UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO

PROGRAMA DE MAESTRÍA Y DOCTORADO EN INGENIERÍA

TEORÍA Y SIMULACIÓN DE UN FLUIDO PERCUS-YEVICK HOMOGÉNEO ASIMÉTRICO DE ESFERAS DURAS

TESIS DE MAESTRÍA

QUE PARA OPTAR POR EL GRADO DE:

MAESTRO EN INGENIERÍA

PRESENTA:

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TEMIXCO, MORELOS 17 DE DICIEMBRE DE 2021

Summary

We study the analytical and numerical solution of the Percus-Yevick integral equation of a complex hard spheres fluid. To test our findings, we performed molecular dynamics simulations of a two-species hard spheres fluid. One of the well established analytical solutions of the Percus-Yevick equation for this system was derived by R. J. Baxter, for one species [1]. For a mixture [2] of hard spheres, he generalized his one-species mathematical approach [1]. Unfortunately, there are some mathematical incongruities in his derivations, as we prove in this thesis. Therefore, we review Baxter's derivations and offer a correct derivation. In particular, we propose an alternative set of equations to that given in reference [2]. We, successfully, test our new reformulation of the n-species Percus-Yevick integral equations against other analytical solutions, its finite elements numerical solution, and molecular dynamics simulations. Finally, we demonstrate that the solution derived following Baxter's steps does not coincide with the molecular dynamics results.

Contents

Chapter 1

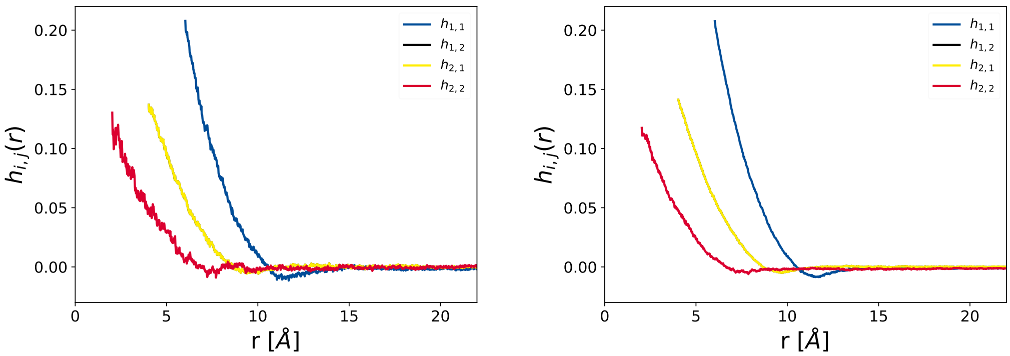
Introduction

Let us consider a system of N particles confined in a volume V. If the number of particles is small and we know their pair-interaction potential, their position and velocity (momenta) can be computed by solving the system's Lagrangian (Hamiltonian). However, if the number of particles is enormous: it would be challenging—sometimes impossible—to compute the system's motion as a function of time by the methods of classical mechanics. In the past, the Newton's equations have been numerically solved for a large, but finite number of particles. In fact, we can obtain macroscopic properties, given the inter-particles potential, by taking averages over the position and velocities of particles. This computer experiment approach is known as molecular dynamics [3]. However, as the system's complexity increases it becomes, sometimes, impossible to use this method. So, how can we study more complex systems?

On the other hand, is it even useful to analyze this many body systems using a particle approach? Even though the objects we encounter in our daily experience are of macroscopic size–large enough to be observed directly–, they are composed of particles. Most of the many body systems in physics, chemistry and biology consist of very many particles of atomic, nanoscopic or microscopic scale, i.e. from atoms ($\gtrsim 1$Å) to complex molecules ($\lesssim 10\mu m$). Hence, macroscopic parameters such as volume, pressure, energy, entropy and temperature depend on the distribution, motion and velocity of the systems particles. Therefore, it is, indeed, worthwhile to analyze such system's under a particle's approach. However, is it useful to know the system's particles' position and momenta as a function time? This, of course, depends on what we want to do; for example, let us consider the following problem: CRISPR-Cas9 is a genome-editing technology which can be programmed to change specific genes in living organisms. Even so, its mechanics at the molecular level is not fully understood yet. Furthermore, since the key steps of the process have to be traced with precision at tiny time jumps, it turns out that molecular dynamics simulations can bring some light on how CRISPR-Cas9 works [4]. Therefore, yes, sometimes it is, to some limited extent, useful knowing the system's particles position as a function of time. Altogether, molecular dynamics is a very reliable tool for simulation of microscopic systems, but simultaneously it might be a very computationally expensive technique. In addition to molecular computer simulations, there are, of course, non-equilibrium statistical mechanics theories to deal with time-dependent phenomena, such as transport theory [5], molecular hydrodynamics [6], and irreversible thermodynamics [7], based on time-dependent correlation functions.

Hence, in general, knowing the system's particles position as a function of time is not so useful. In fact, statistical mechanics has proven that understanding the behavior of the whole system can be achieved not only by knowing individually the behavior of particles, but by understanding its interactions as a whole. Quoting Richard Tolman, the complete explanation "of thermodynamics in terms of ... statistical mechanics is one of the greatest achievements of physics", nonetheless we haven't defined what statistical mechanics is. With this in mind, let us answer our first question, i.e., how can we study more complex systems?

One of the first ideas that comes into one's mind with the words "statistical" and "many" is the mathematical law of large numbers. It basically states: if we were to perform an experiment several times–several as in 10 million of particle collisions or more–the outcomes' average obtained is close and even tends to the expected value as we perform more trials. As an example, in Figure 1.1, we show our molecular dynamics simulation of a system of particles consisting of two hard spheres species immersed in a container. There are no external fields acting over them–the fluid is homogeneous–, the diameter of each species is two and six angstroms respectively, the molar concentrations are 1 $\frac{mol}{cm^3} \equiv M$ for both of them, and the temperature is $298K$. Figure 1.1 shows the *equilibrium* total correlation between particles of species, i and j, $h_{i,j}(r)$, in terms of their distance, r. This illustrates the law of large numbers, i.e., as we perform more collisions (trials): we obtain a better picture of the expected value of the parameter we are looking for (compare Fig. 1.1-b, $6x10^6$ collisions, against Fig. 1.1-a, $6x10^5$ trials). We will properly define $h_{i,j}(r)$ later on this chapter, and discuss extensively Fig. 1.1, in chapters 5 and 6. Moreover, the total correlation functions were computed applying Boltzmann's method [8], in other words, taking the average over a trajectory on the phase space, i.e., over a sequence of possible



(a) (b)

Figure 1.1: Total correlation functions, $h_{i,j}(r)$ $(i, j \in \{1, 2\})$, calculated with molecular dynamics. The system is a two-species of hard spheres fluid, at a temperature $T = 298K$. Their diameters and molar concentrations are $d_1 = 6$Å and $d_2 = 2$Å, and $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively. (a) Total correlation functions after 600,000 collisions. (b) Total correlation functions after 6,000,000 trials.

positions and velocities, given an initial condition. On the other hand, if the expected value was computed over an ensemble of systems–a collection containing system's copies representing all the possible states at least one time–Gibbs's method [8] would've been applied. By definition, the theory of statistical mechanics consists of statistical methods and probability theory applied to large assemblies of microscopic entities. It does not assume or postulate any natural laws, but explains the macroscopic behavior of nature from the behavior of such ensembles.

Therefore, the theory of equilibrium statistical mechanics predicts the expected state of a system. Given initial conditions, we can find an equilibrium state–an average of what it is encountered in nature–however, equilibrium statistical mechanics is not concerned with each particles' behavior.

Let us elaborate on Gibbs's method by explaining the concept of phase space, Γ. Imagine a system of N particles; let Γ be the subset of $\mathbb{R}^{6N}$ comprising all system's accessible positions and momenta. A microstate is an element of Γ governed by Hamilton's equations. A system's macrostate M in equilibrium is described by some state functions such as energy, temperature, pressure and the number of particles. In other words, it is a set comprising tuples whose entries are the state functions' values. To grasp these concepts, let us state the following example. We flip twice a coin, there are four possible outcomes or microstates with the same probability (principle of equal a priori probability):

$$\{(head,\ tail), (head,\ head), (tail,\ tail), (tail,\ head)\},$$

but just three macrostates (not equally probable): two heads, two tails or one head and one tail, i.e., microstates are different ways a system can achieve a macrostate. Gibbs proposed an ensemble (a collection) of microstates. It contains an infinite number of copies of our system, where each possible microstate is represented at least one time. Therefore, there is a distribution of the microstates in the ensemble. Consequently, what we look for is to compute the expected value of a macroscopic property, X, using a probability density function, f, over the phase space [1].

$$E[X] = \int_{\Gamma} X(q,p) f(q,p) dq dp$$

However, how do we find such functions? We could make assumptions over f depending on the system to be modeled–choosing the ensemble–, but, finding X, which describes the system's thermodynamic properties is necessary.

Assuming a system of particles interacting via pair-wise additive forces–since more real assumptions result in more expensive computations–, thermodynamic properties can be expressed as functionals of the radial distribution function, $g_{i,j}(r)$, which is the expected number of $j-$particles at distance r from an $i-$particle divided by the number of $j-$particles at distance r from an $i-$particle if the fluid was an ideal gas. It measures how the fluid's structure deviates from an ideal gas–complete randomness–under the same conditions.

Before talking about such a relationship, let us introduce the reduced distribution function, defined as,

$$f^{(n)}(q^n, p^n; t) = \frac{N!}{(N-n)!} \int\int f(q,p;t) dq^{(N-n)} dp^{(N-n)},$$

where $q^n = (q_1, q_2, .., q_n)$, $dq^{(N-n)} = dq_{n+1} dq_{n+2} \cdots dq_N$, $p^n = (p_1, p_2, .., p_n)$, and $dp^{(N-n)} = dp_{n+1} dp_{n+2} \cdots dp_N$. $f^{(n)}(q^n, p^n; t)$ is the probability that at time t the system's first n general coordinates lie in the volume element $dp^{(n)} dq^{(n)}$ irrespective of the integrated coordinates and momenta of the $(N-$

[1] Note that in this thesis only equations which will be referred to afterwards will be numbered.

n) particles[2]. Let us define $\rho^{(n)}$ by integrating $f^{(n)}$ with respect the momenta,

$$f^{(n)}(q^n) = A\rho^{(n)}(q^n),$$

where A is a constant. Subsequently, the n-particle distribution function, $g^{(n)}$, is defined as

$$g^{(n)}(q_1, q_2, ..., q_n) = \frac{\rho^{(n)}(q_1, q_2, ..., q_n)}{\prod_{i=1}^{n} \rho^{(1)}(q_i)}.$$

If the fluid is homogeneous, then it reduces to

$$\rho^n g^{(n)}(q_1, q_2, ..., q_n) = \rho^{(n)}(q_1, q_2, ..., q_n).$$

If the fluid is also isotropic–its properties are not dependent on the direction along which they are measured–, the pair distribution function depends on the distance between particles and becomes the radial distribution function, $g^{(2)}(|q_i - q_j|) = g_{i,j}(r)$. Nevertheless, how do we compute it? First, let us introduce the total correlation functions, $h_{i,j}$, defined as

$$h_{i,j}(r) = g_{i,j}(r) - 1, \tag{1.1}$$

and the direct correlation functions, $c_{i,j}(r)$, defined by the integral equations, known in the literature as the Ornstein-Zernike (OZ) equations for m species,

$$h_{i,j}(r) = c_{i,j}(r) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(r - r')h_{k,j}(r')dr'. \tag{1.2}$$

General liquid theories have been developed from different balance equations, such as the the Ornstein-Zernike equations. For a review of these theories see, for example, reference [8]. In this thesis, we focus on solving the integral equations 1.2. Thus, expected values of thermodynamic properties can be computed if the total correlation function or the direct correlation functions are found. For the expressions of the thermodynamic properties the reader is referred to [5]. In order to solve equations 1.2, we need to make assumptions or approximations of the direct correlations functions, known in the literature as closure approximations. Some of them are the Percus-Yevick approximation (PY) [9, 1, 10] Hyper-netted Chain approximation (HNC) [8], and the Mean Spherical approximation (MSA) [11]. For a system of hard-spheres the MSA and PY approximations become equal. Different approximations can be combined to obtain new liquid theories. For example,if

[2]Since the fluid is homogeneous it's computed for one subset and multiplied by the number of subsets containing n particles

in equation 1.2 the MSA is taken for $c_{i,k}(r - r')$, and the HNC approximation is used for $c_{i,j}(r)$, the so-called HNC/MSA equation is obtained [12, 13]. The HNC/MSA and MSA integral equations have been widely used in soft-condensed matter physics systems to obtain the correlation functions of, e.g., simple liquids, electrolytes, colloid dispersions, etc. Two simple models have been used to study a large variety of condensed matter fluids: hard spheres and charged hard spheres.

Equation 1.2 is an integral equation with two unknown functions: $h_{i,j}(r)$ and $c_{i,j}(r)$. To solve this system of equations, we need an expression for the direct correlation function. The PY approximation is given by

$$c_{i,j}(r) = \left\{ e^{-\beta W_{i,j}(r)} - e^{-\beta[W_{i,j}(r) - u_{i,j}(r)]} \right\} = g_{i,j}(r)[1 - e^{\beta u_{i,j}(r)}], \tag{1.3}$$

while for the MSA $c_{i,j}(r) = -\beta u_{i,j}(r)$. For a system of hard spheres

$$u_{i,j}(r) = \begin{cases} \infty & r < a_{i,j} \\ 0 & r > a_{i,j}, \end{cases} \tag{1.4}$$

where $u_{i,j}(r)$ is the *unscreened* interaction potential between two particles of the fluid, $W_{i,j}(r)$ is their corresponding potential of mean force, and $a_{i,j} \equiv (a_i + a_j)/2$, such that a_i and a_j are the molecular diameters of the particles of species i and j, respectively. Hence, inserting equation 1.3 or equation 1.4, in equation 1.2, we obtain the MSA integral equation. However, for charged hard spheres, equations 1.3 and 1.4 are not anymore equivalent. An important advantage of this approach is that an analytical solution of the direct correlation function for hard spheres fluids exists, thus providing closed formulas. Although, here we will not go any further with the HNC/MSA equation, let us just add that the HNC direct correlation function is easily obtained from equation 1.3, by expanding to first order the second exponential in the curly brackets. Hence, as pointed out above, the HNC/MSA equation is found by substituting this correlation function in the first term of the right hand side of equation 1.2, while the MSA correlation is used inside its integral term.

The Ornstein-Zernike equation, with the Percus-Yevick approximation for fluid mixtures has been analytically studied by R. J. Baxter [1, 2], L. Blum [14], and J. L. Lebowitz [15], among other authors. Having analytical expressions for the bulk direct correlation function of hard spheres or charged hard spheres have proved to be a good approach for the solution of integral equations derived for more complex fluids, for example, in the study of mixtures of charged nano-particles or colloids [13], where the MSA analytical direct correlation functions are used [11].

In this thesis we are interested in the solution of the OZ equation with the Percus-Yevick approximation for a mixture of hard spheres. To completely understand what the autor wanted to do in reference [1], some mathematical theory is needed. Hence, in chapter 2 a mathematical background is presented, the majority of it is not demonstrated, but it's referenced. In chapter 3, the theory for the Wiener-Hopf factorization method is presented, most of it, is demonstrated and the gaps of reference [16] are filled. In chapter 4, we obtain the main result from reference [1] using the theory from the previous chapters; moreover, it also contains the correct, Baxter couldn't arrive to one, and complete generalization from [2] rigorously proved. This generalization is a set equations, see equations 4.24 and 4.25, that connect the total and direct correlation functions using a function denoted by Q_i. For the case of one species this set of equations allows us to find an analytical solution for the direct correlation function, however for more than one species this set of equations does not allow us to find it. Nevertheless, this generalization provides a new optic to the problem of computing the total and direct correlation functions, in fact it might be better to work with the functions Q_i: given that severe changes in the direct correlation function might produce similar total correlation functions, as it can be seen in section 6.3.2 (figures 6.3.2 and 6.3.2).

Why is this finding relevant? Assume an non-homogeneous fluid comprised by one charged sphere in the center and two species of charged hard spheres–where the difference between diameters is big–around it. The method to obtain the system's total correlation functions [13] uses as input the direct correlations functions estimated with MSA, but those analytical expressions [11] were based on [2] and [10]! So it might be worth to redo the computations involved in obtaining those results. It becomes more relevant since some of the steps are not so transparent, as discussed in section 6.1.2.

In chapter 5, we present the total correlations functions for a fluid comprised of two species at temperature, $T = 298K$, the particles are hard spheres with no long-range inter-molecular forces. Its diameters are $d_1 = 6\text{Å}$ and $d_2 = 2\text{Å}$. Its molar concentrations are $\rho_1 = 1M$ and $\rho_2 = 1M$. The total correlation functions were obtained using two methods, molecular dynamics and finite element. We compare them and use as benchmark the finite element total correlation functions in the next chapter. Finally, in chapter 6, we discuss Hiroike's analytical expressions for the direct correlation functions [10] and compare them to our numerical results. For a binary mixture we validate the main result of chapter 4, additionally, we compare Baxter's work [2], arriving to an analytical expression for the direct correlations functions for a binary mixture, against our numerical results. In summary, Baxter's work is wrong, since the direct correlation functions are very different from our benchmark. Hiroike's analytical solution coincide with our benchmark, but a crucial step is obscure in his work, as commented in section 6.1.2.

As for a synthesis of our contributions:

1. We rigorously proved Baxter's result [1] for one species in section 4.1.
2. We followed Baxter's steps in [2] to obtain analytical expression for the direct correlation function, in the case of a binary mixture in section 6.3.
   (a) We used these analytical expressions as counterexample to prove he was wrong, when we compared them against our results from molecular dynamics and finite element.
   (b) We used these analytical expressions as a way to illustrate how very different direct correlation functions used to solve the OZ equation produce similar total correlation functions.
3. We rigorously derived what Baxter intended to do in [2]. With that we arrived to a set of equations, which reformulate de OZ equation in section 4.2.
   (a) We validated this set of equations for a binary mixture. We did it by comparing them with our results from molecular dynamics and finite element in section 6.2.

Chapter 2

Mathematical background

Let us do a review of definitions, propositions and theorems that will be used in chapter 3. Most of them are from real and complex analysis, nevertheless, there are some definitions that will be used in all the document.

2.1 Complex analysis

Let us recall useful propositions from complex analysis, they will be used in section 3.1.1. The statements and proofs are found in references [17, 18, 19, 20].

Definition 2.1.1 *Let $L : [a, b] \subseteq \mathbb{R} \to \mathbb{C}$ be a curve; we say L is a Jordan curve if it is injective when restricted to (a, b).*

Proposition 2.1.2 *Let G be the interior of closed rectifiable Jordan curve L; if f is analytic in G and continuous in the frontier of G, then*

$$\int_L f(z)dz = 0.$$

Definition 2.1.3 *Let $\delta : [a, b] \subseteq \mathbb{R} \to \mathbb{C}$ be a curve; we say δ is an arc, if $a \neq b$. We say β is an open arc if β is the restriction of δ to (a, b). Moreover, it is rectifiable if it is of finite length.*

Theorem 2.1.4 *Let f_1 and f_2 be functions of a complex variable such that f_1 is analytic in G_1 and f_2 is analytic in G_2, where $G_1 \cap G_2 = \emptyset$, but share an accessible open and rectifiable Jordan boundary arc δ. If f_1 is continuous in $G_1 \cup \delta$, f_2 is continuous in $G_2 \cup \delta$ and for all $z \in \delta$ $f_1(z) = f_2(z)$, then* *there exists a function f analytic in $G_1 \cup \delta \cup G_2$ such that*

$$f(z) = \begin{cases} f_1(z) & z \in G_1 \\ f_1(z) = f_2(z) & z \in \delta \\ f_2(z) & z \in G_2. \end{cases}$$

Theorem 2.1.5 *Let f be an analytic function in a closed disc of radius R with center in the origin. Suppose $r < R$, then*

$$max_{|z|=r}|f(z)| \leq \frac{2r}{R-r} sup_{|z|\leq R} Re(f(z)) + \frac{R+r}{R-r}|f(0)|.$$

Theorem 2.1.6 *Let A and C be positive constants and F an entire function. If*

1. *for all $z \in \mathbb{C}$ $|F(z)| \leq Ce^{A|z|}$ and*
2. *$\int_{-\infty}^{\infty} |F(x)|^2 dx < \infty$,*

then there exists $f \in L^2(-A, A)$ such that for all $z \in \mathbb{C}$

$$F(z) = \int_{-A}^{A} f(t)e^{itz} dt.$$

2.2 Preliminaries

This section contains the definitions that will be used in the document. The propositions where we prove that some set is a ring are useful when we engage in simplifying expressions where the elements are used. In the Fourier subsection we give a recount of used definitions. Finally, the propositions and theorems are from real analysis and they will be used shortly after stating them or in chapter 3. All of the proofs were made by us, in some not all, we filled the blanks left by Krein in reference [16].

2.2.1 Foundations

Definition 2.2.1 *Let L be the set*

$$L = \left\{ f : \mathbb{R} \to \mathbb{C} \,\middle|\, \int_{-\infty}^{\infty} |f(t)| dt \text{ is finite} \right\}$$

with a norm defined as $||f||_L = \int_{-\infty}^{\infty} |f(t)| dt$, and a product defined as

$$f_1 * f_2(t) = \int_{-\infty}^{\infty} f_1(t-s) f_2(s) ds = \int_{-\infty}^{\infty} f_1(s) f_2(t-s) ds.$$

Remark 2.2.2

$$\begin{aligned}
||f_1 * f_2||_L &= \int_{-\infty}^{\infty} \left| \int_{-\infty}^{\infty} f_1(t-s) f_2(s) ds \right| dt \\
&\leq \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |f_1(t-s) f_2(s)| \, dsdt \\
&= \int_{-\infty}^{\infty} |f_2(s)| \int_{-\infty}^{\infty} |f_1(r)| \, drds \\
&= \int_{-\infty}^{\infty} |f_2(s)| \, ||f_1||_L ds \\
&= ||f_1||_L \; ||f_2||_L.
\end{aligned}$$

Proposition 2.2.3 *The set L equipped with the usual sum of functions, the product defined above and the zero function as additive identity is a ring.*

Proof. First, let us show $(L, +, 0)$ is an abelian group.

1. To be demonstrated, $\forall\ a, b \in L\ a + b \in L$.
   Let $a, b \in L$.
   $$\begin{aligned}
   \int_{-\infty}^{\infty} |(a+b)(t)| dt &= \int_{-\infty}^{\infty} |a(t) + b(t)| dt \\
   &\leq \int_{-\infty}^{\infty} |a(t)| dt + \int_{-\infty}^{\infty} |b(t)| dt \\
   &< \infty,
   \end{aligned}$$
   thus $a + b \in L$.

2. To be demonstrated, $\forall\ a, b, c \in L\ (a + b) + c = a + (b + c)$.
   Let $a, b, c \in L$ and $x \in \mathbb{R}$. Since $\mathbb{C}$ is a field,
   $$(a(x) + b(x)) + c(x) = a(x) + (b(x) + c(x)).$$
   Consequently, $(a + b) + c = a + (b + c)$.

3. To be demonstrated, $\forall a, b \in L\ a + b = b + a$.
   Let $a, b \in L$ and $x \in \mathbb{R}$. Seeing that $\mathbb{C}$ is a field,
   $$a(x) + b(x) = b(x) + a(x).$$
   Hence, $a + b = b + a$.

4. To be demonstrated, $\exists\ e \in L$, such that $\forall a \in L\ a + e = e + a = a$.
   Let 0 be the zero function and $a \in L$: $0 \in L$. Since we proved commutativity it suffices to prove $a + 0 = a$. Suppose $x \in \mathbb{R}$, recognizing that $\mathbb{C}$ is a field:
   $$a(x) + 0(x) = a(x) + 0 = a(x).$$
   Therefore, $a + 0 = a$.

5. To be demonstrated, $\forall a \in L \; \exists \; b \in L$, such that $a + b = e = b + a$. Let $a \in L$, i.e. $\int_{-\infty}^{\infty} |a(t)|dt = cte < \infty$, then $-\int_{-\infty}^{\infty} |a(t)|dt < \infty$; $-a \in L$. Let $x \in \mathbb{R}$. Since $\mathbb{C}$ is a field,

$$a(x) + b(x) = b(x) + a(x) = 0(x) :$$

$a + b = b + a = 0$.

Now let us see $(L, *)$ is a semigroup.

1. To be demonstrated, $\forall a, b \in L \; a * b = b * a$.
   Let $a, b \in L$ and $t \in \mathbb{R}$.

$$\begin{aligned} a * b(t) &= \int_{-\infty}^{\infty} a(t-s)b(s)ds \\ &= -\int_{\infty}^{-\infty} a(x)b(t-x)dx \\ &= \int_{-\infty}^{\infty} b(t-x)a(x)dx \\ &= b * a(t). \end{aligned}$$

2. To be demonstrated, $\forall a, b, c \in L \; (a * b) * c = a * (b * c)$.
   Let $a, b, c \in L$ and $t \in \mathbb{R}$.

$$\begin{aligned} (a * b(t)) * c(t) &= \left(\int_{-\infty}^{\infty} a(t-s)b(s)ds\right) * c(t) \\ &= \left(\int_{-\infty}^{\infty} b(t-x)a(x)dx\right) * c(t) \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} b(t-x-s)a(x)dxc(s)ds \\ &= \int_{-\infty}^{\infty} a(x)\int_{-\infty}^{\infty} b(t-x-s)c(s)dsdx \\ &= a(t) * \left(\int_{-\infty}^{\infty} b(t-s)c(s)ds\right) \\ &= a(t) * (b * c(t)). \end{aligned}$$

Finally let us show $\forall a, b, c \in L \; a*(b+c) = (a*b)+(a*c)$. Suppose $a, b, c \in L$ and $t \in \mathbb{R}$.

$$\begin{aligned} (a * b(t)) + (a * c(t)) &= \left(\int_{-\infty}^{\infty} a(t-s)b(s)ds\right) + \left(\int_{-\infty}^{\infty} a(t-s)c(s)ds\right) \\ &= \int_{-\infty}^{\infty} a(t-s)\left[b(s) + c(s)\right]ds \\ &= a(t) * (b + c(t)) : \end{aligned}$$

$a * (b + c) = (a * b) + (a * c)$. $\square$

Definition 2.2.4 *Let us define the following sets:*

$$L_+ = \{f \in L \mid \textit{if } t < 0, \ \textit{then } f(t) = 0\}$$

and

$$L_- = \{f \in L \mid \textit{if } t > 0, \ \textit{then } f(t) = 0\}.$$

Proposition 2.2.5 *$(L_+, +, *, 0)$ and $(L_-, +, *, 0)$ are sub rings of L.*

Proof. Let us show it for $(L_+, +, 0, *)$, the other one is analogous.

1. To be demonstrated, $\forall a, b \in L_+ \ a - b \in L_+$.
   Let $a, b \in L_+$ and $t < 0$. Since $\mathbb{C}$ is a field,

   $$\begin{aligned} (a-b)(t) &= a(t) - b(t) \\ &= 0 + 0 \\ &= 0. \end{aligned}$$

   Furthermore, in view of L being a commutative ring, $a - b \in L$: $a - b \in L_+$.

2. To be demonstrated, $\forall a, b \in L_+ \ a * b \in L_+$.
   Considering L is a commutative ring, $a * b \in L$. Let $t < 0$.

   $$\begin{aligned} a * b(t) &= \int_{-\infty}^{\infty} a(t-s)b(s)ds \\ &= \int_{-\infty}^{0} a(t-s)b(s)ds + \int_{0}^{\infty} a(t-s)b(s)ds \\ &= 0 + 0 : \end{aligned}$$

   $a * b \in L_+$.

□

2.2.2 Fourier transform

Definition 2.2.6 *Let f be a real valued function; we define the Fourier transform of f as $\hat{f}(y) = \int_{-\infty}^{\infty} f(x)e^{ixy}dx$ if $\hat{f}(y)$ is finite.*

Theorem 2.2.7 *Suppose a function g exists such that,*

$$g(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \hat{f}(t)e^{ixt}dt \quad x \in \mathbb{R}.$$

If $f \in L$ and $\hat{f} \in L$, then g is continuous and $f = g$ except in a set of measure zero. If f is continuous: $f = g$.

2.2.3 Useful propositions and theorems

Proposition 2.2.8 *If $f \in L$, $\hat{f}(y) \to 0$ when $|y| \to \infty$.*

Proof. Suppose $f \in L$:

$$\begin{aligned}
\hat{f}(y) &= \int_{-\infty}^{\infty} f(x)e^{iyx}dx \\
&= \int_{-\infty}^{\infty} f\left(t+\frac{\pi}{y}\right)e^{iy\left(t+\frac{\pi}{y}\right)}dt \\
&= \int_{-\infty}^{\infty} f\left(x+\frac{\pi}{y}\right)e^{iyx}e^{i\pi}dx \\
&= -\int_{-\infty}^{\infty} f\left(x+\frac{\pi}{y}\right)e^{iyx}dx,
\end{aligned}$$

then

$$2\hat{f}(y) = \int_{-\infty}^{\infty}\left[f(x) - f\left(x+\frac{\pi}{y}\right)\right]e^{iyx}dx.$$

$$\begin{aligned}
|\hat{f}(y)| &= \left|\frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[f(x) - f\left(x+\frac{\pi}{y}\right)\right]e^{iyx}dx\right| \\
&\leq \frac{1}{2}\int_{-\infty}^{\infty}\left|\left[f(x) - f\left(x+\frac{\pi}{y}\right)\right]\right|dx.
\end{aligned}$$

By the dominated convergence theorem we can move the limit inside the integral: for all $\epsilon > 0$ there exists a $Y > 0$ such that for all $|y| > Y$ $||\hat{f}(y)| - 0| < \epsilon$. It follows that $|\hat{f}(y)| < \epsilon$, moreover $\hat{f}(y) \to 0$ given that $|y| \to \infty$. $\square$

Remark 2.2.9 *The Fourier transform of f, $\hat{f}$, is continuous.*

Remark 2.2.10 *It's well known that given f and $g \in L$, the Fourier transform of $h = f * g$ is $\hat{h} = \hat{f}\hat{g}$.*

Definition 2.2.11 *Let us define de following set:*

$$\mathfrak{R}^0 = \{\hat{f} \mid f \in L\}.$$

Proposition 2.2.12 *The algebraic structure $(\mathfrak{R}^0, +, \cdot, 0)$ is a ring where $\cdot$ is the usual product of functions.*

$\square$

Definition 2.2.13 *Let $\mathfrak{R}$ be a set such that*

$$\mathfrak{R} = \left\{ c + \int_{-\infty}^{\infty} f(t) e^{ity} dt \mid c \in \mathbb{C},\ f \in L \right\}.$$

Remark 2.2.14 *$\mathcal{F} \in \mathfrak{R}$:*

$$\begin{aligned} \mathcal{F}(y) &= c + \int_{-\infty}^{\infty} f(t) e^{ity} dt \\ &= \int_{-\infty}^{\infty} \left[c\delta(t) + f(t) \right] e^{ity} dt \end{aligned}$$

where δ is Dirac's delta function. Therefore,

$$\mathfrak{R} = \left\{ \int_{-\infty}^{\infty} \left[c\delta(t) + f(t) \right] e^{ity} dt \mid f \in L,\ c \in \mathbb{C} \right\},$$

i.e., $\mathfrak{R}$ contains all the integrable functions' Fourier transformation of the form $c\delta + f$.

Proposition 2.2.15 *Let $\tilde{L} = \{c\delta + f \mid f \in L,\ c \in \mathbb{C}\}$; $(\mathfrak{R}, +, \cdot, 0, 1)$ and $(\tilde{L}, +, *, 0, \delta)$ are rings.*

□

Definition 2.2.16 *We denote the upper and lower complex plane as*

$$\Pi_+ = \{z \in \mathbb{C} \mid Im(z) \geq 0\} \quad \textit{and} \quad \Pi_- = \{z \in \mathbb{C} \mid Im(z) \leq 0\}.$$

Definition 2.2.17 *Let us define the following sets:*

$$\begin{aligned} \mathfrak{R}_+ &= \left\{ c + \int_0^{\infty} f(t) e^{ity} dt \mid c \in \mathbb{C},\ f \in L_+ \right\} \subset \mathfrak{R} \\ \mathfrak{R}_+^0 &= \left\{ \int_0^{\infty} f(t) e^{ity} dt \mid f \in L_+ \right\} \subset \mathfrak{R}_+ \\ \mathfrak{R}_- &= \left\{ c + \int_{-\infty}^{0} f(t) e^{ity} dt \mid c \in \mathbb{C},\ f \in L_- \right\} \subset \mathfrak{R} \\ \mathfrak{R}_-^0 &= \left\{ \int_{-\infty}^{0} f(t) e^{ity} dt \mid f \in L_- \right\} \subset \mathfrak{R}_-. \end{aligned}$$

Proposition 2.2.18 *If $\mathcal{F}_+ \in \mathfrak{R}_+$ and $\mathcal{F}_- \in \mathfrak{R}_-$, they can be extended to holomorphic functions in the interior and continuous on $\Pi_\pm$.*

Proof. Suppose $\mathcal{F}_+ \in \mathfrak{R}_+$, i.e., $\mathcal{F}_+(y) = c + \int_0^\infty f(t)e^{ity}dt$ and let $z \in \mathbb{C}$.

$$\begin{aligned} \left|c + \int_0^\infty f(t)e^{itz}dt\right| &= \left|c + \int_0^\infty f(t)e^{itz_1}e^{-tz_2}dt\right| \\ &\leq |c| + \int_0^\infty |f(t)|e^{-tz_2}dt \\ \text{if } T \text{ is big enough} &\leq |c| + \int_0^T |f(t)|e^{-tz_2}dt + \int_T^\infty |f(t)|dt \\ &< \infty. \end{aligned}$$

$$\begin{aligned} \left|c + \int_0^\infty itf(t)e^{itz}dt\right| &= \left|c + \int_0^\infty itf(t)e^{itz_1}e^{-tz_2}dt\right| \\ &\leq |c| + \int_0^\infty |tf(t)|e^{-tz_2}dt \\ \text{if } T \text{ is big enough} &\leq |c| + \int_0^T |tf(t)|e^{-tz_2}dt + \int_T^\infty |f(t)|dt \\ &< \infty. \end{aligned}$$

Using remark 2.2.9 $\mathcal{F}_+$ can be extended to a holomorphic function in the interior and continuous on Π_+. Similarly, $\mathcal{F}_-$ is a holomorphic function in the interior and continuous on Π_-. $\square$

Examples.

1. $\frac{1}{y-z} = -i\int_0^\infty e^{-izt}e^{iyt}dt \in \mathfrak{R}_+^0 \subset \mathfrak{R}_+$ $Im(z) < 0$. $Im(z) < 0$ is asked so $f(t) = e^{-izt} = e^{-iz_1t}e^{z_2t} \in L_+ \iff Im(z) < 0$. Using proposition 2.2.18,
$$\frac{1}{\zeta - z} = -i\int_0^\infty e^{-izt}e^{i\zeta t}dt.$$

2. $\frac{1}{y-z} = i\int_{-\infty}^0 e^{-izt}e^{iyt}dt \in \mathfrak{R}_-^0$ $Im(z) > 0$. $Im(z) > 0$ is asked so $f(t) = e^{-izt} = e^{-iz_1t}e^{z_2t} \in L_- \iff Im(z) > 0$. Using proposition 2.2.18,
$$\frac{1}{\zeta - z} = i\int_{-\infty}^0 e^{-izt}e^{i\zeta t}dt.$$

Proposition 2.2.19 *Suppose $\mathcal{F} \in \mathfrak{R}_+^0$ and consider its extension to Π_+. If $z = Re^{i\theta}$ and $\theta \in [0, \pi]$, then $|\mathcal{F}(z)| \to 0$ uniformly as $R \to \infty$.*

Proof. Let $\mathcal{F} \in \mathfrak{R}_+^0$ and consider its extension to Π_+, i.e.,

$$\mathcal{F}(z) = \int_0^\infty f(t)e^{izt}dt$$

where $f \in L_+$. Let $\epsilon > 0$ and consider $g(x) = \begin{cases} 1 & x \in (a,b) \\ 0 & otherwise \end{cases}$: for $b > a \geq 0$

$$\begin{aligned} \int_0^\infty g(x) e^{i(Rcos\theta + iRsen\theta)x} dx &= \int_a^b e^{i(Rcos\theta + iRsen\theta)x} dx \\ &= \frac{e^{iRcos(\theta)b} e^{-Rsen(\theta)b} - e^{iRcos(\theta)a} e^{-Rsen(\theta)a}}{iR(cos\theta + isen\theta)}. \end{aligned}$$

$$\begin{aligned} \left| \int_0^\infty g(x) e^{i(Rcos\theta + iRsen\theta)} dx \right| &\leq \frac{e^{-Rsen(\theta)b}}{R} + \frac{e^{-Rsen(\theta)a}}{R} \\ \text{given that } sin(\theta) \leq 1 \text{ for } \theta \in [0,\pi] &\leq \frac{e^{-Rb}}{R} + \frac{e^{-Ra}}{R} \\ \text{if } R \to \infty &\to 0. \end{aligned}$$

Let g be a simple function, $g = \sum_{i=1}^n c_i \chi_{(a,b)}$. Using additive properties of limits and integrals, we get the same result. Consequently, there exists $N \in \mathbb{N}$ such that if $R > N$,

$$\left| \int_0^\infty g(x) e^{izx} dx \right| < \frac{\epsilon}{2}.$$

Since the simple functions are dense in L [17],

$$\int_{-\infty}^\infty |f(t) - g(t)| \, dt < \frac{\epsilon}{2}.$$

$$\begin{aligned} \int_0^\infty |f(t) - g(t)| \, dt &\leq \int_{-\infty}^\infty |f(t) - g(t)| \, dt \\ &< \frac{\epsilon}{2}. \end{aligned}$$

For $\theta \in [0, \pi]$

$$\begin{aligned} \int_0^\infty |f(t) - g(t)| \, e^{-Rsen(\theta)x} dt &\leq \int_0^\infty |f(t) - g(t)| \, e^{-Rx} dt \\ \text{given } R \text{ big enough} &\leq \int_0^\infty |f(t) - g(t)| \, dt \\ &< \frac{\epsilon}{2} : \end{aligned}$$

$$\begin{aligned} \left| \int_0^\infty f(x) e^{izx} dx \right| &= \left| \int_0^\infty (f-g)(x) e^{izx} dx + \int_0^\infty g(x) e^{izx} dx \right| \\ &\leq \int_0^\infty |f(t) - g(t)| \, e^{-Rsen(\theta)x} dt + \left| \int_0^\infty g(x) e^{izx} dx \right| \\ &< \epsilon \quad . \end{aligned}$$

$\square$

Proposition 2.2.20 *Suppose $\mathcal{F} \in \mathfrak{R}^0_-$ and consider its extension to Π_-. If $z = Re^{i\theta}$ and $\theta \in [\pi, 2\pi]$, then $|\mathcal{F}(z)| \to 0$ uniformly as $R \to \infty$.*

Proof. The demonstration is analogous to the previous proposition. □

Proposition 2.2.21 *Let $\mathcal{F} \in \mathfrak{R}_+$, in other words there exists $f \in L_+$ such that $\mathcal{F} = c + \int_0^\infty f(t)e^{izt}dt$. If we consider the extension of $\mathcal{F}$ to Π_+, thus $\mathcal{F}(z) \leq M$ for all $z \in \Pi_+$ where $M > 0$. In a similar manner, if $\mathcal{F} \in \mathfrak{R}_-$, then $\mathcal{F}$ is bounded on Π_-.*

Proof.

$$\begin{aligned} \left| c + \int_0^\infty f(t)e^{izt}dt \right| &\leq |c| + \left| \int_0^\infty f(t)e^{izt}dt \right| \\ &\leq |c| + \epsilon \\ &= M. \end{aligned}$$

□

Proposition 2.2.22 *Let $\mathcal{F} \in \mathfrak{R}_+$, in other words there exists $f \in L_+$ such that $\mathcal{F} = c + \int_0^\infty f(t)e^{izt}dt$. If we consider the extension of $\mathcal{F}$ to Π_+, $\mathcal{F}$ is continuous on $\Pi_+ \cup \{\infty\}$. In a similar manner, if $\mathcal{F} \in \mathfrak{R}_-$, then $\mathcal{F}$ is continuous on $\Pi_- \cup \{\infty\}$.*

Proof. Let $\mathcal{F} \in \mathfrak{R}_+$, in other words there exists $f \in L_+$ such that $\mathcal{F} = c + \int_0^\infty f(t)e^{izt}dt$. Consider the extension of $\mathcal{F}$ to Π_+. Since it is holomorphic on Π_+, we just need to check it is continuous on ∞. Let $\{z_n\}$ be a succession of points tending to ∞. Let $\epsilon > 0$, by proposition 2.2.19 there exists $R > 0$ and N a natural number such that for all $n > N$ $|\int_0^\infty f(t)e^{izt}dt| < \epsilon$:

$$\begin{aligned} |\mathcal{F}(z_n) - c| &= \left| c + \int_0^\infty f(t)e^{iz_n t}dt - c \right| \\ &= \left| \int_0^\infty f(t)e^{iz_n t}dt \right| \\ &< \epsilon. \end{aligned}$$

Consequently, $\mathcal{F}$ is continuous. □

The following theorem is of great importance; it won't be demonstrated, but reference to it can be found in [16].

Theorem 2.2.23 *Let $G : \mathbb{C} \to \mathbb{C}$ be a holomorphic function in $D \subset \mathbb{C}$ and $\mathcal{F} \in \mathfrak{R}$ such that for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$ $\mathcal{F}(y) \in D$, therefore $G \circ \mathcal{F} \in \mathfrak{R}$.*

Definition 2.2.24 *Let $\alpha : \mathbb{R} \cup \{-\infty, \infty\} \to \mathbb{C}$ be a closed curve oriented in the complex plane with respect to the origin, i.e., $\alpha(\infty) = \alpha(-\infty)$ and $(\forall t\ \alpha(t) \neq 0)$. We define its index as*

$$ind(\alpha) = \frac{1}{2\pi}\, arg(\alpha(t))|_{-\infty}^{\infty}.$$

Remark 2.2.25 *If the curve α admits an extension over Π_+ (Π_-), i.e., is holomorphic in the interior and continuous in the region including the frontier–even the point at infinity–, thus $ind(\alpha)$ is the number of zeros (the number of zeros with negative sign) where every zero is counted as much as its multiplicity.*

Corolary 2.2.26 *Suppose $\mathcal{F} \in \mathfrak{R}$ such that $\lim_{|y|\to\infty} \mathcal{F}(y) = 1$ for all $y \in \mathbb{R}$ $\mathcal{F}(y) \neq 0$ and $ind(\mathcal{F}) = 0$, then for an adequate logarithm branch there exists $l \in L$ such that*

$$ln\,(\mathcal{F}(y)) = \int_{-\infty}^{\infty} l(t)e^{iyt}dt \qquad y \in \mathbb{R}.$$

Proof. With the hypothesis we can define a branch where the logarithm is analytic, and the image of $\mathcal{F}$ stays in it. Using theorem 2.2.23 there exists $l \in L$ such that

$$ln\,(\mathcal{F}(y)) = c + \int_{-\infty}^{\infty} l(t)e^{iyt}dt \qquad y \in \mathbb{R},\ c \in \mathbb{C}.$$

We must prove $c = 0$, first let us show

$$\lim_{|y|\to\infty} ln\,(\mathcal{F}(y)) = 0.$$

Let $\epsilon > 0$. Since $ln[\ ]$ is continuous in 1, for ϵ there exists δ such that for all $|z-1| < \delta$ $|lnz| < \epsilon$. Given that $\mathcal{F}(y) \to 1$ when $|y| \to \infty$, for δ there exists a $Y > 0$ such that for all $|y| > Y$ $|\mathcal{F} - 1| < \delta$. Since $|\mathcal{F} - 1| < \delta$, $|ln\,[\mathcal{F}(y)]\,| < \epsilon$: for all $\epsilon > 0$ there exists $Y > 0$ such that for all $|y| > Y$ $|ln\,[\mathcal{F}(y)]\,| < \epsilon$, in other words $ln\,[\mathcal{F}(y)] \to 0$ as $|y| \to \infty$. Substituting our findings,

$$\begin{aligned} 0 &= ln\,(\mathcal{F}(\infty)) \\ &= c + 0 : \end{aligned}$$

$$ln\,(\mathcal{F}(y)) = \int_{-\infty}^{\infty} l(t)e^{iyt}dt \qquad y \in \mathbb{R},\ c \in \mathbb{C}.$$

$\square$

The following theorems won't be demonstrated, reference to them can be found on [16], even though they are of great importance.

Theorem 2.2.27 *Let $G : \mathbb{C} \to \mathbb{C}$ be a function holomorphic on $D \subset \mathbb{C}$ and $\mathcal{F} \in \mathfrak{R}_+$. Let us consider its extension to Π_+; if for all $z \in \Pi_+ \cup \{-\infty, \infty\}$ $\mathcal{F}(z) \in D$, then $G \circ \mathcal{F} \in \mathfrak{R}_+$.*

Theorem 2.2.28 *Let $G : \mathbb{C} \to \mathbb{C}$ be a function holomorphic on $D \subset \mathbb{C}$ and $\mathcal{F} \in \mathfrak{R}_-$. Let us consider its extension to Π_-; if for all $z \in \Pi_- \cup \{-\infty, \infty\}$ $\mathcal{F}(z) \in D$, then $G \circ \mathcal{F} \in \mathfrak{R}_-$.*

Chapter 3

The factorization problem

As pointed out in the introduction, we are interested in finding the radial distribution function $g_{i,j}(r)$; since $g_{i,j}(r) - 1 = h_{i,j}(r)$, one approach is to solve the system of integral equations

$$h_{i,j}(|r|) = c_{i,j}(|r|) + \sum_{k=1}^{M} \rho_k \int c_{i,k}(|r - r'|)h_{k,j}(|r'|)dr'$$

called Ornstein-Zernike for M species. We have M equations and $2M$ unknowns $(h_{i,j}, c_{i,j})$. We will start by assuming that c and h behave well–so their Fourier transformation exists–, and $M = 1$:

$$h(|r|) = c(|r|) + \rho \int c(|r - r'|)h(|r'|)dr'.$$

After some computations, we can use the Wiener-Hopf factorization to solve it. In this chapter, we will fill the gaps of some theory exposed in references [16, 21]. In the next chapter, we will follow Baxter's steps [1] and see what follows for the general case, furthermore we will complete and correct what he did in reference [2].

3.1 Factorization on the line

Definition 3.1.1 *A factorization of a continuous function,*

$$f : \mathbb{R} \cup \{-\infty, \infty\} \to \mathbb{C},$$

is a representation of the form

$$f(y) = f_+(y)f_-(y) \quad y \in \mathbb{R} \cup \{-\infty, \infty\}$$

where f_+ and f_- are holomorphic functions in the interior and continuous on Π_+ and Π_-, respectively, and $f_+(\pm\infty) = 1 = f_-(\pm\infty)$. We say it's a proper factorization if at least one factor f_+ or f_- is different from zero in their domain (Π_+ and Π_-). Furthermore, it's canonical if both factors are different from zero in its domain. On mathematical notation

1. *its proper* $\iff$ $(\forall\ z \in \Pi_+ \quad f_+(z) \neq 0)$ *o* $(\forall\ z \in \Pi_- \quad f_-(z) \neq 0)$ *and*
2. *its canonical* $\iff$ $(\forall\ z \in \Pi_+ \quad f_+(z) \neq 0)$ *and* $(\forall\ z \in \Pi_- \quad f_-(z) \neq 0)$.

Remark 3.1.2 *We will be interested in studying functions of the form $f(y) = 1 - \hat{g}$, with $g \in L$. Using proposition 2.2.8, $f \to 1$ as $|y| \to \infty$.*

Theorem 3.1.3 *Let $f \in \mathfrak{R}$ be a function such that $\lim_{|y|\to\infty} f(y) = 1$. The function f admits a canonical factorization if and only if*

$$\forall y \in \mathbb{R} \cup \{-\infty, \infty\} \quad f(y) \neq 0 \quad \textit{and} \quad ind(f) = 0.$$

Moreover, if f admits a canonical factorization, then it is the only proper factorization. In addition, the factors f_+ and f_- are elements of $\mathfrak{R}_+$ and $\mathfrak{R}_-$, respectively, and $f_+,\ f_- \to 1$ as $|y| \to \infty$.

Proof. Let $f \in \mathfrak{R}$ such that $\lim_{|y|\to\infty} f(y) = 1$. First, suppose f admits a canonical factorization. Let us assume there exists $y \in \mathbb{R} \cup \{-\infty, \infty\}$ such that $f(y) = 0$: $0 = f(y) = f_+(y)f_-(y)$. Wherewith, $f_+(y) = 0$ or $f_-(y) = 0$. But that is a contradiction, since the factorization was canonical. Then, for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$ $f(y) \neq 0$. Given that $arg(z_1 z_2) = arg(z_1) + arg(z_2)$, $ind(f) = ind(f_+) + ind(f_-)$. Considering that f_+ and f_- have no zeros in Π_+ and Π_-, respectively, and using remark 2.2.25,

$$ind(f) = 0 + 0 = 0.$$

Suppose

$$\forall y \in \mathbb{R} \cup \{-\infty, \infty\} \quad f(y) \neq 0 \quad y \quad ind(f) = 0.$$

Using corollary 2.2.26 there exists $l \in L$ such that for all $y \in \mathbb{R}$

$$f(y) = exp\left(\int_{-\infty}^{\infty} l(t)e^{iyt}dt\right).$$

Let us define the following functions:

$$l_+(t) = \begin{cases} l(t) & t \geq 0 \\ 0 & t < 0 \end{cases} \quad \textit{and} \quad l_-(t) = \begin{cases} 0 & t > 0 \\ l(t) & t \leq 0 \end{cases}.$$

In view of

$$\int_0^\infty |l(t)|dt \leq \int_{-\infty}^\infty |l(t)|dt < \infty \quad and \quad \int_{-\infty}^0 |l(t)|dt \leq \int_{-\infty}^\infty |l(t)|dt < \infty \quad l_+, l_- \in L,$$

by inspection $l_+ \in L_+$ and $l_- \in L_-$:

$$\int_0^\infty l_+(t)e^{iyt}dt \in \mathfrak{R}_+ \quad and \quad \int_{-\infty}^0 l_+(t)e^{iyt}dt \in \mathfrak{R}_-.$$

For all $y \in \mathbb{R}$ we define:

$$f_+(y) = exp\left(\int_0^\infty l_+(t)e^{iyt}dt\right) \quad and \quad f_-(y) = exp\left(\int_{-\infty}^0 l_-(t)e^{iyt}dt\right).$$

Using proposition 2.2.18 we can extend f_+ to Π_+ and f_- to Π_-. Let us consider that

1. $$\int_0^\infty l_+(t)e^{iyt}dt \in \mathfrak{R}_+ \quad and \quad \int_{-\infty}^0 l_+(t)e^{iyt}dt \in \mathfrak{R}_-$$
   can be extended to Π_+ and Π_-, respectively, and
2. $exp(\ )$ is holomorphic in $\mathbb{C}$.

Therefore, by theorems 2.2.27 and 2.2.28: $f_+ \in \mathfrak{R}_+$ and $f_- \in \mathfrak{R}_-$. Furthermore,

$$\begin{aligned} f_+f_- &= exp\left(\int_0^\infty l_+(t)e^{iyt}dt\right) exp\left(\int_{-\infty}^0 l_-(t)e^{iyt}dt\right) \\ &= exp\left(\int_0^\infty l_+(t)e^{iyt}dt + \int_{-\infty}^0 l_-(t)e^{iyt}dt\right) \\ &= exp\left(\int_{-\infty}^\infty l(t)e^{iyt}dt\right) \\ &= f. \end{aligned}$$

Let us prove $f_+,\ f_- \to 1$ as $|y| \to \infty$. We do it for f_+, the proof for f_- is analogous. Seeing that $l_+ \in L_+$ and $l_- \in L_-$, $l_+, l_- \in L$; using proposition 2.2.8 $\hat{l}_+(y),\ \hat{l}_-(y) \to 0$ as $|y| \to \infty$. Since $exp(\ )$ is continuous, using an argument of continuity, $f_+(y) \to 1$ if $|y| \to \infty$.

Let g_+ and g_- be a proper factorization of f; without loss of generality suppose $g_+(z) \neq 0$–definition of proper factorization–on Π_+. We define the function G as

$$G = \frac{f_+}{g_+} = \frac{g_-}{f_-}.$$

For this reason G is analytic in $\mathbb{C}$. Since G is continuous and $\mathbb{C} \cup \{\infty\}$ is compact, the image of G is bounded; using Liouville's theorem G is constant. By theorems 2.2.19 and 2.2.20,

1. if $z = Re^{i\theta}$ y $\theta \in [0, \pi]$, then $|f_+(z)| \to 1$ when $R \to \infty$ and $|g_+(z)| \to 1$ when $R \to \infty$, and

2. if $z = Re^{i\theta}$ y $\theta \in [\pi, 2\pi]$, then $|f_-(z)| \to 1$ when $R \to \infty$ and $|g_-(z)| \to 1$ when $R \to \infty$.

For Π_+ we use $\frac{f_+}{g_+}$ and for Π_-, $\frac{f_-}{g_-}$. By taking the limit when $R \to \infty$ $|G(z)| \to 1$, $G = 1$: $f_+ = g_+$ and $f_- = g_-$. □

Corolary 3.1.4 *Let $f \in \mathfrak{R}$; suppose $\lim_{|y| \to \infty} f(y) = 1$, in other words there exists $g \in L$ such that $f(y) = 1 + \int_{-\infty}^{\infty} e^{iyt} g(t) dt$. If f admits a canonical factorization and g is even, hence $\overline{f_+}(z) = f_-(z) = f_+(-z)$ and $\overline{f_-}(z) = f_+(z) = f_-(-z)$.*

Proof. Let $f \in \mathfrak{R}$ and suppose $\lim_{|y| \to \infty} f(y) = 1$: there exists $g \in L$ such that $f(y) = 1 + \int_{-\infty}^{\infty} e^{iyt} g(t) dt$. Assume g is even and f admits a canonical factorization, $f = f_+ f_-$. Since $f_+ \in \mathfrak{R}_+$, $f_- \in \mathfrak{R}_-$, $f_+(\infty) = 1$, and $f_-(\infty) = 1$, therefore

$$
\begin{aligned}
f_+(z) &= 1 + \int_0^{\infty} e^{izt} g_+(t) dt \quad z \in \Pi_+ \\
f_-(z) &= 1 + \int_{-\infty}^{0} e^{izt} g_-(t) dt \quad z \in \Pi_-.
\end{aligned}
$$

$$
\begin{aligned}
\overline{f_+}(y) &= \overline{f_+(\overline{y})} \\
&= \overline{f_+(y)} \\
&= \overline{1 + \int_0^{\infty} e^{iyt} g_+(t) dt} \\
&= 1 + \int_0^{\infty} e^{-iyt} \overline{g_+(t)} dt \\
&= 1 + \int_0^{\infty} e^{-iyt} \overline{g_+}(t) dt \\
&= 1 + \int_{-\infty}^{0} e^{iys} \overline{g_+}(-s) ds.
\end{aligned}
$$

First, let us prove that $\overline{g_+}(-s) \in L_-$.

$$\begin{aligned}\int_{-\infty}^{0} |\overline{g_+}(-s)|ds &= \int_{0}^{\infty} |\overline{g_+}(x)|dx \\ &= \int_{0}^{\infty} |\overline{g_+(\overline{x})}|dx \\ &= \int_{0}^{\infty} |\overline{g_+(x)}|dx \\ &= \int_{0}^{\infty} |g_+(x)|dx \\ &< \infty.\end{aligned}$$

Wherefore, $\overline{g_+}(-s) \in L_-$: $\overline{f_+}(y)$ can be extended to an analytical function in the interior and continuous on Π_-, furthermore $\overline{f_+}(\pm\infty) = 1$. Let us prove that $\overline{f_+}(z) \neq 0$ for all z in Π_-. Let $z \in \Pi_-$. Suppose $\overline{f_+}(z) = 0$, therefore

$$\begin{aligned}0 &= \overline{f_+}(z) \\ &= \overline{f_+(\overline{z})}.\end{aligned}$$

Taking the conjugate from both sides,

$$0 = f_+(\overline{z}).$$

Which is a contradiction, since $\overline{z} \in \Pi_+$ and f_+ can't be zero on Π_+: $\overline{f_+}(z) \neq 0$ in Π_-. It is analogous to prove that $\overline{f_-}(z) \neq 0$ on Π_+, is analytic on the interior and continuous on Π_+, and $\overline{f_-}(\pm\infty) = 1$. Considering that f has a canonical factorization, there is only one proper factorization. It only remains to be proved that $f = \overline{f_-}\ \overline{f_+}$ on the real line to obtain, $\overline{f_+}(z) = f_-(z)$ and $\overline{f_-}(z) = f_+(z)$.

$$\begin{aligned}f(y) &= 1 + \int_{-\infty}^{\infty} e^{iyt} g(t)dt \\ &= 1 + \int_{-\infty}^{\infty} cos(yt)g(t)dt + i\int_{-\infty}^{\infty} sen(yt)g(t)dt \\ sen(yt)g(t) \text{ is odd} \quad &= 1 + \int_{-\infty}^{\infty} cos(yt)g(t)dt,\end{aligned}$$

in other words, $f(y)$ is a real number.

$$\begin{aligned}& f(y) = \overline{f(y)} \\ \iff\ & f(y) = \overline{f_-(y)f_+(y)} \\ \iff\ & f(y) = \overline{f_-(y)}\ \overline{f_+(y)} \\ \iff\ & f(y) = \overline{f_-(\overline{y})}\ \overline{f_+(\overline{y})} \\ \iff\ & f(y) = \overline{f_-}(y)\ \overline{f_+}(y).\end{aligned}$$

Hence, $\overline{f_-}$ and $\overline{f_+}$ is a proper factorization of f. Using the uniqueness, $\overline{f_+}(z) = f_-(z)$ and $\overline{f_-}(z) = f_+(z)$.

Given that g is even, f is even:

$$\begin{aligned} f(y) &= f(-y) \\ &= f_+(-y)f_-(-y). \end{aligned}$$

Wherefore $f_+(-y)$ and $f_-(-y)$ are candidates for a proper factorization of f. Since f_+ and f_- are holomorphic functions in the interior and continuous on Π_+ and Π_-, respectively, $f_-(-z)$ and $f_+(-z)$ are holomorphic functions in the interior and continuous on Π_+ and Π_-, respectively. Clearly, $f_+(\mp\infty) = 1 = f_-(\mp\infty) = 1$ given that $f_+(\pm\infty) = 1 = f_-(\pm\infty) = 1$. Moreover, $f_+(z) \neq 0$ for all $z \in \Pi_+$, hence $f_+(-z) \neq 0$ for all $z \in \Pi_-$: $f_+(-z)$ and $f_-(-z)$ is a proper factorization of f. Given that f admits a canonical factorization, using the uniqueness, $f_+(z) = f_-(-z)$ and $f_-(z) = f_+(-z)$. $\square$

Proposition 3.1.5 *Let $F \in \mathfrak{R}^0_+$ or $F \in \mathfrak{R}^0_-$; if we consider its extension to Π_+ or Π_-, respectively, then $|F(k)| \to 0$ uniformly as $|k_1| \to \infty$.*

Proof. Let $F \in \mathfrak{R}^0_+$ be a function, and $\epsilon > 0$.

$$\begin{aligned} F(k) &= \int_0^\infty f(x)e^{i(k_1+ik_2)x}dx \\ &= \int_0^\infty f(x)e^{ikx}dx \\ &= \int_0^\infty f\left(t+\frac{\pi}{k_1}\right)e^{ik\left(t+\frac{\pi}{k_1}\right)}dt \\ &= \frac{1}{\sqrt{2\pi}}\int_0^\infty f\left(x+\frac{\pi}{k_1}\right)e^{i(k_1+ik_2)\left(x+\frac{\pi}{k_1}\right)}dx \\ &= \int_0^\infty f\left(x+\frac{\pi}{k_1}\right)e^{i(k_1+ik_2)x}e^{i\pi}e^{-\frac{k_2\pi}{k_1}}dx \\ &= -\int_0^\infty f\left(x+\frac{\pi}{k_1}\right)e^{i(k_1+ik_2)x}e^{-\frac{k_2\pi}{k_1}}dx : \end{aligned}$$

$$2F(k) = \int_0^\infty \left[f(x) - f\left(x+\frac{\pi}{k_1}\right)e^{-\frac{k_2\pi}{k_1}}\right]e^{ik_1}e^{-k_2x}dx.$$

$$\begin{aligned}
|F(k)| &= \left|\frac{1}{2}\int_0^\infty \left[f(x) - f\left(x+\frac{\pi}{k_1}\right)e^{-\frac{k_2\pi}{k_1}}\right]e^{ik_1}e^{-k_2x}dx\right| \\
&\leq \frac{1}{2}\int_0^\infty \left|\left[f(x) - f\left(x+\frac{\pi}{k_1}\right)e^{-\frac{k_2\pi}{k_1}}\right]\right|e^{-k_2x}dx \\
&= \frac{1}{2}\int_0^\infty \left|\left[f(x) - f\left(x+\frac{\pi}{k_1}\right)e^{-\frac{k_2\pi}{k_1}} + f(x)e^{-\frac{k_2\pi}{k_1}} - f(x)e^{-\frac{k_2\pi}{k_1}}\right]\right|e^{-k_2x}dx \\
&\leq e^{-\frac{k_2\pi}{k_1}}\int_0^\infty \left|f(x) - f\left(x+\frac{\pi}{k_1}\right)\right|e^{-k_2x}dx + \left|1-e^{-\frac{k_2\pi}{k_1}}\right|\int_0^\infty |f(x)|e^{-k_2x}dx.
\end{aligned}$$

By inspection the first term can be made smaller than $\frac{\epsilon}{2\int_0^\infty \left|f(x)-f\left(x+\frac{\pi}{k_1}\right)\right|e^{-k_2x}dx}$ for some $K > |k_1|$; since $exp(\ )$ is continuous in 0, there exists $\delta > 0$ such that for all $|t| < \delta$ $|e^t - 1| < \frac{\epsilon}{2\int_0^\infty |f(x)|e^{-k_2x}dx}$. Therefore, we can choose K sufficiently big such that what we described happens,

$$\begin{aligned}
|F(k)| &< \frac{\epsilon}{2} + \frac{\epsilon}{2} \\
&= \epsilon.
\end{aligned}$$

In other words, $|F(k)| \to 0$ uniformly when $|k_1| \to \infty$. $\square$

Remark 3.1.6 *Given that $f_+ \in \mathfrak{R}_+$, $f_- \in \mathfrak{R}_-$, $f_+(\infty) = 1$, and $f_-(\infty) = 1$:*

$$\begin{aligned}
f_+(z) &= 1 + \int_0^\infty e^{izt}g_+(t)dt \quad z \in \Pi_+ \\
f_-(z) &= 1 + \int_{-\infty}^0 e^{izt}g_-(t)dt \quad z \in \Pi_-.
\end{aligned}$$

Furthermore,

$$\begin{aligned}
f_-(z) &= 1 + \int_{-\infty}^0 e^{izt}g_-(t)dt \quad z \in \Pi_- \\
&= 1 - \int_\infty^0 e^{-izx}g_-(-x)dx \quad z \in \Pi_- \\
&= 1 + \int_0^\infty e^{-izx}g_\tau(x)dx \quad z \in \Pi_-
\end{aligned}$$

where $g_\tau(x) = g_-(-x)$. Hence, for all $x < 0$ $g_\tau = 0$ and $g_\tau \in L_+$.

3.1.1 Entire functions of exponential type

Let $g \in L$ such that $g(x) = 0$ for all $x \notin [a_-, a_+]$. We want to know the canonical factorization of functions $f \in \mathfrak{R}$ such that

$$f(y) = 1 + \lambda\int_{a_-}^{a_+} g(t)e^{iyt}dt.$$

Remark 3.1.7 *1. The function f is entire.*

2. If $0 < a_- < a_+$: the problem degenerates to $f = fh$ where $h = 1$. Without loss of generality, let us suppose $a_- < 0 < a_+$.

Proposition 3.1.8 *Let $a_- < 0 < a_+$ and $f(y) = 1 + \lambda \int_{a_-}^{a_+} g(t)e^{iyt}dt$ where $g \in L$. The following statements are true.*

1. *There exists $C > 0$ such that $\forall z \in \Pi_+$ $|f(z)| \leq Ce^{-a_-|Im(z)|}$.*
2. *There exists $C > 0$ such that $\forall z \in \Pi_-$ $|f(z)| \leq Ce^{a_+|Im(z)|}$.*
3. *There exists $C > 0$ such that $\forall z \in \mathbb{C}$ $|f(z)| \leq Ce^{a|Im(z)|}$*

where $a = max(a_+, -a_-)$.

Proof. Let $a = max(a_+, -a_-)$.

$$|f(z)| \;\leq\; 1 + |\lambda| \int_{a_-}^{a_+} |g(t)|e^{-z_2 t}dt.$$

If $z_2 \geq 0$

$$\begin{array}{rl} & a_- \leq t \leq a_+ \\ \Longleftrightarrow & z_2 a_- \leq z_2 t \leq z_2 a_+ \\ \Longleftrightarrow & -z_2 a_- \geq -z_2 t \geq -z_2 a_+ \\ \Longleftrightarrow & e^{-a_-|Im(z)|} = e^{-z_2 a_-} \geq e^{-z_2 t}, \end{array}$$

therefore

$$\begin{aligned} |f(z)| &\leq 1 + |\lambda| \int_{a_-}^{a_+} |g(t)|e^{-a_-|Im(z)|}dt \\ &= Ce^{-a_-|Im(z)|} \leq Ce^{a|Im(z)|}. \end{aligned}$$

If $z_2 < 0$, $-z_2 > 0$:

$$\begin{array}{rl} & a_- \leq t \leq a_+ \\ \Longleftrightarrow & -z_2 a_- \leq -z_2 t \leq -z_2 a_+ \\ \Longleftrightarrow & e^{-z_2 t} \leq e^{-z_2 a_+} = e^{a_+|Im(z)|}. \end{array}$$

Thus,

$$\begin{aligned} |f(z)| &\leq 1 + |\lambda| \int_{a_-}^{a_+} |g(t)|e^{a_+|Im(z)|}dt \\ &= Ce^{a_+|Im(z)|} \leq Ce^{a|Im(z)|}. \end{aligned}$$

□

Theorem 3.1.9 *Let $a_- < 0 < a_+$, $g \in L$ such that $g(x) = 0$ for all $x \notin [a_-, a_+]$, and*

$$f(y) = 1 + \lambda \int_{a_-}^{a_+} g(t) e^{iyt} dt \in \mathfrak{R}.$$

If

$$\forall y \in \mathbb{R} \cup \{-\infty, \infty\} \quad f(y) \neq 0 \quad \text{and} \quad ind(f) = 0,$$

then there exists $f_+ \in \mathfrak{R}_+$ and $f_- \in \mathfrak{R}_-$ such that

1. *$f_\pm \to 1$ as $|y| \to \infty$,*
2. *$f(y) = f_+(y) f_-(y)$ for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$–in fact $f(z) = f_+(z) f_-(z)$ for all $z \in \mathbb{C}^-$,*
3. *the extensions of f_+ and f_- are entire functions,*
4. *$(\forall\ z \in \Pi_+ \quad f_+(z) \neq 0)$ and $(\forall\ z \in \Pi_- \quad f_-(z) \neq 0)$, and*
5. *is the only proper factorization.*

Furthermore,

$$f_+(z) = 1 + \int_0^{a_+} e^{izt} g_+(t) dt, \quad \text{and} \quad f_-(z) = 1 + \int_{a_-}^0 e^{izt} g_-(t) dt$$

where $g_+ \in L_+$, $g_- \in L_-$, $g_+(t) = 0$ for all $t \geq a_+$, and $g_-(t) = 0$ for all $t \leq a_-$.

Proof. Let $a_- < 0 < a_+$, $g \in L$ such that $g(x) = 0$ for all $x \notin [a_-, a_+]$, and

$$f(y) = 1 + \lambda \int_{a_-}^{a_+} g(t) e^{iyt} dt \in \mathfrak{R}.$$

Suppose that for all

$$y \in \mathbb{R} \cup \{-\infty, \infty\} \quad f(y) \neq 0, \quad \text{and} \quad ind(f) = 0.$$

Using theorem 3.1.3 there exist $f_+ \in \mathfrak{R}_+$, and $f_- \in \mathfrak{R}_-$ such that

1. $f_\pm \to 1$ if $|y| \to \infty$,
2. $f(y) = f_+(y) f_-(y)$ for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$,
3. the extensions of f_+ and f_- are holomorphic and continuous on Π_+ and Π_-, respectively,
4. $(\forall\ z \in \Pi_+ \quad f_+(z) \neq 0)$ and $(\forall\ z \in \Pi_- \quad f_-(z) \neq 0)$, and

5. it is the only proper factorization.

To be demonstrated:

1. the extensions of f_+ and f_- are entire,
2. $f(z) = f_+(z)f_-(z)$ for all $z \in \mathbb{C}$,
3. f and f_+ have zeros in the interior of Π_+,
4. f and f_- have zeros in the interior of Π_-, and
5. $$f_+(z) = 1 + \int_0^{a_+} e^{izt}\gamma_+(t)dt \quad y \quad f_-(z) = 1 + \int_{a_-}^{0} e^{izt}\gamma_-(t)dt$$
   where $\gamma_+ \in L_+$, $\gamma_- \in L_-$, $\gamma_+(t) = 0$ for all $t > a_+$ and $\gamma_-(t) = 0$ for all $t < a_-$.

Let us define

$$g_+(z) = \begin{cases} f_+(z) & 0 \leq Im(z) < \infty \\ ff_-^{-1}(z) & -\infty < Im(z) < 0 \end{cases}$$

and

$$g_-(z) = \begin{cases} ff_+^{-1}(z) & 0 < Im(z) < \infty \\ f_-(z) & -\infty < Im(z) \leq 0. \end{cases}$$

f_+ is continuous on Π_+, ff_-^{-1} is continuous on Π_-, and on the intersection–the real line–they are equal: using the pasting lemma[1] g_+ is continuous on $\mathbb{C}$; similarly, g_- is continuous on $\mathbb{C}$. Given that f_+ is analytical on the interior of Π_+ and ff_-^{-1} is analytical on the interior of Π_-, g_+ is analytical on $\mathbb{C} - \{z \in \mathbb{C} \mid Im(z) = 0\}$; the analyticity of g_+ in $\mathbb{C}$ follows from using a similar argument used in theorem's 2.1.4 demonstration. Analogously, g_- is analytical on $\mathbb{C}$: point 1 is proven.

In view of the fact that g_+ has the same characteristics of f_+ on Π_+ and g_- the same as f_- on Π_-, it is a proper factorization of f in the real line, where we have used the uniqueness, $f_+ = g_+$ and $f_- = g_-$. Therefore, f_+ and f_- are entire functions. Because of how we defined g_- and g_+: $f = f_+f_-$ in all $\mathbb{C}$, which proves point 2.

[1]Let X , Y be both closed (or both open) subsets of a topological space A such that $A = X \cup Y$, and let B also be a topological space. If $f : A \to B$ is continuous when restricted to both X and Y, then f is continuous.

Next, let us prove that f_+ has at least one zero–in fact, there is an infinity of zeros. Suppose f_+ doesn't have a zero for $Im(z) < 0$, hence f_+ has no zeros on $\mathbb{C}$. Given that f_+ is an entire function, there exists an entire function g such that $f_+(z) = e^{g(z)}$ $\left(\text{consider the following function } g'(z) = \frac{f'_+(z)}{f_+(z)}\right)$. It follows from theorem 2.2.28, that $f_-^{-1} \in \mathfrak{R}_-$; by proposition 2.2.21 there exists M_+ and M_- such that

$$\forall z \in \Pi_+ \quad |f_+(z)| \leq M_+ \quad and \quad \forall z \in \Pi_- \quad |f_-^{-1}(z)| \leq M_-.$$

Furthermore, by proposition 3.1.8 there exists $C > 0$ such that $\forall z \in \Pi_-$ $|f(z)| \leq Ce^{a_+|Im(z)|}$. Since $f_+ = ff_-^{-1}$, for all $z \in \Pi_-$ $|f_+(z)| \leq M_-Ce^{a_+|Im(z)|} = Ae^{a_+|Im(z)|}$. Moreover, M_+ or A are as big as we want, so

$$\forall z \in \Pi_- \quad |f_+(z)| \leq M_+e^{a_+|Im(z)|}.$$

Because $f_+ \neq 0$, then $lnf_+ = g$ is analytical and $|f_+(z)| = e^{Re(g(z))}$. For this reason, $ln|f_+(z)| = Re(g(z))$:

$$\begin{aligned} Re(g(z)) &\leq ln(M_+) \leq ln(M_+) + a_+|Im(z)| \quad \forall z \in \Pi_+ \quad and \\ Re(g(z)) &\leq ln(M_+) + a_+|Im(z)| \quad \forall z \in \Pi_-. \end{aligned}$$

Wherefore, for all $z \in \mathbb{C}$

$$Re(g(z)) \leq ln(M_+) + a_+|Im(z)| \leq ln(M_+) + a_+|z|.$$

Using theorem 2.1.5 for $R < 2R$,

$$\begin{aligned} max_{|z|=R}|g(z)| &\leq \frac{2R}{2R-R} sup_{|z|\leq 2R} Re(g(z)) + \frac{3R}{2R-R}|g(0)| \\ &= 2sup_{|z|\leq 2R} Re(g(z)) + 3|g(0)| \\ &\leq 2ln(M_+) + 2a_+|z| + 3|g(0)| \\ &= 2a_+|z| + M_1 \quad M_1 > 0 : \end{aligned}$$

for $|z| < R$

$$|g(z)| < 2a_+|z| + M_1.$$

Let us observe the last statement is valid for all $R > 0$, therefore for all $z \in \mathbb{C}$

$$|g(z)| < 2a_+|z| + M_1.$$

Thus, $g(z) = cz + b$ where $c, b \in \mathbb{C}$.

$$g(z) = c_1z_1 + ic_1z_2 + ic_2z_1 - c_2z_2 + b_1 + ib_2.$$

$$Re(g(z)) = c_1 z_1 + b_1 - c_2 z_2.$$

Let $z_2 = 0$.

$$Re(g(z)) = c_1 z_1 + b_1 \leq ln(M_+).$$

Suppose $c_1 < 0$. When $z_1 \to -\infty$, $Re(g(z)) \to \infty$ and it's not bounded, which is a contradiction: $c_1 \geq 0$. Let $c_1 > 0$. When $z_1 \to \infty$, $Re(g(z)) \to \infty$ and it's not bounded, again it's a contradiction: $c_1 \leq 0$. Consequently $c_1 = 0$. Let $z = ix$ for $x \geq 0$, hence

$$Re(g(z)) = b_1 - c_2 x \leq ln(M_+).$$

Therefore, $c_2 \geq 0$, in other words $c_2 = a$ with $a \geq 0$. If $z = -ix$ with $x > 0$:

$$\begin{aligned} Re(g(z)) &= b_1 + ax \\ &\leq ln(M_+) + a_+|x| \\ &= ln(M_+) + a_+ x. \end{aligned}$$

If $A = b_1 - ln(M_+)$:

$$\frac{A}{x} + a \leq a_+.$$

Taking the limit when $x \to \infty$: $a \leq a_+$, thus

$$f_+(z) = e^b e^{iaz} = Ce^{iaz} \quad 0 \leq a \leq a_+.$$

Seeing that $|f_+(x)| \to 1$ when $|x| \to \infty$, we obtain $C = 1$.

$$\begin{aligned} |f_+(z)| &= |e^{iaRcos(\theta)} e^{-aRsen(\theta)}| \\ &= |e^{-aRsen(\theta)}| \\ &\leq e^{-aR}. \end{aligned}$$

Taking the limit $R \to \infty$ given that $\theta \in [0, \pi]$ and $|f_+(Re^{i\theta})| \to 1$, implies $1 \leq 0$. Consequently, $a = 0$ and $f_+(z) = 1$, where we have used the following result found in [16],

$$\limsup_{r \to \infty} \frac{ln|f(-ir)|}{r} = \limsup_{r \to \infty} \frac{ln|f_+(-ir)|}{r} = a_+.$$

Since $f_+(z) = 1$, $a_+ = 1$, but that is a contradiction given that a_+ is arbitrary. Consequently, f_+ has at least one zero in the interior of Π_-. Therefore, f has it too. In a similar way we obtain that f_- has at least one zero in the interior of Π_+, thus f has it too: we have proved point 3. Let α be in the interior of Π_- and a zero of f_+. We define the following function

$$F(z) = \frac{f_+(z)}{z-\alpha} e^{-i\frac{a_+}{2}z}.$$

Since $f_+ e^{-i\frac{a_+}{2}z}$ is entire and the singularity is removable in α, F is an entire function. Consider a ball with radius R containing α, $B_R(\alpha)$, such that it is contained in the interior of Π_-. Inside the ball $F(z)$ is bounded, let us assume by $M_1 > 0$. Outside of the ball and in the interior of Π_-

$$|f_+(z)| \leq M_+ e^{a_+|Im(z)|}, \quad \frac{1}{|z-\alpha|} \leq \frac{1}{|\alpha_0 - \alpha|} = M_2, \quad \textit{and}$$

$$\left| e^{-i\frac{a_+}{2}z} \right| = e^{z_2 \frac{a_+}{2}} = e^{-|Im(z)|\frac{a_+}{2}}$$

where $\alpha_0 \in B_R(\alpha)$. Hence,

$$\begin{aligned} |F(z)| &\leq M_+ M_2 e^{a_+|Im(z)|} e^{-|Im(z)|\frac{a_+}{2}} \\ &= N e^{|Im(z)|\frac{a_+}{2}}. \end{aligned}$$

On Π_+

$$|f_+(z)| \leq M_+, \quad \frac{1}{|z-\alpha|} \leq \frac{1}{|\alpha_0 - \alpha|} = M_2, \quad \textit{and} \quad \left| e^{-i\frac{a_+}{2}z} \right| = e^{|Im(z)|\frac{a_+}{2}}.$$

Therefore,

$$\begin{aligned} |F(z)| &\leq M_+ M_2 e^{|Im(z)|\frac{a_+}{2}} \\ &= N e^{|Im(z)|\frac{a_+}{2}}. \end{aligned}$$

Consequently, for all $z \in \mathbb{C}$

$$|F(z)| \leq N e^{|Im(z)|\frac{a_+}{2}}.$$

For $t \in \mathbb{R}$

$$|F(t)|^2 = \frac{|f_+(t)|^2}{|t-\alpha|^2} :$$

$$\begin{aligned}
\int_{-\infty}^{\infty}|F(t)|^2dt &= \int_{-\infty}^{\infty}\frac{|f_+(t)|^2}{|t-\alpha|^2}dt \\
&= \int_{-A}^{A}\frac{|f_+(t)|^2}{|t-\alpha|^2}dt+\int_{-\infty}^{-A}\frac{1}{|t-\alpha|^2}dt+\int_{A}^{\infty}\frac{1}{|t-\alpha|^2}dt \\
&= \int_{-A}^{A}\frac{|f_+(t)|^2}{|t-\alpha|^2}dt+\int_{-\infty}^{-A}\frac{1}{(t-\alpha_1)^2+\alpha_2^2}dt+\int_{A}^{\infty}\frac{1}{(t-\alpha_1)^2+\alpha_2^2}dt \\
&= B+\int_{-\infty}^{-A-\alpha_1}\frac{1}{x^2+\alpha_2^2}dt+\int_{A-\alpha_1}^{\infty}\frac{1}{x^2+\alpha_2^2}dt \\
&= B+\frac{1}{\alpha_2}\left[arctan\left(\frac{-A-\alpha_1}{\alpha_2}\right)-\left(-\frac{\pi}{2}\right)\right]+\frac{1}{\alpha_2}\left[\frac{\pi}{2}-arctan\left(\frac{A-\alpha_1}{\alpha_2}\right)\right] \\
&< \infty.
\end{aligned}$$

Using theorem 2.1.6 there exists $h \in L_2\left(-\frac{a_+}{2}, \frac{a_+}{2}\right)$ such that

$$F(z)=\int_{-\frac{a_+}{2}}^{\frac{a_+}{2}} e^{izt}h(t)dt.$$

Substituting $F(z)$ in its definition,

$$\begin{aligned}
\frac{f_+(z)}{z-\alpha} &= \int_{-\frac{a_+}{2}}^{\frac{a_+}{2}} e^{izt}e^{i\frac{a_+}{2}z}h(t)dt \\
&= \int_{-\frac{a_+}{2}}^{\frac{a_+}{2}} e^{iz\left(t+\frac{a_+}{2}\right)}h(t)dt \\
&= \int_{0}^{a_+} e^{izx}h\left(x-\frac{a_+}{2}\right)dx.
\end{aligned}$$

On the other hand, we know that

$$\begin{aligned}
f_+(z) &= 1+\int_0^{\infty} e^{izt}\gamma_+(t)dt \\
&= \int_{-\infty}^{\infty} e^{izt}\left(\delta+\gamma_+\right)(t)dt.
\end{aligned}$$

Since $Im(\alpha)<0$,

$$\frac{1}{z-\alpha}=-i\int_0^{\infty} e^{-i\alpha t}e^{izt}dt.$$

Let g be a function such that $g(t) = -ie^{-i\alpha t}$ for all $t \geq 0$ and $g(t) = 0$ for all $t < 0$, thus

$$\begin{aligned}
\frac{f_+(z)}{z-\alpha} &= \int_{-\infty}^{\infty} e^{izt} \int_{-\infty}^{\infty} g(s)\,(\delta + \gamma_+)\,(t-s)ds \\
&= \int_{-\infty}^{\infty} e^{izt} \left(g(t) + \int_{-\infty}^{\infty} g(s)\gamma_+(t-s)ds \right) dt \\
&= \int_{-\infty}^{\infty} e^{izt} g(t)dt + \int_{-\infty}^{\infty} e^{izt} \int_{-\infty}^{\infty} g(s)\gamma_+(t-s)dsdt \\
&= \int_{0}^{\infty} e^{izt} g(t)dt + \int_{-\infty}^{\infty} e^{izt} \int_{0}^{t} g(s)\gamma_+(t-s)dsdt \\
&= \int_{0}^{\infty} e^{izt} g(t)dt + \int_{0}^{\infty} e^{izt} \int_{0}^{t} g(s)\gamma_+(t-s)dsdt \\
&= \int_{0}^{\infty} e^{izt} \left(g(t) + \int_{0}^{t} g(s)\gamma_+(t-s)ds \right) dt \\
&= \int_{0}^{\infty} e^{izt} \left(g(t) - \int_{t}^{0} g(t-x)\gamma_+(x)dx \right) dt \\
&= \int_{0}^{\infty} e^{izt} \left(g(t) + \int_{0}^{t} g(t-s)\gamma_+(s)ds \right) dt \\
&= \int_{0}^{\infty} e^{izt} g_\alpha(t)dt
\end{aligned}$$

where $g_\alpha(t) = g(t) + \int_0^t g(t-s)\gamma_+(s)ds = -ie^{-i\alpha t} - i\int_0^t e^{-i\alpha(t-s)}\gamma_+(s)ds$.

$$g_\alpha(t) = -ie^{-i\alpha t} - ie^{-i\alpha t}\int_0^t e^{i\alpha s}\gamma_+(s)ds:$$

$$\begin{aligned}
g'_\alpha(t) &= \alpha e^{-i\alpha t} + \alpha e^{-i\alpha t}\int_0^t e^{i\alpha s}\gamma_+(s)ds - ie^{-i\alpha t}e^{i\alpha t}\gamma_+(t) \\
&= \alpha e^{-i\alpha t} + \alpha e^{-i\alpha t}\int_0^t e^{i\alpha s}\gamma_+(s)ds - i\gamma_+(t).
\end{aligned}$$

Wherefore,

$$g'_\alpha(t) + i\alpha g_\alpha(t) = -i\gamma_+(t).$$

Given that

$$\int_0^\infty e^{izt} g_\alpha(t)dt = \frac{f_+(z)}{z-\alpha} = \int_0^{a_+} e^{izx} h\left(x - \frac{a_+}{2}\right) dx,$$

if we define $h\left(x - \frac{a_+}{2}\right) = 0$ outside of $[0, a_+)$:

$$\int_0^\infty e^{izt}\left(g_\alpha(t) - h\left(t - \frac{a_+}{2}\right)\right) dt = 0.$$

Therefore, it is integrable. Using the theorem 2.2.7 $g_\alpha(t) = h\left(t - \frac{a_+}{2}\right)$ except in a zero measure set and $g_\alpha(t) = 0$ outside of $[0, a_+)$ (because of the continuity of the zero function). Using the last assertion and that $g'_\alpha(t) + i\alpha g_\alpha(t) = -i\gamma_+(t)$, for all $t \notin [0, a_+)$

$$\gamma_+(t) = 0,$$

and

$$f_+(z) = 1 + \int_0^{a_+} e^{izt}\gamma_+(t)dt.$$

Similarly,

$$f_-(z) = 1 + \int_{a_-}^{0} e^{izt}\gamma_-(t)dt$$

where $\gamma_-(t) = 0$ for all $t \leq a_-$. □

Corolary 3.1.10 *Let $0 < a_+$, $g \in L$ such that $g(x) = 0$ for all $x \notin [-a_+, a_+]$ and*

$$f(y) = 1 + \lambda \int_{-a_+}^{a_+} g(t)e^{iyt}dt \in \mathfrak{R}.$$

If

$$\forall y \in \mathbb{R} \cup \{-\infty, \infty\} \quad f(y) \neq 0, \quad ind(f) = 0 \quad \textit{and} \quad f \textit{ is } \textbf{even},$$

then there exists $f_+ \in \mathfrak{R}_+$ such that

1. *$f_+ \to 1$ as $|y| \to \infty$,*
2. *$f(y) = f_+(y)f_+(-y)$ for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$–in fact $f(z) = f_+(z)f_+(-z)$ for all $z \in \mathbb{C}-$,*
3. *the extensions of $f_+(z)$ and $f_+(-z)$ are entire functions,*
4. *$(\forall\ z \in \Pi_+ \quad f_+(z) \neq 0)$, $(\forall\ z \in \Pi_- \quad f_+(-z) \neq 0)$,*
5. *f and f_+ have zeros in the interior of Π_+, f and f_- have zeros in the interior of Π_-, and*
6. *is its only proper factorization.*

Furthermore,

$$f_+(z) = 1 + \int_0^{a_+} e^{izt}\gamma_+(t)dt \quad \textit{and} \quad f_+(-z) = 1 + \int_{-a_+}^{0} e^{izt}\gamma_+(-t)dt$$

where $\gamma_+ \in L_+$ and $\gamma_+(t) = 0$ for all $t \geq a_+$.

Proof. Let $0 < a_+$, $g \in L$ such that $g(x) = 0$ for all $x \notin [-a_+, a_+]$ and

$$f(y) = 1 + \lambda \int_{-a_+}^{a_+} g(t)e^{iyt}dt \in \mathfrak{R}.$$

Suppose

$$\forall y \in \mathbb{R} \cup \{-\infty, \infty\} \;\; f(y) \neq 0, \quad ind(f) = 0 \quad and \quad f \text{ is an even function},$$

using theorem 3.1.9 there exist $f_+ \in \mathfrak{R}_+$ and $f_- \in \mathfrak{R}_-$ such that

1. $f_\pm \to 1$ as $|y| \to \infty$,
2. $f(y) = f_+(y)f_-(y)$ for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$–in fact $f(z) = f_+(z)f_-(z)$ for all $z \in \mathbb{C}$–,
3. the extensions of f_+ and f_- are entire functions;
4. $(\forall\ z \in \Pi_+ \;\; f_+(z) \neq 0)$, $(\forall\ z \in \Pi_- \;\; f_-(z) \neq 0)$,
5. f and f_+ have zeros in the interior of Π_+, f and f_- have zeros in the interior of Π_-, and
6. is its only proper factorization.

Furthermore,

$$f_+(z) = 1 + \int_0^{a_+} e^{izt}\gamma_+(t)dt \quad and \quad f_-(z) = 1 + \int_{a_-}^0 e^{izt}\gamma_-(t)dt$$

where $\gamma_+ \in L_+$, $\gamma_- \in L_-$, $\gamma_+(t) = 0$ for all $t \geq a_+$ and $\gamma_-(t) = 0$ for all $t \leq a_-$. Hence, what we need to prove is $f_+(z) = f_-(-z)$.

$$\begin{aligned} f(z) &= f(-z) \quad f \text{ is even} \\ &= f_+(-z)f_-(-z), \end{aligned}$$

thus $f_+(-z)$ and $f_-(-z)$ are candidates for a proper factorization of f. Since f_+ and f_- are holomorphic functions in the interior and continuous in all Π_+ and Π_-, respectively, $f_-(-z)$ and $f_+(-z)$ are holomorphic functions in the interior and continuous in all Π_+ and Π_-, respectively. $f_+(\pm\infty) = 1 = f_-(\pm\infty) = 1$: $f_+(\mp\infty) = 1 = f_-(\mp\infty) = 1$. Moreover, since $f_+(z) \neq 0$ for all $z \in \Pi_+$, $f_+(-z) \neq 0$ for all $z \in \Pi_-$. Wherefore, $f_+(-z)$ and $f_-(-z)$ is a proper factorization of f. Using the uniqueness given by the theorem used at the start, $f_+(z) = f_-(-z)$ and $f_-(z) = f_+(-z)$. Finally,

1. $f(y) = f_+(y)f_+(-y)$ for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$–in fact $f(z) = f_+(z)f_+(-z)$ for all $z \in \mathbb{C}$–,

2. the extensions of $f_+(z)$ and $f_+(-z)$ are entire functions,

3. $(\forall\ z \in \Pi_+ \quad f_+(z) \neq 0)$, $(\forall\ z \in \Pi_- \quad f_+(-z) \neq 0)$, and

4. is its only proper factorization.

Moreover,

$$\begin{aligned} f_+(-z) &= 1 + \int_0^{a_+} e^{izt}\gamma_+(t)dt \\ &= 1 + \int_{-a_+}^{0} e^{izt}\gamma_+(-t)dt. \end{aligned}$$

Since $\gamma_+(t) = 0$ for all $t \geq a_+$, $\gamma_+(-t) = 0$ for all $t \leq -a_+$. $\square$

Proposition 3.1.11 *Let $f : \mathbb{C} \to \mathbb{C}$. If there exist $A > 0$ and $a \geq 0$ such that for all $z \in \mathbb{C}$ $|f(z)| \leq Ae^{a|Im(z)|}$, then there exists $B > 0$ such that for all $z \in \mathbb{C}$ $|1 + f(z)| \leq Be^{a|Im(z)|}$.*

Proof. Let $f : \mathbb{C} \to \mathbb{C}$. Suppose there exist $A > 0$ and $a \geq 0$ such that for all $z \in \mathbb{C}$ $|f(z)| \leq Ae^{a|Im(z)|}$.

$$\begin{aligned} |1 + f(z)| &\leq 1 + |f(z)| \\ &\leq e^{a|Im(z)|} + Ae^{a|Im(z)|} \\ &= (A+1)e^{a|Im(z)|} \\ &= Be^{a|Im(z)|}. \end{aligned}$$

$\square$

Proposition 3.1.12 *Let $c \in \mathbb{C}$, $g_+ \in L_+$, and $f(y) = c + \int_0^\infty g_+(t)e^{iyt}dt$ be an entire function. Suppose there exists $a \geq 0$ and $A > 0$ such that for all $z \in \Pi_-$ $|f(z)| \leq Ae^{a|Im(z)|}$, and $\alpha \in \Pi_+$ such that $f(\alpha) = 0$. Therefore, $\frac{f(z)}{z-\alpha}$ is an entire function, for all $z \in \Pi_+$*

$$\frac{f(z)}{z-\alpha} = \int_0^\infty e^{izt}g_\alpha(t)dt,$$

and there exists $B > 0$ such that for all $z \in \Pi_-$ $|\frac{f(z)}{z-\alpha}| \leq Be^{a|Im(z)|}$.

Proof. Let $g_\alpha(t) = ie^{-i\alpha t}\int_t^\infty e^{i\alpha s}g_+(s)ds$ for all $t \geq 0$ and $g_\alpha(t) = 0$ for all $t < 0$.

$$\begin{aligned} g'_\alpha(t) &= \alpha e^{-i\alpha t}\int_t^\infty e^{i\alpha s}g_+(s)ds - ie^{-i\alpha t}e^{i\alpha t}g_+(s) \\ ig'_\alpha(t) &= \alpha g_\alpha(t) + g_+(t) \\ g_+(t) &= ig'_\alpha(t) - \alpha g_\alpha(t). \end{aligned}$$

Let $z \in \Pi_+$.

$$\begin{aligned} f(z) &= c + \int_0^\infty g_+(t)e^{izt}dt \\ &= c + \int_0^\infty \left[ig'_\alpha(t) - \alpha g_\alpha(t)\right]e^{izt}dt \\ &= c + \int_0^\infty ig'_\alpha(t)e^{izt}dt - \alpha\int_0^\infty g_\alpha(t)e^{izt}dt \\ &= c + ie^{izt}g_\alpha\Big|_0^\infty + z\int_0^\infty g_\alpha(t)e^{izt} - \alpha\int_0^\infty g_\alpha(t)e^{izt}dt \\ &= 0 + f(\alpha) + (z-\alpha)\int_0^\infty g_\alpha(t)e^{izt}dt \\ &= (z-\alpha)\int_0^\infty g_\alpha(t)e^{izt}dt. \end{aligned}$$

Therefore,

$$\frac{f(z)}{z-\alpha} = \int_0^\infty e^{izt}g_\alpha(t)dt.$$

It is entire since we can remove the singularity. Since α is an isolated zero, there exists B an open ball such that $\alpha \in B$ and no other zero of f belongs to it. Let $z \in \Pi_-$. If $z \in B$, then $\frac{f(z)}{z-a}$ is bounded. Let us say by M_1. Let $\alpha_0 \in B - \{\alpha\}$. If $z \notin B$,

$$\frac{f(z)}{z-a} \leq Max\left(M_1e^{aIm(z)}, \frac{Ae^{aIm(z)}}{\alpha_0-\alpha}\right).$$

□

Proposition 3.1.13 *Let $\lambda \in \{0,1\}$, $g_+ \in L_+$, and $f(y) = \lambda + \int_0^\infty g_+(t)e^{iyt}dt$ an entire function such that $\lim_{|y|\to\infty} f(x+iy) = 1$. If there exist $a \geq 0$ and $A > 0$ such that for all $z \in \Pi_-$ $|f(z)| \leq Ae^{a|Im(z)|}$, and g_+ is not the function zero or the function zero except in a zero measure set: $g_+(t) = 0$ for all $t \notin [0,a]$.*

Proof. Let $\lambda \in \{0,1\}$, $g_+ \in L_+$, and $f(y) = \lambda + \int_0^\infty g_+(t)e^{iyt}dt$ be an entire function. Suppose there exist $a \geq 0$ and $A > 0$ such that for all $z \in \Pi_-$ $|f(z)| \leq Ae^{a|Im(z)|}$, and g_+ is not the function zero or the function zero except in a zero measure set.

Remark 3.1.14 *The function f can only have a finite number of zeros in Π_+. Suppose there are an infinity number of zeros in Π_+. Since $\Pi_+ \cup \{\infty\}$ is compact in the complex sphere: there's an accumulation point for those zeros. It can be on Π_+ or in ∞. If it is in Π_+, given that it is entire, the function is zero. But that is a contradiction since $f(y) = 1 + \lambda \int_0^\infty g_+(t)e^{iyt}dt$. If the limit point is at ∞: any succession of zeros would tend to 1 because of proposition 2.2.19, that's a contradiction.*

Consequently, we can use proposition 3.1.12 the right number of times to obtain a function h such that

1. it is entire,
2. there exists $B > 0$ such that for all $z \in \Pi_-$ $h(z) \leq Be^{a|Im(z)|}$,
3. h and f share the same zeros in Π_-,
4. $\lim_{|y|\to\infty} h(y) = 0$, and
5. for all $z \in \Pi_+$ $h(z) = \int_0^\infty e^{izt}p_+(t)dt \in \mathfrak{R}_+$.

We are looking for a zero, α, in the interior of Π_-, in order to define

$$F(z) = \frac{f(z)}{z-\alpha}e^{-i\frac{a_+}{2}z}.$$

Suppose h doesn't have a zero in the interior of Π_-, hence h has no zeros on $\mathbb{C}$. Given that h is an entire function, there exists an entire function g such that $h(z) = e^{g(z)}$ $\left(\text{consider the following function } g'(z) = \frac{h'(z)}{h(z)}\right)$. Since $h \in \mathfrak{R}_+$ there exists M_+ such that

$$\forall z \in \Pi_+ \quad |h(z)| \leq M_+.$$

Because $h \neq 0$, $lnh = g$ is analytical and $|h(z)| = e^{Re(g(z))}$: $ln|h(z)| = Re(g(z))$. Consequently,

$$\begin{aligned} Re(g(z)) &\leq ln(M_+) \leq ln(M_+) + a|Im(z)| \quad \forall z \in \Pi_+ \quad \textit{and} \\ Re(g(z)) &\leq ln(M_+) + a|Im(z)| \quad \forall z \in \Pi_-. \end{aligned}$$

Wherefore, for all $z \in \mathbb{C}$

$$Re(g(z)) \leq ln(M_+) + a|Im(z)| \leq ln(M_+) + a|z|.$$

Using theorem 2.1.5 for $R < 2R$,

$$\begin{aligned} max_{|z|=R}|g(z)| &\leq \frac{2R}{2R-R} sup_{|z|\leq 2R} Re(g(z)) + \frac{3R}{2R-R}|g(0)| \\ &= 2sup_{|z|\leq 2R} Re(g(z)) + 3|g(0)| \\ &\leq 2ln(M_+) + 2a|z| + 3|g(0)| \\ &= 2a|z| + M_1 \quad M_1 > 0 : \end{aligned}$$

for $|z| < R$

$$|g(z)| < 2a|z| + M_1.$$

The last statement is valid for all $R > 0$, thus for all $z \in \mathbb{C}$

$$|g(z)| < 2a|z| + M_1 :$$

$g(z) = cz + b$ where $c, b \in \mathbb{C}$.

$$g(z) = c_1z_1 + ic_1z_2 + ic_2z_1 - c_2z_2 + b_1 + ib_2.$$

$$Re(g(z)) = c_1z_1 + b_1 - c_2z_2.$$

Let $z_2 = 0$.

$$Re(g(z)) = c_1z_1 + b_1 \leq ln(M_+).$$

Suppose $c_1 < 0$. When $z_1 \to -\infty$ $Re(g(z)) \to \infty$, it's not bounded, is a contradiction: $c_1 \geq 0$. Let $c_1 > 0$. When $z_1 \to \infty$ $Re(g(z)) \to \infty$, it's not bounded, is a contradiction: hence $c_1 \leq 0$. Consequently, $c_1 = 0$. Let $z = ix$ for $x \geq 0$.

$$Re(g(z)) = b_1 - c_2x \leq ln(M_+).$$

$c_2 \geq 0$, because $Re(g(z))$ is bounded. Let $a_0 \geq 0$ such that $a_0 = c_2$. If $z = -ix$ with $x > 0$:

$$\begin{aligned} Re(g(z)) &= b_1 + a_0x \\ &\leq ln(M_+) + a|x| \\ &= ln(M_+) + ax. \end{aligned}$$

If $A = b_1 - ln(M_+)$:

$$\frac{A}{x} + a_0 \leq a.$$

Taking the limit when $x \to \infty$, $a_0 \leq a$. Thus,

$$h(z) = e^b e^{ia_0 z} = Ce^{ia_0 z} \quad 0 \leq a_0 \leq a.$$

Seeing that $|h(x)| \to 0$ when $|x| \to \infty$, $C = 0$:

$$\int_0^\infty e^{izt} g(t) dt = h(z) = 0.$$

Therefore, g is the function zero or the function zero except in a zero measure set, but we made the assumption that it wasn't. Consequently, h has at least one zero in the interior of Π_-: f has it too.

Let α be in the interior of Π_- such that $f(\alpha) = 0$. Let us define F as

$$F(z) = \frac{f(z)}{z - \alpha} e^{-i\frac{a}{2}z}.$$

Since $fe^{-i\frac{a}{2}z}$ is entire and the singularity is removable in α, F is an entire function. Let us take a ball with radius R containing α and that is contained in the interior of Π_-. Inside the ball $F(z)$ is bounded, let us say by $M_1 > 0$. Outside of the ball and in the interior of Π_-,

$$|f(z)| \leq M_+ e^{a|Im(z)|}, \quad \frac{1}{|z - \alpha|} \leq \frac{1}{|\alpha_0 - \alpha|} = M_2 \quad and$$

$$\left| e^{-i\frac{a}{2}z} \right| = e^{z_2 \frac{a}{2}} = e^{-|Im(z)| \frac{a}{2}}$$

where $\alpha_0 \in B_R(\alpha)$. Hence,

$$\begin{aligned} |F(z)| &\leq M_+ M_2 e^{a|Im(z)|} e^{-|Im(z)|\frac{a}{2}} \\ &= Ne^{|Im(z)|\frac{a}{2}}. \end{aligned}$$

On Π_+

$$|f_+(z)| \leq M_+, \quad \frac{1}{|z - \alpha|} \leq \frac{1}{|\alpha_0 - \alpha|} = M_2, \quad and \quad \left| e^{-i\frac{a}{2}z} \right| = e^{|Im(z)|\frac{a}{2}} :$$

$$\begin{aligned} |F(z)| &\leq M_+ M_2 e^{|Im(z)|\frac{a}{2}} \\ &= Ne^{|Im(z)|\frac{a}{2}}. \end{aligned}$$

Consequently, for all $z \in \mathbb{C}$

$$|F(z)| \leq Ne^{|Im(z)|\frac{a}{2}}.$$

For $t \in \mathbb{R}$

$$|F(t)|^2 = \frac{|f(t)|^2}{|t-\alpha|^2}.$$

$$\begin{aligned}
\int_{-\infty}^{\infty} |F(t)|^2 dt &= \int_{-\infty}^{\infty} \frac{|f(t)|^2}{|t-\alpha|^2} dt \\
&= \int_{-A}^{A} \frac{|f(t)|^2}{|t-\alpha|^2} dt + \int_{-\infty}^{-A} \frac{1}{|t-\alpha|^2} dt + \int_{A}^{\infty} \frac{1}{|t-\alpha|^2} dt \\
&= \int_{-A}^{A} \frac{|f(t)|^2}{|t-\alpha|^2} dt + \int_{-\infty}^{-A} \frac{1}{(t-\alpha_1)^2+\alpha_2^2} dt + \int_{A}^{\infty} \frac{1}{(t-\alpha_1)^2+\alpha_2^2} dt \\
&= B + \int_{-\infty}^{-A-\alpha_1} \frac{1}{x^2+\alpha_2^2} dt + \int_{A-\alpha_1}^{\infty} \frac{1}{x^2+\alpha_2^2} dt \\
&= B + \frac{1}{\alpha_2}\left[arctan\left(\frac{-A-\alpha_1}{\alpha_2}\right) - \left(-\frac{\pi}{2}\right)\right] + \frac{1}{\alpha_2}\left[\frac{\pi}{2} - arctan\left(\frac{A-\alpha_1}{\alpha_2}\right)\right] \\
&< \infty.
\end{aligned}$$

Using theorem 2.1.6, there exists $h \in L_2\left(-\frac{a}{2}, \frac{a}{2}\right)$ such that

$$F(z) = \int_{-\frac{a}{2}}^{\frac{a}{2}} e^{izt} h(t) dt.$$

Substituting $F(z)$ in its definition,

$$\begin{aligned}
\frac{f(z)}{z-\alpha} &= \int_{-\frac{a}{2}}^{\frac{a}{2}} e^{izt} e^{i\frac{a}{2}z} h(t) dt \\
&= \int_{-\frac{a}{2}}^{\frac{a}{2}} e^{iz\left(t+\frac{a}{2}\right)} h(t) dt \\
&= \int_{0}^{a} e^{izx} h\left(x - \frac{a}{2}\right) dx.
\end{aligned}$$

On the other hand we know that

$$\begin{aligned}
f(z) &= 1 + \int_{0}^{\infty} e^{izt} g_+(t) dt \\
&= \int_{-\infty}^{\infty} e^{izt} \left(\delta + g_+\right)(t) dt.
\end{aligned}$$

Since $Im(\alpha) < 0$,

$$\frac{1}{z-\alpha} = -i \int_{0}^{\infty} e^{-i\alpha t} e^{izt} dt.$$

Let g be a function such that $g(t) = -ie^{-i\alpha t}$ for all $t \geq 0$ and $g(t) = 0$ for all $t < 0$, then

$$\begin{aligned}
\frac{f(z)}{z-\alpha} &= \int_{-\infty}^{\infty} e^{izt} \int_{-\infty}^{\infty} g(s)\left(\delta + g_+\right)(t-s)ds \\
&= \int_{-\infty}^{\infty} e^{izt} \left(g(t) + \int_{-\infty}^{\infty} g(s) g_+(t-s)ds \right) dt \\
&= \int_{-\infty}^{\infty} e^{izt} g(t)dt + \int_{-\infty}^{\infty} e^{izt} \int_{-\infty}^{\infty} g(s)g_+(t-s)dsdt \\
&= \int_{0}^{\infty} e^{izt} g(t)dt + \int_{-\infty}^{\infty} e^{izt} \int_{0}^{t} g(s)g_+(t-s)dsdt \\
&= \int_{0}^{\infty} e^{izt} g(t)dt + \int_{0}^{\infty} e^{izt} \int_{0}^{t} g(s)g_+(t-s)dsdt \\
&= \int_{0}^{\infty} e^{izt} \left(g(t) + \int_{0}^{t} g(s) g_+(t-s)ds \right) dt \\
&= \int_{0}^{\infty} e^{izt} \left(g(t) - \int_{t}^{0} g(t-x) g_+(x)dx \right) dt \\
&= \int_{0}^{\infty} e^{izt} \left(g(t) + \int_{0}^{t} g(t-s) g_+(s)ds \right) dt \\
&= \int_{0}^{\infty} e^{izt} g_\alpha(t)dt
\end{aligned}$$

where $g_\alpha(t) = g(t) + \int_0^t g(t-s)g_+(s)ds = -ie^{-i\alpha t} - i\int_0^t e^{-i\alpha(t-s)} g_+(s)ds$.

$$g_\alpha(t) = -ie^{-i\alpha t} - ie^{-i\alpha t}\int_0^t e^{i\alpha s} g_+(s)ds.$$

$$\begin{aligned}
g'_\alpha(t) &= \alpha e^{-i\alpha t} + \alpha e^{-i\alpha t} \int_0^t e^{i\alpha s} g_+(s)ds - ie^{-i\alpha t}e^{i\alpha t} g_+(t) \\
&= \alpha e^{-i\alpha t} + \alpha e^{-i\alpha t} \int_0^t e^{i\alpha s} g_+(s)ds - ig_+(t).
\end{aligned}$$

Wherefore,

$$g'_\alpha(t) + i\alpha g_\alpha(t) = -ig_+(t).$$

Given that

$$\int_0^\infty e^{izt} g_\alpha(t)dt = \frac{f(z)}{z-\alpha} = \int_0^a e^{izx} h\left(x - \frac{a}{2}\right) dx,$$

if we define $h\left(x - \frac{a}{2}\right) = 0$ outside of $[0, a]$,

$$\int_0^\infty e^{izt}\left(g_\alpha(t) - h\left(t - \frac{a}{2}\right)\right) dt = 0.$$

Therefore, it is integrable. Using the theorem 2.2.7, $g_\alpha(t) = h\left(t - \frac{a}{2}\right)$ except in a zero measure set and $g_\alpha(t) = 0$ outside of $[0, a]$ (because of the continuity of the zero function). Using the last assertion and that $g'_\alpha(t) + i\alpha g_\alpha(t) = -ig_+(t)$, for all $t \notin [0, a]$

$$g_+(t) = 0$$

and

$$f(z) = 1 + \int_0^a e^{izt} g_+(t) dt.$$

$\square$

Proposition 3.1.15 *Let $\lambda \in \mathbb{R}$, $g_- \in L_-$, and $f(y) = 1 + \lambda \int_{-\infty}^0 g_-(t)e^{iyt}dt$ be an entire function such that $\lim_{|y|\to\infty} f(x+iy) = 1$. If there exist $a \geq 0$ and $A > 0$ such that for all $z \in \Pi_+$ $|f(z)| \leq Ae^{a|Im(z)|}$, then $g_-(t) = 0$ for all $t \notin [-a, 0]$.*

Proof. The proof is almost analogous to one of the last proposition. $\square$

3.2 Factorization of nonsingular matrices

The following theorems and propositions won't be demonstrated, the reader can find proof of them in reference [21].

Definition 3.2.1 *A left standard factorization of a continuous nonsingular matrix function $\mathfrak{M}(y)$ $(-\infty < y < \infty)$ is a representation of $\mathfrak{M}$ such that*

$$\mathfrak{M}(y) = \mathfrak{R}_+(y)\mathfrak{D}(y)\mathfrak{R}_-(y)$$

where $\mathfrak{D}(y)$ is a diagonal matrix function,

$$\mathfrak{D}(y) = \left[\left(\frac{y-i}{y+i}\right)^{\kappa_j} \delta_{jk}\right],$$

$\kappa_1 \geq \kappa_2 \geq ... \geq \kappa_n$ are integer numbers, and the matrix functions $\mathfrak{R}_\pm(y)$ admit

1. *analytic extensions, holomorphic in the interior and continuous on $\Pi_\pm$,*
2. *whose determinant is not zero, i.e.,*

$$det(\mathfrak{R}_+)(z) \neq 0 \quad \forall z \in \Pi_+, \quad det(\mathfrak{R}_-)(z) \neq 0 \quad \forall z \in \Pi_-.$$

If the factors $\mathfrak{R}_\pm(y)$ are interchanged, then the factorization from $\mathfrak{R}(y)$ is called right standard factorization.

Theorem 3.2.2 *Every nonsingular matrix function $\mathfrak{M}(y) \in \mathfrak{R}_{(n\times n)}$ has a left (right) standard factorization and for every standard factorization the factors $\mathfrak{R}_\pm(y) \in \mathfrak{R}^{\pm}_{(n\times n)}$.*

Definition 3.2.3 *If all the left exponents (κ_i) of the nonsingular matrix $\mathfrak{M}(y)$ are zero, i.e.,*

$$\mathfrak{M}(y) = \mathfrak{R}_+(y)\mathfrak{R}_-(y)$$

and $\mathfrak{R}_+(\infty) = I$: the left standard factorization is canonical. In a similar manner the right standard factorization

$$\mathfrak{M}(y) = \mathfrak{R}_-(y)\mathfrak{R}_+(y)$$

such that $\mathfrak{R}_-(\infty) = I$ is called right canonical factorization.

Proposition 3.2.4 *We have the following uniqueness property. Let $\mathfrak{R}_+$ and $\mathfrak{R}_-$ be a left canonical factorization. Suppose $\mathfrak{G}_+$ and $\mathfrak{G}_-$ is another left canonical factorization,*

$$\mathfrak{R}_+ = \mathfrak{G}_+ \quad \mathfrak{R}_- = \mathfrak{G}_-.$$

Proof. Let $\mathfrak{R}_+$ and $\mathfrak{R}_-$ be a left canonical factorization. Suppose $\mathfrak{G}_+$ and $\mathfrak{G}_-$ are another left canonical factorization. They are standard factorizations, hence

$$\mathfrak{G}_+^{-1}(y)\mathfrak{R}_+(y) = \mathfrak{G}_-(y)\mathfrak{R}_-^{-1}(y) \quad y \in \mathbb{R}.$$

Given that $\mathfrak{G}_\pm^{-1}(y)\mathfrak{R}_+(y)$ is holomorphic on $\Pi_\pm$, let

$$G(z) = \begin{cases} \mathfrak{G}_+^{-1}(z)\mathfrak{R}_+(z) & z \in \Pi_+ \\ \mathfrak{G}_-(z)\mathfrak{R}_-^{-1}(z) & z \in \Pi_-. \end{cases}$$

$G(\infty) = I$: is a constant matrix function–$G(z) = I$. Wherefore,

$$\mathfrak{G}_+^{-1}(y)\mathfrak{R}_+(y) = \mathfrak{G}_-(y)\mathfrak{R}_-^{-1}(y) = I.$$

Proposition 3.2.5 *If the matrix function $\mathfrak{M}(y)$ has a left canonical factorization, i.e., there exist $\mathfrak{G}_+(y) \in \mathfrak{R}^+_{(n\times n)}$ and $\mathfrak{G}_-(y) \in \mathfrak{R}^-_{(n\times n)}$ such that*

$$\mathfrak{M}(y) = \mathfrak{G}_+(y)\mathfrak{G}_-(y) \; y \in \mathbb{R} \quad \textit{and} \quad \mathfrak{G}_+(\infty) = I$$

where $\mathfrak{G}_\pm(y)$ can be extended to be holomorphic in the interior and continuous on $\Pi_\pm$. Then,

$$\left(\forall z \in \Pi_+ \mathfrak{G}_+(z) \neq \left[0\right]\right) \;\; \textit{or} \;\; \left(\forall z \in \Pi_- \mathfrak{G}_-(z) \neq \left[0\right]\right).$$

3.2.1 Factorization of hermitian matrices

Let us denote $\mathfrak{M}^*(z)$ as the conjugated hermitian matrix function of $\mathfrak{M}(z)$: $\mathfrak{M}^*(z) = \overline{\mathfrak{M}^T(\overline{z})}$ where the bar denotes taking the conjugate and ^{T} the transpose.

Definition 3.2.6 *We say a matrix function $\mathfrak{M}$ is hermitian if*

$$\mathfrak{M}(z) = \mathfrak{M}^*(z).$$

Definition 3.2.7

$$\begin{aligned} Re\,(\mathfrak{M}(z)) &= \mathfrak{M}_R(z) = \frac{\mathfrak{M}(z) + \mathfrak{M}^*(z)}{2} \\ Im\,(\mathfrak{M}(z)) &= \mathfrak{M}_J(z) = \frac{\mathfrak{M}(z) - \mathfrak{M}^*(z)}{2i}. \end{aligned}$$

Remark 3.2.8 *The matrix functions $\mathfrak{M}_R(z)$ and $\mathfrak{M}_J(z)$ are hermitian.*

Definition 3.2.9 *We say a matrix function $\mathfrak{M}(z)$ is definite if for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$ the quadratic form*

$$\zeta^*\mathfrak{M}(y)\zeta,$$

where $\zeta \in \mathbb{C}^n$, only has real values different from zero and with constant sign.

Remark 3.2.10 *Every definite matrix function is hermitian.*

Proposition 3.2.11 *The hermitian matrix function $\mathfrak{M}(y)$ is definite if and only if $\mathfrak{M}(y)$ is nonsingular and $\mathfrak{M}(y)$ is definite for at least one point.*

Proposition 3.2.12 *If the real or the imaginary part of the nonsingular matrix function $\mathfrak{M}(y)$ is definite, then all left (right) exponents of the matrix $\mathfrak{M}(y)$ are zero, i.e., the factorization is canonical.*

Theorem 3.2.13 *A matrix function $\mathfrak{M}(y) \in \mathfrak{R}_{(n\times n)}$ has a representation of the form*

$$\mathfrak{M}(y) = \mathfrak{F}_+(y)\mathfrak{F}_+^*(y),$$

where the matrix function $\mathfrak{F}_+(y) \in \mathfrak{R}^+_{(n\times n)}$ and $det(\mathfrak{F}_+(z)) \neq 0$ for all $z \in \Pi_+$, if and only if $\mathfrak{M}(y)$ is positive definite.

Chapter 4

Factoring the Ornstein-Zernike equation

Definition 4.0.1 *A homogeneous fluid is a fluid in absence of external forces. Conversely, a nonhomogeneous fluid is a fluid in which an external force field is acting over it.*

Let a homogeneous fluid with m species have densities ρ_k with $k \in \{1, ..., m\}$. Our principal objective is to solve the system of integral equations

$$h_{i,j}(r_i, r_j) = c_{i,j}(r_i, r_j) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(r_i, r_k) h_{k,j}(r_k, r_j) dr_k \tag{4.1}$$

for $h_{i,j}(r)$ and $c_{i,j}(r)$. We will refer to this system as the Ornstein-Zernike equation for m species. The functions $h_{i,j}(r)$ and $c_{i,j}(r)$ are called the total and direct correlation function, respectively. The integral equations 4.1 are part of the general liquid theories developed from balance equations [22, 23, 24]. If equations 4.1 are solved we can compute the system's thermodynamic properties with them, see reference [5]. In this chapter we will use the Wiener-Hopf factorization method to transform equations 4.1 into a new set of equations, which we will show below that, together with the Percus-Yevick approximation, can be analytically solved for a one species of hard spheres model or conveniently numerically resolved for some more complex systems. In the case of one species, it is possible to solve equation 4.1 using the factorization method. For now, let us assume particles are hard spheres. Each particle has a diameter d_k ordered such that if $i \leq j$, then $d_i \geq d_j$.

Definition 4.0.2 *A fluid is isotropic if its properties are not dependent on the direction along which they are measured.*

It turns out that if the fluid is isotropic the Ornstein-Zernike equation for M species becomes

$$h_{i,j}(|r_i - r_j|) \;\;=\;\; c_{i,j}(|r_i - r_j|) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|r_i - r_k|)h_{k,j}(|r_k - r_j|)dr_k.$$

In other words, $h_{i,j}$ and $c_{i,j}$ are functions of the distance between particles i and j. Furthermore, if we suppose particle j is at the origin:

$$h_{i,j}(|r_i|) \;\;=\;\; c_{i,j}(|r_i|) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|r_i - r_k|)h_{k,j}(|r_k|)dr_k.$$

We will use all the tools developed in previous chapters to get more information from it. In the next section, we analytically solve the Percus-Yevick approximation for one species of hard spheres.

4.1 One species

Let us assume we only have one species:

$$h_{1,1}(|r_1|) \;\;=\;\; c_{1,1}(|r_1|) + \sum_{k=1}^{1} \rho_1 \int c_{1,1}(|r_1 - r_1'|)h_{1,1}(|r_1'|)dr_1'.$$

We will drop the subscripts,

$$h(|r|) \;\;=\;\; c(|r|) + \rho_1 \int c(|r - r'|)h(|r'|)dr'.$$

If we make a change of variable:

$$h(|r|) \;\;=\;\; c(|r|) + \rho_1 \int c(|r'|)h(|r - r'|)dr'.$$

We will put vectors in bold letters to highlight the fact that they are not scalars,

$$h(|\mathbf{r}|) = c(|\mathbf{r}|) + \rho \int c(|\mathbf{r'}|)h(|\mathbf{r} - \mathbf{r'}|)d\mathbf{r'}.$$

Baxter in [1] used the Winer-Hopf factorization in order to obtain the direct correlation function. In this section we will develop what was done in [1] using the theory from the last chapter.

Let us suppose c and h are elements of L, see definition 2.2.1. Multiplying both sides of the Ornstein-Zernike equation by $e^{i\langle \mathbf{r},\mathbf{k}\rangle}$ and integrating over $\mathbb{R}^3$ with respect to $\mathbf{r}$,

$$\int_{\mathbb{R}^3} e^{i\langle \mathbf{r},\mathbf{k}\rangle} h(|\mathbf{r}|)d\mathbf{r} = \int_{\mathbb{R}^3} e^{i\langle \mathbf{r},\mathbf{k}\rangle} c(|\mathbf{r}|)d\mathbf{r} + \rho \left(\int_{\mathbb{R}^3} e^{i\langle \mathbf{r},\mathbf{k}\rangle} \left[\int c(|\mathbf{r'}|)h(|\mathbf{r} - \mathbf{r'}|)d\mathbf{r'} \right] d\mathbf{r} \right).$$

We just applied the Fourier transform to the Ornstein-Zernike equation:

$$\hat{h}(\mathbf{k}) = \hat{c}(\mathbf{k}) + \rho\hat{c}(\mathbf{k})\hat{h}(\mathbf{k}). \tag{4.2}$$

Let us take as a base of $\mathbb{R}^3$, $\left\{\mathbf{x}, \mathbf{y}, \frac{\mathbf{k}}{|\mathbf{k}|}\right\}$. Any element, $\mathbf{r}$, of $\mathbb{R}^3$ can be represented as $\mathbf{r} = x\mathbf{x} + y\mathbf{y} + z\frac{\mathbf{k}}{|\mathbf{k}|}$ where x, y and z are real numbers. If $|\mathbf{k}| = k$:

$$\begin{aligned} \hat{h}(\mathbf{k}) &= \int_{\mathbb{R}^3} e^{ik\langle \mathbf{r}, \hat{\mathbf{k}}\rangle} h(|\mathbf{r}|)dxdydz \\ &= \int_{\mathbb{R}^3} e^{izk} h(|\mathbf{r}|)dxdydz. \end{aligned}$$

Changing to spherical coordinates,

$$\begin{aligned} \hat{h}(\mathbf{k}) &= \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{iRcos(\phi)k} h(R)R^2 sen(\phi)d\theta d\phi dR \\ &= 2\pi \int_0^\infty \int_0^\pi e^{iRcos(\phi)k} h(R)R^2 sen(\phi)d\phi dR. \end{aligned} \tag{4.3}$$

If we define $t = cos\phi$:

$$\begin{aligned} \int_0^\pi e^{iRcos(\phi)k} sen(\phi)d\phi &= -\int_1^{-1} e^{iRkt}dt \\ &= \int_{-1}^1 e^{iRkt}dt \\ &= \left.\frac{e^{iRkt}}{iRk}\right|_{-1}^1 \\ &= \frac{e^{iRk} - e^{-iRk}}{iRk} \\ &= \frac{2isen(Rk)}{iRk} \\ &= \frac{2sen(Rk)}{Rk}. \end{aligned}$$

Substituting the last result in equation 4.3,

$$\begin{aligned} \hat{h}(\mathbf{k}) &= 2\pi \int_0^\infty \int_0^\pi e^{iRcos(\phi)k} h(R)R^2 sen(\phi)d\phi dR \\ &= \frac{4\pi}{k} \int_0^\infty h(R)Rsen(kR)dR. \end{aligned}$$

Since $\hat{h}$ only depends on k: $\hat{h}(\mathbf{k}) = \hat{h}(k)$, i.e.

$$\hat{h}(k) = \frac{4\pi}{k} \int_0^\infty h(R)Rsen(kR)dR \quad k \geq 0. \tag{4.4}$$

Similarly,

$$\hat{c}(k) = \frac{4\pi}{k}\int_0^{\infty} c(R)Rsen(kR)dR \quad k \geq 0.$$

Now comes the interesting part, let us define

$$J(x) = \begin{cases} \int_x^{\infty} th(t)dt & x \geq 0 \\ \int_{-x}^{\infty} th(t)dt & x < 0 \end{cases}$$

and integrate by parts equation 4.4, where

$$u = sen(kx) \quad , \quad dv = xh(x)dx$$

$$du = kcos(kx)dx \quad and \quad v = -\int_x^{\infty} th(t)dt :$$

$$\begin{aligned} \hat{h}(k) &= \frac{4\pi}{k}\left[-sen(kx)\int_x^{\infty} th(t)dt\Big|_0^{\infty} + \int_0^{\infty} kcos(kx)J(x)dx\right] \\ &= 0 + 4\pi\int_0^{\infty} cos(kx)J(x)dx \\ &= 4\pi\int_0^{\infty} cos(kx)J(x)dx \quad k \geq 0. \end{aligned}$$

In a similar way, let us define

$$S(x) = \begin{cases} \int_x^{\infty} tc(t)dt & x \geq 0 \\ \int_{-x}^{\infty} tc(t)dt & x < 0 : \end{cases}$$

$$\hat{c}(k) = 4\pi\int_0^{\infty} cos(kx)S(x)dx \quad k \geq 0.$$

We want to find a relation between the functions $\hat{J}$ and $\hat{h}$, hence we need to check if there exists the Fourier transform of J.

$$\begin{aligned} \int_{-\infty}^{0} J(x)dx &= -\int_{\infty}^{0} J(-x)dx \\ &= \int_0^{\infty} J(-x)dx \\ &= \int_0^{\infty}\int_{-(-x)}^{\infty} th(t)dtdx \\ &= \int_0^{\infty} J(x)dx \\ &= \frac{\hat{h}(0)}{4\pi} \\ &< \infty, \end{aligned}$$

therefore

$$\begin{aligned} \hat{J}(k) &= \int_{-\infty}^{\infty} J(x)e^{ixk}dx \\ &= \int_{-\infty}^{\infty} J(x)cos(kx)dx + i\left(\int_{-\infty}^{\infty} J(x)sen(kx)dx\right). \end{aligned}$$

Remark 4.1.1 *J and S are even functions.*

Using remark 4.1.1, $J(x)cos(kx)$ is even and $J(x)sen(kx)$ is odd. Then,

$$\begin{aligned}\hat{J}(k) &= 2\int_0^\infty J(x)cos(kx)dx + 0 \\ &= 2\int_0^\infty J(x)cos(kx)dx \quad k \in \mathbb{R}\end{aligned}$$

and

$$\hat{S}(k) = 2\int_0^\infty S(x)cos(kx)dx \quad k \in \mathbb{R}.$$

Wherefore, for all $k \geq 0$

$$\hat{c}(k) = (2\pi)\hat{S}(k) \quad and \quad \hat{h}(k) = (2\pi)\hat{J}(k).$$

Substituting in equation 4.2, the OZ equation becomes,

$$(2\pi)\hat{J}(k) = (2\pi)\hat{S}(k) + (2\pi)^2\rho\hat{J}(k)\hat{S}(k).$$

Hence, defining $\lambda = (2\pi)\rho$, we obtain.

$$\hat{J}(k) = \hat{S}(k) + \lambda\hat{J}(k)\hat{S}(k) : \tag{4.5}$$

$$\hat{J}(1 - \lambda\hat{S}) = \hat{S} \quad and \quad \hat{J} = (1 + \lambda\hat{J})\hat{S}.$$

Solving for $1 + \lambda\hat{J}$,

$$\frac{1}{\mathcal{F}} = 1 + \lambda\hat{J} \tag{4.6}$$

where $\mathcal{F} \equiv (1 - \lambda\hat{S})$.

Remark 4.1.2 *Since $\hat{J}$ is the Fourier transform of J, $\frac{1}{\mathcal{F}}$ doesn't have poles in the real line. Thus, $\mathcal{F}$ does not have zeros in the real line, i.e. for all $y \in \mathbb{R}$ $\mathcal{F}(y) \neq 0$. Therefore, $\mathcal{F}$ satisfies one of the hypothesis of corollary 3.1.10.*

Now, we want to factor $\mathcal{F}$, i.e. apply last chapter's theory, to obtain a new expression of (4.5), for hard spheres. Remark 4.1.2 is the first step to do it, and in the next section we will make an additional assumption to continue in our develepment.

4.1.1 Correlation function for hard spheres

Let us make the following supposition about the inter-molecular potential. If a is the particles' diameter, then

$$U(x) = \begin{cases} \infty & x < d \\ 0 & x \geq 0. \end{cases}$$

In other words,

$$h(x) = -1 \quad \forall\ x \leq d \quad and \quad c(x) = 0 \quad \forall x > d.$$

Proposition 4.1.3 *For all* $|x| > d$ $S(x) = 0$.

Proof. Let $|x| > d$. If $x > d$, then $S(x) = \int_x^\infty tc(t)dt$. Since $c(x) = 0$ for all $x > d$, $S(x) = 0$. If $x < -d$, then $S(x) = \int_{-x}^\infty tc(t)dt$. But, $-x > d$: $S(x) = 0$. □

Using proposition 4.1.3,

$$\hat{S}(y) = \int_{-d}^{d} e^{iyt} S(t)dt.$$

By proposition 3.1.8,

$$\left|\hat{S}(z)\right| \leq e^{d|Im(z)|} \int_{-d}^{d} |S(t)|dt = Ce^{d|Im(z)|}.$$

Proposition 4.1.4 *Let* $\mathcal{F} \in \mathfrak{R}$ *such that* $\mathcal{F}$ *is even. If for all* $y \in \mathbb{R}$ $\mathcal{F}(y) \neq 0$, *then* $ind(\mathcal{F}) = 0$.

Proof.

$$\begin{aligned}
0 &= ind(1) \\
&= ind\left(\frac{\mathcal{F}(y)}{\mathcal{F}(y)}\right) \\
&= ind(\mathcal{F}(y)) - ind(\mathcal{F}(y)) \\
&= ind(\mathcal{F}(y)) - ind(\mathcal{F}(-y)) \\
&= ind(\mathcal{F}(y)) - (-ind(\mathcal{F}(y))) \\
&= 2ind(\mathcal{F}(y)) :
\end{aligned}$$

$ind(\mathcal{F}(y)) = 0$. □

Using proposition 4.1.4, $ind(\mathcal{F}(y)) = 0$. Since $\mathcal{F}(y) \neq 0$ and $ind(\mathcal{F}(y)) = 0$, by corollary 3.1.10 there exists $\mathcal{F}_+ \in \mathfrak{R}_+$ such that

1. $\mathcal{F}_+ \to 1$ as $|y| \to \infty$,

2. $\mathcal{F}(y) = \mathcal{F}_+(y)\mathcal{F}_+(-y)$ for all $y \in \mathbb{R} \cup \{-\infty, \infty\}$–in fact $\mathcal{F}(z) = \mathcal{F}_+(z)\mathcal{F}_+(-z)$ for all $z \in \mathbb{C}$–,

3. the extensions of $\mathcal{F}_+(z)$ and $\mathcal{F}_+(-z)$ are entire functions,

4. $(\forall\ z \in \Pi_+\ \ \mathcal{F}_+(z) \neq 0)$, $(\forall\ z \in \Pi_-\ \ \mathcal{F}_+(-z) \neq 0)$,

5. f and $\mathcal{F}_+$ have zeros in the interior of Π_+, $\mathcal{F}$ and $\mathcal{F}_-$ have zeros in the interior of Π_-, and

6. is its only proper factorization.

Furthermore,

$$\mathcal{F}_+(z) = 1 + \int_0^d e^{izt} g_+(t)dt \quad and \quad \mathcal{F}_+(-z) = 1 + \int_{-d}^0 e^{izt} g_+(-t)dt \tag{4.7}$$

where $g_+ \in L_+$ and $g_+(t) = 0$ for all $t \geq d$.

$$\begin{aligned}
1 - \lambda\hat{S}(z) &= \mathcal{F} \\
&= \mathcal{F}_+(z)\mathcal{F}_-(z) \\
&= \left(1 + \int_0^d e^{izt} g_+(t)dt\right)\left(1 + \int_{-d}^0 e^{izt} g_-(t)dt\right) \\
&= \left(1 + \int_{-\infty}^{\infty} e^{izt} g_+(t)dt\right)\left(1 + \int_{-\infty}^{\infty} e^{izt} g_-(t)dx\right) \\
&= 1 + \int_{-\infty}^{\infty} e^{izt} g_+(t)dt + \int_{-\infty}^{\infty} e^{izt} \int_{-\infty}^{\infty} g_-(t-s)\left[\delta + g_+\right](s)dsdt.
\end{aligned}$$

$$\begin{aligned}
-\lambda\hat{S}(z) &= \int_{-\infty}^{\infty} e^{izt} g_+(t)dt + \int_{-\infty}^{\infty} e^{izt}\left[\int_{-\infty}^{\infty} g_-(t-s)\delta(s)ds + \int_{-\infty}^{\infty} g_-(t-s)g_+(s)ds\right]dt \\
&= \int_{-\infty}^{\infty} e^{izt} g_+(t)dt + \int_{-\infty}^{\infty} e^{izt}\left[\int_{-\infty}^{\infty} g_-(x)\delta(t-x)dx + \int_{-\infty}^{\infty} g_-(t-s)g_+(s)ds\right]dt \\
&= \int_{-\infty}^{\infty} e^{izt} g_+(t)dt + \int_{-\infty}^{\infty} e^{izt}\left[\int_{-\infty}^{\infty} g_-(x)\delta(-(x-t))dx + \int_{-\infty}^{\infty} g_-(t-s)g_+(s)ds\right]dt \\
&= \int_{-\infty}^{\infty} e^{izt} g_+(t)dt + \int_{-\infty}^{\infty} e^{izt}\left[\int_{-\infty}^{\infty} g_-(x)\delta(x-t)dx + \int_{-\infty}^{\infty} g_-(t-s)g_+(s)ds\right]dt \\
&= \int_{-\infty}^{\infty} e^{izt} g_+(t)dt + \int_{-\infty}^{\infty} e^{izt}\left[g_-(t) + \int_{-\infty}^{\infty} g_-(t-s)g_+(s)ds\right]dt :
\end{aligned}$$

$$\int_{-\infty}^{\infty} e^{izt}\left[\lambda S(t) + g_+(t) + g_-(t) + \int_{-\infty}^{\infty} g_-(t-s)g_+(s)ds\right]dt \;=\; 0.$$

Hence, except in a zero measure set,

$$\lambda S(t) + g_+(t) + g_-(t) + \int_{-\infty}^{\infty} g_-(t-s)g_+(s)ds \;=\; 0.$$

Since $g_+(t) = 0$ for all $t \notin [0, d)$,

$$\lambda S(t) + g_+(t) + g_-(t) + \int_0^d g_-(t-s)g_+(s)ds \;=\; 0.$$

Given that $g_+(-x) = g_-(x)$,

$$\lambda S(t) \;=\; -g_+(t) - g_+(-t) - \int_0^d g_+(s)g_+(s-t)ds.$$

Definition 4.1.5 *Let us define the function Q as*

$$Q(t) = -\frac{1}{\lambda} g_+(t).$$

Therefore,

$$S(t) = Q(t) + Q(-t) - \lambda \int_0^d Q(s)Q(s-t)ds.$$

Suppose $t > 0$, then

$$S(t) = Q(t) - \lambda \int_t^d Q(s)Q(s-t)ds.$$

$$S(t) = Q(t) - \lambda \int_t^d Q(s)Q(s-t)ds$$

or if $x = t - s$, then

$$S(t) = Q(t) + \lambda \int_0^{t-d} Q(t-x)Q(-x)dx.$$

Remark 4.1.6 *By corollary 3.1.4, $\overline{\mathcal{F}_+}(y) = \mathcal{F}_+(-y)$.*

$$\overline{\mathcal{F}_+}(z) = \mathcal{F}_+(-z) \quad \textit{and} \quad \overline{\mathcal{F}_+ - 1}(z) = \mathcal{F}_+(-z) - 1,$$

in other words it is hermitian. It's well known that a function is real valued if and only if its Fourier transform is hermitian. Consequently, g_+ is real valued. Therefore, we can compute the derivative of Q with respect to a real variable.

$$\begin{aligned} -tc(t) &= S'(t) \\ &= Q'(t) + \lambda \left(Q(d)Q(d-t) + \int_0^{t-d} Q'(t-x)Q(-x)dx \right). \end{aligned}$$

Since $Q(d) = 0$,

$$-tc(t) = Q'(t) + \lambda \int_0^{t-d} Q'(t-x)Q(-x)dx.$$

Let $s = t - x$, then

$$-tc(t) = Q'(t) - \lambda \int_t^d Q'(s)Q(s-t)ds. \tag{4.8}$$

Since $\frac{1}{\mathcal{F}} = 1 + \lambda\hat{J}$,

$$\mathcal{F}_-^{-1}(y) = (1+\lambda\hat{J})\mathcal{F}_+(y). \tag{4.9}$$

Using corollary 2.2.28 $\mathcal{F}_-^{-1} \in \mathfrak{R}_-$, $\mathcal{F}_-^{-1} = 1 + \int_{-\infty}^{0} e^{iyt}p_-(t)dt$. Substituting the expression for $\mathcal{F}_-^{-1}$ and equation 4.7 in equation 4.9:

$$\begin{aligned}
1+\int_{-\infty}^{0} e^{iyt}p_-(t)dt &= \left(1+\lambda\int_{-\infty}^{\infty} J(t)e^{iyt}dt\right)\left(1+\int_{0}^{d} e^{iyt}g_+(t)dt\right)\\
\int_{-\infty}^{0} e^{iyt}p_-(t)dt &= \lambda\int_{-\infty}^{\infty} J(t)e^{iyt}dt + \left(\int_{-\infty}^{\infty}\left[\delta(t)+\lambda J(t)\right]e^{iyt}dt\right)\left(\int_{0}^{d} e^{iyt}g_+(t)dt\right)\\
\int_{-\infty}^{0} e^{iyt}p_-(t)dt &= \lambda\int_{-\infty}^{\infty} J(t)e^{iyt}dt + \int_{-\infty}^{\infty} e^{iyt}\int_{-\infty}^{\infty} g_+(s)\left[\delta(t-s)+\lambda J(t-s)\right]dsdt\\
\int_{-\infty}^{0} e^{iyt}p_-(t)dt &= \lambda\int_{-\infty}^{\infty} J(t)e^{iyt}dt + \int_{-\infty}^{\infty} e^{iyt}g_+(t)dt + \int_{-\infty}^{\infty} e^{iyt}\int_{-\infty}^{\infty}\lambda g_+(s)J(t-s)dsdt.
\end{aligned}$$

$$\int_{-\infty}^{\infty} e^{iyt}\left(-p_-(t)+\lambda J(t)+g_+(t)+\int_{-\infty}^{\infty}\lambda g_+(s)J(t-s)ds\right)dt = 0.$$

So, except in a zero measure set,

$$-p_-(t)+\lambda J(t)+g_+(t)+\int_{-\infty}^{\infty}\lambda g_+(s)J(t-s)ds = 0.$$

Since, if $t>0$, then $p_-(t)=0$:

$$\lambda J(t)+g_+(t)+\int_{-\infty}^{\infty}\lambda g_+(s)J(t-s)ds = 0 \quad t>0.$$

$$\begin{aligned}
J(t) &= -\frac{1}{\lambda}g_+(t) - \int_0^d g_+(s)J(t-s)ds\\
Q(t) = -\frac{1}{\lambda}g_+(t) &= Q(t)+\lambda\int_0^d Q(s)J(t-s)ds.
\end{aligned}$$

$$\begin{aligned}
-th(t) &= J'(t)\\
&= Q'(t)+\lambda\int_0^d Q(s)J'(t-s)ds\\
&= Q'(t)+\lambda\int_0^t Q(s)J'(t-s)ds+\lambda\int_t^d Q(s)J'(t-s)ds\\
&= Q'(t)-\lambda\int_0^t Q(s)(t-s)h(t-s)ds-\lambda\int_t^d Q(s)(-(t-s))h(-(t-s))(-1)ds\\
&= Q'(t)-\lambda\int_0^t Q(s)(t-s)h(t-s)ds-\lambda\int_t^d Q(s)(t-s)h(-(t-s))ds\\
&= Q'(t)-\lambda\int_0^d Q(s)(t-s)h(|t-s|)ds:
\end{aligned}$$

$$-th(t) = Q'(t) - \lambda \int_0^d Q(s)(t-s)h(|t-s|)ds \quad t > 0. \tag{4.10}$$

Equations 4.8 and 4.10 are the reformulation of the OZ equation, (4.5), which have been derived with a rigorous mathematical procedure, *where every step has been demonstrated*, in contrast to Baxter's procedure in reference [1], which has some unproved mathematical assertions.

In the next subsection we present an analytical solution to Eqs. (4.8) and (4.10).

4.1.2 Analytical solution for hard spheres

From equation 4.10, for all $t \in (0, d)$

$$\begin{aligned}
-th(t) &= t \\
&= Q'(t) - \lambda \int_0^d Q(s)(t-s)h(|t-s|)ds \\
&= Q'(t) + \lambda \int_0^d Q(s)(t-s)ds \\
&= Q'(t) + t\lambda \int_0^d Q(s)ds - \lambda \int_0^d sQ(s)ds.
\end{aligned}$$

Solving for $Q'(t)$,

$$\begin{aligned}
Q'(t) &= at + b, \\
a &= 1 - \lambda \int_0^d Q(s)ds \\
b &= \lambda \int_0^d sQ(s)ds.
\end{aligned}$$

Integrating,

$$Q(t) = \frac{a}{2}t^2 + bt + P.$$

Since $Q(d) = 0$,

$$P = -\frac{a}{2}d^2 - bd.$$

Wherefore,

$$\begin{aligned}
a &= 1-\lambda\int_0^d \left(\frac{a}{2}s^2+bs+P\right)ds \\
&= 1-\lambda\left(\frac{a}{6}s^3+\frac{b}{2}s^2+Ps\right)\Big|_0^d \\
&= 1-\lambda\left[\frac{a}{6}d^3+\frac{b}{2}d^2+Pd\right] \\
&= 1-\lambda\left[\frac{a}{6}d^3+\frac{b}{2}d^2-\frac{a}{2}d^3-bd^2\right] \\
&= 1+\lambda\left[\frac{a}{3}d^3+\frac{b}{2}d^2\right].
\end{aligned}$$

Simplifying, we obtain,

$$\left(1-\lambda\frac{d^3}{3}\right)a-\lambda\frac{d^2}{2}b=1. \tag{4.11}$$

Substituting in the other equation,

$$\begin{aligned}
b &= \lambda\int_0^d s\left(\frac{a}{2}s^2+bs+P\right)ds \\
&= \lambda\int_0^d \left(\frac{a}{2}s^3+bs^2+Ps\right)ds \\
&= \lambda\left(\frac{a}{8}s^4+\frac{b}{3}s^3+\frac{P}{2}s^2\right)\Big|_0^d \\
&= \frac{\lambda d^4}{8}a+\frac{\lambda d^3}{3}b+\frac{\lambda}{2}d^2\left(-\frac{a}{2}d^2-bd\right) \\
&= \frac{\lambda d^4}{8}a+\frac{\lambda d^3}{3}b-\frac{\lambda d^4}{4}a-\frac{\lambda d^3}{2}b \\
&= -\frac{\lambda d^4}{8}a-\frac{\lambda d^3}{6}b.
\end{aligned}$$

Hence,

$$\frac{\lambda d^4}{8}a+\left(1+\frac{\lambda d^3}{6}\right)b=0. \tag{4.12}$$

If ($\lambda = 2\pi\rho$), the linear system consisting of the two equations 4.11 and 4.12 is

$$\begin{bmatrix}\left(1-\frac{2\pi\rho d^3}{3}\right) & -\pi\rho d^2 \\ \frac{\pi\rho d^4}{4} & \left(1+\frac{\pi\rho d^3}{3}\right)\end{bmatrix}\begin{bmatrix}a\\ b\end{bmatrix}=\begin{bmatrix}1\\ 0\end{bmatrix}.$$

Solving it by hand or using Wolfram Mathematica, we find,

$$a = \frac{12(3+\rho\pi d^3)}{(6-\rho\pi d^3)^2} \quad and \quad b = \frac{-9\rho\pi d^4}{(6-\rho\pi d^3)^2}.$$

Simplifying the equations,

$$a = \frac{1+2\eta}{(1-\eta)^2} \quad and \quad b = -\frac{3}{2}\frac{d\eta}{(1-\eta)^2}$$

where $\eta = \frac{1}{6}\pi\rho d^3$. Let us remember that for all $t \in (0, d)$

$$Q(t) \;=\; \frac{a}{2}t^2 + bt - \frac{a}{2}d^2 - bd.$$

Substituting in equation 4.8,

$$\begin{aligned}
-tc(t) &= Q'(t) - \lambda \int_t^d Q'(s)Q(s-t)ds \quad t \in (0, d] \\
&= at + b - 2\pi\rho \int_t^d (as+b)\left(\frac{a}{2}(s-t)^2 + b(s-t) + P\right) ds \\
&= at + b - 2\pi\rho \int_t^d (as+b)\left(\frac{a}{2}(s^2 - 2st + t^2) + b(s-t) + P\right) ds \\
&= at + b \\
&- 2\pi\rho \int_t^d \left(\frac{1}{2}a^2s^3 - a^2s^2t + \frac{1}{2}a^2st^2 + abs^2 - abst + asP\right) ds - \\
&- 2\pi\rho \int_t^d \left(\frac{1}{2}abs^2 - abst + \frac{1}{2}abt^2 + b^2s - b^2t + bP\right) ds \\
&= at + b - 2\pi\rho \int_t^d \Big[As^3 + Bs^2 + Cs + D\Big] ds \\
&= at + b - 2\pi\rho \left(\frac{1}{4}As^4 + \frac{1}{3}Bs^3 + \frac{1}{2}Cs^2 + Ds\right)\Big|_t^d \\
&= at + 2\pi\rho \left(\frac{1}{4}At^4 + \frac{1}{3}Bt^3 + \frac{1}{2}Ct^2 + Dt\right) \\
&+ b - 2\pi\rho \left(\frac{1}{4}Ad^4 + \frac{1}{3}Bd^3 + \frac{1}{2}Cd^2 + Dd\right)
\end{aligned}$$

where

$$\begin{aligned}
A &= \frac{1}{2}a^2, \\
B &= -a^2t + ab + \frac{1}{2}ab = -a^2t + \frac{3}{2}ab, \\
C &= \frac{1}{2}a^2t^2 - abt + aP - abt + b^2 = \frac{1}{2}a^2t^2 - 2abt + aP + b^2, and \\
D &= \frac{1}{2}abt^2 - b^2t + bP.
\end{aligned}$$

Simplifying the result with Wolfram Mathematica,

$$\begin{aligned}-tc(t) &= \frac{-3(1-\eta)^2 d(6\eta - \pi\rho d^3)}{12(1-\eta)^4} + \frac{2(1+2\eta)(6[1-\eta]^2 - [-4+\eta]\pi\rho d^3)t}{12(1-\eta)^4} \\ &- \frac{3(2+\eta)^2\pi\rho d^2 t^2}{12(1-\eta)^4} + \frac{(1+2\eta)^2\pi\rho t^4}{12(1-\eta)^4},\end{aligned}$$

or

$$-tc(t) = \frac{12(1+2\eta)^2}{12(1-\eta)^4}t - \frac{6\left(1+\frac{\eta}{2}\right)^2\eta\frac{1}{d}}{(1-\eta)^4}t^2 + \frac{(1+2\eta)^2\eta\frac{1}{2d^3}}{(1-\eta)^4}t^4.$$

Given that $t > 0$,

$$c(t) = -\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{6\left(1+\frac{\eta}{2}\right)^2\eta\frac{1}{d}}{(1-\eta)^4}t - \frac{(1+2\eta)^2\eta\frac{1}{2d^3}}{(1-\eta)^4}t^3. \tag{4.13}$$

Which is the analytical expression for the Percus-Yevick approximation for hard spheres found by Wertheim in reference [9]. In the next section we generalize most of the results for one species, except the analytical solution, following the same ideas.

4.2 More than one species

The Ornstein-Zernike equation for m species,

$$h_{i,j}(|\mathbf{r}|) = c_{i,j}(|\mathbf{r}|) + \sum_{k=1}^{m}\rho_k \int c_{i,k}(|\mathbf{r'}|)h_{k,j}(|\mathbf{r}-\mathbf{r'}|)d\mathbf{r'}.$$

Suppose $c_{i,j}$ and $h_{i,j}$ are elements of L for all i and j. As for one species, using the Fourier transform:

$$\sqrt{\rho_i\rho_j}\hat{h}_{i,j}(\mathbf{k}) = \sqrt{\rho_i\rho_j}\hat{c}_{i,j}(\mathbf{k}) + \sum_{k=1}^{m}\sqrt{\rho_i\rho_k}\hat{c}_{i,k}(\mathbf{k})\sqrt{\rho_k\rho_j}\hat{h}_{k,j}(\mathbf{k}) \tag{4.14}$$

where $\hat{h}_{i,j}(\mathbf{k}) = \int_{\mathbb{R}^3} e^{i\langle\mathbf{r},\mathbf{k}\rangle}h_{i,j}(\mathbf{r})d\mathbf{r}$ and $\hat{c}_{i,j}(\mathbf{k}) = \int_{\mathbb{R}^3} e^{i\langle\mathbf{r},\mathbf{k}\rangle}c_{i,j}(\mathbf{r})d\mathbf{r}$. For each equation, we use the same method as in section 4.1:

$$\hat{h}_{i,j}(k) = \frac{4\pi}{k}\int_0^\infty h_{i,j}(R)Rsen(kR)dR \quad k \geq 0 \quad and \quad \hat{c}_{i,j}(k) = \frac{4\pi}{k}\int_0^\infty c_{i,j}(R)Rsen(kR)dR \quad k \geq 0$$

where $k = |\mathbf{k}|$. Let us define

$$J_{i,j}(x) = \begin{cases}\int_x^\infty th_{i,j}(t)dt & x \geq 0\\ \int_{-x}^\infty th_{i,j}(t)dt & x < 0\end{cases} \quad and \quad S_{i,j}(x) = \begin{cases}\int_x^\infty tc_{i,j}(t)dt & x \geq 0\\ \int_{-x}^\infty tc_{i,j}(t)dt & x < 0.\end{cases}$$

Similarly as in section 4.1, for all $k \in \mathbb{R}$

$$\hat{J}_{i,j}(k) = 2\int_0^\infty J_{i,j}(x)cos(kx)dx \quad and \quad \hat{S}_{i,j}(k) = 2\int_0^\infty S_{i,j}(x)cos(kx)dx.$$

Integrating by parts the expressions for $\hat{c}_{i,j}$ and $\hat{h}_{i,j}$, for all $k \geq 0$

$$\hat{h}_{i,j}(k) = 4\pi\int_0^\infty cos(kx)J_{i,j}(x)dx \quad and \quad \hat{c}_{i,j}(k) = 4\pi\int_0^\infty cos(kx)S_{i,j}(x)dx.$$

Wherefore,

$$\hat{h}_{i,j}(k) = 2\pi\hat{J}_{i,j}(k) \quad and \quad \hat{c}_{i,j}(k) = 2\pi\hat{S}_{i,j}(k).$$

Substituting in equation 4.14,

$$2\pi\sqrt{\rho_i\rho_j}\hat{J}_{i,j}(y) = 2\pi\sqrt{\rho_i\rho_j}\hat{S}_{i,j}(y) + (2\pi)^2\sum_{k=1}^{m}\sqrt{\rho_i\rho_k}\hat{S}_{i,k}(y)\sqrt{\rho_k\rho_j}\hat{J}_{k,j}(y).$$

Let us define the following matrix functions as

$$\mathfrak{J}_{i,j} = 2\pi\sqrt{\rho_i\rho_j}\hat{J}_{i,j}(y) \quad and \quad \mathfrak{S}_{i,j} = 2\pi\sqrt{\rho_i\rho_j}\hat{S}_{i,j}(y):$$

$$\mathfrak{J} = \mathfrak{S} + \mathfrak{S}\mathfrak{J}.$$

By inspection,

$$(I - \mathfrak{S})\mathfrak{J} = \mathfrak{S}.$$

Proposition 4.2.1 *The matrix function $(I - \mathfrak{S})$ is nonsingular.*

Proof.

$$\begin{aligned} & \mathfrak{J} = \mathfrak{S} + \mathfrak{S}\mathfrak{J} \\ \iff & I + \mathfrak{J} - \mathfrak{S} - \mathfrak{S}\mathfrak{J} = I \\ \iff & (I - \mathfrak{S})(I + \mathfrak{J}) = I. \end{aligned}$$

Therefore, $(I + \mathfrak{J})$ is the inverse of $(I - \mathfrak{S})$ and $(I - \mathfrak{S})$ is a nonsingular matrix. □

Proposition 4.2.2 *The matrix function $(I - \mathfrak{S})$ is positive definite.*

Proof. Since $(I - \mathfrak{S})(\infty) = I$ is nonsingular and positive definite at ∞, by proposition 3.2.11 $(I - \mathfrak{S})$ is positive definite. □

Using theorem 3.2.13, propostions 3.2.5 and 3.2.12: there exists $\mathfrak{F}_+(y) \in \mathfrak{R}^+_{(n\times n)}$ and $\mathfrak{F}_-(y) \in \mathfrak{R}^-_{(n\times n)}$ such that

1. $I - \mathfrak{S}(y) = \mathfrak{F}_+(y)\mathfrak{F}_-(y)$,

2. $\mathfrak{F}_-(y) = \mathfrak{F}_+^*(y)$,
3. $det(\mathfrak{F}_+(z)) \neq 0 \ \forall \ z \in \Pi_+$ and $det(\mathfrak{F}_-(z)) \neq 0 \ \forall \ z \in \Pi_-$,
4. $\mathfrak{F}_+(\infty) = I$ y $\mathfrak{F}_-(\infty) = I - \mathfrak{S}(\infty) = I$,
5. the factors admit analytic continuations, holomorphic in the interior and continuous on $\Pi_\pm$, and
6. for all $z \in \Pi_+$ $\mathfrak{F}_+(z) \neq \begin{bmatrix} 0 \end{bmatrix}$ and for all $z \in \Pi_-$ $\mathfrak{F}_-(z) \neq \begin{bmatrix} 0 \end{bmatrix}$.

Since $I - \mathfrak{S}(y)$ is symmetric, even and

$$I - \mathfrak{S}(y) \quad = \quad \mathfrak{F}_+(y)\mathfrak{F}_-(y),$$

then

$$I - \mathfrak{S}(y) \quad = \quad \mathfrak{F}_-^T(-y)\mathfrak{F}_+^T(-y)$$

where the super-index T denotes the transpose. Hence, $\mathfrak{F}_-^T(-y)$ and $\mathfrak{F}_+^T(-y)$ are candidates for a canonical factorization of $I - \mathfrak{S}(y)$. Doing a change of variable in the elements of $\mathfrak{F}_-^T(y)$ and $\mathfrak{F}_+^T(y)$, $\mathfrak{F}_-^T(-y) \in \mathfrak{R}_{(n\times n)}^+$ and $\mathfrak{F}_+^T(-y) \in \mathfrak{R}_{(n\times n)}^-$. Wherefore, they admit an analytical continuation, holomorphic in the interior and continuous on $\Pi_\pm$. Moreover, since $\mathfrak{F}'_-(-\infty) = I$, it is a left canonical factorization and by proposition 3.2.4.

$$\mathfrak{F}_+^T(-y) = \mathfrak{F}_+^*(y) \quad \mathfrak{F}_-^T(-y) = \mathfrak{F}_+(y).$$

Remark 4.2.3 *Each element of $\mathfrak{F}_+$ is an hermitian function, since*

$$\begin{aligned} & \mathfrak{F}_+^T(-y) = \mathfrak{F}_+^*(y) \\ \iff \quad & \mathfrak{F}_+(-y) = \overline{\mathfrak{F}_+(y)}. \end{aligned}$$

Remark 4.2.4 *Given that $\mathfrak{F}_+(\infty) = I = \mathfrak{F}_-(\infty)$,*

$$\begin{aligned} \forall \ k = j \quad \mathfrak{F}_+^{k,j}(y) \quad &= \quad 1 + \int_0^\infty g_+^{k,j}(t)e^{ity}dt, \\ \forall \ k \neq j \quad \mathfrak{F}_+^{k,j}(y) \quad &= \quad \int_0^\infty g_+^{k,j}(t)e^{ity}dt, \\ \forall \ k = j \quad \mathfrak{F}_-^{k,j}(y) \quad &= \quad 1 + \int_{-\infty}^0 g_-^{k,j}(t)e^{ity}dt, \quad \textit{and} \\ \forall \ k \neq j \quad \mathfrak{F}_-^{k,j}(y) \quad &= \quad \int_{-\infty}^0 g_-^{k,j}(t)e^{ity}dt. \end{aligned}$$

Furthermore, by remark 4.2.3 the functions $g_+^{k,j}$ and $g_-^{k,j}$ are real valued for all k and j in $\{1, 2, 3, ..., m\}$.

$$\delta_{i,j} - \mathfrak{S}_{i,j}(y) \;=\; \sum_{k=1}^{m} \mathfrak{F}_{+}^{i,k}(y)\mathfrak{F}_{-}^{k,j}(y).$$

If $i = j$, then

$$\begin{aligned}
1 - \mathfrak{S}_{i,i}(y) &= \sum_{k=1}^{m} \mathfrak{F}_{+}^{i,k}(y)\mathfrak{F}_{-}^{k,i}(y) \\
&= \mathfrak{F}_{+}^{i,i}(y)\mathfrak{F}_{-}^{i,i}(y) + \sum_{k\neq i} \mathfrak{F}_{+}^{i,k}(y)\mathfrak{F}_{-}^{k,i}(y) \\
&= \left(1 + \int_0^\infty e^{iyt} g_+^{i,i}(t)dt\right)\left(1 + \int_{-\infty}^0 e^{iyt} g_-^{i,i}(t)dt\right) \\
&+ \sum_{k\neq i}\left(\int_0^\infty e^{iyt} g_+^{i,k}(t)dt\right)\left(\int_{-\infty}^0 e^{iyt} g_-^{k,i}(t)dt\right) \\
&= 1 + \int_0^\infty e^{iyt} g_+^{i,i}(t)dt + \int_{-\infty}^0 e^{iyt} g_-^{i,i}(t)dt \\
&+ \int_{-\infty}^\infty e^{iyt} \int_{-\infty}^\infty g_+^{i,i}(s) g_-^{i,i}(t-s)dsdt \\
&+ \sum_{k\neq i}\int_{-\infty}^\infty e^{iyt} \int_{-\infty}^\infty g_+^{i,k}(s) g_-^{k,i}(t-s)dsdt \\
&= 1 + \int_0^\infty e^{iyt} g_+^{i,i}(t)dt + \int_{-\infty}^0 e^{iyt} g_-^{i,i}(t)dt \\
&+ \sum_{k=1}^{m}\int_{-\infty}^\infty e^{iyt} \int_{-\infty}^\infty g_+^{i,k}(s) g_-^{k,i}(t-s)dsdt.
\end{aligned}$$

Since $\mathfrak{S}_{i,j} = 2\pi\sqrt{\rho_i\rho_j}\hat{S}_{i,j}(y)$ and substituting in the last equation,

$$0 \;=\; \int_{-\infty}^\infty e^{iyt}dt\left[2\pi\sqrt{\rho_i\rho_j}S_{i,i}(t) + g_+^{i,i}(t) + g_-^{i,i}(t) + \sum_{k=1}^{m}\int_{-\infty}^\infty ds g_+^{i,k}(s)g_-^{k,i}(t-s)\right].$$

Then, except in a zero measure set,

$$0 = 2\pi\sqrt{\rho_i\rho_j}S_{i,i}(t) + g_+^{i,i}(t) + g_-^{i,i}(t) + \sum_{k=1}^{m}\int_{-\infty}^\infty ds g_+^{i,k}(s)g_-^{k,i}(t-s). \quad (4.15)$$

Definition 4.2.5 *Let* $\lambda_k = 2\pi\rho_k$,

$$Q_{i,j}^+ = -\frac{g_+^{i,j}}{2\pi\sqrt{\rho_i\rho_j}} \quad and \quad Q_{i,j}^- = -\frac{g_-^{i,j}}{2\pi\sqrt{\rho_i\rho_j}}.$$

Solving for $S_{i,i}$ in equation 4.15,

$$\begin{aligned}
S_{i,i}(t) &= Q_{i,i}^+(t) + Q_{i,i}^-(t) - \sum_{k=1}^{m}\lambda_k\int_{-\infty}^\infty dsQ_{i,k}^+(s)Q_{k,i}^-(t-s) \\
&= Q_{i,i}^+(t) + Q_{i,i}^-(t) - \sum_{k=1}^{m}\lambda_k\int_{t}^\infty dsQ_{i,k}^+(s)Q_{k,i}^-(t-s).
\end{aligned}$$

If $i \neq j$, then

$$
\begin{aligned}
-\mathfrak{S}_{i,j}(y) &= \sum_{k=1}^{m} \mathfrak{F}_{+}^{i,k}(y)\mathfrak{F}_{-}^{k,j}(y) \\
&= \mathfrak{F}_{+}^{i,i}(y)\mathfrak{F}_{-}^{i,j}(y) + \mathfrak{F}_{+}^{i,j}(y)\mathfrak{F}_{-}^{j,j}(y) + \sum_{k\neq i,j} \mathfrak{F}_{+}^{i,k}(y)\mathfrak{F}_{-}^{k,j}(y) \\
&= \left(1 + \int_0^\infty e^{iyt} g_{+}^{i,i}(t)dt\right) \int_{-\infty}^0 e^{iyt} g_{-}^{i,j}(t)dt \\
&+ \int_0^\infty e^{iyt} g_{+}^{i,j}(t)dt \left(1 + \int_{-\infty}^0 e^{iyt} g_{-}^{j,j}(t)dt\right) \\
&+ \sum_{k\neq i,j} \left(\int_0^\infty e^{iyt} g_{+}^{i,k}(t)dt\right)\left(\int_{-\infty}^0 e^{iyt} g_{-}^{k,j}(t)dt\right) \\
&= \int_0^\infty e^{iyt} g_{+}^{i,j}(t)dt + \int_{-\infty}^0 e^{iyt} g_{-}^{i,j}(t)dt \\
&+ \int_{-\infty}^\infty e^{iyt} \int_{-\infty}^\infty g_{+}^{i,i}(s) g_{-}^{i,j}(t-s) ds dt \\
&+ \int_{-\infty}^\infty e^{iyt} \int_{-\infty}^\infty g_{+}^{i,j}(s) g_{-}^{j,j}(t-s) ds dt \\
&+ \sum_{k\neq i,j} \int_{-\infty}^\infty e^{iyt} \int_{-\infty}^\infty g_{+}^{i,k}(s) g_{-}^{k,j}(t-s) ds dt \\
&= \int_0^\infty e^{iyt} g_{+}^{i,j}(t)dt + \int_{-\infty}^0 e^{iyt} g_{-}^{i,j}(t)dt \\
&+ \sum_{k=1}^{m} \int_{-\infty}^\infty e^{iyt} \int_{-\infty}^\infty g_{+}^{i,k}(s) g_{-}^{k,j}(t-s) ds dt.
\end{aligned}
$$

Since $\mathfrak{S}_{i,j} = 2\pi\sqrt{\rho_i\rho_j}\hat{S}_{i,j}(y)$ and substituting in the last equation,

$$
0 = \int_{-\infty}^\infty e^{iyt} dt \left[2\pi\sqrt{\rho_i\rho_j} S_{i,j}(t) + g_{+}^{i,j}(t) + g_{-}^{i,j}(t) + \sum_{k=1}^{m} \int_{-\infty}^\infty ds g_{+}^{i,k}(s) g_{-}^{k,j}(t-s)\right].
$$

Then, except in a zero measure set,

$$
0 = 2\pi\sqrt{\rho_i\rho_j} S_{i,j}(t) + g_{+}^{i,j}(t) + g_{-}^{i,j}(t) + \sum_{k=1}^{m} \int_{-\infty}^\infty ds g_{+}^{i,k}(s) g_{-}^{k,j}(t-s).
$$

Solving for $S_{i,j}$,

$$
\begin{aligned}
S_{i,j}(t) &= Q_{i,j}^{+}(t) + Q_{i,j}^{-}(t) - \sum_{k=1}^{m} \lambda_k \int_{-\infty}^\infty ds Q_{i,k}^{+}(s) Q_{k,j}^{-}(t-s) \\
&= Q_{i,j}^{+}(t) + Q_{i,j}^{-}(t) - \sum_{k=1}^{m} \lambda_k \int_{t}^\infty ds Q_{i,k}^{+}(s) Q_{k,j}^{-}(t-s).
\end{aligned}
$$

Comparing both equations, we get that for all i and j in $\{1, 2, 3, ..., M\}$

$$S_{i,j}(t) = Q^+_{i,j}(t) + Q^-_{i,j}(t) - \sum_{k=1}^{m} \lambda_k \int_t^\infty dsQ^+_{i,k}(s)Q^-_{k,j}(t-s). \tag{4.16}$$

Or in matrix notation,

$$S(t) = Q^+(t) + Q^-(t) - \int_t^\infty dsQ^+(s)Q^-(t-s). \tag{4.17}$$

For the equation relating J with Q^+,

$$\begin{aligned} & (I - \mathfrak{S})(I + \mathfrak{J}) = I \\ \Longleftrightarrow \quad & (I + \mathfrak{J}) = (I - \mathfrak{S})^{-1} \\ \Longleftrightarrow \quad & (I + \mathfrak{J}) = \mathfrak{F}_-^{-1}\mathfrak{F}_+^{-1} \\ \Longleftrightarrow \quad & (I + \mathfrak{J})\mathfrak{F}_+ = \mathfrak{F}_-^{-1} \\ \Longleftrightarrow \quad & \mathfrak{F}_+ + \mathfrak{J}\mathfrak{F}_+ = \mathfrak{F}_-^{-1}. \end{aligned}$$

$$\begin{aligned} \mathfrak{F}_+^{i,j} + \sum_{k=1}^{m} \mathfrak{J}_{i,k}\mathfrak{F}_+^{k,j} &= (\mathfrak{F}_-^{-1})_{i,j} \\ \mathfrak{F}_+^{i,j} + \sum_{k \neq j} \mathfrak{J}_{i,k}\mathfrak{F}_+^{k,j} + \mathfrak{J}_{i,j}\mathfrak{F}_+^{j,j} &= (\mathfrak{F}_-^{-1})_{i,j} : \end{aligned}$$

Substituting the values from $\mathcal{F}_+$ (remark 4.2.4), $\mathfrak{J}$ and doing something similar as in section 4.1:

$$0 = \int_{-\infty}^{\infty} e^{iyt} \left(g^+_{i,j}(t) + 2\pi\sqrt{\rho_i\rho_j} J_{i,j}(t) + \sum_{k=1}^{m} 2\pi\sqrt{\rho_i\rho_k} \int_{-\infty}^{\infty} J_{i,k}(t-s)g^+_{k,j}(s)ds - (g_-^{-1})_{i,j}(t) \right) dt.$$

Except in a zero measure set,

$$-2\pi\sqrt{\rho_i\rho_j}J_{i,j}(t) = g^+_{i,j}(t) + \sum_{k=1}^{m} 2\pi\sqrt{\rho_i\rho_k} \int_{-\infty}^{\infty} J_{i,k}(t-s)g^+_{k,j}(s)ds - (g_-^{-1})_{i,j}(t) :$$

for $t > 0$

$$J_{i,j}(t) = Q^+_{i,j}(t) + \sum_{k=1}^{m} \lambda_k \int_0^\infty J_{i,k}(t-s)Q^+_{k,j}(s)ds. \tag{4.18}$$

Or in matrix notation

$$J(t) = Q^+(t) + \int_0^\infty J(t-s)Q^+(s)ds. \tag{4.19}$$

Equations 4.17 and 4.19 are the generalizations of equations 4.8 and 4.10. In the next subsection we will see their form for the special case of hard spheres.

4.2.1 Direct correlation function for hard spheres

Suppose

$$U_{i,j}(x) = \begin{cases} \infty & x < \frac{d_i+d_j}{2} \\ 0 & x \geq \frac{d_i+d_j}{2}. \end{cases}$$

In other words we have

$$h_{i,j}(x) = -1 \quad \forall\, x \leq \frac{d_i+d_j}{2} \quad \textit{and} \quad c(x) = 0 \quad \forall x > \frac{d_i+d_j}{2}.$$

Remark 4.2.6 *For all* $|x| > \frac{d_i+d_j}{2}$ $\;S_{i,j}(x) = 0.$

Hence, $I - \mathfrak{S}_{i,j}$ is an entire function for all i and j in $\{1, 2, 3, ..., m\}$.

Proposition 4.2.7 $\mathfrak{F}_+^{i,j}$ *and* $\mathfrak{F}_-^{i,j}$ *are entire functions for all* i, j*, and*

$$I - \mathfrak{S}(z) = \mathfrak{F}_+(z)\mathfrak{F}_-(z) \quad z \in \mathbb{C}.$$

Proof. Since for all $z \in \Pi_+$ $det\,(\mathfrak{F}_+(z)) \neq 0$ and for all $z \in \Pi_-$ $det\,(\mathfrak{F}_-(z)) \neq 0$,

$$\mathfrak{G}_+(z) = \begin{cases} \mathfrak{F}_+(z) & 0 \leq Im(z) < \infty \\ (I - \mathfrak{S})\mathfrak{F}_-^{-1}(z) & -\infty < Im(z) < 0 \end{cases}$$

and

$$\mathfrak{G}_-(z) = \begin{cases} (I - \mathfrak{S})\mathfrak{F}_+^{-1}(z) & 0 < Im(z) < \infty \\ \mathfrak{F}_-(z) & -\infty < Im(z) \leq 0. \end{cases}$$

Given that $\mathfrak{F}_+$ is continuous on Π_+, $(I - \mathfrak{S})\mathfrak{F}_-^{-1}$ is continuous on Π_-. In the intersection they are equal, then by the pasting lemma $\mathfrak{G}_+$ is continuous on $\mathbb{C}$. Similarly, $\mathfrak{G}_-$ is continuous in $\mathbb{C}$. Given that $\mathfrak{F}_+$ is holomorphic in the interior of Π_+ and $(I - \mathfrak{S})\mathfrak{F}_-^{-1}$ is holomorphic in the interior of Π_-, $\mathfrak{G}_+$ is holomorphic on $\mathbb{C} - \{z \in \mathbb{C} \mid Im(z) = 0\}$. Using lemma 2.1.4 or a similar argument to its demonstration, we get that $\mathfrak{G}_+$ and $\mathfrak{G}_-$ are entire.

Since $\mathfrak{G}_+$ has the same characteristics that $\mathfrak{F}_+$ on Π_+ and $\mathfrak{G}_-$ the same characteristics that $\mathfrak{F}_-$ on Π_-, then it is a canonical factorization of $I - \mathfrak{S}$ in the real line. By the uniqueness, we have that $\mathfrak{F}_+ = \mathfrak{G}_+$ and $\mathfrak{F}_- = \mathfrak{G}_-$. Therefore, $\mathfrak{F}_+$ and $\mathfrak{F}_-$ are entire, and by how we defined $\mathfrak{G}_-$ and $\mathfrak{G}_+$, $(I - \mathfrak{S}) = \mathfrak{F}_+\mathfrak{F}_-$ on $\mathbb{C}$. $\square$

We want to find similar equations as in the one species case, we will continue with the proofs of auxiliary propositions used in the demonstration of theorem 4.2.12.

Proposition 4.2.8 *There exists $A_{i,j} > 0$ such that for all $z \in \mathbb{C}$*

$$\mathfrak{F}_+^{i,j}(z) \leq A_{i,j} e^{\frac{d_1+d_i}{2}|Im(z)|}.$$

Proof. Let $\mathfrak{F} = I - \mathfrak{S}$.

$$\mathfrak{F} = \mathfrak{F}_+ \mathfrak{F}_-.$$

$$\mathfrak{F}_{i,j} = \sum_{k=1}^{m} \mathfrak{F}_+^{i,k} \mathfrak{F}_-^{k,j}.$$

Fixing i, we get the following system of linear equations,

$$\begin{aligned}
\mathfrak{F}_{i,1} &= \sum_{k=1}^{m} \mathfrak{F}_+^{i,k} \mathfrak{F}_-^{k,1} \\
\mathfrak{F}_{i,2} &= \sum_{k=1}^{m} \mathfrak{F}_+^{i,k} \mathfrak{F}_-^{k,2} \\
&\vdots \\
\mathfrak{F}_{i,M} &= \sum_{k=1}^{m} \mathfrak{F}_+^{i,k} \mathfrak{F}_-^{k,M}.
\end{aligned}$$

It is equivalent to

$$Y = \mathfrak{F}_- X$$

where

$$Y = \begin{bmatrix} \mathfrak{F}_{i,1} \\ \mathfrak{F}_{i,2} \\ \vdots \\ \mathfrak{F}_{i,m} \end{bmatrix} \quad and \quad X = \begin{bmatrix} \mathfrak{F}_+^{i,1} \\ \mathfrak{F}_+^{i,2} \\ \vdots \\ \mathfrak{F}_+^{i,m}. \end{bmatrix}$$

Using Cramer's rule,

$$X_l = \frac{det\left(\begin{bmatrix} \mathfrak{F}_-^1 & \dots & \mathfrak{F}_-^{l-1} & Y & \mathfrak{F}_-^{l+1} & \dots & \mathfrak{F}_-^m \end{bmatrix}\right)}{det(\mathfrak{F}_-)}.$$

Let $z \in \Pi_-$. Since $det(\mathfrak{F}_-) \in \mathfrak{R}_-$ and $\forall z \in \Pi_-$ $det(\mathfrak{F}_-) \neq 0$, by theorem 2.2.28 $\frac{1}{det(\mathfrak{F}_-)} \in \mathfrak{R}_-$. Given that $\mathfrak{R}_-$ is a ring and by properties of the determinant,

$$det\left(\begin{bmatrix} \mathfrak{F}_-^1 & \dots & \mathfrak{F}_-^{l-1} & Y & \mathfrak{F}_-^{l+1} & \dots & \mathfrak{F}_-^m \end{bmatrix}\right) = \sum_{k=1}^{m} \mathfrak{F}_{i,k} a_k$$

where $a_k \in \mathfrak{R}_-$. Again, since $\mathfrak{R}_-$ is a ring, $b_k = \frac{a_k}{det(\mathfrak{F}_-)} \in \mathfrak{R}_-$ and

$$\mathfrak{F}_+^{i,l} = X^l \quad = \quad \sum_{k=1}^{m} b_k \mathfrak{F}_{i,k}. \tag{4.20}$$

Using proposition 3.1.8, there exists $A > 0$ such that for all $z \in \Pi_-$

$$|\mathfrak{F}_{i,k}(z)| \leq A_k e^{\frac{d_i+d_k}{2}|Im(z)|}.$$

Since we ordered the species so that $d_1 \geq d_k$,

$$\mathfrak{F}_+^{i,l} \leq B_{i,l} e^{\frac{d_1+d_i}{2}|Im(z)|}$$

where $B_{i,l} = Max(A_k)_{k=1}^m$. By proposition 2.2.21, there exists $M_{i,l} > 0$ such that

$$\mathfrak{F}_+^{i,l} \leq M_{i,l} :$$

if $A_{i,l} = Max(M_{i,l}, B_{i,l})$, then for all $z \in \mathbb{C}$

$$\mathfrak{F}_+^{i,l} \leq A_{i,l} e^{\frac{d_1+d_i}{2}|Im(z)|}.$$

□

Definition 4.2.9 *For hard spheres in the short-range,* **two species are the same if they have the same diameter**.

Remark 4.2.10 *In our model the only parameters we encounter are the diameter of particles and the number of particles per unit of volume. Hence, we can add the densities and take as the same species two particles with the same diameter. We will use this fact in the next proposition's proof.*

Proposition 4.2.11 *For all i and j in $\{1, 2, 3, ..., m\}$ $g_+^{i,j}$ is not the zero function and $g_+^{i,j}$ is not the zero function except in a measure zero set.*

Proof. Let $i, j \in \{1, 2, 3, ..., m\}$. We are going to do the proof by contradiction. Suppose $g_+^{i,j}$ is the zero function or $g_+^{i,j}$ is the zero function except in a measure zero set:

$$\mathfrak{F}_+^{i,j} = \delta_{i,j}.$$

Substituting in equation 4.20,

$$\delta_{i,j} \quad = \quad \sum_{k=1}^{m} b_k \mathfrak{F}_{i,k}. \tag{4.21}$$

Using proposition 3.1.8, there exists A_k such that

$$\mathfrak{F}_{i,k} \leq A_k e^{\frac{d_i+d_k}{2}|Im(z)|}.$$

Hence, for an appropriate $A > 0$, for all $z \in \Pi_-$

$$b_1\mathfrak{F}_{i,1} \quad = \quad \delta_{i,j} - \sum_{k\neq 1} b_k \mathfrak{F}_{i,k} \leq Ae^{\frac{d_i+d_2}{2}|Im(z)|}.$$

Let $y < 0$. Since b_1 is bounded on Π_-,

$$\begin{aligned} sup\left(\left\{\frac{ln|b_1\mathfrak{F}_{i,1}(-ir)|}{r}\middle| r \geq -y\right\}\right) &\leq sup\left(\left\{\frac{lnA}{r}\middle| r\geq -y\right\}\right) + \frac{d_i+d_2}{2} \\ &= \frac{lnA}{-y} + \frac{d_i+d_2}{2}. \end{aligned}$$

Taking the infimum on both sides,

$$\begin{aligned} &\limsup_{r\to\infty} \frac{ln|\mathfrak{F}_{i,1}(-ir)|}{r} \leq 0 + \frac{d_i+d_2}{2} \\ \iff \quad &\limsup_{r\to\infty} \frac{ln|b_1\mathfrak{F}_{i,1}(-ir)|}{r} \leq \frac{d_i+d_2}{2}. \end{aligned}$$

By [25],

$$\limsup_{r\to\infty} \frac{ln|b_1\mathfrak{F}_{i,1}(-ir)|}{r} = \frac{d_i+d_1}{2} :$$

$$\frac{d_i+d_1}{2} \leq \frac{d_i+d_2}{2}.$$

Which is a contradiction, since $d_1 > d_2$. □

Theorem 4.2.12 *For all $k, j \in \{1, 2, 3, ..., m\}$*

$$\begin{aligned} \mathfrak{F}_+^{k,j}(y) &= \delta_{k,j} + \int_0^{\frac{d_1+d_k}{2}} g_+^{k,j}(t)e^{ity}dt \quad and \\ \mathfrak{F}_-^{k,j}(y) &= \delta_{i,j} + \int_{-\frac{d_1+d_k}{2}}^0 g_-^{k,j}(t)e^{ity}dt. \end{aligned}$$

Furthermore, for all $t \notin \left(0, \frac{d_1+d_k}{2}\right)$ $g_+^{k,j}(t) = 0$ and for all $t \notin \left(-\frac{d_1+d_k}{2}, 0\right)$ $g_-^{k,j}(t) = 0$.

Proof. Using propositions 3.1.13, 4.2.8 and 4.2.11, we get the result for $\mathfrak{F}_+^{k,j}$. Given that $\mathfrak{F}_-^T(-y) = \mathfrak{F}_+(y)$, we get it for $\mathfrak{F}_-^{k,j}$. $\square$

Using the last theorem, equations 4.18 and 4.17 become,

$$S_{i,j}(t) = Q_{i,j}^+(t) + Q_{i,j}^-(t) - \sum_{k=1}^{m} \lambda_k \int_t^{\frac{d_1+d_i}{2}} ds Q_{i,k}^+(s) Q_{k,j}^-(t-s) \tag{4.22}$$

$$J_{i,j}(t) = Q_{i,j}^+(t) + \sum_{k=1}^{m} \lambda_k \int_0^{\frac{d_1+d_k}{2}} J_{i,k}(t-s) Q_{k,j}^+(s) ds. \tag{4.23}$$

Differentiating with respect to $t > 0$ (we have already proved they are real valued) and if $Q_{i,j}^+ = Q_{i,j}$, as in section 4.1,

$$-tc_{i,j}(t) = Q'_{i,j}(t) - \sum_{k=1}^{m} \lambda_k \int_t^{\frac{d_1+d_i}{2}} ds Q'_{i,k}(s) Q_{j,k}(s-t), \tag{4.24}$$

and

$$-th_{i,j}(t) = Q'_{i,j}(t) + \sum_{k=1}^{m} \lambda_k \int_0^{\frac{d_1+d_k}{2}} (t-s) h_{i,k}(|t-s|) Q_{k,j}(s) ds. \tag{4.25}$$

Equations 4.24 and 4.25 are the result of assuming a hard spheres potential in equations 4.17 and 4.19. *Together, these equations are a new, useful, reformulation of the PY equation for a mixture of hard spheres.* Let us refer to these equations as the m-species Rivera-Baxter (mRB) equations. Unfortunately, following Baxter's approach [1], we were not able to solve them analytically, due to what we think is an inconsistency in his derivation. However, *in chapter 6 we will validate our new mRB integral equations using finite element computational techniques [26, 27, 28] for a particular case, presented in chapter 5.*

1. In chapter 5 we will obtain the total and direct correlation functions for a system of hard spheres using molecular dynamics and finite element techniques. The systems comprise particles of diameters $R_1 = 6\text{Å}$ and $R_2 = 2\text{Å}$, and molar concentrations of $\rho_1 = 1M$ and $\rho_2 = 1M$. We will compare our finite element results with our molecular dynamics simulations, so we can use the finite element total and direct correlation functions as our benchmark.

2. In chapter 6, section 6.1, we will discuss and compare Hiroike's analytical expression for the direct correlation functions [29] with our finite element results from chapter 5.

3. In section 6.2, we will use Hiroike's analytical direct correlation functions presented in chapter 6 to numerically obtain the $Q_{i,j}(r)$ functions and validate the integral equations 4.24 and 4.25.

4. Finally, in section 6.3 we will follow article [2] and compute Baxter's direct correlation functions. Then, we will obtain their corresponding total correlations functions, using the Ornstein-Zernike equations, and we will compare the direct correlations functions to Hiroike's analytical solutions and our results from finite element computations.

Chapter 5

Numerical simulations

We want to numerically test the short range direct correlation functions proposed in references [2, 10], chapter 6. For this reason we developed a molecular dynamics computer simulation program, and ran it for some specific parameters. The basis of this technique can be consulted in reference [3]. Additionally, we wrote a fortran 90 program to numerically solve, using a finite element method [26], the Percus-Yevick integral equations:

$$\begin{aligned}
f_{i,j}(|r|) &= c_{i,j}(|r|) \quad 0 < |r| \leq d_{i,j} \\
f_{i,j}(|r|) &= h_{i,j}(|r|) \quad d_{i,j} < |r| \\
-1 &= f_{i,j}(|r|) + \sum_{k=1}^{m} \rho_k \int f_{i,k}(|r - r_k|) f_{k,j}(|r_k|) dr_k \quad 0 < |r| \leq d_{i,j} \\
f_{i,j}(|r|) &= \sum_{k=1}^{m} \rho_k \int f_{i,k}(|r - r_k|) f_{k,j}(|r_k|) dr_k d_{i,j} < |r|,
\end{aligned}$$

obtained from the Ornstein-Zernike equations.

5.1 Molecular dynamics

Molecular dynamics is a computer experiment for a given model fluid, where the Newton's equations of motion are solved, as a function of time, for a number of particles interacting through a simplified model of a given real system. Let us suppose that these particles are hard spheres. Hence, the kinetic energy is conserved and there are no long-range inter-molecular forces. Given those suppositions, we wrote a program to take pictures–we will clarify later–of the fluid's particles every time a collision occurred. For that, we needed to identify the closest collision to occur given the position and velocities of the particles at a given time. Then, advance the system until that collision to take the picture and compute the new velocity vectors of the particles colliding. Again, we look for the closest collision and repeat the process. It's computationally expensive, because we need to compute all the possible collisions between an enormous number of particles, then find the one that will occur first, while we take care of not having overlaps between particles. Now, let us clarify what we mean by taking pictures. Each time a collision occurs we position ourselves in one specific particle and we count how many particles of each species are at a distance r from it. Immediately, we store that data, we do it for all the system's particles and we use it to compute the radial distribution function. As for the initial conditions we assumed the particles were in a lattice, using a Maxwell velocity distribution function we randomly assigned velocity vectors to the particles in accordance with the system's temperature and finally we let the system evolve for a convenient number of collisions.

In this thesis, we will perform a molecular dynamics simulation for a system of two species of hard spheres and calculate their total correlation functions, $h_{i,j}(r)$. We use periodic boundary conditions at the frontier, that is, every time a particle leaves the box; another particle enters in an adequate way. We will use these results to test our analytical solutions of the PY equation for hard spheres. We assume a system comprised by two species, the particles are hard spheres with no long-range inter-molecular forces. Their diameters are $d_1 = 6\text{Å}$ and $d_2 = 2\text{Å}$, and their molar concentrations are $\rho_1 = 1M$ and $\rho_2 = 1M$. We used a box with sides equal to 104.43Å and 686 particles for each species. In figures 5.1, 5.2, and 5.3 we present our results for $h_{1,1}(r)$, $h_{1,2}(r)$, $h_{2,1}(r)$ and $h_{2,2}(r)$, after $600,000$, $1,000,000$, $3,000,000$ and $6,000,000$ collisions. Of course, the larger the number of collisions allowed in the simulation, the smoother are the calculated correlation functions. All the total correlation functions exhibit the same qualitative behavior, i.e., $h_{i,j}(r)$ has a first maximum at the inter-particles contact value, $r = r_c$, while it tends to zero for $r \to \infty$, where $r_c \equiv (d_i + d_j)/2$. This behavior reveals the existence of effective liquid cohesion forces, although no attractive forces are present in our model. When the number of particles is lowered to a concentration of the order of that of an ideal gas, the total correlation becomes equal to $0, \forall r \geq (d_i + d_j)/2$ (not shown), showing that this effective many-body attraction is an entropy effect.

In Fig. 5.1 we show the total correlation distribution function, $h_{1,1}(r)$, as a function of the inter-particles distance r among particles of species 1, i.e., the larger particles in the system with $d_1 = 3d_2$. At the particles contact point, $r_c \equiv (d_1 + d_1)/2 = 6\text{Å}$, $h_{1,1}(r_c) = 0.2076$, while it shows a first minimum of $h_{1,1}(r = 11.71) = -8.63x10^{-3}$. In particles diameters, this minimum is

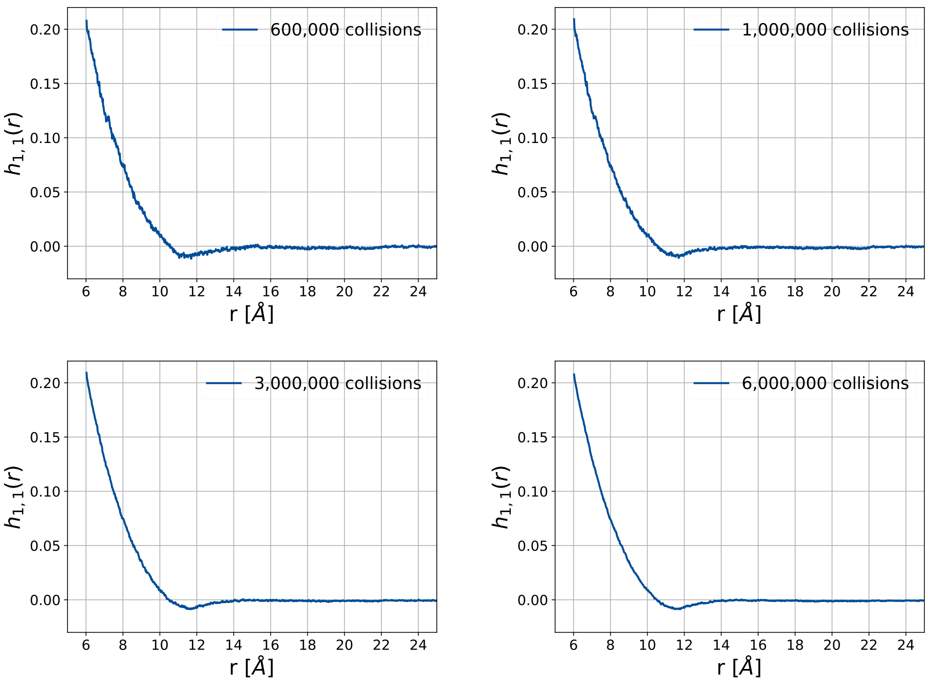


Figure 5.1: Total correlation function, $h_{1,1}(r)$, among particles of species 1 as a function of the inter-particles distance, r. The system is a two species hard spheres fluid with temperature $T = 298K$. Their diameters and molar concentrations are $d_1 = 6$Å and $d_2 = 2$Å, and $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively. The results were obtained through a molecular dynamics simulation. The different plots correspond to an increasing number of collisions.

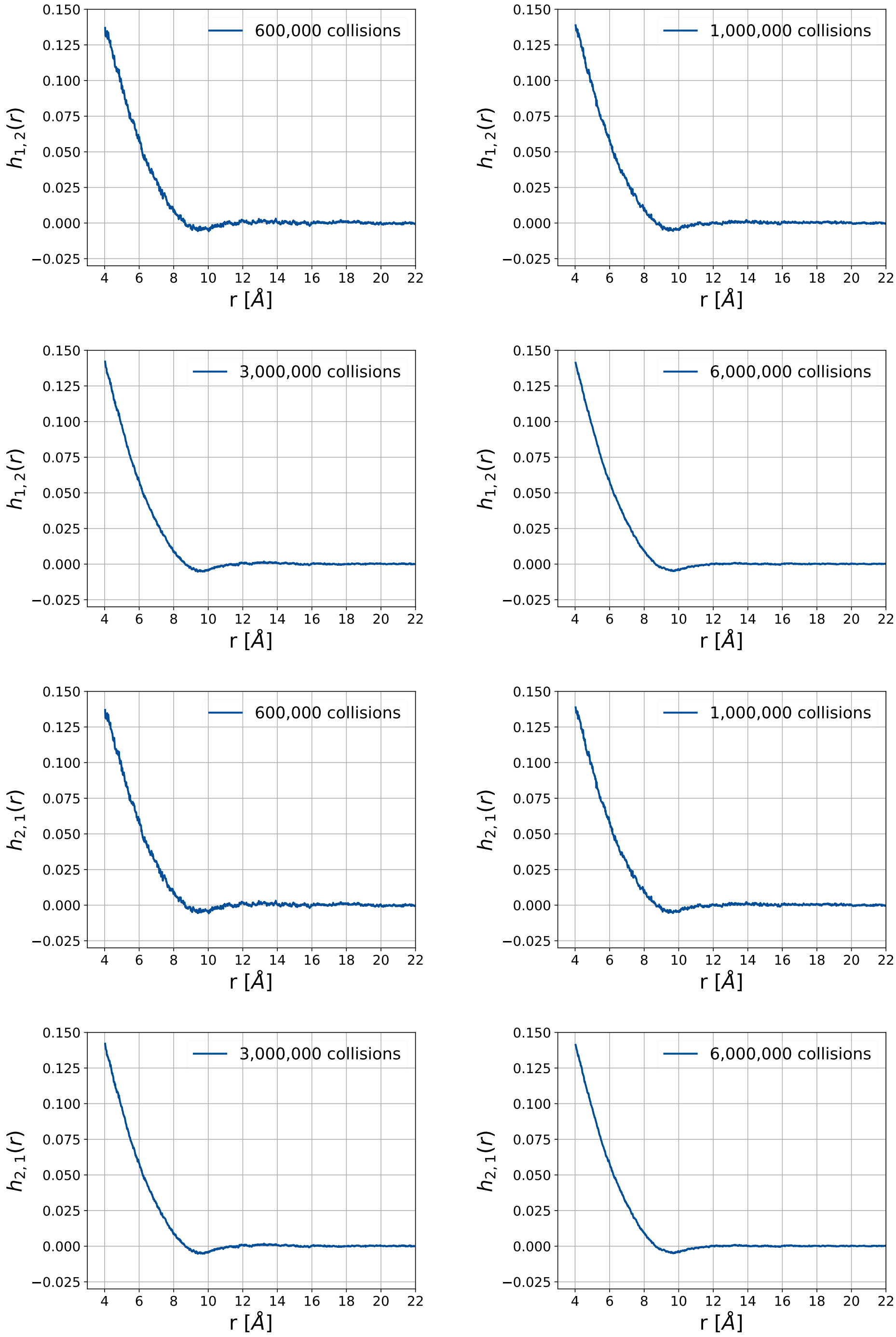


Figure 5.2: Total correlation functions, $h_{1,2}(r)$ and $h_{2,1}(r)$, between particles of species 1 and 2, as a function of the inter-particles distance, r. The system parameters are the same as in Fig. 5.1.

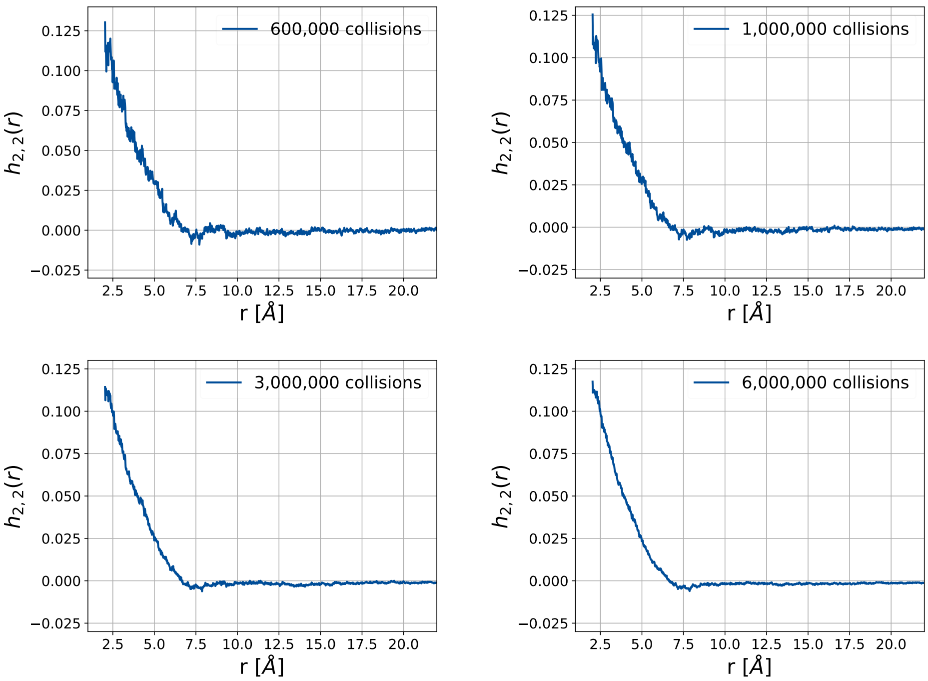


Figure 5.3: Total correlation function, $h_{2,2}(r)$, among particles of species 2, as a function of the inter-particles distance, r. The system parameters are the same as in Figs. 5.1 and 5.2.

located at $r = 1.952d_1$ (or $r = 5.85d_2$) from the center of the reference central particle, indicating that after a first layer of adsorbed hard spheres, the particles concentration decreased to an under-bulk concentration. Then, it becomes a bit higher than one. Hence this total correlation shows an oscillatory behavior, as has been long recognized in the literature [5, 8].

In Fig. 5.2 we depict the $h_{1,2}(r)$ and $h_{2,1}(r)$ total correlation functions. Of course $h_{1,2}(r) = h_{2,1}(r)$. We show both here to exhibit the consistency of our MD calculations. For this case $r_c \equiv (d_1 + d_2)/2 = 4$Å, and $h_{1,2}(r_c) = 0.1413$, while it shows a minimum of $h_{2,1}(r = 9.69) = -5.01x10^{-3}$. In particles diameters, this minimum is located at $r = 1.615d_1$ (or $r = 4.845d_2$), indicating a particles depletion below their bulk value a bit after the contact between two particles of species 1.

Finally, in In Fig. 5.3, we depict the $h_{2,2}(r)$ total correlation function. Here, $r_c \equiv (d_2+d_2)/2 = 2$Å, and $h_{2,2}(r_c) = 0.1175$, while it shows a minimum of $h_{2,2}(r = 7.87) = -6.12x10^{-3}$. In particles radius, this minimum is located at $r = 1.312d_1$ (or $r = 3.935d_2$), indicating a particles depletion below their bulk value a in-between two particles of species 2. Higher contact values, together with longer location of the minimum implies an increasing available system volume, thus an increase in its entropy.

In the next section we will numerically solve the OZ equation with the PY approximation for the direct correlation function, with a finite elements method, and compare these solutions with our MD simulations.

5.2 Finite element

We want to approximate the total and direct correlation functions. Let us define a node as an element of the function's domain we want to approximate. The finite element method we employ assumes that the functions we seek can be expressed as a linear combination of polynomial basis functions, ϕ_l, which at their central node take the value of one, and in the other nodes their value is zero. For our numerical computations we assumed quadratic basis functions. For the first node, we use a geometric transformation, $t(x)$, that sends the second node to the origin, the first node to -1 and the third node to 1. Then,

$$\phi_l(t) = \begin{cases} \frac{t(t-1)}{2} & |t| \leq 1 \\ 0 & t > 1. \end{cases}$$

For the even nodes, we use a transformation, $t(x)$, that sends the central node to the origin and the adjacent nodes to -1 and 1. Then,

$$\phi_l(t) = \begin{cases} \frac{1-t^2}{2} & |t| \leq 1 \\ 0 & t > 1. \end{cases}$$

For the odd nodes, we use two transformations, the first one sends $k-2$ to -1, $k-1$ to 0 and k to 1. The second one sends k to -1, $k+1$ to 0 and $k+2$ to 1. Then, if $x \leq k$,

$$\phi_l(t) = \begin{cases} \frac{t(t+1)}{2} & |t| \leq 1 \\ 0 & t > 1. \end{cases}$$

Else,

$$\phi_l(t) = \begin{cases} \frac{t(t-1)}{2} & |t| \leq 1 \\ 0 & t > 1. \end{cases}$$

Finally, for the last node, we use a transformation, $t(x)$, that sends the $L-2$ node to -1, $L-1$ to 0 and L to 1. Then,

$$\phi_l(t) = \begin{cases} \frac{t(t+1)}{2} & |t| \leq 1 \\ 0 & t > 1. \end{cases}$$

Substituting the basis functions on the Percus-Yevick integral equations; they become a system of linear equations, where the unknowns are the scalar coefficients. For m species the OZ equation is

$$h_{i,j}(r_i, r_j) = c_{i,j}(r_i, r_j) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(r_i, r_k) h_{k,j}(r_k, r_j) dr_k.$$

Hence, in terms of the inter-particles distance,

$$h_{i,j}(|r_i - r_j|) = c_{i,j}(|r_i - r_j|) + \sum_{k=1}^{m} \int c_{i,k}(|r_i - r_k|) h_{k,j}(|r_k - r_j|) dr_k.$$

If we set particle i at the origin,

$$h_{i,j}(|r_j|) = c_{i,j}(|r_j|) + \sum_{k=1}^{m} \int c_{i,k}(|r_k|) h_{k,j}(|r_k - r_j|) dr_k.$$

Taking coordinates such that particle j is at the z axis,

$$h_{i,j}(z) = c_{i,j}(z) + \sum_{k=1}^{m} \int c_{i,k}(|r_k|) h_{k,j}(|r_k - \vec{z}|) dr_k.$$

Changing to spherical coordinates, $(s, \theta, \varphi) \mapsto t(cos\theta sen\varphi, sen\theta sen\varphi, cos\varphi)$, we obtain

$$\begin{aligned} h_{i,j}(z) &= c_{i,j}(z) + \sum_{k=1}^{m} 2\pi\rho_k \int_0^\infty \int_0^\pi h_{k,j}\left(\sqrt{z^2+t^2-2ztcos\varphi}\right) c_{i,k}(t) t^2 sen\varphi d\varphi dt \\ &= c_{i,j}(z) + \sum_{k=1}^{m} \frac{2\pi\rho_k}{z} \int_0^{\frac{R_i+R_k}{2}} dt c_{i,k}(t) t \int_{|z-t|}^{|z+t|} ds h_{k,j}(s)\, s. \end{aligned}$$

Now, with the Percus-Yevick approximation, given by,

$$f_{i,j}(z) = \begin{cases} c_{i,j}(z) & z \le \frac{R_i+R_j}{2} \\ h_{i,j}(z) & z > \frac{R_i+R_j}{2}. \end{cases}, \quad C_{i,j}(z) = \begin{cases} f_{i,j}(z) & z \le \frac{R_i+R_j}{2} \\ 0 & z > \frac{R_i+R_j}{2}, \end{cases},$$

$$and \;\; H_{i,j}(z) = \begin{cases} -1 & z \le \frac{R_i+R_j}{2} \\ f_{i,j}(z) & z > \frac{R_i+R_j}{2}. \end{cases}$$

The OZ equation becomes:

1. For all $0 < |r| \le \frac{R_i+R_j}{2}$,

$$-1 = f_{i,j}(|r|) + \sum_{k=1}^{m} \frac{2\pi\rho_k}{z} \int_0^{\frac{R_i+R_k}{2}} dt C_{i,k}(t) t \int_{|z-t|}^{|z+t|} ds H_{k,j}(s)\, s.$$

2. For all $\frac{R_i+R_j}{2} < |r|$,

$$f_{i,j}(|r|) = \sum_{k=1}^{m} \frac{2\pi\rho_k}{z} \int_0^{\frac{R_i+R_k}{2}} dt C_{i,k}(t) t \int_{|z-t|}^{|z+t|} ds H_{k,j}(s)\, s.$$

From the last system we make the following observations. We are looking for linear combinations of ϕ_l such that,

$$f_{i,j} \simeq \sum_{l=1}^{n} w_{i,j}^l \phi_l(z),$$

where $w_{i,j}$ are scalars and n is the number of nodes in our mesh. Therefore, our system of integral equations becomes a linear system of algebraic equations, whose unknowns are $w_{i,j}$. It is not a simple task to obtain the system given the diameters of the particles, since, the range of the integrals and the functions C and H depend on the particles' diameters. For example, the system won't be the same when the diameters of the particles are similar or when one diameter is 10 times the other.

We used the Newton-Rhapson method to solve this system of equations. In figure 5.4 we compare the different total correlation functions, $h_{i,j}(r)$, obtained through our finite elements solution of the PY integral equations, with those calculated in our MD simulations. On the other hand, since MD does not give directly the direct correlation function, we have substituted our MD results for the total correlation functions into the PY integral equations to compute hybrid direct correlation functions, and compare them with those obtained directly from the full solution of the PY integral equation. We tested the consistency of both, the finite elements and MD calculations. In figure 5.5 we show a comparison of the different $c_{i,j}(r)$ obtained from the PY integral equation with these hybrid direct correlation functions. As it can be appreciated in these figures the finite element results show a good agreement with MD simulations; *we would like to highlight that we got an excellent agreement due to the fact we are working with low density values.* In figure 5.6 we highlight the direct correlation functions' symmetry using only finite element calculations.

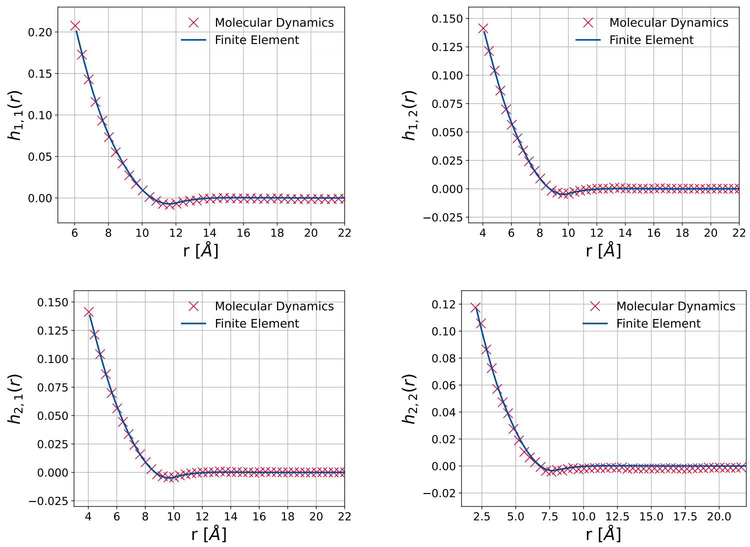


Figure 5.4: Total correlation functions, $h_{i,j}(r)$ such that $i, j \in \{1, 2\}$, calculated with molecular dynamics and finite element. The system is a two species hard spheres fluid, with temperature, $T = 298K$. Their diameters and molar concentrations are $d_1 = 6$Å and $d_2 = 2$Å, and $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively.

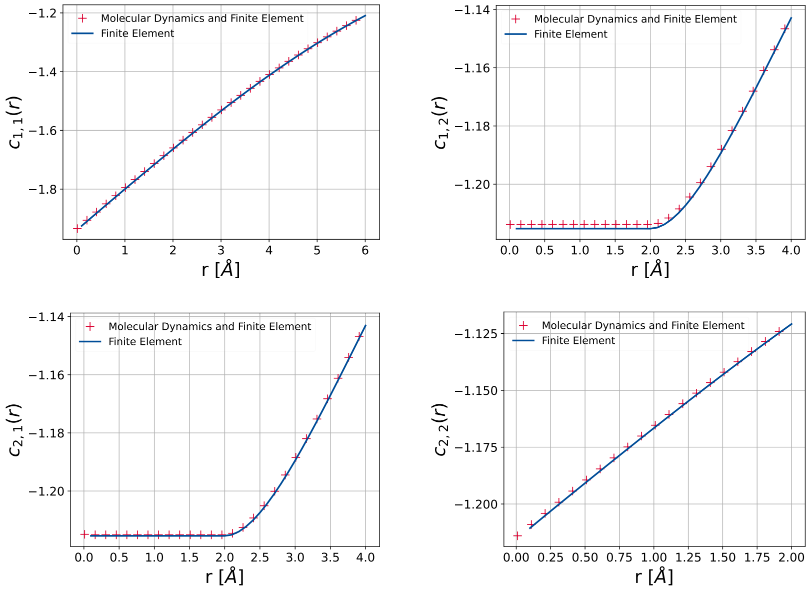


Figure 5.5: Direct correlation functions, $c_{i,j}(r)$ such that $i, j \in \{1, 2\}$, calculated with molecular dynamics and finite element. The system is a two species hard spheres fluid, with temperature, $T = 298K$. Their diameters and molar concentrations are $d_1 = 6$Å and $d_2 = 2$Å, and $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively.

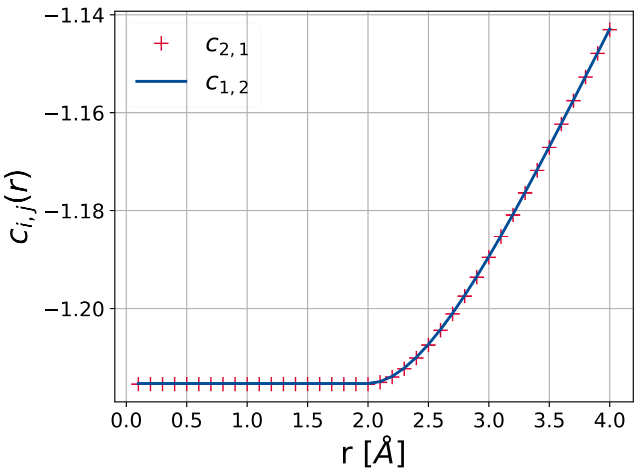


Figure 5.6: Symmetry in direct correlation functions, $c_{1,2}(r)$ and $c_{2,1}(r)$, calculated with finite element. The system is a two species hard spheres fluid, with temperature, $T = 298K$. Their diameters and molar concentrations are $d_1 = 6$Å and $d_2 = 2$Å, and $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively.

Chapter 6

Analytical direct correlation functions for hard spheres

We initiate this chapter discussing the work done by Kazuo Hiroike [10, 29], where he proposed an analytical expression for the finite range direct correlation functions for a mixture of hard spheres. Next, we discuss the work done by Baxter [1, 2]; we compare Baxter's solution with our derivation, presented in chapter 4, and Hiroike's work. We briefly mention the correction we made to Baxter's work in order to complete it and compare his results to the numerical direct correlation functions.

6.1 Hiroike's work

We will start with nomenclature; our goal is to derive equation 2.7 from Hiroike's derivation published in 1969 [10], which is the basis of Hiroike's proposed analytical solution (hereinafter referred to as Hiroioke1). His derivation lacks clearness in his paper of 1970 [29], hereinafter referred to as Hiroike2.

6.1.1 Nomenclature

The Ornstein-Zernike equation for m species is:

$$h_{i,j}(r_i, r_j) \quad = \quad c_{i,j}(r_i, r_j) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(r_i, r_k) h_{k,j}(r_1, r_k) dr_k.$$

Given the right assumptions, it only depends on the distance between particle i and particle j:

$$h_{i,j}(|r_i - r_j|) \quad = \quad c_{i,j}(|r_i - r_j|) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|r_i - r_k|) h_{k,j}(|r_k - r_j|) dr_k.$$

If the particle i is centered at the origin,

$$h_{i,j}(|r_j|) \;=\; c_{i,j}(|r_j|) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|r_k|)h_{1,j}(|r_k - r_j|)dr_k.$$

Let us take the coordinates of $\mathbb{R}^3$ such that the particle j lies on $e_3 = (0,0,1)$:

$$h_{i,j}(z) \;=\; c_{i,j}(z) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|r_k|)h_{k,j}(|r_k - e_3|)dr_k.$$

Using spherical coordinates in the integral,

$$(x,y,z) \;\mapsto\; s(cos\theta sin\varphi, sin\theta sin\varphi, cos\varphi),$$

$$\begin{aligned} h_{i,j}(z) &= c_{i,j}(z) + 2\pi \sum_{k=1}^{m} \rho_k \int_0^\infty ds \int_0^\pi d\varphi h_{k,j}\left(\sqrt{z^2+s^2-2zscos\varphi}\right) c_{i,k}(s)s^2 sen\varphi \\ &= c_{i,j}(z) + \frac{2\pi}{z} \sum_{k=1}^{m} \rho_k \int_0^\infty ds c_{i,k}(s)s \int_{|z-s|}^{z+s} dt h_{k,j}(t)\, t. \end{aligned}$$

Multiplying both sides by $2\pi\sqrt{\rho_i\rho_j}z$,

$$2\pi\sqrt{\rho_i\rho_j}zh_{i,j}(z) \;=\; 2\pi\sqrt{\rho_i\rho_j}zc_{i,j}(z) + \sum_{k=1}^{m}\int_0^\infty ds 2\pi\sqrt{\rho_i\rho_k}sc_{i,k}(s)\int_{|z-s|}^{z+s} dt 2\pi\sqrt{\rho_k\rho_j}th_{k,j}(t).$$

If $z = r$, $H_{i,j}(r) = 2\pi\sqrt{\rho_i\rho_j}rh_{i,j}(r)$ and $C_{i,j}(r) = 2\pi\sqrt{\rho_i\rho_j}rc_{i,j}(r)$, then

$$H_{i,j}(r) \;=\; C_{i,j}(r) + \sum_{k=1}^{m}\int_0^\infty ds C_{i,k}(s)\int_{|r-s|}^{r+s} dt H_{k,j}(t):$$

$$H(r) \;=\; C(r) + \int_0^\infty ds \int_{|r-s|}^{r+s} dt C(s)H(t).$$

Remark 6.1.1 *The matrices H and C are symmetric: they are equal to their transpose matrix.*

$$H(r) = H^T(r) \quad and \quad C(r) = C^T(r).$$

Wherefore,

$$H(r) - C(r) - \int_0^\infty ds \int_{|r-s|}^{r+s} dt C(s)H(t) = 0_{m\times m} \quad and \tag{6.1}$$

$$H(r) - C(r) - \int_0^\infty ds \int_{|r-s|}^{r+s} dt H(t)C(s) = 0_{m\times m}. \tag{6.2}$$

Remark 6.1.2

$$\begin{aligned} h_{i,j}(|r_j|) &= c_{i,j}(|r_j|) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|r_k|) h_{1,j}(|r_k - r_j|) dr_k \\ &= c_{i,j}(|r_j|) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|r_j - x_k|) h_{1,j}(|x_k|) dx \\ &= c_{i,j}(|r_j|) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|x_k - r_j|) h_{1,j}(|x_k|) dx. \end{aligned}$$

Taking the coordinates of $\mathbb{R}^3$ *such that the particle* j *lies on* $\vec{z} = (0,0,1)$,

$$h_{i,j}(z) = c_{i,j}(z) + \sum_{k=1}^{m} \rho_k \int c_{i,k}(|x_k - \vec{z}|) h_{k,j}(|x_k|) dr_k.$$

Hence,

$$H(r) - C(r) - \int_0^\infty dt \int_{|r-s|}^{r+s} ds C(s) H(t) = 0_{m\times m} \quad \textit{and} \tag{6.3}$$

$$H(r) - C(r) - \int_0^\infty dt \int_{|r-s|}^{r+s} ds H(t) C(s) = 0_{m\times m}. \tag{6.4}$$

6.1.2 Hiroike's $D(r)$ equation

$$\begin{aligned} 0_{m\times m} &= H(r) - C(r) - \int_0^\infty ds \int_{|r-s|}^{r+s} dt C(s) H(t) \\ &= H(r) - C(r) - \int_0^\infty ds \int_{|r-s|}^{r+s} dt C(s) H(t) + 0_{m\times m}. \end{aligned}$$

$$
\begin{aligned}
0_{m\times m} &= H(r)-C(r)-\int_0^\infty ds\int_{|s-r|}^{s+r} dtC(s)H\left(t\right) \\
&- \int_0^\infty ds\int_s^{s+r} dt\left[H(s)-C(s)-\int_0^\infty du\int_{|u-s|}^{u+s} dvH\left(v\right)C(u)\right]H(t) \\
&+ \int_0^\infty ds\int_{|s-r|}^{s} dtH(t)\left[H(s)-C(s)-\int_0^\infty du\int_{|u-s|}^{u+s} dvC(u)H\left(v\right)\right] \\
&= H(r)-C(r)-\int_0^\infty ds\int_{|s-r|}^{s+r} dtC(s)H\left(t\right) \\
&- \int_0^\infty ds\int_s^{s+r} dtH(s)H(t)+\int_0^\infty ds\int_s^{s+r} dtC(s)H(t) \\
&+ \int_0^\infty ds\int_s^{s+r} dt\left[\int_0^\infty du\int_{|u-s|}^{u+s} dvH\left(v\right)C(u)\right]H(t) \\
&+ \int_0^\infty ds\int_{|s-r|}^{s} dtH(t)H(s)-\int_0^\infty ds\int_{|s-r|}^{s} dtH(t)C(s) \\
&- \int_0^\infty ds\int_{|s-r|}^{s} dtH(t)\left[\int_0^\infty du\int_{|u-s|}^{u+s} dvC(u)H\left(v\right)\right] \\
&= H(r)-C(r)-\int_0^\infty ds\int_{|s-r|}^{s} dt\left[C(s)H\left(t\right)+H(t)C(s)\right] \\
&- \int_0^\infty ds\int_s^{s+r} dtH(s)H(t)+\int_0^\infty ds\int_{|r-s|}^{s} dtH(t)H(s) \\
&+ \int_0^\infty ds\int_0^\infty du\left[\int_{|u-s|}^{u+s} dv\int_s^{s+r} dtH\left(v\right)C(u)H(t)\right. \\
&- \left.\int_{|s-r|}^{s} dt\int_{|u-s|}^{u+s} dvH(t)C(u)H\left(v\right)\right] \\
&= H(r)-C(r)-\int_0^\infty ds\int_{|s-r|}^{s} dt\left[C(s)H\left(t\right)+H(t)C(s)\right] \\
&+ \left[-\int_0^\infty dt\int_t^{t+r} ds+\int_0^\infty ds\int_{|r-s|}^{s} dt\right]H(t)H(s) \\
&+ \int_0^\infty ds\int_0^\infty du\left[\int_{|u-s|}^{u+s} dt\int_s^{s+r} dv-\int_{|s-r|}^{s} dt\int_{|u-s|}^{u+s} dv\right]H(t)C(u)H\left(v\right) \\
&= D(r)
\end{aligned}
$$

where $D(r)$ its just the name of the expression given in Hiroike1 [10].

Remark 6.1.3 *Careful consideration of the integration limits, and the use of Fubini's theorem of calculus [17], we find that*

$$\begin{aligned}\int_0^\infty ds \int_{|r-s|}^{s} dt &= -\int_0^{\frac{r}{2}} ds \int_s^{r-s} dt + \int_{\frac{r}{2}}^{r} ds \int_{r-s}^{s} dt + \int_r^\infty ds \int_{s-r}^{s} dt \\ &= -\int_0^{\frac{r}{2}} dt \int_0^{t} ds - \int_{\frac{r}{2}}^{r} dt \int_0^{r-t} ds + \int_0^{\frac{r}{2}} dt \int_{r-t}^{r+t} ds + \int_{\frac{r}{2}}^{\infty} dt \int_t^{r+t} ds\end{aligned}$$

$$-\int_0^\infty ds \int_{|s-r|}^{s} dtH(t) \left[\int_0^\infty du \int_{|u-s|}^{u+s} dvC(u)H(v)\right] = -\int_0^\infty ds \int_{|s-r|}^{s} dtH(t)F(s)$$

$$\begin{aligned}= &\left[-\int_0^{\frac{r}{2}} dt \int_0^{t} ds - \int_{\frac{r}{2}}^{r} dt \int_0^{r-t} ds + \int_0^{\frac{r}{2}} dt \int_{r-t}^{r+t} ds + \int_{\frac{r}{2}}^{\infty} dt \int_t^{r+t} ds\right] H(t) * \\ * &\left[\int_0^\infty du \int_{|u-s|}^{u+s} dvC(u)H(v)\right].\end{aligned}$$

Consequently,

$$\left[-\int_0^\infty dt \int_t^{t+r} ds + \int_0^\infty ds \int_{|r-s|}^{s} dt\right] H(t)H(s) = -\int_0^r dt \int_0^{r-t} dsH(t)H(s).$$

It agrees with what is exposed in references [10, 29]. The last term of equation 2.7 in Hiroike1 [10] or equation 2.3 in Hiroike2 [29] is

$$\int_0^r dt \left[\int_t^\infty ds \int_0^s du \int_{|s-u-t|}^{s-|u-t|} dv - \int_0^t ds \int_0^t du \int_{|t-u-s|}^{t-|u-s|} dv\right] H(u)C(s)H(v),$$

or in the nomenclature we are using,

$$\int_0^r ds \left[-\int_s^\infty du \int_0^u dt \int_{|u-t-s|}^{u-|t-s|} dv + \int_0^s du \int_0^s dt \int_{|s-t-u|}^{s-|t-u|} dv\right] H(t)C(u)H(v). \tag{6.5}$$

We tried to derive the last expression from

$$\int_0^\infty ds \int_0^\infty du \left[\int_{|u-s|}^{u+s} dt \int_s^{s+r} dv - \int_{|s-r|}^{s} dt \int_{|u-s|}^{u+s} dv\right] H(t)C(u)H(v), \tag{6.6}$$

but we were unsuccessful. Since Hiroike used elementary calculations and applied Fubini's Theorem, we integrated

$$f(u) = e^{-u}$$

over the two regions to test if the regions are equivalent under those computations. We did it in Wolfram Mathematica. We obtained that over the region of equation 6.5

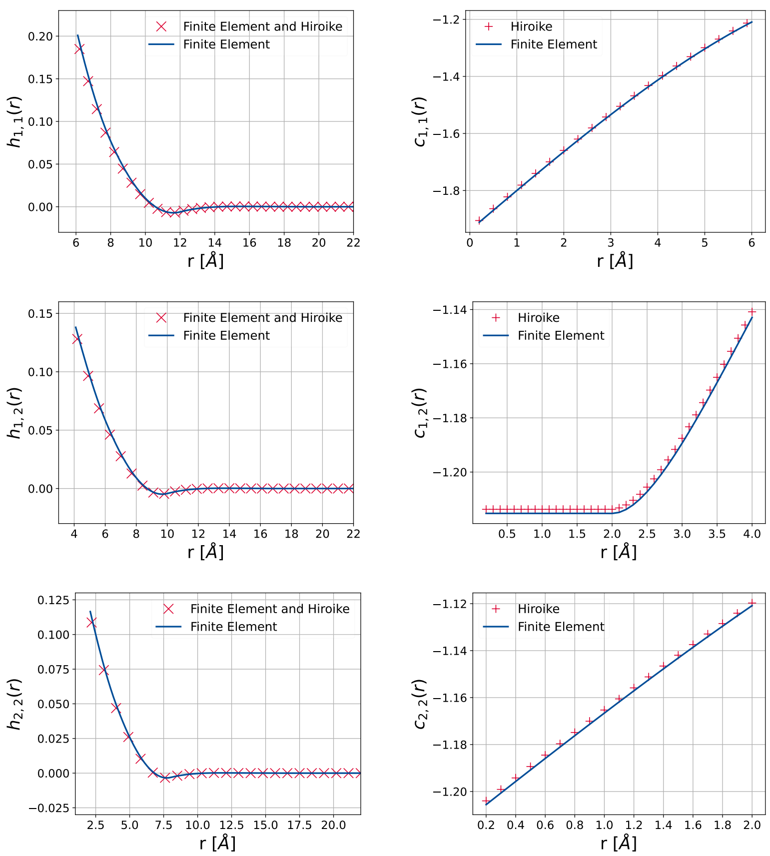
$$\int_0^r ds \left[-\int_s^\infty du \int_0^u dt \int_{|u-t-s|}^{u-|t-s|} dv + \int_0^s du \int_0^s dt \int_{|s-t-u|}^{s-|t-u|} dv\right] f(u) = -4e^{-r} + (r-2)^2,$$

nevertheless over the region of equation 6.6,

$$\int_0^\infty ds \int_0^\infty du \left[\int_{|u-s|}^{u+s} dt \int_s^{s+r} dv - \int_{|s-r|}^{s} dt \int_{|u-s|}^{u+s} dv\right] f(u)$$

diverges. Therefore, the regions are not equivalent under elementary calculations and the use of Fubini's theorem. *It is unclear how to proceed to analytically obtain Hiroike's general expression for the direct correlations functions. However, in this chapter we test its validity against our finite element numerical solutions of equation 4.1 for the direct correlation functions. Furthermore, substituting his analytical expressions for $c_{i,j}(r)$ in equation 4.1 and solving it numerically with finite element, we obtain their corresponding total correlations functions, $h_{i,j}(r)$, and compare them with our finite element results in chapter 5.*

In figures 6.1 and 6.2 we present a comparison of $h_{i,j}(r)$ and $c_{i,j}(r)$ of a mixture of hard spheres calculated with Hiroike's analytical solution and the numerical solution of the PY integral equation, solved with a finite elements method and MD simulations. As can be seen in figure 6.1 there is an excellent agreement of Hiroike's solutions with our finite elements solution of the PY integral equation, and, by extension, also with our previously presented results of MD (see figure 5.4, 5.5, and 5.6). These results validate, by consistency, our three approaches to the solution of the PY integral equation. In figure 6.2, we present results for $h_{i,j}(r)$ and $c_{i,j}(r)$ for a highly asymmetric mixture of two species of hard spheres, and compare $h_{i,j}(r)$, obtained from the numerical solution of the PY equation using the finite element method, with the MD simulation. In the same figure, we also compare Hiroike's direct correlation functions, $c_{i,j}(r)$, with the numerical solution of the PY equation. As can be seen, in all cases, there is a good agreement among our different approaches, even for a highly asymmetric system of hard spheres.



(a) (b)

Figure 6.1: (a) Total correlation functions, $h_{i,j}(r)$, calculated by solving the PY integral equation with a finite elements methods, and those obtained through the OZ equation with the PY approximation, but using the direct correlation functions, $c_{i,j}(r)$, given by Hiroike's analytical solution. (b) Finite element solution of the Ornstein-Zernike equation against Hiroike's analytical solution for the direct correlation functions, $c_{i,j}(r)$.

The system is a two species hard spheres fluid, with temperature, $T = 298K$. Their diameters and molar concentrations are $d_1 = 6$Å and $d_2 = 2$Å, and $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively.

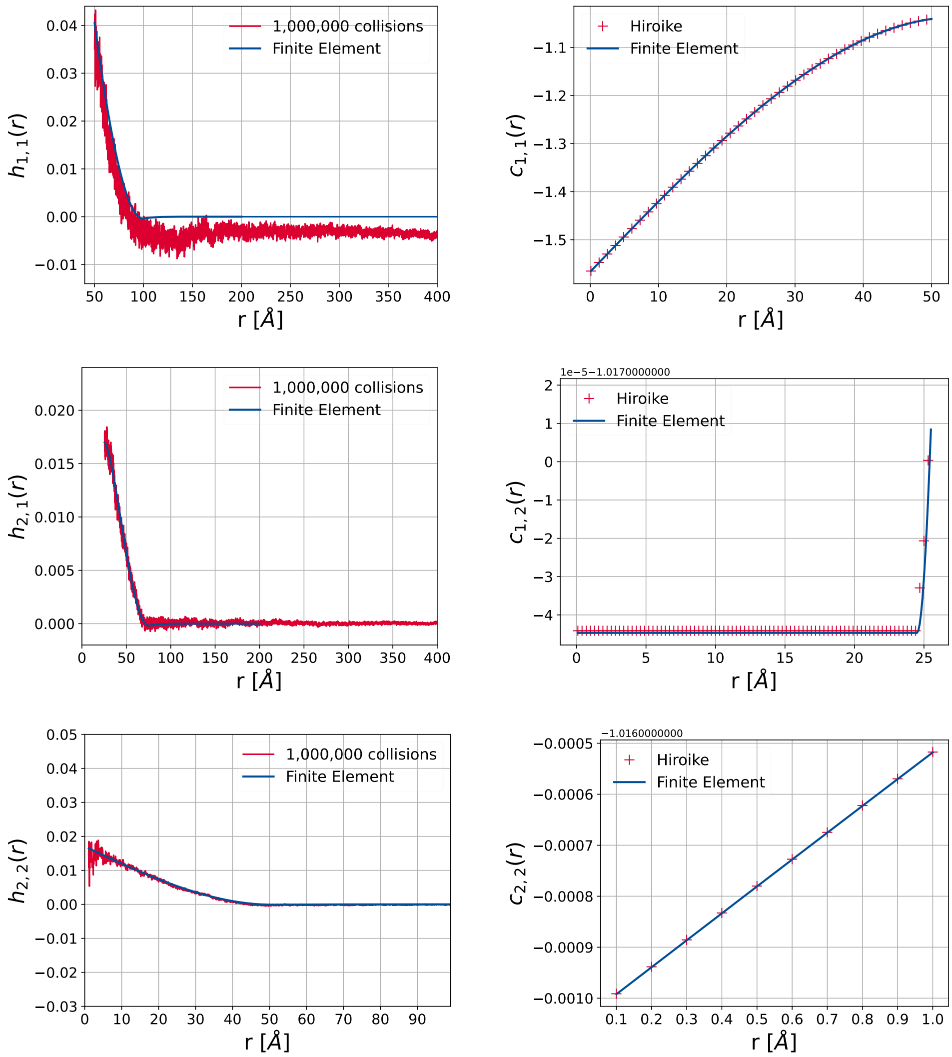


Figure 6.2: On the left hand side, MD total correlation functions computed after 1,000,000 collisions and compared to the finite element solution of the PY integral equation. On the right hand side, the direct correlation functions computed using finite elements to solve the PY integral equation and Hiroike's analytical solution. The system is a highly asymmetric mixture of two species of hard spheres with temperature $T = 298K$.
Their diameters and molar concentrations are $d_1 = 50$Å and $d_2 = 1$Å, and $\rho_1 = 0.0004M$ and $\rho_2 = 0.01M$, respectively. For the molecular dynamics computations we used a box with sides of 1033.56Å containing 266 particles of the first species and 6646 particles of the second species.

6.2 Our integral equations' validation

Now, we want to numerically validate our system of equations, given by

$$-tc_{i,j}(t) = Q'_{i,j}(t) - \sum_{k=1}^{m} \lambda_k \int_{t}^{\frac{d_1+d_i}{2}} dsQ'_{i,k}(s)Q_{j,k}(s-t),$$

and

$$-th_{i,j}(t) = Q'_{i,j}(t) + \sum_{k=1}^{m} \lambda_k \int_{0}^{\frac{d_1+d_k}{2}} (t-s)h_{i,k}(|t-s|)Q_{k,j}(s)ds.$$

In order to do it, we used the finite elements method [26] to solve equation

$$S_{i,j}(t) = Q^{+}_{i,j}(t) + Q^{-}_{i,j}(t) - \sum_{k=1}^{m} \lambda_k \int_{t}^{\frac{d_1+d_i}{2}} dsQ^{+}_{i,k}(s)Q^{-}_{k,j}(t-s).$$

We used as an input Hiroike's analytical expression for the direct correlation function to numerically compute $Q_{i,j}(r)$. Then, we solved equation

$$J_{i,j}(t) = Q^{+}_{i,j}(t) + \sum_{k=1}^{m} \lambda_k \int_{0}^{\frac{d_1+d_k}{2}} J_{i,k}(t-s)Q^{+}_{k,j}(s)ds.$$

and differentiated $J_{i,j}(r)$ to find $h_{i,j}(r)$. As it can be observed in figure 6.3, our theorem 4.2.12 is validated by these numerical results, since the functions $Q_{i,j}(r) = 0$ for all $r \geq \frac{R_1+R_i}{2}$–refuting what Baxter claimed in reference [2]. Moreover, from figure 6.4 we conclude the functions $h_{i,j}(r)$, obtained using the equations derived in chapter 4, coincide with our benchmark obtained in chapter 5.

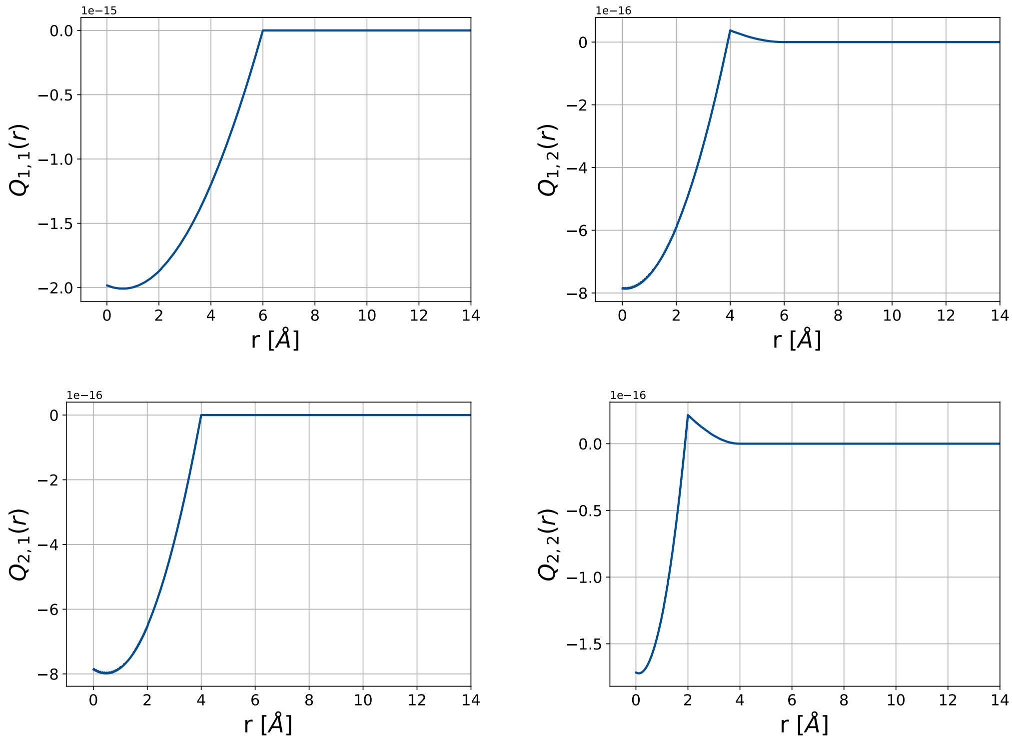


Figure 6.3: Functions $Q_{i,j}(r)$, for a mixture of two species of hard spheres, at temperature $T = 298K$. Their diameters are $d_1 = 6$Å and $d_2 = 2$Å, and their molar concentrations are $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively.

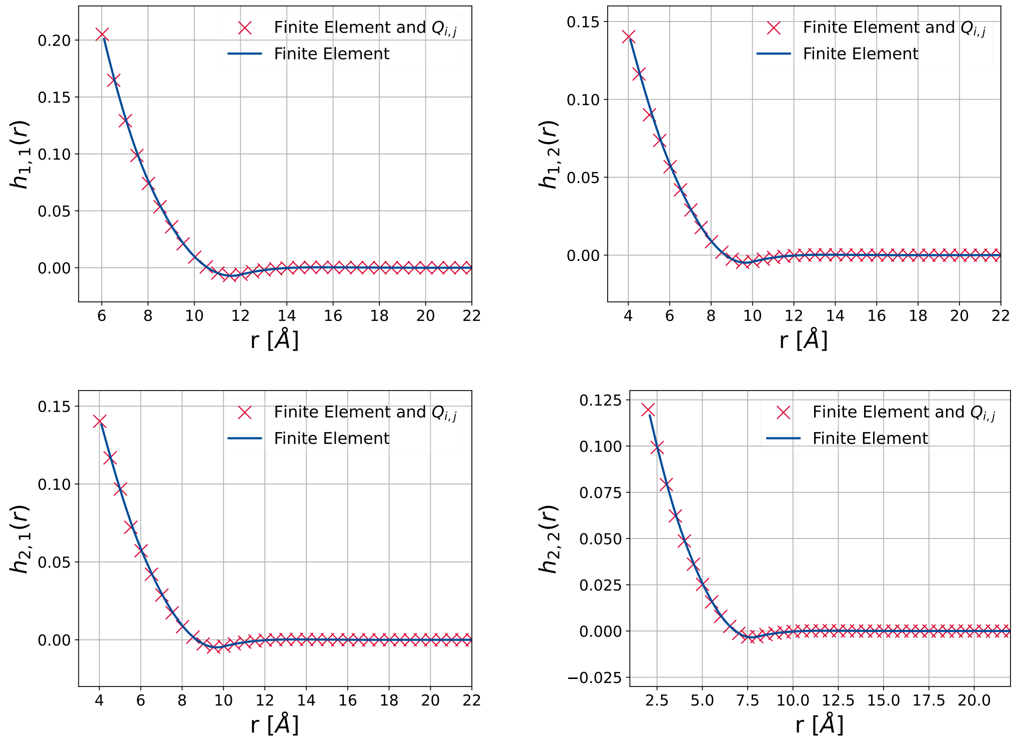


Figure 6.4: Total correlation functions, $h_{i,j}(r)$, numerically computed for a mixture of two species of hard spheres at temperature $T = 298K$. Their diameters are $d_1 = 6$Å and $d_2 = 2$Å, and their molar concentrations are $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively.

6.3 Baxter's work

6.3.1 One species

As Baxter in reference [1], we arrived to the same results in our section 4.1 for a system of only one species of hard spheres. *However, we must point out that we could not follow Baxter's logical deductions, since we found a lack of mathematical rigorousness. Hence, we recurred to methods for the solution of integral equations on a half-line with kernel depending upon the difference of the arguments [16], in order to develop section 4.1.* Nevertheless, we arrived at the same results of Baxter, i.e.,

$$-th(t) = Q'(t) - \lambda \int_0^R Q(s)(t-s)h(|t-s|)ds \quad t > 0 \quad and$$

$$-tc(t) = Q'(t) - \lambda \int_t^R Q'(s)Q(s-t)ds.$$

6.3.2 More than one species

Although, we were able to obtain the same result of Baxter, for a one species fluid of hard spheres presented in reference [1], we were unable to reproduce, with mathematical rigorousness, his derivation for a multi-component mixture of hard spheres [2]. In fact, as we shall show below, his resultant direct correlation functions, $c_{i,j}(r)$, seem to be incorrect. In his article [2] Baxter claimed,

$$\mathfrak{F}_+^{k,j}(y) = \hat{g}_+^{k,j}(y) \quad = \quad \delta_{k,j} + \int_{\frac{R_k - R_j}{2}}^{\frac{R_k + R_j}{2}} dt e^{iyt} g_+^{k,j}(t).$$

But a direct consequence of theorem 4.2.12 is that the support of the functions $Q_{k,j}$ is $\left(0, \frac{R_1+R_k}{2}\right)$ and not $\left(\frac{R_k-R_j}{2}, \frac{R_k+R_j}{2}\right)$, as claimed by Baxter. Baxter's claim should have been suspicious from the start since the functions $Q_{k,j}$ are elements of L_+, and $\frac{R_k-R_j}{2}$ can be a negative number. Moreover, when it is a positive number the integral is missing $\left(0, \frac{R_k-R_j}{2}\right)$, which can be very large if the difference is big enough. Nevertheless, let us make the exercise of following Baxter's steps and compare the result with the numerical direct correlation functions for hard spheres. Baxter's equation 25 in our notation is

$$rh_{i,j}\left(|r|\right) \quad = \quad -Q'_{i,j}(r) + 2\pi \sum_{k=1}^{M} \rho_k \int_{\frac{R_i - R_k}{2}}^{\frac{R_i + R_k}{2}} dt Q_{i,k}(t)(r-t)h_{k,j}(|r-t|),$$

where $r \in \left(\frac{R_i-R_j}{2}, \frac{R_i+R_j}{2}\right)$. Using the assumptions for the PY approximation,

$$-r = -Q'_{i,j}(r) - 2\pi \sum_{k=1}^{M} \rho_k \int_{\frac{R_i-R_k}{2}}^{\frac{R_i+R_k}{2}} dt Q_{i,k}(t)(r-t).$$

Solving for $Q'_{i,j}$,

$$\begin{aligned} Q'_{i,j}(r) &= r - 2\pi \sum_{k=1}^{M} \rho_k \int_{\frac{R_i-R_k}{2}}^{\frac{R_i+R_k}{2}} dt Q_{i,k}(t)(r-t) \\ &= \left(1 - 2\pi \sum_{k=1}^{M} \rho_k \int_{\frac{R_i-R_k}{2}}^{\frac{R_i+R_k}{2}} dt Q_{i,k}(t)\right) r + \left(2\pi \sum_{k=1}^{M} \rho_k \int_{\frac{R_i-R_k}{2}}^{\frac{R_i+R_k}{2}} dt Q_{i,k}(t)\right) \\ &= a_i r + b_i. \end{aligned}$$

These equations differ from Baxter's equations 38 and 39 by 2π [2], but let us think it was a transcription mistake. Suppose we have two species, the first with diameter $R_1 = 6 * 10^{-8} cm$, density $\rho_1 = 6.023 * 10^{20}$ particles per liter; the second with diameter $R_2 = 2 * 10^{-8} cm$ and density $\rho_2 = 6.023 * 10^{20}$ particles per liter. Making the calculations with Wolfram Mathematica,

$$\begin{aligned} a_1 &= 1.4239 \quad , \quad b_1 = -4.2717 * 10^{-15}, \\ a_2 &= 1.1638 \quad and \quad b_2 = -8.5917 * 10^{-10}. \end{aligned}$$

But, if we use Baxter equations 40 and 41 from reference [2], then

$$\begin{aligned} a_1 &= 1.3389 \quad , \quad b_1 = -7.8868 * 10^{-9}, \\ a_2 &= 1.1636 \quad and \quad b_2 = -8.7631 * 10^{-10}. \end{aligned}$$

Let us continue with the first set of numbers derived. Using equation 24 of Baxter's work [2],

$$c_{1,1}(r) = -2.1539 - \frac{1.3219 \times 10^{-8}}{r} 1.7758 \times 10^{7} r + 0.0125 r^2 - 5.3321 * 10^{20} r^3.$$

The corresponding Hiroike's analytical expression for $c_{1,1}(r)$ is given by,

$$c_{1,1}(r) = -1.9329 + 1.3878 * 10^{7} r - 4.8211 * 10^{20} r^3.$$

In figure 6.5 we compare all the resultant direct correlation functions, $c_{i,j}(r)$, following Baxter's steps, as indicated above, against the results obtained from

1. the numerical solution from the Ornstein-Zernike equation, with the PY approximation and

2. Hiroike's analytical expression.

It is clearly seen that the Baxter solution has significant quantitative and qualitative disagreements with the the PY integral equation and the analytical solution of Hiroike, and, by extension, also with our MD simulation (see figure 5.5). This is a counterexample, since we just need to show that for one specific case the equations derived do not work. Hence, Baxter derivation in reference [2] is incorrect. Finally, in figure 6.6 we compare the total correlation functions, $h_{i,j}(r)$, corresponding to Baxter's direct correlation functions analytical solutions, with those from finite elements. It is interesting that although there are major disagreements between the Baxter's and finite elements direct correlation function, we find a qualitative agreement among the corresponding total correlation functions.

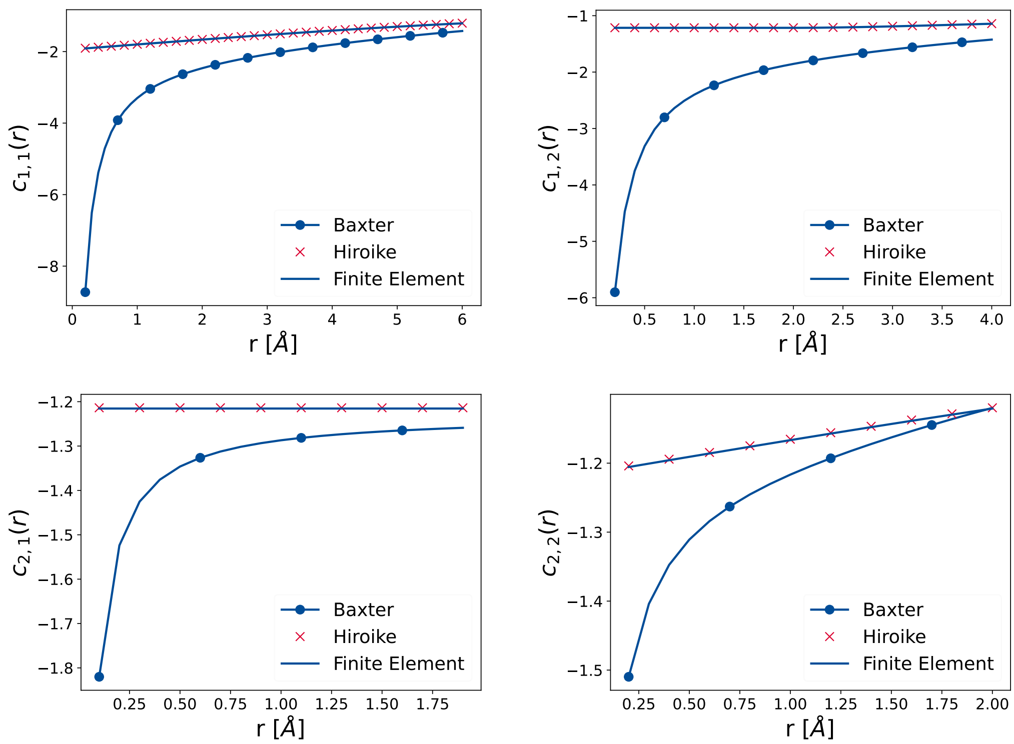


Figure 6.5: Direct correlation function, $c_{i,j}(r)$, calculated with Baxter's method, Hiroike's analytical solution and the finite element method. The system is a two species hard spheres fluid, with temperature, $T = 298K$. Their diameters and molar concentrations are $d_1 = 6$Å and $d_2 = 2$Å, and $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively.

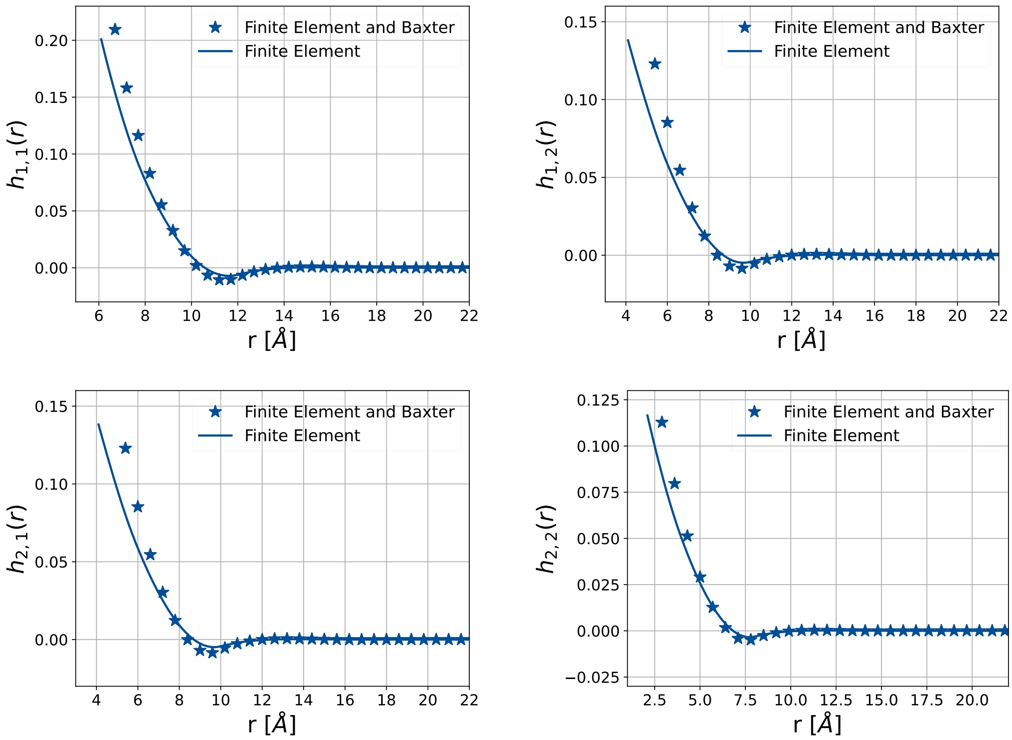


Figure 6.6: Total correlation function, $h_{i,j}(r)$, numerically computed using the Ornstein-Zernike equation and Baxter's analytical solutions for the direct correlation functions. The system is a two species hard spheres fluid at temperature $T = 298K$. The particles' diameters and molar concentrations are $d_1 = 6$Å and $d_2 = 2$Å, and $\rho_1 = 1M$ and $\rho_2 = 1M$, respectively.

Chapter 7

Conclusions

In this thesis we focus on the solution of the Percus-Yevick integral equations for an n-species hard spheres fluid. In particular, we review the Baxter's solutions for one species [1] and n-species [2] of hard spheres. We found mathematical inconsistencies in Baxter's solutions for the one species case, and frankly an incorrect derivation of Baxter's result for n-species. Hence, we have reformulated, both, the one species, see section 4.1 equations 4.8 and 4.10, and n-species Baxter's derivations for the solution of the Percus-Yevick equation, see section 4.2 equations 4.24 and 4.25. As for this part of the thesis, we conclude that further inspections need to be made on works like [14] and [11], since the first one is based on what Baxter did and the second one does not provide the derivation of the findings.

Although, we have rigorously mathematically derived a reformulation of the Percus-Yevich equations in chapter 4, we have revised the analytical solution of Hiroike (section 6.1), numerically solved the Percus-Yevick equation and performed molecular dynamics simulations for a binary mixture of hard spheres, both in chapter 5. With the simulations we calculated the direct correlation functions, $c_{i,j}(r)$, and total correlation functions, $h_{i,j}(r)$, and we found an excellent agreement with our derived functions (see section 6.2). It might be possible to work just with the Q_i,make assumptions over them, in order to estimate the direct and total correlation functions.

We found agreement with Hiroike's analytical solution, for it see section 6.1, but some steps need to be clarified, since a particular case does not imply it's validity for all cases. In section 6.3 we showed that Baxter's method to obtain an analytical solution for the direct correlation functions is inconsistent with our findings. It is also interesting that the total correlation functions obtained with the Baxter's direct correlations functions are in qualitative good agreement with our correct solution, but they are still different functions. We point out that even if they are quantitatively close functions they may lead to important differences in the fluid's thermodynamic properties. This is particularly important, since some approximations might appear to be good ones, but may lead to very different results compared to what we observe in nature. We want that our simulations be as close to reality in order to perform experiments using the computer, in conclusion we should be careful on what we think is a good estimation for the total correlation function.

As for this thesis contributions:

1. We rigorously proved Baxter's result [1] for one species in section 4.1.

2. We followed Baxter's steps in [2] to obtain analytical expression for the direct correlation function, in the case of a binary mixture in section 6.3.

    (a) We used these analytical expressions as counterexample to prove he was wrong, when we compared them against our results from molecular dynamics and finite element.

    (b) We used these analytical expressions as a way to illustrate how very different direct correlation functions used to solve the OZ equation produce similar total correlation functions.

3. We rigorously derived what Baxter intended to do in [2]. With that we arrived to a set of equations, which reformulate de OZ equation in section 4.2.

    (a) We validated this set of equations for a binary mixture. We did it by comparing them with our results from molecular dynamics and finite element in section 6.2.

Finally, what comes next? When one person is new to field, he has to start with old papers, there's the responsibility of re-doing the theory to check and understand what previous authors said. I'd say that the first half of this thesis gave me experience in the field of integral equations, explicitly in the ones that look like the OZ equation. The second half of the thesis gave me experience in molecular dynamics and finite element computations. Hard spheres with no charge is the first step to tackle more complicated problems as charged hard spheres, confined charged hard spheres or charged spheres where a force field is acting over them (in-homogeneous fluids). Knowing the analytical expression for the direct correlations functions in the bulk has been used to compute the total correlation of in-homogeneous fluids (see [30]). Furthermore, when dealing with particles with very different sizes as in colloids, it becomes important to know the direct correlation functions in bulk to be able to compute the total correlations functions as Dr. Lozada did in [13]. In general, this thesis could be used or has repercussions in the study of nanoparticles and colloidal particles.

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