's eries for the last series, we have to multiply f by h^2 so that we get :

$$D_{per} = D_0 + \frac{k_B T}{3} \left(\frac{H}{8L^2 \eta} + \frac{L}{\eta} \frac{\alpha^2}{2\pi^2} \sum_{\mathbf{n} \neq (0,0)} \left(\int_{\mathbb{R}^2} e^{-\alpha^2 L^2 \|(l,m)\|^2} \left(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m) + \mathbf{n}\|} \right) dl dm \right) \\ + \frac{1}{\eta 2\pi L} \sum_{(m_1,m_2) \neq (0,0)} \frac{1}{\|(m_1,m_2)\|} e^{-\frac{\pi^2 \|(m_1,m_2)\|^2}{L^2 \alpha^2}} - \frac{\alpha}{2\pi^{1/2} \eta} + \frac{H}{8L^2 \eta} \frac{1}{h^2} \sum_{(m_1,m_2) \neq 0} f(\|(m_1,m_2)\|h)h^2 \right).$$

$$(6.165)$$

This being valid $\forall \alpha > 0$, it is true in particular for $\alpha = \frac{1}{L}(> 0)$ and we then obtain, recalling

also that $h = \frac{\pi H}{L}$:

$$D_{per} = D_0 + \frac{k_B T}{3} \left(\frac{H}{8L^2 \eta} + \frac{1}{2\pi^2 L \eta} \sum_{\mathbf{n} \neq (0,0)} \left(\int_{\mathbb{R}^2} e^{-\|(l,m)\|^2} \left(\frac{1}{\|\mathbf{n}\|} - \frac{1}{\|-(l,m) + \mathbf{n}\|} \right) dl dm \right) + \frac{1}{\eta 2\pi L} \sum_{(m_1,m_2) \neq (0,0)} \frac{1}{\|(m_1,m_2)\|} e^{-\pi^2 \|(m_1,m_2)\|^2} - \frac{1}{2\pi^{1/2} L \eta} + \frac{1}{8\pi^2 H \eta} \sum_{(m_1,m_2) \neq 0} f(\|(m_1,m_2)\|h)h^2 \right).$$

$$(6.166)$$

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 $H/L \rightarrow 0$:

$$\sum_{(m_1,m_2)\neq 0} f(\|(m_1,m_2)\|h)h^2 \to \int_{\mathbb{R}^2} f(\mathbf{x})d\mathbf{x} := I.$$
(6.167)

We then have :

$$D_{per} = D_0 + \frac{k_B T}{3} \frac{I}{8\pi^2 H \eta} \left(1 + o\left(\frac{H}{L}\right) \right). \tag{6.168}$$

For large L, we know with theorem 9 that the first term of expansion in H is :

$$\frac{-3k_bT}{16\pi H\eta} \tag{6.169}$$

so that it can be conjecture that 4:

$$I = \frac{-9\pi}{2}.$$
 (6.170)

If we want to obtain the second order for the expansion of D_{per} , we have on the one hand the three terms in the begining of (6.143) (not 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 $P_{m_1,m_2} = [m_1h - \frac{h}{2}, m_1h + \frac{h}{2}] \times [m_2h - \frac{h}{2}, m_2h + \frac{h}{2}]$ of size h^2 and centered on point (x_{m1}, x_{m2}) with $x_{mi} = m_i h$ (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. :

$$\int_{\mathbb{R}^2} f(\mathbf{x}) d\mathbf{x} = \sum_{(m_1, m_2)} \int_{P_{m_1, m_2}} f(\mathbf{x}) d\mathbf{x}$$
(6.171)

with

$$f(\mathbf{x}) = f(x_{m1}, x_{m2}) + (x - x_{m1})\frac{\partial f}{\partial x}(x_{m1}, x_{m2}) + (y - x_{m2})\frac{\partial f}{\partial y}(x_{m1}, x_{m2}) + \frac{1}{2}(x - x_{m1})^2\frac{\partial^2 f}{\partial x^2}(x_{m1}, x_{m2}) + \frac{1}{2}(y - x_{m2})^2\frac{\partial^2 f}{\partial y^2}(x_{m1}, x_{m2}) + (x - x_{m1})(y - x_{m2})\frac{\partial^2 f}{\partial x \partial y}(x_{m1}, x_{m2}) + o(h^2).$$
 (6.172)

^{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 :

$$\int_{P_{m_1,m_2}} \frac{1}{2} (x - x_{m_1})^2 \frac{\partial^2 f}{\partial x^2} (x_{m_1}, x_{m_2}) dx dy = \frac{h^4}{24} \frac{\partial^2 f}{\partial x^2} (m_1 h, m_2 h)$$
(6.173)

and

$$\int_{P_{m_1,m_2}} \frac{1}{2} (y - x_{m_2})^2 \frac{\partial^2 f}{\partial y^2}(x_{m_1}, x_{m_2}) dx dy = \frac{h^4}{24} \frac{\partial^2 f}{\partial y^2}(m_1 h, m_2 h).$$
(6.174)

We then have :

$$\sum_{(m_1,m_2)} \int_{P_{m_1,m_2}} f(\mathbf{x}) d\mathbf{x} = \sum_{(m_1,m_2)} \left(f(x_{m1}, x_{m2}) h^2 + \frac{h^4}{24} \frac{\partial^2 f}{\partial x^2}(m_1 h, m_2 h) + \frac{h^4}{24} \frac{\partial^2 f}{\partial y^2}(m_1 h, m_2 h) \right).$$
(6.175)

For the last two terms, we have :

$$\sum_{(m_1,m_2)} \frac{h^4}{24} \frac{\partial^2 f}{\partial x^2}(m_1 h, m_2 h) = \frac{h^2}{24} \sum_{(m_1,m_2)} \frac{\partial^2 f}{\partial x^2}(m_1 h, m_2 h)h^2$$
(6.176)

$$\sum_{(m_1,m_2)} \frac{h^4}{24} \frac{\partial^2 f}{\partial y^2}(m_1h, m_2h) = \frac{h^2}{24} \sum_{(m_1,m_2)} \frac{\partial^2 f}{\partial y^2}(m_1h, m_2h)h^2$$
(6.177)

where, for $h \to 0,$ we have, as Riemann's series :

$$\sum_{(m_1,m_2)} \frac{\partial^2 f}{\partial x^2}(m_1h, m_2h)h^2 \to \int_{\mathbb{R}^2} \frac{\partial^2 f}{\partial x^2}(x, y)dxdy$$
(6.178)

$$\sum_{(m_1,m_2)} \frac{\partial^2 f}{\partial y^2}(m_1h,m_2h)h^2 \to \int_{\mathbb{R}^2} \frac{\partial^2 f}{\partial y^2}(x,y)dxdy.$$
(6.179)

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_{per} as :

$$D_{per} = D_0 - \frac{3k_B T}{16\pi H\eta} \left(1 - \frac{8}{9}C_2 \frac{H}{L} + o\left(\left(\frac{H}{L}\right)\right) \right)$$

$$(6.180)$$

with :

$$C_2 = \frac{1}{\pi} C_1 + \sum_{(m_1, m_2) \neq (0, 0)} \frac{1}{\|(m_1, m_2)\|} e^{-\pi^2 \|(m_1, m_2)\|^2} - \pi^{1/2}$$
(6.181)

where we recall that C_1 is defined in (6.130).

We numerically have

$$C_1 \simeq -6.2387$$
 and $\sum_{(m_1, m_2) \neq (0, 0)} \frac{1}{\|(m_1, m_2)\|} e^{-\pi^2 \|(m_1, m_2)\|^2} \simeq 2.069 \ 10^{-4}$ (6.182)

so that

$$C_2 \simeq -3.7579.$$
 (6.183)

Finally, we get :

$$D_{per} \simeq D_0 - \frac{3k_B T}{16\pi H\eta} \left(1 + 3.3403 \frac{H}{L} + o\left(\left(\frac{H}{L}\right)\right) \right). \tag{6.184}$$

With that expansion, we can easily see that when $H \to \infty$ and $H/L \to 0$ we have $D_{per} \to D_0$, 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 $\frac{1}{D_0}$ 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 $\frac{\left(D_0 - \frac{3kT}{16\pi\eta H}\right)}{D_0}$ found in the previous section in the non-periodic case

$$\frac{\left(D_0 - \frac{3kT}{16\pi\eta H} \left(1 + 3.3403\frac{H}{L}\right)\right)}{D_0}, \text{ i.e. t}$$

On the graph (figure 33), we can observe the behavior of $\frac{1}{D_0}$, 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 $\frac{\left(D_0 - \frac{3kT}{16\pi\eta H}\right)}{D_0}$ 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 $H \to \infty$ and $H/L \to 0$ we have $D_{per} \to D_0$, 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 ϵ_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 A, 36,342 A and 53,000 A, and containing a Na⁺, an ion 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 Ax = b and have a complexity in $O(n \log_2^{\alpha}(n))$ (*n* being the number of unknowns).

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