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XVI CICLO DEL
DOTTORATO DI RICERCA IN FISICA

Classical liquids: exact results, integral equations theory, and Monte Carlo simulations

DOTTORANDO

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Chapter 1

Introduction

The relation between interaction and structure and thermodynamic properties in condensed matter is a central issue for the theory. Liquid phases have often been considered very difficult to describe by theory since they lack the possibilities of controlled approximations like in dilute (gas) or symmetric (crystalline) phases. However, the source of the difficulties, the partial disorder of the relevant configurations, makes them ideal for studying the interactions in condensed matter phases. Notwithstanding many theories have been developed in the last half century, this remains an active field of research witnessed by recent progress in colloidal science or in confined liquid theory. In the present thesis work we have studied issues related to some unsolved problems in this area. The final thesis has been confined to those problems for which we could give either a definite solution or an original discussion.

The outline of the thesis is as follows. In the second chapter we briefly present some background notions necessary to have a clear picture of where the arguments treated in the thesis are collocated in the realm of theoretical physics: a classical liquid is defined, the creation of a mathematical model of a real fluid is discussed, and a brief outline of the experimental methods used to analyze a real fluid and of the simulation methods used to analyze its mathematical models is given. In chapters 3, 4, 5, and 6 we study various aspects of the integral equations theory. These are approximate theories which allow to gain some insight into the structure and thermodynamics of a given model. In chapter 4 we give particular emphasis to the analytic solutions of such theories. While in chapter 5 and 6 we concentrate on their numerical solutions. In chapter 7 we carry out a Monte Carlo simulation aimed to study the structure of some simple models. Up until 1961 the statistical mechanics of the one dimensional Coulomb gas was an unsolved problem. At more or less the same time the problem was solved by Lenard [1] and by Prager [2] independently. A powerful alternative method of solution using functional integration was subsequently found by Edwards and Lenard [3]. In chapter 9 we give a review of their method of solution and show how it is suitable to study other one dimensional fluid models. The two dimensional Coulomb gas may also be solved exactly at a temperature $\beta q^2 = 2$ [4]. In chapter 8 we find some exact results for a particular two dimensional Coulomb gas: one in a disk on the surface of a pseudosphere. We will now give a brief abstract for each of the chapters three to nine, stressing whether they contain original results or not.

In chapter 3 there are no original results. We try to give a unified introduction to the theory of classical fluids, introducing the density functional theory as a development of the grand canonical formalism of statistical mechanics, defining the free energy and the most commonly used correlation functions, as well as the Ornstein-Zernike (OZ) equation. We use Percus method to introduce the most commonly known integral equations [like the Random Phase Approximation (RPA), the Percus-Yevick (PY) approximation, and the hypernetted chain (HNC) approxima-

tion]. At the end of the chapter we present the mean spherical approximation (MSA) which (together with PY) admits an analytic solutions for a number of fluid models of physical interest.

In chapter 4 there are no published results. We present the analytic solutions of the MSA for the three dimensional mixture of charged hard spheres, obtained using the Wiener-Hopf factorization (see appendix B). The original subject of this chapter, presented in the last section, is the discussion of the impossibility to use the Wiener-Hopf technique to find an analytic solution of the PY approximation for the three dimensional non additive hard spheres. Such solution has not yet been found.

Chapter 5 contains original results published on [5]. We discuss and illustrate through numerical examples the relations between generating functionals, thermodynamic consistency (in particular the virial-free energy one), and uniqueness of the solution, in the integral equation theory of liquids. We propose a new approach for deriving closures automatically satisfying such characteristics. Results from a first exploration of this program are presented and discussed.

In chapter 6 we present some original results published on [6]. A recently proposed connection between the threshold for the stability of the iterative solution of integral equations for the pair correlation functions of a classical fluid and the structural instability of the corresponding real fluid is carefully analyzed. Direct calculation of the Lyapunov exponent of the standard iterative solution of HNC and PY integral equations for the 1D hard rods fluid shows the same behavior observed in 3D systems. Since no phase transition is allowed in such 1D system, our analysis shows that the proposed one phase criterion, at least in this case, fails. We argue that the observed proximity between the numerical and the structural instability in 3D originates from the enhanced structure present in the fluid but, in view of the arbitrary dependence on the iteration scheme, it seems uneasy to relate the numerical stability analysis to a robust one-phase criterion for predicting a thermodynamic phase transition.

Chapter 7 contains original results which are in course of publication on Physica A [7]. We calculate, through Monte Carlo numerical simulations, the partial total and direct correlation functions of the three dimensional symmetric Widom-Rowlinson mixture. We find that the differences between the partial direct correlation functions from simulation and from the Percus-Yevick approximation (calculated analytically by Ahn and Lebowitz) are well fitted by Gaussians. We provide an analytical expression for the fit parameters as function of the density. We also present Monte Carlo simulation data for the direct correlation functions of a couple of non additive hard sphere systems to discuss the modification induced by finite like diameters.

In chapter 8 we present original results published on [8]. The classical (i.e. non-quantum) equilibrium statistical mechanics of a two-dimensional one-component plasma (a system of charged point-particles embedded in a neutralizing background) living on a pseudosphere (an infinite surface of constant negative curvature) is considered. In the case of a flat space, it is known that, for a one-component plasma, there are several reasonable definitions of the pressure, and that some of them are not equivalent to each other. In this chapter, this problem is revisited in the case of a pseudosphere. General relations between the different pressures are given. At one special temperature, the model is exactly solvable in the grand canonical ensemble. The grand potential and the one-body density are calculated in a disk, and the thermodynamic limit is investigated. The general relations between the different pressures are checked on the solvable model.

In chapter 9 there are no published results. Following Edwards and Lenard paper [3] we describe a way of simplifying the calculation of the grand canonical partition function of an ensemble of classical particles living in a one dimensional world and interacting with a given pair potential. Using the notion of a general Gaussian random process and of Kac's theorem, we show how it is possible to express the grand partition function as a one dimensional integral of

the fundamental solution of a given partial differential equation. The kind of partial differential equation will be fixed by the kind of diffusion equation satisfied by the Gaussian random process. Following [3] we see how the Wiener process allows to treat the "Edwards model". We then show how other stochastic processes can be used to treat other fluid models: we use the Ornstein-Uhlenbeck process to simplify the calculation of the grand partition function of the "Kac-Baker model" and the generalized Ornstein-Uhlenbeck process to treat a fluid with a "general" pair potential.

Chapter 2

Background

This thesis presents results on a few issues of the theory of classical liquids.

A liquid is a particular phase of matter which occurs at intermediate values of pressure, temperature, and volume. In figure 2.1 we draw the typical phase diagram of a monatomic

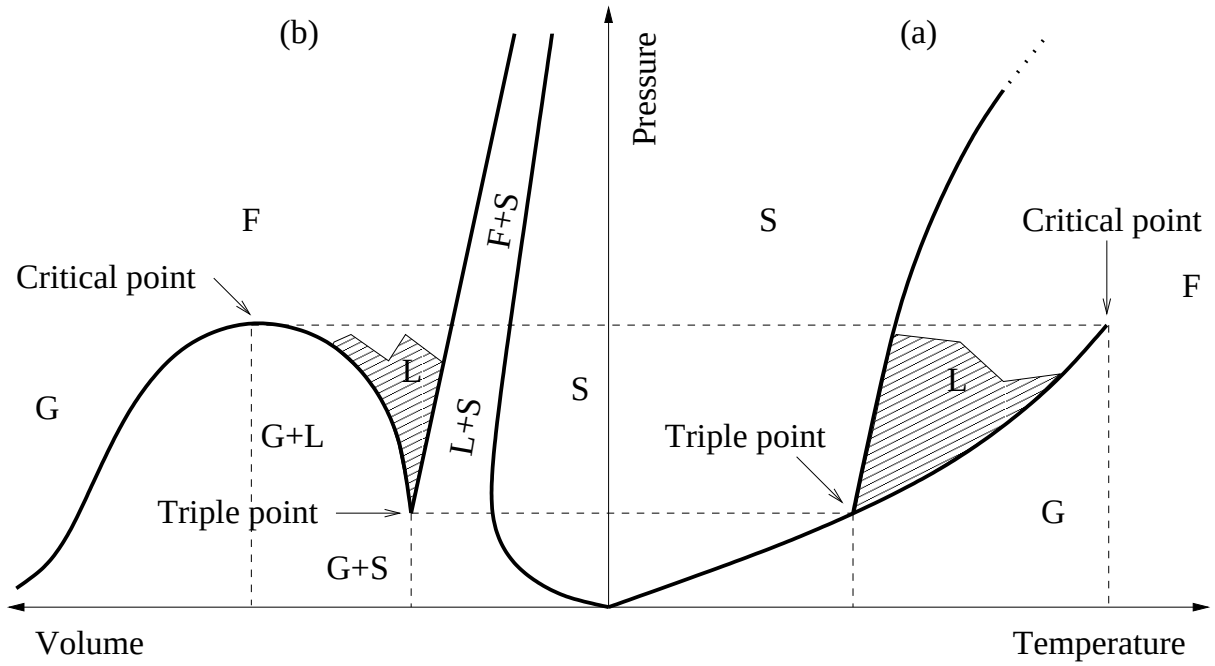

FIGURE 2.1: Phase diagram of a typical monatomic substance. The solid lines indicate the boundaries between solid (S), liquid (L), vapor (G) or fluid (F) phases. (a) is the projection in the pressure-temperature plane and (b) is that in the pressure-volume plane. The shaded regions indicate the part of these diagrams considered as a dense liquid. The limits of the liquid state are marked triple and critical points.

substance (for example argon). From the figure we can see that the liquid phase (bounded above by the critical point and below by the triple point) occupies a relatively small region of the phase diagram.

The temperatures at which most substances are liquid are high enough that the system may be considered classical.

From the point of view of the dynamical and structural properties a liquid distinguishes itself from a solid by the presence of an important diffusion and by the lack of long range order, and

from a gas by the importance of collisional processes and short range correlations.

The work done by physicists when studying liquids can be described by the block diagram shown in figure 2.2. To understand theoretically the behavior of a liquid we need a model for the

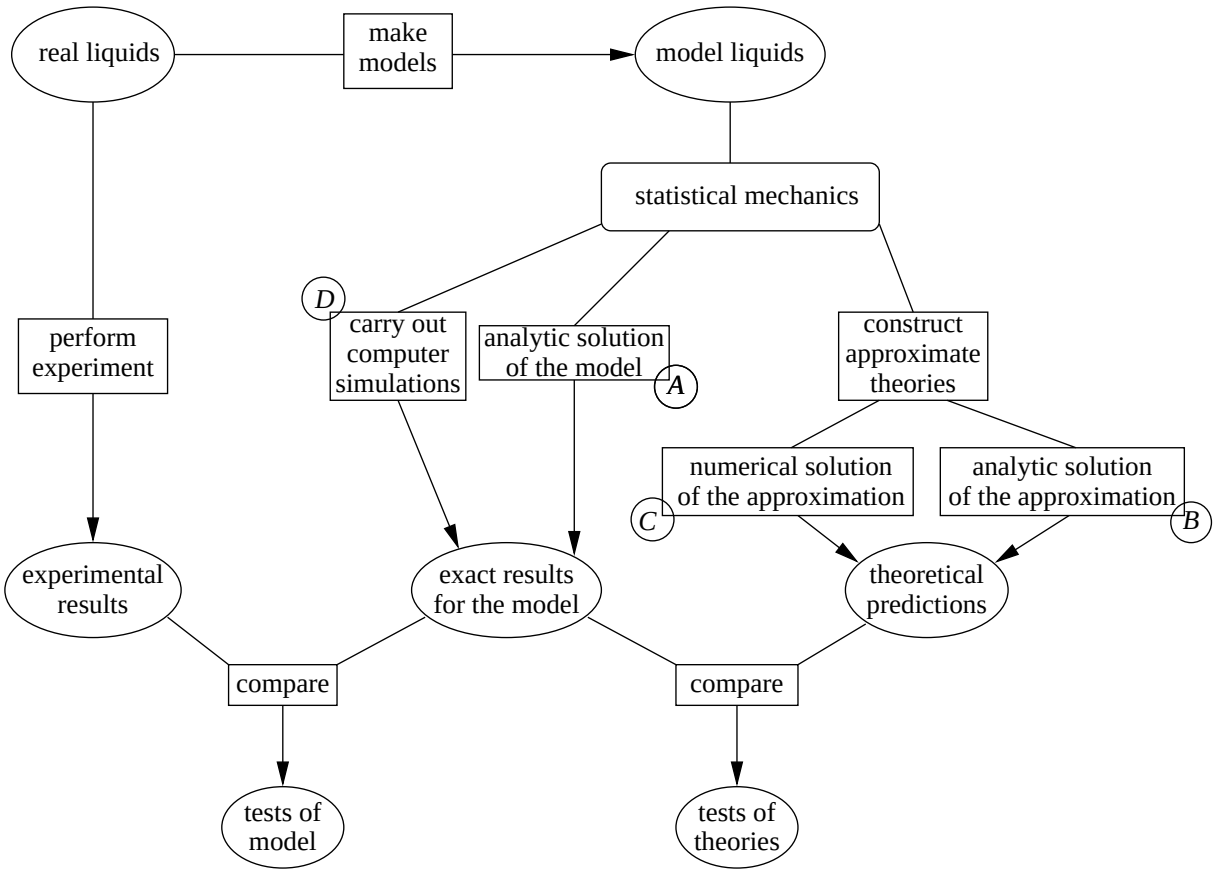

FIGURE 2.2: Block diagram showing the processes needed to test a particular model of a liquid and the ones needed to test a particular theory for a given model. In the thesis we will present some examples to illustrate those parts of the diagram which have a circle beneath them.

interactions. Then we need to compare the results obtained from the experiments with the ones obtained from the numerical simulations or the rarely available analytic solution of the model. While to test theories constructed from a particular model we need to compare the latter with the results from numerical or analytical (when available) solutions of the theories. In this thesis we will give some examples of "analytic solution of a model" (see chapters 8 and 9), some examples of "analytic solution of the approximation" (see chapter 4), some examples of "numerical solution of the approximation" (see chapters 5 and 6), and some examples of "computer simulations" (see chapter 7). We will also see how to "construct approximate theories" (see chapters 3, 5, and 6). Since we will not talk about how to "make models", how to "perform experiment", and how to "carry out computer simulations" we will spend some words on this arguments in this introductory chapter.

i How to make a model

When creating a physical model of a real liquid one usually makes two basic hypothesis: the system, in absence of an external potential, has to be homogeneous and isotropic, in the bulk. The main ingredient to be chosen when creating a physical model of a real liquid is the type of interaction amongst the particles.

i.1 The interaction potential

The most general potential energy for a system of N pointwise particles is

$$V_N(r^N) = \sum_{i=1}^{N} v_1(\mathbf{r}_1) + \sum_{1\le i<j\le N} v_2(\mathbf{r}_i,\mathbf{r}_j) + \sum_{1\le i<j<k\le N} v_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) + \dots \quad , \tag{2.i:1}$$

where the first term represents the effect of an external field and the remaining terms represent particle interactions. The usual assumption behind this expansion is that the pair interaction v_2 will be dominant, followed by the three particles correction term v_3, and hopefully successively smaller terms which may be neglected.

If the particles are not spherically symmetric, as for rigid molecules for example, the definition of the potentials $v_2, v_3, \dots$ must be widened to include the orientations dependence.

Even if the three body term is undoubtedly important at liquid densities, in many calculations they are either omitted or included by defining an 'effective' pair potential

$$V_N(r^N) \approx \sum_{i=1}^{N} v_1(\mathbf{r}_i) + \sum_{1\le i<j\le N} v_2^{eff}(r_{ij}) \quad , \tag{2.i:2}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. In general an effective potential will depend upon the property to be calculated and it will also be functionally dependent on the thermodynamic state parameters. However such issues are important only if one is interested in modeling real liquids but the main features of the liquid behavior do not depend on the details of the interaction model.

The most important feature of the pair potential of a liquid is the strong repulsion that appears at short range and is due to the overlap of the outer electron shells inhibited by the Pauli exclusion principle. This strongly repulsive forces are responsible for the short range order characteristic of the liquid state. The attractive forces acting at long range are much more smooth and play only a minor role in determining the structure of the liquid. They provide an almost uniform attractive background giving rise to the cohesive energy that stabilizes the liquid.

Then, the simplest model of a fluid is a system of hard spheres. That is a system of pointwise particles whose pair potential is

$$v_2(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \ge \sigma \end{cases} \quad , \tag{2.i:3}$$

where σ is the diameter of the spheres. The equilibrium properties for this potential may be expressed in terms of the coupling parameter ρ/ρ_0, where $\rho_0 = \sqrt{2}/\sigma^3$ is the number density of hard spheres at closest packing. For this fluid the absence of attractive forces means that there is only one single fluid phase.

Another simple model without attractive forces is the inverse power potential fluid (see chapter 5 subsection iii.1) also called the soft sphere model. Its pair potential is chosen to be

continuous

$$v_2(r) = \epsilon \left(\frac{\sigma}{r}\right)^n \quad , \tag{2.i:4}$$

where ϵ and σ are two positive parameters and n is usually chosen to be an integer. The appropriate coupling parameter for this liquid is $z = (\rho\sigma^3/\sqrt{2})(\beta\epsilon)^{3/n}$.

Both the hard spheres and the inverse power potential fluids are idealized model which may have only one fluid phase. A simple model that can describe a true liquid phase is obtained by adding to the hard spheres potential a square well attraction.

$$v_2(r) = \begin{cases} \infty & r < \sigma_1 \\ -\epsilon & \sigma_1 \leq r < \sigma_2 \\ 0 & \sigma_2 \leq r \end{cases} \quad , \tag{2.i:5}$$

where ϵ, σ_1, and σ_2 are all positive parameters.

In the search for more realistic pair potentials for neutral atoms one can consider the continuous Lennard-Jones potential (see chapter 5 subsection iii.2)

$$v_2(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \quad . \tag{2.i:6}$$

It involves two positive parameters: ϵ is the depth of the attractive well and σ the point at which $v_2 = 0$. The Lennard-Jones potential provides a fair description of the interaction between pairs of rare gas atoms. Computer experiments [9] show that the triple point of the Lennard-Jones fluid is at $\rho\sigma^3 \simeq 0.85$ and $1/(\beta\epsilon) \simeq 0.68$.

For ions, these potentials are not sufficient to represent the long range interactions. A simple approach is to supplement one of the above pair potentials with the Coulomb interaction (see chapter 4 section i)

$$v_2(r_{ij}) = \frac{z_i z_j e^2}{\epsilon_0 r_{ij}} \quad , \tag{2.i:7}$$

where $z_i e$ and $z_j e$ are the charges on ions i and j and ϵ_0 is the dielectric constant of the surrounding medium.

When making a model of a liquid we also need to choose the space in which the particles are allowed to move. In most cases this will be an Euclidean space but nothing forbids us to choose more general Riemannian spaces (for example in chapter 8 we will study the one component Coulomb plasma on a pseudosphere). The first thing to choose is the dimensionality of such a space.

Often the choice of the space has an influence on the interaction potential amongst the particles. Let us consider for example, charged particles (ions for example) free to move in a two dimensional Euclidean space. In this case we have two possible choices for the Coulomb pair potential. We can infact choose a model in which the particles still interact through an electric field with field lines in the three dimensional space, in this case we would choose a $1/r$ Coulomb potential, but we may also choose a model in which the particles interact through an electric field with field lines which do not come out of the plane, in this case we would choose a $-\ln(r/r_0)$ (with r_0 a given length scale) Coulomb potential.

Choosing a lower dimensionality often increases the chances of finding an exactly soluble model. Some examples for this are the two dimensional one component plasma considered in chapter 8 and the one dimensional models studied in chapter 9. The existence of an analytic

solution for a particular model has often been considered a sufficient condition to tag that model as an interesting one, even when the model itself did not offer an immediate description of any real liquid known. The interest in simple exactly soluble models often lies in the fact that one can use them as paradigmatic examples useful to build approximations for more complicated and realistic models.

The dimensionality of the space can have an influence on the phase diagram. For example it has been proven that one dimensional systems with finite range pairwise potential can never have a phase transition [10].

ii Experimental methods

The main reason to mention experimental methods in a theoretical work is that the quantities which are directly measurable play a critical role in the comparison between theory and experiment. The experimental methods used when studying a real liquid fall in two categories: experiments which measure macroscopic quantities and those which measure microscopic quantities. The macroscopic data can usually be measured to a higher accuracy (0.1%) than the microscopic data (1.0%).

ii.1 Measurements on a macroscopic scale

Typical macroscopic measurements are experiments done to measure the pressure P, density ρ, and temperature T of a liquid. Integration of these measurements yields other thermodynamic quantities such as the internal energy, the heat capacities, or the compressibilities.

Measurements on a macroscopic scale are often needed to measure the transport coefficients of a liquid such as the shear and bulk viscosity, the thermal conductivity, or the diffusion coefficient.

ii.2 Measurements on a microscopic scale

The most important class of microscopic measurements are the radiation scattering experiments. Among these three are particularly valuable: neutrons, X-rays, and and laser light scattering. We will now give a brief description of a scattering experiment to stress the connection between measured quantities (the cross section) and theoretical concepts (the structure factor).

A typical layout of a scattering experiment on a liquid is shown in figure 2.3. The incident particles are wave packets with average momenta $\langle \mathbf{p} \rangle = \hbar \mathbf{k}_0$ and average impact parameter $\langle \rho \rangle$. They are assumed to be uniformly distributed on the $z = z_0 \to -\infty$ plane for $\rho \lesssim \rho_{max}$. The range of the scattering potential $\mathcal{V}(\mathbf{r})$ is $r_0 \ll \rho_{max}$.

We want to calculate the differential cross section $d\sigma/d\Omega$ defined as

$$\left[\frac{d\sigma}{d\Omega}(\theta,\phi)\right] d\Omega \equiv \frac{\text{number of particles scattered in } d\Omega/\text{second}}{\text{number of incident particles/(second} \times \text{area on the } z = z_0 \text{ plane)}} \quad .(2.\text{ii:}1)$$

Let us now assume, for simplicity, that the particles in the incident beam are neutrons[1]. The scattering of the neutron with the liquid occurs as a result of interactions with the atomic nuclei of the atoms of the liquid. These interactions are very short ranged, and the total scattering potential $\mathcal{V}(\mathbf{r})$ may therefore be approximated by a sum of delta function pseudopotentials of

[1]Things are only slightly different for X-rays and light scattering. See later on in the text.

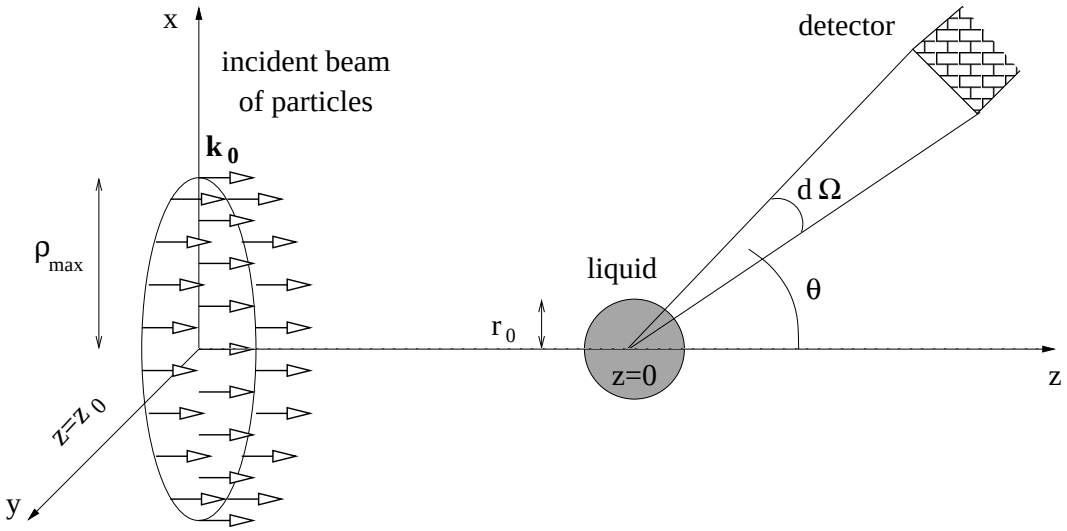

FIGURE 2.3: Diagram showing a general scattering experiment for the measurement of the static structure factor. The incident beam of radiation is made up of particles with average momenta $\hbar\mathbf{k}_0$, uniformly distributed on the $z = z_0 \to -\infty$ plane for $\rho = \sqrt{x^2 + y^2} \lesssim \rho_{max}$. The dimensions of the liquid r_0 are much smaller than ρ_{max}. The detector counts the number of scattered particles falling in the solid angle $d\Omega$ per second.

the form

$$\mathcal{V}(\mathbf{r}) = \frac{2\pi\hbar^2}{m} \sum_{i=1}^{N} b_i \delta(\mathbf{r} - \mathbf{r}_i) \quad , \tag{2.ii:2}$$

where b_i is the scattering length of the ith nucleus. For most nuclei, b_i is positive, but it can also be negative and even complex; it varies both with isotopic species and with the spin state of the nucleus. Using the Born approximation one finds the following result for the differential cross section (see for example [11] chapter 19)

$$\frac{d\sigma}{d\Omega} = \left\langle \sum_{i=1}^{N} \sum_{i=j}^{N} b_i b_j e^{-i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle \quad , \tag{2.ii:3}$$

where $\langle \ldots \rangle$ is the thermal average and $\mathbf{k} = \mathbf{k}_1 - \mathbf{k}_0$, with $\mathbf{k}_1 = k_0 \hat{\boldsymbol{r}}$ the wavevector of the particles collected by the detector. A more useful result is obtained taking a statistical average of the scattering lengths over both the isotopic species present in the sample and the spin states of the nuclei; this can be done independently of the thermal averaging over the coordinates. We therefore introduce the notation

$$\begin{aligned} \langle b_i^2 \rangle &= \langle b^2 \rangle \quad , \\ \langle b_i b_j \rangle &= \langle b_i \rangle \langle b_j \rangle = \langle b \rangle^2 = b_{coh}^2 \quad , \\ (\langle b^2 \rangle - \langle b \rangle^2) &= b_{inc}^2 \quad , \end{aligned}$$

where the subscript "coh" stands for coherent and "inc" for incoherent, and rewrite equation

(2.ii:3) as

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= N\langle b^2\rangle + \langle b\rangle^2 \left\langle \sum_{i\neq j}^{N} e^{-i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)} \right\rangle \\ &= N(\langle b^2\rangle - \langle b\rangle^2) + \langle b\rangle^2 \left\langle \left| \sum_{i=1}^{N} e^{-i\mathbf{k}\cdot\mathbf{r}_i} \right|^2 \right\rangle \\ &= Nb_{inc}^2 + Nb_{coh}^2 S(\mathbf{k}) \quad . \end{aligned} \tag{2.ii:4}$$

We then see that within the coherent contribution to the cross section appear the function $S(\mathbf{k})$ called the *static structure factor* of the liquid. It gives information on the structure of the liquid since for an homogeneous liquid its Fourier transform

$$\rho^2 g^{(2)}(\mathbf{r}) = \rho \int e^{i\mathbf{k}\cdot\mathbf{r}} [S(\mathbf{k}) - 1] \frac{d\mathbf{k}}{(2\pi)^3} \quad , \tag{2.ii:5}$$

represents [see equation (3.i:17)] the probability density of finding a particle on the origin and another at $\mathbf{r}$. For a liquid that is also isotropic $g^{(2)}(r)$ is called the *radial distribution function*. The static structure factor for a multicomponent fluid is discussed in appendix D section i.

A similar calculation can be made for the cross section of elastic scattering of X-rays. In this case only the coherent part gives a contribution and, since X-rays are scattered by the atomic electrons, the analog of b is the atomic form factor.

When the energy of the incident particles is comparable to the thermal energies of the atoms of the liquid, as for thermal neutrons, the scattering cannot be considered elastic any more. The cross section can therefore be measured as a function of energy transfer as well as momentum transfer. By this means it is possible to extract information on wavenumber and frequency dependent fluctuations in liquids at wavelengths comparable with the spacing between particles (see [12] chapter 7). Light scattering experiments yield similar results to thermal neutron scattering, but the accessible range of momentum transfer limits the method to the study of fluctuations of wavelengths of order 10^{-5}cm, corresponding to the hydrodynamic regime.

iii Numerical simulations

Numerical simulations of classical liquids [13, 14], some times called computer experiments, can be of two types: the ones using the method of molecular dynamics [15] and the ones using the Monte Carlo method of Metropolis [16].

These computer experiments give exact results for the particular model studied. Since computers cannot deal with an Avogadro' s number of particles the usefulness of these methods rests in the fact that a model containing a relatively small number of particles (several hundreds) is in most cases sufficiently large to simulate the behavior of a macroscopic system when periodic boundary conditions [17] are employed. Moreover with a computer experiment is possible to obtain informations on quantities of theoretical importance that are not readily measurable in the laboratory.

Molecular dynamics is especially valuable since it allows the study of time dependent phenomena. While to study the static properties of a system the Monte Carlo method is often more suitable, primarily because the implementation of phase averages in any statistical ensemble is simpler than in Molecular dynamics.

iii.1 Molecular dynamics

In a typical molecular dynamic calculation a system of N particles (atoms, molecules, ions, ...) is placed in a cubical box of fixed volume with periodic boundary conditions. A set of initial velocities is assigned to each particle. The velocities are usually drawn from a Maxwell-Boltzmann distribution appropriate to the temperature of interest and selected in such a way as to have the net linear momentum initially equal to zero.

The trajectory of the particles are then calculated by integration of the classical equations of motion

$$m_i \mathbf{r}_i \quad = \quad \mathbf{f}_i = -\nabla_i V_N(r^N) \quad , \tag{2.iii:1}$$

where m_i is the mass of particle i, $\mathbf{r}_i$ is its position, and V_N is the total potential energy already introduced in 2.i:1. The dynamical states that the method generates represent a sample from a microcanonical ensemble.

In the early stages of the calculation it is normal for the temperature to drift away from the value at which it was originally set, and an occasional rescaling of the particles velocities is therefore necessary. Once equilibrium is reached, the system is allowed to evolve undisturbed, with both kinetic and potential energies fluctuating around steady mean values.

The coordinates r^N and momenta p^N of the particles are stored for later analysis. For example if $\mathcal{O}[r^N, p^N]$ is a function of the $6N$ coordinates and momenta, and O is the associated thermodynamic property, the simplest way to obtain O is through a time average of $\mathcal{O}$ over the dynamical history of the system

$$O = \langle \mathcal{O} \rangle_t = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \mathcal{O}[r^N(t), p^N(t)]\, dt \quad . \tag{2.iii:2}$$

iii.2 Monte Carlo

Apart from the choice of initial conditions, a molecular dynamics simulation is, in principle, entirely deterministic in nature. By contrast, as the name suggests, any Monte Carlo computation is essentially probabilistic.

The canonical ensemble average of any property $\mathcal{O}$ function of the particles coordinates can be written as

$$\langle \mathcal{O} \rangle = \frac{\int \mathcal{O}(r^N) e^{-\beta V_N(r^N)}\, dr^N}{\int e^{-\beta V_N(r^N)}\, dr^N} \quad . \tag{2.iii:3}$$

The presence of multidimensional integrals rules out the possibility to use deterministic quadrature methods to calculate $\langle \mathcal{O} \rangle$. We could instead attempt to generate a large number of random configurations of particles $\{s_0, s_1, s_2, \ldots, s_P\}$ with $s_i = (r^N)_i$ and evaluate $\langle \mathcal{O} \rangle$ as

$$\langle \mathcal{O} \rangle \simeq \frac{\sum_{m=1}^{P} \mathcal{O}(s_m) e^{-\beta V_N(s_m)}}{\sum_{m=1}^{P} e^{-\beta V_N(s_m)}} \quad . \tag{2.iii:4}$$

This crude approach is in practice very inefficient because a randomly constructed configuration is likely to have a very small Boltzmann factor.

It is then necessary to introduce importance sampling [18], *i.e* sample configurations in such a way that the regions of configuration space that make the largest contribution to the integrals

in equation (2.iii:3) are also the regions that are sampled most frequently. If $\pi(s_m)$ is the probability of choosing a configuration m, equation (2.iii:4) must be replaced by

$$\langle \mathcal{O} \rangle \simeq \frac{\sum_{m=1}^{P} \mathcal{O}(s_m) e^{-\beta V_N(s_m)} / \pi(s_m)}{\sum_{m=1}^{P} e^{-\beta V_N(s_m)} / \pi(s_m)} \quad . \tag{2.iii:5}$$

If one can sample on the Boltzmann distribution itself

$$\pi(s_m) = \frac{e^{-\beta V_N(s_m)}}{\sum_{m=1}^{P} e^{-\beta V_N(s_m)}} \quad , \tag{2.iii:6}$$

(2.iii:5) reduces to

$$\langle \mathcal{O} \rangle \simeq \frac{1}{P} \sum_{m=1}^{P} \mathcal{O}(s_m) \quad . \tag{2.iii:7}$$

However, in the usual statistical mechanics calculations, the normalization denominator in (2.iii:6) is not known and only relative probabilities of different configurations are easily accessible. The problem of finding a scheme for sampling configuration space according to a specific probability distribution is most easily formulated in terms of the theory of stochastic processes.

In a random walk (Markov chain) one changes the state of the system randomly according to a fixed transition rule $\mathcal{P}(s \to s')$, thus generating a random walk through state space $\{s_0, s_1, s_2, \ldots\}$. The definition of a Markov process is that the next step is chosen from a probability distribution that depends only on the "present" position. $\mathcal{P}(s \to s')$ is a probability distribution so it satisfies

$$\sum_{s'} \mathcal{P}(s \to s') = 1 \quad , \tag{2.iii:8}$$

and

$$\mathcal{P}(s \to s') \geq 0 \quad . \tag{2.iii:9}$$

The transition probability often satisfies the detailed balance property: the transition rate from s to s' equals the reverse rate

$$\pi(s)\mathcal{P}(s \to s') = \pi(s')\mathcal{P}(s' \to s) \quad . \tag{2.iii:10}$$

If the pair $\pi(s)$, $\mathcal{P}(s \to s')$ satisfies the detailed balance and if $\mathcal{P}(s \to s')$ is ergodic [2], then the random walk must eventually have π as its equilibrium asymptotic distribution. Detailed balance is one way of making sure that we sample π; it is a sufficient condition.

The Metropolis (rejection) method is a particular way of ensuring that the transition rules satisfy detailed balance. It does this by splitting the transition probability into an "a priori" sampling distribution $T(s \to s')$ (a probability distribution that we can directly sample) and an acceptance probability $A(s \to s')$ where $0 \leq A \leq 1$

$$\mathcal{P}(s \to s') = T(s \to s')A(s \to s') \quad . \tag{2.iii:11}$$

[2] Ergodicity is ensured if: (1) one can move from any state to any other state in a finite number of steps with a nonzero probability, (2) the transition probability is not periodic (always true if $\mathcal{P}(s \to s) > 0$), (3) the average return time to any state is finite. This is always true in a finite system (*e.g.* periodic boundary conditions).

In the generalized Metropolis procedure [19], trial moves are accepted according to

$$A(s \to s') = \min[1, q(s \to s')] \quad , \tag{2.iii:12}$$

where

$$q(s \to s') = \frac{\pi(s')T(s' \to s)}{\pi(s)T(s \to s')} \quad . \tag{2.iii:13}$$

It is easy to verify detailed balance and hence asymptotic convergence with this procedure by looking at the three cases: $s = s'$ (trivial), $q(s \to s') \leq 1$, and $q(s \to s') \geq 1$.

This is the generalized Metropolis algorithm:

1. Decide what distribution to sample $[\pi(s)]$ and how to move from one state to another $T(s \to s')$.
2. Initialize the state, pick s_0.
3. To advance the state from s_n to s_{n+1}:
   - Sample s' from $T(s_n \to s')$.
   - Calculate the ratio
   $$q = \frac{\pi(s')T(s' \to s_n)}{\pi(s_n)T(s_n \to s')} \quad . \tag{2.iii:14}$$
   - Accept or reject: if $q > u_n$ where u_n is a uniformly distributed random number in (0,1) set $s_{n+1} = s'$, otherwise set $s_{n+1} = s_n$.
4. Throw away the first κ states as being out of equilibrium (κ being the "warm-up" time).
5. Collect averages every so often and block them to get error bars.

Consider the sampling of the classical Boltzmann distribution $\exp(-\beta V_N(s))$. In the original Metropolis procedure [16], $T(s \to s')$ was chosen to be a constant distribution inside a cube and zero outside. This is the "classic" rule: a single atom at a single "time" slice is displaced uniformly and the cube side Δ is adjusted to achieve an efficient sampling of the configuration space. acceptance. Since T is a constant, it drops out of the acceptance formula. So the update rule is

$$\mathbf{r}' = \mathbf{r} + (\mathbf{u} - 1/2)\Delta \quad , \tag{2.iii:15}$$

where $\mathbf{u} = (u_1, u_2, u_3)$ with u_n uniformly distributed random numbers in (0,1). The acceptance is based on $q = \exp\{-\beta[V_N(s') - V_N(s)]\}$: moves that lower the potential energy are always accepted, moves that raise the potential energy are often accepted if the energy cost (relative to $1/\beta$) is small.

Some things to note about Metropolis:

- The acceptance ratio (number of successful moves/total number of trials) is a key quantity to keep track of and to quote. If it is very small one is doing a lot of work without moving through phase space, if it is close to 1 one could use larger steps and get faster convergence.
- One nice feature is that particles can be moved one at a time.
- The normalization of π is not needed, only ratios enter in.
- One can show that Metropolis acceptance formula is optimal among formulas of this kind which satisfy detailed balance (the average acceptance ratio is as large as possible).

Chapter 3

The theory of classical fluids

The motivation for this chapter is to try to summarize the relevant results of the statistical theory of classical fluids, in a modern perspective based on the classical version of the density functional theory (DFT). In section i we introduce the grand canonical formalism, in section ii we follow Percus method to introduce some well known integral equations: Yvon approximation, Percus-Yevick (PY), hypernetted-chain (HNC), and the Born-Green equations. In section iii we present the mean spherical approximation (MSA).

i Grand canonical formalism

In this section we will closely follow a recent paper of J. M. Caillol [20] to introduce DFT from the grand canonical formalism for a one component classical fluid (the generalization to a multicomponent system is given in appendix iii).

Let us consider a classical fluid in a volume V of an Euclidean space of dimension d in the presence of an external potential $\varphi(\mathbf{r})$. Given the system of pointwise, identical, classical particles in thermodynamic equilibrium at a temperature T, the probability density of finding the system with N particles occupying the positions $r^N = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$ and with momenta $p^N = (\mathbf{p}_1, \ldots, \mathbf{p}_N)$ is

$$\mathcal{F}(r^N, p^N, N) = \frac{1}{\Theta} \frac{z^N}{h^{dN} N!} e^{-\beta \mathcal{H}_N(r^N, p^N)} \quad , \tag{3.i:1}$$

where $1/\beta = K_B T$ with K_B the Boltzmann constant, $z = \exp(\beta\mu)$ is the fugacity with μ the chemical potential, and the Hamiltonian $\mathcal{H}_N = K(p^N) + W(r^N) + \sum_{i=1}^N \varphi(\mathbf{r}_i)$ with K the kinetic energy and W the internal potential energy. The normalizing factor $\Theta = \Theta(\mu, V, T)$ is the *grand partition function*. Integrating (3.i:1) over the momenta we find

$$\begin{aligned} f(r^N, N) &= \int \mathcal{F}(r^N, p^N, N)\, dp^N \\ &= \frac{1}{\Theta} \frac{1}{\Lambda^{dN} N!} e^{-\beta W + \sum_{i=1}^N u(\mathbf{r}_i)} \quad , \end{aligned} \tag{3.i:2}$$

where for $K = \sum_i \mathbf{p}_i^2/(2m)$ we have $\Lambda = \sqrt{2\pi\beta\hbar^2/m}$ for the de Broglie thermal wavelength. We also introduced the generalized potential $u(\mathbf{r}) = \beta\mu - \beta\varphi(\mathbf{r})$.

We will now introduce the following notation:

i) a configuration of the system $\omega = (N, r^N)$,

ii) the measure $d\omega = dr^N/(\Lambda^{dN} N!)$,

iii) the system measure $d\mu(\omega) = d\omega\, e^{-\beta W(\omega)}$,

iv) the equilibrium phase space density $f_0(\omega) = f(\omega)\Lambda^{dN} N!$,

v) the microscopic density of particles $\hat{\rho}(\mathbf{r};\omega) = \sum_{i=1}^{N} \delta^d(\mathbf{r} - \mathbf{r}_i)$,

vi) the average of a microscopic variable $\langle A(\omega)\rangle = \sum_{N=0}^{\infty} \int d\omega\, f_0(\omega) A(\omega)$

vii) the scalar product $\langle f(\mathbf{r})|g(\mathbf{r})\rangle = \int d^d\mathbf{r}\, f(\mathbf{r}) g(\mathbf{r})$.

The partition function can then be rewritten as the following functional of the generalized potential

$$\Theta[u] = \int d\mu(\omega)\, e^{\langle \hat{\rho}|u\rangle} \quad . \tag{3.i:3}$$

We define next the set of functions $\mathcal{U} = \{u : V \to \mathbb{R} | \Theta[u] < \infty\}$. We restrict ourselves to the case of $\mathcal{H}$-stable systems in the sense of Ruelle, i.e. systems such that $W(\omega) \geq -NB$ with $B < \infty$ a constant independent of N. We have that

$$\begin{aligned} \Theta[u] &= \sum_{N=0}^{\infty} \frac{1}{N!} \frac{1}{\Lambda^{dN}} \int e^{-\beta W + \sum_{i=1}^{N} u(\mathbf{r}_i)}\, d\mathbf{r}_1 \cdots d\mathbf{r}_N \\ &\leq \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{1}{\Lambda^d} e^{-\beta B} \int_V e^{u(\mathbf{r})} d\mathbf{r} \right)^N \\ &= \exp\left(\frac{1}{\Lambda^d} e^{-\beta B} \int_V e^{u(\mathbf{r})} d\mathbf{r} \right) \quad . \end{aligned} \tag{3.i:4}$$

Then the set $\mathcal{U}$ restricts to $\mathcal{U} = \{u : V \to \mathbb{R} | e^u \in L^1(\mathbb{R}^d, d\mathbf{r})\}$. Since the exponential function is a convex function it is immediate to show that $\mathcal{U}$ is a convex set. Moreover, using Hölder inequality, we can prove [20] that the grand potential $\Omega[u] = -\ln \Theta[u]/\beta$ is a strictly concave functional of u.

i.1 Free energy as the Legendre transform of $\ln \Theta$

Taking the logarithm of f_0 we find

$$\beta W(\omega) + \ln f_0(\omega) = -\ln \Theta + \langle \hat{\rho}(\mathbf{r};\omega)|u(\mathbf{r})\rangle \quad . \tag{3.i:5}$$

We now take the average to obtain

$$\begin{aligned} \langle \beta W(\omega) + \ln f_0(\omega)\rangle &= -\ln \Theta + \langle \langle \hat{\rho}(\mathbf{r};\omega)\rangle | u(\mathbf{r})\rangle \\ &= -\ln \Theta + \langle \rho(\mathbf{r})|u(\mathbf{r})\rangle \quad , \end{aligned} \tag{3.i:6}$$

where we have defined the density function as

$$\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r};\omega)\rangle = \frac{\delta \ln \Theta[u]}{\delta u(\mathbf{r})} \quad . \tag{3.i:7}$$

We define a functional of ρ and u as follows

$$\beta A[\rho, u] = \langle \rho | u\rangle - \ln \Theta[u] \quad . \tag{3.i:8}$$

Notice that for a homogeneous system in absence of external field $A[\rho, \beta\mu] = \Omega[\beta\mu] + N\mu$ is the free energy of the fluid. Moreover, for a given function $\rho(\mathbf{r})$, A is a strictly concave functional of $u(\mathbf{r})$. Which tells us that if A has a maximum for $\bar{u} \in \mathcal{U}$ it has to be unique. We then define the Helmholtz free energy as

$$\beta\bar{A}[\rho] = \beta A[\rho, \bar{u}] = \sup_{u\in\mathcal{U}} \beta A[\rho, u] \quad . \tag{3.i:9}$$

Noticing that $\bar{u}$ is such that $\delta A/\delta u|_{\bar{u}} = 0$, or also (3.i:7), we conclude that the functional of the density $\beta\bar{A}$ is the Legendre transform of $\ln\Theta$ in ρ.

It remains to show the existence of $\bar{u}$ given ρ. We can make the following observations:

(1) If $\rho(\mathbf{r})$ is negative at some $\mathbf{r}$ then, due to the convexity of $\ln\Theta$ (3.i:7) has no solutions;

(2) For the ideal gas $\rho > 0$, is sufficient to ensure that a solution to (3.i:7) exists. Indeed when $W = 0$ (3.i:7) gives

$$\bar{u} = \ln(\Lambda^d\rho) \quad , \tag{3.i:10}$$

as solution;

(3) For $\mathcal{H}$-stable systems one can show that the set

$$\mathcal{R} = \{\rho : V \to \mathbb{R} | (3.i:7) \text{ has solution}\} \tag{3.i:11}$$

is convex.

Some properties of $\bar{A}[\rho]$ which follows from its definition are:

(1) Young' s inequality

$$\beta\bar{A}[\rho] + \ln\Theta[u] \geq \langle\rho|u\rangle \qquad \forall u \in \mathcal{U}, \rho \in \mathcal{R} \quad ; \tag{3.i:12}$$

(2) $\bar{A}[\rho]$ is a strictly convex functional of ρ;

(3) finally the functional derivative of $\beta\bar{A}[\rho]$ with respect to ρ is easily obtained as

$$\frac{\delta\beta\bar{A}[\rho]}{\delta\rho(\mathbf{r})} = \bar{u}(\mathbf{r}) \quad . \tag{3.i:13}$$

i.2 Correlation functions generated by $\ln\Theta[u]$

The n particles correlation functions can be obtained by a Taylor expansion of $\Theta[u+\delta u]$ around u:

$$\begin{aligned} G^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) &= \frac{1}{\Theta[u]} \frac{\delta^{(n)}\Theta[u]}{\delta u(\mathbf{r}_1)\cdots\delta u(\mathbf{r}_n)} \\ &= \langle \prod_{i=1}^{n} \hat{\rho}(\mathbf{r}_i;\omega)\rangle \quad . \end{aligned} \tag{3.i:14}$$

The correlation function $\rho^{(n)}$ typically used in the theory of liquids [12] are defined as the functional derivatives of $\Theta[u]$ with respect to the generalized fugacity $z^*(\mathbf{r}) = e^{u(\mathbf{r})}$

$$\begin{aligned}\rho^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) &= \prod_{i=1}^{n} z^*(\mathbf{r}_i)\frac{1}{\Theta[z^*]}\frac{\delta^{(n)}\Theta[z^*]}{\delta z^*(\mathbf{r}_1)\cdots\delta z^*(\mathbf{r}_n)} \\ &= \langle\left[\prod_{i=1}^{n}\hat{\rho}(\mathbf{r}_i;\omega)\right]_{DP}\rangle \quad , \end{aligned} \tag{3.i:15}$$

where with the symbol $[\ldots]_{DP}$ we indicate that from the sum of products of delta functions within the square braces we have to neglect the ones which contain more than a delta function referred to the same particle and we have to keep only those with delta functions referred to Different Particles. For example we have

$$G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + \rho^{(1)}(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2) \quad . \tag{3.i:16}$$

The n particles distribution function $g^{(n)}$ are then defined as

$$g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{\rho^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)}{\rho^{(1)}(\mathbf{r}_1)\cdots\rho^{(1)}(\mathbf{r}_n)} \quad . \tag{3.i:17}$$

It is often useful to use the connected correlation functions (also known as the Ursell, or cluster, or irreducible correlation functions), these are defined as follows

$$G_c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{\delta^{(n)}\ln\Theta[u]}{\delta u(\mathbf{r}_1)\cdots\delta u(\mathbf{r}_n)} \quad . \tag{3.i:18}$$

The relationship between $G_c^{(n)}$ and $G^{(n)}$ can be written symbolically as follows

$$G_c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = G^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) - \sum\prod_{m<n} G_c^{(m)}(\mathbf{r}_{i_1},\ldots,\mathbf{r}_{i_n}) \quad , \tag{3.i:19}$$

where the sum of products is carried out over all possible partitions of the set $(1,\ldots,n)$ into subsets of cardinal number $m<n$. For instance we have

$$G_c^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = G^{(2)}(\mathbf{r}_1,\mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \quad , \tag{3.i:20}$$

where $\rho = G^{(1)} = G_c^{(1)}$ is the mean density of particles.

It is often useful to define another type of correlation functions, the total correlation functions $h^{(n)}$ as

$$h^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{\rho_c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)}{\rho^{(1)}(\mathbf{r}_1)\cdots\rho^{(1)}(\mathbf{r}_n)} \quad , \tag{3.i:21}$$

where the $\rho_c^{(n)}$ are defined as in (3.i:19) with G replaced by ρ.

i.3 Correlation functions generated by $\bar{A}[\rho]$

The functional $-\beta\bar{A}[\rho]$ is the generating functional for the n particles direct correlation functions $\hat{c}^{(n)}$

$$\hat{c}^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = -\frac{\delta^{(n)}\beta\bar{A}[\rho]}{\delta\rho(\mathbf{r}_1)\cdots\delta\rho(\mathbf{r}_n)} \quad . \tag{3.i:22}$$

The direct correlation functions $\hat{c}^{(n)}$ and the Ursell correlation functions $G_c^{(n)}$ are related through generalized Ornstein-Zernike relations [21]. For historical reasons [22] one rather defines the *true* direct correlation functions $c^{(n)}$ by

$$\hat{c}^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) + \hat{c}_{id}^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) \quad , \tag{3.i:23}$$

where $\hat{c}_{id}^{(n)}$ are the $\hat{c}^{(n)}$ functions of the ideal gas, so that the $c^{(n)}$ are the functional derivatives of minus the excess free energy. From equations (3.i:13) and (3.i:10) we find

$$\hat{c}_{id}^{(1)}(\mathbf{r}) = -\ln[\Lambda^d \rho(\mathbf{r})] \quad , \tag{3.i:24}$$

and from (3.i:22) and (3.i:24) we find for $n \geq 2$

$$\begin{aligned} \hat{c}_{id}^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n) &= \frac{\delta^{(n-1)}\hat{c}_{id}^{(1)}(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)\cdots\delta\rho(\mathbf{r}_n)} \\ &= (-1)^{n-1}\frac{(n-2)!}{\rho^{n-1}(\mathbf{r}_1)}\prod_{i=2}^{n}\delta(\mathbf{r}_1-\mathbf{r}_i) \quad . \end{aligned} \tag{3.i:25}$$

The $c^{(n)}$ and $\rho^{(n)}$ satisfy the Ornstein-Zernike equations typically used in the theory of liquids [12]. Let us show this for $n = 2$. From equations (3.i:23), (3.i:24) and (3.i:13) follows

$$\begin{aligned} c^{(1)}(\mathbf{r}) &= \hat{c}^{(1)}(\mathbf{r}) - \hat{c}_{id}^{(1)}(\mathbf{r}) \\ &= \bar{u}(\mathbf{r}) + \ln[\Lambda^d\rho(\mathbf{r})] \\ &= \ln[\rho(\mathbf{r})/z^*(\mathbf{r})] + \text{constant} \quad . \end{aligned} \tag{3.i:26}$$

We have then

$$\begin{aligned} c^{(2)}(\mathbf{r}_1,\mathbf{r}_2) &= \frac{\delta\ln[\rho(\mathbf{r}_1)/z^*(\mathbf{r}_1)]}{\delta\rho(\mathbf{r}_2)} \\ &= \frac{1}{\rho(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2) - \frac{\delta\ln z^*(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)} \quad , \end{aligned} \tag{3.i:27}$$

but also

$$\begin{aligned} \delta(\mathbf{r}_1-\mathbf{r}_2) = \frac{\delta\ln z^*(\mathbf{r}_1)}{\delta\ln z^*(\mathbf{r}_2)} &= \int \frac{\delta\ln z^*(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_3)}\frac{\delta\rho(\mathbf{r}_3)}{\delta\ln z^*(\mathbf{r}_2)}\,d\mathbf{r}_3 \\ &= \int [\delta(\mathbf{r}_1-\mathbf{r}_3)/\rho^{(1)}(\mathbf{r}_1) - c^{(2)}(\mathbf{r}_1,\mathbf{r}_3)][\delta(\mathbf{r}_2-\mathbf{r}_3)\rho^{(1)}(\mathbf{r}_3) \\ &\quad +\rho^{(1)}(\mathbf{r}_2)\rho^{(1)}(\mathbf{r}_3)h(\mathbf{r}_2,\mathbf{r}_3)] \quad . \end{aligned} \tag{3.i:28}$$

From which follows at last,

$$h^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = c^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + \int \rho^{(1)}(\mathbf{r}_3)c^{(2)}(\mathbf{r}_1,\mathbf{r}_3)h^{(2)}(\mathbf{r}_3,\mathbf{r}_2)\,d\mathbf{r}_3 \quad , \tag{3.i:29}$$

which is the *Ornstein-Zernike equation* (OZ). The generalization of this equation to a multicomponent system is given in appendix D section ii.

ii Percus method

Consider a system of particles interacting through a pair potential $v(i,j)$. We use index i to denote the position of the i-th particle, $\mathbf{r}_i$. Let us imagine to introduce in the system a particle, called 0, fixed on the origin. The particles of the system are then subject to the external field

$$\phi(i) = v(0,i) \quad . \tag{3.ii:1}$$

The grand partition function of the system of particles plus the particle on the origin is a functional of the external field

$$\Theta[\phi] = \sum_{N=0}^{\infty} \frac{\zeta^N}{N!} \int e^{-\beta \sum_{i=1}^{N} \phi(i)} e^{-\beta V_N} \, d1 \cdots dN \quad , \tag{3.ii:2}$$

where $\zeta = z/\Lambda^3$ is the fugacity and $V_N = \sum_{\substack{i,j=1 \\ i<j}}^{N} v(i,j)$. On the other hand we have

$$V_N + \sum_{i=1}^{N} \phi(i) = \sum_{\substack{i,j=0 \\ i<j}}^{N} v(i,j) = V_{N+1}^0 \quad . \tag{3.ii:3}$$

We can then write

$$\begin{aligned} \Theta[\phi] &= \frac{\Theta[0]}{\zeta} \left(\sum_{N=0}^{\infty} \frac{\zeta^{N+1}}{N!} \int e^{-\beta V_{N+1}^0} \, d1 \cdots dN \right) / \Theta[0] \\ &= \frac{\Theta[0]}{\zeta} \left(\sum_{N=1}^{\infty} \frac{\zeta^{N}}{(N-1)!} \int e^{-\beta V_{N}^0} \, d1 \cdots d(N-1) \right) / \Theta[0] \\ &= \frac{\Theta[0]}{\zeta} \rho^{(1)}(0|\phi=0) \quad . \end{aligned} \tag{3.ii:4}$$

Analogously for the single particle density in the presence of the external field we have

$$\rho^{(1)}(1|\phi) = \frac{1}{\Theta[\phi]\zeta} \sum_{N=1}^{\infty} \frac{\zeta^{N+1}}{(N-1)!} \int e^{-\beta V_{N+1}^0} \, d2 \cdots dN \tag{3.ii:5}$$

$$\begin{aligned} &= \left(\frac{1}{\Theta[0]} \sum_{N=2}^{\infty} \frac{\zeta^{N}}{(N-2)!} \int e^{-\beta V_{N}^0} \, d2 \cdots d(N-1) \right) / \rho^{(1)}(0|\phi=0) \\ &= \rho^{(2)}(0,1|\phi=0)/\rho^{(1)}(0|\phi=0) \quad . \end{aligned} \tag{3.ii:6}$$

Similarly one can show that

$$\rho^{(n)}(1,\ldots,n|\phi) = \rho^{(n+1)}(0,1,\ldots,n|\phi=0)/\rho^{(1)}(0|\phi=0) \quad . \tag{3.ii:7}$$

Percus idea [23] was to recognize that if the system in absence of the external field is uniform then

$$\rho^{(1)}(1|\phi) = \rho g(0,1) \tag{3.ii:8}$$

Let us now consider the external field ϕ as a perturbation. The functionals of ϕ can then be expanded in a Taylor series around $\phi = 0$

$$\delta\mathcal{F}[\phi] = \int \left. \frac{\delta\mathcal{F}}{\delta\phi(1)} \right|_{\phi=0} \delta\phi(1) \, d1 + \frac{1}{2!} \int\int \left. \frac{\delta^2\mathcal{F}}{\delta\phi(1)\delta\phi(2)} \right|_{\phi=0} \delta\phi(1)\delta\phi(2) \, d1d2 + \ldots \tag{3.ii:9}$$

At variance with the quantum version of DFT, where approximations are built on the energy functional, the approximations of the theory of classical liquids for the pair correlations are based on the previous formulae and are directly focused on the particle density induced by an additional particle. They can be derived from the Taylor expansion (3.ii:9) of a suitable function of $\rho^{(1)}(1|\phi)$ and ϕ. For example if we expand $\rho^{(1)}(1|\phi)$, to first order in $\delta\phi$, we have

$$\delta\rho^{(1)}(1|\phi) = \int \left.\frac{\delta\rho^{(1)}(1|\phi)}{\delta\phi(2)}\right|_{\phi=0} \delta\phi(2)\, d2 \quad . \tag{3.ii:10}$$

The functional derivative can be easily calculated as

$$\frac{\delta\rho^{(1)}(1|\phi)}{\delta\phi(i)} = \beta[\rho^{(1)}(i|\phi)\rho^{(1)}(1|\phi) - \delta(1,i)\rho^{(1)}(1|\phi) - \rho^{(2)}(1,i|\phi)] \quad , \tag{3.ii:11}$$

where $\delta(1,i) = \delta(\mathbf{r}_1 - \mathbf{r}_i)$ is the Dirac delta function. When we calculate (3.ii:11) at $\phi = 0$ we find

$$\begin{aligned} \left.\frac{\delta\rho^{(1)}(1|\phi)}{\delta\phi(2)}\right|_{\phi=0} &= \beta[\rho^2 - \rho\delta(1,2) - \rho^{(2)}(1,2|0)] \\ &= -\beta[\rho^2 h(1,2) + \rho\delta(1,2)] \quad . \end{aligned} \tag{3.ii:12}$$

Now we observe that

$$\delta\phi(2) = v(0,2) \quad , \tag{3.ii:13}$$

and

$$\delta\rho^{(1)}(1|\phi) = \rho^{(1)}(1|\phi) - \rho^{(1)}(1|0) = \rho h(0,1) \quad . \tag{3.ii:14}$$

Using (3.ii:12), (3.ii:13), and (3.ii:14) in (3.ii:10) we find *Yvon equation* [24]

$$h(0,1) = -\beta v(0,1) + \rho \int h(1,2)[-\beta v(0,2)]\, d2 \quad . \tag{3.ii:15}$$

From the Ornstein-Zernike equation follows that Yvon approximation amounts to setting

$$c(0,1) = -\beta v(0,1) \quad . \tag{3.ii:16}$$

This is also known as Random Phase Approximation (RPA).

In the low density limit ($\rho \to 0$) this approximation gives the wrong behavior for h. According to Yvon equation $h(0,1) \simeq -\beta v(0,1)$ while we know that the correct behavior is $h(0,1) \simeq f(0,1)$ where $f(0,1) = \exp[-\beta v(0,1)] - 1$ is the Mayer function.

We find better approximations when expansions in powers of $\delta\rho^{(1)}(1|\phi)$ are considered.

ii.1 The Percus-Yevick (PY) approximation

Let us consider, for example, the Taylor expansion of the functional $\rho^{(1)}(1|\phi)/\zeta^*(1)$ ($\zeta^*(i) = \zeta e^{-\beta\phi(i)}$) truncated to first order in $\delta\rho^{(1)}$

$$\begin{aligned} \frac{\rho^{(1)}(1|\phi)}{\zeta^*(1)} &= \frac{\rho^{(1)}(1|0)}{\zeta} + \int \left.\frac{\delta[\rho^{(1)}(1|\phi)/\zeta^*(1)]}{\delta\rho^{(1)}(2|\phi)}\right|_{\phi=0} \delta\rho^{(1)}(2|\phi)\, d2 \\ &= \frac{\rho}{\zeta} + \frac{\rho^2}{\zeta}\int c(1,2)\, h(0,2)\, d2 \quad , \end{aligned}$$

where we used the definition of the direct correlation function c (3.i:27). We find then

$$g(0,1)e^{\beta v(0,1)} = 1 + \rho \int c(1,2)\, h(0,2)\, d2 \quad . \tag{3.ii:17}$$

Using Ornstein-Zernike equation we find the following approximation for c

$$c(0,1) = g(0,1)\left(1 - e^{\beta v(0,1)}\right) \quad . \tag{3.ii:18}$$

Using (3.ii:18) in (3.ii:17) we find an integral equation for g known as the *Percus-Yevick equation* [25] (PY)

$$g(0,1)e^{\beta v(0,1)} = 1 + \rho \int g(1,2)\left(1 - e^{\beta v(1,2)}\right)[g(0,2) - 1]\, d2 \quad . \tag{3.ii:19}$$

ii.2 The hypernetted chain approximation

For the functional $\ln[\rho^{(1)}(1|\phi)/\zeta^*(1)]$ we have to first order in $\delta\rho^{(1)}$

$$\ln\left[\frac{\rho g(0,1)}{\zeta e^{-\beta v(0,1)}}\right] = \ln\left[\frac{\rho}{\zeta}\right] + \int c(1,2)\, \rho h(2,0)\, d2 \quad , \tag{3.ii:20}$$

or

$$\ln[g(0,1)] = -\beta v(0,1) + \rho \int c(1,2)\, h(2,0)\, d2 \quad . \tag{3.ii:21}$$

Using Ornstein-Zernike equation we find the following approximation for c

$$c(0,1) = g(0,1) - 1 - \ln[g(0,1)] - \beta v(0,1) \quad . \tag{3.ii:22}$$

Using (3.ii:22) in (3.ii:21) we find an integral equation 4for g known as the *hypernetted chain equation* (HNC)

$$\ln[g(0,1)] = -\beta v(0,1) \tag{3.ii:23}$$

$$+\rho \int \{g(1,2) - 1 - \ln[g(1,2)] - \beta v(1,2)\}[g(2,0) - 1]\, d2 \; . \tag{3.ii:24}$$

iii The mean spherical approximation

Suppose that the particles of the fluid interact through the following pair potential

$$v(1,2) = \begin{cases} \infty & r_{12} < d \\ v_1(1,2) & r_{12} > d \end{cases} \quad , \tag{3.iii:1}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. This pair potential can be rewritten as

$$v(1,2) = v_{hs}(r_{12}) + v_t(\mathbf{r}_{12}) \quad , \tag{3.iii:2}$$

$$v_{hs}(r) = \begin{cases} \infty & r < d \\ 0 & r > d \end{cases} \quad , \tag{3.iii:3}$$

$$v_t(\mathbf{r}) = \begin{cases} 0 & r < d \\ v_1(\mathbf{r}) & r > d \end{cases} \quad , \tag{3.iii:4}$$

where v_{hs} is the spherical hard spheres potential and v_t is the tail potential, generally attractive ($v_1 < 0$) and without spherical symmetry.

The Mayer function can be thus written

$$\begin{aligned} f(1,2) &= e^{-\beta v(1,2)} - 1 \\ &= e^{-\beta v_{hs}(r_{12})} e^{-\beta v_t(\mathbf{r}_{12})} - 1 \\ &= [1 + f_{hs}(r_{12})] e^{-\beta v_t(\mathbf{r}_{12})} - 1 \quad , \end{aligned} \tag{3.iii:5}$$

where f_{hs} is the Mayer function for the hard spheres potential.

$$f_{hs}(r) = \begin{cases} -1 & r < d \\ 0 & r > d \end{cases} \quad . \tag{3.iii:6}$$

If the tail potential is "small" we can linearize f respect to v_t. We thus obtain

$$\begin{aligned} f &= (1 + f_{hs})(1 - \beta v_t + \ldots) - 1 \\ &\simeq f_{hs} - \beta v_t (1 + f_{hs}) \quad . \end{aligned} \tag{3.iii:7}$$

Let us now consider the Percus-Yevick approximation

$$c(1,2) = g(1,2) \left(1 - e^{\beta v(1,2)} \right) \quad , \tag{3.iii:8}$$

and rewrite it in terms of the Mayer function

$$c = f + f(h - c) \quad , \tag{3.iii:9}$$

where $h = g - 1$. From the density expansion for h and c (see [12]) we know that the term of order zero in ρ is the first term on the right hand side of (3.iii:9) ($\lim_{\rho \to 0} h = \lim_{\rho \to 0} c = f$) and the higher orders terms are contained in the second term on the right hand side of (3.iii:9).

The mean spherical approximation consist in substituting f in the first term on the right hand side of (3.iii:9) with its expression linearized in v_t (3.iii:7), and f in the second term on the right hand side of (3.iii:9) with its expression of order zero in v_t. We then write

$$c = \{ f_{hs} - \beta v_t (1 + f_{hs}) \} + \{ f_{hs} \} (h - c) \quad , \tag{3.iii:10}$$

From which follows the mean spherical approximation (MSA)

$$c = -\beta v_t + \frac{f_{hs}}{1 + f_{hs}} g \quad . \tag{3.iii:11}$$

The mean spherical approximation tells us that

$$c(1,2) = -\beta v_1(1,2) \quad \text{for } r_{12} > d \quad , \tag{3.iii:12}$$

on the other hand we know that it has to hold exactly

$$g(1,2) = 0 \quad \text{for } r_{12} < d \quad . \tag{3.iii:13}$$

The problem is then to find $c(1,2)$ for $r_{12} < d$ using the Ornstein-Zernike equation. Another way to reach MSA is to start from RPA instead than PY.

If in place of v_{hs} we have a pair potential v_0, highly repulsive but continuous, replacing in (3.iii:11) f_{hs} with the Mayer function for v_0, we obtain the so called "soft core" mean spherical approximation

$$c = -\beta v_1 + \left(1 - e^{\beta v_0} \right) g \quad . \tag{3.iii:14}$$

The MSA is among the few integral equation which admits analytic solutions when applied to simple classical fluids (see chapter 4). A technique often used to find the analytic solution is the Wiener-Hopf factorization (see appendix B).

Chapter 4

MSA and PY analytic solutions

The Wiener-Hopf factorization (see appendix B) has long been known as a useful method to find analytic solutions of simple integral equations for simple liquids. Probably the first application of this method of solution was on the PY approximation for a one component fluid of hard spheres [26]. This solution, due to Baxter, was alternative to the one given by Thiele-Wertheim [27–29], and had the advantage that it could be easily generalized to the case when the potential consisted of a hard sphere core plus a tail. Later on Baxter [44] extended his method of solution to the PY approximation for a mixture of additive hard spheres. The Wiener-Hopf factorization has been used by Høye and Blum [45] to find an analytic solution to the MSA of an hard sphere multi-Yukawa fluid (one whose pair potential is given by $\beta v(r) = -\sum_i K_i \exp[-z_i(r-1)]/r \quad r > 1, = \infty \quad r < 1$ where the K_i and the z_i are positive constants). Moreover the Wiener-Hopf technique has been used in studies on colloidal suspensions of neutral particles with adhesive interaction. In such studies, Baxter's "sticky hard spheres" model [30, 31] played an important role. In Baxter's original formulation and its extension to the multicomponent case [32, 33] (refereed in the literature as SHS1 model) the pair potential, in addition to a hard sphere repulsion, contains an infinitely deep and narrow attractive square well, obtained according to a particular limiting procedure ("sticky limit") that keeps the second virial coefficient finite. Now the SHS1 in the PY approximation, when applied to an n components mixtures, requires the solution of a set of $n(n+1)/2$ coupled quadratic equations [32]. So this model cannot be used to describe the properties of polydisperse systems [for which the number n of components may be of order $10^1 \div 10^3$ or more (discrete polydispersity) or infinite (continuous polydispersity)]. More recently there have been attempts to find an alternative SHS model which could be analytically tractable even in the general multicomponent case (see [34] for the references). In particular Brey and co-workers [36] proposed to start from a hard sphere Yukawa potential with $K = zK_0$, with K_0 independent of z. This other Hamiltonian (referred to in the literature as SHS2 model) is supplemented by a "sticky limit" which in this case amounts to taking $z \to \infty$ [36]. For the SHS2 model the OZ equation can be solved analytically within the MSA [37, 38]. It turns out that this solution is readily usable even in the polydisperse multicomponent case (see [34] for references). Recently there has been a lot of investigations on the structural properties of polydisperse fluids using the SHS2 model [39, 40] [41–43]. More recently Gazzillo and co-workers showed that the SHS2 model is ill defined: its Hamiltonian leads to an exact second virial coefficient which diverges [34].

In the first section of this chapter we present an application of the Wiener-Hopf technique to the determination of an analytic solutions of the MSA for the restricted primitive model of charged hard spheres. The presentation of this solution, originally given by Blum [46], will allow us to introduce the general formalism needed to tackle a multicomponent system. In the last

section we show how the Wiener-Hopf technique fails to give useful results when applied to a mixture of non additive hard spheres.

i Restricted primitive model for charged hard spheres

In this section we present a detailed derivation of the analytic solution of the MSA for a mixture of uniformly charged hard spheres, obtained through the Wiener-Hopf method.

The simplest model of a ionic liquid (see [12]) is a system of N hard spheres uniformly charged. In this primitive model the spheres are of n different species. The spheres belonging to specie $\mu = 1, 2, \ldots, n$ have a diameter σ_μ and carry a total charge $z_\mu e$, where e is the elementary charge. The spheres move in a continuum medium of dielectric constant ϵ. The pair potential is then

$$v_{\mu\nu}(r) = \begin{cases} \infty & r < \sigma_{\mu\nu} \quad , \\ v^c_{\mu\nu}(r) = \dfrac{z_\mu z_\nu e^2}{\epsilon r} & r > \sigma_{\mu\nu} \quad , \end{cases} \tag{4.i:1}$$

where $\sigma_{\mu\nu} = (\sigma_\mu + \sigma_\nu)/2$. And we shall take the system to be globally neutral

$$\sum_\mu x_\mu z_\mu = 0 \quad , \tag{4.i:2}$$

where x_μ is the concentration of specie μ.

We want to study such model in the restricted case

$$\begin{aligned} \sigma_\mu &= \sigma \quad \forall\mu \quad , \\ |z_\mu| &= z \quad \forall\mu \quad . \end{aligned}$$

In particular we want to study such restricted primitive model when we have just two species (binary mixture) of opposite charge and same concentration (equimolar mixture)

$$\begin{aligned} z_1 &= -z_2 = 1 \quad , \\ x_1 &= x_2 = 1/2 \quad . \end{aligned}$$

Given the symmetry of the model one can immediately verify that the total partial correlation function must have the following symmetry

$$h_{11}(\mathbf{r}_1, \mathbf{r}_2) = h_{22}(\mathbf{r}_1, \mathbf{r}_2) \quad . \tag{4.i:3}$$

For an homogeneous and isotropic system one also have for the total and direct correlation functions (see section ii)

$$h_{12}(r) = h_{21}(r) \quad , \tag{4.i:4}$$

$$c_{12}(r) = c_{21}(r) \quad . \tag{4.i:5}$$

The OZ equation is

$$\begin{aligned}
h_{11}(r) &= c_{11}(r) + \frac{\rho}{2}\left[\int c_{11}(r')h_{11}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' + \int c_{12}(r')h_{21}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\right] \quad , \\
h_{22}(r) &= c_{22}(r) + \frac{\rho}{2}\left[\int c_{21}(r')h_{12}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' + \int c_{22}(r')h_{22}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\right] \quad , \\
h_{12}(r) &= c_{12}(r) + \frac{\rho}{2}\left[\int c_{11}(r')h_{12}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' + \int c_{12}(r')h_{22}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\right] \quad , \\
h_{21}(r) &= c_{21}(r) + \frac{\rho}{2}\left[\int c_{21}(r')h_{11}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' + \int c_{22}(r')h_{21}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\right] \quad .
\end{aligned}$$

Taking the Fourier transform of the first two equations and comparing them we find

$$c_{11}(r) = c_{22}(r) \quad . \tag{4.i:6}$$

The independent OZ equations reduces then to two

$$\begin{aligned}
h_{11}(r) &= c_{11}(r) + \frac{\rho}{2}\left[\int c_{11}(r')h_{11}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' + \int c_{12}(r')h_{21}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\right] \quad , \\
h_{12}(r) &= c_{12}(r) + \frac{\rho}{2}\left[\int c_{11}(r')h_{12}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' + \int c_{12}(r')h_{22}(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\right] \quad .
\end{aligned}$$

This two equations separates upon the introduction of the following combinations

$$\begin{cases} h_s(r) = \frac{1}{2}[h_{11}(r) + h_{12}(r)] \quad , \\ h_d(r) = h_{11}(r) - h_{12}(r) \quad , \end{cases} \tag{4.i:7}$$

$$\begin{cases} c_s(r) = \frac{1}{2}[c_{11}(r) + c_{12}(r)] \quad , \\ c_d(r) = c_{11}(r) - c_{12}(r) \quad , \end{cases} \tag{4.i:8}$$

where h_s is the *number density* total correlation function and h_d the *charge density* total correlation function. The result being

$$h_s(r) = c_s(r) + \rho \int c_s(r')h_s(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' \quad , \tag{4.i:9}$$

$$h_d(r) = c_d(r) + \frac{\rho}{2} \int c_d(r')h_d(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' \quad . \tag{4.i:10}$$

In the mean spherical approximation (3.iii:11) we have

$$c_{\mu\nu}(r) = -\beta v_{\mu\nu}(r) \qquad r > \sigma_{\mu\nu} \quad . \tag{4.i:11}$$

In addition since the pair potential is infinite for $r < \sigma_{\mu\nu}$ we must have the following exact relation

$$h_{\mu\nu} = -1 \qquad r < \sigma_{\mu\nu} \quad . \tag{4.i:12}$$

In terms of the linear combinations just defined we have

$$\begin{cases} h_s(r) = -1 & r < \sigma \quad , \\ c_s(r) = 0 & r > \sigma \quad , \end{cases} \tag{4.i:13}$$

$$\begin{cases} h_d(r) = 0 & r < \sigma \quad , \\ c_d(r) = -\beta\dfrac{2e^2}{\epsilon r} & r > \sigma \quad , \end{cases} \tag{4.i:14}$$

We see then that the closure for the number density correlations is equivalent to the PY approximation for a one component system of neutral hard spheres, whose solution is known [12] to be [1]

$$c_s(x) = -\lambda_1 - 6\eta\lambda_2 x - \frac{1}{2}\eta\lambda_1 x^3 \quad x < 1 \quad , \tag{4.i:15}$$

where $x = r/\sigma$, $\eta = \rho\pi\sigma^3/6$ is the packing fraction, and λ_1, λ_2 are given by

$$\lambda_1 = a^2 = \frac{(1+2\eta)^2}{(1-\eta)^4} \quad , \tag{4.i:16}$$

$$\lambda_2 = -\frac{(1+\eta/2)^2}{(1-\eta)^4} \quad . \tag{4.i:17}$$

The calculation of c_d has been done independently by Waisman and Lebowitz [48, 49], and by Blum [46]. In the next two sections we will present Blum calculation which relies on a generalization of the methods used to solve the PY equation for the one component system of hard spheres. Following Blum we will do the calculation for the full primitive model and specialize to the restricted one later on.

i.1 Method of solution

Noticing that we can write

$$v^c_{\alpha\beta}(r) = \lim_{\mu\to 0} \frac{z_\alpha z_\beta e^2}{\epsilon}\frac{e^{-\mu r}}{r} \quad , \tag{4.i:18}$$

and recalling that the three dimensional Fourier transform of the Yukawa potential $e^{-\mu r}/r$ is $4\pi/(\mu^2+k^2)$, we can write the Fourier transform of the OZ equation in the following matricial form

$$\lim_{\mu\to 0}\left\{[I + \sqrt{\rho}\tilde{H}(k)\sqrt{\rho}]\left[I - \sqrt{\rho}\left(\tilde{C}^0(k) - D\frac{1}{k^2+\mu^2}\right)\sqrt{\rho}\right]\right\} = I \quad , \tag{4.i:19}$$

where $I_{\alpha\beta} = \delta_{\alpha\beta}$ is the identity matrix, $\rho_{\alpha\beta} = \rho_\alpha\delta_{\alpha\beta}$ with $\rho_\alpha = N_\alpha/V$, $D_{\alpha\beta} = z_\alpha z_\beta \alpha^2$ with $\alpha^2 = 4\pi\beta e^2/\epsilon$,

$$\begin{cases} \tilde{H}_{\alpha\beta}(k) = 2\pi\displaystyle\int_{-\infty}^{\infty} e^{ikr}U_{\alpha\beta}(r)\,dr \quad , \\ U_{\alpha\beta}(r) = \displaystyle\int_r^{\infty} sh_{\alpha\beta}(s)\,ds \quad , \end{cases} \tag{4.i:20}$$

$$\begin{cases} \tilde{C}^0_{\alpha\beta}(k) = 2\pi\displaystyle\int_{-\infty}^{\infty} e^{ikr}V_{\alpha\beta}(r)\,dr \quad , \\ V_{\alpha\beta}(r) = \displaystyle\int_r^{\infty} sc^0_{\alpha\beta}(s)\,ds \quad , \\ c^0_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \beta v^c_{\alpha\beta}(r) \quad , \end{cases} \tag{4.i:21}$$

where the total partial correlation function $h_{\alpha\beta}(r)$ and the direct partial correlation function $c_{\alpha\beta}(r)$ are assumed to extend evenly over $r < 0$.

[1] Notice that the PY approximation for the hard spheres fluid in all odd dimensions has been solved analytically by Leutheusser [47]

We now propose the following Wiener-Hopf factorization and will later prove it to be correct

$$I - \sqrt{\rho}\left(\tilde{C}^0(k) - D\frac{1}{k^2+\mu^2}\right)\sqrt{\rho} = \tilde{Q}(k)\tilde{Q}^T(-k) \quad , \tag{4.i:22}$$

where the T stands for transposition. The $\tilde{Q}(k)$ matrix is given by

$$\tilde{Q}_{\alpha\beta}(k) = \delta_{\alpha\beta} + \sqrt{\rho_\alpha\rho_\beta}\left[-\int_{\lambda_{\beta\alpha}}^{\sigma_{\beta\alpha}} e^{ikr}Q_{\alpha\beta}(r)\,dr + A_{\alpha\beta}\int_{\sigma_{\beta\alpha}}^{\infty} e^{ikr}e^{-\mu r}\,dr\right] \quad , \tag{4.i:23}$$

where we have introduced $\lambda_{\alpha\beta} = (\sigma_\alpha - \sigma_\beta)/2$ and $Q_{\alpha\beta}(r)$ is a function which has support on $[\lambda_{\beta\alpha}, \sigma_{\beta\alpha}]$ and is zero otherwise. We will see in section ii that a factorization of this kind is not possible for a mixture of non additive hard spheres. The main obstacle being the determination of the lower bounds $\lambda_{\alpha\beta}$.

We will now simplify (4.i:22).

i.1.1 Relationship between c^0 and Q

In terms of

$$\hat{Q}_{\alpha\beta}(k) = \int e^{ikr}Q_{\alpha\beta}(r)\,dr \quad . \tag{4.i:24}$$

equation (4.i:23) becomes

$$\tilde{Q}_{\alpha\beta}(k) = \delta_{\alpha\beta} + \sqrt{\rho_\alpha\rho_\beta}\left[-\hat{Q}_{\alpha\beta}(k) + A_{\alpha\beta}e^{(ik-\mu)\sigma_{\alpha\beta}}\frac{1}{\mu-ik}\right] \quad . \tag{4.i:25}$$

We then have

$$\begin{aligned}[\tilde{Q}(k)\tilde{Q}^T(k)]_{\alpha\beta} = \delta_{\alpha\beta} + \sqrt{\rho_\alpha\rho_\beta}\Bigg[&-\hat{Q}_{\alpha\beta}(k) - \hat{Q}_{\beta\alpha}(-k) + A_{\alpha\beta}\frac{e^{(ik-\mu)\sigma_{\alpha\beta}}}{\mu-ik} \\ &+A_{\beta\alpha}\frac{e^{(-ik-\mu)\sigma_{\beta\alpha}}}{\mu+ik}\Bigg] + \sqrt{\rho_\alpha\rho_\beta}\sum_\gamma \rho_\gamma\Bigg[\hat{Q}_{\alpha\gamma}(k)\hat{Q}_{\beta\gamma}(-k) \\ &+A_{\alpha\gamma}A_{\beta\gamma}\frac{e^{ik(\sigma_{\alpha\gamma}-\sigma_{\beta\gamma})}e^{-\mu(\sigma_{\alpha\gamma}+\sigma_{\beta\gamma})}}{\mu^2+k^2} - \hat{Q}_{\alpha\gamma}(k)A_{\beta\gamma}\frac{e^{(-ik-\mu)\sigma_{\beta\gamma}}}{\mu+ik} \\ &-\hat{Q}_{\beta\gamma}(-k)A_{\alpha\gamma}\frac{e^{(ik-\mu)\sigma_{\alpha\gamma}}}{\mu-ik}\Bigg] \quad .\end{aligned} \tag{4.i:26}$$

The term containing the product of two A's can be rewritten as

$$\sqrt{\rho_\alpha\rho_\beta}e^{-\mu\sigma_{\alpha\beta}}\sum_\gamma \rho_\gamma A_{\alpha\gamma}A_{\beta\gamma}e^{-\mu\sigma_\gamma}\left(\frac{e^{ik\lambda_{\alpha\beta}}}{k^2+\mu^2}\right) \quad . \tag{4.i:27}$$

The inverse one dimensional Fourier transform of the term in parenthesis is

$$\frac{1}{2\pi}\frac{e^{-\mu|r-\lambda_{\alpha\beta}|}}{\mu} \quad . \tag{4.i:28}$$

Next we take the one dimensional inverse Fourier transform of the Wiener-Hopf factorization, i.e. we multiply both members of (4.i:22) by e^{-ikr} and integrate on $dk/(2\pi)$ over the whole real axis. We find

$$\begin{aligned}
-2\pi V_{\alpha\beta}(|r|) + D_{\alpha\beta}\frac{e^{-\mu|r|}}{2\pi\mu} = \\
\left[-Q_{\alpha\beta}(r) - Q_{\beta\alpha}(-r) + A_{\alpha\beta}e^{-\mu r}\theta(r-\sigma_{\alpha\beta}) + A_{\beta\alpha}e^{\mu r}\theta(-r-\sigma_{\alpha\beta})\right] \\
+\sum_\gamma \rho_\gamma \left\{ \int Q_{\beta\gamma}(t)Q_{\alpha\gamma}(t+r)\,dt + A_{\alpha\gamma}A_{\beta\gamma}e^{-\mu\sigma_{\alpha\beta}}e^{-\mu\sigma_\gamma}\frac{e^{-\mu|r-\lambda_{\alpha\beta}|}}{2\pi\mu} \right. \\
\left. -A_{\alpha\gamma}\int Q_{\beta\gamma}(t)[e^{-\mu(t+r)}]_{\sigma_{\alpha\gamma}}^{\infty}dt - A_{\beta\gamma}\int Q_{\alpha\gamma}(t+r)[e^{-\mu t}]_{\sigma_{\beta\gamma}}^{\infty}dt \right\} \quad , \qquad (4.i:29)
\end{aligned}$$

where θ is the Heaviside step function and the function $[f(t)]_a^b$ equals $f(t)$ in $[a,b]$ and is zero otherwise.

We have three convolutions

$$\begin{aligned}
I_\gamma^1(r) &= \int Q_{\beta\gamma}(t)Q_{\alpha\gamma}(t+r)\,dt \quad , \\
I_\gamma^2(r) &= \int Q_{\beta\gamma}(t)[e^{-\mu(t+r)}]_{\sigma_{\alpha\gamma}}^{\infty}dt \quad , \\
I_\gamma^3(r) &= \int Q_{\alpha\gamma}(t+r)[e^{-\mu t}]_{\sigma_{\beta\gamma}}^{\infty}dt \quad .
\end{aligned}$$

The integration intervals in each one of the convolutions are

$$\begin{aligned}
I_\gamma^1 &: \quad [\lambda_{\gamma\beta},\sigma_{\gamma\beta}] \cap [\lambda_{\gamma\alpha}-r,\sigma_{\gamma\alpha}-r] \quad , \\
I_\gamma^2 &: \quad [\lambda_{\gamma\beta},\sigma_{\gamma\beta}] \cap [\sigma_{\gamma\alpha}-r,\infty] \quad , \\
I_\gamma^3 &: \quad [\sigma_{\gamma\beta},\infty] \cap [\lambda_{\gamma\alpha}-r,\sigma_{\gamma\alpha}-r] \quad .
\end{aligned}$$

For $r=\sigma_{\alpha\beta}$ we have

$$\begin{aligned}
I_\gamma^1 &: \quad [\lambda_{\gamma\beta},\sigma_{\gamma\beta}] \cap [\lambda_{\gamma\beta}-\sigma_\alpha,\lambda_{\gamma\beta}] \quad , \\
I_\gamma^2 &: \quad [\lambda_{\gamma\beta},\lambda_{\gamma\beta}+\sigma_\beta] \cap [\lambda_{\gamma\beta},\infty] \quad , \\
I_\gamma^3 &: \quad [\lambda_{\gamma\beta}+\sigma_\beta,\infty] \cap [\lambda_{\gamma\beta}-\sigma_\alpha,\lambda_{\gamma\beta}] \quad .
\end{aligned}$$

We then see that for $r>\sigma_{\alpha\beta}$ we have

$$I_\gamma^1 = 0 \quad \forall\gamma \quad , \qquad (4.i:30)$$

$$I_\gamma^3 = 0 \quad \forall\gamma \quad , \qquad (4.i:31)$$

and the integration interval for I_γ^2 is $[\lambda_{\gamma\beta},\sigma_{\gamma\beta}]$. The Wiener-Hopf factorization in real space, equation (4.i:29), for $r>\sigma_{\alpha\beta}$ becomes then

$$\begin{aligned}
D_{\alpha\beta}\frac{e^{-\mu r}}{2\pi\mu} &= e^{-\mu\sigma_{\alpha\beta}}\left(\sum_\gamma \rho_\gamma A_{\alpha\gamma}A_{\beta\gamma}e^{-\mu\sigma_\gamma}\right)\frac{e^{-\mu(r-\lambda_{\alpha\beta})}}{2\pi\mu} \\
&\quad -\sum_\gamma \rho_\gamma A_{\alpha\gamma}\int_{\lambda_{\gamma\beta}}^{\sigma_{\gamma\beta}} Q_{\beta\gamma}(t)[e^{-\mu(t+r)}]_{\sigma_{\alpha\gamma}}^{\infty}dt + A_{\alpha\beta}e^{-\mu r} \quad . \qquad (4.i:32)
\end{aligned}$$

Let us now make two observations:

(1) multiplying both members of (4.i:32) by μ and taking the limit $\mu \to 0$ we find

$$D_{\alpha\beta} = \sum_\gamma \rho_\gamma A_{\alpha\gamma} A_{\beta\gamma} \quad , \tag{4.i:33}$$

recalling that $D_{\alpha\beta} = z_\alpha z_\beta \alpha^2$ we need then

$$A_{\alpha\beta} = z_\alpha a_\beta \quad . \tag{4.i:34}$$

Therefore (4.i:33) becomes

$$\alpha^2 = \sum_\gamma \rho_\gamma a_\gamma^2 \quad . \tag{4.i:35}$$

(2) if we call $\Delta^\mu_{\alpha\beta}(r)$ the difference between the left hand side and the first term on the right hand side of (4.i:32) we have

$$\begin{aligned} \lim_{\mu\to 0} \Delta^\mu_{\alpha\beta}(r) &= A_{\alpha\beta} - \sum_\gamma \rho_\gamma A_{\alpha\gamma} \int Q_{\beta\gamma}(t)\, dt \\ &= A_{\beta\alpha} - \sum_\gamma \rho_\gamma A_{\beta\gamma} \int Q_{\alpha\gamma}(t)\, dt = \text{constant} \quad , \end{aligned} \tag{4.i:36}$$

where the second equality follows looking at the real space Wiener-Hopf factorization for $r < -R_{\alpha\beta}$.

We now study the integration intervals of the three convolutions when $r = \lambda_{\beta\alpha}$

$$\begin{aligned} I^1_\gamma &: \quad [\lambda_{\gamma\beta}, \sigma_{\gamma\beta}] \cap [\lambda_{\gamma\beta}, \lambda_{\gamma\beta} + \sigma_\alpha] \quad , \\ I^2_\gamma &: \quad [\lambda_{\gamma\beta}, \sigma_{\gamma\beta}] \cap [\lambda_{\gamma\beta} + \sigma_\alpha, \infty] \quad , \\ I^3_\gamma &: \quad [\sigma_{\gamma\beta}, \infty] \cap [\lambda_{\gamma\beta}, \lambda_{\gamma\beta} + \sigma_\alpha] \quad . \end{aligned}$$

Then for $r \geq \lambda_{\beta\alpha}$ we have

$$\begin{aligned} I^1_\gamma &: \quad [\lambda_{\gamma\beta}, \min\{\sigma_{\gamma\beta}, \sigma_{\gamma\alpha} - r\}] \quad , \\ I^2_\gamma &: \quad [\max\{\lambda_{\gamma\beta}, \sigma_{\gamma\alpha} - r\} \sigma_{\gamma\beta}] \quad , \\ I^3_\gamma &: \quad [\sigma_{\gamma\beta}, \sigma_{\gamma\alpha} - r] \quad . \end{aligned}$$

Taking into account observation (2), the Wiener-Hopf factorization (4.i:29) in the limit $\mu \to 0$, in the interval $\lambda_{\beta\alpha} \leq r \leq \sigma_{\beta\alpha}$ becomes

$$\begin{aligned} -2\pi V_{\alpha\beta}(|r|) &= -Q_{\alpha\beta}(r) + A_{\alpha\beta}[\theta(r - \sigma_{\alpha\beta}) - 1] + \sum_\gamma \rho_\gamma \left[\int Q_{\beta\gamma}(t) Q_{\alpha\gamma}(t + r)\, dt \right. \\ &\quad - A_{\alpha\gamma} \left(\int_{\sigma_{\alpha\gamma} - r}^\infty Q_{\beta\gamma}(t)\, dt - \int Q_{\beta\gamma}(t)\, dt \right) \\ &\quad \left. - A_{\beta\gamma} \int_{\sigma_{\beta\gamma}}^\infty Q_{\alpha\gamma}(t + r)\, dt \right] \quad . \end{aligned} \tag{4.i:37}$$

Once $V_{\alpha\beta}(r)$ is known iterating over Q is then formally possible to find $Q_{\alpha\beta}(r)$. This proves that the factorization proposed (4.i:22) and (4.i:23) is indeed correct. This is the relationship between V and Q. Taking a derivative with respect to r one finds the relationship between c^0 and Q we are looking for. Before we do this we will make two observations:

(1) From equation (4.i:37) follows

$$\lim_{r\to\sigma_{\alpha\beta}^-} Q_{\alpha\beta}(r) = -A_{\alpha\beta} \quad , \tag{4.i:38}$$

(2) since $c^0_{\alpha\beta}(r)$ is symmetric, $V_{\alpha\beta}(r)$ is symmetric, then taking into account the remark (4.i:36) follows

$$Q_{\alpha\beta}(\lambda_{\beta\alpha}) = Q_{\beta\alpha}(\lambda_{\alpha\beta}) \quad . \tag{4.i:39}$$

Indeed we have

$$\begin{aligned}\int Q_{\beta\gamma}(t)Q_{\alpha\gamma}(t+\lambda_{\beta\alpha})\,dt &= \int Q_{\beta\gamma}(s-\lambda_{\beta\alpha})Q_{\alpha\gamma}(s)\,ds \\ &= \int Q_{\alpha\gamma}(s)Q_{\beta\gamma}(s+\lambda_{\alpha\beta})\,ds \quad ,\end{aligned}$$

and

$$\begin{aligned}&\sum_\gamma \rho_\gamma \left[A_{\alpha\gamma}\int_{\sigma_{\alpha\gamma}-\lambda_{\beta\alpha}}^\infty Q_{\beta\gamma}(t)\,dt + A_{\beta\gamma}\int_{\sigma_{\beta\gamma}+\lambda_{\beta\alpha}}^\infty Q_{\alpha\gamma}(t)\,dt\right] = \\ &\sum_\gamma \rho_\gamma \left[A_{\alpha\gamma}\int_{\sigma_{\alpha\gamma}+\lambda_{\alpha\beta}}^\infty Q_{\beta\gamma}(t)\,dt + A_{\beta\gamma}\int_{\sigma_{\beta\gamma}-\lambda_{\alpha\beta}}^\infty Q_{\alpha\gamma}(t)\,dt\right] = \\ &\sum_\gamma \rho_\gamma \left[A_{\beta\gamma}\int_{\sigma_{\beta\gamma}-\lambda_{\alpha\beta}}^\infty Q_{\alpha\gamma}(t)\,dt + A_{\alpha\gamma}\int_{\sigma_{\alpha\gamma}+\lambda_{\alpha\beta}}^\infty Q_{\beta\gamma}(t)\,dt\right] \quad .\end{aligned}$$

Let us now take the derivative with respect to r of equation (4.i:37). We find for $\lambda_{\beta\alpha} \le r \le \sigma_{\beta\alpha}$

$$\begin{aligned}2\pi r c^0_{\alpha\beta}(|r|) = -Q'_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \Bigg[&\frac{dI^1_\gamma}{dr} - A_{\alpha\gamma}Q_{\beta\gamma}(\sigma_{\alpha\gamma}-r) \\ &+A_{\beta\gamma}Q_{\alpha\gamma}(\sigma_{\beta\gamma}+r)\Bigg] \quad ,\end{aligned} \tag{4.i:40}$$

The third term in the square braces exists for $-\sigma_{\alpha\beta} \le r \le \lambda_{\alpha\beta}$. The second term in the square braces exists for $\lambda_{\alpha\beta} \le r \le \sigma_{\alpha\beta}$. The first term in the square braces is

$$\begin{aligned}\frac{dI^1_\gamma}{dr} &= \frac{d}{dr}\int_{\lambda_{\gamma\beta}}^{\min\{\sigma_{\gamma\beta},\sigma_{\gamma\alpha}-r\}} Q_{\beta\gamma}(t)Q_{\alpha\gamma}(t+r)\,dt \\ &= \begin{cases} \displaystyle\int Q_{\beta\gamma}(t)Q'_{\alpha\gamma}(t+r)\,dt & r < \lambda_{\alpha\beta} \quad , \\ \displaystyle Q_{\beta\gamma}(\sigma_{\gamma\alpha}-r)A_{\alpha\gamma} + \int Q_{\beta\gamma}(t)Q'_{\alpha\gamma}(t+r)\,dt & r \ge \lambda_{\alpha\beta} \quad ,\end{cases}\end{aligned} \tag{4.i:41}$$

where we used equation (4.i:38). So we can rewrite equation (4.i:40) as follows

$$2\pi r c^0_{\alpha\beta}(|r|) = -Q'_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \left[\int Q_{\beta\gamma}(t)Q'_{\alpha\gamma}(t+r)\,dt + A_{\beta\gamma}Q_{\alpha\gamma}(\sigma_{\beta\gamma+r})\right] \quad , \tag{4.i:42}$$

where the last term exists only when $\lambda_{\beta\alpha} \leq r \leq \lambda_{\alpha\beta}$ (we are considering the worst case possible when $\sigma_\alpha > \sigma_\beta$).

In particular when all the diameters are equal, $\sigma_{\alpha\beta} = \sigma$, $\lambda_{\alpha\beta} = 0$, and $Q_{\alpha\beta}(r)$ has support on $[0, \sigma]$. We find then for $0 \leq r \leq \sigma$

$$2\pi c^0_{\alpha\beta}(r) = -Q'_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \int_0^{\sigma-r} Q_{\beta\gamma}(t) Q'_{\alpha\gamma}(t+r)\, dt \quad . \tag{4.i:43}$$

i.1.2 Relationship between U and Q

Introducing the Wiener-Hopf factorization (4.i:22) into the OZ equation 4.i:19 we find in matricial notation

$$[I + \sqrt{\rho}\tilde{H}(k)\sqrt{\rho}]\tilde{Q}(k) - I = [\tilde{Q}^T(-k)]^{-1} - I \quad . \tag{4.i:44}$$

When we take the inverse one dimensional Fourier transform of this expression the right hand side give zero contribution for $r > \lambda_{\beta\alpha}$ [44] infact:

(1) form equation (4.i:23) follows that for $ik \to \infty$

$$\tilde{Q}_{\alpha\beta}(-k) \sim \delta_{\alpha\beta} + e^{-ik\lambda_{\beta\alpha}} \left[l_{\alpha\beta}(k) + m_{\alpha\beta}(k) e^{-ik(\sigma_{\alpha\beta} - \lambda_{\beta\alpha})} \right] \quad , \tag{4.i:45}$$

where $l_{\alpha\beta}(k)$ and $m_{\alpha\beta}(k)$ are $O(1/k)$. Then we must have

$$\left\{ [\tilde{Q}^T(-k)]^{-1} - I \right\}_{\alpha\beta} \sim e^{ik\lambda_{\beta\alpha}} n_{\alpha\beta}(k) \quad , \tag{4.i:46}$$

with $\lim_{ik\to\infty} n_{\alpha\beta}(k) = 0$. From which follows that for $r > \lambda_{\beta\alpha}$

$$e^{-ikr} \left\{ [\tilde{Q}^T(-k)]^{-1} - I \right\}_{\alpha\beta} \overset{ik\to\infty}{\longrightarrow} 0 \quad . \tag{4.i:47}$$

When taking the inverse Fourier transform of the right hand side of (4.i:44) we can then close the path of integration on the lower half imaginary $k = x + iy$ plane. Since the contribution from the path at $y < 0$ gives zero contribution to the total integral;

(2) the matrix elements of $\tilde{Q}^T(-k)$ are analytic functions of k on the whole complex plane (being the Fourier transforms of functions with finite support). The same then holds for the elements of $[\tilde{Q}^T(-k)]^{-1}$. Then the path integral considered at point (1) must vanish by Cauchy' s theorem.

The inverse one dimensional Fourier transform of (4.i:44) is then

$$2\pi U_{\alpha\beta}(|r|) = Q_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \left[2\pi \int_{\lambda_{\beta\gamma}}^{\sigma_{\beta\gamma}} Q_{\gamma\beta}(s) U_{\gamma\alpha}(|r-s|)\, ds \right.$$
$$\left. -2\pi A_{\gamma\beta} \int_{\sigma_{\beta\gamma}}^{\infty} e^{-\mu s} U_{\gamma\alpha}(|r-s|)\, ds \right] \quad . \tag{4.i:48}$$

or in the limit $\mu \to 0$

$$2\pi U_{\alpha\beta}(|r|) = Q_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \left[2\pi \int_{\lambda_{\beta\gamma}}^{\sigma_{\beta\gamma}} Q_{\gamma\beta}(s) U_{\gamma\alpha}(|r-s|)\, ds \right. \tag{4.i:49}$$
$$\left. -2\pi A_{\gamma\beta} \int_{\sigma_{\beta\gamma}-r}^{\infty} U_{\gamma\alpha}(|t|)\, dt \right] \quad . \tag{4.i:50}$$

We now use the charge sum rule to simplify the last term. The normalization condition for the partial pair distribution function can be written (see (D.iii:6))

$$\rho_\mu \int g_{\mu\nu}(r)\, d\mathbf{r} = N_\mu - \delta_{\mu\nu} \quad . \tag{4.i:51}$$

Multiplying this expression by z_μ, summing over μ, and using the neutrality condition (4.i:2) we find for $h_{\mu\nu} = g_{\mu\nu} - 1$

$$\sum_\mu \rho_\mu \int h_{\mu\nu}(r)\, d\mathbf{r} = -z_\nu \quad . \tag{4.i:52}$$

Multiplying by a_γ and recalling (4.i:34) we find

$$4\pi \sum_\mu A_{\mu\gamma}\rho_\mu \int_0^\infty h_{\mu\nu}(r) r^2\, dr = -A_{\nu\gamma} \quad . \tag{4.i:53}$$

Integrating by parts we have

$$\int_0^r r[r h_{\mu\nu}(r)]\, dr = \left[-r\int_r^\infty r h_{\mu\nu}(r)\right]_0^\infty + \int_0^\infty \left[\int_r^\infty r' h_{\mu\nu}(r')\, dr'\right] dr \quad . \tag{4.i:54}$$

Since $\hat{h}_{\mu\nu}(k=0)$ must be finite, then $h_{\mu\nu}(r)$ must behave as $1/r^{3+\epsilon}$, $\epsilon > 0$ for $r \to \infty$. Then the first term in the right hand side of (4.i:54) must vanish also in $r = \infty$ and we find

$$2\pi \sum_\mu A_{\mu\gamma}\rho_\mu \int_0^\infty U_{\mu\nu}(r)\, dr = -\frac{A_{\nu\gamma}}{2} \quad . \tag{4.i:55}$$

Then the relationship between U and Q becomes

$$\begin{aligned} 2\pi U_{\alpha\beta}(|r|) = Q_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \Bigg[& 2\pi \int_{\lambda_{\beta\gamma}}^{\sigma_{\beta\gamma}} Q_{\gamma\beta}(s) U_{\gamma\alpha}(|r-s|)\, ds \\ & -2\pi A_{\gamma\beta} \int_0^{\sigma_{\beta\gamma}-r} U_{\gamma\alpha}(|t|)\, dt \Bigg] + \frac{A_{\alpha\beta}}{2} \quad . \end{aligned} \tag{4.i:56}$$

For $r \le \sigma_{\alpha\beta}$ we must have $g_{\alpha\beta}(r) = 0$. We can then write

$$\begin{aligned} U_{\alpha\beta}(r) &= \int_r^\infty s h_{\alpha\beta}(s)\, ds = \int_0^\infty s h_{\alpha\beta}(s)\, ds + \frac{r^2}{2} \\ &= \frac{J_{\alpha\beta}}{2\pi} + \frac{r^2}{2} \qquad r, \le \sigma_{\alpha\beta} \quad , \end{aligned} \tag{4.i:57}$$

where we have defined the constants

$$J_{\alpha\beta} = 2\pi \int_0^\infty s h_{\alpha\beta}(s)\, ds = J_{\beta\alpha} \quad . \tag{4.i:58}$$

It is easy to verify that the relationship (4.i:56) between U and Q on the interval $\lambda_{\beta\alpha} < r < \sigma_{\beta\alpha}$ involves the function $U_{\alpha\beta}(r)$ only on the interval $0 \le r < \sigma_{\beta\alpha}$. Given $U_{\alpha\beta}(r)$ on $0 \le r < \sigma_{\beta\alpha}$, is then possible to find $Q_{\alpha\beta}(r)$ as a function of $A_{\alpha\beta}$ and $J_{\alpha\beta}$. This is done in appendix E. Moreover we know that

$$\lim_{r \to \sigma_{\beta\alpha}^-} Q_{\alpha\beta}(r) = -A_{\alpha\beta} \quad , \tag{4.i:59}$$

and we continuously extend $Q_{\alpha\beta}(r)$ in $\lambda_{\beta\alpha}$

$$Q_{\alpha\beta}(\lambda_{\beta\alpha}) = \lim_{r \to \lambda_{\beta\alpha}^+} Q_{\alpha\beta}(r) \quad . \tag{4.i:60}$$

ii PY solution for non additive hard spheres

An interesting problem which has not yet been solved is the determination of a complete analytic solution of the PY integral equations for a system of three dimensional non additive hard spheres (NAHS). In some early papers Lebowitz and co-workers [50, 51] found the exact correlation functions as well as the solution of the PY integral equation for NAHS in one dimension with some restriction on the non additivity parameter $(R_{\alpha\beta} - (R_\alpha + R_\beta)/2)$, but their extension to the three dimensional system was not complete and they could not provide a closed analytical expression for the direct correlation functions.

The NAHS model is interesting because the inclusion of a negative $(R_{\alpha\beta} < (R_\alpha + R_\beta)/2)$ or positive $(R_{\alpha\beta} > (R_\alpha + R_\beta)/2)$ non additivity is crucial to model several experimental results on binary systems (compound forming alloys, aqueous electrolyte solutions as well as molten salts are good examples for negative non additivity. Positive non-additivity could be used to model the tendency to phase separation in liquid alloys, some alkali metals alloys, or supercritical aqueous solutions of NaCl. See [52] for the references). Ordering phenomena (compound alternation or segregation) can often be interpreted in terms of the excluded volume effects due to non additivity in the repulsive cores.

In this section we will show which are the main difficulties in trying to generalize to NAHS the work of Baxter [44] on the analytic solution of the PY approximation for a mixture of additive hard spheres.

Let us consider an homogeneous and isotropic fluid of density ρ made of n different types of hard spheres of diameter $R_1, R_2, \ldots, R_n$. Let ρ_α be the density of the hard spheres of type $\alpha = 1, 2, \ldots, n$. Moreover let the distance of closest approach between two spheres be

$$R_{\alpha\beta} = \begin{cases} R_\alpha & \alpha = \beta \\ \frac{1}{2}(R_\alpha + R_\beta)(1 + \Delta_{\alpha\beta}) & \alpha \neq \beta \end{cases} \quad , \tag{4.ii:1}$$

where $\Delta_{\alpha\beta}$ are the parameters which rules the non additivity: for $\Delta_{\alpha\beta} = 0$ the spheres are said to be additive.

The Ornstein-Zernike (OZ) equation (D.ii:1) give a relationship between the partial total correlation functions $h_{\alpha\beta}$ and the partial direct correlation functions $c_{\alpha\beta}$

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \int c_{\alpha\gamma}(s) h_{\gamma\beta}(|\mathbf{r} - \mathbf{s}|) \quad , \tag{4.ii:2}$$

where $r = |\mathbf{r}|$ and $s = |\mathbf{s}|$.

Since the pair interaction potential $\phi_{\alpha\beta}(r)$ is infinite for $r < R_{\alpha\beta}$ we must have

$$h_{\alpha\beta}(r) = -1 \quad \text{for } r < R_{\alpha\beta} \quad . \tag{4.ii:3}$$

Since $\phi_{\alpha\beta}(r)$ is zero for $r > R_{\alpha\beta}$, the PY approximation states that we must have

$$c_{\alpha\beta}(r) = 0 \quad \text{for } r > R_{\alpha\beta} \quad . \tag{4.ii:4}$$

The problem consists in the solution of the system of equations (4.ii:2), (4.ii:3), and (4.ii:4).

ii.1 The Wiener-Hopf factorization is ill defined

Multiplying the OZ equation (4.ii:2) times $\sqrt{\rho_\alpha \rho_\beta} e^{i\mathbf{k}\cdot\mathbf{r}}$ and integrating over the whole space in $d\mathbf{r}$ we find in matricial form

$$\tilde{H}(k) = \tilde{C}(k) + \tilde{C}(k)\tilde{H}(k) \quad , \tag{4.ii:5}$$

where $k = |\mathbf{k}|$ and

$$\begin{cases} \tilde{H}_{\alpha\beta}(k) = 2\pi \displaystyle\int_{-\infty}^{\infty} e^{ikr} U_{\alpha\beta}(r)\, dr \\ U_{\alpha\beta}(r) = \displaystyle\int_{r}^{\infty} \sqrt{\rho_\alpha \rho_\beta}\, s h_{\alpha\beta}(s)\, ds \end{cases} , \tag{4.ii:6}$$

$$\begin{cases} \tilde{C}_{\alpha\beta}(k) = 2\pi \displaystyle\int_{-\infty}^{\infty} e^{ikr} V_{\alpha\beta}(r)\, dr \\ V_{\alpha\beta}(r) = \displaystyle\int_{r}^{\infty} \sqrt{\rho_\alpha \rho_\beta}\, s c_{\alpha\beta}(s)\, ds \end{cases} . \tag{4.ii:7}$$

We follow the convention of choosing $h_{\alpha\beta}(-r) = h_{\alpha\beta}(r)$ and $c_{\alpha\beta}(-r) = c_{\alpha\beta}(r)$ so that $U_{\alpha\beta}$ and $V_{\alpha\beta}$ are even functions.

Now we note that $I - \tilde{C}(k)$, where I is the identity matrix, is a symmetric matrix and an even function of k. So following Baxter we perform the following Wiener-Hopf factorization

$$I - \tilde{C}(k) = [I + \tilde{H}(k)]^{-1} = \tilde{Q}^T(-k)\tilde{Q}(k) \quad , \tag{4.ii:8}$$

where we use the superscript T to denote the transposed matrix and

$$\tilde{Q}_{\alpha\beta}(k) = \delta_{\alpha\beta} - \int_{S_{\alpha\beta}}^{R_{\alpha\beta}} e^{ikr} Q_{\alpha\beta}(r)\, dr \equiv \delta_{\alpha\beta} - \hat{Q}_{\alpha\beta}(k) \quad . \tag{4.ii:9}$$

The $Q_{\alpha\beta}(r)$ are real functions with support in $[S_{\alpha\beta}, R_{\alpha\beta}]$ and zero everywhere else. The parameters $S_{\alpha\beta}$ are for the moment unknowns. We will now prove that they are ill defined for the NAHS.

We first rewrite equation (4.ii:8) as follows

$$\tilde{C}_{\alpha\beta}(k) = \hat{Q}_{\alpha\beta}(k) + \hat{Q}_{\beta\alpha}(-k) - \sum_{\gamma} \hat{Q}_{\gamma\alpha}(-k)\hat{Q}_{\gamma\beta}(k) \quad . \tag{4.ii:10}$$

Then we multiply both sides by e^{-ikr} and integrate in $dk/(2\pi)$ over the whole real axis. We find for $r > R_{\alpha\beta}$

$$2\pi V_{\alpha\beta}(r) = -\sum_{\gamma} \int Q_{\gamma\alpha}(t) Q_{\gamma\beta}(t + r)\, dt \quad , \tag{4.ii:11}$$

where the integration in dt is over the interval

$$[S_{\gamma\alpha}, R_{\gamma\alpha}] \cap [S_{\gamma\beta} - r, R_{\gamma\beta} - r] \quad . \tag{4.ii:12}$$

Now from (4.ii:4) and (4.ii:7) follows that $V_{\alpha\beta}(r) = 0$ for $r > R_{\alpha\beta}$. So also the sum of the n integrals in (4.ii:11) must vanish. One can readily verify that each one of the n integrals vanishes if we choose

$$S_{\gamma\alpha} = R_{\gamma\beta} - R_{\alpha\beta} \quad . \tag{4.ii:13}$$

For additive hard sphere this choice reduces to $S_{\gamma\alpha} = (R_\gamma - R_\alpha)/2$ independent from β, which is Baxter' s choice. We readily realize looking at (4.ii:1) that using (4.ii:13) for NAHS, would lead to a dependence of $S_{\gamma\alpha}$ from an intermediate index β, occurrence which is not admissible.

ii.2 Symmetric binary mixture

For a symmetric binary mixture $n = 2$, $\Delta_{11} = \Delta_{22} = \Delta_{12} = \Delta_{21} = \Delta$, $R_1 = R_2 = R$, and $\rho_1 = \rho_2 = \rho/2$. The problem reduces to determine the direct correlation function for like species $c_{11}(r)$ and for unlike species $c_{12}(r)$. A good approximation to the true direct correlation functions has been given by Gazzillo [53].

In this case the determination of the 4 $S_{\alpha\beta}$ is much simplified. Following the argument given in the previous subsection we have studied the interval (4.ii:12) for $r = R_{\alpha\beta}$ in the 8 cases of interest, determining in each case the $S_{\alpha\beta}$ for which the intersection vanishes for $r > R_{\alpha\beta}$. We found:

- $\alpha = \beta = 1$
  $\gamma = 1$ $[S_{11}, R] \cap [S_{11} - R, 0]$. The intersection vanishes for $S_{11} = 0$.
  $\gamma = 2$ $[S_{21}, (1+\Delta)R] \cap [S_{21} - R, \Delta R]$. The intersection vanishes for $S_{21} = \Delta R$.

- $\alpha = \beta = 2$
  $\gamma = 1$ $[S_{12}, (1+\Delta)R] \cap [S_{12} - R, \Delta R]$. The intersection vanishes for $S_{12} = \Delta R$.
  $\gamma = 2$ $[S_{22}, R] \cap [S_{22} - R, 0]$. The intersection vanishes for $S_{22} = 0$.

- $\alpha = 1, \beta = 2$
  $\gamma = 1$ $[S_{11}, R] \cap [S_{12} - (1+\Delta)R, 0]$.
  $\gamma = 2$ $[S_{21}, (1+\Delta)R] \cap [S_{22} - (1+\Delta)R, -\Delta R]$.

- $\alpha = 2, \beta = 1$
  $\gamma = 1$ $[S_{12}, (1+\Delta)R] \cap [S_{11} - (1+\Delta)R, -\Delta R]$.
  $\gamma = 2$ $[S_{22}, R] \cap [S_{21} - (1+\Delta)R, 0]$.

We see that with the choice $S_{11} = S_{22} = 0$ and $S_{12} = S_{21} = \Delta R$ each integral in (4.ii:11) vanishes. Once the $S_{\alpha\beta}$ have been chosen the determination of the partial direct correlation function through Baxter' s method is straightforward. With our choice of the $S_{\alpha\beta}$ we had to restrict $0 < \Delta < 1/2$ and we found for the like direct correlation function

$$c_{11}(r) = a_1 + a_2 r + a_4 r^3 \quad \text{for } 0 < r < R \quad , \tag{4.ii:14}$$

where a_1, a_2, and a_4 are functions of Δ and R. The solution has the correct limit (4.i:15) as $\Delta \to 0$. Unfortunately despite having the correct functional form and the correct $\Delta \to 0$ limit this solution does not compare well with Gazzillo's approximation or with the numerically generated function.

For the unlike direct correlation function we found

$$c_{12}(r) = c_1 \quad \text{for } 0 < r < \Delta R \quad , \tag{4.ii:15}$$

$$c_{12}(r) = a_0/r + a_1 + a_2 r + a_4 r^3 \quad \text{for } \Delta R < r < (1-\Delta)R \quad , \tag{4.ii:16}$$

$$c_{12}(r) = b_0/r + b_1 + \tfrac{1}{2} a_2 r + \tfrac{1}{2} a_4 r^3 \quad \text{for } (1-\Delta)R < r < (1+\Delta)R \quad , \tag{4.ii:17}$$

where c_1, a_0, b_0, and b_1 are functions of Δ and R. $c_{12}(r)$ is discontinuous at $r = \Delta R$,

$$\lim_{r \to \Delta R^+} c'_{12}(r) = 0 \quad , \tag{4.ii:18}$$

and $c'_{12}(r)$ is discontinuous at $r = (1-\Delta)R$. The discontinuities are unphysical.

So it looks as if the Wiener-Hopf factorization does not give any good result for the NAHS. An element in favor of this conclusion come from the analysis of the Widom-Rowlinson model in the next subsection.

ii.3 The Widom-Rowlinson model

The Widom-Rowlinson model [54] is obtained from the binary mixture of hard spheres by setting

$$\Delta = d/R \quad , \tag{4.ii:19}$$

and letting $R \to 0$.

Ahn and Lebowitz find the following solution in one dimension

$$\tilde{C}_{11}(k) = 0 \quad , \tag{4.ii:20}$$

$$\tilde{C}_{12}(k) = 2\mu \frac{\sin[d(k^2+4\mu^2)^{1/2}]}{(k^2+4\mu^2)^{1/2}} \quad , \tag{4.ii:21}$$

where μ is a parameter which can be determined from the following equation

$$\mu = \sqrt{\rho_1 \rho_2}\cos(2\mu d) \tag{4.ii:22}$$

It is possible to find a factorization like in (4.ii:10) and (4.ii:9). For example choosing $\hat{Q}_{11} = \hat{Q}_{22}$, $\hat{Q}_{12} = \hat{Q}_{21}$, and $\hat{Q}_{11}$, $\hat{Q}_{12}$ real functions one finds

$$\hat{Q}_{11} = \frac{\tilde{C}_{12} - 2\sqrt{(1-\sqrt{1-\tilde{C}_{12}^2})/2} + 2[(1-\sqrt{1-\tilde{C}_{12}^2})/2]^{3/2}}{\tilde{C}_{12}} \overset{\tilde{C}_{12}\to 0}{\longrightarrow} \tilde{C}_{12}^2/8 + O[\tilde{C}_{12}^4] \quad ,$$

$$\hat{Q}_{12} = \sqrt{(1-\sqrt{1-\tilde{C}_{12}^2})/2} \overset{\tilde{C}_{12}\to 0}{\longrightarrow} \tilde{C}_{12}/2 + O[\tilde{C}_{12}^3] \quad ,$$

where amongst the 4 solutions to (4.ii:10) we have chosen the one for which $\lim_{\tilde{C}_{12}\to 0}\hat{Q}_{11} = \lim_{\tilde{C}_{12}\to 0}\hat{Q}_{12} = 0$. Notice that the solution found indeed give for $\hat{Q}_{11}(k)$ and $\hat{Q}_{12}(k)$ even, real functions. Infact for a symmetric binary mixture, the partial structure factors $S_{\alpha\beta}(k) = (\sqrt{\rho_\alpha \rho_\beta}/\rho)\{[I - \tilde{C}(k)]^{-1}\}_{\alpha\beta}$ are given by

$$S(k) = \frac{1}{2}\frac{1}{1-\tilde{C}_{12}^2(k)} \begin{pmatrix} 1 & \tilde{C}_{12}(k) \\ \tilde{C}_{12}(k) & 1 \end{pmatrix} \quad .$$

But since $\lim_{k\to\infty}\tilde{C}_{12}(k) = 0$ and the $S_{\alpha\beta}(k)$ has to remain finite for all k then we must have $\tilde{C}_{12}^2(k) < 1$ for all k.

However even if a factorization is possible, in the Widom-Rowlinson model the $h_{11}(r)$ is unknown for all r. For the Wiener-Hopf factorization technique to be useful it is necessary that in the relationship between the $Q(r)$ and the $h(r)$, the $h(r)$ are involved only over the interval where they are known. But this is not possible in the Widom-Rowlinson model for what we just said. So it seems as if the Wiener-Hopf factorization is not a useful technique to solve the Widom-Rowlinson model or the more general non additive hard spheres model in the PY approximation.

In chapter 7 the structure of the three dimensional Widom-Rowlinson model will be studied in detail starting from Monte Carlo simulation results. We will also point out several misprints in the portion of the paper of Ahn and Lebowitz [54] dealing with the three dimensional Widom-Rowlinson model.

iii Hard spheres with surface adhesion

In studies on colloidal suspensions of neutral particles with adhesive interaction, Baxter's "sticky hard spheres" model [30, 31] has often been used. In Baxter's original formulation and its extension to the multicomponent case [32, 33] (refereed in the literature as SHS1 model) the pair potential, in addition to a hard sphere repulsion, contains an infinitely deep and narrow attractive square well, obtained according to a particular limiting procedure ("sticky limit") that keeps the second virial coefficient finite.

This model has the following positive features:

- when studied within the PY approximation an analytic solution can be found,
- such analytic solution exhibits a gas-liquid phase transition,
- it is appropriate for the description of some properties of colloidal suspensions, micelles, microemulsions, and protein solutions with short range interactions. It can also describe some aspects of adsorption, flocculation, and percolation phenomena, solvent-mediated forces, ionic mixtures, solutions with a small degree of size polydispersity, and fluid of chain-like molecules (see [34] for a list of references).

Its main drawbacks are:

- Stell found [35] that sticky hard spheres of the same diameter, in the Baxter limit, when treated exactly, are not thermodynamically stable,
- more importantly, colloidal suspensions are rather commonly polydisperse. Polydispersity means that mesoscopic suspended particles of a same chemical specie are not necessarily identical, but some of their properties (size, charge, etc.)may exhibit a discrete or continuous distribution of values. Even when all macroparticles belong to a unique chemical specie, a polydisperse fluid must therefore be treated as a multicomponent mixture. The number n of components may be of order $10^1 \div 10^3$ or more (discrete polydispersity) or infinite (continuous polydispersity). Now the SHS1 in the PY approximation, when applied to mixtures, requires the solution of a set of $n(n+1)/2$ coupled quadratic equations [32] a task which cannot be accomplished analytically.

More recently there have been attempts to find an alternative SHS model which could be analytically tractable even in the general multicomponent case (see [34] for the references). In particular Brey and co-workers [36] proposed to start from a hard sphere Yukawa potential

$$\beta\phi(r) = \begin{cases} +\infty & r < R \\ -Ke^{-z(r-R)}/r & r \geq R \end{cases} \quad , \tag{4.iii:1}$$

with $K = zK_0$, $K_0 = \epsilon_0^* R^2$, $\epsilon_0^* = \beta\epsilon_0 \equiv 1/(12T^*)$, R denotes the hard sphere diameter, z the Yukawa inverse range, ϵ_0 an energy, and T^* a reduced temperature. This other Hamiltonian (referred to in the literature as SHS2 model) is supplemented by a "sticky limit" which in this case amounts to taking $z \to \infty$ [36].

For the SHS2 model the OZ equation can be solved analytically within the MSA [37, 38]. It turns out that this solution is readily usable even in the polydisperse multicomponent case (see [34] for references). Recently there has been a lot of investigations on the structural properties of polydisperse fluids using a version of the SHS2 model in which the coupling (stickiness) parameters which define the strength of the Yukawa attraction are *factorizable* [39, 40] and one

in which they are *non-factorizable* [41][2][42, 43]. More recently Gazzillo and co-workers showed that the SHS2 model is ill defined: its Hamiltonian leads to an exact second virial coefficient which diverges [34]. They propose a third model of SHS.

In this section we present the analytic solution to the Percus-Yevick approximation for the SHS1 model. The derivation is in part alternative to the one originally given by R. J. Baxter [30] since we use as method of solution the Wiener-Hopf factorization (see section B). The same method was later used by Baxter himself [31]. The derivation was done without being aware of the existence of [31] so it is in some sense original. We hope that it may be a useful exercise, for the reader, in which Dirac delta functions are used within the Wiener-Hopf factorization method.

Let us consider a system of particles interacting through a pair potential $\phi^{\Delta}(r)$ of the following kind (see figure 4.1)

$$\beta\phi^{\Delta}(r) = \begin{cases} +\infty & r < R - \Delta \\ \epsilon(\Delta) < 0 & R - \Delta < r < R \\ 0 & r > R \end{cases} \quad , \tag{4.iii:2}$$

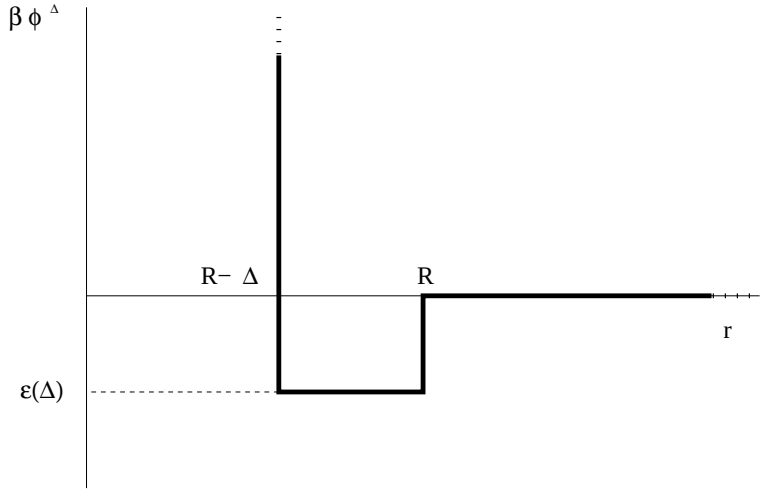

FIGURE 4.1: Potential (4.iii:2).

The Mayer function is $f^{\Delta}(r) = e^{-\beta\phi^{\Delta}(r)} - 1$, see figure 4.2
Moreover let

$$\lim_{\Delta \to 0} \epsilon(\Delta) = -\infty \quad . \tag{4.iii:3}$$

We want to study the system in the limit of Δ going to zero. We choose for ϵ the following expression

$$\epsilon(\Delta) = \ln\left(\frac{12\tau\Delta}{R}\right) \quad . \tag{4.iii:4}$$

[2]Notice that there must be a misprint in their equations (8), (9), and (10).

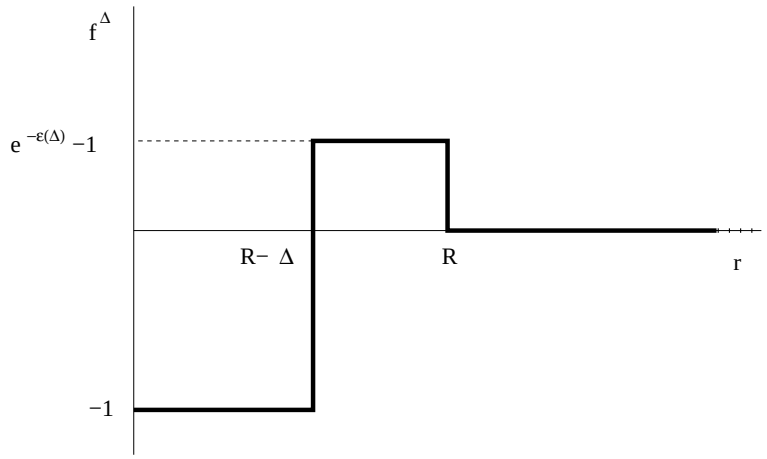

FIGURE 4.2: Mayer function for the potential (4.iii:2).

It can be shown that in the limit of Δ going to zero, the Mayer cluster integrals $g_n(r)$ (see [12] section 5.3) remain finite for $r = R$. For example for $g_1(r)$ we have

$$\begin{aligned} g_1^\Delta(r) &= \int f^\Delta(|\mathbf{r}-\mathbf{r}'|) f^\Delta(\mathbf{r}')\, d\mathbf{r}' \\ &= 2\pi \int_0^R ds\, s f^\Delta(s) \int_{|r-s|}^{r+s} dt\, t f^\Delta(t) \quad . \end{aligned} \tag{4.iii:5}$$

In the limit $\Delta \to 0$ we have

$$f(r) = \lim_{\Delta\to 0} f^\Delta(r) = -\theta(R-r) + \frac{R}{12\tau}\delta(r-R) \quad , \tag{4.iii:6}$$

where $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ otherwise, is the Heaviside step function, and $\delta(x)$ is the Dirac delta function. We then find

$$\begin{aligned} g_1(R) &= \lim_{\Delta\to 0} g_1^\Delta(R) \\ &= -2\pi \int_0^R ds\, s \int_{R-s}^{R+s} dt\, t f(t) + 2\pi \left(\frac{R^2}{12\tau}\right) \int_0^{2R} dt\, t f(t) \\ &= -2\pi \int_0^R ds\, s \frac{1}{2}\left[s^2 - 2sR + \frac{R^2}{12\tau}\right] + 2\pi \left(\frac{R^2}{12\tau}\right)\left(-\frac{R^2}{2} + \frac{R^2}{12\tau}\right) \\ &= 2\pi \left[\frac{5R^4}{24} - \frac{R^4}{12\tau} + \left(\frac{R^2}{12\tau}\right)^2\right] < \infty \quad . \end{aligned} \tag{4.iii:7}$$

Since $\phi^\Delta(r) = \infty$ for $r < R - \Delta$ we must have for the pair distribution function

$$g^\Delta(r) = 0 \qquad r < R - \Delta \quad . \tag{4.iii:8}$$

From the virial expansion for g^Δ we find

$$\begin{aligned} g^\Delta(r) &= e^{-\beta\phi^\Delta(r)}[1 + \sum_{n=1}^{\infty} \rho^n g_n^\Delta(r)] \\ &= \frac{R}{12\tau\Delta}[1 + \sum_{n=1}^{\infty} \rho^n g_n^\Delta(r)] \qquad R - \Delta < r < R \quad , \end{aligned} \tag{4.iii:9}$$

Where ρ is the number density of the fluid. Let us call

$$\lambda^{\Delta}(r) = [1 + \sum_{n=1}^{\infty} \rho^n g_n^{\Delta}(r)]/\tau \quad , \tag{4.iii:10}$$

we then have

$$\lambda = \lim_{\Delta \to 0} \lambda^{\Delta}(R) < \infty \quad . \tag{4.iii:11}$$

So we find

$$g(r) = \lim_{\Delta \to 0} g^{\Delta}(r) = \frac{R\lambda}{12}\delta(r-R) \quad r \leq R \quad . \tag{4.iii:12}$$

Let us introduce next the function $H(r) = rh(r) = r[g(r) - 1]$. We will have

$$H(r) = \frac{R^2\lambda}{12}\delta(r-R) - r \quad r \leq R \quad . \tag{4.iii:13}$$

In the Percus-Yevick approximation the direct correlation function is

$$c(r) = \left(1 - e^{\beta\phi(r)}\right) g(r) \quad , \tag{4.iii:14}$$

where $\phi(r) = \lim_{\Delta \to 0} \phi^{\Delta}(r)$. Since $\phi(r) = 0$ when $r > R$ we have

$$c(r) = 0 \quad r > R \quad . \tag{4.iii:15}$$

This allows us to solve the Ornstein-Zernike equation using the Wiener-Hopf factorization (see section B). This involves the functions $H(r)$ and $C(r) = rc(r)$ only over the interval $r \in [0, R]$ and may be written as follows (see equations (B.:44) and (B.:46))

$$H(r) = -Q'(r) + 2\pi\rho \int_0^R H(|r-s|)\mathrm{sgn}(r-s)Q(s)\,ds \quad , \tag{4.iii:16}$$

$$C(r) = -Q'(r) + 2\pi\rho \int_r^R Q'(s)Q(s-r)\,ds \quad , \tag{4.iii:17}$$

where the prime stands for derivative and $Q(r)$ is an auxiliary function that must be continue on $[0, R[$ and zero on $]R, \infty]$.

From (4.iii:16) we find Q' in the interval $[0, R]$

$$\begin{aligned} Q'(r) = & - \frac{R^2\lambda}{12}\delta(r-R) + r - 2\pi\rho \int_0^R (r-s)Q(s)\,ds \\ & + 2\pi\rho \int_0^R \frac{R^2\lambda}{12}\delta(|r-s|-R)\mathrm{sgn}(r-s)Q(s)\,ds \\ = & - \frac{R^2\lambda}{12}\delta(r-R) + ar + b \quad , \end{aligned} \tag{4.iii:18}$$

where

$$a = 1 - 2\pi\rho \int_0^R Q(s)\,ds \quad , \tag{4.iii:19}$$

$$b = 2\pi\rho \int_0^R sQ(s)\,ds \quad . \tag{4.iii:20}$$

Since we must have $Q(r) = 0$ for $r > R$ it has to be

$$Q(r) = \frac{1}{2}ar^2 + br + \gamma \quad , \tag{4.iii:21}$$

$$Q(R) = \frac{R^2\lambda}{12} \quad . \tag{4.iii:22}$$

Using (4.iii:21) into equations (4.iii:19), (4.iii:20), and (4.iii:22) we have three equations in the three unknown a, b, and γ. Calling $\mu = \lambda\eta(1-\eta)$ we find

$$\begin{cases} a = (1 + 2\eta - \mu)/(1-\eta)^2 \quad , \\ b = \dfrac{R}{2}(\mu - 3\eta)/(1-\eta)^2 \quad , \\ \gamma = -\dfrac{R^2}{12}(6 - \mu/\eta)/(1-\eta) \quad , \end{cases} \tag{4.iii:23}$$

where $\eta = \rho R^3\pi/6$ is the hard sphere packing fraction. Notice that we recover the case of hard spheres [equations (C.:10),(C.:11), and (C.:12)] by setting $\lambda = 0$ in equations (4.iii:23).

From (4.iii:17) we find $C(r)$ in the interval $[0, R]$

$$C(r) = \tilde{C}(r) + \frac{R^2\lambda}{12}\delta(r-R) \quad , \tag{4.iii:24}$$

$$\tilde{C}(r) = C_0 + C_1 r + C_2 r^2 + C_4 r^4 \quad , \tag{4.iii:25}$$

where

$$\begin{cases} C_0 = -\dfrac{R}{12}\lambda^2\eta \quad , \\ C_1 = -(1 + 2\eta - \mu)^2/(1-\eta)^4 \quad , \\ C_2 = \dfrac{1}{2R}[3\eta(2+\eta)^2 - 2\mu(1 + 7\eta + \eta^2) + \mu^2(2+\eta)]/(1-\eta)^4 \quad , \\ C_4 = \dfrac{\eta}{2R^3}C_1 \quad . \end{cases} \tag{4.iii:26}$$

We are left with the task of determining λ. Equating the coefficients of the Dirac deltas in the Percus-Yevick closure we have

$$(f(r) + 1)C(r) = f(r)(H(r) + r) \quad , \tag{4.iii:27}$$

where on the interval $[0, R]$

$$\begin{aligned} f(r) + 1 &= \frac{R}{12\tau}\delta(r-R) \quad , \\ C(r) &= \frac{R^2\lambda}{12}\delta(r-R) + \tilde{C}(r) \quad , \\ H(r) + r &= \frac{R^2\lambda}{12}\delta(r-R) \quad . \end{aligned}$$

We then find

$$\frac{R}{12\tau}\tilde{C}(R) = (-1)\frac{R^2\lambda}{12} \quad , \tag{4.iii:28}$$

or $\tilde{C}(R) = -R\lambda\tau$. From this follows

$$\frac{1+\eta/2}{(1-\eta)^2}\frac{1}{\lambda} - \frac{\eta}{1-\eta} + \frac{\eta}{12}\lambda - \tau = 0 \quad . \tag{4.iii:29}$$

Equation (4.iii:29) multiplied by $\lambda(1-\eta)^2$ is a quadratic equation in λ which admits two real roots $\lambda_\pm(\tau,\eta)$ when the discriminant is non-negative

$$D = (5 - 12\tau + 6\tau^2)\eta^2 + (-2 + 12\tau - 12\tau^2)\eta + 6\tau \geq 0 \quad . \tag{4.iii:30}$$

The solutions of $D = 0$ are

$$\eta_\pm = \frac{1 - 6\tau + 6\tau^2 \pm \sqrt{1 - 12\tau + 18\tau^2}}{5 - 12\tau + 6\tau^2} \overset{\tau\to\infty}{\longrightarrow} 1 \tag{4.iii:31}$$

The solutions of $a = 5 - 12\tau + 6\tau^2 = 0$ are

$$\begin{cases} \tau_1 = (6+\sqrt{6})/6 \\ \tau_2 = (6-\sqrt{6})/6 \end{cases} \tag{4.iii:32}$$

The solutions of $d = 1 - 12\tau + 18\tau^2 = 0$ are

$$\begin{cases} \tau_3 = (2+\sqrt{2})/6 \\ \tau_4 = (2-\sqrt{2})/6 \end{cases} \tag{4.iii:33}$$

We then have the situation depicted in figure (4.3) We will call τ_4 the critical temperature

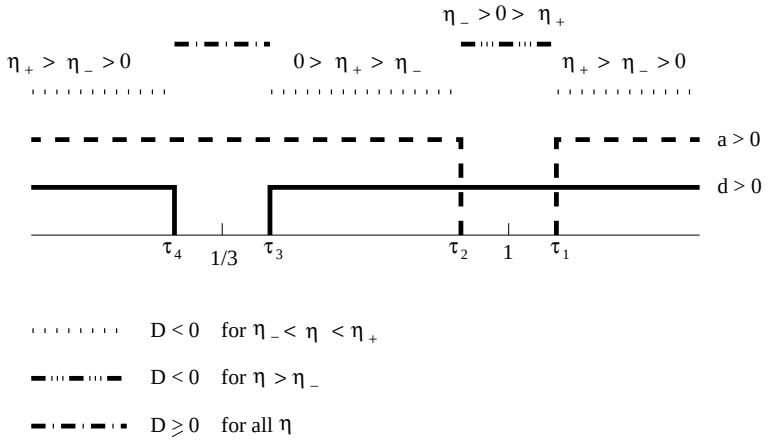

FIGURE 4.3: Sign of the discriminant D.

$$\tau_c = \tau_4 \simeq 0.09763 \quad . \tag{4.iii:34}$$

We have the following cases

$\tau < \tau_c$	(4.iii:29) has no solutions for $\eta_- < \eta < \eta_+$
$\tau_c < \tau < \tau_2$	(4.iii:29) has two real solutions for all η
$\tau_2 < \tau < \tau_1$	(4.iii:29) has no solutions for $\eta > \eta_- > 1$
$\tau_1 < \tau$	(4.iii:29) has no solutions for $\eta_+ > \eta > \eta_- > 1$

Notice that the value physically accessible for the density are $\eta \in [0, \eta_0]$ where $\eta_0 = \pi/(3\sqrt{2})$ is the maximum packing density. Corresponding to the critical temperature τ_c we have a critical density

$$\eta_c = \eta_\pm(\tau_c) = \frac{\sqrt{2}}{6 + 2^{5/2}} \simeq 0.12132 \quad . \tag{4.iii:35}$$

We are left with the problem of deciding which one of the two solutions $\lambda_\pm$ is the physically acceptable one. From the virial expansion for g (4.iii:10), follows that

$$\lim_{\eta \to 0} \lambda(\tau, \eta) = \frac{1}{\tau} \quad . \tag{4.iii:36}$$

It follows then from equation (4.iii:29) that the physically acceptable solution is λ_+ the other one diverging as η goes to 0.

There is one more physical constraint that must be fulfilled, namely the radial distribution function has to be a bounded function. Multiplying equation (4.iii:16) times e^{-tr} and integrating over r from 0 to ∞ (we change variables from (r, s) to $(y = r - s, s)$ and integrate first over y) we find

$$\begin{aligned} \bar{H}(t) &= -\bar{Q}'(t) + 2\pi\rho\bar{Q}(t)\bar{H}(t) + 2\pi\rho I(t) \quad , \\ I(t) &= \int_0^R dy\, y e^{ty} \int_y^R ds\, Q(s) e^{-ts} \quad , \\ \bar{f}(t) &\equiv \int_0^\infty f(r) e^{-tr}\, dr \quad . \end{aligned} \tag{4.iii:37}$$

From which follows

$$\bar{H}(t) = \frac{-\bar{Q}'(t) + 2\pi\rho I(t)}{1 - 2\pi\rho\bar{Q}(t)} \quad . \tag{4.iii:38}$$

Moreover we have

$$\bar{Q}(t) = E(t) + F(t)e^{-Rt} \quad , \tag{4.iii:39}$$

$$E(t) = (a + bt + ct^2)/t^3 \quad , \tag{4.iii:40}$$

$$F(t) = (aR^2/2 + bR + c)/t + (Ra + b)/t^2 + a/t^3 \quad . \tag{4.iii:41}$$

The function $1 - 2\pi\rho\bar{Q}(t)$ tends to 1 for $t \to \infty$ and behaves as $-2\pi\rho(-Ra)/t^2$ near $t = 0$. Then if $a < 0$ it must have at least a zero on the positive real axis. We thus conclude that for $\mu > 1 + 2\eta$, $H(r)$ (or $g(r)$) is an unbounded function.

In figure 4.4 we plot the function $\lambda_+(\tau, \eta)$ (bold lines) and $\lambda_-(\tau, \eta)$ for different values of τ. For $\tau < \tau_c$, $\lambda_\pm$ end on the curve

$$A(\eta) = \lambda_+(\tau_-(\eta), \eta) = \sqrt{\frac{6(2 + \eta)}{\eta(1 - \eta)^2}} \quad , \tag{4.iii:42}$$

where $\tau_\pm(\eta)$ are the solutions to $D = 0$. For solutions above the curve

$$B(\eta) = \frac{2\eta + 1}{\eta(1 - \eta)} \quad , \tag{4.iii:43}$$

the radial distribution function is unbounded. The physical region is the one below the two curves A and B. This two curves meet at $\eta = \eta_c$.

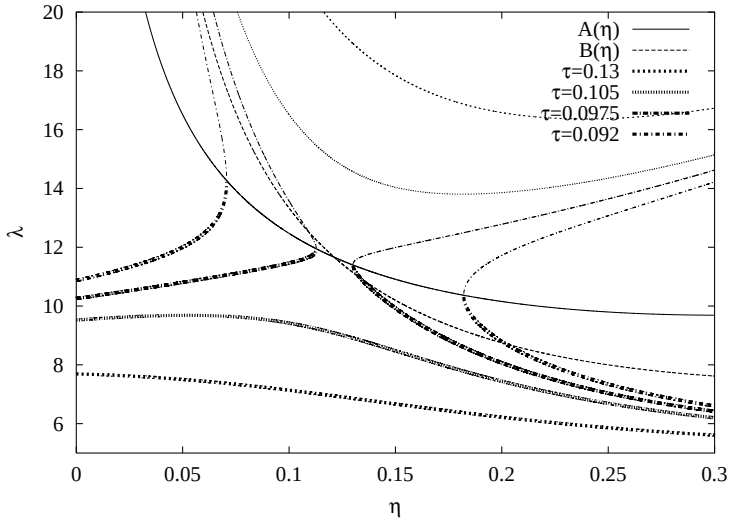

FIGURE 4.4: Plot of $A(\eta)$ (4.iii:42), $B(\eta)$ (4.iii:43), and $\lambda_{\pm}(\tau,\eta)$ for $\tau = 0.13, 0.105, 0.0975$, and 0.092. The physical region for the solutions to equation (4.iii:29) is the one below the two curves A and B.

iii.1 Compressibility Pressure

The pressure from the compressibility equation is given by

$$\begin{aligned}
\beta \left.\frac{\partial P}{\partial \rho}\right|_T &= \frac{1}{S(0)} = \frac{1}{1+\rho\hat{h}(0)} = 1-\rho\hat{c}(0) \\
&= 1 - 4\pi\rho\int_0^R sC(s)\,ds \\
&= -C_1 \\
&= [1+2\eta-\lambda_-(\tau,\eta)\eta(1-\eta)]^2/(1-\eta)^4 \quad , \qquad \text{(4.iii:44)}
\end{aligned}$$

where $S(k)$ is the static structure factor and a hat denotes a Fourier transform. Note that the isothermal compressibility is positive for all η and τ, and diverges on $\lambda = B(\eta)$.

We find the pressure integrating over η. If we call $v_0 = \pi R^3/6$ the volume of a sphere we find

$$\begin{aligned}
\beta v_0 P(\tau,\eta) &= \int_0^\eta (1+2\eta'-\mu(\tau,\eta'))^2/(1-\eta')^4\,d\eta' \qquad \text{(4.iii:45)} \\
&= \frac{1}{3\,(-1+\eta)^3}[-3\,\eta\,(1+\eta\,(-11+19\,\eta))+18\,(-1+\eta)\,\eta \\
&\quad \times(-2+11\,\eta)\,\tau - 216\,(-1+\eta)^2\,\eta\,\tau^2 + 72\,(-1+\eta)^3\,\tau^3 - \\
&\quad 2\sqrt{6}\left(\eta\,(-2+5\,\eta) - 12\,(-1+\eta)\,\eta\,\tau + 6\,(-1+\eta)^2\,\tau^2\right)^{\frac{3}{2}}]
\end{aligned}$$

We see from figure 4.5 that, with the Percus-Yevick closure, there is a non accessible region on the plane (pressure,volume). That region is delimited by the curve

$$\begin{aligned}
C(\eta) &= \beta v_0 P(\tau_-(\eta),\eta) \\
&= \frac{\eta}{3(\eta-1)^3}[-3-3\eta-3\eta^2+\sqrt{\eta(2+\eta)}(\sqrt{6}\eta+\sqrt{24})] \quad . \qquad \text{(4.iii:46)}
\end{aligned}$$

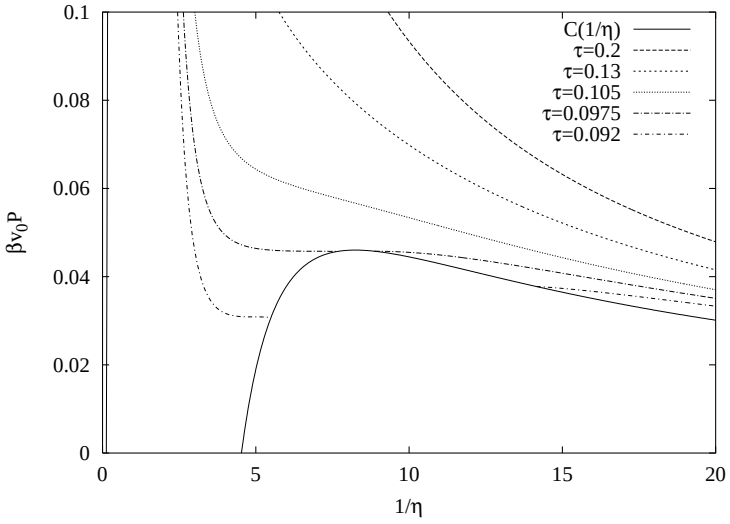

FIGURE 4.5: Plot of several isotherms at $\tau = 0.2, 0.13, 0.105, 0.0975$, and 0.092. The equation of state is obtained from the compressibility equation (4.iii:44). We plot $\beta v_0 P$ against $1/\eta$, the dimensionless volume per particle. The region below the curve $C(1/\eta)$ (4.iii:46) is unaccessible with the Percus-Yevick closure.

At the critical point we find

$$\beta v_0 P_c = \frac{2(4+3\sqrt{2})}{9(2+\sqrt{2})^3} \simeq 0.04602 \quad , \tag{4.iii:47}$$

where $P_c = P(\tau_c, \eta_c)$. The critical isotherm $P_c(\eta) = P(\tau_c, \eta)$ has the following behavior near the critical point

$$P_c(\eta) - P_c = \begin{cases} \omega_+(\eta-\eta_c)^3 + O[(\eta-\eta_c)^4] & \eta > \eta_c \\ \omega_-(\eta-\eta_c)^3 + O[(\eta-\eta_c)^4] & \eta < \eta_c \end{cases} \tag{4.iii:48}$$

where $\omega_\pm = \lim_{\eta\to\eta_c\pm} \partial^3 P_c/\partial\eta^3$ with $\omega_- \approx 34\omega_+$.

iii.2 Virial pressure

From the virial theorem we have

$$\frac{\beta P}{\rho} = \lim_{\Delta\to 0}\left\{1 - \frac{2}{3}\pi\beta\rho\int_0^\infty r^3 g^\Delta(r)\frac{d\phi^\Delta(r)}{dr}\,dr\right\} \quad . \tag{4.iii:49}$$

Because this equation involves the derivative of the pair potential, it cannot be used directly in the calculation of the equation of state. This problem can be overcome rewriting the equation in terms of the function $N(r)^\Delta$ defined as

$$N^\Delta(r) = re^{\beta\phi^\Delta(r)}g^\Delta(r) \quad . \tag{4.iii:50}$$

Indeed it can be shown that this function must be a continuous function even when g^Δ and ϕ^Δ are discontinuous. Using equation (4.iii:50) in (4.iii:49) we find

$$\begin{aligned} \frac{\beta P}{\rho} &= \lim_{\Delta\to 0}\left\{1 - \frac{2}{3}\pi\beta\rho\int_0^\infty r^2 N^\Delta(r)e^{-\beta\phi^\Delta(r)}\frac{d\phi^\Delta(r)}{dr}\,dr\right\} \\ &= \lim_{\Delta\to 0}\left\{1 + \frac{4\eta}{R^3}\int_0^\infty r^2 N^\Delta(r)\frac{de^{-\beta\phi^\Delta(r)}}{dr}\,dr\right\} \quad . \end{aligned} \tag{4.iii:51}$$

The discontinuities in the pair potential are such (see figure 4.1) that the derivative of the Boltzmann factor is

$$\frac{de^{-\beta\phi^{\Delta}(r)}}{dr} = e^{-\epsilon(\Delta)}\delta(r-R') - \left(e^{-\epsilon(\Delta)}-1\right)\delta(r-R) \quad , \tag{4.iii:52}$$

where $R' = R - \Delta$ and $e^{-\epsilon(\Delta)} = R/(12\tau\Delta)$ (see equation (4.iii:4)). We find then

$$\begin{aligned} \frac{\beta P}{\rho} &= \lim_{\Delta\to 0}\left\{1 + \frac{4\eta}{R^3}\frac{R}{12\tau\Delta}R'^2 N^{\Delta}(R') - \frac{4\eta}{R^3}\left(\frac{R}{12\tau\Delta}-1\right)R^2 N^{\Delta}(R)\right\} \\ &= \lim_{\Delta\to 0}\left\{1 + \frac{4\eta}{R}N^{\Delta}(R) - \frac{\eta}{3\tau}\left[\frac{R^2 N^{\Delta}(R) - R'^2 N^{\Delta}(R')}{R^2\Delta}\right]\right\} \quad . \end{aligned} \tag{4.iii:53}$$

We now observe that from the Percus-Yevick closure follows $N^{\Delta}(r) = r + H^{\Delta}(r) - C^{\Delta}(r)$. From equations (4.iii:13) and (4.iii:24) then follows $N^{\Delta}(r) \stackrel{\Delta\to 0}{\longrightarrow} N(r) = -\tilde{C}(r)$ for $r \le R$.Using equation (4.iii:28) we further find that the second term on the right hand side of equation (4.iii:53) equals $4\eta\lambda\tau$. To calculate the third term one has to carefully evaluate the $\Delta \to 0$ limit. Assuming we can evaluate it as follows

$$\frac{\eta}{3\tau}\lim_{\Delta\to 0}\left[\frac{R^2\tilde{C}(R) - R'^2\tilde{C}(R')}{R^2\Delta}\right] = \frac{\eta}{3\tau}[(2/R)C_0 + 3C_1 + 4RC_2 + 6R^3C_4] \quad , \tag{4.iii:54}$$

we find for the virial pressure the following expression

$$\beta v_0 P = \eta\left(\frac{\beta P}{\rho}\right) = \eta\left\{1 + 4\eta\lambda_+\tau + \frac{\eta}{3\tau}[(2/R)C_0 + 3C_1 + 4RC_2 + 6R^3C_4]\right\} \quad . \tag{4.iii:55}$$

This expression coincides with equation (38) in [30] apart from the lack of the additional term $\eta^2\lambda^3/24$ within the square brackets, present in Baxter's equation. Indeed the function $N^{\Delta}(r)$ is not differentiable in $r = R$. So our assumption was wrong: we cannot substitute N^{Δ} with N and then take the limit $\Delta \to 0$. The task of calculating N^{Δ} is a little bit more laborious, since one cannot work with delta functions, and is left as an exercise to the reader.

Chapter 5

Generating functionals, consistency, and uniqueness in the integral equation theory of liquids

In chapter 3 we introduced the most common integral equation theories (IET). IET of the liquid state statistical mechanics are valuable tools for studying structural and thermodynamic properties of pairwise interacting fluid systems [12, 55]. Many of these approximations to the exact relation between pair potential and pair correlation functions have been proposed in the last half century, starting from the pioneering works [56–58] to the most refined and modern approximations [59–63] which may approach the accuracy of computer simulation with a negligible computational cost.

The functional method in statistical mechanics [12] provides the most general and sound starting point to introduce IET as approximations of the exact functional relations and it is the classical statistical mechanics counterpart of the quantum density functional theory.

Notwithstanding the success of present IET to describe the structure of simple one component systems, considerable work is still devoted to derive improved approximations which could accurately describe the thermodynamics as well. Also applications to non simple or multicomponent systems are still subject of current studies.

Actually, the description of thermodynamics is one weak point of IET approaches: reasonable and apparently harmless approximations to the potential-correlation relations usually result in a dramatically inconsistent thermodynamics where many, if not all, among the exact sum rules derived from statistical mechanics, are violated.

The problem of thermodynamic inconsistency, *i.e.* the inequivalence between different routes to thermodynamics, actually plagues the IET approach to the point that the degree of inconsistency between different formulae for the same quantity is used as an intrinsic measurement of the quality of a closure.

In the past, some discussion of the thermodynamic consistency appeared in the literature. Hypernetted chain approximation (HNC) was recognized as a closure directly derivable from an approximation for the free energy functional [64] , thus exhibiting consistency between the virial formula and the thermodynamic expression for the pressure. However, this limited consistency is not enough to guarantee a unique and faithful description of the phase diagram. Apart the problem of the remaining inconsistencies, the descriptions of the critical points and spinodal lines are seriously inadequate.

Extensive work on HNC [65–67] showed that in place of a true spinodal line, it is more

appropriate to describe the numerical results as due to a region in the thermodynamic plane where no real solution of the integral equation exists. In particular, Belloni[65] showed that the disappearance of the solution originates from a branching point where two solutions merge, instead than from a line of diverging compressibility. Thus, we have direct evidence that HNC may have multiple solutions, at least in part of the phase diagram.

Empirical improvements on HNC have been proposed [59, 62, 63] providing in many cases excellent results for one-component simple fluids. However, although reduced, the thermodynamic inconsistency problem remains and the multiple solution problem is completely untouched.

In this work we start an investigation of a new approach to IET directly addressing the two points of uniqueness of the solution and thermodynamic consistency. The basic idea is to constrain the search for new closures within the class of generating functionals which are strictly convex free-energy functionals, thus enforcing the virial-energy consistency as well as the uniqueness of the solution.

In particular, in the present chapter we try to answer the following questions: i) does at least one strictly convex free-energy functional of the pair correlation function exist? ii) what is the nature of the resulting spinodal line (if any), iii) what is the quality of the resulting thermodynamic and structural results? iv) does the simultaneous requirement of consistency and uniqueness automatically provide improved results?

As we will show, we have a positive answer for i), a thorough and interesting characterization for ii), some interesting indications for iii), and a partly negative answer for iv).

However, we can show that it is possible to exploit the control provided by the generating functional approach to easily generate new closures and we feel our procedure could be the basis of a more systematic approach to IET.

In section i we recall the connections between closures, generating functionals, thermodynamic consistency and uniqueness of solutions and we illustrate them in the well known case of HNC approximation. In section ii we introduce two straightforward extensions of HNC intended to cure its problems. In Section iii numerical results are presented and discussed. In section iv we show two possible improvements of the closures studied.

i Thermodynamic consistency and uniqueness of the solution of integral equations

Since the work by Olivares and McQuarrie [68] it is known the general method to obtain the generating functional whose extremum with respect to variations of the direct ($c(r)$) or total ($h(r)$) correlation functions results in the closure relation, provided the Ornstein-Zernike equation is satisfied. In a way, here we address the inverse problem of the derivation of a closure: given a closure (whatever was the way of deriving it) what is the functional of the correlation functions which has the closure as extremum value equation?

For example, if we have a closure of the form

$$\rho^2 c(r) = \Psi\{h(r), \beta\phi(r)\} \quad , \tag{5.i:1}$$

where $\phi(r)$ is the pair interaction potential and Ψ is an arbitrary function, the functional

$$\begin{aligned} Q[h(r), \beta\phi(r)] \;=\; & \frac{1}{2\beta\rho}\left(\int \frac{d\mathbf{k}}{(2\pi)^3}\{\rho\hat{h}(k) - \ln[1-\rho\hat{h}(k)]\} - \right. \\ & \left. \int d\mathbf{r}\, h(r) \int_0^1 dt\, \Psi\{t h(r), \beta\phi(r)\} + \text{constant}\right) \quad , \end{aligned} \tag{5.i:2}$$

is such that the extremum condition

$$\frac{\delta Q}{\delta h(r)} = 0 \quad , \tag{5.i:3}$$

is equivalent to

$$\rho^2 h(r) = \Psi\{h(r), \beta\phi(r)\} + \rho \int h(|\mathbf{r} - \mathbf{r}'|)\Psi\{h(r'), \beta\phi(r')\}\, d\mathbf{r}' \quad . \tag{5.i:4}$$

Olivares and McQuarrie also showed how to find the generating functional if the closure is expressed in the form

$$\rho^2 h(r) = \Psi\{c(r), \beta\phi(r)\} \quad . \tag{5.i:5}$$

In section iv.3 we discuss the extension of their method to the case of a closure written as

$$\rho^2 c(r) = \Psi\{\gamma(r), \beta\phi(r)\} \quad , \tag{5.i:6}$$

where $\gamma(r) = h(r) - c(r)$ is the indirect correlation function. Notice that most of the modern closures correspond to this last case.

The possibility of translating the original integral equation into an extremum problem allows to get an easy control on two important characteristics of the approximation: thermodynamic consistency between energy and virial routes to the thermodynamics and uniqueness of the solution.

Indeed, once we get the generating functional Q, due to the approximations induced by the closure, there is no guarantee that its value at the extremum is an excess free energy. In order to be a free energy, the functional should satisfy the condition

$$\frac{\delta Q}{\delta \phi(r)} = \frac{\rho}{2} g(r) \quad , \tag{5.i:7}$$

where $g(r) = h(r) + 1$ is the pair distribution function.

Even if this condition is not new, and mention to it is present in the literature [69], we discuss it in appendix F as well as its consequences on the thermodynamic consistency between the virial pressure and the density derivative of the free energy.

Another issue where the generating functional approach is useful is the problem of multiple solutions of the integral equations [65]. In particular, the analysis of the convexity properties of the generating functional is a very powerful tool [70, 71].

Let us illustrate this techniques in the case of HNC closure. It is well known [64, 68] that the HNC equation with closure

$$c(r) = h(r) - \ln\left[g(r)e^{\beta\phi(r)}\right] \quad , \tag{5.i:8}$$

can be derived from the variational principle

$$\frac{\delta \mathcal{F}[h]}{\delta h(r)} = 0 \quad , \tag{5.i:9}$$

where

$$\mathcal{F}[h] = \mathcal{F}_{OZ}[h] + \mathcal{F}_{HNC}[h] \quad , \tag{5.i:10}$$

with

$$\begin{cases} \mathcal{F}_{OZ}[h] = \int \frac{d\mathbf{k}}{(2\pi)^3}\{\rho\hat{h}(k) - \ln[1+\rho\hat{h}(k)]\} \quad , \\ \\ \mathcal{F}_{HNC}[h] = \rho^2 \int d\mathbf{r}\left\{1 + g(r)\left[\ln\left(g(r)e^{\beta\phi(r)}\right) - 1\right] - h^2(r)/2\right\} \quad . \end{cases} \tag{5.i:11}$$

Let us call $\bar{h}(r)$ the extremum of $\mathcal{F}$, solution of the variational principle (5.i:9). It can be shown (see appendix F) that, within an additive constant, $\mathcal{F}[\bar{h}]/(2\beta\rho)$ is the excess Helmholtz free energy per particle of the liquid. This ensure thermodynamic consistency between the route to the pressure going through the partial derivative of the free energy and the one going through the virial theorem (see appendix F). In addition, it allows to get a closed expression for the excess chemical potential without further approximations [72, 73]. This feature is highly desirable for applications of IET to the determination of the phase diagrams.

Moreover if we can prove that $\mathcal{F}$, defined on some convex set of trial correlation functions D_c, is a strictly convex functional, then we know that if a solution to (5.i:9) exists, it corresponds to a minimum and is unique. A functional $\mathcal{F}$ is strictly convex if for all $y(r) \in D_c$ and $y(r) \neq 0$, we have

$$A = \int y(r)\frac{\delta^2\mathcal{F}[h]}{\delta h(r)\delta h(r')}y(r')\,d\mathbf{r}\,d\mathbf{r}' > 0 \quad . \tag{5.i:12}$$

We calculate the second functional derivatives as follows

$$\begin{cases} \frac{\delta^2\mathcal{F}_{OZ}[h]}{\delta h(r)\delta h(r')} = \rho^2 \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{r}')} \frac{1}{[1+\rho\hat{h}(k)]^2} \quad , \\ \\ \frac{\delta^2\mathcal{F}_{HNC}[h]}{\delta h(r)\delta h(r')} = \rho^2\delta(\mathbf{r}-\mathbf{r}')\left(\frac{1}{g(r)} - 1\right) \quad . \end{cases} \tag{5.i:13}$$

Recalling that the static structure factor $S(k) = 1 + \rho\hat{h}(k)$, we find for A

$$A/\rho^2 = \int \frac{d\mathbf{k}}{(2\pi)^3}\frac{\hat{y}^2(k)}{S^2(k)} + \int d\mathbf{r}\, y^2(r)\left(\frac{1}{g(r)} - 1\right) \quad . \tag{5.i:14}$$

Now, the most interesting results would be to show the strict convexity of the HNC functional over the convex set of all the admissible pair correlation functions (all the $h(r) \geq -1$ and properly decaying to zero at large distance.

However, this is not the case for HNC. It has not been possible to show the positive definiteness of equation (5.i:14) and it has been shown [65] that in some region of the thermodynamic plane HNC does exhibit multiple solutions.

The best we can do is to obtain a more limited result. Calling $g_1 = \sup g(r)$ ($g_1 > 1$ is the height of the first peak of the pair distribution function) and using Parseval theorem, we find

$$A/\rho^2 > \int \frac{d\mathbf{k}}{(2\pi)^3}\hat{y}^2(k)\left(\frac{1}{S^2(k)} - 1 + \frac{1}{g_1}\right) \quad , \tag{5.i:15}$$

from which we deduce that $A > 0$ on the following set of functions

$$D = \left\{h(r)\,|\,0 < S(k) < \sqrt{g_1/(g_1-1)} \quad \forall k\right\} \quad . \tag{5.i:16}$$

We conclude that $\mathcal{F}$ defined on any convex set of functions $D_c \subset D$ is strictly convex. Near the triple point we are sure we are out from such set since the first peak of the pair distribution function for the Lennard-Jones fluid is $g_1 \simeq 3$ [74], so that $\sqrt{g_1/(g_1-1)} \simeq 1.2$. The first peak of the static structure factor is also close to 3. Then we are not inside D and the HNC approximation may have multiple solutions [65].

Instead, if we are in the weak coupling regime, the previous conditions tells us that there is a range where the branch of solutions going to the perfect gas limit is unique and quite isolated from other solutions.

ii Extensions of HNC

The generating functional approach can be used in a systematic way to look for better closures. We think that this way, we can obtain a less empirical search method for improving closures.

In the following we report some preliminary analysis we have done. As a first test of our program, we have restricted our investigations to simple modifications of HNC functional. As we will discuss later, such a choice is certainly not optimal. However, we can learn enough to consider the approach worthwhile of further investigations and we feel the results are interesting in order to reveal more details about the characteristics of the solutions of the highly non linear IET.

ii.1 The HNC/H2 approximation

We want to modify the HNC closure in order to have an integral equation with a generating functional which is strictly convex without having to restrict its definition domain. We choose as our modified HNC (HNC/H2) closure [1]

$$c(r) = h(r) - \ln[g(r)] - \beta\phi(r) - \alpha h^2(r) \quad , \tag{5.ii:1}$$

with α a parameter to be determined. The new closure generating functional is

$$\mathcal{F}_{HNC/H2}[h] = \rho^2 \int d\mathbf{r} \left\{ 1 + g(r) \left[\ln\left(g(r) e^{\beta\phi(r)} \right) - 1 \right] - h^2(r)/2 + \alpha h^3(r)/3 \right\} \ . \tag{5.ii:2}$$

Its second functional derivative with respect to h is

$$\frac{\delta^2 \mathcal{F}_{HNC/H2}[h]}{\delta h(r) \delta h(r')} = \rho^2 \delta(\mathbf{r} - \mathbf{r}') \left[\frac{1}{g(r)} - 1 + 2\alpha h(r) \right] \quad . \tag{5.ii:3}$$

Recalling that $h = g - 1$ and $g(r) > 0$ for all r, we see that for $\alpha = 1/2$

$$\frac{1}{g} - 1 + 2\alpha h = \frac{(1-g)^2}{g} \geq 0 \quad \forall g \quad . \tag{5.ii:4}$$

Then $\mathcal{F}_{HNC/H2}$ is a convex functional and since $\mathcal{F}_{OZ}$ is unchanged and strictly convex (see appendix G), their sum, the generating functional of the integral equation, is strictly convex.

Moreover $\{\mathcal{F}_{OZ}[\bar{h}] + \mathcal{F}_{HNC/H2}[\bar{h}]\}/(2\beta\rho)$ continues to be the excess Helmholtz free energy per particle of the liquid since equation (5.i:7) holds (see appendix F).

[1] Our first trial should really be $c = -\ln g - \beta\phi$. Which should be called HNC/H1. We have tested numerically this closure and we found that it performed worst than HNC/H2 both for the structure and for the thermodynamics of the system under exam.

We have then an integral equation which is both thermodynamically consistent (the pressure calculated from the virial theorem coincides with that one calculated from the Helmholtz free energy) and with a solution which, when it exists, is unique.

ii.2 The HNC/H3 approximation

In the same spirit as in subsection ii.1 we can try to add a term h^3 in the HNC/H2 closure

$$c(r) = h(r) - \ln[g(r)] - \beta\phi(r) - \alpha h^2(r) - \gamma h^3(r) \quad , \tag{5.ii:5}$$

with α and γ parameters to be determined. We call this approximation HNC/H3. The closure generating functional is

$$\mathcal{F}_{HNC/H3}[h] = \rho^2 \int d\mathbf{r} \ \left\{1 + g(r)\left[\ln\left(g(r)e^{\beta\phi(r)}\right) - 1\right] - h^2(r)/2 + \alpha h^3(r)/3 + \gamma h^4(r)/4\right\} \quad . \tag{5.ii:6}$$

Its second functional derivative with respect to h is

$$\begin{aligned}\frac{\delta^2\mathcal{F}_{HNC/H3}[h]}{\delta h(r)\delta h(r')} &= \rho^2\delta(\mathbf{r}-\mathbf{r}')\left[\frac{1}{g(r)} - 1 + 2\alpha h(r) + 3\gamma h^2(r)\right] \\ &= \rho^2\delta(\mathbf{r}-\mathbf{r}')\frac{1-g(r)}{g(r)}\{1 - 2\alpha g(r) + 3\gamma g(r)[1-g(r)]\} \quad .\end{aligned} \tag{5.ii:7}$$

In order to have the right hand side of this expression positive for $g > 0$ the only choice we have is to set $\alpha = 1/2$. In this way

$$(1-g)[1 - 2\alpha g + 3\gamma g(1-g)] = (1-g)^2(1+3\gamma g) \quad , \tag{5.ii:8}$$

and we see that $\mathcal{F}_{HNC/H3}$ is a convex functional if we additionally choose $\gamma > -1/[3\sup g(r)]$.

Once again $\{\mathcal{F}_{OZ}[\bar{h}] + \mathcal{F}_{HNC/H3}[\bar{h}]\}/(2\beta\rho)$ is the excess Helmholtz free energy per particle of the liquid and the thermodynamic consistency virial-free energy is ensured.

iii Numerical results

To solve numerically the OZ plus closure system of nonlinear equations we used Zerah' s algorithm [75]. We performed Fourier transforms using a fast Fourier transform routine taken from CERN library. In the code we always work with adimensional thermodynamic variables $T^* = 1/(\beta\epsilon)$,$\rho^* = \rho\sigma^3$, and $P^* = P\sigma^3/\epsilon$, where σ and ϵ are the characteristic length and characteristic energy of the system respectively.We always used 1024 grid points and a step size $\Delta r = 0.025\sigma$.

The thermodynamic quantities were calculated according to the statistical mechanics formulae for: the excess internal energy per particle

$$U^{exc}/N = 2\pi\rho\int_0^\infty \phi(r)g(r)r^2\,dr \quad , \tag{5.iii:1}$$

the excess virial pressure

$$\beta P^v/\rho - 1 = -\frac{2}{3}\pi\beta\rho\int_0^\infty \frac{d\phi(r)}{dr}g(r)r^3\,dr \quad , \tag{5.iii:2}$$

the bulk modulus calculated from the compressibility equation

$$B_c = \frac{\beta}{\rho\chi_T} = \frac{1}{S(k=0)} \quad , \tag{5.iii:3}$$

where χ_T is the isothermal compressibility, and the bulk modulus calculated from the virial equation

$$\begin{aligned} B_p &= \beta\frac{\partial P^v}{\partial\rho} \\ &= 1 - \frac{4}{3}\pi\beta\rho\int_0^\infty \frac{d\phi(r)}{dr}g(r)r^3\,dr - \frac{2}{3}\pi\beta\rho^2\int_0^\infty \frac{d\phi(r)}{dr}\frac{\partial g(r)}{\partial\rho}r^3\,dr \quad . \end{aligned} \tag{5.iii:4}$$

For the calculation of B_p once $g(r)$ and $c(r)$ had been calculated, Lado' s scheme for Fourier transforms [76] was used to determine $\partial\hat{g}(k)/\partial\rho$. Even if slow, this allows us to explicitly calculate and later invert the coefficients matrix of the linear system of equations which enters the calculation of $\partial\hat{g}(k)/\partial\rho$.

iii.1 Inverse power potentials

The general form of the inverse power potential is

$$\phi(r) = \epsilon\left(\frac{\sigma}{r}\right)^n \quad , \tag{5.iii:5}$$

where $3 < n < \infty$. For this class of fluids the thermodynamics depends only from the dimensionless coupling parameter

$$z = (\rho\sigma^3/\sqrt{2})(\beta\epsilon)^{3/n} \quad . \tag{5.iii:6}$$

In this subsection we choose to fix $\rho^* = 1$ so that equation (5.iii:6) gives the relation between z and T^*.

We performed our calculations on the n =12, 6, and 4 fluids at the freezing point. We compared three kind of closures: the thermodynamically consistent one of Rogers and Young [77] (RY) with thermodynamic consistency virial-compressibility and known to be very close to the simulation results, the hypernetted-chain (HNC) closure, and the HNC/H2 described in subsection ii.1. In each case we compared our data with the Monte Carlo (MC) results of Hansen and Schiff [78].

iii.1.1 The inverse 12th power potential

The freezing point for this fluid is at $z = 0.813$. In figure 5.1 we compare the MC and RY results for the pair distribution function. The RY α parameter to achieve thermodynamic consistency at this value of z is 0.603. Notice that we express α in units of σ and not of $a = (3/4\pi\rho)^{1/3}$ as in the original Rogers and Young' s paper [77]. In figure 5.2 we compare the MC, the HNC, and the HNC/H2 results for the pair distribution function.

In table 5.1 we compare various thermodynamic quantities (the excess internal energy per particle, the excess virial pressure, the bulk moduli) obtained from the RY, the HNC, and the HNC/H2 closures. In the MC calculation of Hansen and Schiff the excess internal energy per particle is 2.675, the excess virial pressure is 18.7, and the bulk modulus 72.7.

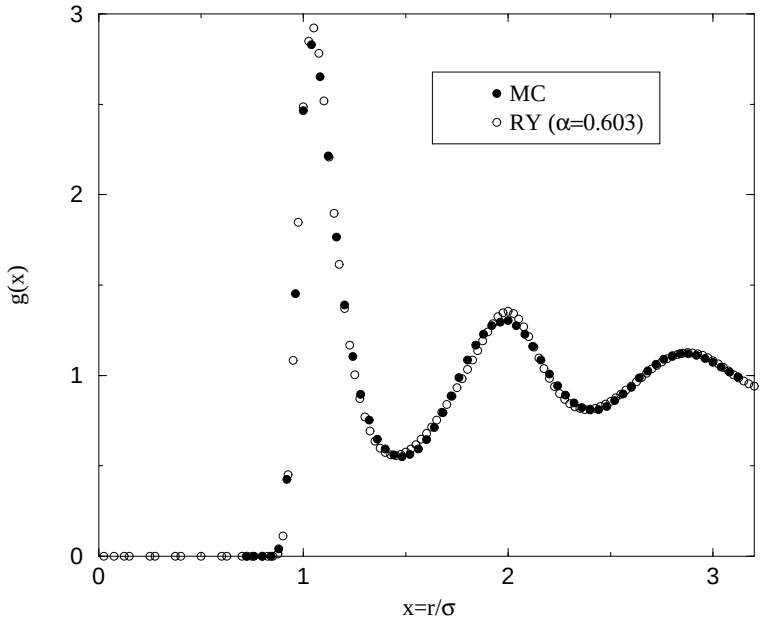

FIGURE 5.1: Comparison of the Monte Carlo (MC) and Rogers Young (RY) results for the pair distribution function of the inverse 12th-power fluid at $z = 0.813$.

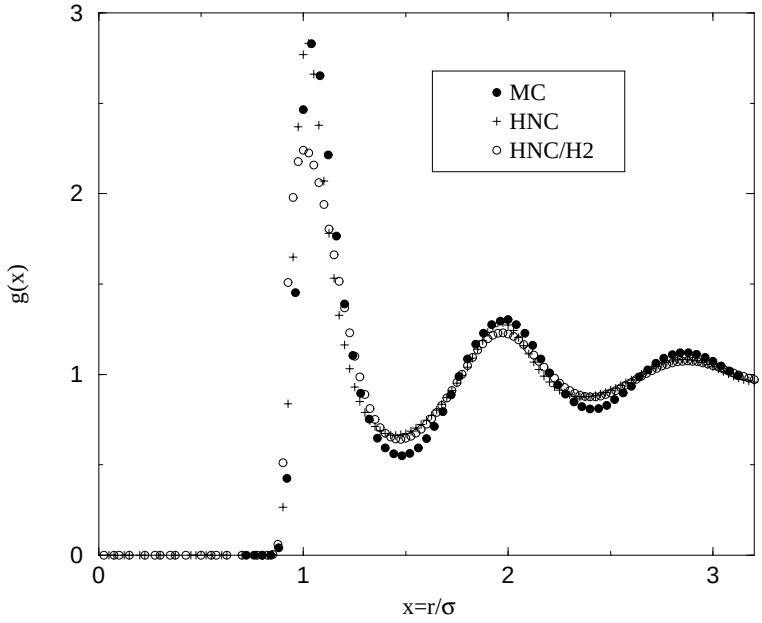

FIGURE 5.2: Comparison of the Monte Carlo (MC), the HNC, and HNC/H2 results for the pair distribution function of the inverse 12th-power fluid at $z = 0.813$.

iii.1.2 The inverse 6th power potential

The freezing point for this fluid is at $z = 1.54$. In figure 5.3 we compare the MC and RY results for the pair distribution function. The RY α parameter to achieve thermodynamic consistency at this value of z is 1.209. In figure 5.4 we compare the MC, the HNC, and the HNC/H2 results for the pair distribution function.

closure	$U^{exc}/(N\epsilon)$	$\beta P^{(v)}/\rho - 1$	B_c	B_p
RY ($\alpha = 0.603$)	2.626	18.359	69.782	70.125
HNC	3.009	21.036	45.278	80.430
HNC/H2	3.200	22.372	52.661	87.255

TABLE 5.1: We compare various thermodynamic quantities as obtained from the RY, the HNC, and the HNC/H2 closure, for the inverse 12th-power fluid at the freezing point ($z = 0.813$). $U^{exc}/(N\epsilon)$ is the excess internal energy per particle, $\beta P^{(v)}/\rho - 1$ the excess virial pressure, B_c and B_p are the bulk moduli from the compressibility and the virial equation respectively.

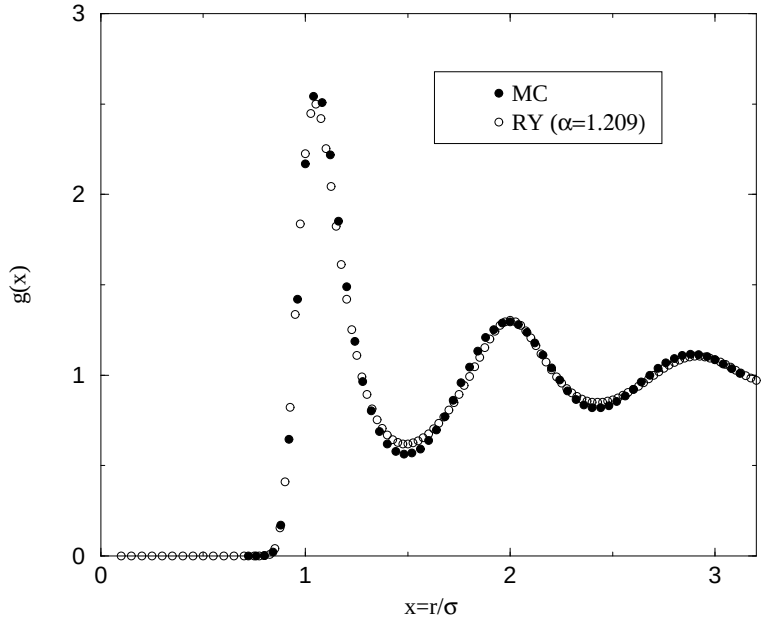

FIGURE 5.3: Comparison of the Monte Carlo (MC) and Rogers Young (RY) results for the pair distribution function of the inverse 6th-power fluid at $z = 1.54$.

In table 5.2 we compare various thermodynamic quantities (the excess internal energy per particle, the excess virial pressure, the bulk moduli) obtained from the RY, the HNC, and the HNC/H2 closures. In the MC calculation of Hansen and Schiff the excess internal energy per particle is 4.090, the excess virial pressure is 38.8 and the bulk modulus 110.1.

iii.1.3 The inverse 4th power potential

The freezing point for this fluid is at $z = 3.92$. In figure 5.5 we compare the MC and RY results for the pair distribution function. The RY α parameter to achieve thermodynamic consistency at this value of z is 1.794. In figure 5.6 we compare the MC, the HNC, and the HNC/H2 results for the pair distribution function.

In table 5.3 we compare various thermodynamic quantities (the excess internal energy per particle, the excess virial pressure, the bulk moduli) obtained from the RY, the HNC, and the HNC/H2 closures. In the MC calculation of Hansen and Schiff the excess internal energy per particle is 8.233, the excess virial pressure is 107.7 and the bulk modulus 156.

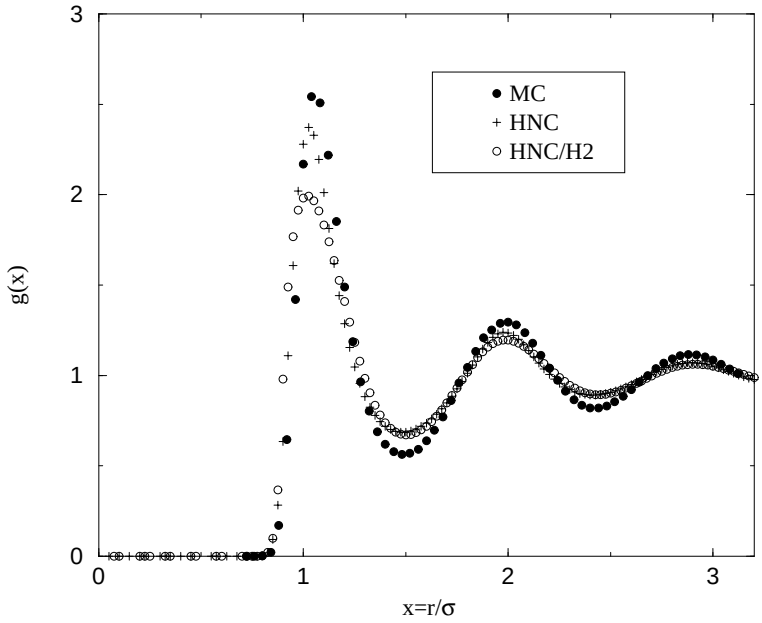

FIGURE 5.4: Comparison of the Monte Carlo (MC), the HNC, and HNC/H2 results for the pair distribution function of the inverse 6th-power fluid at $z = 1.54$.

closure	$U^{exc}/(N\epsilon)$	$\beta P^{(v)}/\rho - 1$	B_c	B_p
RY ($\alpha = 1.209$)	4.114	39.027	110.952	111.420
HNC	4.235	40.178	84.016	113.733
HNC/H2	4.283	40.635	88.289	115.757

TABLE 5.2: We compare various thermodynamic quantities as obtained from the RY, the HNC, and the HNC/H2 closure, for the inverse 6th-power fluid at the freezing point ($z = 1.54$). $U^{exc}/(N\epsilon)$ is the excess internal energy per particle, $\beta P^{(v)}/\rho - 1$ the excess virial pressure, B_c and B_p are the bulk moduli from the compressibility and the virial equation respectively.

iii.2 The spinodal line

In this subsection we study a pair potential with a minimum In particular we chose the Lennard-Jones potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \quad , \tag{5.iii:7}$$

where ϵ and σ are positive parameters. The critical point for this fluid is at [79]

$$\begin{aligned} T_c^* &= 1.3120 \pm 0.0007 \\ \rho_c^* &= 0.316 \pm 0.001 \\ P_c^* &= 0.1279 \pm 0.0006 \end{aligned}$$

Integral equations fail to have a solution at low temperature and intermediate density, i.e. in the two-phase unstable region of the phase diagram. In particular it is well known that the HNC approximation is unable to reproduce the *spinodal line*, the locus of points of infinite compressibility in the phase diagram [65]. This is due to the loss of solution as one approaches

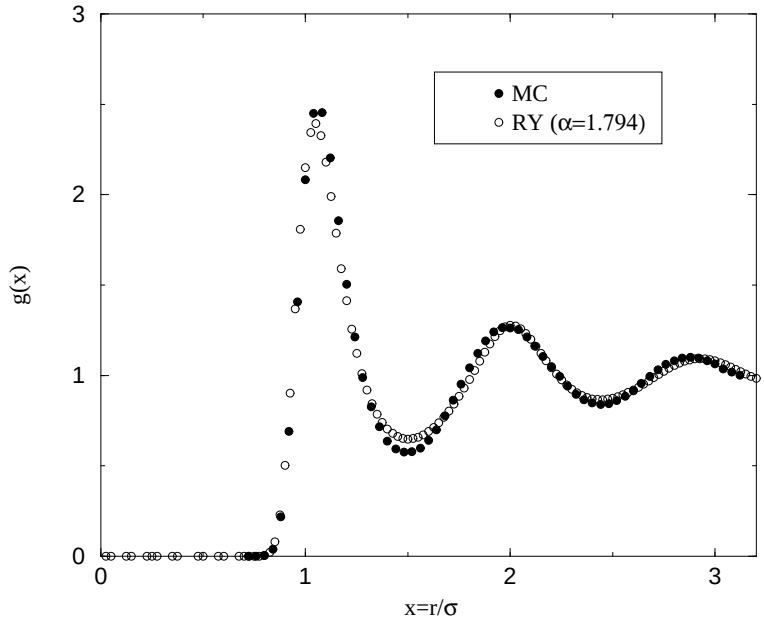

FIGURE 5.5: Comparison of the Monte Carlo (MC) and Rogers Young (RY) results for the pair distribution function of the inverse 4th-power fluid at $z = 3.92$.

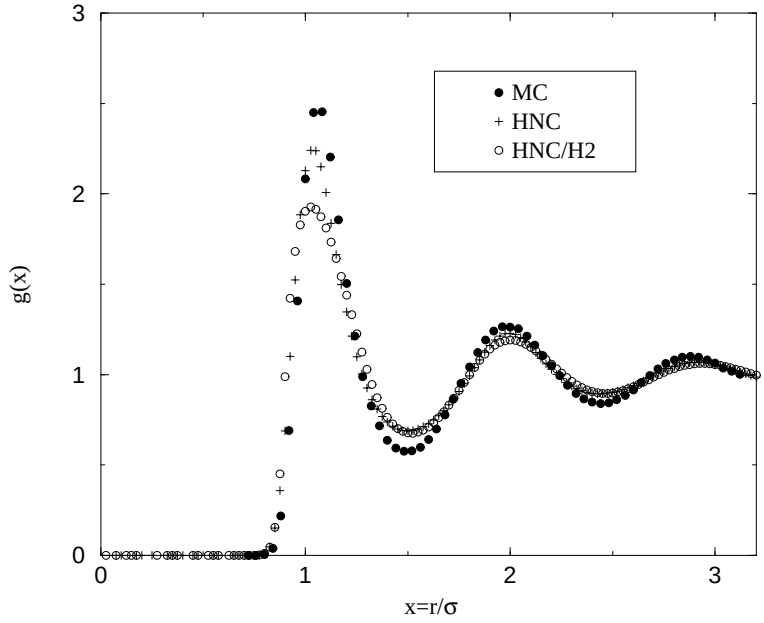

FIGURE 5.6: Comparison of the Monte Carlo (MC), HNC, and HNC/H2 results for the pair distribution function of the inverse 4th-power fluid at $z = 3.92$.

the spinodal line on an isotherm from high or from low densities. The line of loss of solution, in the phase diagram, is called *termination line*. The loss of solution for the HNC approximation is due to the loss of strict convexity of the generating functional [80]. Indeed, using HNC approximation, we computed the bulk modulus from the compressibility equation B_c, on several isotherms as a function of the density. At low temperatures we found that both at high density and at low density we were unable to continue the isotherm at low values of B_c. Zerah' s

closure	$U^{exc}/(N\epsilon)$	$\beta P^{(v)}/\rho - 1$	B_c	B_p
RY ($\alpha = 1.794$)	8.001	104.664	250.106	242.948
HNC	8.047	105.277	223.328	244.212
HNC/H2	8.068	105.542	226.966	257.678

TABLE 5.3: We compare various thermodynamic quantities as obtained from the RY (notice that the bulk moduli were not given in the Rogers and Young' s paper and the value of the virial pressure as reported in our table was not corrected to take into account the long range nature of the potential), the HNC and the HNC/H2 closure, for the inverse 4th-power fluid at the freezing point ($z = 3.92$). $U^{exc}/(N\epsilon)$ is the excess internal energy per particle, $\beta P^{(v)}/\rho - 1$ the excess virial pressure, B_c and B_p are the bulk moduli from the compressibility and the virial equation respectively.

algorithm either could not get to convergence or it would converge at a non physical solution (with a structure factor negative at some wavevector k). Since HNC/H2 has, by construction, an always strictly convex generating functional, we expect it to be able to reproduce a spinodal line (there should be no termination line).

In Figure 5.7 we show the behavior of B_c on several isotherms as a function of density,

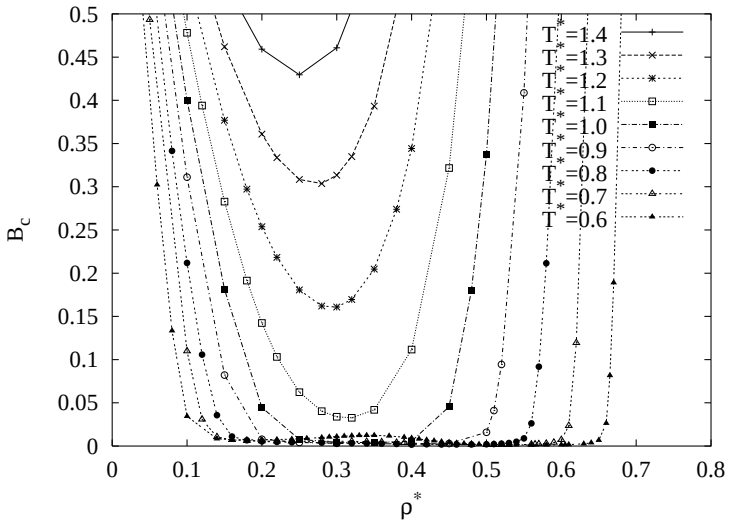

FIGURE 5.7: Behavior of B_c of the Lennard-Jones fluid, on several isotherms as a function of the density for the HNC/H2 approximation.

calculated with the HNC/H2 approximation. We see that now there are no termination points. B_c never becomes exactly zero and the low temperature isotherms develop a bump in the intermediate density region. The same plot for the bulk modulus calculated from the virial pressure B_p, shows that at low temperatures this bulk modulus indeed becomes zero along the isotherms both at high and low densities.

In figure 5.8 the pressure is plotted as a function of the density on several isotherms for the HNC/H2 approximation. Apart from the fact that we find negative pressures, the isotherms has a Van der Waals like behavior.

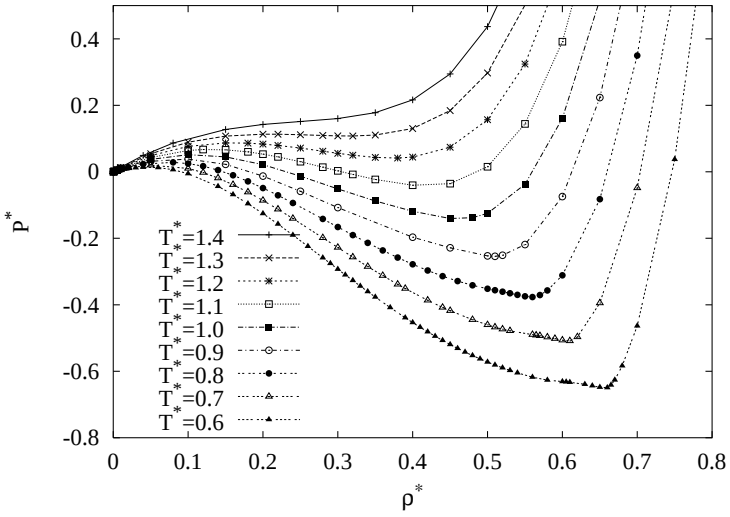

FIGURE 5.8: Behavior of the pressure of the Lennard-Jones fluid, on several isotherms as a function of the density for the HNC/H2 approximation.

iv Improving the closures

The numerical results for HNC/H2 exhibit interesting features as far as the coexistence region is concerned but show unambiguously a worst agreement with the MC structural data in correspondence with a marginal improvement in the thermodynamics.

We feel that the main problem is the difficulty of an accurate description of the bridge functions in terms of powers of the pair correlation function. Recent investigations on improved closures seem to point to the indirect correlation function $\gamma(r)$ or some renormalized version of it, as the best starting point for progress. However, before moving to more complex relations or functional dependences, we have explored two possible directions for improving the HNC/H2 closure. In the first approach we have tried to follow the MHNC approach by Lado *et al.* [81]. In the second we have explored the possibilities of optimization offered by the numerical coefficient of the cubic term in the generating functional.

iv.1 The reference HNC/H2 approximation

From the graphical analysis of the pair distribution function it is known [12] that $g(r)$ may be written as

$$g(r) = e^{-\beta\phi(r)+\gamma(r)+B(r)} \quad , \tag{5.iv:1}$$

where $\gamma(r) = h(r) - c(r)$ is the sum of all the series type diagrams and $B(r)$ the sum of bridge type diagrams. If we take

$$B(r) = -\frac{1}{2}h^2(r) + G(r) \quad , \tag{5.iv:2}$$

we have that our HNC/H2 approximation amounts to setting $G(r) = 0$. Rosenfeld and Ashcroft [59] proposed that $B(r)$ should be essentially the same for all potentials $\phi(r)$. We now make the same proposal for the G function. In the same spirit of the RHNC approximation of Lado [81] we will approximate $G(r)$ with the G function of a short range (reference) potential $\phi_0(r)$.

Assuming known the properties of the reference system, we can calculate the G function as follows

$$G_0(r) = \ln\left[g_0(r)e^{\beta\phi_0(r)}\right] - \gamma_0(r) + \frac{1}{2}h_0^2(r) \quad . \tag{5.iv:3}$$

The reference HNC/H2 (RHNC/H2) approximation is then

$$g(r) = e^{-\beta\phi(r)+\gamma(r)-\frac{1}{2}h^2(r)+G_0(r)} \quad . \tag{5.iv:4}$$

An expression for the free energy functional can be obtained *turning on* the potential $\phi(r)$ in two stages: first, from the noninteracting state to the reference potential $\phi_0(r)$ and then from there to the full potential $\phi(r)$. To this end we write

$$\phi(r;\lambda_0,\lambda_1) = \lambda_0\phi_0(r) + \lambda_1\Delta\phi(r) \quad , \tag{5.iv:5}$$

with $\Delta\phi(r) = \phi(r) - \phi_0(r)$. Following the same steps as in [60] we obtain for the excess free energy per particle

$$f^{exc} = f_1 + f_2 + f_3^{(0)} + \Delta f_3 \tag{5.iv:6}$$

where the first two terms were already encountered in section i

$$\beta f_1 = \frac{1}{2}\rho\int d\mathbf{r}\left\{1 + g(r)\left[\ln\left(g(r)e^{\beta\phi(r)}\right) - 1\right] - h^2(r)/2 + h^3(r)/6\right\} \quad , \tag{5.iv:7}$$

$$\beta f_2 = \frac{1}{2\rho}\int\frac{d\mathbf{k}}{(2\pi)^3}\{\rho\hat{h}(k) - \ln[1+\rho\hat{h}(k)]\} \quad . \tag{5.iv:8}$$

The third term is assumed known

$$\beta f_3^{(0)} = -\frac{1}{2}\rho\int d\mathbf{r}\int_0^1 d\lambda_0 G(r;\lambda_0,0)\frac{\partial g(r;\lambda_0,0)}{\partial\lambda_0} = \beta(f^{(0)} - f_1^{(0)} - f_2^{(0)}) \quad , \tag{5.iv:9}$$

here $f^{(0)}$ is the excess free energy per particle of the reference system and $f_1^{(0)}, f_2^{(0)}$ are defined as in equations (5.iv:7), (5.iv:8) for the reference potential and its corresponding correlation functions. The last term is

$$\beta\Delta f_3 = -\frac{1}{2}\rho\int d\mathbf{r}\int_0^1 d\lambda_1 G(r;1,\lambda_1)\frac{\partial g(r;1,\lambda_1)}{\partial\lambda_1} \quad . \tag{5.iv:10}$$

According to our proposal, G is insensitive to a change in potential from ϕ_0 to ϕ. We may then approximate this last term as follows

$$\beta\Delta f_3 \approx -\frac{1}{2}\rho\int d\mathbf{r}G_0(r)[g(r) - g_0(r)] \quad . \tag{5.iv:11}$$

Now that we have the free energy we may consider it as a functional of both $h(r)$ and $G_0(r)$ and take its variation with respect to these functions. We find,

$$\begin{aligned}\beta\,\delta f^{exc} = {} & \frac{1}{2}\rho\int d\mathbf{r}\left\{c(r) - h(r) + h^2(r)/2 + \ln\left[g(r)e^{\beta\phi(r)}\right] - G_0(r)\right\}\delta h(r) - \\ & \frac{1}{2}\rho\int d\mathbf{r}[g(r) - g_0(r)]\delta G_0(r) \quad .\end{aligned} \tag{5.iv:12}$$

It follows that the free energy is minimized when both the RHNC/H2 closure (equation (5.iv:4)) is satisfied and when the following constraint

$$\int d\mathbf{r}[g(r) - g_0(r)]\delta G_0(r) = 0 \quad , \tag{5.iv:13}$$

is fulfilled.

Taking the second functional derivative of f^{exc} with respect to $h(r)$ we find that also this free energy is a strictly convex functional of the total correlation function. This property was lacking in the RHNC theory and constitutes the main feature of the RHNC/H2 closure. As already stressed in section ii.1 it ensures that if a solution to the integral equation exists it has to be unique.

The constraint, as for RHNC, gives a certain thermodynamic consistency to the theory (see [60]). If we choose a reference potential $\phi_0(r) = \phi_0(r;\sigma,\epsilon)$ which depends on some length and energy parameters σ and ϵ, the optimum values of the parameters that minimize the free energy can be determined by the constraint (5.iv:13) which becomes

$$\int d\mathbf{r}[g(r) - g_0(r)]\frac{\partial G_0(r)}{\partial \sigma} = 0 \quad , \tag{5.iv:14}$$

and

$$\int d\mathbf{r}[g(r) - g_0(r)]\frac{\partial G_0(r)}{\partial \epsilon} = 0 \quad , \tag{5.iv:15}$$

However, neither the hard-sphere pseudo bridge functions nor some empirical attempt to model the unknown function via a Yukawa function provided useful results.

iv.1.1 Results from the RHNC/H2 approximation

For the Lennard-Jones fluid near its triple point ($\rho^* = 0.85$ and $T^* = 0.719$) we tried to mimic the G function with a Yukawian. We chose

$$G_0(r) = -A\frac{e^{-r/\lambda}}{r} \quad , \tag{5.iv:16}$$

where A and λ are two positive constants. Setting λ equal to the first minimum of the pair distribution function obtained from a molecular dynamics simulation [74] ($\lambda \simeq 1.5$), we varied A to fit the excess internal energy obtained in the simulation [82] ($U^{exc}/(N\epsilon) = -6.12$). The resulting value for A was around 124. The values of the pressure and of the bulk modulus did not match with the ones of the simulation and the pair distribution function had a lower first peak and the successive peaks shifted forward respect to the $g(r)$ of the simulation as is shown in figure 5.9.

iv.2 Optimized HNC/H3 approximation

For $\gamma = 0$ HNC/H3 reduces to HNC/H2. For $\gamma > 0$ the first peak of the pair distribution function is dumped respect to the one of the pair distribution function calculated with HNC/H2. For $\gamma < 0$ the first peak increases giving in general a better fit to the simulation data.

In figure 5.10 we compare the pair distribution function of the Lennard-Jones fluid near its triple point, calculated with a molecular dynamic simulation [74], the HNC/H2 approximation, the approximation HNC/H3 with $\gamma = -0.203$ (at lower values of γ Zerah' s algorithm would fail

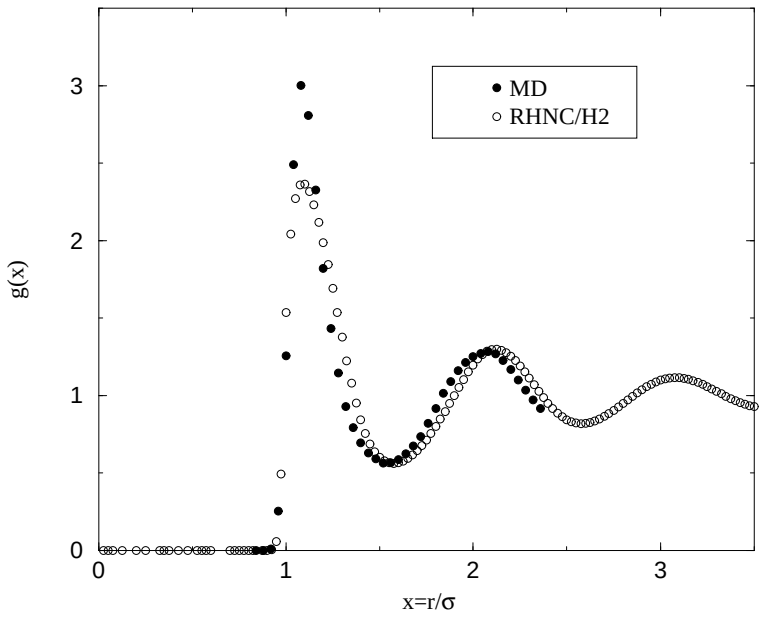

FIGURE 5.9: Comparison of the pair distribution function computed from the RHNC/H2 with a yukawian G function and from a molecular dynamics (MD) simulation, for a Lennard-Jones fluid at $\rho^* = 0.85$ and $T^* = 0.719$.

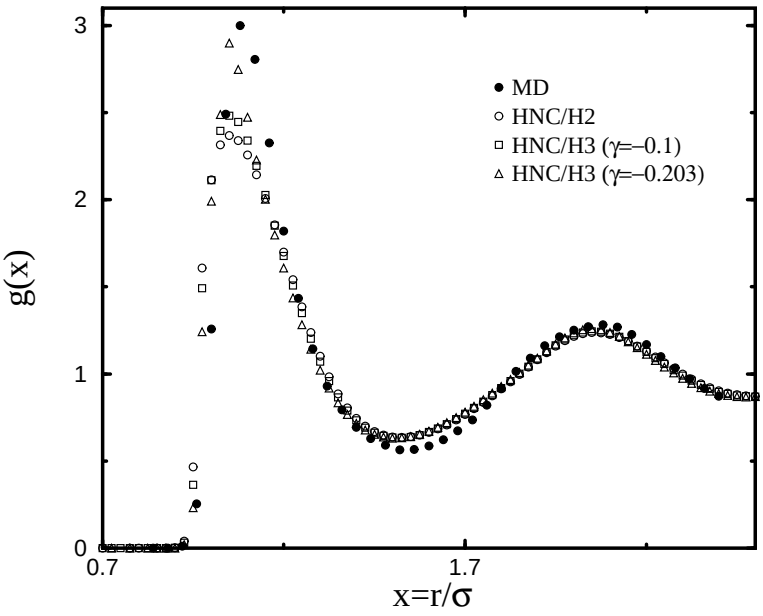

FIGURE 5.10: Comparison of the pair distribution function of a Lennard-Jones fluid at $\rho^* = 0.85$ and $T^* = 0.719$ computed from the molecular dynamic (MD) simulation of Verlet, the HNC/H2 approximation, and the HNC/H3 approximation. For HNC/H3 we present results obtained setting $\gamma = -0.1$ (when the generating functional of the approximation is still strictly convex) and $\gamma = -0.203$ (which gives the best fit possible to the simulation data but does not ensure the strict convexity of the generating functional).

to converge), and the approximation HNC/H3 with $\gamma = -0.1$ (when the generating functional of HNC/H3 is still strictly convex). As we can see HNC/H3 fits the simulation data better than

HNC/H2 even if the first peak is still slightly displaced to the left of the simulation data, a well known problem of the HNC approximation [59].

The best results are given by HNC/H3 with $\gamma = -0.203$. Note that the HNC/H3 generating functional at this value of γ is not strictly convex (strict convexity is lost for $\gamma \lesssim -1/9$). The first peak of the static structure factor is at $k\sigma \simeq 6.75$ and has a magnitude of 2.41, a quite low value for a liquid near the triple point. We have calculated the pressure and the internal energy. We found $\beta P/\rho \simeq 3.87$ and $U^{exc}/(N\epsilon) \simeq -5.72$ (very close to the HNC results $\beta P/\rho \simeq 3.12$ and $U^{exc}/(N\epsilon) \simeq -5.87$) to be compared with the simulation results [82] 0.36 and -6.12 respectively. The bulk moduli are $B_c \simeq 11.74$ and $B_p \simeq 36.61$ which shows that at the chosen value of γ we do not have the thermodynamic consistency virial-compressibility and we do not improve on HNC inconsistency (using HNC we find $B_c \simeq 7.09$ and $B_p \simeq 32.72$).

iv.3 Functionals of γ

Often in the numerical solution of the OZ + closure integral equation use is made of the auxiliary function $\gamma(r) = h(r) - c(r)$. Suppose that the closure relation can be written as

$$\rho^2 c(r) = -\Psi\{\gamma(r)\} \quad , \tag{5.iv:17}$$

where Ψ is a function of a function.

We want to translate the integral equation into a variational principle involving functionals of $\gamma(r)$. Then we introduce a closure functional $\mathcal{F}_{cl}[\gamma]$ such that

$$\frac{\delta \mathcal{F}_{cl}[\gamma]}{\delta \gamma(r)} = \Psi\{\gamma(r)\} \quad , \tag{5.iv:18}$$

and an OZ functional $\mathcal{F}_{OZ,c}[\gamma]$ such that, when $c(r)$ and $\gamma(r)$ satisfy the OZ equation, we have

$$\frac{\delta \mathcal{F}_{OZ,c}[\gamma]}{\delta \gamma(r)} = \rho^2 c(r) \quad . \tag{5.iv:19}$$

Then when both the closure and the OZ relations are satisfied, the functional $\mathcal{F} = \mathcal{F}_{cl} + \mathcal{F}_{OZ,c}$ is stationary with respect to variations of $\gamma(r)$, i.e.

$$\frac{\delta \mathcal{F}[\gamma]}{\delta \gamma(r)} = 0 \quad . \tag{5.iv:20}$$

This is the variational principle sought.

We want now find $\mathcal{F}_{OZ,c}$. The OZ equation in k space is

$$\rho \hat{c}^2(k) + \rho \hat{\gamma}(k)\hat{c}(k) - \hat{\gamma}(k) = 0 \quad . \tag{5.iv:21}$$

When we solve it for $\hat{c}$ we find two solutions

$$\hat{c} = \frac{-\hat{\Gamma} \pm \sqrt{\hat{\Gamma}^2 + 4\hat{\Gamma}}}{2\rho} \quad , \tag{5.iv:22}$$

where $\hat{\Gamma}(k) = \rho\hat{\gamma}(k)$ is always positive since

$$\hat{\Gamma} = \rho^2 \hat{h}\hat{c} = \rho^2 \frac{\hat{h}^2}{1 + \rho\hat{h}} = \rho^2 \frac{\hat{h}^2}{S(k)} \quad , \tag{5.iv:23}$$

$S(k)$ being the liquid static structure factor which is positive definite for all k. Since $\hat{c}(k)$ is a function which oscillates around 0, where $\hat{c}$ is negative we have to choose the solution with the minus sign, where it is positive the one with the plus sign. In particular if the isothermal compressibility of the liquid χ_T, is smaller than the one of the ideal gas χ_T^0, we have that

$$\hat{c}(0) = \frac{1}{\rho}\left(1 - \frac{\chi_T^0}{\chi_T}\right) < 0 \quad , \tag{5.iv:24}$$

and we have to start with the minus sign.

The functional we are looking for is then (see equation (30) in [68] with the constant set equal to zero)

$$\mathcal{F}_{OZ,c}[\gamma] = \int_0^1 dt \int d\mathbf{r}\, \gamma(r) \int \frac{d\mathbf{k}}{(2\pi)^3}\frac{\rho}{2} e^{i\mathbf{k}\cdot\mathbf{r}} \left[-t\hat{\Gamma}(k) + s_c(k)\sqrt{t^2\hat{\Gamma}^2(k) + 4t\hat{\Gamma}(k)}\right] \quad , \tag{5.iv:25}$$

where $s_c(k)$ is +1 when $\hat{c}(k) \geq 0$ and -1 when $\hat{c}(k) < 0$. Rearranging the integrals and making the change of variable $y = t\hat{\Gamma}$ we find

$$\begin{aligned}
\mathcal{F}_{OZ,c}[\gamma] &= \frac{1}{2}\int \frac{d\mathbf{k}}{(2\pi)^3} \int_0^{\hat{\Gamma}(k)} dy \left(-y + s_c(k)\sqrt{y^2+4y}\right) \\
&= \int \frac{d\mathbf{k}}{(2\pi)^3} \left\{ -\hat{\Gamma}^2/4 + s_c(k) \left[\left(1+\hat{\Gamma}/2\right)\sqrt{\left(1+\hat{\Gamma}/2\right)^2 - 1} \right.\right. \\
&\qquad \left.\left. - \ln\left(1 + \hat{\Gamma}/2 + \sqrt{\left(1+\hat{\Gamma}/2\right)^2 - 1}\right)\right]\right\} \quad .
\end{aligned} \tag{5.iv:26}$$

If the closure relation was

$$\rho^2 h(r) = -\Psi\{\gamma(r)\} \quad , \tag{5.iv:27}$$

we would have introduced a closure functional $\mathcal{F}_{cl}[\gamma]$ such that

$$\frac{\delta \mathcal{F}_{cl}[\gamma]}{\delta\gamma(r)} = \Psi\{\gamma(r)\} \quad , \tag{5.iv:28}$$

and an OZ functional $\mathcal{F}_{OZ,h}[\gamma]$ such that, when $h(r)$ and $\gamma(r)$ satisfy the OZ equation, we have

$$\frac{\delta \mathcal{F}_{OZ,h}[\gamma]}{\delta\gamma(r)} = \rho^2 h(r) \quad . \tag{5.iv:29}$$

To find $\mathcal{F}_{OZ,h}$ we notice that the OZ equation in k space relating $\hat{h}$ and $\hat{\gamma}$, now is

$$\rho\hat{h}^2(k) - \rho\hat{\gamma}(k)\hat{h}(k) - \hat{\gamma}(k) = 0 \quad . \tag{5.iv:30}$$

When we solve it for $\hat{h}$ we find

$$\hat{h} = \frac{\hat{\Gamma} \pm \sqrt{\hat{\Gamma}^2 + 4\hat{\Gamma}}}{2\rho} \quad . \tag{5.iv:31}$$

We now have,

$$\begin{aligned}
\mathcal{F}_{OZ,h}[\gamma] = \int \frac{d\mathbf{k}}{(2\pi)^3} \left\{ \hat{\Gamma}^2/4 + s_h(k) \left[\left(1+\hat{\Gamma}/2\right)\sqrt{\left(1+\hat{\Gamma}/2\right)^2 - 1} \right.\right. \\
\left.\left. - \ln\left(1 + \hat{\Gamma}/2 + \sqrt{\left(1+\hat{\Gamma}/2\right)^2 - 1}\right)\right]\right\} \quad ,
\end{aligned} \tag{5.iv:32}$$

where $s_h(k)$ is +1 when $\hat{h}(k) > 0$ and -1 when $\hat{h}(k) \leq 0$. Note that since $\hat{h}\hat{c} \geq 0$ (see (5.iv:23)) we must have $s_h = s_c$.

The second functional derivative of $\mathcal{F}_{OZ,h}$ is

$$\frac{\delta^2 \mathcal{F}_{OZ,h}[\gamma]}{\delta\Gamma(r)\delta\Gamma(r')} = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{r}')} \frac{\sqrt{\hat{\Gamma}^2 + 4\hat{\Gamma}} + s_h(k)(2+\hat{\Gamma})}{2\sqrt{\hat{\Gamma}^2 + 4\hat{\Gamma}}} \quad , \tag{5.iv:33}$$

which shows that due to the presence of the sign s_h the functional $\mathcal{F}_{OZ,h}$ is neither convex nor concave. Thus, any check of the convexity properties of generating functionals of the $\gamma(r)$ function should be done on the full functional.

v Conclusions

In this chapter we have analyzed the relations between generating functionals, thermodynamic consistency and uniqueness of the solution of the integral equations of liquid state theory. We think that the requirement of deriving from a free energy and the uniqueness of the solution are two important ingredients to enforce in the quest for better closures. The former requirement is of course crucial to get virial-energy consistency. But it is also important to get integral equations able to provide a closed formula for the chemical potential without additional approximations. This last issue looks highly desirable for applications of IET to the determination of phase diagrams. The latter is certainly a useful constraint from the numerical point of view but it is also a very strong condition, probably able to avoid some non physical behavior in the coexistence region, although this point would deserve further investigation. Most of the existing closures fail to satisfy the condition of uniqueness of the solution. Among them, only the Optimized Random Phase Approximation by Andersen and Chandler [71, 83] satisfies both constraints although they were not used in the original derivation of the approximation. One obvious question is whether the enforcement of these constraints automatically results in improved closures.

In this work, we have started an exploration of the capabilities of the combined requirement of consistency and uniqueness, starting with simple modifications to the HNC closure, corresponding to the addition of a square and a cubic power of $h(r)$ in the HNC functional. We found a couple of approximations (HNC/H2 and HNC/H3), which have built in the virial-free energy thermodynamic consistency and have a unique solution.

We numerically tested these closures on inverse power and the Lennard-Jones fluid. From the tests on the inverse power potential fluids one can see that the HNC/H2 approximation is comparable to HNC for the thermodynamic quantities and performs worst than RY and even HNC for structural properties. The tests on the Lennard-Jones fluid revealed as this approximation does not suffer from the presence of a termination line (present in HNC and almost all the existing closures). This allowed us to follow isotherms from the low density to the high density region and this behavior would be very useful in the study of the phase coexistence. However, the thermodynamic results show only a marginal improvement on HNC and the structure is definitely worse.

Our trials to improve HNC/H2 in the same spirit of the modified HNC approaches did not succeed. We feel that the main reason is in the difficulty of modeling the real bridge functions through a polynomial in the function $h(r)$. In this respect, approaches based on generating functionals depending on the indirect correlation function $\gamma(r)$ look more promising but we have not tried them yet.

Much better results for the structure are found with HNC/H3 as is shown in figure 5.10. However, probably for the same reasons just discussed, one has to renounce to have an approximation with a strictly convex generating functional depending on $h(r)$. The thermodynamics

reproduced by HNC/H3 is not yet satisfactory: due to the slight left shift of the main peak of the $g(r)$ the calculated pressure misses the simulation result. Nonetheless the presence of the free parameter γ in HNC/H3 leaves open the possibility of imposing the thermodynamic consistency virial-compressibility. If the value of the parameter needed to have the consistency is bigger than $-1/[3 \sup g(r)]$ then we would have an approximation which is completely thermodynamically consistent and have a unique solution. This strategy may eventually lead to discover that the price we have to pay to have a completely thermodynamically consistent approximation is the loss of strict convexity of the generating functional.

Chapter 6

Stability of the iterative solutions of integral equations as one phase freezing criterion

A recently proposed connection between the threshold for the stability of the iterative solution of integral equations for the pair correlation functions of a classical fluid and the structural instability of the corresponding real fluid is carefully analyzed. Direct calculation of the Lyapunov exponent of the standard iterative solution of HNC and PY integral equations for the 1D hard rods fluid shows the same behavior observed in 3D systems. Since no phase transition is allowed in such 1D system, our analysis shows that the proposed one phase criterion, at least in this case, fails. We argue that the observed proximity between the numerical and the structural instability in 3D originates from the enhanced structure present in the fluid but, in view of the arbitrary dependence on the iteration scheme, it seems uneasy to relate the numerical stability analysis to a robust one-phase criterion for predicting a thermodynamic phase transition.

i Introduction

When studying the structure and thermodynamics of classical fluids one is often faced with the task of solving the nonlinear integral equation which stems out of the combination of the Ornstein-Zernike equation and an approximate relation between pair potential and correlation functions (the closure) [12]. Integral equations can be generally written in the form

$$\gamma(r) = A\gamma(r) \quad , \tag{6.i:1}$$

where $\gamma(r) \in S$ may be the total correlation function $h(r)$, the direct correlation function $c(r)$, or a combination of the two, S is a set of a metric space of functions, and $A : S \to S$ is a non linear operator mapping S into itself.

Numerical analysis of integral equations suggests the use of the following combination

$$\gamma(r) = h(r) - c(r) \quad , \tag{6.i:2}$$

since γ is a much smoother function than h or c, especially in the core region.

It has been pointed out by Malescio *et. al.* [84–86] that, amongst the different numerical schemes that one may choose to solve (6.i:1), the *simple iterative scheme of Picard* plays a special

role. Picard scheme consists in generating successive approximations to the solution through the relationship

$$\gamma_{n+1} = A\gamma_n \quad , \tag{6.i:3}$$

starting from some initial value γ_0. If the sequence of successive approximations $\{\gamma_n\}$ converges toward a value $\gamma^\star$, then $\gamma^\star$ is a fixed point for the operator A, i.e. it is a solution of Eq. (6.i:1), $\gamma^\star = A\gamma^\star$. Banach' s fixed point theorem (see chapter 1 in [87] especially theorem 1.A) states that, given an operator $A : S \to S$, where S is a closed nonempty set in a complete metric space, the simple iteration (6.i:3) may converge toward the only fixed point in S (A is k contractive) or it may not converge (A is non expansive). So the simple iterative method can be used to signal a fundamental change in the properties of the underlying operator.

The operator A will in general depend on the thermodynamic state of the fluid. In order to determine the properties of the operator at a given state we can proceed as follows. First, we find the fixed point $\gamma^\star$ using a numerical scheme (more refined then Picard' s) capable of converging in the high density region. Next, we perturb the fixed point with an arbitrary initial perturbation $\delta_0(r)$ so that

$$A(\gamma^\star + \delta_0) \simeq A\gamma^\star + \left.\frac{\partial A}{\partial \gamma}\right|_{\gamma^\star} \delta_0 = \gamma^\star + M\delta_0 \quad , \tag{6.i:4}$$

where we have introduced the Floquet matrix M. Now $\delta_1 = M\delta_0$ may be considered as the new perturbation. We then generate the succession $\{\delta_n\}$ where

$$\delta_n = M\delta_{n-1} \quad . \tag{6.i:5}$$

If the succession converges to zero then the operator A is k contractive, if it diverges the operator is non expansive. Malescio *et. al.* call $\{\delta_n\}$ *fictitious dynamics* and associate to the resulting fate of the initial perturbation the nature of the *structural equilibrium* of the fluid. If the succession converges to zero they say that the fluid is *structurally stable* and *structurally unstable* otherwise. We will call ρ_{inst} the density where the transition between a structurally stable and unstable fluid occurs.

Following Malescio *et. al.* it is possible to define a *measure* for the structural stability of the system as follows. We define

$$S_i = \frac{||M\delta_i(r)||}{||\delta_i(r)||} \quad , \tag{6.i:6}$$

where $||f(r)|| = \sqrt{\sum_{i=1}^{N} f^2(r_i)}$ is the norm of a function f defined over a mesh of N points. We assume that the norm of the perturbation depends exponentially on the number of iterations

$$||\delta_n|| = ||\delta_0|| 2^{\lambda n} \quad , \tag{6.i:7}$$

where λ is the Lyapunov exponent related to the fictitious dynamics. Then one can write the average exponential stretching of initially nearby points as

$$\lambda = \lim_{n\to\infty} \frac{1}{n} \log_2 \left(\prod_{i=0}^{n-1} S_i \right) \quad . \tag{6.i:8}$$

Malescio *et. al.* have calculated the dependence of λ on the density for various simple three dimensional liquids (and various closures): hard spheres [84], Yukawa, inverse power and

Lennard-Jones potentials [85]. For all these systems they found that λ increases with the density and the density at which λ becomes positive, ρ_{inst}, falls close to the freezing density ρ_f of the fluid system. This occurrence lead them to propose this kind of analysis as a one-phase criterion to predict the freezing transition of a dense fluid and to estimate ρ_f. However, we think that there are some practical and conceptual difficulties with such one-phase criterion.

First of all, it does not depend only on the closure adopted but also on the kind of algorithm used to solve the integral equation. Indeed, different algorithms give different ρ_{inst} and Malescio *et. al.* choose to use as instability threshold for their criterion the one obtained using Picard algorithm, thus giving to it a special status. However, it is hard to understand why the particular algorithm adopted in the solution of the integral equation should be directly related to a phase boundary.

Moreover, one would expect that the estimate of ρ_{inst} would improve in connection with improved closures. This is not the case, at least in the one component hard sphere fluid.

Even a more serious doubt about the validity of the proposed criterion comes from its behavior in one dimensional systems. In this chapter we present the same Lyapunov exponent analysis on a system of hard rods in one dimension treated using either the Percus-Yevick (PY) or the hypernetted chain (HNC) approximations. What we find is that the Lyapunov exponent as a function of density has the same behavior as that for the three dimensional system (hard spheres): it becomes positive beyond a certain ρ_{inst}. Since it is known [10] that a one dimensional fluid of hard rods does not have a phase transition, our result sheds some doubts on the validity of the proposed criterion.

ii Technical details

As numerical scheme to calculate the fixed point we used Zerah' s algorithm [75] for the three dimensional systems and a modified iterative method for the hard rods in one dimension. In the modified iterative method input and output are mixed at each iteration

$$\gamma_{n+1} = A_{mix}\gamma_n = \alpha A\gamma_n + (1-\alpha)\gamma_n \quad , \tag{6.ii:1}$$

where α is a real parameter $0 < \alpha < 1$. Note that while for a non expansive operator A the Picard iterative method (6.i:3) needs not converge, one can prove convergence results on an Hilbert space for the modified iterative method with fixed α (see proposition 10.16 in [87]). In all the computations we used a uniform grid of $N = 1024$ points with a spacing $\delta r = 0.025$. Generally, we observed a marginal increase of ρ_{inst} by lowering N.

A method to find a Lyapunov exponent, equivalent but more accurate than the one of Malescio *et. al.* (6.i:8), goes through the diagonalization of the Floquet matrix. Note that in general this matrix is non symmetric, thus yielding complex eigenvalues. A Lyapunov exponent can then be defined as [88]

$$\lambda' = \log\left[\max_i\left(\sqrt{er_i^2 + ei_i^2}\right)\right] \quad , \tag{6.ii:2}$$

where er_i and ei_i are respectively the real and imaginary part of the i-th eigenvalue. In our numerical computations we always used recipe (6.ii:2) to calculate the Lyapunov exponents since it is explicitly independent from the choice of an initial perturbation.

We constructed the Floquet matrix in the following way [89]. In a Picard iteration we start from $\gamma(r)$ we calculate $c(r)$ from the closure approximation, we calculate its Fourier transform

$\tilde{c}(k)$, we calculate $\tilde{\gamma}(k)$ from the OZ equation, and finally we anti transform $\tilde{\gamma}$ to get $\gamma'(r)$. For example for a three dimensional system a PY iteration in discrete form can be written as follows

$$c_i = (1+\gamma_i)\left(e^{-\beta\phi_i}-1\right) \quad , \tag{6.ii:3}$$

$$\tilde{c}_j = \frac{4\pi\delta r}{k_j}\sum_{i=1}^{N-1} r_i \sin(k_j r_i) c_i \quad , \tag{6.ii:4}$$

$$\tilde{\gamma}_j = \rho\tilde{c}_j^2/(1-\rho\tilde{c}_j) \tag{6.ii:5}$$

$$\gamma'_i = \frac{\delta k}{2\pi^2 r_i}\sum_{j=1}^{N-1} k_j \sin(k_j r_i)\tilde{\gamma}_j \quad , \tag{6.ii:6}$$

where $r_i = i\delta r$ are the N mesh points in r space, $k_j = j\delta k$ are the N mesh points in k space, with $\delta k = \pi/(N\delta r)$, $c_i = c(r_i)$, $\gamma_i = \gamma(r_i)$, $\tilde{c}_j = \tilde{c}(k_j)$, $\tilde{\gamma}_j = \tilde{\gamma}(k_j)$, and $\phi_i = \phi(r_i)$ is the interparticle potential calculated on the grid points. The Floquet matrix will then be

$$\begin{aligned} M_{ij} &= \frac{\partial\gamma'_i}{\partial\gamma_j} = \sum_{m=1}^{N-1}\frac{\partial\gamma'_i}{\partial\tilde{\gamma}_m}\frac{\partial\tilde{\gamma}_m}{\partial\tilde{c}_m}\frac{\partial\tilde{c}_m}{\partial c_j}\frac{\partial c_j}{\partial\gamma_j} \\ &= \frac{\delta r\delta k}{\pi}\left(\frac{r_j}{r_i}\right)\left(e^{-\beta\phi_j}-1\right)(D_{i-j}-D_{i+j}) \quad , \end{aligned} \tag{6.ii:7}$$

where

$$D_l = \sum_{m=1}^{N-1}\cos(k_m r_l)\left[\frac{2\rho\tilde{c}_m}{1-\rho\tilde{c}_m}+\left(\frac{\rho\tilde{c}_m}{1-\rho\tilde{c}_m}\right)^2\right] \quad . \tag{6.ii:8}$$

The HNC case can be obtained replacing in (6.ii:7) $[\exp(-\beta\phi_j)-1]$ with $[\exp(-\beta\phi_j+\gamma_j)-1]$ and the Martynov Sarkisov (MS) [62] closure can be implemented replacing it with $[\exp(-\beta\phi_j+\sqrt{1+2\gamma_j}-1)/\sqrt{1+2\gamma_j}-1]$.

To derive the expression for the Floquet matrix valid for the one dimensional system and consistent with a trapezoidal discretization of the integrals, we need to replace (6.ii:4) and (6.ii:6) with

$$\tilde{c}_j = 2\delta r\left(\sum_{i=1}^{N-1}\cos(k_j r_i)c_i+\frac{1}{2}c_0\right) \quad , \tag{6.ii:9}$$

$$\gamma'_i = \frac{\delta k}{\pi}\left(\sum_{i=1}^{N-1}\cos(k_j r_i)\tilde{\gamma}_j+\frac{1}{2}\tilde{\gamma}_0\right) \quad . \tag{6.ii:10}$$

iii Numerical results

iii.1 Three dimensional systems

We have calculated the Lyapunov exponent (6.ii:2) as a function of the density for a three dimensional hard spheres fluid and a Lennard-Jones fluid at a reduced temperature $T^* = 2.74$, using both the PY and the HNC closures. For the hard spheres we have also used the MS closure. The results of the calculations are shown in figure 6.1 and 6.2 respectively. In good agreement with the results of Malescio *et. al.* [84, 85], we can see how the slope of the curves starts high at low densities and decreases rapidly with ρ. At high densities the Lyapunov exponent becomes

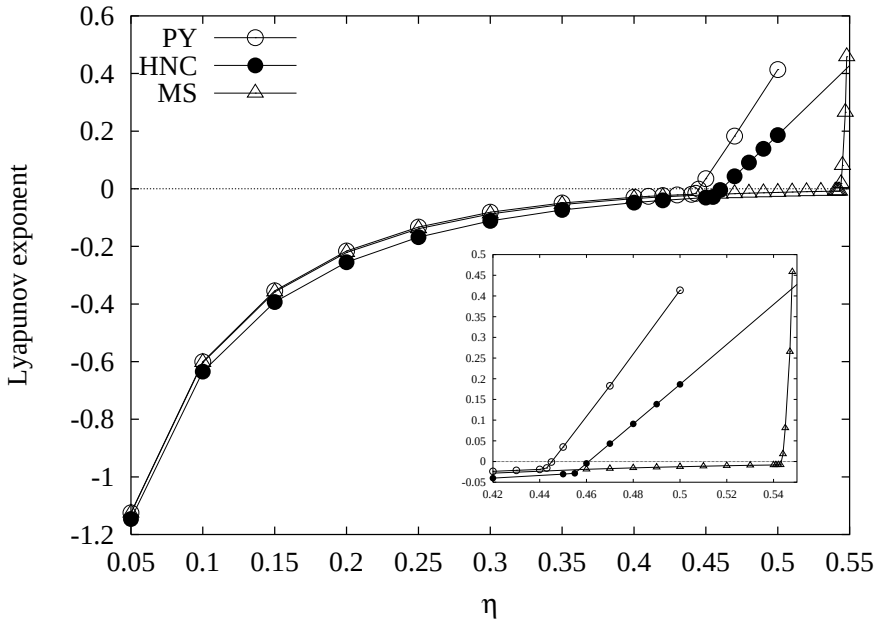

FIGURE 6.1: We show the Lyapunov exponent as a function of the packing fraction $\eta = \rho\pi d^3/6$ for a system of three dimensional hard spheres of diameter d as calculated using the PY, the HNC, and the MS closures.

zero at ρ_{inst}. Before reaching the instability threshold the curves show a rapid change in their slope at $\rho_c < \rho_{inst}$. The insets show a magnification of the region around ρ_c from which we are lead to conclude that, within the numerical accuracy of the calculations, the slope of the curves $d\lambda'/d\rho$ undergoes a jump at ρ_c.

For the hard spheres fluid we found $\eta_{inst} = \rho_{inst}\pi d^3/6$ of about 0.445 in the PY approximation, around 0.461 in the HNC approximation, and around 0.543 in the MS approximation. For the Lennard-Jones fluid our results were indistinguishable from those of Malescio *et. al.* [85]. We found a reduced instability density ρ^*_{inst} around 1.09 in the PY approximation and around 1.06 in the HNC approximation.

iii.2 The one dimensional hard spheres

We have calculated the Lyapunov exponent (6.ii:2) as a function of the density for a one dimensional hard spheres fluid using both PY and HNC closures. The results of the calculation are shown in figure 6.3. The curves show the same qualitative behavior as the ones for the three dimensional fluids.

iii.3 The Floquet matrix

In figure 6.4 we show a surface plot of the non-zero region of the Floquet matrix (6.ii:7) as calculated for the three dimensional hard spheres fluid in HNC approximation at $\eta = 0.3$. As we approach the critical density the peaks near $i = 1$ accentuate themselves. This suggests that the trace of the transition of operator A from k contractive to nonexpansive can be found in a local change of the Floquet matrix.

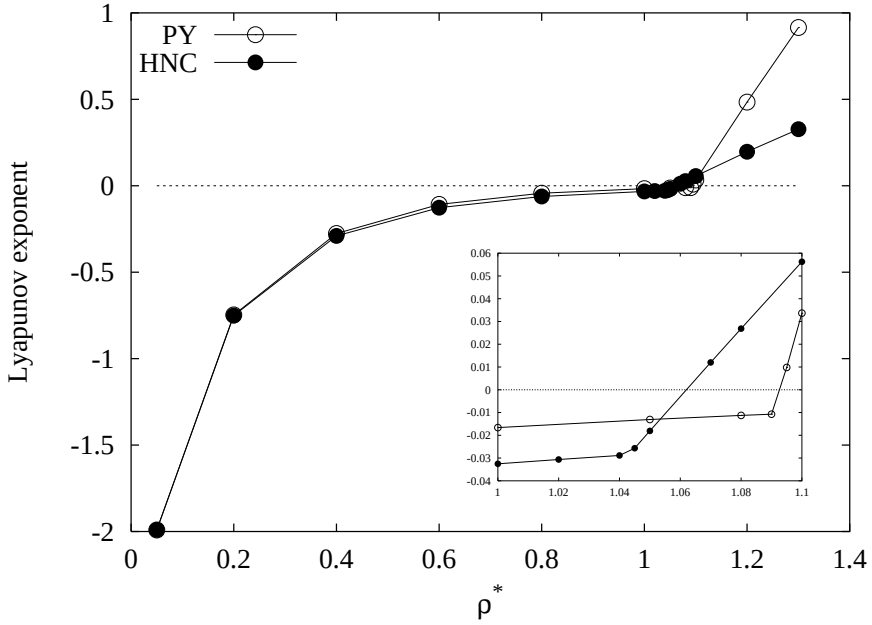

FIGURE 6.2: We show the Lyapunov exponent as a function of the reduced density for a Lennard-Jones fluid at a reduced temperature $T^* = 2.74$ as calculated using the PY and the HNC closures.

iv Conclusions

The fictitious dynamics associated to the iterative solution of an integral equation can signal the transition of the map of the integral equation from k contractive to non expansive. If the Lyapunov exponent is negative the map is k contractive, if it is positive the map is non expansive.

Since it is possible to modify in an arbitrary way the fictitious dynamics keeping the same fixed point, it is difficult to understand a deep direct connection between the stability properties of the map and a one-phase criterion for a thermodynamic transition.

Admittedly the correlations shown by Malescio et al. are striking. We calculated the Lyapunov exponent as a function of the density for various fluids (hard spheres in one and three dimensions and three dimensional Lennard-Jones fluid) both in the HNC and PY approximations. For the three dimensional fluids the instability density falls close to the freezing density ρ_f. For example, the Lennard-Jones fluid studied with HNC should undergo a freezing transition at $\rho^* \simeq 1.06$ or at $\rho^* \simeq 1.09$, if studied with PY , rather close to the freezing density $\rho_f^* \simeq 1.113$. For hard spheres ρ_{inst}^* is about 10% smaller than $\rho_f^* \sim 0.948$. The Hansen-Verlet "rule" states that a simple fluid freezes when the maximum of the structure factor is about 2.85 [9]. According to this rule the three dimensional hard spheres fluid studied with HNC should undergo a freezing transition at $\rho \simeq 1.01$ while when studied with PY the transition should be at $\rho \simeq 0.936$. The corresponding estimates obtained through ρ_{inst}^*, 0.879 (HNC) and 0.850 (PY) are poorer and, more important, are not consistent with the well known better performance of PY in the case of hard spheres.

In one dimension, a fluid of hard spheres (hard rods), cannot undergo a phase transition [10]. From Fig. 6.3 we see that the system still becomes structurally unstable. This can be explained by observing that the structural stability as defined by Malescio *et. al.* is a property of the map A and in particular of the algorithm used to get solution of the integral equation under study. As such, it is not directly related to the thermodynamic properties even at the approximate level

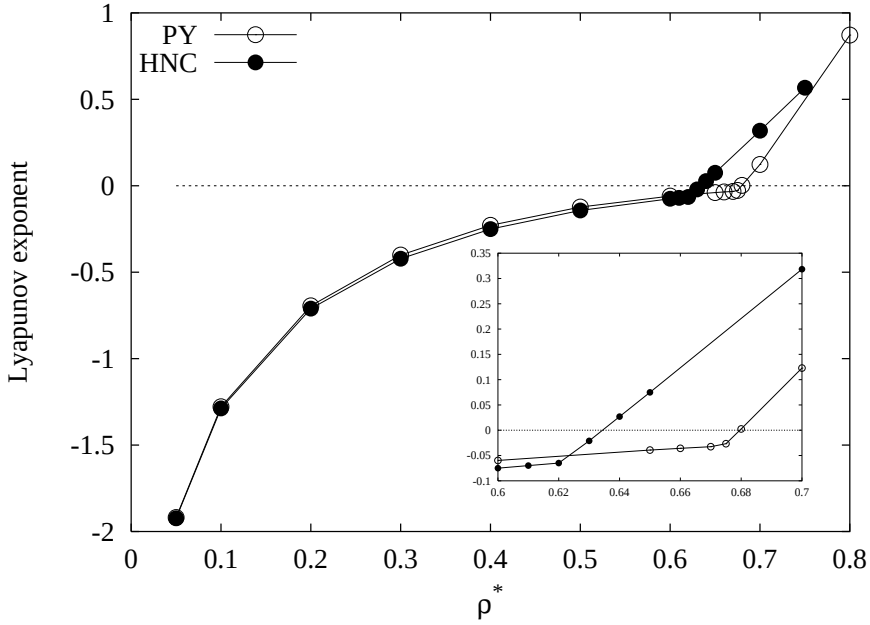

FIGURE 6.3: We show the Lyapunov exponent as a function of the reduced density for a one dimensional fluid of hard spheres as calculated using the PY and the HNC closures.

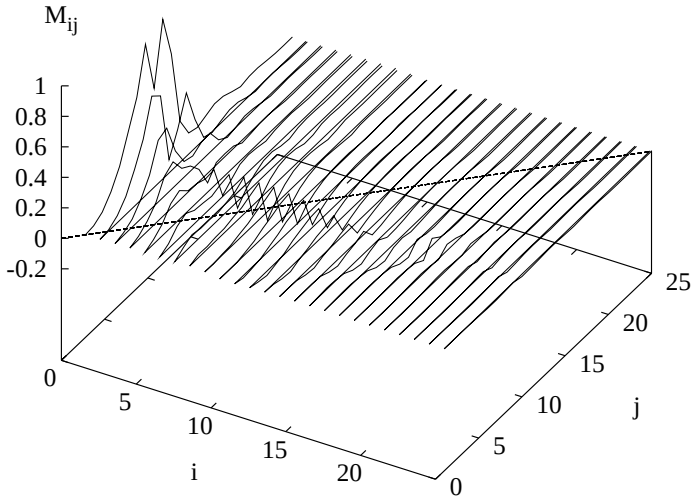

FIGURE 6.4: We show a surface plot of the Floquet matrix (6.ii:7) calculated for three dimensional hard spheres in HNC approximation at $\eta = 0.3$. The matrix was generated using $N = 256$ grid points but only the region significantly different from zero is shown.

of the theory (there is no direct relation between the contractiveness properties of A and the thermodynamics). It looks more reasonable that the increase of the correlations would be the common origin of the numerical instability of the Picard iteration and, whenever it is possible, of thermodynamic phase transitions.

Chapter 7

Direct correlation functions of the Widom-Rowlinson model

In this chapter we calculate, through Monte Carlo numerical simulations, the partial total and direct correlation functions of the three dimensional symmetric Widom-Rowlinson mixture. We find that the differences between the partial direct correlation functions from simulation and from the Percus-Yevick approximation (calculated analytically by Ahn and Lebowitz) are well fitted by Gaussians. We provide an analytical expression for the fit parameters as function of the density. We also present Monte Carlo simulation data for the direct correlation functions of a couple of non additive hard sphere systems to discuss the modification induced by finite like diameters.

i Introduction

Fluid binary mixtures may exhibit the phenomenon of phase separation. The simplest system able to undergo a demixing phase transition is the model introduced by Widom and Rowlinson some years ago [90]. Consider a binary mixture of non-additive hard spheres. This is a fluid made of hard spheres of specie 1 of diameter R_{11} and number density ρ_1 and hard spheres of specie 2 of diameter R_{22} and number density ρ_2, with a pair interaction potential between species i and j that can be written as follows

$$v_{ij}(r) = \begin{cases} \infty & r < R_{ij} \\ 0 & r > R_{ij} \end{cases} \quad , \tag{7.i:1}$$

where $R_{12} = (R_{11} + R_{22})/2 + \alpha$. The Widom-Rowlinson (WR) model is obtained choosing the diameters of the spheres equal to 0,

$$R_{11} = R_{22} = 0 \quad , \tag{7.i:2}$$

so that there is no interaction between like spheres and there is a hard core repulsion of diameter α between unlike spheres. The symmetry of the system induces the symmetry of the unlike correlations $[h_{12}(r) = h_{21}(r), \quad c_{12}(r) = c_{21}(r)]$. The WR model has been studied in the past by exact [91] and approximate [54, 92–94] methods and it has been shown that it exhibits a phase transition at high density. More recently, additional studies have appeared and theoretical predictions have been confirmed by Monte Carlo (MC) computer simulations [95–100]

In this chapter we will study the three dimensional symmetric Widom-Rowlinson mixture for which $\rho_1 = \rho_2 = \rho/2$, where ρ is the total number density of the fluid, and

$$h_{11}(r) = h_{22}(r) \ , \tag{7.i:3}$$
$$c_{11}(r) = c_{22}(r) \ . \tag{7.i:4}$$

Moreover we know from (7.i:1) that the partial pair correlation function $g_{ij} = h_{ij} + 1$ must obey

$$g_{ij}(r) = 0 \quad \text{for } r < R_{ij} \ . \tag{7.i:5}$$

Our main goal is to focus on the direct correlation functions (dcf) of the WR model as a simplified prototype of non-additive hard spheres (NAHS) systems. The reasons to focus on the dcf's is twofold: on the one hand, they are easier functions to model and fit. On the other hand, they play a central role in approximate theories like the Percus-Yevick approximation or mean spherical approximation (MSA) [12]. We hope that a better understanding of the dcf's properties in the WR model, could help in developing accurate analytical theories for the NAHS systems.

We calculate through Monte Carlo simulations the like $g_{11}^{(MC)}(r)$ and unlike $g_{12}^{(MC)}(r)$ pair distribution functions for a system large enough to allow a meaningful determination of the correspondent partial direct correlation functions $c_{11}^{(MC)}(r)$ and $c_{12}^{(MC)}(r)$, using the Ornstein-Zernike equation [12]. We compare the results for the unlike direct correlation function with the results of the Percus-Yevick (PY) analytic solution found by Ahn and Lebowitz [54, 92]. In the same spirit as the work of Grundke and Henderson for a mixture of additive hard spheres [101], we propose a fit for the functions $\Delta_{11}^c(r) = c_{11}^{(MC)}(r)$ and $\Delta_{12}^c(r) = c_{12}^{(MC)}(r) - c_{12}^{(PY)}(r)$.

At the end of the chapter we also show the results from two Monte Carlo simulations on a mixture of non-additive hard spheres with equal diameter spheres $R_{11} = R_{22} = R_{12}/2$ and on one with different diameter spheres $R_{11} = 0$ and $R_{22} = R_{12}$ to study the effect of non zero like diameters on the WR dcf's.

ii Monte Carlo simulation and PY solution

The Monte Carlo simulation was performed with a standard NVT Metropolis algorithm [14] using $N = 4000$ particles. Linked lists [14] have been used to reduce the computational cost. We generally used 5.2×10^8 Monte Carlo steps where one step corresponds to the attempt to move a single particle. The typical CPU time for each density was around 20 hours (runs at higher densities took longer than runs at smaller densities) on a Compaq AlphaServer 4100 5/533.

We run the simulation of WR model at 6 different densities $\bar{\rho} = \rho\alpha^3 = 0.28748$, 0.4, 0.45, 0.5, 0.575, and 0.65. Notice that the most recent computer simulation calculations [97, 98] give consistent estimates of the critical density around 0.75. Our data at the highest density (0.65) are consistent with a one phase system.

The Monte Carlo simulation returned the $g_{ij}(r)$ over a range not less than 9.175α for the densest system. In all the studied cases the pair distribution functions attained their asymptotic value well inside the maximum distance they were evaluated. Thus, it has been possible to obtain accurate Fourier transforms of the correlation functions $[h_{ij}(k)]$. To obtain the $c_{ij}(r)$ we used

Ornstein-Zernike equation as follows

$$c_{11}(k) = \frac{h_{11}(k)\left[1+\frac{\rho}{2}h_{11}(k)\right]-\frac{\rho}{2}h_{12}^2(k)}{\left[1+\frac{\rho}{2}h_{11}(k)\right]^2-\left[\frac{\rho}{2}h_{12}(k)\right]^2} \tag{7.ii:1}$$

$$c_{12}(k) = \frac{h_{12}(k)}{\left[1+\frac{\rho}{2}h_{11}(k)\right]^2-\left[\frac{\rho}{2}h_{12}(k)\right]^2} \tag{7.ii:2}$$

From the $h_{ij}(k)$ and $c_{ij}(k)$ we get the difference $\gamma_{ij}(k) = h_{ij}(k) - c_{ij}(k)$ which is the Fourier transform of a continuous function in real space. So it is safe to transform back in real space [to get $\gamma_{ij}(r)$]. Finally, the dcf's are obtained from the differences $h_{ij}(r) - \gamma_{ij}(r)$.

While for a system of non-additive hard sphere in three dimensions a closed form solution to the PY approximation is still lacking, Ahn and Lebowitz have found an analytic solution of this approximation for the WR model (in one and three dimensions).

The PY approximation consists of the assumption that $c_{ij}(r)$ does not extend beyond the range of the potential

$$c_{ij}(r) = 0 \quad \text{for } r > R_{ij} \quad . \tag{7.ii:3}$$

Combining this with the exact relation (7.i:5) and using the Ornstein-Zernike equation we are left with a set of equations for $c_{ij}(r)$ and $g_{ij}(r)$ which have been solved analytically by Ahn and Lebowitz.

Their solution is parameterized by a parameter z_0. They introduce the following two functions of z_0 (which can be written in terms of elliptic integrals of the first and third kind)

$$I_1 \equiv \int_{z_0}^{\infty} \frac{dz}{z\sqrt{z^3+4z/z_0-4}} \quad , \tag{7.ii:4}$$

$$I_2 \equiv \int_{z_0}^{\infty} \frac{dz}{\sqrt{z^3+4z/z_0-4}} \quad , \tag{7.ii:5}$$

and define z_0 in terms of the partial densities ρ_1 and ρ_2 as follows

$$\eta \equiv 2\pi\sqrt{\rho_1\rho_2} = \frac{(I_2/2)^3}{\cos I_1} \quad . \tag{7.ii:6}$$

They then define the following functions (note that in the last equality of equation (3.76) in [54] there is a misprint)

$$\bar{c}_{12}(k) \equiv -\frac{2}{\sqrt{\rho_1\rho_2}}\sqrt{\frac{1+Y}{z_0^3Y^3+4Y+4}} \times \sin\left[\frac{1}{2}\sqrt{z_0^3Y^3+4Y+4}\int_1^{\infty}\frac{dz}{(z+Y)\sqrt{z_0^3z^3+4z-4}}\right] \quad , \tag{7.ii:7}$$

$$\bar{h}_{12}(k) \equiv \bar{c}_{12}(k)[1-\rho_1\rho_2\bar{c}_{12}^2(k)]^{-1} \quad , \tag{7.ii:8}$$

where $Y \equiv (2k/I_2)^2$.

We also realized that some other misprint should be present in the Ahn and Lebowitz paper since we have found empirically that the PY solution (with k in units of α) should be given by

$$c_{12}(k) = \bar{c}_{12}(ks) \quad , \tag{7.ii:9}$$

where s is a scale parameter to be determined as follows

$$s = -[\bar{h}_{12}(r=0)]^{1/3} \quad . \tag{7.ii:10}$$

Notice that for the symmetric case $\rho_1 = \rho_2 = \rho/2$ and $\eta = \pi\rho = 0.90316\ldots$ we find $z_0 = 1$ and $s = 1$.

In Figs. 7.1, 7.2, and 7.3 we show three cases corresponding to the extreme and one intermediate density. In the figures, we compare the MC simulation data with the PY solution for

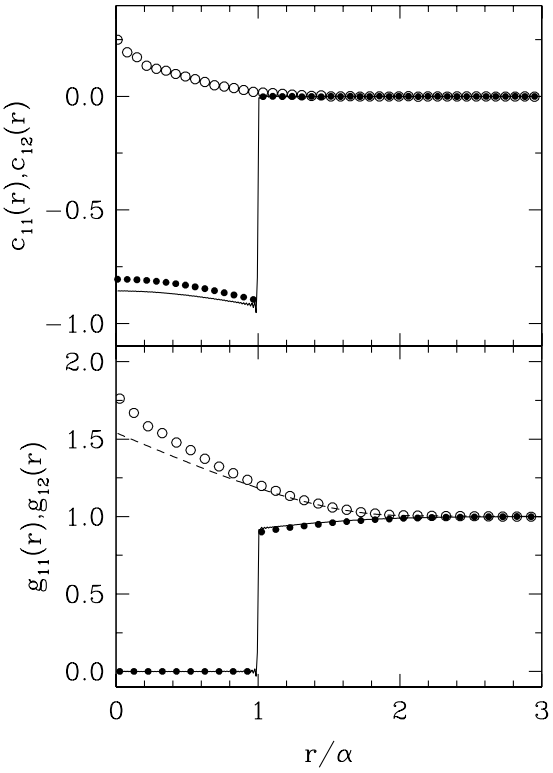

FIGURE 7.1: Top panel: partial direct correlation functions obtained from the Monte Carlo simulation (points) with the $c_{12}^{(PY)}(r)$ obtained from the PY approximation (line) at a density $\rho\alpha^3 = 0.28748$. Bottom panel: partial pair distribution functions obtained from the Monte Carlo simulation compared with the ones obtained from the PY approximation at the same density. The open circles and the dashed line: the like correlation functions. Closed circles and the continuous line: the unlike correlation functions.

the partial pair distribution functions and the partial direct correlation functions. Our results for the partial pair distribution functions at $\rho\alpha^3 = 0.65$ are in good agreement with the ones of Shew and Yethiraj [97]. The figures show how the like correlation functions obtained from the PY approximation are the ones that differ most from the MC simulation data. The difference is more marked in a neighborhood of $r = 0$ and becomes more pronounced as the density increases.

In Fig. 7.4 we also show the results for the partial direct correlation function in k space at a density $\rho\alpha^3 = 0.28748$.

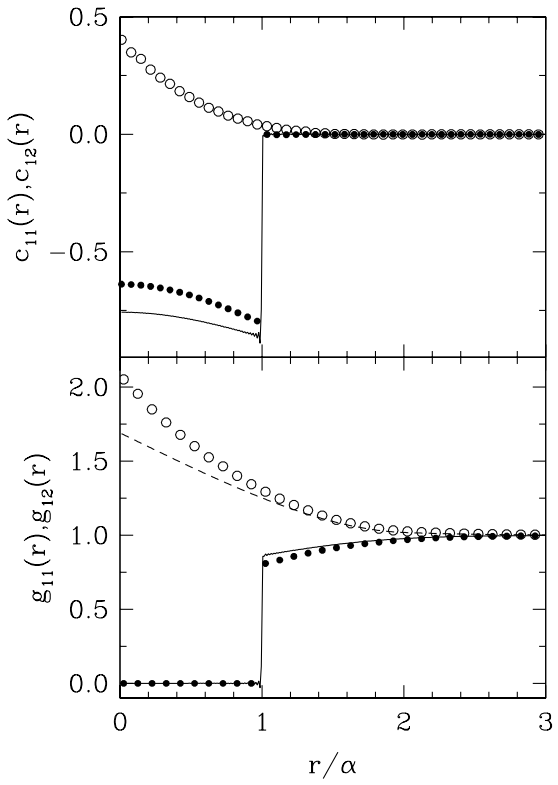

FIGURE 7.2: Same as in Fig. 7.1 at a density $\rho\alpha^3 = 0.4$.

iii Fit of the data

From the simulations we found that $c_{12}^{(MC)}(r) < 8 \times 10^{-3}$ for $r > \alpha$ at all the densities studied. This allows us to say that $\Delta_{12}^c(r) \simeq 0$ for $r > \alpha$. Moreover we found that both $\Delta_{12}^c(r)$ for $r < \alpha$, and $\Delta_{11}^c(r)$ are very well fitted by Gaussians

$$\Delta_{11}^c(r) \simeq b_{11} \exp[-a_{11}(r + d_{11})^2] \quad \text{for all } r > 0, \tag{7.iii:1}$$

$$\Delta_{12}^c(r) \simeq b_{12} \exp[-a_{12} r^2] \quad \text{for } 0 < r < \alpha, \tag{7.iii:2}$$

In Figs. 7.5 and 7.6 we show the behaviors of the parameters of the best fit (7.iii:1) and (7.iii:2), with density. In order to check the quality of the fit, we did not use the data at $\bar{\rho} = 0.45$ in the determination of the parameters. The points for a_{12} and b_{12} are well fitted by a straight line or a parabola. As shown in Fig. 7.5 the best parabolae are

$$a_{12}(\bar{\rho}) = 0.839 + 0.096\bar{\rho} - 1.287\bar{\rho}^2 \ , \tag{7.iii:3}$$

$$b_{12}(\bar{\rho}) = -0.155 + 0.759\bar{\rho} - 0.159\bar{\rho}^2 \ . \tag{7.iii:4}$$

Fig. 7.6 shows how the parameters for $\Delta_{11}^c(r)$ are much more scattered and hard to fit. The quartic polynomial going through the five points, for each coefficient, are

$$a_{11}(\bar{\rho}) = -55.25 + 504.8\bar{\rho} - 1659.\bar{\rho}^2 + 2364.\bar{\rho}^3 - 1236.\bar{\rho}^4 \ , \tag{7.iii:5}$$

$$b_{11}(\bar{\rho}) = 171.4 - 1556.\bar{\rho} + 5166.\bar{\rho}^2 - 7421.\bar{\rho}^3 + 3906.\bar{\rho}^4 \ , \tag{7.iii:6}$$

$$d_{11}(\bar{\rho}) = 128.9 - 1144.\bar{\rho} + 3747.\bar{\rho}^2 - 5328.\bar{\rho}^3 + 2782.\bar{\rho}^4 \ , \tag{7.iii:7}$$

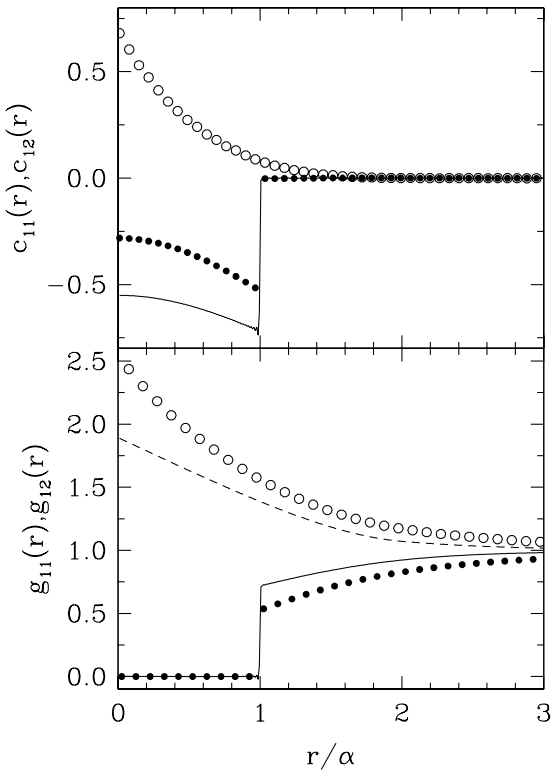

FIGURE 7.3: Same as in Fig. 7.1 at a density $\rho\alpha^3 = 0.65$.

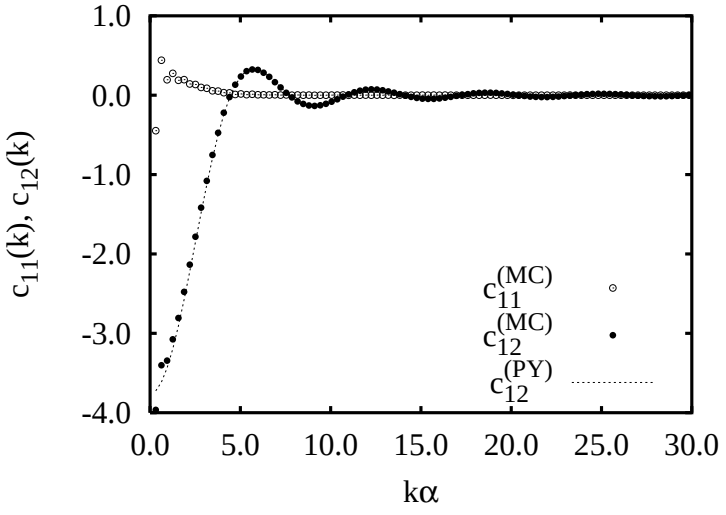

FIGURE 7.4: We compare the partial direct correlation function in k space obtained from the Monte Carlo simulation (with superscript MC) with the one obtained from the PY approximation (with superscript PY) at a density $\rho\alpha^3 = 0.28748$.

The difficulty in finding a good fit for these parameters may be twofold: first we are fitting $\Delta_{11}^{c}(r)$ with a three (instead of two) parameters curve and second the partial pair distribution

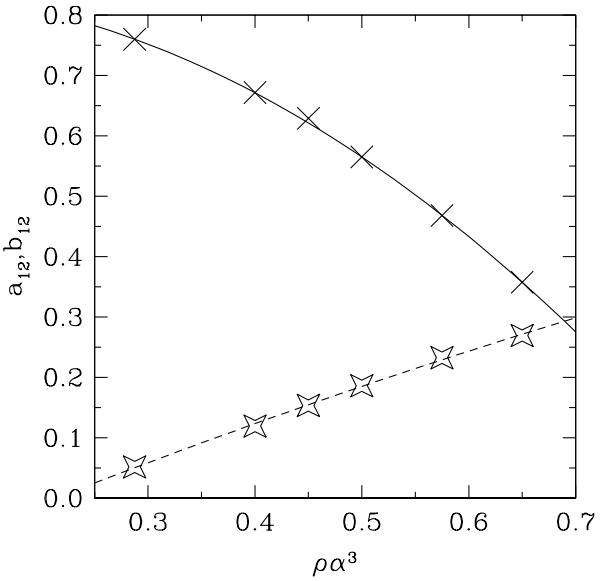

FIGURE 7.5: We plot, for five different values of the density, the parameters a_{12} (diagonal crosses) and b_{12} (starred crosses) of the best Gaussian fit (7.iii:2) to $\Delta^c_{12}(r)$ for $r < \alpha$, and fit them with parabolae (lines). The parameters at $\rho\alpha^3 = 0.45$ where not used for the parabolic fit and give an indication of the quality of the fit.

functions obtained from the Monte Carlo simulation are less accurate in a neighborhood of the origin (due to the reduced statistics there). This inaccuracy is amplified in the process of finding the partial direct correlation functions. Such inaccuracy will not affect significantly $\Delta^c_{12}(r)$ which has a derivative very close or equal to zero near the origin, but it will significantly affect $\Delta^c_{11}(r)$ which is very steep near the origin.

In order to estimate the quality of the fit we have used the simulation data at $\bar{\rho} = 0.45$. From Fig. 7.5 we can see how the parabolic fit is a very good one. In Fig. 7.6 the point at $\bar{\rho} = 0.45$ gives an indication of the accuracy of the quartic fit. We have also compared the pair distribution and direct correlation functions obtained from the fit with those from MC: both the like and unlike distribution functions are well reproduced while there is a visible discrepancy in the dcf from the origin up to $r = 0.5\alpha$. However we expect that moving on the high density or low density regions (where the quartic polynomial becomes more steep) the quality of the fit will get worst. In particular the predicted negative values for a_{11}, in those regions, are completely unphysical and the fit should not be used to extrapolate beyond the range $0.28 < \bar{\rho} < 0.65$.

iv From WR to non additive hard spheres

In order to see how the structure, and in particular the dcf's of the Widom-Rowlinson model change as one switches on the spheres diameters we have made two additional Monte Carlo simulations. In the first one we chose $\rho_1 = \rho_2 = 0.65/R^3_{12}$ and $R_{11} = R_{22} = R_{12}/2$. The resulting partial pair distribution functions and partial direct correlation functions are shown in Fig. 7.7. From a comparison with Fig. 7.3 we see how in this case the switching on of the like diameters causes both $c_{12}(r)$ for $r < R_{12}$ and $g_{12}(r)$ for $r > R_{12}$ to approach $r = R_{12}$ with a slope close to zero.

In the second simulation we chose $\rho_1 = \rho_2 = 0.65/R^3_{12}$ and $R_{11} = 0$, $R_{22} = R_{12}$. The

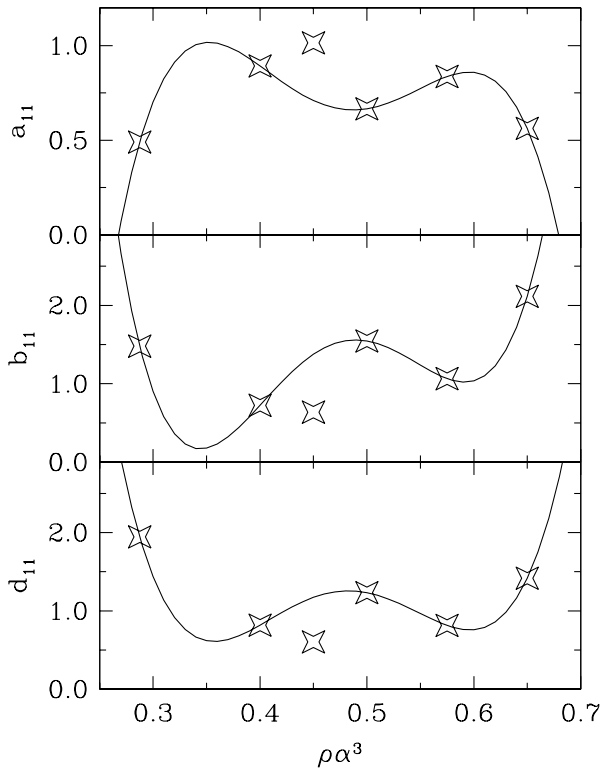

FIGURE 7.6: We plot, for five different values of the density, the parameters a_{11}, b_{11} and d_{11} (stars) of the best Gaussian fit (7.iii:1) to $\Delta^c_{11}(r)$, and draw the quartic polynomial (lines) through them. The parameters at $\rho\alpha^3 = 0.45$ where not used to determine the quartic polynomial and give an indication of the quality of the fit.

resulting partial pair distribution functions and partial direct correlation functions are shown in Fig. 7.8. From a comparison with Fig. 7.3 we see how in this case the switching on of the like diameters causes both $g_{11}(0)$ and $c_{11}(0)$ to increase, and $c_{12}(r)$ to lose the nearly zero slope at $r = 0$. As in the previous case $g_{12}(r)$ for $r > R_{12}$ approaches $r = R_{12}$ with a slope close to zero. The like 22 correlation functions for $r > R_{12}$ vary over a range comparable to the one over which vary the like 11 correlation functions of the WR model.

For both these cases there is no analytic solution of the PY approximation available and a better understanding of the behavior of the direct correlation functions may help in finding approximate expressions [53].

v Conclusions

In this chapter we have evaluated the direct correlation functions of a Widom-Rowlinson mixture at different densities through Monte Carlo simulation and we have studied the possibility of fitting the difference between MC data and the PY dcf's. We found a very good parameterization of $c_{12}(r)$ for $r < \alpha$ [see equations (7.iii:2) and (7.iii:3)-(7.iii:4)] and a poorer one for $c_{11}(r)$ [see equations (7.iii:1) and (7.iii:5)-(7.iii:7)]. The difficulty in this last case probably arises from the necessity of using three parameters [instead of just two needed for parameterizing $c_{12}(r)$], although it cannot be completely excluded some effect of the decreasing precision of the

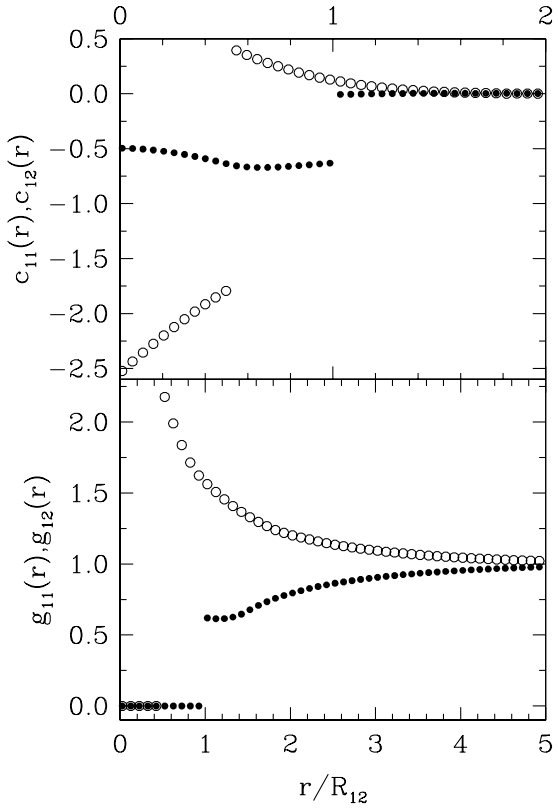

FIGURE 7.7: Monte Carlo results at a density $\rho = \rho_1 = \rho_2 = 0.65/R_{12}^3$ for the partial direct correlation function (on top) and the partial pair distribution function (below) of a mixture of non additive hard spheres with $R_{11} = R_{22} = R_{12}/2$. The open circles denote the like correlation functions. The closed circles denote the unlike correlation functions.

simulation data near the origin.

In the last part of the chapter we have illustrated with additional Monte Carlo data the changes induced in the WR dcf's by a finite size of the excluded volume of like correlations. These results are meant to provide a guide in the search of a manageable, simple analytical parameterization of the structure of mixtures of non additive hard spheres which is still not available although highly desirable.

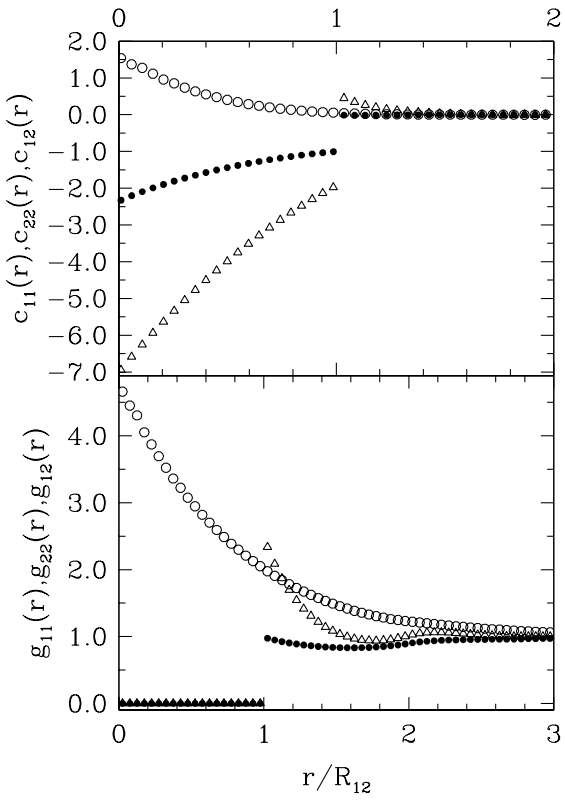

FIGURE 7.8: Monte Carlo results at a density $\rho = \rho_1 = \rho_2 = 0.65/R_{12}^3$ for the partial direct correlation function (on top) and the partial pair distribution function (below) of a mixture of non additive hard spheres with $R_{11} = 0$ and $R_{22} = R_{12}$. The open circles denote the like 11 correlation functions. The open triangles denote the like 22 correlation functions. The closed circles denote the unlike correlation functions.

Chapter 8

Pressures for a One-Component Plasma on a pseudosphere

The classical (i.e. non-quantum) equilibrium statistical mechanics of a two dimensional one component plasma (a system of charged point-particles embedded in a neutralizing background) living on a pseudosphere (an infinite surface of constant negative curvature) is considered. In the case of a flat space, it is known that, for a one-component plasma, there are several reasonable definitions of the pressure, and that some of them are not equivalent to each other. In the present chapter, this problem is revisited in the case of a pseudosphere. General relations between the different pressures are given. At one special temperature, the model is exactly solvable in the grand canonical ensemble. The grand potential and the one-body density are calculated in a disk, and the thermodynamic limit is investigated. The general relations between the different pressures are checked on the solvable model.

We study the ergodicity of a classical finite dynamical system moving in a connected and compact domain of a pseudosphere. In particular we derive a condition on its potential and kinetic energy sufficient for the system to be ergodic. We discuss the existence and uniqueness of the grand canonical Gibbs distribution as the limit distribution for the system with an infinite number of particles. We consider the special case of the one component Coulomb plasma on a pseudosphere and prove the ergodicity of the system obtained by switching off the mutual interaction amongst the particles.

We also derive an equation of state for the one component Coulomb plasma on a pseudosphere using a field theoretical argument, and argue that the same equation of state holds for the same system on a large class of Riemannian surfaces.

i Introduction

This chapter is divided into four parts: in the first part (from subsection i.1 to subsection iii.1) we study a two dimensional one component Coulomb plasma (2D OCP) as a dynamical system moving in a connected and compact domain of a pseudosphere. In the second part (from subsection iii.2 to subsection iii.6) we compare four different definitions for the pressure of this system and derive some general sum rules. In the third part (section iv) we study a swarm of free particles moving on a pseudosphere and coupled to a massive scalar field, a Yukawa field. This is a field theoretical description of a system of particles interacting through a screened Coulomb potential of the Debye-Yukawa form. When the Yukawa interaction tends to the Coulomb interaction the system reduces to a one component Coulomb plasma. In the last part (section

v) we solve exactly the 2D OCP on a finite disk of the pseudosphere, in the grand canonical ensemble, at a special temperature. The thermodynamic limit is also investigated and the sum rules among the different definitions for the pressure are checked.

Coulomb systems such as plasmas or electrolytes are made of charged particles interacting through Coulomb' s law. The simplest model of a Coulomb system is the one component plasma, also called Jellium: an assembly of identical point charges, embedded in a neutralizing uniform background of the opposite sign. Here we consider the classical (i.e. non quantum) equilibrium statistical mechanics of the one component plasma. Although many features of more realistic systems are correctly reproduced, this model has the peculiarity that there are several reasonable definitions of its pressure, and some of these definitions are not equivalent to each other [102, 103].

The two-dimensional version of the one component plasma has been much studied. Provided that the Coulomb potential due to a point-charge is defined as the solution of the Poisson equation in a two-dimensional world (i.e. is a logarithmic function $-\ln r$ of the distance r to that point-charge), the two dimensional one component plasma mimics many generic properties of the three-dimensional Coulomb systems. Of course, this toy logarithmic model does not describe real charged particles, such as electrons, confined on a surface, which nevertheless interact through the three dimensional Coulomb potential $1/r$ (with the electric field lines coming out of the surface). One motivation for studying the two dimensional one component plasma is that its equilibrium statistical mechanics is exactly solvable at one special temperature: both the thermodynamical quantities and the correlation functions are available [104].

How the properties of a system are affected by the curvature of the space in which the system lives is a question which arises in general relativity. This is an incentive for studying simple models. Thus, the problem of a two dimensional one component plasma on a pseudosphere has been considered [105].

For this two dimensional one component plasma on a pseudosphere, the problem of studying and comparing the different possible definitions of the pressure also arises. This is the subject of the present chapter.

A pseudosphere is a non compact Riemannian surface of constant negative curvature. Unlike the sphere it has an infinite area and it is not embeddable in the three dimensional Euclidean space. The property of having an infinite area makes it interesting from the point of view of Statistical Physics because one can take the thermodynamic limit on it.

Riemannian surfaces of negative curvature play a special role in the theory of dynamical systems [106]. Hadamard study of the geodesic flow of a point particle on a such surface [107] has been of great importance for the future development of ergodic theory and of modern chaos theory. In 1924 the mathematician Emil Artin [108] studied the dynamics of a free point particle of mass m on a pseudosphere closed at infinity by a reflective boundary (a billiard). Artin' s billiard belongs to the class of the so called Anosov systems. All Anosov systems are ergodic and posses the mixing property [109]. Sinai [110] translated the problem of the Boltzmann-Gibbs gas into a study of the by now famous "Sinai' s billiard", which in turn could relate to Hadamard' s model of 1898. Recently, smooth experimental versions of Sinai' s billiard have been fabricated at semiconductor interfaces as arrays of nanometer potential wells and have opened the new field of mesoscopic physics [111].

The following important theorem holds for Anosov systems [112],[113]:

Theorem i.1 *Let M be a connected, compact, orientable analytic surface which serves as the configurational manifold of a dynamical system whose Hamiltonian is $H = T + U$. Let the dynamical system be closed and its total energy be h. Consider the manifold $\mathcal{M}$ defined by*

the Maupertuis Riemannian metric $(ds)^2 = 2(h-U)T(dt)^2$ *on* M*. If the curvature of* $\mathcal{M}$ *is negative everywhere then the dynamical system is an Anosov system and in particular is ergodic on* $M_h = \{h = H\}$*.*

If the dynamical system is composed of N particles, the same conclusions hold, we need only require that the curvature be negative when we keep the coordinates of all the particles but anyone constant.

A simple example for the application of this theorem is given by the free symmetrical top. In this case the configurational manifold M is given by the Euler angles $\vec{q} = (q^\theta, q^\varphi, q^\psi) = (\theta, \varphi, \psi)$. Since the potential energy U is zero the Maupertuis Riemannian metric is $ds^2/(2h) = T\,dt^2 = g_{\mu,\nu} dq^\mu dq^\nu$ where the kinetic energy is

$$T = \frac{1}{2}\{\dot\theta^2 I_1 + \dot\varphi^2[I_3 + (I_2 - I_3)\sin^2\theta] + \dot\psi^2 I_3 + \dot\varphi\dot\psi 2I_3\cos\theta\} \quad , \tag{8.i:1}$$

with $I_1 = I_2$, and I_3 the three moments of inertia. The manifold $\mathcal{M}$ is then SO(3) with the following metric tensor

$$\begin{cases} g_{\theta\theta} = \frac{1}{2} I_1 \quad , \\ g_{\varphi\varphi} = \frac{1}{2}[I_3 + (I_2 - I_3)\sin^2\theta] \quad , \\ g_{\psi\psi} = \frac{1}{2} I_3 \quad , \\ g_{\varphi\psi} = \frac{1}{2} I_3 \cos\theta \quad . \end{cases}$$

If we calculate the scalar curvature of $\mathcal{M}$, this is what we find

$$R = \frac{1}{I_1}\left[4 - \frac{I_3}{I_2}\right] \quad . \tag{8.i:2}$$

We conclude that when $I_3 > 4I_2$ the system is ergodic. This is also shown at the end of section 37 of [114] where it is said that "...the top does not at any time return exactly at its original position".

The chapter has the following structure. In subsection i.1 we give a brief description of the pseudosphere. In subsection i.2 we introduce the one component Coulomb plasma as a dynamical system confined in a connected and compact domain of the pseudosphere.

We discuss the ergodicity of the system in section ii: we calculate the curvature of $\mathcal{M}$ for a general dynamical system with potential energy U. Requiring the curvature to be negative we find a disequality containing T and partial derivatives of U whose fulfillment we are able to prove for the one component Coulomb plasma with the Coulomb interaction amongst the particles switched off. In subsection ii.3 we discuss the thermodynamic limit from the point of view of ergodic theory.

In section iii we compare four different definitions of pressure for the one component plasma on the pseudosphere. In subsection iii.1 we use the virial theorem to derive an expression for the *virial pressure* of the finite or infinite one component plasma in terms of the one and two particle correlation functions. It is known that, due to the presence of an inert background without kinetic energy, the *thermal pressure* of a flat one component plasma is negative for particular values of the temperature [115, 116] (this pathology occurs also in three dimensions). A pressure that is always positive is the *kinetic pressure* which is defined [102, 103] as one would define the pressure in the kinetic theory of gases. In subsection iii.2 we show the equivalence between the virial pressure and the kinetic pressure for the one component plasma on the pseudosphere. In subsection iii.3 we derive a relationship between the thermal pressure and the kinetic pressure in the thermodynamic limit (although for usual fluids the thermal pressure

and the kinetic pressure are equivalent, in the presence of a background they are different). In subsection iii.4 we extend a "contact theorem" proved by Totsuji [117] for the flat one component plasma, to the plasma on the pseudosphere. In subsection iii.5 we treat the non neutral one component plasma on the pseudosphere: we review the previous definitions of pressure, define the *mechanical pressure* [102], and determine the relationship between the mechanical pressure and the kinetic pressure in the thermodynamic limit. In subsection iii.6 we derive expressions of the thermal and mechanical pressures appropriate for the grand canonical ensemble. These will be used in the last section.

On a pseudosphere since the area of a large domain is of the same order as the area of the neighborhood of the boundary, all the above definitions of pressure depend on the boundary conditions. In section iv we show that a bulk pressure independent of the boundary conditions can be defined from the Maxwell stress tensor [118, 119] at some point well inside the fluid. We derive an equation of state for this *Maxwell tensor pressure* and show that it holds for the one component plasma on a large class of Riemannian surfaces including the plane, the sphere, and the pseudosphere.

In the last section v, we illustrate the general properties of the one component plasma on the pseudosphere at the special value of the Coulombic coupling constant at which all properties can be explicitly and exactly calculated. The grand potential and the one particle density are calculated in a disk, and the thermodynamic limit is investigated. The general relations between the different pressures are checked on the solvable model.

i.1 The pseudosphere

There are at least three commonly known sets of coordinates to describe a pseudosphere $\mathcal{S}$.

The one which render explicit the "similarity" with the sphere is $\vec{q} = (q^1, q^2) = (q^\tau, q^\varphi) = (\tau, \varphi)$ with $\tau \in [0, \infty[$ and $\varphi \in [0, 2\pi)$ the metric being,

$$ds^2 = g_{\mu\nu}\, dq^\mu dq^\nu = a^2(d\tau^2 + \sinh^2\tau\, d\varphi^2) \quad . \tag{8.i:3}$$

Another set of coordinates often used is (r, φ) with $r = \tanh(\tau/2)$. They are the polar coordinates of the unitary disk,

$$\mathcal{D} = \{\omega \in \mathbb{C} \mid |\omega| < 1\} \quad . \tag{8.i:4}$$

The metric in terms of this new coordinates is,

$$ds^2 = 4a^2 \frac{dr^2 + r^2 d\varphi^2}{(1 - r^2)^2} \quad . \tag{8.i:5}$$

The unitary disk with such a metric is called the *Poincaré disk* [1] .

A third set of coordinates used is (x, y) obtained from (r, φ) through the Cayley transformation,

$$z \equiv x + iy = \frac{\omega + i}{1 + i\omega} \quad . \tag{8.i:6}$$

which establishes a bijective transformation between the unitary disk and the complex half plane,

$$\mathcal{H} = \{z = x + iy \mid x \in \mathbb{R}, y > 0\} \quad . \tag{8.i:7}$$

[1] Notice that in this chapter, instead of working with a dimensionless r, we preferred to work with $r = 2a\tanh(\tau/2)$, so that at small r, the geodesic distance (8.i:9) of a point (r, φ) from the origin would simply have r as its leading term.

The center of the unitary disk corresponds to the point $z_o = i$, "the center of the plane". The metric becomes,

$$ds^2 = a^2 \frac{dx^2 + dy^2}{y^2} \quad . \tag{8.i:8}$$

The complex half plane with such a metric is called the *hyperbolic plane*, and the metric the *Poincaré' s metric*.

Cayley transformation is a particular Möbius transformation. Poincaré metric is invariant under Möbius transformations. And any transformation that preserves Poincaré metric is a Möbius transformation.

The geodesic distance d_{01} between any two points $q_0 = (\tau_0, \varphi_0)$ and $q_1 = (\tau_1, \varphi_1)$ on $\mathcal{S}$ is given by,

$$\cosh(d_{01}/a) = \cosh\tau_1 \cosh\tau_0 - \sinh\tau_1 \sinh\tau_0 \cos(\varphi_1 - \varphi_0) \quad . \tag{8.i:9}$$

Given the set of points Ω_d at a geodesic distance from the origin less or equal to d,

$$\Omega_d = \{(\tau, \varphi) \mid \tau a \leq d, \varphi \in [0, 2\pi)\} \quad , \tag{8.i:10}$$

that we shall call a disk of radius d, we can determine its circumference,

$$\begin{aligned} \mathcal{C} &= \mathcal{L}(\partial\Omega_d) = a \int_{\tau = d/a} \sqrt{\dot\tau^2 + \sinh^2\tau\, \dot\varphi^2}\, dt \\ &= 2\pi\, a\, \sinh\left(\frac{d}{a}\right) \underset{d \to \infty}{\sim} \pi\, a\, e^{d/a} \quad , \end{aligned} \tag{8.i:11}$$

and its area,

$$\begin{aligned} \mathcal{A} &= \mathcal{V}(\Omega_d) = \int_0^{2\pi} d\varphi \int_0^{d/a} d\tau\, a^2 \sinh\tau \\ &= 4\pi\, a^2\, \sinh^2\left(\frac{d}{2a}\right) \underset{d \to \infty}{\sim} \pi\, a^2\, e^{d/a} \quad . \end{aligned} \tag{8.i:12}$$

The Laplace-Beltrami operator on $\mathcal{S}$ is,

$$\begin{aligned} \Delta &= \frac{1}{\sqrt{g}} \frac{\partial}{\partial q^\mu} \left(\sqrt{g}\, g^{\mu\nu} \frac{\partial}{\partial q^\nu} \right) \\ &= \frac{1}{a^2} \left(\frac{1}{\sinh\tau} \frac{\partial}{\partial\tau} \sinh\tau \frac{\partial}{\partial\tau} + \frac{1}{\sinh^2\tau} \frac{\partial^2}{\partial\varphi^2} \right) \quad , \end{aligned} \tag{8.i:13}$$

where g is the determinant of the metric tensor $g = det||g_{\mu\nu}||$.

The curvature is expressed in terms of the Riemannian tensor which for a surface has $2^2(2^2 - 1)/12 = 1$ independent components. For a pseudosphere if we choose the coordinates (τ, φ), the metric tensor is,

$$||g_{\mu\nu}|| = \begin{pmatrix} a^2 & 0 \\ 0 & a^2 \sinh^2\tau \end{pmatrix} \quad . \tag{8.i:14}$$

The characteristic component of the Riemann tensor is,

$$R^\tau{}_{\varphi\tau\varphi} = -\sinh^2\tau \quad . \tag{8.i:15}$$

The Gaussian curvature is given by

$$R^{\tau\varphi}{}_{\tau\varphi} = g^{\varphi\varphi} R^{\tau}{}_{\varphi\tau\varphi} = -\frac{1}{a^2} \quad . \tag{8.i:16}$$

Contraction gives the components of the Ricci tensor,

$$R^{\tau}{}_{\tau} = R^{\varphi}{}_{\varphi} = -\frac{1}{a^2} \quad , \qquad R^{\tau}{}_{\varphi} = 0 \quad , \tag{8.i:17}$$

and further contraction gives the scalar curvature,

$$R = -\frac{2}{a^2} \quad . \tag{8.i:18}$$

i.2 The one component Coulomb plasma

The one component Coulomb plasma is an ensemble of N identical pointwise particles of mass m and charge q, constrained to move in a connected and compact domain $\Omega \subset \mathcal{S}$ by an infinite potential barrier on the boundary of the domain $\partial\Omega$. The total charge of the system is neutralized by a background surface charge distribution uniformly smeared on Ω with density $\rho_b = -nq$ (ρ_b is 0 outside of Ω), where $n = N/\mathcal{V}(\Omega)$ is the particle number density.

The pair Coulomb potential between two unit charges a geodesic distance d apart, satisfies Poisson equation on $\mathcal{S}$,

$$\Delta v(d) = -2\pi\delta^{(2)}(d) \quad , \tag{8.i:19}$$

where $\delta^{(2)}(d_{01}) = \delta(\vec{q}_0 - \vec{q}_1)/\sqrt{g}$ is the Dirac delta function on the curved manifold. Poisson equation admits a solution vanishing at infinity,

$$v(d_{ij}) = -\ln\left[\tanh\left(\frac{d_{ij}}{2a}\right)\right] \quad . \tag{8.i:20}$$

The electrostatic potential of the background $w(\vec{q})$ satisfies,

$$\Delta w(\vec{q}) = -2\pi\rho_b \quad . \tag{8.i:21}$$

If we choose $\Omega = \Omega_{a\tau_0}$, the electrostatic potential of the background inside Ω can be chosen to be just a function of τ (see appendix J),

$$w(\tau) = 2\pi a^2 qn \left\{\ln\left[\frac{1-\tanh^2(\tau_0/2)}{1-\tanh^2(\tau/2)}\right] + \sinh^2(\tau_0/2)\ln[\tanh^2(\tau_0/2)]\right\} \quad . \tag{8.i:22}$$

The self energy of the background is (see equation (J.:9)),

$$v_0 = -\frac{1}{2}(2\pi a^2 qn)^2\{1 - \cosh\tau_0 + 4\,\ln[\cosh(\tau_0/2)] + 2\sinh^4(\tau_0/2)\ln[\tanh^2(\tau_0/2)]\} \quad . \tag{8.i:23}$$

The total potential energy of the system is then,

$$U = v_0 + v_{pb} + v_{pp} \quad , \tag{8.i:24}$$

where v_{pp} is the potential energy due to the interactions amongst the particles,

$$v_{pp} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} q^2 \, v(d_{ij}) \quad , \tag{8.i:25}$$

and v_{pb} is the potential energy due to the interaction between the particles and the background,

$$v_{pb} = \sum_{i=1}^{N} q \, w(\tau_i) \quad . \tag{8.i:26}$$

This expression can be rewritten as follows,

$$v_{pb} = v_1 + \bar{v}_{pb} \quad , \tag{8.i:27}$$

where,

$$v_1 = N \, 2\pi a^2 \, q^2 n \, \{\ln[1 - \tanh^2(\tau_0/2)] + \sinh^2(\tau_0/2) \ln[\tanh^2(\tau_0/2)]\} \quad , \tag{8.i:28}$$

is a constant and,

$$\bar{v}_{pb} = \sum_{i=1}^{N} q \bar{w}(\tau_i) \quad , \tag{8.i:29}$$

with,

$$\bar{w}(\tau) = -2\pi a^2 \, qn \, \ln[1 - \tanh^2(\tau/2)] \geq 0 \quad \forall \ \ \tau \tag{8.i:30}$$

Since the interaction between the particles is repulsive we conclude that, up to an additive constant $(v_0 + v_1)$, the potential U is a positive function of the coordinates of the particles.

ii Ergodicity

Consider a closed one component Coulomb plasma of N charges and total energy h, confined in the domain $\Omega_{a\tau_0} \subset \mathcal{S}$. Let the coordinates of particle i be $\vec{q}_i = {q_{(i)}}^{\alpha} \vec{e}_\alpha = ({q_{(i)}}^1, {q_{(i)}}^2) \in \Omega_{a\tau_0}$, where $\vec{e}_\alpha = \partial/\partial q^\alpha$ $(\alpha = 1, 2)$ is a coordinate basis for $\mathcal{S}$. The trajectory of the dynamical system,

$$\mathcal{T}_{t_0} = \{q^N(t) \equiv (\vec{q}_1, \ldots, \vec{q}_N) \mid t \in [0, t_0]\} \quad , \tag{8.ii:1}$$

is a geodesic on the $2N$ dimensional manifold $\mathcal{M}$ defined by the metric,

$$\mathcal{G}_{\alpha\beta} = (h - U) g_{\mu\nu}(\vec{q}_i) \otimes \cdots \otimes g_{\mu\nu}(\vec{q}_N) \quad , \tag{8.ii:2}$$

on $\mathcal{S}^N$. Since $\bar{v}_{pb}$ and v_{pp} are positive on $\Omega_{a\tau_0}$ we have,

$$\mathcal{G}_{\alpha\beta} < \mathcal{G}'_{\alpha\beta} = (h - v_0 - v_1) g_{\mu\nu}(\vec{q}_i) \otimes \cdots \otimes g_{\mu\nu}(\vec{q}_N) \quad , \tag{8.ii:3}$$

where $\mathcal{G}'$ has a negative curvature along the coordinates of any given particle. In the next subsection we will calculate the curvature of $\mathcal{G}$ along the coordinates of one particle. According to the theorem stated in the introduction we will require the curvature to be negative everywhere

on $\mathcal{S}^N$. This will determine a condition on the kinetic and potential energy of the system, sufficient for its ergodicity to hold on M_h.

Let $\tilde{p}_i = p_{(i)_\alpha}\tilde{\omega}^\alpha$ be the momentum of charge i, where $\tilde{\omega}^\alpha = \tilde{d}q^\alpha$ are the 1-forms of the dual coordinate basis, and define $p^N(t) \equiv (\tilde{p}_1, \ldots, \tilde{p}_N)$. The ergodicity of the system tells us that given any dynamical quantity $A(q^N, p^N)$, its time average,

$$\langle A\rangle_t = \lim_{T\to\infty}\frac{1}{T}\int_0^T A(q^N,p^N)\,dt \quad , \tag{8.ii:4}$$

coincides with its microcanonical phase space average,

$$\langle A\rangle_h = \frac{\int_{M_{ps}} A(q^N,p^N)\,\delta(h-H)\,d^{4N}\mu_{ps}}{\int_{M_{ps}}\delta(h-H)\,d^{4N}\mu_{ps}} \quad , \tag{8.ii:5}$$

where the phase space of the system is,

$$\begin{aligned} M_{ps} = \{(q^N,p^N) \quad | \quad & \vec{q}_i \in \mathcal{S} \quad i=1,\ldots,N; \\ & p_{(i)_\alpha} \in [-\infty,\infty] \quad i=1,\ldots,N, \alpha = 1,2\} \quad , \end{aligned} \tag{8.ii:6}$$

the phase space measure is,

$$d^{4N}\mu_{ps} = \prod_{\alpha=1}^{2} dq_{(1)}{}^\alpha \cdots dq_{(N)}{}^\alpha dp_{(1)_\alpha}\cdots dp_{(N)_\alpha} \quad , \tag{8.ii:7}$$

and δ is the Dirac delta function.

ii.1 Calculation of the curvature of $\mathcal{M}$

We calculate the curvature of $\mathcal{M}$ along particle 1 using Cartan structure equations. Let $T = h - U(\tau,\varphi)$ be the kinetic energy of the N particle system of total energy h, as a function of the coordinates of particle 1 (all the other particles having fixed coordinates). We choose an orthonormal basis,

$$\begin{cases} \tilde{\omega}^{\hat{\tau}} = a\sqrt{T}\tilde{d}\tau \\ \tilde{\omega}^{\hat{\varphi}} = a\,\sinh(\tau)\sqrt{T}\tilde{d}\varphi \end{cases} \tag{8.ii:8}$$

By Cartan second theorem we know that the connection 1-form satisfies $\tilde{\omega}_{\hat{\alpha}\hat{\beta}} + \tilde{\omega}_{\hat{\beta}\hat{\alpha}} = 0$. Then we must have,

$$\begin{cases} \tilde{\omega}^{\hat{\tau}}{}_{\hat{\tau}} = \tilde{\omega}^{\hat{\varphi}}{}_{\hat{\varphi}} = 0 \\ \tilde{\omega}^{\hat{\tau}}{}_{\hat{\varphi}} = -\tilde{\omega}_{\hat{\varphi}}{}^{\hat{\tau}} = -\tilde{\omega}^{\hat{\varphi}}{}_{\hat{\tau}} \end{cases} \tag{8.ii:9}$$

We use Cartan first theorem to calculate $\tilde{\omega}^{\hat{\tau}}{}_{\hat{\varphi}}$,

$$\begin{aligned} \tilde{d}\tilde{\omega}^{\hat{\tau}} &= -\tilde{\omega}^{\hat{\tau}}{}_{\hat{\varphi}} \wedge \tilde{\omega}^{\hat{\varphi}} \\ &= \tilde{d}(a\sqrt{T}\tilde{d}\tau) \\ &= a\,T^{\frac{1}{2}}{}_{,\varphi}\,\tilde{d}\varphi\wedge\tilde{d}\tau = 0 \quad , \end{aligned} \tag{8.ii:10}$$

where in the last equality we used the fact that the pair interaction is a function of $\varphi_i - \varphi_j$ and that the interaction with the background is a function of τ only (being the system confined in a

domain which is symmetric under translations of φ). We must then conclude that $\tilde{\omega}^{\hat{\tau}}{}_{\hat{\varphi}}$ is either zero or proportional to $\tilde{\omega}^{\hat{\varphi}}$. We proceed then calculating,

$$\begin{aligned} \tilde{d}\tilde{\omega}^{\hat{\varphi}} &= -\tilde{\omega}^{\hat{\varphi}}{}_{\hat{\tau}} \wedge \tilde{\omega}^{\hat{\tau}} \\ &= \tilde{d}(a\,\sinh(\tau)\sqrt{T}\tilde{d}\varphi) \\ &= a(\sinh(\tau)T^{\frac{1}{2}})_{,\tau}\,\tilde{d}\tau \wedge \tilde{d}\varphi \quad , \end{aligned} \tag{8.ii:11}$$

which tells us that indeed,

$$\tilde{\omega}^{\hat{\varphi}}{}_{\hat{\tau}} = \frac{(\sinh(\tau)T^{\frac{1}{2}})_{,\tau}}{a\,\sinh(\tau)T}\tilde{\omega}^{\hat{\varphi}} \quad . \tag{8.ii:12}$$

Next we calculate the characteristic component of the curvature 2-form $\mathcal{R}^{\hat{\alpha}}{}_{\hat{\beta}} = \tilde{d}\tilde{\omega}^{\hat{\alpha}}{}_{\hat{\beta}} + \tilde{\omega}^{\hat{\alpha}}{}_{\hat{\gamma}} \wedge \tilde{\omega}^{\hat{\gamma}}{}_{\hat{\beta}}$,

$$\begin{aligned} \mathcal{R}^{\hat{\tau}}{}_{\hat{\varphi}} &= \tilde{d}\tilde{\omega}^{\hat{\tau}}{}_{\hat{\varphi}} \\ &= \tilde{d}[-(\sinh(\tau)T^{\frac{1}{2}})_{,\tau}T^{-\frac{1}{2}}\tilde{d}\varphi] \\ &= -\frac{[(\sinh(\tau)T^{\frac{1}{2}})_{,\tau}T^{-\frac{1}{2}}]_{,\tau}}{a^2\,\sinh(\tau)T}\tilde{\omega}^{\hat{\tau}} \wedge \tilde{\omega}^{\hat{\varphi}} \quad . \end{aligned} \tag{8.ii:13}$$

and use Cartan third theorem to read off the characteristic component of the Riemann tensor,

$$R^{\hat{\tau}}{}_{\hat{\varphi}\hat{\tau}\hat{\varphi}} = -\frac{[(\sinh(\tau)T^{\frac{1}{2}})_{,\tau}T^{-\frac{1}{2}}]_{,\tau}}{a^2\,\sinh(\tau)T} \quad . \tag{8.ii:14}$$

We find then for the scalar curvature,

$$\begin{aligned} R = R^{\hat{\alpha}\hat{\beta}}{}_{\hat{\alpha}\hat{\beta}} &= 2R^{\hat{\tau}\hat{\varphi}}{}_{\hat{\tau}\hat{\varphi}} \\ &= -\frac{2}{a^2}\left\{\frac{[(\sinh(\tau)\,T^{\frac{1}{2}})_{,\tau}T^{-\frac{1}{2}}]_{,\tau}}{\sinh(\tau)\,T}\right\} \quad , \end{aligned} \tag{8.ii:15}$$

which can be rewritten in terms of the Laplacian as follows,

$$R = -\frac{2}{a^2T}\left\{1 + \frac{1}{2T}\left[-a^2\Delta U + \frac{U_{,\varphi\varphi}}{\sinh^2\tau} - \frac{(U_{,\tau})^2}{T}\right]\right\} \quad . \tag{8.ii:16}$$

For finite values of h, the condition for R to be negative on all the accessible region of $\mathcal{S}^N$ is then,

$$2\pi a^2\,q^2 n - \frac{U_{,\varphi\varphi}}{\sinh^2\tau} + \frac{(U_{,\tau})^2}{T} < 2T \quad . \tag{8.ii:17}$$

ii.2 Ergodicity of the semi-ideal Coulomb plasma

Consider a one component Coulomb plasma where we switch off the mutual interactions between the particles, leaving unchanged the interaction between the particles and the neutralizing background ($U = v_0 + v_{pb}$). We will call it the "semi-ideal" system. Define,

$$\Omega(h, \tau_0) = \{q^N | \vec{q}_i \in \Omega_{a\tau_0} \;\; \forall i, h - U(q^N) \geq 0\} \quad , \tag{8.ii:18}$$

and call $\bar{h} = h - v_0 - v_1$ and

$$\begin{aligned} f(N) &= -N\ln[1-\tanh^2(\tau_0/2)] = N\ln[1+\sinh^2(\tau_0/2)] \\ &= N\ln\left(1+\frac{N}{4\pi a^2 n}\right) \quad . \end{aligned} \tag{8.ii:19}$$

We will have ($\alpha = 2\pi a^2 n q^2$)

$$r = \inf_{q^N\in\Omega(h,\tau_0)} 2T^2 = \begin{cases} 2[\bar{h}-\alpha f(N)]^2 & \bar{h} > \alpha f(N) \\ 0 & \bar{h} \le \alpha f(N) \end{cases} \quad , \tag{8.ii:20}$$

Notice that for large N, at constant n, we have

$$-v_0/\alpha = \frac{\alpha}{q^2}\left[-2\frac{N}{4\pi a^2 n} + \ln\left(1+\frac{N}{4\pi a^2 n}\right) + \frac{1}{2}\right] + O(1/N) \quad , \tag{8.ii:21}$$

$$-v_1/\alpha = f(N) + N - \frac{\alpha}{q^2} + O(1/N) \quad . \tag{8.ii:22}$$

Using the extensive property of the energy we may assume that $h = Nh_0$, where h_0 is the total energy per particle. Then for large N we will have

$$\bar{h} = Nh_0 + \alpha f(N) + \left(\frac{\alpha}{q}\right)^2\left[\ln\left(1+\frac{N}{4\pi a^2 n}\right) - \frac{1}{2}\right] + O(1/N) > \alpha f(N) \quad , \tag{8.ii:23}$$

if $h_0 \ge 0$.

On the other hand for $\bar{h} > \alpha f(N)$ we have

$$\begin{aligned} l &= \sup_{q^N\in\Omega(h,\tau_0)} [\alpha T + (U_{,\tau})^2] \le \sup_{q^N\in\Omega(h,\tau_0)} [\alpha T] + \sup_{q^N\in\Omega(h,\tau_0)} [(U_{,\tau})^2] \\ &= l_+ = \alpha\bar{h} + \alpha^2\tanh^2(\tau_0/2) \quad , \end{aligned} \tag{8.ii:24}$$

Condition (8.ii:17) is always satisfied if $l < r$. Then the semi-ideal system is ergodic if,

$$\bar{h} > \bar{h}_+ = \alpha f(N) + \frac{\alpha}{4}\left[1+\sqrt{1+8f(N)+8\tanh^2(\tau_0/2)}\right] \quad , \tag{8.ii:25}$$

where $\bar{h}_+$ is the largest root of the equation $l_+ = r$. Recalling that $\tanh^2(\tau_0/2) \to 1$ at lare N, one can verify that, given equation (8.ii:23), equation (8.ii:25) must be satisfied at large N if $h_0 > 0$.

We conclude that the semi ideal system is certainly ergodic if the total enery is extensive and the total energy per particle is positive.

ii.3 The thermodynamic limit

From the point of view of ergodic theory, given the microcanonical phase space probability distribution for the N particle dynamical system,

$$P_N(q^N, p^N) = \frac{\delta(h_N - H_N)}{\int_{M_{ps}} \delta(h_N - H_N)\, d^{4N}\mu_{ps}} \quad , \tag{8.ii:26}$$

it is natural to assume the existence of an asymptotic probability distribution $P(\gamma)$ with $\gamma = (N, q^N, p^N)$ as the number of particles tends to infinity [120]. One usually has,

$$P_N \xrightarrow[\substack{N\to\infty \\ n = \frac{N}{\mathcal{V}(\Omega)} \text{ constant}}]{} P \quad , \tag{8.ii:27}$$

where in the limit process one has to take into account the extensive property of h_N. This freedom in taking the limit translate itself in the existence of an whole family of limit distribution $\{P_\beta\}$ parameterized by the temperature $1/\beta$ of the infinite system.

By the theorem of equivalence of ensembles [121] we know that P_β indeed exists and is the grand-canonical Gibbs distribution, which is well defined for the one component Coulomb plasma [105]. The uniqueness of the limit distribution is discussed in [122].

Given the existence and uniqueness of the limit distribution one can reach the averages of the infinite system using the following procedure,

$$\langle A\rangle_\Omega = \int_{M_\Omega} A\,P\,d\gamma \underset{\Omega\to\mathcal{S}}{\longrightarrow} \langle A\rangle = \int_{M_\mathcal{S}} A\,P\,d\gamma \quad , \tag{8.ii:28}$$

where A is any given dynamical variable and,

$$\begin{aligned} M_\Omega = \{(N, q^N, p^N) \quad | \quad & N\in\mathbb{N}; \vec{q}_i\in\Omega \quad i=1,\dots,N; \\ & {p_{(i)}}_\alpha \in [-\infty,\infty] \quad i=1,\dots,N, \alpha=1,2\} \quad , \end{aligned} \tag{8.ii:29}$$

iii Pressures of the one component Coulomb plasma

For a one component Coulomb plasma several different definitions of the pressure are possible [102]. In this section we review four of them. We treat the neutral system in the first four subsections and the non neutral system in the last subsection.

iii.1 The virial theorem

The Hamiltonian of our dynamical system of N particles is,

$$H(q^N,p^N) = T(q^N,p^N) + \bar{U}(q^N) \quad , \tag{8.iii:1}$$

where we are assuming the particles confined in $\Omega_{a\tau_0}$ (we will omit the subscript $a\tau_0$ unless explicitly needed), with $\bar{U} = U+$ confining potential. The kinetic energy is,

$$T = \frac{1}{2m}\sum_{i=1}^{N} g^{\alpha\beta}(\vec{q}_i){p_{(i)}}_\alpha {p_{(i)}}_\beta \quad . \tag{8.iii:2}$$

The Roman indices label the particles, and the lower or upper Greek indices denote covariant or contravariant components respectively. A sum over repeated Greek indices is tacitly assumed.

The equations of motion for particle i are,

$$\begin{cases} \dot{{q_{(i)}}^\alpha} = \dfrac{\partial H}{\partial {p_{(i)}}_\alpha} = \dfrac{1}{m} g^{\alpha\beta}(\vec{q}_i){p_{(i)}}_\beta \\ \\ \dot{{p_{(i)}}_\alpha} = -\dfrac{\partial H}{\partial {q_{(i)}}^\alpha} = -\dfrac{1}{2m} {g^{\mu\nu}}_{,\alpha}(\vec{q}_i){p_{(i)}}_\mu {p_{(i)}}_\nu - \bar{U}_{,\alpha}(\vec{q}_i) \end{cases} , \tag{8.iii:3}$$

where the comma stands for partial differentiation and the dot for total derivative with respect to time.

If we take the time derivative of $\sum_i {q_{(i)}}^\tau p_{(i)_\tau}$ we find [2],

$$\begin{aligned}\frac{d}{dt}\sum_{i=1}^{N} {q_{(i)}}^\tau p_{(i)_\tau} &= \frac{1}{m}\sum_{i=1}^{N} g^{\tau\nu}(\vec{q_i}) p_{(i)_\tau} p_{(i)_\nu} - \frac{1}{2m}\sum_{i=1}^{N} {q_{(i)}}^\tau g^{\mu\nu}{}_{,\tau}(\vec{q_i}) p_{(i)_\mu} p_{(i)_\nu} \\ &\quad - \sum_{i=1}^{N} {q_{(i)}}^\tau \bar{U}_{,\tau}(\vec{q_i}) \quad , \end{aligned} \tag{8.iii:4}$$

where the last term is called the *virial* of the system.

Since the system is confined in Ω the coordinates ${q_{(i)}}^\tau(t)$ and their canonically conjugated momenta $p_{(i)_\tau}(t)$ remain finite at all times. We then must have,

$$\langle \frac{d}{dt}\sum_{i=1}^{N} {q_{(i)}}^\tau p_{(i)_\tau} \rangle_t = 0 \quad . \tag{8.iii:5}$$

We define the virial pressure $P_\Omega^{(v)}$ of the system as minus the time average of the force per unit length exerted by the confining potential on the particles. By the ergodic hypothesis we have,

$$\begin{aligned} P_\Omega^{(v)} \oint_{\partial\Omega} q^\tau d^1\Sigma_\tau &= \frac{1}{m}\langle \sum_{i=1}^{N} g^{\tau\nu}(\vec{q_i}) p_{(i)_\tau} p_{(i)_\nu} \rangle_t - \frac{1}{2m}\langle \sum_{i=1}^{N} {q_{(i)}}^\tau g^{\mu\nu}{}_{,\tau}(\vec{q_i}) p_{(i)_\mu} p_{(i)_\nu} \rangle_t \\ &\quad - \langle \sum_{i=1}^{N} {q_{(i)}}^\tau U_{,\tau}(\vec{q_i}) \rangle_t \quad , \end{aligned} \tag{8.iii:6}$$

where $d^1\Sigma_\alpha = \sqrt{g}\prod_{\beta=1;\beta\neq\alpha}^{2} dq^\beta$, is the elementary "surface" element, on the pseudosphere, orthogonal to the direction α. The line integral is,

$$\oint_{\partial\Omega_{a\tau_0}} q^\tau d^1\Sigma_\tau = \int_0^{2\pi} \tau_0\, a^2\, \sinh\tau_0\, d\varphi = \tau_0 a \mathcal{L}(\partial\Omega_{a\tau_0}) \quad . \tag{8.iii:7}$$

Moreover the ergodic hypothesis allows us to replace the time averages with microcanonical phase space averages. To reach the thermodynamic limit we further replace the microcanonical averages with grand-canonical phase space averages over M_Ω and let $\Omega \to \mathcal{S}$. We call $P^{(v)}$ the virial pressure of the system in the thermodynamic limit,

$$P^{(v)} = \lim_{\substack{\Omega\to\mathcal{S} \\ n \ constant}} P_\Omega^{(v)} \quad . \tag{8.iii:8}$$

[2] One may be tempted to start with the time derivative of $\sum_i \vec{q_i}\cdot\vec{p_i}$. Note however that this quantity does not remain finite at all times. This is because, when you follow the motion of a particle colliding with the boundary, it may go around the origin indefinitely, and φ (which must be defined as a continuous variable, without any 2π jumps) may increase indefinitely. Thus the time average of the time derivative of this quantity does not vanish.

We calculate next the three terms contributing to the pressure. The first one is,

$$\frac{1}{m}\langle\sum_{i=1}^{N} g^{\tau\nu}(\vec{q}_i)p_{(i)_\tau}p_{(i)_\nu}\rangle_\Omega =$$
$$2\frac{\sum_{N=0}^{\infty}\frac{z^N}{h^{2N}N!}\int e^{-\beta(T+U)}\,\frac{1}{2m}\sum_i^N g^{\tau\nu}(\vec{q}_i)p_{(i)_\tau}p_{(i)_\nu}\,d^{4N}\mu_{ps}}{\sum_{N=0}^{\infty}\frac{z^N}{h^{2N}N!}\int e^{-\beta(T+U)}\,d^{4N}\mu_{ps}} =$$
$$\frac{1}{\beta}\frac{\sum_{N=0}^{\infty}\frac{z^N}{\lambda^{2N}N!}N\int_\Omega e^{-\beta U}\,dS_1\cdots dS_N}{\sum_{N=0}^{\infty}\frac{z^N}{\lambda^{2N}N!}\int_\Omega e^{-\beta U}\,dS_1\cdots dS_N} = \frac{\langle N\rangle}{\beta} = \frac{n}{\beta}\mathcal{V}(\Omega) \quad , \tag{8.iii:9}$$

where z is the fugacity of the system, $\lambda = \sqrt{2\pi\beta\hbar^2/m}$ is the de Broglie thermal wavelength, and $dS = \sqrt{g}\prod_{\alpha=1}^{2} dq^\alpha = a^2\,\sinh\tau\,d\varphi\,d\tau$ is the elementary area element on the pseudosphere. In the following we will introduce a generalized fugacity $\zeta = z/\lambda^2$. Since $\mathcal{V}(\Omega_{a\tau_0})$ diverges less rapidly than $\tau_0\mathcal{L}(\partial\Omega_{a\tau_0})$ as $\tau_0\to\infty$, this term does not contribute to the pressure.

The second term is,

$$-\frac{1}{2m}\langle\sum_{i=1}^{N} {q_{(i)}}^\tau g^{\mu\nu}{}_{,\tau}(\vec{q}_i)p_{(i)_\mu}p_{(i)_\nu}\rangle_\Omega =$$
$$-\frac{1}{2m}\langle\sum_{i=1}^{N}\tau_i\, g^{\varphi\varphi}{}_{,\tau}(\vec{q}_i)[p_{(i)_\varphi}]^2\rangle_\Omega =$$
$$\frac{1}{2m}\langle\sum_{i=1}^{N}\tau_i\,\frac{g_{\varphi\varphi,\tau}(\vec{q}_i)}{[g_{\varphi\varphi}(\vec{q}_i)]^2}[p_{(i)_\varphi}]^2\rangle_\Omega =$$
$$2\langle\sum_{i=1}^{N}\frac{\tau_i}{\tanh\tau_i}\frac{(p_{(i)_\varphi})^2}{2ma^2\sinh^2\tau_i}\rangle_\Omega =$$
$$\frac{1}{\beta}\langle\sum_{i=1}^{N}\frac{\tau_i}{\tanh\tau_i}\rangle_\Omega =$$
$$\frac{1}{\beta}\int_\Omega n_\Omega^{(1)}(\vec{q}_1)\frac{\tau_1}{\tanh\tau_1}\,dS_1 \quad , \tag{8.iii:10}$$

where $n_\Omega^{(1)}$ is the one particle correlation function,

$$n_\Omega^{(1)}(\vec{q}_1) = \frac{\sum_{N=1}^{\infty}\frac{\zeta^N}{N!}N\int_\Omega e^{-\beta U}dS_2\cdots dS_N}{\sum_{N=0}^{\infty}\frac{\zeta^N}{N!}\int_\Omega e^{-\beta U}dS_1\cdots dS_N} \quad . \tag{8.iii:11}$$

Since for the infinite system U does not depend on the choice of the pseudosphere origin we must have $n_{\mathcal{S}}^{(1)}(\vec{q}_1) = n$. In the event that $n_{\Omega_{a\tau_0}}^{(1)}(\tau)\sim n$ near the boundary (see appendix I),

comparing the asymptotic behaviors of $2\pi a^2 \int_0^{\tau_0} \tau \cosh\tau \, d\tau$ and $\tau_0 \mathcal{L}(\partial\Omega_{a\tau_0})$ as $\tau_0 \to \infty$ we find that the second term gives a contribution n/β to the pressure.

The third term is,

$$\begin{aligned} -\langle \sum_{i=1}^{N} q_{(i)}{}^{\tau} U_{,\tau}(\vec{q}_i) \rangle_\Omega &= q \int_\Omega n_\Omega^{(1)}(\vec{q}_1)\, \tau_1\, \bar{w}_{,\tau}(\tau_1)\, dS_1 \\ &\quad -\frac{q^2}{2} \int_\Omega n_\Omega^{(2)}(\vec{q}_1, \vec{q}_2)\, (q_{(1)}{}^{\tau} v_{,\tau_1}(d_{12}) + q_{(2)}{}^{\tau} v_{,\tau_2}(d_{12}))\, dS_1\, dS_2 \ , \end{aligned} \tag{8.iii:12}$$

where $n_\Omega^{(2)}$ is the two particle correlation function,

$$n_\Omega^{(2)}(\vec{q}_1, \vec{q}_2) = \frac{\displaystyle\sum_{N=2}^{\infty} \frac{\zeta^N}{N!} N(N-1) \int_\Omega e^{-\beta U} dS_3 \cdots dS_N}{\displaystyle\sum_{N=0}^{\infty} \frac{\zeta^N}{N!} \int_\Omega e^{-\beta U} dS_1 \cdots dS_N} \quad , \tag{8.iii:13}$$

which for the infinite system can be rewritten as $n_{\mathcal{S}}^{(2)}(\vec{q}_1, \vec{q}_2) = n^2\, g(d_{12})$, where g is the usual pair correlation function. Notice that since the charges are indistinguishable we must have $n_\Omega^{(2)}(\vec{q}_1, \vec{q}_2) = n_\Omega^{(2)}(\vec{q}_2, \vec{q}_1)$. Then equation (8.iii:12) can be rewritten as follows,

$$\begin{aligned} -\langle \sum_{i=1}^{N} q_{(i)}{}^{\tau} U_{,\tau}(\vec{q}_i) \rangle_\Omega &= q \int_\Omega n_\Omega^{(1)}(\vec{q}_1)\, \tau_1\, \bar{w}_{,\tau}(\tau_1)\, dS_1 \\ &\quad -q^2 \int_\Omega n_\Omega^{(2)}(\vec{q}_1, \vec{q}_2)\, q_{(1)}{}^{\tau} v_{,\tau_1}(d_{12})\, dS_1\, dS_2 \quad , \end{aligned} \tag{8.iii:14}$$

When $n_{\Omega_{a\tau_0}}^{(1)}(\tau) \sim n$ near the boundary (see appendix I), we find the contribution of the background to the pressure comparing the asymptotic behaviors of,

$$\int_{\mathcal{S}} \tau \bar{w}_{,\tau}(\tau)\, dS = 2\pi a^2\, nq \left(-2\pi a^2 \int_0^{\tau_0} \tau\, \tanh(\tau/2)\, \sinh\tau \, d\tau \right) \quad , \tag{8.iii:15}$$

and $\tau_0 \mathcal{L}(\partial\Omega_{a\tau_0})$ as $\tau_0 \to \infty$. So doing we find that the background contributes to the pressure a term $-2\pi a^2 (nq)^2$.

We then reach the following expression for the pressure in terms of the one and two particle correlation functions,

$$\begin{aligned} P^{(v)} = \lim_{\tau_0 \to \infty} \frac{1}{a\tau_0 \mathcal{L}(\partial\Omega_{a\tau_0})} \Bigg[&\frac{1}{\beta} \int_{\Omega_{a\tau_0}} n_{\Omega_{a\tau_0}}^{(1)}(\vec{q}_1) \frac{\tau_1}{\tanh\tau_1}\, dS_1 + \\ &q \int_{\Omega_{a\tau_0}} n_{\Omega_{a\tau_0}}^{(1)}(\vec{q}_1)\, \tau_1\, \bar{w}_{,\tau}(\tau_1)\, dS_1 - q^2 \int_{\Omega_{a\tau_0}} n_{\Omega_{a\tau_0}}^{(2)}(\vec{q}_1, \vec{q}_2)\, \tau_1 v_{,\tau_1}(d_{12})\, dS_1\, dS_2 \Bigg] \ . \end{aligned} \tag{8.iii:16}$$

iii.2 Equivalence of virial and kinetic pressures

The average force exerted by the particles on a perimeter element $ds = a \sinh\tau_0 \, d\varphi$ of the boundary $\partial\Omega_{a\tau_0}$, is $[n_\Omega^{(1)}(\tau_0)/\beta] ds$ where $n_\Omega^{(1)}(\tau)$ is the one particle density at a distance $a\tau$ from the origin. Therefore the kinetic pressure is,

$$P_\Omega^{(k)} = n_\Omega^{(1)}(\tau_0)/\beta \quad . \tag{8.iii:17}$$

We assume that this quantity has a limit when $\tau_0 \to \infty$. It will now be shown that the virial pressure $P_\Omega^{(v)}$, is the same as $P_\Omega^{(k)}$.

Replacing the virial pressure with the kinetic pressure in the left hand side of equation (8.iii:6) we have,

$$P_\Omega^{(k)} \oint_{\partial\Omega} q^\tau \, d^1\Sigma_\tau = \frac{1}{\beta} \oint_{\partial\Omega} n_\Omega^{(1)}(\vec{q}) q^\tau \, d^1\Sigma_\tau \quad . \tag{8.iii:18}$$

Using Gauss theorem we find,

$$\begin{aligned} P_\Omega^{(k)} \oint_{\partial\Omega} q^\tau \, d^1\Sigma_\tau &= \frac{1}{\beta} \int_\Omega \frac{(\sqrt{g(\vec{q}_1)} {q_{(1)}}^\tau)_{,\tau_1}}{\sqrt{g(\vec{q}_1)}} n_\Omega^{(1)}(\vec{q}_1) \, dS_1 + \\ & \frac{1}{\beta} \int_\Omega {q_{(1)}}^\tau {n_\Omega^{(1)}}_{,\tau_1}(\vec{q}_1) \, dS_1 \quad . \end{aligned} \tag{8.iii:19}$$

The first term on the right hand side of this equation can be further developed into,

$$\frac{\langle N \rangle}{\beta} + \frac{1}{\beta} \int_\Omega \frac{(\sqrt{g})_{,\tau_1}}{\sqrt{g}} {q_{(1)}}^\tau n_\Omega^{(1)}(\vec{q}_1) \, dS_1 \quad . \tag{8.iii:20}$$

We see then that we recover the term (8.iii:9) plus the term (8.iii:10) of the virial pressure.

In the second term on the right hand side of equation (8.iii:19) we can replace the gradient of the one particle correlation function with its expression in terms of one and two particle correlation functions. We know that the equilibrium states of the finite system contained in the domain Ω are described by correlation functions which are solutions of the BGY hierarchy,

$$\begin{aligned} & \frac{1}{\beta q^2} {n_\Omega^{(m)}}_{,\alpha_1}(\vec{q}_1, \ldots, \vec{q}_m) = \\ & \left[-n \int_\Omega F_{\alpha_1}(d_{10}) \, dS_0 + \sum_{j=2}^{m} F_{\alpha_1}(d_{1j}) \right] n_\Omega^{(m)}(\vec{q}_1, \ldots, \vec{q}_m) \\ & + \int_\Omega F_{\alpha_1}(d_{10}) n_\Omega^{(m+1)}(\vec{q}_1, \ldots, \vec{q}_m, \vec{q}_0) \, dS_0 \quad , \end{aligned} \tag{8.iii:21}$$

where $F_{\alpha_1}(d_{10}) = -v_{,\alpha_1}(d_{10})$. For $m = 1$ we have,

$$\frac{1}{\beta q^2} {n_\Omega^{(1)}}_{,\alpha_1}(\vec{q}_1) = \int_\Omega F_{\alpha_1}(d_{10}) [n_\Omega^{(2)}(\vec{q}_1, \vec{q}_0) - n n_\Omega^{(1)}(\vec{q}_1)] \, dS_0 \quad , \tag{8.iii:22}$$

which when inserted into the second term on the right hand side of equation (8.iii:19) gives the term (8.iii:14) of the virial pressure. We then find that,

$$P_\Omega^{(k)} = P_\Omega^{(v)} \quad . \tag{8.iii:23}$$

iii.3 The thermal pressure in the Canonical ensemble

The thermal pressure is defined as the partial derivative with respect to the area of the Helmholtz free energy $F(\beta, \mathcal{A}, N)$ keeping the number of particles N, the background charge, and the temperature T constants,

$$P_\Omega^{(t)} = -\left(\frac{\partial F}{\partial \mathcal{A}} \right)_{\beta, N} \quad . \tag{8.iii:24}$$

The free energy is related to the logarithm of the partition function $Q(\beta, \mathcal{A}, N)$ as follows,

$$F = -\frac{1}{\beta} \ln Q \quad . \tag{8.iii:25}$$

and the partition function is defined as,

$$\begin{aligned} Q(N, \mathcal{A}, T) &= \frac{h^{-2N}}{N!} \int e^{-\beta H(q^N, p^N)} \, d^{4N}\mu_{ps} \\ &= \frac{\lambda^{-2N}}{N!} \int_\Omega e^{-\beta U(q^N)} \, dS_1 \cdots dS_N \quad , \end{aligned} \tag{8.iii:26}$$

where $\lambda = \sqrt{2\pi\beta\hbar^2/m}$ is the de Broglie thermal wavelength.

We calculate the thermal pressure using the dilatation method. We make the following change of variables in the definition of the partition function,

$$\left\{ \begin{array}{ll} \varphi_i \to \varphi_i & \varphi_i \in [0, 2\pi) \\ \tau_i \to \tau_0 t_i & t_i \in [0, 1] \end{array} \right. \tag{8.iii:27}$$

This enables us to calculate the partial derivative with respect to $\mathcal{A} = 2\pi a^2(\cosh\tau_0 - 1)$ through a partial derivative with respect to τ_0,

$$\begin{aligned} P_\Omega^{(t)} &= \frac{d\tau_0}{d\mathcal{A}} \frac{\partial}{\partial\tau_0} \left[\frac{1}{\beta} \ln Q(\tau_0) \right] \\ &= \frac{1}{2\pi a^2 \sinh\tau_0} \frac{1}{\beta} \frac{1}{Q(\tau_0)} \frac{\partial Q(\tau_0)}{\partial\tau_0} \quad , \end{aligned} \tag{8.iii:28}$$

where,

$$Q(\tau_0) = \frac{\lambda^{-2N}}{N!} \int_\Omega e^{-\beta U_{\tau_0}} \, a^{2N} \tau_0^N \prod_{i=1}^N \sinh(\tau_0 t_i) \, dt_i d\varphi_i \quad , \tag{8.iii:29}$$

with,

$$\begin{aligned} U_{\tau_0} &= q^2 \left\{ \frac{1}{2} \sum_{i \neq j} v([d_{ij}]_{\tau_0}) \right. \\ &\quad -\frac{N}{\mathcal{A}} \sum_i \int v([d_{ip}]_{\tau_0}) a^2 \sinh(\tau_0 t_p) \tau_0 \, dt_p d\varphi_p \\ &\quad \left. \frac{1}{2} \left(\frac{N}{\mathcal{A}} \right)^2 \int v([d_{pq}]_{\tau_0}) a^4 \sinh(\tau_0 t_p) \sinh(\tau_0 t_q) \tau_0^2 \, dt_p d\varphi_p dt_q d\varphi_q \right\} \quad , \end{aligned} \tag{8.iii:30}$$

and,

$$\cosh([d_{ij}]_{\tau_0}/a) = \cosh(\tau_0 t_i)\cosh(\tau_0 t_j) - \sinh(\tau_0 t_i)\sinh(\tau_0 t_j)\cos(\varphi_i - \varphi_j) \quad . \tag{8.iii:31}$$

At the end of the calculation we undo the change of variables going back to (τ_i, φ_i).

We find then,

$$P_\Omega^{(t)} = \frac{1}{2\pi a^2 \sinh\tau_0} \frac{1}{\beta} \left\{ \frac{N}{\tau_0} + \frac{1}{\tau_0} \langle \sum_i \frac{\tau_0 t_i}{\tanh(\tau_0 t_i)} \rangle_\Omega - \frac{\beta}{\tau_0} \langle \tau_0 \frac{\partial U_{\tau_0}}{\partial\tau_0} \rangle_\Omega \right\} \quad . \tag{8.iii:32}$$

Recalling that $a\tau_0\mathcal{L}(\partial\Omega) = \tau_0 2\pi a^2 \sinh\tau_0$ we see that for the ideal gas ($U = 0$) the thermal pressure coincides with the virial pressure [see terms (8.iii:9) and (8.iii:10)]. It remains to calculate the excess thermal pressure,

$$\begin{aligned} P^{(t)}_{\Omega,exc} &= -\frac{1}{a\tau_0\mathcal{L}(\partial\Omega)}\langle\tau_0\frac{\partial U_{\tau_0}}{\partial\tau_0}\rangle_\Omega \\ &= P^{(t)}_{\Omega,pp} + P^{(t)}_{\Omega,pb} + P^{(t)}_{\Omega,bb} \quad , \end{aligned} \tag{8.iii:33}$$

which is made up of three contributions: the one from the particle-particle interactions, the one from the particle-background interactions, and the one from the background-background interaction.

Let us calculate $P^{(t)}_{\Omega,pp}$. Since,

$$\tau_0\frac{\partial v([d_{ij}]_{\tau_0})}{\partial\tau_0} = \left(t_i\frac{\partial}{\partial t_i} + t_j\frac{\partial}{\partial t_j}\right)v([d_{ij}]_{\tau_0}) \quad ,$$

we find,

$$P^{(t)}_{\Omega,pp} = -\frac{q^2}{a\tau_0\mathcal{L}(\partial\Omega)}\langle\sum_{i\neq j}\tau_i\, v_{,\tau_i}(d_{ij})\rangle_\Omega \quad , \tag{8.iii:34}$$

which coincides with the second term on the right hand side of equation (8.iii:14).

Let us calculate next $P^{(t)}_{\Omega,pb}$,

$$\begin{aligned} P^{(t)}_{\Omega,pb} = -\frac{q^2}{a\tau_0\mathcal{L}(\partial\Omega)} \quad & \Bigg\{ -n\langle\sum_i\int_\Omega[\tau_i\, v_{,\tau_i}(d_{ip}) + \tau_p\, v_{,\tau_p}(d_{ip})]\, dS_p\rangle_\Omega \\ & -n\langle\sum_i\int_\Omega v(d_{ip})\, dS_p\rangle_\Omega \\ & -n\langle\sum_i\int_\Omega v(d_{ip})\frac{\tau_p}{\tanh\tau_p}\, dS_p\rangle_\Omega \\ & + n\frac{a\tau_0\mathcal{L}(\partial\Omega)}{\mathcal{A}}\langle\sum_i\int_\Omega v(d_{ip})\, dS_p\rangle_\Omega\Bigg\} \\ = \frac{q^2}{a\tau_0\mathcal{L}(\partial\Omega)} \quad & \Bigg\{ n\langle\sum_i\int_\Omega\tau_i\, v_{,\tau_i}(d_{ip})\, dS_p\rangle_\Omega \\ & +n\langle\sum_i\oint_{\partial\Omega}\tau_p\, v(d_{ip})\, d^1\Sigma_{p_\tau}\rangle_\Omega \\ & - n\frac{a\tau_0\mathcal{L}(\partial\Omega)}{\mathcal{A}}\langle\sum_i\int_\Omega v(d_{ip})\, dS_p\rangle_\Omega\Bigg\} \quad . \end{aligned} \tag{8.iii:35}$$

We see that the first term on the right hand side coincides with the first term on the right hand side of equation (8.iii:14).

Let us calculate in the end $P^{(t)}_{\Omega,bb}$,

$$\begin{aligned} P^{(t)}_{\Omega,bb} = -\frac{q^2}{a\tau_0\mathcal{L}(\partial\Omega)} \quad & \left\{ \frac{n^2}{2}\int_\Omega\int_\Omega [\tau_p\, v_{,\tau_p}(d_{pq}) + \tau_q\, v_{,\tau_q}(d_{pq})]\, dS_p dS_q \right. \\ & +n^2\int_\Omega\int_\Omega v(d_{pq})\, dS_p dS_q \\ & +\frac{n^2}{2}\int_\Omega\int_\Omega v(d_{pq})\left[\frac{\tau_p}{\tanh\tau_p}+\frac{\tau_q}{\tanh\tau_q}\right] dS_p dS_q \\ & \left. -\, n^2\frac{a\tau_0\mathcal{L}(\partial\Omega)}{\mathcal{A}}\int_\Omega\int_\Omega v(d_{pq})\, dS_p dS_q \right\} \\ = -\frac{q^2}{a\tau_0\mathcal{L}(\partial\Omega)} \quad & \left\{ n^2\int_\Omega\oint_{\partial\Omega} \tau_p\, v(d_{pq})\, d^1\Sigma_{p_\tau} dS_q \right. \\ & \left. -n^2\frac{a\tau_0\mathcal{L}(\partial\Omega)}{\mathcal{A}}\int_\Omega\int_\Omega v(d_{pq})\, dS_p dS_q \right\} \quad . \end{aligned} \tag{8.iii:36}$$

We find then the following relationship between the thermal and the virial pressure,

$$\begin{aligned} P^{(t)}_\Omega = P^{(v)}_\Omega \quad & - \quad q^2\frac{n}{\mathcal{A}}\int_\Omega\int_\Omega v(d_{pq})[n^{(1)}_\Omega(\tau_p) - n]\, dS_p dS_q \\ & + \quad q^2\frac{n}{a\tau_0\mathcal{L}(\partial\Omega)}\int_\Omega\oint_{\partial\Omega} \tau_p\, v(d_{pq})[n^{(1)}_\Omega(\tau_q) - n]\, d^1\Sigma_{p_\tau} dS_q \ . \end{aligned} \tag{8.iii:37}$$

The second integral on the right hand side of this equation is zero: the electric potential at $\vec{q}_p$ created by the total charge distribution (particles plus background) is given by the quantity $q\int_\Omega v(d_{pq})[n^{(1)}_\Omega(\tau_q) - n]\, dS_q$. Since the total charge is zero, by Newton's theorem the above potential vanishes on the disk's boundary $\tau_p = \tau_0$. In the first integral on the right hand side of equation (8.iii:37) $-qn\int_\Omega v(d_{pq})\, dS_q$ is the electric potential created by the background at $\vec{q}_p$. We then have,

$$P^{(t)}_\Omega = P^{(v)}_\Omega + q\frac{1}{\mathcal{A}}\int_\Omega w(\tau_p)[n^{(1)}_\Omega(\tau_p) - n]\, dS_p \quad . \tag{8.iii:38}$$

We want to find an expression for the difference between the thermal and the virial pressure in the thermodynamic limit. Since $n^{(1)}_\Omega(\tau_p) - n$ is localized near the boundary (see appendix I) we change the integration variable from τ to $\sigma = \tau_0 - \tau$ and take the limit $\tau_0 \to \infty$. We have that the electric potential of the background behaves as,

$$w(\sigma) \underset{\tau_0\to\infty}{\sim} 2\pi a^2 qn(-\sigma - 1) \quad , \tag{8.iii:39}$$

Then using the normalization condition for the one particle correlation function we find,

$$P^{(t)} - P^{(v)} = -2\pi a^2 nq^2\int_0^\infty [n^{(1)}_{\mathcal{S}}(\sigma) - n]\sigma e^{-\sigma}\, d\sigma \quad . \tag{8.iii:40}$$

This latter formula is the same as in the case of a flat system in the thermodynamic limit (half-space), except for the factor $\exp(-\sigma)$ (see [102] section 5.1.2. The flat system expression is recovered taking the limit $a \to \infty, \sigma \to 0, a\sigma = x$).

iii.4 Difference between thermal and kinetic pressure

In a flat half space (thermodynamic limit of a disc) the difference between the thermal and the kinetic pressure $P^{(t)} - P^{(k)}$ is related to the potential difference between the surface and the bulk [117]. We want to give the analog of this relation in the case of a pseudosphere. In this subsection we will omit the subscripts on the correlation functions.

Let us first review the flat case. In reference [102] the last equation of section 5.1.2. becomes in our notation,

$$P^{(t)} - P^{(k)} = -2\pi q^2 n \int_0^\infty x[n^{(1)}(x) - n]\, dx \quad ,$$

where x is the distance from the boundary. The electric potential $\phi(x)$ obeys the Poisson equation,

$$\frac{d^2\phi(x)}{dx^2} = -2\pi q\,[n^{(1)}(x) - n] \quad .$$

After an integration by parts, and taking into account that $x d\phi/dx$ vanishes at $x = 0$ (because of the overall neutrality) and at $x = \infty$ (because the electric field goes fast to zero in the bulk), one finds,

$$P^{(t)} - P^{(k)} = -qn\,[\phi_{\rm bulk} - \phi_{\rm surface}] \quad . \tag{8.iii:41}$$

This equation (8.iii:41) can be found in [117], equations (2.18) and (2.20).

Let us now give another, more pictorial, proof of equation (8.iii:41). We consider a large disk filled with a one component Coulomb plasma, of area $\mathcal{A}$. For compressing it a little, changing the area by $d\mathcal{A} < 0$, we must provide the reversible work $\delta W = P^{(t)}|d\mathcal{A}|$. We may achieve that compression in two steps. First, one compresses the particles only, leaving the background behind; the corresponding work is $\delta W^{(1)} = P^{(k)}|d\mathcal{A}|$, since $P^{(k)}$ is the force per unit length exerted on the wall by the particles alone. Then, one compresses the background, i.e. brings the charge $-qn_b|d\mathcal{A}|$ from a region where the potential is $\phi_{\rm surface} = 0$ into the plasma, spreading it uniformly; the corresponding work is $\delta W^{(2)} = -[qn|d\mathcal{A}|/\mathcal{A}] \int \phi(r) dS$, where $\phi(r)$ is the potential at distance r from the center. Therefore,

$$P^{(t)} = P^{(k)} - \frac{qn}{\mathcal{A}} \int \phi(r)\, dS \quad . \tag{8.iii:42}$$

Since $\phi(r)$ differs from $\phi_{\rm bulk}$ only in the neighborhood of the boundary circle, in the large disc limit,

$$\frac{1}{\mathcal{A}} \int \phi(r)\, dS \sim \phi_{\rm bulk} \quad , \tag{8.iii:43}$$

and (8.iii:42) becomes (8.iii:41).

Let us now follow the same steps on a pseudosphere (see figure 8.1). We again get (8.iii:42), with $\phi(\tau)$ instead of $\phi(r)$. But now, the neighborhood of the boundary circle has an area of the same order of magnitude as the whole area $\mathcal{A}$, and (8.iii:43) is no longer valid. In the large disc limit, we rather have,

$$\frac{1}{\mathcal{A}} \int \phi(\tau)\, dS \sim e^{-\tau_0} \int_0^{\tau_0} \phi(\tau) e^{\tau}\, d\tau \quad . \tag{8.iii:44}$$

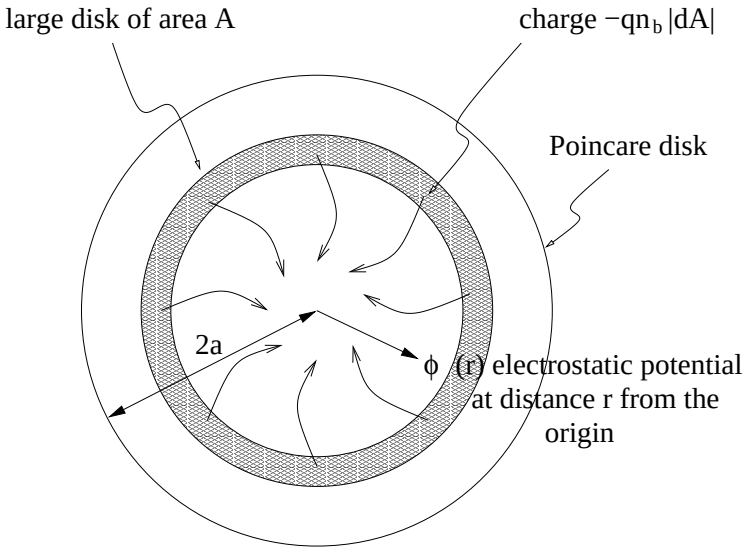

FIGURE 8.1: Shows the Poincaré disk, the disk of area $\mathcal{A}$ initially containing the 2D OCP, and the disk of area $\mathcal{A} - d\mathcal{A}$ containing the compressed 2D OCP. Since we are working at constant β, N, N_b, the leftover background charge $qn_b d\mathcal{A}$ must be spreaded uniformly within the compressed disk.

Using (8.iii:44) in (8.iii:42), we recover, after some manipulation, equation (8.iii:40),

$$P^{(t)} - P^{(k)} \sim -2\pi a^2 nq^2 \int_0^{\tau_0} [n^{(1)}(\tau) - n](\tau_0 - \tau) e^{\tau - \tau_0}\, d\tau \quad . \tag{8.iii:45}$$

Indeed, in (8.iii:45) $[n^{(1)}(\tau) - n]$ can be expressed in terms of $\phi(\tau)$ through the Poisson equation, $\Delta\phi(\tau) = -2\pi q[n^{(1)}(\tau) - n]$. Since the charge density is localized at large τ, we can use for the Laplacian $\Delta \sim a^{-2}[d^2/d\tau^2 + d/d\tau]$. After integrations by parts, (8.iii:45) becomes,

$$P^{(t)} - P^{(k)} \sim -qn\, e^{-\tau_0} \int_0^{\tau_0} \phi(\tau) e^{\tau}\, d\tau \quad , \tag{8.iii:46}$$

which is the same as (8.iii:42) in the large τ_0 limit.

In conclusion, (8.iii:41) valid for a large flat disc generalizes into (8.iii:46) on a pseudosphere

iii.5 Non neutral system and the mechanical pressure

In this subsection we want to revisit the various definitions of pressure and the relations between them for a *non neutral* one component Coulomb plasma, i.e. a system with $\rho_b = -n_b q$ with $n_b \neq n$. It is convenient to introduce the number of elementary charges in the background: $N_b = n_b \mathcal{A}$

In this case we find for the virial and kinetic pressure of the finite system,

$$\begin{aligned} P_\Omega^{(k)} = P_\Omega^{(v)} \quad = \quad & \frac{1}{a\tau_0 \mathcal{L}(\partial\Omega)} \left\{ \frac{\langle N \rangle}{\beta} + \frac{1}{\beta} \int_\Omega n_\Omega^{(1)}(\tau_1) \frac{\tau_1}{\tanh \tau_1}\, dS_1 \right. \\ & \left. - q^2 \int_\Omega \int_\Omega \tau_1 v_{,\tau_1}(d_{10}) [n_\Omega^{(2)}(\vec{q}_1, \vec{q}_2) - n_b n_\Omega^{(1)}(\tau_1)]\, dS_0 dS_1 \right\} \quad . \end{aligned} \tag{8.iii:47}$$

The thermal pressure becomes equation (8.iii:37) with n replaced by n_b,

$$\begin{aligned} P_\Omega^{(t)} = P_\Omega^{(v)} &- q^2 \frac{n_b}{\mathcal{A}} \int_\Omega \int_\Omega v(d_{pq})[n_\Omega^{(1)}(\tau_p) - n_b]\, dS_p dS_q \\ &+ q^2 \frac{n_b}{a\tau_0 \mathcal{L}(\partial\Omega)} \int_\Omega \oint_{\partial\Omega} \tau_p\, v(d_{pq})[n_\Omega^{(1)}(\tau_q) - n_b]\, d^1\Sigma_{p_\tau} dS_q \quad . \end{aligned} \tag{8.iii:48}$$

For the non neutral system we can introduce a fourth type of pressure: the *mechanical pressure*, or partial pressure due to the particles. For a fluid parameterized by $(\beta, \mathcal{A}, N, n_b)$ the mechanical pressure is defined as follows,

$$P_\Omega^{(m)} = -\left(\frac{\partial F}{\partial \mathcal{A}}\right)_{\beta,N,n_b} \quad . \tag{8.iii:49}$$

Using the dilatation method again, we find,

$$P_\Omega^{(m)} = P_\Omega^{(v)} + q^2 \frac{n_b}{a\tau_0 \mathcal{L}(\partial\Omega)} \int_\Omega \oint_{\partial\Omega} \tau_p\, v(d_{pq})[n_\Omega^{(1)}(\tau_q) - n_b]\, d^1\Sigma_{\tau_p} dS_q \quad . \tag{8.iii:50}$$

Using Newton's theorem this expression can be simplified as follows,

$$\begin{aligned} P_\Omega^{(m)} - P_\Omega^{(v)} &= q^2 (N - N_b) \frac{n_b}{a\tau_0 \mathcal{L}(\partial\Omega)} \oint_{\partial\Omega} \tau_p v(d_{p0}) d^1\Sigma_{\tau_p} \\ &= q^2 n_b (N - N_b) v(a\tau_0) \quad . \end{aligned} \tag{8.iii:51}$$

The difference between the thermal and the mechanical pressure can be rewritten as,

$$P_\Omega^{(t)} - P_\Omega^{(m)} = \frac{q}{\mathcal{A}} \int_\Omega w(\tau)[n_\Omega^{(1)}(\tau) - n_b]\, dS \quad . \tag{8.iii:52}$$

In the thermodynamic limit we find,

$$P^{(m)} - P^{(v)} = 2\pi a^2 q^2 n_b (n - n_b) \quad . \tag{8.iii:53}$$

In equation (8.iii:52) $[n_\Omega^{(1)}(\tau) - n_b]$ differs from zero just in a neighborhood of the disk boundary (the system tends to be electrically neutral in the bulk). Then changing variables from τ to the distance from the boundary $\sigma = \tau_0 - \tau$ we find,

$$P^{(t)} - P^{(m)} = \frac{2q}{e^{\tau_0}} \int_0^{\tau_0} w(\sigma)[n_\mathcal{S}^{(1)}(\sigma) - n_b] \sinh(\tau_0 - \sigma)\, d\sigma \quad . \tag{8.iii:54}$$

Using the asymptotic expansion (8.iii:39) for the background potential we have,

$$\begin{aligned} P^{(t)} - P^{(m)} &= q \int_0^\infty 2\pi a^2 q n_b (-\sigma - 1)[n_\mathcal{S}^{(1)}(\sigma) - n_b] e^{-\sigma}\, d\sigma \\ &= -2\pi a^2 q^2 n_b (n - n_b) \\ &\quad -2\pi a^2 n_b\, q^2 \int_0^\infty [n_\mathcal{S}^{(1)}(\sigma) - n_b] \sigma e^{-\sigma}\, d\sigma \quad , \end{aligned} \tag{8.iii:55}$$

where we used the asymptotic form for the normalization condition of the one particle correlation function. We also have,

$$P^{(t)} - P^{(v)} = -2\pi a^2 n_b\, q^2 \int_0^\infty [n_\mathcal{S}^{(1)}(\sigma) - n_b] \sigma e^{-\sigma}\, d\sigma \quad . \tag{8.iii:56}$$

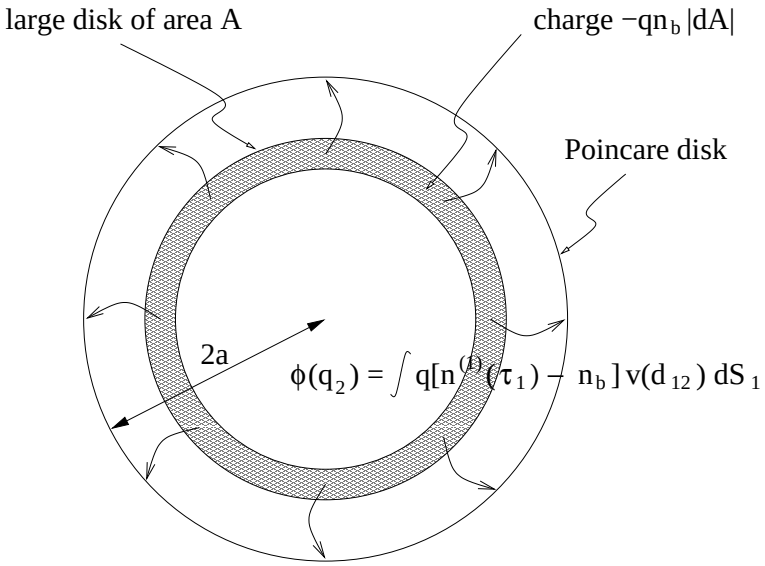

FIGURE 8.2: Shows the Poincaré disk, the disk of area $\mathcal{A}$ initially containing the 2D OCP, and the disk of area $\mathcal{A} - d\mathcal{A}$ containing the compressed 2D OCP. Since we are working at constant β, N, n_b, the leftover background charge $qn_b d\mathcal{A}$ must be sent to infinity.

The difference $P^{(m)} - P^{(k)}$ can be obtained by a slight change in the argument of subsection iii.4 (see figure 8.2). Again we consider a large disk filled with a one component Coulomb plasma of area $\mathcal{A}$, and we compress it infinitesimally, changing its area by $d\mathcal{A} < 0$, now at constant β, N, n_b, providing the reversible work $\delta W = -P^{(m)} d\mathcal{A}$, in two steps. First one compresses the particles only, leaving the background behind, and the corresponding work is $\delta W^{(1)} = -P^{(k)} d\mathcal{A}$. Then one must withdraw the leftover background charge $qn_b d\mathcal{A}$, bringing it from the surface, where the potential is ϕ_{surface} to infinity, where the potential vanishes. The corresponding work is $\delta W^{(2)} = -qn_b d\mathcal{A}\phi_{\text{surface}}$. Therefore one finds, $P^{(m)} - P^{(k)} = qn_b\phi_{\text{surface}}$. In the thermodynamic limit on the pseudosphere, $\phi_{\text{surface}} \to 2\pi a^2 q(n - n_b)$.

iii.6 Thermal and mechanical pressures in the Grand Canonical ensemble

In the following we shall also need an expression of the thermal and mechanical pressures appropriate for the grand canonical ensemble. It should be remembered that, for a one component plasma, the grand canonical partition function must be defined [123] as an ensemble of systems with any number N of particles in a fixed area and with a *fixed background charge density* $-qn_b$ (using am ensemble of neutral systems, i.e. varying n_b together with N does not give a well behaved grand partition function). Thus the grand partition function Ξ and the corresponding grand potential $\Omega = -\ln \Xi/\beta$ are functions of $\beta, \mathcal{A}, \zeta, n_b$, where ζ is the fugacity. We assume that even on a pseudosphere, the grand potential is extensive, i.e. of the form $\Omega = \mathcal{A}\omega(\beta, \zeta, n_b)$. The usual Legendre transformation from F to Ω and from N to ζ changes (8.iii:24) into,

$$P^{(t)} = -\left(\frac{\partial \Omega}{\partial \mathcal{A}}\right)_{\beta,\zeta,N_b} \quad . \tag{8.iii:57}$$

Since ω depends on $\mathcal{A}$ through $n_b = N_b/\mathcal{A}$, (8.iii:57) becomes,

$$P^{(t)} = -\omega + n_b \frac{\partial \omega}{\partial n_b} \quad . \tag{8.iii:58}$$

Note the difference with an ordinary fluid, without a background, for which $P^{(t)} = -\omega$.

The mechanical pressure (8.iii:49) is changed by the Legendre transformation into,

$$P^{(m)} = -\left(\frac{\partial\Omega}{\partial\mathcal{A}}\right)_{\beta,\zeta,n_b} = -\omega \tag{8.iii:59}$$

iv The Yukawa fluid and the Maxwell tensor pressure

In the previous sections we have described a method for calculating the virial and kinetic pressures exerted by the Coulomb plasma on the "surface" of its container comparing them with the thermal pressure. In this section, following closely a derivation due to Jancovici [119], we will calculate the *Maxwell tensor pressure* $P^{(\theta)}$ of the plasma on the Riemannian surface, using a field theoretical argument. This bulk pressure has been shown to be equivalent to the thermal pressure as defined by Choquard, for the flat plasma. On a pseudosphere, since the surface of a large domain is of the same order of magnitude as the volume, the thermal pressure would depend on the boundary conditions and probably would be different from the Maxwell tensor pressure.

A field theoretical description of a one component Coulomb plasma on a Riemannian manifold $\mathcal{R}$ can be obtained as follows. Consider a system of particles of mass m and charge q living on the whole manifold with a number density n, immersed in a uniform neutralizing background charge distribution of charge density $\rho_b = -nq$, and coupled to a scalar field ϕ of "mass" α. This we will call a Yukawa fluid. In the limit of a vanishing α the Yukawa fluid reduces to the one component Coulomb plasma.

Let us introduce the mass density of particle i,

$$\rho_i = m\,\delta(\vec{q} - \vec{q}_i)/\sqrt{g} \quad , \tag{8.iv:1}$$

where $\vec{q}_i$ is the position of particle i, and the total charge density as,

$$\begin{aligned} \rho &= \rho_p + \rho_b \quad , \\ \rho_p &= q\sum_i \delta(\vec{q} - \vec{q}_i)/\sqrt{g} \quad . \end{aligned} \tag{8.iv:2}$$

The Hamiltonian of the fluid can be written as,

$$H = H_p + H_\phi + H_{p\phi} \quad , \tag{8.iv:3}$$

where H_p is the kinetic energy of the particles,

$$\begin{aligned} H_p &= \int \mathcal{H}_p \sqrt{g}\, d\vec{q} \quad , \\ \mathcal{H}_p &= \frac{1}{2}\sum_i \rho_i\, g^{\mu\nu}(\vec{q}_i)(p_{(i)_\mu}/m)(p_{(i)_\nu}/m) \quad , \end{aligned} \tag{8.iv:4}$$

and $H_\phi + H_{p\phi}$ is their total "electrostatic" potential energy. If the dimension of the manifold is d we have,

$$\begin{aligned} H_\phi &= \int \mathcal{H}_\phi \sqrt{g}\, d\vec{q} \quad , \\ \mathcal{H}_\phi &= -\frac{1}{2\epsilon_d}[g^{\mu\nu}\phi_{,\mu}\phi_{,\nu} + \alpha^2\phi^2] \quad , \end{aligned} \tag{8.iv:5}$$

where $\epsilon_1 = 2$, $\epsilon_2 = 2\pi$, $\epsilon_3 = 4\pi$, and,

$$\begin{aligned} H_{p\phi} &= \int \mathcal{H}_{p\phi}\sqrt{g}\, d\vec{q} \quad , \\ \mathcal{H}_{p\phi} &= \rho\phi \quad . \end{aligned} \tag{8.iv:6}$$

The Lagrangian density $\mathcal{L}\sqrt{g} = (\mathcal{L}_p + \mathcal{L}_\phi)\sqrt{g}$ has a particle contribution,

$$\mathcal{L}_p = \frac{1}{2}\sum_i \rho_i\, g_{\mu\nu}(\vec{q}_i)\dot{q_{(i)}}^\mu \dot{q_{(i)}}^\nu \quad , \tag{8.iv:7}$$

and a field contribution,

$$\mathcal{L}_\phi = -(\mathcal{H}_\phi + \mathcal{H}_{p\phi}) \quad . \tag{8.iv:8}$$

The field equation of motion is,

$$\frac{\partial}{\partial q^\mu}\left[\frac{\partial(\mathcal{L}_\phi\sqrt{g})}{\partial\phi_{,\mu}}\right] = \frac{\partial[\mathcal{L}_\phi\sqrt{g}]}{\partial\phi} \quad , \tag{8.iv:9}$$

which reduces to Helmholtz equation,

$$(-\Delta + \alpha^2)\phi = \epsilon_d\rho \quad , \tag{8.iv:10}$$

whose solution may be written in terms of its Green function G, as follows,

$$\phi(\vec{q}_0) = \int G(d_{01})\rho(\vec{q}_1)\sqrt{g}\, d\vec{q}_1 \quad . \tag{8.iv:11}$$

In appendix H we give a collection of Green functions for the Euclidean spaces of dimension $d \leq 3$ and for some simple Riemannian manifolds of dimension $d = 2$ and $d = 3$.

Performing an integration by parts and neglecting the "surface" contribution of the field at infinity (when such "surface" does not reduce to a "point" as in finite manifolds) we can rewrite the energy density of the Yukawa fluid as,

$$\begin{aligned} (\mathcal{H}_\phi + \mathcal{H}_{p\phi})\sqrt{g} &= \frac{1}{2\epsilon_d}[g^{\mu\nu}\phi_{,\mu}\phi_{,\nu} + \alpha^2\phi^2]\sqrt{g} \\ &\quad \frac{1}{2}\,\rho\,\phi\,\sqrt{g} \quad . \end{aligned} \tag{8.iv:12}$$

The total stress tensor is,

$$T_{\mu\nu} = -\frac{2}{\sqrt{g}}\frac{\delta[\mathcal{L}\sqrt{g}]}{\delta g^{\mu\nu}} = (T_p)_{\mu\nu} + (T_\phi)_{\mu\nu} \quad . \tag{8.iv:13}$$

It has a particle contribution,

$$(T_p)_{\mu\nu} = -\sum_i \rho_i \frac{p_{(i)_\mu}}{m}\frac{p_{(i)_\nu}}{m} \quad , \tag{8.iv:14}$$

and a field contribution,

$$\begin{aligned} (T_\phi)_{\mu\nu} &= -2\frac{\delta\mathcal{L}_\phi}{\delta g^{\mu\nu}} + g_{\mu\nu}\mathcal{L}_\phi \\ &= \frac{1}{\epsilon_d}[\phi_{,\mu}\phi_{,\nu} - \frac{1}{2}g_{\mu\nu}(\phi^{,\gamma}\phi_{,\gamma} + \alpha^2\phi^2)] \quad . \end{aligned} \tag{8.iv:15}$$

The mass current density of particle i is,

$$J_{i_\mu} = \rho_i \frac{{p_{(i)}}_\mu}{m} \quad . \tag{8.iv:16}$$

From the conservation of the mass of a particle (${J_{i_\mu}}_;^{i_\mu} = 0$, where the semicolon stands for covariant derivative), the equation of motion of the particles, and the equation of motion of the field, follows the conservation of the stress tensor (${T_{\mu\nu}}_;^{\nu} = 0$).

The Maxwell tensor pressure of the Yukawa fluid is given by,

$$\begin{aligned} P^{(\theta)} &= -\langle T^{11}\rangle_{\mathcal{R}} & (8.iv:17)\\ &= -\frac{1}{d}\langle T^{\mu\mu}\rangle_{\mathcal{R}} \quad , & (8.iv:18)\end{aligned}$$

where as in the previous sections $\langle \ldots \rangle_{\mathcal{R}}$ stands for the grand-canonical average and fluid isotropy was used in the last equality. The particle contribution to the pressure is,

$$\begin{aligned} P_p^{(\theta)} &= -\langle (T_p)^{11}\rangle_{\mathcal{R}} \\ &= -\langle (T_p)^{\hat{1}\hat{1}}\rangle_{\hat{\mathcal{R}}} \\ &= \frac{2}{\beta}\langle \sum_i \frac{\hat{\rho}_i}{m}\left[\frac{\beta}{2m}(p_{(i)\hat{1}})^2\right]\rangle_{\hat{\mathcal{R}}} \quad , \end{aligned}$$

where in the second equality we changed coordinate basis on $\mathcal{R}^N$: from the coordinate basis $\{\vec{e}_{i_\mu}\}$ to the non-coordinate orthonormal reference frame $\{\vec{e}_{i_{\hat{\mu}}}\}$, defined by,

$$\vec{e}_{i_{\hat{\mu}}} = {L^{i_\mu}}_{i_{\hat{\mu}}}\vec{e}_{i_\mu} \tag{8.iv:19}$$

where the transition matrix satisfies,

$$g^{i_\mu i_\nu}{L^{i_{\hat{\mu}}}}_{i_\mu}{L^{i_{\hat{\nu}}}}_{i_\nu} = g^{i_{\hat{\mu}} i_{\hat{\nu}}} \quad ,$$

with $g^{i_{\hat{\mu}} i_{\hat{\nu}}} = \delta_{i_{\hat{\mu}} i_{\hat{\nu}}}$. We denoted with $\langle \ldots \rangle_{\hat{\mathcal{R}}}$ the grand-canonical average using the new phase space coordinates,

$$\begin{cases} {q_{(i)}}^{\hat{\mu}} = {L^{i_{\hat{\mu}}}}_{i_\mu}{q_{(i)}}^{\mu} \\ {p_{(i)}}_{\hat{\mu}} = {L^{i_\mu}}_{i_{\hat{\mu}}}{p_{(i)}}_{\mu} \end{cases} \quad ,$$

and with $\hat{\rho}_i$ the mass density in the local orthonormal frame. Carrying out the integration over the momenta we find,

$$P_p^{(\theta)} = \frac{1}{\beta}\langle \sum_i \frac{\hat{\rho}_i}{m}\rangle_{\hat{\mathcal{R}}} \quad .$$

Switching back to the original coordinate basis yields,

$$\begin{aligned} P_p^{(\theta)} &= \frac{1}{\beta}\langle \sum_i \delta(\vec{q} - \vec{q}_i)/\sqrt{g}\rangle_{\mathcal{R}} \\ &= \frac{n}{\beta} \quad . & (8.iv:20)\end{aligned}$$

We see then that the field contribution to the pressure turns out to be the excess pressure over the one of the ideal fluid. Making use of the rotational symmetry of the fluid, the excess pressure may be written as,

$$\begin{aligned} P_\phi^{(\theta)} &= -\frac{1}{d}\langle (T_\phi)^{\mu\mu}\rangle_{\mathcal{R}} \\ &= -\frac{1}{d}\langle (T_\phi)^{\hat{\mu}\hat{\mu}}\rangle_{\hat{\mathcal{R}}} \\ &= -\frac{1}{d}\frac{1}{\epsilon_d}\langle \phi_{,\hat{\mu}}\phi_{,\hat{\mu}} - \frac{d}{2}(\phi_{,\hat{\mu}}\phi_{,\hat{\mu}} + \alpha^2\phi^2)\rangle_{\hat{\mathcal{R}}} \\ &= \frac{1}{\epsilon_d}\langle \phi_{,\mu}\phi_{,\mu}(1/2 - 1/d) + \alpha^2\phi^2/2)\rangle_{\mathcal{R}} \quad . \end{aligned} \tag{8.iv:21}$$

In particular for a two dimensional manifold we have,

$$P_\phi^{(\theta)} = \frac{\alpha^2}{4\pi}\langle \phi^2\rangle_{\mathcal{R}} \quad . \tag{8.iv:22}$$

Using equation (8.iv:11) we find,

$$P_\phi^{(\theta)} = \frac{\alpha^2}{4\pi}\langle [q\sum_i G(d_{0i}) - nqI_G][q\sum_j G(d_{0j}) - nqI_G]\rangle_{\mathcal{R}} \quad , \tag{8.iv:23}$$

where $I_G = \int G(d_{01})\, dS_1$. The homogeneity and isotropy of the fluid allows us to rewrite the excess pressure as sum of two terms,

$$P_\phi^{(\theta)} = P_{self}^{(\theta)} + P_{non-self}^{(\theta)} \quad , \tag{8.iv:24}$$

where the *self* term is,

$$P_{self}^{(\theta)} = \lim_{\bar{d}\to 0}[P_0^{(\theta)}(\bar{d}) + P_1^{(\theta)}(\bar{d})] \quad , \tag{8.iv:25}$$

$$P_0^{(\theta)}(\bar{d}) = \text{regularized term (see next subsection)} \quad , \tag{8.iv:26}$$

$$P_1^{(\theta)}(\bar{d}) = \frac{\alpha^2}{4\pi}nq^2\int_{d_{01}>\bar{d}} G^2(d_{01})\, dS_1 \quad , \tag{8.iv:27}$$

and the *non-self* term is,

$$P_{non-self}^{(\theta)} = \frac{\alpha^2}{4\pi}n^2q^2\int G(d_{01})G(d_{02})h(d_{12})\, dS_1 dS_2 \quad . \tag{8.iv:28}$$

where $h = g - 1$ is the pair correlation function.

iv.1 Calculation of the self part of the excess pressure

In the calculation of the self part of the excess pressure care is needed in neglecting the force that each particle exerts on itself [118]. Such contribution is responsible for the divergence of the self part of the excess pressure at small geodesic distances from the origin when one calculates it, for example, on the $q^1 = 0$ "surface" (without taking advantage of the rotational symmetry of the fluid, i.e. from equation (8.iv:17) instead of equation (8.iv:18)). In order to cure such divergence one can employ the prescription described in equation (8.iv:25): split $P_{self}^{(\theta)}$ into the

contributions $P_0^{(\theta)}$ of geodesic distance from the origin $d_{01} < \bar{d}$ and $P_1^{(\theta)}$ of geodesic distance from the origin $d_{01} > \bar{d}$, and let $\bar{d} \to 0$ in the end. Now $P_1^{(\theta)}$ is convergent and can be computed using the rotational symmetry as shown in equation (8.iv:27). For a pseudosphere one finds [124],

$$\begin{aligned} P_1^{(\theta)} = \lim_{\bar{d}\to 0} P_1^{(\theta)}(\bar{d}) &= \frac{\alpha^2}{4\pi} nq^2\, 2\pi a^2 \int_1^\infty Q_\nu^2(y)\, dy \\ &= \frac{(a\alpha)^2}{2} nq^2 \frac{\psi'(\nu+1)}{2\nu+1} \quad , \end{aligned} \tag{8.iv:29}$$

where ψ is the psi function (the logarithmic derivative of the gamma function). $P_0^{(\theta)}$ must be regularized by the prescription that no particle sits on the $q^1 = 0$ "surface". This can be realized by removing from the integration domain a thin slab $|q^1| < \varepsilon$ and taking the limit $\varepsilon \to 0$ afterwards,

$$\begin{aligned} P_0^{(\theta)} &= -\frac{nq^2}{\epsilon_2} \lim_{\varepsilon\to 0} \int_{\substack{d_{01}<\bar{d} \\ |q^1|>\varepsilon}} dS_1 \left\{ {G_{,1}}^2(d_{01}) - \frac{1}{2}[G_{,\mu}(d_{01}) G_{,\mu}(d_{01}) + \alpha^2 G^2(d_{01})] \right\} \\ &= -\frac{nq^2}{2\epsilon_2} \lim_{\varepsilon\to 0} \int_{\substack{d_{01}<\bar{d} \\ |q^1|>\varepsilon}} dS_1 [{G_{,1}}^2(d_{01}) - {G_{,2}}^2(d_{01})] \quad , \end{aligned} \tag{8.iv:30}$$

where in the last equality we kept just the divergent part of the integrand. Since $\bar{d}$ can be taken arbitrarily small, the regularized $P_0^{(\theta)}$ can be computed using the small d form of $G(d)$, which is just the Coulomb potential in $\mathbb{R}^2$,

$$\begin{aligned} & d \longrightarrow r = \sqrt{x^2+y^2} \quad , \\ & G(d) \longrightarrow G(r) = -\ln r + \text{constant} \quad . \end{aligned}$$

We then find for $P_0^{(\theta)}$,

$$P_0^{(\theta)}(\bar{d}) = -\frac{nq^2}{2\epsilon_2} \lim_{\varepsilon\to 0} \int_{\varepsilon<|x|<\bar{d}} dx \int_{-\sqrt{\bar{d}^2-x^2}}^{\sqrt{\bar{d}^2-x^2}} dy \frac{x^2-y^2}{(x^2+y^2)^2} = -\frac{nq^2}{4} \quad .$$

We finally find for the self part of the excess pressure of the Yukawa fluid on the pseudosphere,

$$P_{self}^{(\theta)} = -\frac{nq^2}{4} + \frac{(a\alpha)^2}{2} nq^2 \frac{\psi'(\nu+1)}{2\nu+1} \tag{8.iv:31}$$

iv.2 Calculation of the non-self part of the excess pressure

First note that since the integrand in (8.iv:28) depends only on the shape of the geodesic triangle $(0,1,2)$, the integration can be performed on another pair of positions $(0,2)$ rather than $(1,2)$.

$$P_{non-self}^{(\theta)} = \frac{\alpha^2}{4\pi} n^2 q^2 \int \left[\int G(d_{01}) G(d_{02})\, dS_0 \right] h(d_{12})\, dS_2 \quad . \tag{8.iv:32}$$

Using Dirac notation,

$$G(d_{ij}) = \left\langle i \left| \frac{\epsilon_2}{-\Delta + \alpha^2} \right| j \right\rangle \quad ,$$

where i, j are positions, gives for the integral on 0 in (8.iv:32),

$$\begin{aligned}\int G(d_{01})G(d_{02})\,dS_0 &= \int dS_0 \left\langle 1 \left| \frac{\epsilon_2}{-\Delta+\alpha^2} \right| 0 \right\rangle \left\langle 0 \left| \frac{\epsilon_2}{-\Delta+\alpha^2} \right| 2 \right\rangle \\ &= \left\langle 1 \left| \frac{(\epsilon_2)^2}{(-\Delta+\alpha^2)^2} \right| 2 \right\rangle \\ &= -\epsilon_2 \frac{\partial G(d_{12})}{\partial \alpha^2} \quad .\end{aligned}$$

Thus equation (8.iv:32) becomes,

$$P^{(\theta)}_{non-self} = -\frac{n^2q^2}{4} \int \alpha \frac{\partial G(d_{12})}{\partial \alpha} h(d_{12})\,dS_2 \quad .$$

Restricting ourselves to the pseudosphere case, since G depends on α only through the combination $(a\alpha)$ we find,

$$P^{(\theta)}_{non-self} = -\frac{n^2q^2}{4} \int a \frac{\partial G(\tau)}{\partial a} h(\tau)\,dS \quad . \tag{8.iv:33}$$

iv.3 The Coulomb limit on the pseudosphere

The Yukawa interaction is a screened Coulomb interaction. In the limit of an infinite screening length $1/\alpha$, the Yukawa interaction reduces to the Coulomb potential. As $\alpha \to 0$, $\nu \to 0$, $G(\tau) \to Q_0(\cosh\tau) = -\ln(\tanh\tau/2)$, and $a\partial G/\partial a \to 0$. Thus,

$$P^{(\theta)}_{non-self} = 0 \quad , \tag{8.iv:34}$$

Moreover since $\psi'(1) = \pi^2/6$ is finite,

$$P^{(\theta)}_{self} = -\frac{nq^2}{4} \quad . \tag{8.iv:35}$$

We find then that the excess pressure entirely comes from the self part,

$$P^{(\theta)}_{\phi} = P^{(\theta)}_{self} = -\frac{nq^2}{4} \quad . \tag{8.iv:36}$$

iv.4 Range of validity of the equation of state

It has been shown by Jancovici [119] that the same equation of state (8.iv:36) holds for the plasma on the plane, the sphere, and the pseudosphere.

More generally we can state that such equation of state holds on any surface with the following property,

$$\lim_{\alpha\to 0} \left\{ \int G^2(d_{01})\,dS_1 - 2\pi n \int \frac{\partial G(d_{01})}{\partial \alpha^2} h(d_{01})\,dS_1 \right\} = 0 \quad , \tag{8.iv:37}$$

where G is the Green function of Helmholtz equation (H.:1), and h is the pair correlation function satisfying the following charge sum rule,

$$n \int h(d_{01})\,dS_1 = -1 \quad . \tag{8.iv:38}$$

v Exact results at $\beta q^2 = 2$

When the Coulombic coupling constant is $\beta q^2 = 2$, all the thermodynamic properties and correlation functions of the two-dimensional one-component plasma can be computed exactly in several geometries [4, 125, 126] including the pseudosphere [105]. In reference [105] the density and correlation functions in the bulk, on a pseudosphere, were computed. Here we are interested in these quantities near the boundary. In reference [105] the calculations were done for a system with a $-\ln\sinh(d/2a)$ interaction and it was shown that this interaction gives the same results as the real Coulomb interaction $-\ln\tanh(d/2a)$, as far as the bulk properties are concerned. The argument in favor of this equivalence no longer holds for the density and other quantities near the boundary; therefore we shall concentrate on the real Coulomb system with a $-\ln\tanh(d/2a)$ interaction. This system was briefly considered in the Appendix of reference [105]. For the sake of completeness, we revisit here the reduction of the statistical mechanics problem to the study of a certain operator.

v.1 The grand potential

Working with the set of coordinates (r, φ) on the pseudosphere (the Poincaré disk representation), the particle i-particle j interaction term in the Hamiltonian can be written as [105]

$$v(d_{ij}) = -\ln\tanh(d_{ij}/2a) = -\ln\left|\frac{(z_i - z_j)/(2a)}{1 - (z_i\bar{z}_j/4a^2)}\right| \tag{8.v:1}$$

where $z_j = r_j e^{i\varphi_j}$ and $\bar{z}_j$ is the complex conjugate of z_j. This interaction (8.v:1) happens to be the Coulomb interaction in a flat disc of radius $2a$ with ideal conductor walls. Therefore, it is possible to use the techniques which have been developed [127, 128] for dealing with ideal conductor walls, in the grand canonical ensemble.

The grand canonical partition function of the OCP at fugacity ζ with a fixed background density n_b, when $\beta q^2 = 2$, is

$$\Xi = C_0\left[1 + \sum_{N=1}^{\infty}\frac{1}{N!}\int\prod_{i=1}^{N}\frac{r_i dr_i d\varphi_i}{[1-(r_i^2/4a^2)]}\prod_{i<j}\left|\frac{(z_i - z_j)/(2a)}{1 - (z_i\bar{z}_j/4a^2)}\right|^2\prod_{i=1}^{N}\zeta(r_i)\right] \tag{8.v:2}$$

where for $N = 1$ the product $\prod_{i<j}$ must be replaced by 1. We have defined a position-dependent fugacity $\zeta(r) = \zeta[1 - r^2/(4a^2)]^{4\pi n_b a^2 - 1}e^C$ which includes the particle-background interaction (8.i:22) and only one factor $[1 - r^2/(4a^2)]^{-1}$ from the integration measure $dS = [1 - r^2/(4a^2)]^{-2}\, d\mathbf{r}$. This should prove to be convenient later. The e^C factor is

$$e^C = \exp\left[4\pi n_b a^2\left(\ln\cosh^2\frac{\tau_0}{2} - \sinh^2\frac{\tau_0}{2}\ln\tanh^2\frac{\tau_0}{2}\right)\right] \tag{8.v:3}$$

which is a constant term coming from the particle-background interaction term (8.i:22) and

$$\ln C_0 = \frac{(4\pi n_b a^2)^2}{2}\left[\ln\cosh^2\frac{\tau_0}{2} + \sinh^2\frac{\tau_0}{2}\left(\sinh^2\frac{\tau_0}{2}\ln\tanh^2\frac{\tau_0}{2} - 1\right)\right] \tag{8.v:4}$$

which comes from the background-background interaction (8.i:23). Notice that for large domains, when $\tau_0 \to \infty$, we have

$$e^C \sim \left[\frac{e^{\tau_0+1}}{4}\right]^{4\pi n_b a^2} \tag{8.v:5}$$

and

$$\ln C_0 \sim -\frac{(4\pi n_b a^2)^2 e^{\tau_0}}{4} \tag{8.v:6}$$

Let us define a set of reduced complex coordinates $u_i = (z_i/2a)$ inside the Poincaré disk and its corresponding images $u_i^* = (2a/\bar{z}_i)$ outside the disk. By using Cauchy identity

$$\det\left(\frac{1}{u_i - u_j^*}\right)_{(i,j)\in\{1,\cdots,N\}^2} = (-1)^{N(N-1)/2}\,\frac{\prod_{i<j}(u_i-u_j)(u_i^*-u_j^*)}{\prod_{i,j}(u_i-u_j^*)} \tag{8.v:7}$$

the particle-particle interaction term together with the $[1-(r_i^2/4a^2)]^{-1}$ other term from the integration measure can be cast into the form

$$\prod_{i<j}\left|\frac{(z_i-z_j)/(2a)}{1-(z_i\bar{z}_j/4a^2)}\right|^2 \prod_{i=1}^{N}[1-(r_i^2/4a^2)]^{-1} = \det\left(\frac{1}{1-u_i\bar{u}_j}\right)_{(i,j)\in\{1,\cdots,N\}^2} \tag{8.v:8}$$

The grand canonical partition function then is

$$\Xi = \left[1+\sum_{N=1}^{\infty}\frac{1}{N!}\int\prod_{i=1}^{N}d^2\mathbf{r}_i\prod_{i=1}^{N}\zeta(r_i)\det\left(\frac{1}{1-u_i\bar{u}_j}\right)\right]C_0 \tag{8.v:9}$$

We shall now show that this expression can be reduced to an infinite continuous determinant, by using a functional integral representation similar to the one which has been developed for the two-component Coulomb gas [21]. Let us consider the Gaussian partition function

$$Z_0 = \int \mathcal{D}\psi\mathcal{D}\bar{\psi}\,\exp\left[\int\bar{\psi}(\mathbf{r})M^{-1}(z,\bar{z}')\psi(\mathbf{r}')\,d^2\mathbf{r}\,d^2\mathbf{r}'\right] \tag{8.v:10}$$

The fields ψ and $\bar{\psi}$ are anticommuting Grassmann variables. The Gaussian measure in (8.v:10) is chosen such that its covariance is equal to[3]

$$\left\langle\bar{\psi}(\mathbf{r}_i)\psi(\mathbf{r}_j)\right\rangle = M(z_i,\bar{z}_j) = \frac{1}{1-u_i\bar{u}_j} \tag{8.v:11}$$

where $\langle\ldots\rangle$ denotes an average taken with the Gaussian weight of (8.v:10). By construction we have

$$Z_0 = \det(M^{-1}) \tag{8.v:12}$$

Let us now consider the following partition function

$$Z = \int \mathcal{D}\psi\mathcal{D}\bar{\psi}\exp\left[\int\bar{\psi}(\mathbf{r})M^{-1}(z,\bar{z}')\psi(\mathbf{r}')d^2\mathbf{r}d^2\mathbf{r}' + \int\zeta(r)\bar{\psi}(\mathbf{r})\psi(\mathbf{r})\,d^2\mathbf{r}\right] \tag{8.v:13}$$

which is equal to

$$Z = \det(M^{-1}+\zeta) \tag{8.v:14}$$

and then

$$\frac{Z}{Z_0} = \det[M(M^{-1}+\zeta)] = \det[1+K] \tag{8.v:15}$$

where

$$K(\mathbf{r},\mathbf{r}') = M(z,\bar{z}')\,\zeta(r') = \frac{\zeta(r')}{1-u\bar{u}'} \tag{8.v:16}$$

[3]Actually the operator M should be restricted to act only on analytical functions for its inverse M^{-1} to exist.

The results which follow can also be obtained by exchanging the order of the factors M and $M^{-1} + \zeta$ in (8.v:15), i.e. by replacing $\zeta(r')$ by $\zeta(r)$ in (8.v:16), however using the definition (8.v:16) of K is more convenient. Expanding the ratio Z/Z_0 in powers of ζ we have

$$\frac{Z}{Z_0} = 1 + \sum_{N=1}^{\infty} \frac{1}{N!} \int \prod_{i=1}^{N} d^2\mathbf{r}_i \prod_{i=1}^{N} \zeta(r_i) \left\langle \bar{\psi}(\mathbf{r}_1)\psi(\mathbf{r}_1) \cdots \bar{\psi}(\mathbf{r}_N)\psi(\mathbf{r}_N) \right\rangle \tag{8.v:17}$$

Now, using Wick theorem for anticommuting variables [21], we find that

$$\left\langle \bar{\psi}(\mathbf{r}_1)\psi(\mathbf{r}_1) \cdots \bar{\psi}(\mathbf{r}_N)\psi(\mathbf{r}_N) \right\rangle = \det M(z_i, \bar{z}_j) = \det\left(\frac{1}{1 - u_i \bar{u}_j}\right) \tag{8.v:18}$$

Comparing equations (8.v:17) and (8.v:9) with the help of equation (8.v:18) we conclude that

$$\Xi = C_0 \frac{Z}{Z_0} = C_0 \det(1 + K) \tag{8.v:19}$$

The problem of computing the grand canonical partition function has been reduced to finding the eigenvalues of the operator K. The eigenvalue problem for K reads

$$\int \zeta e^C \frac{\left(1 - \dfrac{r'^2}{4a^2}\right)^{4\pi n_b a^2 - 1}}{1 - \dfrac{z\bar{z}'}{4a^2}} \Phi(\mathbf{r}')\, r'\, dr' d\varphi' = \lambda \Phi(\mathbf{r}) \tag{8.v:20}$$

For $\lambda \neq 0$ we notice from equation (8.v:20) that $\Phi(\mathbf{r}) = \Phi(z)$ is an analytical function of z. Because of the circular symmetry it is natural to try $\Phi(z) = \Phi_\ell(z) = z^\ell = r^\ell e^{i\ell\varphi}$ with ℓ a positive integer. Expanding

$$\frac{1}{1 - \dfrac{z\bar{z}'}{4a^2}} = \sum_{n=0}^{\infty} \left(\frac{z\bar{z}'}{4a^2}\right)^n \tag{8.v:21}$$

and replacing $\Phi_\ell(z) = z^\ell$ in equation (8.v:20) one can show that Φ_ℓ is actually an eigenfunction of K with eigenvalue

$$\lambda_\ell = 4\pi a^2 \zeta e^C B_{t_0}(\ell + 1, 4\pi n_b a^2) \tag{8.v:22}$$

with $t_0 = r_0^2/(4a^2) = \tanh^2(\tau_0/2)$ and

$$B_{t_0}(\ell + 1, 4\pi n_b a^2) = \int_0^{t_0} (1 - t)^{4\pi n_b a^2 - 1} t^\ell \, dt \tag{8.v:23}$$

the incomplete beta function. So we finally arrive to the result for the grand potential

$$\beta\Omega = -\ln \Xi = -\ln C_0 - \sum_{\ell=0}^{\infty} \ln\left(1 + 4\pi a^2 \zeta e^C B_{t_0}(\ell + 1, 4\pi n_b a^2)\right) \tag{8.v:24}$$

with e^C and $\ln C_0$ given by equations (8.v:3) and (8.v:4). This result is valid for any disk domain of radius $a\tau_0$. Later, in Section v.3, we will derive a more explicit expression of the grand potential for large domains $\tau_0 \to \infty$.

v.2 The density

As usual one can compute the density by doing a functional derivative of the grand potential with respect to the position-dependent fugacity:

$$n^{(1)}(\mathbf{r}) = \left(1 - \frac{r^2}{4a^2}\right)^2 \zeta(r) \frac{\delta \ln \Xi}{\delta \zeta(r)} \tag{8.v:25}$$

The factor $[1-(r^2/4a^2)]^2$ is due to the curvature [105], so that $n^{(1)}(\mathbf{r})\, dS$ is the average number of particles in the surface element $dS = [1-(r^2/4a^2)]^{-2}\, d\mathbf{r}$. Using a Dirac-like notation, one can formally write

$$\ln \Xi = \mathrm{Tr} \ln(1+K) + \ln C_0 = \int \langle \mathbf{r} \left| \ln(1 + \zeta(r) M) \right| \mathbf{r} \rangle \; d\mathbf{r} + \ln C_0 \tag{8.v:26}$$

Then, doing the functional derivative (8.v:25), one obtains

$$n^{(1)}(\mathbf{r}) = \left(1 - \frac{r^2}{4a^2}\right)^2 \zeta(r) \left\langle \mathbf{r} \left| (1+K)^{-1} M \right| \mathbf{r} \right\rangle = 4\pi a \left(1 - \frac{r^2}{4a^2}\right)^2 \zeta(r) \tilde{G}(\mathbf{r}, \mathbf{r}) \tag{8.v:27}$$

where we have defined $\tilde{G}(\mathbf{r}, \mathbf{r}')$ by[4] $\tilde{G} = (1+K)^{-1} M/(4\pi a)$. More explicitly, $\tilde{G}$ is the solution of $(1+K)\tilde{G} = M/(4\pi a)$, that is

$$\tilde{G}(\mathbf{r}, \mathbf{r}') + \zeta e^C \int \tilde{G}(\mathbf{r}'', \mathbf{r}') \frac{\left(1 - \dfrac{r''^2}{4a^2}\right)^{4\pi n_b a^2 - 1}}{1 - \dfrac{z\bar{z}''}{4a^2}} \, d\mathbf{r}'' = \frac{1}{4\pi a \left[1 - \dfrac{z\bar{z}'}{4a^2}\right]} \tag{8.v:28}$$

and the density is given by

$$n^{(1)}(\mathbf{r}) = 4\pi a \zeta e^C \left(1 - \frac{r^2}{4a^2}\right)^{4\pi n_b a^2 + 1} \tilde{G}(\mathbf{r}, \mathbf{r}) \tag{8.v:29}$$

From the integral equation (8.v:28) one can see that $\tilde{G}(\mathbf{r}, \mathbf{r}')$ is an analytical function of z. Trying a solution of the form

$$\tilde{G}(\mathbf{r}, \mathbf{r}') = \sum_{\ell=0}^{\infty} a_\ell(\mathbf{r}') z^\ell \tag{8.v:30}$$

into equation (8.v:28) yields

$$\tilde{G}(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi a} \sum_{\ell=0}^{\infty} \left(\frac{z\bar{z}'}{4a^2}\right)^\ell \frac{1}{1 + 4\pi a^2 \zeta e^C B_{t_0}(\ell+1, 4\pi n_b a^2)} \tag{8.v:31}$$

Then the density is given by

$$n^{(1)}(r) = \zeta e^C \left(1 - \frac{r^2}{4a^2}\right)^{4\pi n_b a^2 + 1} \sum_{\ell=0}^{\infty} \left(\frac{r^2}{4a^2}\right)^\ell \frac{1}{1 + 4\pi a^2 \zeta e^C B_{t_0}(\ell+1, 4\pi n_b a^2)} \tag{8.v:32}$$

[4] the factor $4\pi a$ is there just to keep the same notations as in reference [105].

After some calculation (see Appendix K), it can be shown that, in the limit $a \to \infty$, the result for the flat disk in the canonical ensemble [104]

$$\frac{n^{(1)}(r)}{n_b} = \exp(-\pi n_b r^2) \sum_{\ell=0}^{N_b-1} \frac{(\pi n_b r^2)^\ell}{\gamma(\ell+1,\, N_b)} \tag{8.v:33}$$

is recovered. up to a correction due to the non-equivalence of ensembles in finite systems. In (8.v:33), γ is the incomplete gamma function

$$\gamma(\ell+1,\, x) = \int_0^x t^\ell e^{-t} dt \tag{8.v:34}$$

In that flat-disk case, in the thermodynamic limit (half-space), $n^{(1)}(r_0) = n_{\text{contact}} \to n_b \ln 2$.

v.3 Large domains

We are now interested in large domains $\tau_0 \to \infty$. In this thermodynamic limit we will show that the sums in equations (8.v:24) and (8.v:32) can be replaced by integrals. For pedagogical reasons we will first consider the case $4\pi n_b a^2 = 1$ in which the calculations are simpler, and afterwards deal with the general case.

v.3.1 The case $4\pi n_b a^2 = 1$

In this case the incomplete beta function that appears in equations (8.v:24) and (8.v:32) simply is

$$B_{t_0}(\ell+1, 1) = \frac{t_0^{\ell+1}}{\ell+1} = \frac{[\tanh^2(\tau_0/2)]^{\ell+1}}{\ell+1} \tag{8.v:35}$$

When $\tau_0 \to \infty$ we have

$$B_{t_0}(\ell+1, 1) \sim \frac{\exp(-4(\ell+1)e^{-\tau_0})}{\ell+1} \tag{8.v:36}$$

Then the sum appearing in the grand potential (8.v:24) takes the form

$$\sum_{\ell=0}^{\infty} \ln\left(1 + \frac{\zeta e}{n_b} \frac{\exp(-4(\ell+1)e^{-\tau_0})}{4(\ell+1)e^{-\tau_0}}\right) \tag{8.v:37}$$

where we have used the asymptotic expression (8.v:5) for e^C. This sum can be seen as a Riemann sum for the variable $x = 4(\ell+1)e^{-\tau_0}$. Indeed, for large values of τ_0, the variable x varies in small steps $dx = 4e^{-\tau_0}$. The sum (8.v:37) then converges, when $\tau_0 \to \infty$, to the integral

$$\int_0^\infty \ln\left(1 + \frac{\zeta e}{n_b} \frac{e^{-x}}{x}\right) \frac{dx}{4e^{-\tau_0}} \tag{8.v:38}$$

This expression together with equation (8.v:6) for the constant $\ln C_0$ gives the grand potential in the thermodynamic limit $\tau_0 \to \infty$

$$\beta\Omega \sim -\frac{e^{\tau_0}}{4}\left[\int_0^\infty \ln\left(1 + \frac{\zeta e}{n_b} \frac{e^{-x}}{x}\right) dx - 1\right] \tag{8.v:39}$$

We notice that the grand potential is extensive as expected. The area of the system being $\mathcal{A} = 4\pi a^2 \sinh^2(\tau_0/2) \simeq \pi a^2 e^{\tau_0}$, we find that the grand potential per unit area $\omega = \Omega/\mathcal{A}$ is given by

$$\beta\omega = -n_b\left[\int_0^\infty \ln\left(1 + \frac{\zeta e}{n_b} \frac{e^{-x}}{x}\right) dx - 1\right] \tag{8.v:40}$$

Similar calculations lead from equation (8.v:32) to the density $n^{(1)}(\sigma)$ near the boundary as a function of the distance from that boundary $a\sigma = a(\tau_0 - \tau)$,

$$n^{(1)}(\sigma) = \zeta e\, e^{2\sigma} \int_0^\infty \frac{e^{-xe^\sigma}}{1 + \dfrac{\zeta e}{n_b}\dfrac{e^{-x}}{x}}\, dx \tag{8.v:41}$$

After the change of variable $xe^\sigma \to x$, this can be written as

$$\frac{n^{(1)}(\sigma)}{n_b} = \int_0^\infty \frac{xe^{-x}\, dx}{\dfrac{xe^{-\sigma}}{(\zeta e/n_b)} + e^{-xe^{-\sigma}}} \tag{8.v:42}$$

The average density $n = N/\mathcal{A}$ can be obtained integrating the density profile (8.v:42) or by using the thermodynamic relation $N = -\beta\zeta(\partial\Omega/\partial\zeta)$. We find

$$\frac{n}{n_b} = \int_0^\infty \frac{e^{-x}\, dx}{\dfrac{x}{(\zeta e/n_b)} + e^{-x}} \tag{8.v:43}$$

v.3.2 The general case

With the case $4\pi n_b a^2 = 1$ we have illustrated the general procedure for computing the thermodynamic limit. Now we proceed to compute it in the more general case where $4\pi n_b a^2$ has any positive value. To simplify the notations let us define $\alpha = 4\pi n_b a^2$. The main difficulty is to find a suitable asymptotic expression of the incomplete beta function

$$B_{t_0}(\ell + 1, \alpha) = \int_0^{t_0} (1-t)^{\alpha-1} t^\ell\, dt \tag{8.v:44}$$

when $t_0 \to 1$ which is valid for large ℓ. As we have noticed in the previous section the main contribution from the sum in ℓ that appears in the grand potential comes from large values of ℓ which are of order e^{τ_0}. For these values of ℓ the integrand in the definition of the beta function $(1-t)^{\alpha-1}t^\ell$ is very peaked around $t = t_0$ and decays very fast when $t \to 0$. So the main contribution to the incomplete beta function comes from values of t near t_0. It is then natural to do the change of variable in the integral $t = t_0 - v$ where with the new variable v the integral is mainly dominated by small values of v. Then we have

$$B_{t_0}(\ell + 1, \alpha) = \int_0^{t_0} (1 - t_0 + v)^{\alpha-1} e^{\ell \ln(t_0 - v)}\, dv \tag{8.v:45}$$

Replacing t_0 by its asymptotic value $t_0 \sim 1 - 4e^{-\tau_0}$ and taking into account that v is small (of order $e^{-\tau_0}$), we find, at first order in $e^{-\tau_0}$,

$$B_{t_0}(\ell + 1, \alpha) \sim \frac{1}{\ell^\alpha}\, \Gamma(\alpha, x) \tag{8.v:46}$$

where we have introduced once more the variable $x = 4\ell e^{-\tau_0}$ (at first order in $e^{-\tau_0}$ it is the same variable $x = 4(\ell+1)e^{-\tau_0}$ introduced in the case $\alpha = 1$) and

$$\Gamma(\alpha, x) = \int_x^\infty y^{\alpha-1} e^{-y}\, dy \tag{8.v:47}$$

is an incomplete gamma function. With this result and equation (8.v:5) the term $e^C B_{t_0}(\ell+1,\alpha)$ in the expressions (8.v:24) and (8.v:32) appears as a function of the continuous variable $x = 4\ell e^{-\tau_0}$

$$e^C B_{t_0}(\ell+1,\alpha) \sim e^\alpha \, \frac{\Gamma(\alpha,x)}{x^\alpha} \tag{8.v:48}$$

With this result we can replace the sums for ℓ in equations (8.v:24) and (8.v:32) by integrals over the variable x and we find the following expressions for the grand potential per unit area

$$\beta\omega = \frac{1}{4\pi a^2}\left\{(4\pi n_b a^2)^2 - \int_0^\infty \ln\left[1 + 4\pi a^2 \zeta e^{4\pi n_b a^2} \frac{\Gamma(4\pi n_b a^2, x)}{x^{4\pi n_b a^2}}\right] dx\right\} \tag{8.v:49}$$

and the density

$$n^{(1)}(\sigma) = \zeta e^{4\pi n_b a^2} e^{(4\pi n_b a^2+1)\sigma} \int_0^\infty \frac{e^{-xe^\sigma}\ dx}{1 + 4\pi a^2 \zeta e^{4\pi n_b a^2} \dfrac{\Gamma(4\pi n_b a^2, x)}{x^{4\pi n_b a^2}}} \tag{8.v:50}$$

In particular the contact value of the density, that is when $\sigma = 0$, is

$$n_{\text{contact}} = n^{(1)}(0) = \zeta e^{4\pi n_b a^2} \int_0^\infty \frac{e^{-x}\ dx}{1 + 4\pi a^2 \zeta e^{4\pi n_b a^2} \dfrac{\Gamma(4\pi n_b a^2, x)}{x^{4\pi n_b a^2}}} \tag{8.v:51}$$

After some calculation (see Appendix K), it can be shown that, in the limit $a \to \infty$, the result for the flat disk in the thermodynamic limit $n_{\text{contact}} = n_b \ln 2$ is again recovered.

An alternative expression for the density which we will also use is obtained by doing the change of variable $xe^\sigma \to x$ and introducing again $\alpha = 4\pi n_b a^2$

$$\frac{n^{(1)}(\sigma)}{n_b} = \int_0^\infty \frac{x^\alpha e^{-x}\ dx}{\dfrac{x^\alpha e^{-\alpha\sigma}}{(\zeta e^\alpha / n_b)} + \alpha\Gamma(\alpha, xe^{-\sigma})} \tag{8.v:52}$$

From this expression it can be seen that in the bulk, when $\sigma \to \infty$ and $e^{-\sigma} \to 0$, the density is equal to the background density, $n^{(1)}(\sigma) \to n_b$. The system is neutral in the bulk. The excess charge, which is controlled by the fugacity ζ, concentrates as usual on the boundary.

The average total number of particles N and the average density $n = N/\mathcal{A}$ can be computed either by using the thermodynamic relation

$$N = -\beta\zeta \frac{\partial\Omega}{\partial\zeta} \tag{8.v:53}$$

or by integrating the density profile (8.v:50)

$$N = \int_{\tau<\tau_0} n^{(1)}(\sigma)\, dS = \pi a^2 e^{\tau_0} \int_0^\infty n^{(1)}(\sigma)\, e^{-\sigma}\, d\sigma \tag{8.v:54}$$

The two methods yield the same result, as expected,

$$n = \frac{N}{\mathcal{A}} = \zeta e^{4\pi n_b a^2} \int_0^\infty \frac{\Gamma(4\pi n_b a^2, x)\, dx}{x^{4\pi n_b a^2} + 4\pi a^2 \zeta e^{4\pi n_b a^2} \Gamma(4\pi n_b a^2, x)} \tag{8.v:55}$$

The ratio of the average density and the background density can be put in the form

$$\frac{n}{n_b} = \int_0^\infty \frac{\Gamma(\alpha, x)\, dx}{\dfrac{x^\alpha}{(\zeta e^\alpha / n_b)} + \alpha\Gamma(\alpha, x)} \tag{8.v:56}$$

As seen on equations (8.v:52) and (8.v:56) the density profile $n^{(1)}(\sigma)$ and the average density n are functions of the parameter $g = \zeta e^{4\pi n_b a^2}/n_b$. Different values of this parameter g give different density profiles and mean densities. Depending on the value of g the system can be globally positive, negative or neutral. From equation (8.v:56) it can be seen that the average density is a monotonous increasing function of the fugacity, as it should be. Therefore there is one unique value of the fugacity for which the system is globally neutral. For the case $4\pi n_b a^2 = 1$, we have determined numerically the value of g needed for the system to be neutral, $n = n_b$. This value is $g = \zeta e/n_b = 1.80237$.

It may be noted that, in the case of a flat disk in the grand canonical ensemble, the 2D OCP remains essentially neutral (the modulus of its total charge cannot exceed one elementary charge q), whatever the fugacity ζ might be [129, 130]; this is because the Coulomb interaction $-\ln(r/L)$ becomes infinite at infinity and bringing an excess charge from a reservoir at infinity to the system already carrying a net charge would cost an infinite energy. On the contrary, in the present case of a 2D OCP on a pseudosphere, the Coulomb interaction (8.i:20) has an exponential decay at large distances, and varying the fugacity does change the total charge of the disk.

Figure 8.3 shows several plots of the density $n^{(1)}(\sigma)$ as a function of the distance σ from the boundary (in units of a), for different values of g, in the case $\alpha = 4\pi n_b a^2 = 1$. It is interesting to notice that for $g \leq 1$ the density is always an increasing function of σ. Far away from the boundary, the density approaches the background density n_b from below. On the other hand when $g > 1$, but not too large, the density profile shows an oscillation: $n^{(1)}(\sigma)$ is no longer a monotonous function of σ. Far away from the boundary, $\sigma \to \infty$, the density now approaches the background density from above. Finally, when g is large enough, the density profile is again monotonous, now a decreasing function of σ. The change of behavior as $\sigma \to \infty$ can actually be shown analytically. Let us define $u = e^{-\sigma}$. From equation (8.v:52) we have

$$\frac{\partial}{\partial u}\left(\frac{n^{(1)}(\sigma)}{n_b}\right) = \int_0^\infty \frac{\alpha x^{2\alpha} u^{\alpha-1} e^{-x-xu}}{\left(\dfrac{(xu)^\alpha}{g} + \alpha\Gamma(\alpha, xu)\right)^2}\left[1 - \frac{e^{xu}}{g}\right] dx \tag{8.v:57}$$

The first term in the integral is always positive. The second term, $1 - (e^{xu}/g)$, in the limit $\sigma \to \infty$ ($u \to 0$) is $1 - (1/g)$. If $g < 1$ it is negative, then $\partial n^{(1)}/\partial u$ is negative and $n^{(1)}(\sigma)$ is then an increasing function of σ when $\sigma \to \infty$ as it was noticed in the last paragraph.

Also, in this case $\alpha = 1$, when $\zeta \to \infty$ the density profile (8.v:42) can be computed explicitly

$$\frac{n^{(1)}(\sigma)}{n_b} = \frac{1}{(1 - e^{-\sigma})^2} \tag{8.v:58}$$

It is clearly a monotonous decreasing function of σ.

v.4 Relations between the different pressures

From the explicit expressions (8.v:49) and (8.v:52) for the grand potential and the density profile, we can check the relations between the different pressures obtained in Section iii. The

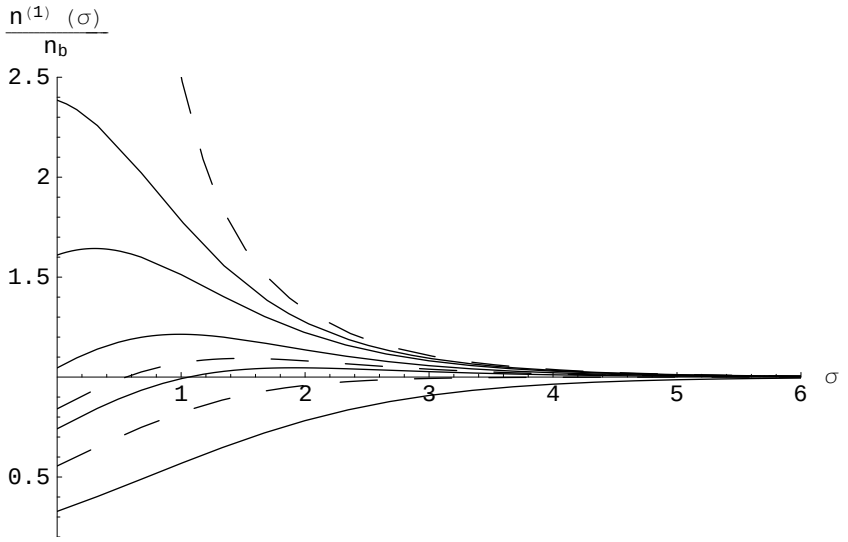

FIGURE 8.3: The density profile $n^{(1)}(\sigma)$ (in units of n_b) as a function of the distance from the boundary σ (in units of a) for different values of the parameter $g = \zeta e/n_b$ in the case $4\pi n_b a^2 = 1$. From bottom to top, in full line $g = 0.5, 1.5, 2.5, 5.0, 10.0$ and in dashed line $g = 1$ (change of behavior between monotonous increasing profile and oscillating profile), $g = 1.80237$ (globally neutral system) and $g \to \infty$.

mechanical pressure simply is $P^{(m)} = -\omega$ and it is given by equation (8.v:49). This expression can be transformed by doing an integration by parts in the integral giving

$$\beta P^{(m)} = -\frac{1}{4\pi a^2}\left\{\int_0^\infty \frac{4\pi a^2 x\zeta e^{4\pi n_b a^2}\dfrac{d}{dx}\left[\dfrac{\Gamma(4\pi n_b a^2, x)}{x^{4\pi n_b a^2}}\right]}{1 + 4\pi a^2\zeta e^{4\pi n_b a^2}\dfrac{\Gamma(4\pi n_b a^2, x)}{x^{4\pi n_b a^2}}}\, dx + (4\pi n_b a^2)^2\right\} \tag{8.v:59}$$

By the replacement

$$\frac{d}{dx}\left[\frac{\Gamma(4\pi n_b a^2, x)}{x^{4\pi n_b a^2}}\right] = -\frac{e^{-x}}{x} - 4\pi n_b a^2 \frac{\Gamma(4\pi n_b a^2, x)}{x^{4\pi n_b a^2+1}} \tag{8.v:60}$$

in equation (8.v:59), one recognizes the expressions (8.v:51) and (8.v:55) for the contact density and the average density, thus giving

$$\beta P^{(m)} = n^{(1)}(0) + 4\pi n_b a^2 (n - n_b) \tag{8.v:61}$$

which is precisely, when $\beta q^2 = 2$, the relation (8.iii:53) between the mechanical pressure $P^{(m)}$ and the kinetic pressure $P^{(k)} = (1/\beta)n^{(1)}(0)$ obtained in Section iii.

The thermal pressure is

$$P^{(t)} = -\omega(\zeta, n_b) + n_b\left(\frac{\partial\omega(\zeta, n_b)}{\partial n_b}\right)_\zeta \tag{8.v:62}$$

The last term in this equation is given by

$$\beta n_b \frac{\partial\omega}{\partial n_b} = \frac{1}{4\pi a^2}\left\{2\alpha^2 - \int_0^\infty \frac{4\pi a^2\zeta}{1 + \dfrac{4\pi a^2\zeta e^\alpha \Gamma(\alpha, x)}{x^\alpha}}\,\alpha\frac{\partial}{\partial\alpha}\left[\frac{e^\alpha\Gamma(\alpha, x)}{x^\alpha}\right] dx\right\} \tag{8.v:63}$$

Making the replacement

$$\alpha \frac{\partial}{\partial \alpha} \left[\frac{e^\alpha \Gamma(\alpha, x)}{x^\alpha} \right] = \alpha e^\alpha \left(\frac{\Gamma(\alpha, x)}{x^\alpha} + \frac{\partial}{\partial \alpha} \left[\frac{\Gamma(\alpha, x)}{x^\alpha} \right] \right) \tag{8.v:64}$$

in equation (8.v:63), one recognizes in the first term the average density n, thus obtaining

$$\beta n_b \frac{\partial \omega}{\partial n_b} = \alpha(2n_b - n) - \alpha I \tag{8.v:65}$$

where

$$I = \int_0^\infty \frac{\zeta e^\alpha}{1 + \dfrac{4\pi a^2 \zeta e^\alpha \Gamma(\alpha, x)}{x^\alpha}} \frac{\partial}{\partial \alpha} \left[\frac{\Gamma(\alpha, x)}{x^\alpha} \right] dx \tag{8.v:66}$$

So the thermal pressure is given by

$$\beta P^{(t)} = n^{(1)}(0) + \alpha n_b - \alpha I \tag{8.v:67}$$

On the other hand the integral appearing in the general relation (8.iii:56) between the thermal pressure and the kinetic pressure

$$J = \int_0^\infty (n^{(1)}(\sigma) - n_b)\, e^{-\sigma} \sigma \, d\sigma \tag{8.v:68}$$

can be split into two parts

$$J = -n_b + I' \tag{8.v:69}$$

with

$$I' = \int_0^\infty n^{(1)}(\sigma) \sigma e^{-\sigma} \, d\sigma \tag{8.v:70}$$

Using the actual integral representation for the density profile given by equation (8.v:50) yields

$$I' = \int_0^\infty \frac{\zeta e^\alpha}{1 + \dfrac{4\pi a^2 \zeta e^\alpha \Gamma(\alpha, x)}{x^\alpha}} \left\{ \int_0^\infty e^{\alpha\sigma} e^{-x e^\sigma} \sigma \, d\sigma \right\} dx \tag{8.v:71}$$

The integral over σ can be cast in the form

$$\frac{\partial}{\partial \alpha} \left[\int_0^\infty e^{\alpha\sigma} e^{-x e^\sigma} \, d\sigma \right] \tag{8.v:72}$$

By doing the change of variable $y = xe^\sigma$ one immediately recognizes the integral representation of the incomplete gamma function. The above expression is then equal to

$$\frac{\partial}{\partial \alpha} \left[\frac{\Gamma(\alpha, x)}{x^\alpha} \right] \tag{8.v:73}$$

Thus we have proven that $I' = I$ and finally we have the relation

$$\beta(P^{(t)} - P^{(k)}) = -4\pi n_b a^2 \int_0^\infty (n^{(1)}(\sigma) - n_b)\, e^{-\sigma} \sigma \, d\sigma \tag{8.v:74}$$

which is relation (8.iii:56) in the solvable case $\beta q^2 = 2$.

vi Conclusions

We have shown that a closed one component Coulomb plasma of N charges confined in a compact connected domain Ω of the pseudosphere is certainly ergodic if we switch off the Coulomb interaction amongst the particles leaving intact the Coulomb interaction amongst the particle and the background. It is left as an open problem to prove that the system remains ergodic if we switch on the mutual interaction between the particles, i.e. to show that for $q^N \in \Omega(h, \tau_0)$ the disequality (8.ii:17) with U given by (8.i:24), holds true at least in the large N (constant n) limit. If this could be proven than taking the thermodynamic limit $N \to \infty$ (keeping n constant) one would recover the Statistical Physics of the one component Coulomb plasma. Taking the limit $a \to 0$ one would recover the Statistical Physics of the flat plasma. This derivation would be alternative to the one of Sari and Merlini [131] which goes through "H-stability" and the "cheese theorem" to prove the existence of the thermodynamic limit.

In a flat space, the neighborhood of the boundary of a large domain has a volume which is a negligible fraction of the whole volume. This is why, for the statistical mechanics of ordinary fluids, usually there is a thermodynamic limit: when the volume becomes infinite, quantities such as the free energy per unit volume or the pressure have a unique limit, independent of the domain shape and of the boundary conditions. However, even in a flat space, the one-component plasma is special. For the OCP, it is possible to define several non-equivalent pressures, some of which, for instance the kinetic pressure, obviously are surface-dependent even in the infinite-system limit.

Even for ordinary fluids, statistical mechanics on a pseudosphere is expected to have special features, which are essentially related to the property that, for a large domain, the area of the neighborhood of the boundary is of the same order of magnitude as the whole area. Although some bulk properties, such as correlation functions far away from the boundary, will exist, extensive quantities such as the free energy or the grand potential are strongly dependent on the boundary neighborhood and surface effects. For instance, in the large-domain limit, no unique limit is expected for the free energy per unit area $F/\mathcal{A}$ or the pressure $-(\partial F/\partial \mathcal{A})_{\beta,N}$.

In the present chapter, we have studied the 2D OCP on a pseudosphere, for which surface effects are expected to be important for both reasons: because we are dealing with a one-component plasma and because the space is a pseudosphere. Therefore, although the correlation functions far away from the boundary have unique thermodynamic limits [105], many other properties are expected to depend on the domain shape and on the boundary conditions. This is why we have considered a special well-defined geometry: the domain is a disk bounded by a plain hard wall, and we have studied the corresponding large-disk limit. Our results have been derived only for that geometry.

We have been especially interested by different pressures which can be defined for this system. It has been shown that the virial pressure $P^{(v)}$ (defined through the virial theorem) and the kinetic pressure $P^{(k)}$ (the force per unit length that the particles alone exert on the wall) are equal to each other. We have also considered the thermal pressure $P^{(t)}$, the definition of which includes contributions from the background. It should be noted that this thermal pressure is also dependent on surface effects, since it is defined by (8.iii:24) and (8.iii:57) in terms of the free energy or the grand potential, and the corresponding partition functions include relevant contributions from the surface region. The thermal pressure is not equal to the previous ones. We have also considered the so-called mechanical pressure $P^{(m)}$ which differs from the kinetic one only for charged systems. General relations among these different pressures have been established for the finite Coulomb plasma. Using the notion that in the thermodynamic limit the one particle correlation function differs from the background density just in a neighborhood of

the boundary $\partial\Omega$ (the system tend to be electrically neutral in the bulk) we have given, whenever possible, the thermodynamic limit of the various relations found. All the above definitions of the pressure depend on the boundary conditions. A definition of a bulk pressure independent of the boundary conditions has been looked for. After an erroneous attempt [105], it has been argued [118, 119] that a bulk pressure $P^{(\theta)}$ could be defined from the Maxwell stress tensor at some point well inside the fluid. The result was

$$P^{(\theta)} = n_b \left(1 - \frac{\beta q^2}{4} \right) \quad , \tag{8.vi:1}$$

That same equation of state holds for the 2D OCP on a plane, a sphere, or a pseudosphere.

When $\beta q^2 = 2$, the model is exactly solvable, in the grand canonical ensemble. Explicit expressions have been obtained for the grand potential, the density profile, and the pressures. The general relations between the different pressures have been checked.

A bulk pressure, independent of the surface effects, can be defined from the Maxwell stress tensor. It is not astonishing that this bulk pressure is different from the previous ones, all of which depend on surface effects.

Chapter 9

Functional integration in one dimensional classical statistical mechanics

The physics of one dimensional systems is simpler than that one of three dimensional ones. Specifically the free energy of an interacting gas has had an exact solution only in one dimension. The apparent simplicity of restricting motion to one spatial dimension is well known and has had much appeal. But what is the relation between the exactly soluble models of the one dimensional world and the richer and puzzling problems of the tree dimensional one? A one dimensional gas was once thought to be incapable even of condensation. Later with the introduction of infinite range forces it has been made to condense, but even so this liquid can never freeze. What one finds is that these models are useful tests of approximate mathematical methods, the solutions of these models are surprisingly complex and interesting, physical applications are often and unexpectedly discovered, and more importantly they educate us to the need of rigorous and exact analysis with which one can have a better definition of reality. The fact that particles can get around each other is responsible for much of the structure of the ordinary world, and is also responsible for the difficulties which the mathematical physicist encounter in studying it. In one dimension we renounce to some of the structure in favor of the possibility of obtaining an exact solution.

The importance of one dimensional physics also lies in the fact that a number of many-body problems in higher dimensions can be accurately mapped into one dimensional problems.

One dimensional models with short range two particles forces do not have a phase transition at a non zero temperature [10].

In this chapter I will describe a way of simplifying the calculation of the grand canonical partition function of an ensemble of classical particles living in a one dimensional world and interacting with a given pair potential v, originally described by Edwards and Lenard in their paper [3] which I will call EL from now on. Using the notion of a general Gaussian random process and Kac's theorem, they show how it is possible to express the grand partition function as a one dimensional integral of the fundamental solution of a given partial differential equation. The kind of partial differential equation will be fixed by the kind of *diffusion equation* satisfied by the Gaussian random process. In sections i, ii, and iii I will present EL's functional integration technique. In subsection iv.2 I will show how, in EL, the properties of the Wiener process are used to solve "Edwards' model". I will then show, in subsection iv.1, how one can use the properties of the Ornstein-Uhlenbeck process to solve the "Kac-Baker's model", and, in

section vii, how the generalized Ornstein-Uhlenbeck process can be used to solve models with a more general pair interaction potential. Even though in EL is mentioned the generality of their technique they just apply it to the "Edwards' model". In Section v we show how EL propose to extract thermodynamical informations from their treatment and in section vi we show, following EL, how it is possible to reduce the search of the grand partition function, to a characteristic value problem, when the diffusion equation is independent of time.

More recently [132] the functional integral technique of Edwards and Lenard has been used to solve the statistical mechanics of a one dimensional Coulomb gas with boundary interactions as a one dimensional model for a colloidal and soap film.

i The Problem

The problem is to simplify the calculation of the grand canonical partition function of a system of particles in the segment $[0, L]$ whose positions are labeled by x_i with $i = 1, 2, \ldots, N$, namely,

$$\Omega = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_0^L dx_N \cdots \int_0^L dx_1 \exp\left\{ -\frac{V_N(x1, \ldots, x_N)}{\theta} \right\} \quad . \tag{9.i:1}$$

EL consider the total potential energy of the system to be,

$$V_N(x_1, \ldots, x_N) = \sum_{i=1}^{N} \sum_{j=1}^{N} w(x_i, x_j) \quad , \tag{9.i:2}$$

where $w(x_i, x_j)$ is a function of two variables depending on the pair potential $v(|x_i - x_j|)$ and the kind of reservoir exchanging particles with the system.

The main idea of EL, is to rewrite the grand partition function as a functional average,

$$\begin{aligned} \Omega &= \left\langle \exp \int_0^L dx' F(\phi(x')) \right\rangle \\ &= \left\langle \sum_{N=0}^{\infty} \frac{1}{N!} \int_0^L dx_N \cdots \int_0^L dx_1 \prod_{i=1}^{N} F(\phi(x_i)) \right\rangle \quad . \end{aligned} \tag{9.i:3}$$

And then choose $F(\phi) = z \exp(i\sigma\phi)$, to get,

$$\Omega = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_0^L dx_N \cdots \int_0^L dx_1 \left\langle \exp\left\{ i\sigma \sum_{i=1}^{N} \phi(x_i) \right\} \right\rangle \quad , \tag{9.i:4}$$

where in interchanging the average with the sum and the integrals they use the linearity of the average. we haven' t defined the average yet so we will do it next.

ii Averaging over a general Gaussian Random Process

A general Gaussian random process $\phi(x)$ is defined by the postulate that for any finite number of points $x_1, \ldots, x_N$ the joint probability density for $\phi(x_k)$ in $d\phi_k$ (we will often make use of the abbreviation $\phi_i \equiv \phi(x_i)$) is of the form,

$$P(\phi_1, \ldots, \phi_N) = \frac{\sqrt{\det B}}{(2\pi)^{N/2}} \exp\left\{ -\frac{1}{2} \sum_{k=1}^{N} \sum_{l=1}^{N} B_{kl} \phi_k \phi_l \right\} \quad , \tag{9.ii:1}$$

where $B_{ij} = B_{ij}(x_1, \ldots, x_N)$ are the elements of the positive definite matrix B.

Let α_k be N arbitrary real numbers. Then,

$$\left\langle \exp\left\{ i \sum_{i=1}^{N} \alpha_i \phi_i \right\} \right\rangle = \exp\left\{ -\frac{1}{2} \sum_{k=1}^{N} \sum_{l=1}^{N} C_{kl} \alpha_k \alpha_l \right\} \quad , \tag{9.ii:2}$$

$$\text{where} \quad C = B^{-1} \quad .$$

Differentiating with respect to α_k and α_l (not excluding $k = l$) and then setting all α to zero, one obtains,

$$\langle \phi(x_k)\phi(x_l) \rangle = C_{kl} = C(x_k, x_l) \quad , \tag{9.ii:3}$$

where C is a function of two variables only, called the *covariance function*. From equations (9.ii:2) and (9.ii:3) follows that also $B_{ij} = B(x_i, x_j)$ is a function of just two variables. The covariance completely characterizes the statistical nature of $\phi(x)$

Replacing all the α' s in equation (9.ii:2) with σ and comparing (9.ii:2) and (9.i:4) with (9.i:1) and (9.i:2) one recognizes that,

$$C(x_1, x_2) = \frac{2}{\theta \sigma^2} w(x_1, x_2) \quad . \tag{9.ii:4}$$

This imposes a restriction to the systems that one can treat. Namely we need w to be positive definite.

Why is all this useful is explained in the next section.

iii Kac's Theorem

Consider a Markoffian process $\phi(x)$, i.e. one for which, given any increasing sequence of times $x_0, x_1, \ldots, x_n$ (with $x_0 < x_1 < \cdots < x_n$), the probability that $\phi(x_k)$ is in $d\phi_k$ (with $k = 0, 1, \ldots, n$) is the product,

$$P(\phi_1, \ldots, \phi_n) = \left(\int_{-\infty}^{\infty} d\phi_0 \prod_{k=1}^{n} P(\phi_k, x_k | \phi_{k-1}, x_{k-1}) R(\phi_0, x_0) d\phi_0 \right) \quad , \tag{9.iii:1}$$

where $P(\phi_1, x_1 | \phi_0, x_0)$ is the conditional probability that $\phi(x_1)$ is in an element $d\phi_1$ around ϕ_1 given that $\phi(x_0) = \phi_0$ and $R(\phi, x)$ is the initial probability distribution for the process. [1] Both the conditional probabilities and the initial distribution are assumed to be normalized to unity over the interval $\phi \in [-\infty, +\infty]$,

$$\int_{-\infty}^{\infty} d\phi_1 P(\phi_1, x_1 | \phi_0, x_0) = \int_{-\infty}^{\infty} d\phi R(\phi, x) = 1 \quad . \tag{9.iii:2}$$

Any quantity which is an expression involving $\phi(x)$ is a random variable whose average value may be determined using the probability (9.iii:1).

One is interested in averages of the form,

$$W(x, x_0) = \left\langle \exp \int_{x_0}^{x} dx' F(\phi(x'), x') \right\rangle \tag{9.iii:3}$$

$$= 1 + \sum_{n=1}^{\infty} \int_{x_0}^{x} dx_n \int_{x_0}^{x_n} dx_{n-1} \cdots \int_{x_0}^{x_2} dx_1 \langle F(\phi_n, x_n) \cdots F(\phi_1, x_1) \rangle \ .$$

[1] Equation (9.iii:1) defines what is often called a *Wiener measure* in the space of continuous functions $\phi(x)$.

Kac' s theorem takes advantage of the Markoffian property (9.iii:1) to relate to each other the successive terms of this series by an integral-recursion formula. It can be seen by inspection that,

$$W(x,x_0) = \int_{-\infty}^{\infty} d\phi Q(\phi, x|\phi_0, x_0) \quad , \tag{9.iii:4}$$

$$Q = \sum_{n=0}^{\infty} Q_n \quad ,$$

$$\begin{cases} Q_0(\phi, x|\phi_0, x_0) = \int_{-\infty}^{\infty} d\phi_0 P(\phi, x|\phi_0, x_0) R(\phi_0, x_0) \\ Q_n(\phi, x|\phi_0, x_0) = \int_{x_0}^{x} dx' \int_{-\infty}^{\infty} d\phi' P(\phi, x|\phi', x') F(\phi', x') Q_{n-1}(\phi', x'|\phi_0, x_0) \end{cases}$$

Then one can write the following integral equation for Q,

$$Q(\phi, x|\phi_0, x_0) = Q_0 + \sum_{n=1}^{\infty} Q_n = \int d\phi_0 PR + \sum_{n=1}^{\infty} \int dx' \int d\phi' PFQ_{n-1}$$

$$= \int_{-\infty}^{\infty} d\phi_0 P(\phi, x|\phi_0, x_0) R(\phi_0, x_0)$$

$$+ \int_{x_0}^{x} dx' \int_{-\infty}^{\infty} d\phi' P(\phi, x|\phi', x') F(\phi', x') Q(\phi', x'|\phi_0, x_0) \quad . \tag{9.iii:5}$$

This is the main result of Kac' s theorem.

Now assuming that the stochastic process $\phi(x)$ satisfies a forward Fokker-Planck equation,

$$\begin{aligned} \frac{\partial}{\partial x} P(\phi, x|\phi_0, x_0) &= \mathcal{L}(\phi, x) P(\phi, x|\phi_0, x_0) \\ P(\phi, x_0|\phi_0, x_0) &= \delta(\phi - \phi_0) \quad \text{initial condition} \end{aligned} \tag{9.iii:6}$$

it immediately follows from the integral formula (9.iii:5), that Q satisfies,

$$\begin{aligned} \frac{\partial}{\partial x} Q(\phi, x|\phi_0, x_0) &= [\mathcal{L}(\phi, x) + F(\phi, x)] Q(\phi, x|\phi_0, x_0) \\ Q(\phi, x_0|\phi_0, x_0) &= R(\phi, x_0) \quad \text{initial condition} \end{aligned} \tag{9.iii:7}$$

If we now further assume $\phi(x)$ to be a Gaussian process (so that equation (9.iii:1) is of the form (9.ii:1)) then we can put together the result of the previous section (9.ii:4) and Kac' s theorem, to say that,

$$\boxed{\Omega = W(L,0) = \int_{-\infty}^{\infty} d\phi Q(\phi, L|0, 0)} \quad , \tag{9.iii:8}$$

where $Q = Q(\phi, x|\phi_0, x_0)$ is the solution of the partial differential equation (9.iii:7) with $F(\phi, x)$ $= F(\phi) = z \exp(i\sigma\phi)$. This is the simplification found by EL. Note the following points:

- This certainly is a simplification from a computational point of view (see chapter 6 of "Lectures in Non-equilibrium Statistical Mechanics" by Klaus Shulten, lecture notes for the 498NSM course held at the University of Illinois at Urbana Champaign during fall 2003).

- When the operator $\mathcal{L}$ is independent of 'time' (we keep calling x time because it comes natural from the notion of random process. In the present contest though x is the position of a particle along his one dimensional world.) then both $P(\phi, x|\phi_0, x_0)$ and $Q(\phi, x|\phi_0, x_0)$ depend only on the difference $x - x_0$ since F does not depend explicitly on x.
- For a non-stationary random process $\phi(x)$ it simplifies things if one takes a delta function as initial distribution, i.e. $R(\phi, x_0) = \delta(\phi - \phi_0)$, where $\phi_0 = \phi(x_0)$. In this case Q is the *fundamental solution* of the partial differential equation (9.iii:7).
- For a non-stationary random process the covariance function $C(x_1, x_2) = \langle \phi(x_1)\phi(x_2) \rangle$ is not a function of $x_2 - x_1$ alone. The identification of the covariance with the inter particle potential v demands that the process be stationary because the inter particle potential is a function of the difference of the two position variables. But in some cases (due for example to the presence of the reservoir) w may differ from v (see subsection iv.2).

As a final remark, in EL is stressed the importance of the Markoffian nature of the process. They observe that the concept of a Markoffian process involves the idea of a succession in 'time' and this is meaningless when there is more then one independent variable. So it seems to be hard to extend the technique just described even to a two dimensional system.

In the following section we will apply the functional integration technique described to some concrete examples.

iv Examples

Let us see now how all this works for two well known Markoffian, Gaussian stochastic processes:

iv.1 The Ornstein-Uhlenbeck process

The *Ornstein-Uhlenbeck process* is a stationary process defined as follows,

$$R(\phi_0) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\phi_0^2}{2}\right) \quad , \tag{9.iv:1}$$

$$P(\phi, x|\phi_0, x_0) = \frac{1}{\sqrt{2\pi S(\Delta x)}} \exp -\frac{(\phi - \phi_0 e^{-\gamma \Delta x})^2}{2S(\Delta x)} \quad , \tag{9.iv:2}$$

$$\text{with} \quad \Delta x = |x - x_0| \quad ,$$

$$S(\Delta x) = 1 - e^{-2\gamma \Delta x} \quad ,$$

where γ is the inverse of the characteristic time constant of the process, i.e. a positive real number. Due to the stationarity the following identity holds,

$$R(\phi) = \int_{-\infty}^{\infty} d\phi_0 P(\phi, x|\phi_0, x_0) R(\phi_0) \quad . \tag{9.iv:3}$$

The covariance for this process is,

$$C(x_1, x_2) = \exp -\gamma |x_1 - x_2| \quad . \tag{9.iv:4}$$

The Fokker-Planck equation satisfied by the process is the Smoluchowski diffusion equation for an harmonic oscillator,

$$\mathcal{L}(\phi) = \gamma \left(\frac{\partial^2}{\partial \phi^2} + \frac{\partial}{\partial \phi} \phi \right) \quad . \tag{9.iv:5}$$

So this process can be used to describe a system of particles whose potential energy is,

$$w(x_1, x_2) = \frac{\theta\sigma^2}{2} \exp -\gamma|x_1 - x_2| \quad . \tag{9.iv:6}$$

Adding a hard-core part to this long range potential and making it attractive by choosing σ pure imaginary, gives the so called "Kac-Baker model". Yang and Lee showed that the presence of the hard core part is sufficient to ensure the existence of the thermodynamic potential for the infinite system ($L \to \infty$). This was calculated exactly by Kac who also proved that the model has no phase transitions (because of the infinite range of the potential, Van Hove' s proof is not applicable here). Later Baker showed that if one sets,

$$\sigma = i\sqrt{\frac{\alpha_0\gamma}{\theta}} \quad , \tag{9.iv:7}$$

(so that the integral of the potential is independent of γ) and then takes the limit $\gamma \to 0$ *after* the limit $L \to \infty$, *then a phase transition of the classical Van der Waals type is obtained.* A model with exponential repulsive pair potential (exactly like the one in (9.iv:6)) was studied by D. S. Newman, who concluded that there was no phase transition for such a model, not even in the long range limit of Baker [133].

iv.2 The Wiener process

We follow EL and introduce the *Wiener process.* It is a non-stationary process defined by (if $x > x_0$),

$$R(\phi_0) = \frac{1}{\sqrt{4\pi D x_0}} \exp -\frac{\phi_0^2}{4Dx_0} \tag{9.iv:8}$$

$$P(\phi, x|\phi_0, x_0) = \frac{1}{\sqrt{4\pi D\Delta x}} \exp -\frac{\Delta\phi^2}{4D\Delta x} \quad , \tag{9.iv:9}$$

$$\text{with} \quad \Delta x = x - x_0 \quad ,$$

$$\Delta\phi = \phi - \phi_0 \quad ,$$

where D is the diffusion constant of the Brownian process, i.e. a positive real number.

The covariance for this process is,

$$C(x_1, x_2) = 2D \min(x_1, x_2) \quad . \tag{9.iv:10}$$

The Fokker-Planck equation satisfied by the process is the Einstein diffusion equation,

$$\mathcal{L}(\phi) = D\frac{\partial^2}{\partial\phi^2} \quad . \tag{9.iv:11}$$

So this process can be used to describe a system of particles whose potential energy is,

$$w(x_1, x_2) = D\theta\sigma^2 \min(x_1, x_2) \quad . \tag{9.iv:12}$$

It was S. F. Edwards, see EL, who first realized that this is a Coulomb system: electrons of charge e living in the segment $[0, L]$ are in contact with an infinite reservoir (in the region $x < 0$, say). The reservoir exchanges particles with the system of electrons giving rise to the statistical fluctuations in particle number. Take the system plus reservoir electrically neutral as

a whole and imagine the system containing N electrons. Then there is a total charge $-Ne$ in the reservoir. Gauss' s theorem then tells that in the region $x \geq 0$ there is a constant electric field of magnitude $2\pi Ne$, due to the presence of the reservoir. Now choosing,

$$D = \frac{2\pi}{\theta} \quad , \tag{9.iv:13}$$

$$\sigma = e \quad , \tag{9.iv:14}$$

one can rewrite the total potential energy of the system as,

$$\begin{aligned} V_N &= 2\pi e^2 \sum_{k=1}^{N}\sum_{l=1}^{N} \min(x_k, x_l) \\ &= 2\pi e^2 \sum_{k=1}^{N}\sum_{l=1}^{N} \left[-\frac{|x_k - x_l|}{2} + \frac{x_k + x_l}{2} \right] \\ &= -2\pi e^2 \sum_{k<l} |x_k - x_l| + 2\pi e^2 \sum_{k=1}^{N}\sum_{l=1}^{N} x_l \\ &= -2\pi e^2 \sum_{k<l} |x_k - x_l| + 2\pi N e^2 \sum_{l=1}^{N} x_l \quad . \end{aligned} \tag{9.iv:15}$$

Which is readily recognized as the expected result for the "Edwards' model". We are assuming that the line is the real world in which each charge lives. So that also its field lines cannot escape from the line. Then the electric potential of each charge is the solution of $d^2\psi(x)/dx^2 = -4\pi\delta(x)$, i.e. $\psi(x) = -2\pi|x|$.

Note that due to the presence of the neutralizing reservoir, w is not just a function of $|x_i - x_j|$ and consequently the random process is not just a stationary one as in the Kac-Baker example.

In this case Edwards has not been able to answer in a definite way to the problem of continuity of the thermodynamic functions.

v Thermodynamics

Following EL, we want now comment briefly on the relevance of all this from the point of view of the thermodynamics of the system of particles. Given the grand canonical partition function $\Omega = \Omega(z, L, \theta)$ the equation of state follows from eliminating z between the two following equations,

$$\frac{P}{\theta} = \frac{1}{L} \ln \Omega(z, L, \theta) \quad , \tag{9.v:1}$$

$$n = z \frac{\partial}{\partial z} \frac{1}{L} \ln \Omega(z, L, \theta) \quad . \tag{9.v:2}$$

where P is the pressure and n the number density of particles. Sometimes one talks about *chemical potential* μ (of the one-component system), instead of z. The two are related by,

$$z = \left(\frac{m\theta}{2\pi\hbar^2} \right)^{1/2} e^{\mu/\theta} \quad , \tag{9.v:3}$$

where m is the mass of the particles. All the other thermodynamic functions can be obtained from the internal energy,

$$U(N,L,S) = -\frac{d}{d(1/\theta)} \ln \Omega(z,L,\theta) \tag{9.v:4}$$

$$= L(-P + \theta \frac{\partial P}{\partial \theta} + \mu n) \quad , \tag{9.v:5}$$

where S is the entropy of the system. Or alternatively from the Helmholtz free energy,

$$A(N,L,\theta) = \mu N - \theta \ln \Omega(z,L,\theta) \quad . \tag{9.v:6}$$

It is often useful to simplify the problem by studying just the asymptotic behavior of Ω in the infinite system limit $L \to \infty$. This usually allows the recognition of eventual phase transitions (as in the Yang & Lee theory and L. Van Hove theorems) as singularities in the equation of state. The equation of state for the infinite system becomes then,

$$\boxed{\begin{cases} \dfrac{P}{\theta} = \Phi(z,v,\theta) = \lim\limits_{L\to\infty} \left[\dfrac{1}{L} \ln \Omega(z,L,\theta) \right] \quad , \\ n = \dfrac{1}{v} = \lim\limits_{L\to\infty} \left[z \dfrac{\partial}{\partial z} \dfrac{1}{L} \ln \Omega(z,L,\theta) \right] \quad , \end{cases}} \tag{9.v:7}$$

where the limit may not be freely interchanged with the differentiation.

vi Characteristic value problem

Both the examples reported have the common feature that $\mathcal{L}$ is independent of time x. Under this circumstance the problem of calculating the grand canonical partition function Ω may be simplified even further, as shown in EL.

Since the coefficient function $F(\phi)$ in equation (9.iii:7) is periodic with period 2π it is possible to reduce the problem (9.iii:7) to the characteristic value problem of an ordinary differential operator on a finite interval of the independent variable ϕ. Let,

$$\tilde{Q}(\phi,x) = \sum_{n=-\infty}^{\infty} Q(\phi + 2\pi n, x|0,0) \quad . \tag{9.vi:1}$$

This function is the *periodic fundamental solution* of the partial differential equation (9.iii:7), i.e. for $x = 0$ it reduces to,

$$\tilde{Q}(\phi,0) = \sum_{n=-\infty}^{\infty} R(\phi + 2\pi n) \quad . \tag{9.vi:2}$$

For the "Kac-Baker model" one finds for example $\tilde{Q}(\phi,0) = \theta_3(\phi/2, 1/\sqrt{e})/(2\pi)$ and for the "Edwards' model" $\tilde{Q}(\phi,0) = \sum_{n=-\infty}^{\infty} \delta(\phi + 2\pi n)$. It then follows that,

$$\Omega = \int_{-\pi}^{\pi} d\phi \tilde{Q}(\phi, L) \quad . \tag{9.vi:3}$$

Since F and $\mathcal{L}$ do not depend on x, in solving (9.iii:7) for $\tilde{Q}$, one may use the method of separation of variables. This leads to the characteristic value problem,

$$\begin{aligned} [\mathcal{L}(\phi) + F(\phi)]\, y(\phi) &= \lambda y(\phi) \quad , \\ y(\phi + 2\pi) &= y(\phi) \quad . \end{aligned} \tag{9.vi:4}$$

Then one looks for a complete orthonormal set of eigenfunctions y_m with relative eigenvalues λ_m $(m = 0, 1, 2, \ldots)$,

$$\int_{-\pi}^{\pi} d\phi y_m(\phi) y_{m'}(\phi) = \delta_{m,m'} \quad . \tag{9.vi:5}$$

The expansion of $\tilde{Q}$ in terms of these functions is,

$$\tilde{Q}(\phi, x) = \sum_{m=0}^{\infty} e^{\lambda_m x} B_m y_m(\phi) \quad , \tag{9.vi:6}$$

$$B_m = \int_{-\pi}^{\pi} d\phi \tilde{Q}(\phi, 0) y_m(\phi) \quad . \tag{9.vi:7}$$

For example $B_m = y_m(0)$ for the "Edwards' model". The grand partition function becomes,

$$\Omega(L) = \sum_{m=0}^{\infty} A_m e^{\lambda_m L} \quad , \tag{9.vi:8}$$

$$A_m = y_m(0) \int_{-\pi}^{\pi} d\phi y_m(\phi) \quad . \tag{9.vi:9}$$

The λ_m and the y_m depends parametrically on z which enters into the definition of $F(\phi)$.

Now assume that among the sequence of eigenvalue λ_m there is one λ_0 *that is real and is bigger than the real part of all the others* then the following simplification holds,

$$\boxed{\Omega(L \to \infty) \sim A_0 \exp(\lambda_0 L)} \quad . \tag{9.vi:10}$$

The equation of state for the infinite system then becomes,

$$P = \theta \lambda_0(z) \quad , \tag{9.vi:11}$$

$$n = \lim_{L \to \infty} \left[z \frac{\partial}{\partial z} \left(\frac{\ln A_0(z)}{L} + \lambda_0(z) \right) \right]$$

$$= z \frac{\partial}{\partial z} \lambda_0(z) \quad . \tag{9.vi:12}$$

For example for an ideal gas $\lambda_0(z) = az$ (a constant).

Let us summarize the characteristic value problem for the two examples reported ($' = d/d\phi$):
(1) repulsive "Kac-Baker model":

$$\gamma[y'' + (\phi y)'] + z e^{-i\sigma\phi} y = \lambda y \quad , \tag{9.vi:13}$$

(2) "Edwards' model":

$$\frac{2\pi}{\theta} y'' + z e^{-ie\phi} y = \lambda y \quad , \tag{9.vi:14}$$

where in both cases $y(\phi)$ is a function of period 2π (for the attractive Kac-Baker model the periodicity is lost but the characteristic value problem is still valid).

vii General potential

In the two examples reported we started from known stochastic processes to find which physical model they may be able to describe. Actually one wants to do the reverse: given a physical model, i.e. given w (a positive definite function (9.ii:4)), determine the stochastic process that allows the desired simplification for the grand canonical partition function. It turns out that this is quite easily accomplished when w is a function of the inter particles distance alone.

For this purpose it is useful to reconsider the Ornstein-Uhlenbeck process in a more general way. Consider the following stationary stochastic process,

$$\begin{aligned} R(\phi) &= \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\phi^2}{2}\right) \quad , & \text{(9.vii:1)} \\ P(\phi, x|\phi_0, x_0) &= \frac{1}{\sqrt{2\pi S(\Delta x)}} \exp -\frac{(\phi - \phi_0 A(\Delta x))^2}{2S(\Delta x)} \quad , & \text{(9.vii:2)} \\ \text{with} \quad \Delta x &= |x - x_0| \quad , \\ S(\Delta x) &= 1 - A^2(\Delta x) \quad , \end{aligned}$$

where the last definition assures the validity of the stationarity property (9.iv:3).

The covariance for this process is,

$$C(x_1, x_2) = \frac{2}{\sigma\theta} w(x_1, x_2) = A(|x_1 - x_2|) \quad . \tag{9.vii:3}$$

It can be readily verified that the transition density of this process satisfies the following forward Fokker-Planck equation,

$$\mathcal{L}(\phi, x) = -\frac{\dot{A}}{A}\left(\frac{\partial^2}{\partial\phi^2} + \frac{\partial}{\partial\phi}\phi\right) \quad , \tag{9.vii:4}$$

where the dot means differentiation with respect to time. Introducing the function $B^2(x) = -2d \ln A(x)/dx$ one can then say that the process satisfies the following stochastic differential equation,

$$\dot{\phi}(x) = -\frac{B^2(x)}{2}\phi(x) + B(x)\eta(x) \quad , \tag{9.vii:5}$$

where $\eta(x)$ is Gaussian white noise.

All this allows for example to simplify the thermodynamics of a system of particles interacting with a potential,

$$w(x_1, x_2) = 1/|x_1 - x_2| \quad , \tag{9.vii:6}$$

for which $B(x) = \sqrt{2/x}$.

In the more general case one has to deal with w' s which are not functions of the inter particle interaction alone. For example one may be interested in modifying "Edwards' model" for the case of a Coulomb system living in $[-L, L]$ and neutralized by a uniform background (containing quadratic terms). This problem has been solved by R. J. Baxter [133] who developed a method for finding the partition function when the pair potential satisfies a linear differential equation with constant coefficients. His method still leads to an eigenvalue problem but do not employ functional averaging.

Chapter 10

Conclusions

In the thesis have been examined various simple classical fluids. Among the one component systems we have studied:

- The one dimensional hard spheres (hard rods). A peculiarity of this system is that, due to its low dimensionality, it cannot undergo the fluid-solid transition. Direct calculations of the Lyapunov exponent of the simple iterative scheme of Picard of HNC and PY integral equations for this system showed the same behavior observed in three dimensional systems (see chapter 6). So at least in this case, the recently proposed [84–86] connection between the threshold for the stability of the iterative solution of integral equations for the pair correlation functions of a classical fluid and its freezing phase transition, failed.

- The three dimensional inverse power potential and Lennard-Jones fluids. We used (see chapter 5) these systems to test the performance of some new closures (HNC/H2, HNC/H3) built in such a way to admit a unique solution and to be thermodynamically consistent (the pressure calculated from the virial theorem coincides with the one obtained from the partial derivatives of the free energy). In particular we showed how for the Lennard-Jones fluid treated with HNC/H2, one could follow the isotherms from the low density to the high density regions without the appearance of termination points. The isotherms had a van der Waals like behavior. A drawback of these new closures is that they were worst than the more common closures (as HNC or RY) in reproducing the structure or thermodynamics of these fluids. If one drops the constraint of the uniqueness of the solution, within HNC/H3, better results, in this sense, were obtained.

- The one component Coulomb plasma on a pseudosphere. It has long been known that at some special temperature ($\beta q^2 = 2$) the partition function and distribution functions of a flat two dimensional one component plasma can be exactly computed in the thermodynamic limit, in the canonical ensemble, using the properties of the Vandermonde determinant [4, 134]. The two dimensional one component plasma on a pseudosphere was first considered by Jancovici and Téllez [105] who were able to extend the exact solution to this system. They still studied only the thermodynamic limit and found consistent results working either in the canonical or in the grand canonical ensembles. In the thesis (see chapter 8) we extended this work to a one component plasma confined into a finite disk of the pseudosphere. Again the grand potential and the one body density were calculated exactly at the special temperature but now we were forced to use the grand canonical ensemble. The thermodynamic limit was also investigated to check, at the special temperature, some sum rules between different definitions of the pressure of the system that had

been previously determined on general grounds.

In the thesis we also stressed the important role played by the pseudosphere in the theory of dynamical systems. In particular Sinai [110] proved the ergodicity of a gas of free particles on a pseudosphere closed at infinity by a reflective boundary. We posed the question: is the two dimensional one component plasma on a pseudosphere ergodic? Due to the difficulty in handling the pair interactions we could not reach a definitive answer.

- The Kac-Baker and Edwards one dimensional fluids. We described in details the functional integration technique used by Edwards and Lenard [3] to reduce the calculation of the grand canonical partition function of one dimensional systems with pair wise interactions, to the solution of a particular partial differential equation (see chapter 9). We reported the treatment of the Edwards model discussed in the Edwards and Lenard paper and showed how one could treat the Kac-Baker model with similar means. We also discussed a possible extension of the method to a system with a "general" pair interaction potential.

Among the multicomponent systems we have studied:

- the restricted primitive model for charged hard spheres. This is the simplest model for a ionic fluid. We reproduced in detail (see chapter 4 section i and appendix E) the calculation of the charge density direct correlation function, originally given by Blum [46]. With the hope of learning something on how to apply the Wiener-Hopf technique to a multicomponent system.

- The mixture of three dimensional non additive hard spheres. A solution of the PY approximation for this system has not yet been found. In the thesis (see chapter 4 section ii) we showed how any attempt to find such a solution using the Wiener-Hopf technique (by an extension of the known solution to the PY approximation for a mixture of additive hard spheres given by Baxter [44]) is bound to be unsuccessful. We motivated this failure by looking at a particular case: the Widom-Rowlinson model.

  We also presented Monte Carlo simulation data for the direct correlation functions of a symmetric mixture and a mixture with equal concentrations but different like diameters.

- The Widom-Rowlinson model. The PY approximation for this system has been solved analytically both in one dimension and in three dimensions by Ahn and Lebowitz [54]. We have calculated (see chapter 7), through Monte Carlo numerical simulations, the partial total and direct correlation functions of the three dimensional symmetric Widom-Rowlinson mixture, and we have found that the difference between the partial direct correlation function from the simulation and the one from the PY approximation (note that there are misprints in the Ahn and Lebowitz paper) are well fitted by Gaussians.

In this thesis work we have explored different aspects of the theory of classical liquid. We have shown how it is not possible to try to find an analytic solution of the PY approximation for the three dimensional mixture of non additive hard spheres, using the Wiener-Hopf technique (see chapter 4). We have seen how to build an integral equation theory starting from two basic requirements: the uniqueness of the solution and the thermodynamic consistency, and how to test it (see chapter 5). We have carefully and critically analyzed a recently proposed one phase freezing criterion (see chapter 6). We have carried out numerical simulations on the Widom-Rowlinson model and on the non additive mixture of hard spheres (see chapter 7). We have seen how the one component Coulomb plasma on a finite disk of the pseudosphere admits exact analytic solutions for the grand potential and the correlation functions at a particular value of

the temperature. We have also seen how to obtain sum rules for different definitions of pressure for this system checking them on the solvable model (see chapter 8). And we have seen how the functional integration technique used by Edwards and Lenard to simplify the calculation of the grand canonical partition function of a one dimensional fluid with pairwise interactions, could be generalized to treat models other than the "Edwards model" (see chapter 9).

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Appendix A

The Born-Green approximation

Expanding the functional $\rho^{(1)}(1|\phi)\nabla_1 \ln[1/\zeta^*(1)]$ to first order in $\delta \ln[\rho^{(1)}(1|\phi)/\zeta^*(1)]$ we find

$$\rho g(0,1)\nabla_1 \ln\left[\frac{1}{\zeta e^{-\beta v(0,1)}}\right] = \int f(1,2)\left\{\ln\left[\frac{\rho g(0,2)}{\zeta e^{-\beta v(0,2)}}\right] - \ln\left(\frac{\rho}{\zeta}\right)\right\} d2 \quad , \tag{A.:1}$$

where f is the following functional derivative

$$\begin{aligned} f(1,2) &= \left\{\frac{\delta\{\rho^{(1)}(1|\phi)\nabla_1 \ln[1/\zeta^*(1)]\}}{\delta \ln[\rho^{(1)}(2|\phi)/\zeta^*(2)]}\right\}_{\phi=0} \\ &= -\frac{\rho}{\zeta}\left\{\frac{\delta\{[\rho^{(1)}(1|\phi)/\zeta^*(1)]\nabla_1\zeta^*(1)\}}{\delta[\rho^{(1)}(2|\phi)/\zeta^*(2)]}\right\}_{\phi=0} \\ &= -\left(\frac{\rho}{\zeta}\right)^2 \nabla_1\left\{\frac{\delta\zeta^*(1)}{\delta[\rho^{(1)}(2|\phi)/\zeta^*(2)]}\right\}_{\phi=0} \\ &= -\left(\frac{\rho}{\zeta}\right)^2 \nabla_1 l(1,2) \\ &= \left(\frac{\rho}{\zeta}\right)^2 \nabla_2 l(1,2) \quad , \end{aligned} \tag{A.:2}$$

where l has been defined. We can find an integral equation for l proceeding as follows

$$\delta(1,2) = \frac{\delta\zeta^*(1)}{\delta\zeta^*(2)} = \int \frac{\delta\zeta^*(1)}{\delta[\rho^{(1)}(3|\phi)/\zeta^*(3)]}\frac{\rho^{(1)}(3|\phi)/\zeta^*(3)}{\delta\zeta^*(2)}\, d3 \quad , \tag{A.:3}$$

moreover

$$\begin{aligned} \frac{\rho^{(1)}(3|\phi)/\zeta^*(3)}{\delta\zeta^*(2)} &= \frac{1}{\zeta^*(3)}\frac{\delta\rho^{(1)}(3|\phi)}{\delta\zeta^*(2)} - \frac{\rho^{(1)}(3|\phi)}{{\zeta^*}^2(3)}\delta(3,2) \\ &= \frac{1}{\zeta^*(2)\zeta^*(3)}[\rho^{(1)}(2|\phi)\rho^{(1)}(3|\phi)h(3,2|\phi) + \rho^{(1)}(3|\phi)\delta(3,2)] \\ &\quad -\frac{\rho^{(1)}(3|\phi)}{{\zeta^*}^2(3)}\delta(3,2) \quad . \end{aligned} \tag{A.:4}$$

Taking the limit $\phi = 0$ in the two preceding equations and substituting the second into the first one we find

$$\delta(1,2) = \int l(1,3)\left(\frac{\rho}{\zeta}\right)^2 h(3,2)\, d3 \quad . \tag{A.:5}$$

Now substituting equation (A.:2) into (A.:1) we find

$$\beta\rho g(0,1)\nabla_1 v(0,1) = \int \left(\frac{\rho}{\zeta}\right)^2 \nabla_2 l(1,2)\{\ln[g(0,2)] + \beta v(0,2)\}\, d2 \quad . \tag{A.:6}$$

Integrating by parts the left hand side

$$\beta\rho g(0,1)\nabla_1 v(0,1) = -\int \left(\frac{\rho}{\zeta}\right)^2 l(1,2)\nabla_2\{\ln[g(0,2)] + \beta v(0,2)\}\, d2 \quad , \tag{A.:7}$$

which can be rewritten as

$$\beta\rho g(0,1)\nabla_0 v(0,1) = -\int \left(\frac{\rho}{\zeta}\right)^2 l(1,2)\nabla_0\{\ln[g(0,2)] + \beta v(0,2)\}\, d2 \quad . \tag{A.:8}$$

Multiplying both members times $h(1,3)$ and integrating over $d1$ we find

$$\begin{aligned}\beta\rho \int [\nabla_0 v(0,1)] g(0,1) h(1,3)\, d1 = \\ -\int \left[\int \left(\frac{\rho}{\zeta}\right)^2 l(1,2) h(1,3)\, d1\right] \nabla_0\{\ln[g(0,2) + \beta v(0,2)]\}\, d2 \quad .\end{aligned} \tag{A.:9}$$

Using equation (A.:5), writing everything in terms of the pair distribution function, and relabeling the indices we finally get the *Born-Green equation* [135]

$$\nabla_1\{\ln[g(1,2)] + \beta v(1,2)\} = -\beta\rho \int [\nabla_1 v(1,3)] g(1,3)[g(3,2) - 1]\, d3 \quad . \tag{A.:10}$$

Appendix B

The Wiener-Hopf factorization

In this appendix we present the Wiener-Hopf factorization for the Ornstein-Zernike equation. This is a technique widely used (see for example the works of R. J. Baxter or L. Blum) to find analytic solutions of integral equations (usually PY and MSA) applied to simple systems. Here, for the reference, we give a much more detailed account of this technique than found in the literature.

Let us consider a generic function $f = f(r)$ with $r = |\mathbf{r}|$, in the three dimensional space. Its Fourier transform can be written as follows

$$\begin{aligned} \hat{f}(k) &= \frac{4\pi}{k}\int_0^\infty \sin(kr)[rf(r)]\,dr \qquad \text{(B.:1)} \\ &= 4\pi\int_0^\infty \cos(kr)F(r)\,dr \quad , \qquad \text{(B.:2)} \end{aligned}$$

where

$$F(r) = \int_r^\infty sf(s)\,ds \quad . \qquad \text{(B.:3)}$$

We can always imagine f defined on the whole real axis choosing $f(-r) = f(r)$. In such case

$$F(-r) = \int_{-r}^\infty sf(d)\,ds = \int_r^\infty sf(s)\,ds = F(r) \quad . \qquad \text{(B.:4)}$$

We then have that

$$\hat{f}(k) = 2\pi\int_{-\infty}^\infty e^{ikr}F(r)\,dr = \hat{f}(-k) \quad . \qquad \text{(B.:5)}$$

Suppose we want to study the hard spheres fluid using the PY closure. We will then have the following constraints on the total and direct pair correlations functions

$$\begin{aligned} h(r) &= -1 \quad r < d \quad , \qquad \text{(B.:6)} \\ c(r) &= 0 \quad r > d \quad , \qquad \text{(B.:7)} \end{aligned}$$

where d is the spheres diameter. Let us consider the function

$$\hat{A}(k) = \frac{1}{S(k)} = \frac{1}{1+\rho\hat{h}(k)} = 1 - \rho\hat{c}(k) \quad , \qquad \text{(B.:8)}$$

where $S(k)$ is the static structure factor, ρ the density of the fluid, and in the second equality we used OZ equation for an homogeneous fluid

$$\hat{h}(k) = \hat{c}(k) + \rho\hat{h}(k)\hat{c}(k) \quad . \tag{B.:9}$$

We introduce the two even functions of r

$$S(r) = \int_r^\infty tc(t)\,dt = \int_r^d tc(t)\,dt = 0 \quad r \geq d \quad , \tag{B.:10}$$

$$J(r) = \int_r^\infty sh(s)\,ds \quad , \tag{B.:11}$$

we will then have for $\hat{A}$ and $\hat{h}$

$$\hat{A}(k) = 1 - 2\pi\rho\int_{-\infty}^{\infty} e^{ikr}S(r)\,dr = 1 - 4\pi\rho\int_0^d \cos(kr)S(r)\,dr \quad , \tag{B.:12}$$

$$\hat{h}(k) = 2\pi\int_{-\infty}^{\infty} e^{ikr}J(r)\,dr \quad . \tag{B.:13}$$

Let us consider now the behavior of $\hat{A}(k)$ in the complex plane $k = x + iy$

$$\hat{A}(k) = 1 - 2\pi\rho\hat{B}(k) \quad , \tag{B.:14}$$

$$\hat{B}(k) = \int_{-\infty}^{\infty} e^{ixr}\left[e^{-yr}S(r)\right]\,dr \quad . \tag{B.:15}$$

It is readily verified that $\hat{B}(k)$ is analytic on $\mathbb{C}$. Indeed since $S(r)$ has finite support, the partial derivatives of B respect to x and y exist (can be brought inside the integral sign) and it can be easily verified that $\partial\hat{B}(k)/\partial x = -i\partial\hat{B}(k)/\partial y$ for all $k \in \mathbb{C}$. Moreover it follows from equation (B.:15) that

$$\lim_{|x|\to\infty} \hat{B}(x + iy) = 0 \quad y_1 < y < y_2 \quad , \tag{B.:16}$$

and then

$$\lim_{|x|\to\infty} \ln\hat{A}(x + iy) = 0 \quad y_1 < y < y_2 \quad . \tag{B.:17}$$

Since the structure factor $S(k) < \infty$ for all $k \in \mathbb{R}^+$ then $\hat{A}(x + iy)$ has no zeroes on the real axis ($y = 0$). It is then possible to choose an ϵ such that $\hat{A}$ has no zeroes in the strip $|y| \leq \epsilon$ (being $\hat{A}$ analytic it is continuous). The function $\ln\hat{A}$ will also be analytic in the strip $|y| \leq \epsilon$. We can then apply Cauchy' s theorem around the strip (see figure B.1) to find

$$\ln\hat{A}(k) = \ln\hat{Q}(k) + \ln\hat{P}(k) \quad k = x + iy \quad |y| < \epsilon \quad , \tag{B.:18}$$

with

$$\ln\hat{Q}(k) = \frac{1}{2\pi i}\int_{-i\epsilon-\infty}^{-i\epsilon+\infty} dk'\frac{\ln\hat{A}(k')}{k' - k} \quad , \tag{B.:19}$$

$$\ln\hat{P}(k) = -\frac{1}{2\pi i}\int_{i\epsilon-\infty}^{i\epsilon+\infty} dk'\frac{\ln\hat{A}(k')}{k' - k} \quad , \tag{B.:20}$$

the integrals on the contour at $|x| = \infty$ being zero. Since $\hat{A}(k) = \hat{A}(-k)$ then $\ln\hat{Q}(-k) = \ln\hat{P}(k)$ and we find for $\hat{A}$ the following Wiener-Hopf factorization

$$\hat{A}(k) = \hat{Q}(k)\hat{Q}(-k) \quad |y| < \epsilon \quad . \tag{B.:21}$$

We will now find some properties of the $\hat{Q}$ function which follows from equation (B.:19):

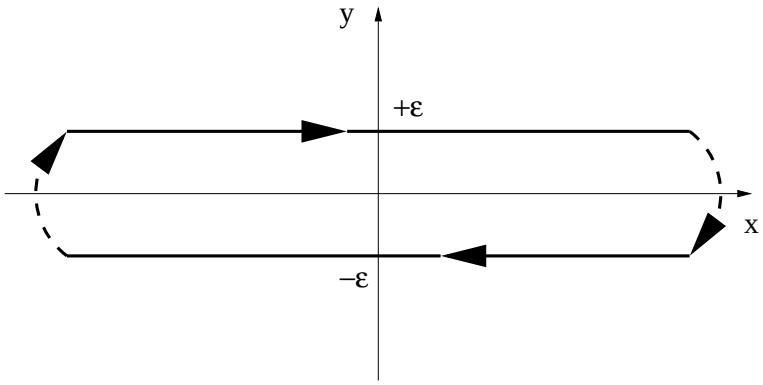

FIGURE B.1: Path of integration.

(1) the function $\ln \hat{Q}(k)$ is analytic for $y \neq -\epsilon$ and $\ln \hat{Q}(-k)$ is analytic for $y \neq +\epsilon$. We conclude that $\hat{Q}(\pm k)$ is analytic for $y \neq \mp\epsilon$ and has no zeroes (it is the exponential of an analytic function);

(2) For $y = 0$ we have

$$\begin{aligned} \ln \hat{Q}^\star(x) &= -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dx' \frac{\ln A^\star(x' - i\epsilon)}{(x' - x) + i\epsilon} \\ &= \frac{1}{2\pi i}\int_{-\infty}^{\infty} dx' \frac{\ln A^\star(-x' - i\epsilon)}{[x' - (-x)] - i\epsilon} \\ &= \frac{1}{2\pi i}\int_{-\infty}^{\infty} dx' \frac{\ln A(x' - i\epsilon)}{[x' - (-x)] - i\epsilon} \\ &= \ln \hat{Q}(-x) \quad , \end{aligned} \tag{B.:22}$$

where a star stands for complex conjugation and in the second to last equality we used $A^\star(x + iy) = A(-x + iy)$;

(3) when $y \neq -\epsilon$ we have $\ln \hat{Q}(x + iy) \sim 1/x$ as $|x| \to \infty$ which means that $\hat{Q}(x + iy) \sim 1 + O(1/x)$;

(4) the expression (B.:19) for $\ln \hat{Q}(k)$ has a singularity at $y = -\epsilon$. It represents two different analytic functions of k for $y < -\epsilon$ and $y > -\epsilon$. We want to find the analytic continuation for $y > -\epsilon$ of the analytic function (B.:19) for $y < -\epsilon$. In the strip $|y| < \epsilon$ we have

$$\hat{Q}(k) = \hat{A}(k)/\hat{Q}(-k) \quad , \tag{B.:23}$$

where $\hat{A}(k)$ is analytic everywhere and $\hat{Q}(-k)$ is analytic for $y < \epsilon$. The analytic function (B.:23) must then coincide with the analytic function (B.:19) for $y > -\epsilon$ in the strip $|y| < \epsilon$. It is then the analytic continuation looked for. Moreover since $\hat{Q}(-k) \to 1$ as $y \to -\infty$ we must have

$$\hat{Q}(k)/e^{-y\alpha} \overset{y\to-\infty}{\longrightarrow} \begin{cases} \infty & \alpha < d \\ 0 & \alpha \geq d \end{cases} \tag{B.:24}$$

as we have

$$\hat{A}(x + iy) = 1 - 2\pi\rho \int_{-d}^{d} e^{ixr} e^{-yr} S(r)\, dr \quad . \tag{B.:25}$$

Now from the properties (1) and (3) follows that for $k \in \mathbb{R}$ the function $1-\hat{Q}(k) \in L^2(-\infty,\infty)$. It is then Fourier integrable along the real axis and a function $Q(r)$ can be defined as

$$2\pi\rho Q(r) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikr}[1-\hat{Q}(k)]\,dk \quad . \tag{B.:26}$$

From property (2) we have that $Q(r)$ is a real function. When $r<0$ we can rewrite

$$2\pi\rho Q(r) = \frac{1}{2\pi}\oint_{\gamma_1+\gamma_2} e^{-ikr}[1-\hat{Q}(k)]\,dk \quad , \tag{B.:27}$$

where γ_1 and γ_2 are the two paths of integration shown in figure B.2. Infact we have $\oint_{\gamma_2}\ldots\to 0$

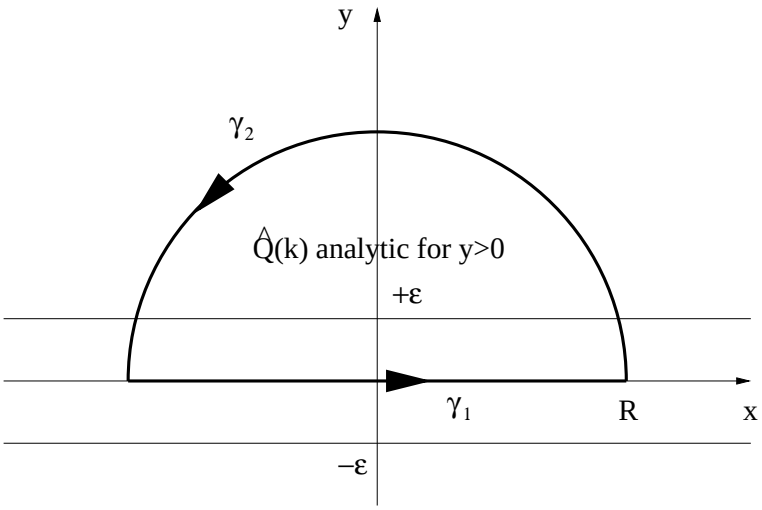

FIGURE B.2: Path of integration.

as $R\to\infty$ when $r<0$ since $[1-\hat{Q}(k)]\to 0$ as $y\to\infty$. Since $\hat{Q}$ is analytic for $y>0$, it follows from Cauchy' s theorem that

$$Q(r) = 0 \quad r<0 \quad . \tag{B.:28}$$

When $r\geq d$ we can rewrite (B.:26) as follows

$$2\pi\rho Q(r) = \frac{1}{2\pi}\oint_{\gamma_1+\gamma_2} e^{-ikr}[1-\hat{Q}(k)]\,dk \quad , \tag{B.:29}$$

where γ_1 and γ_2 are the two paths of integration shown in figure B.3, and for $y>-\epsilon$ we take $\hat{Q}(k)$ to be the analytic continuation found in property (4). Then the limit (B.:24) ensures us that $\oint_{\gamma_2}\ldots\to 0$ as $R\to\infty$ when $r\geq 0$. It again follows from Cauchy' s theorem that,

$$Q(r) = 0 \quad r\geq d \quad . \tag{B.:30}$$

We can then write

$$\hat{Q}(k) = 1 - 2\pi\rho\int_0^d e^{ikr}Q(r)\,dr \quad . \tag{B.:31}$$

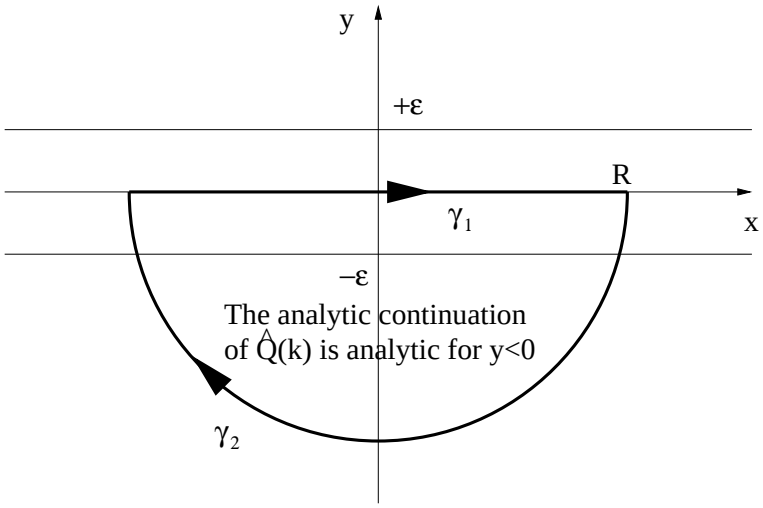

FIGURE B.3: Path of integration.

And from the Wiener-Hopf factorization (B.:21) follows for $k \in \mathbb{R}$

$$1 - 2\pi\rho \int_{-\infty}^{\infty} e^{ikr'} S(r')\, dr' = \left(1 - 2\pi\rho \int_0^d e^{ikr'} Q(r')\, dr'\right) \times \left(1 - 2\pi\rho \int_0^d e^{-ikr'} Q(r')\, dr'\right) \quad , \tag{B.:32}$$

which can be rewritten as

$$\int_{-\infty}^{\infty} e^{ikr'} S(r')\, dr' = \int_0^d e^{ikr'} Q(r')\, dr' + \int_0^d e^{-ikr'} Q(r')\, dr' - 2\pi\rho \int_0^d \int_0^d e^{ik(t-s)} Q(t)Q(s)\, dt\, ds \quad . \tag{B.:33}$$

Multiplying both members times e^{-ikr} and integrating over $dk/(2\pi)$ from $-\infty$ to $+\infty$ we find

$$S(r) = Q(r) + Q(-r) - 2\pi\rho \int_0^d \int_0^d \delta(t - s - r) Q(t)Q(s)\, dt\, ds \quad . \tag{B.:34}$$

Changing variables to $y = t - s$ and $x = t$ we find

$$S(r) = Q(r) + Q(-r) - 2\pi\rho \left[\int_{-d}^{0} dy\, \delta(y - r) \int_0^{d+y} dx\, Q(x)Q(x - y) + \int_0^d dy\, \delta(y - r) \int_y^d dx\, Q(x)Q(x - y)\right] \quad . \tag{B.:35}$$

When $0 < r < d$ we then have

$$S(r) = Q(r) - 2\pi\rho \int_r^d Q(x)Q(x - r)\, dx \quad 0 < r < d \quad . \tag{B.:36}$$

On the other hand from equations (B.:21) and (B.:8) we also have

$$\hat{Q}(k)[1 + \rho\hat{h}(k)] - 1 = \frac{1}{\hat{Q}(-k)} - 1 \tag{B.:37}$$

Multiplying both terms by e^{-ikr} and integrating over dk from $-\infty$ to $+\infty$ we find

$$\begin{aligned}\int_{-\infty}^{\infty} e^{-ikr}\{\hat{Q}(k)[1+\rho\hat{h}(k)]-1\}\,dk &= \int_{-\infty}^{\infty} e^{-ikr}\left[\frac{1}{\hat{Q}(-k)}-1\right]dk \\ &= I(r) \quad . \end{aligned} \tag{B.:38}$$

When $r>0$ we can rewrite

$$I(r)=\oint_{\gamma_1+\gamma_2} e^{-ikr}\left[\frac{1}{\hat{Q}(-k)}-1\right]dk \quad , \tag{B.:39}$$

where γ_1 and γ_2 are the two paths of integration shown in figure B.4. We infact have that

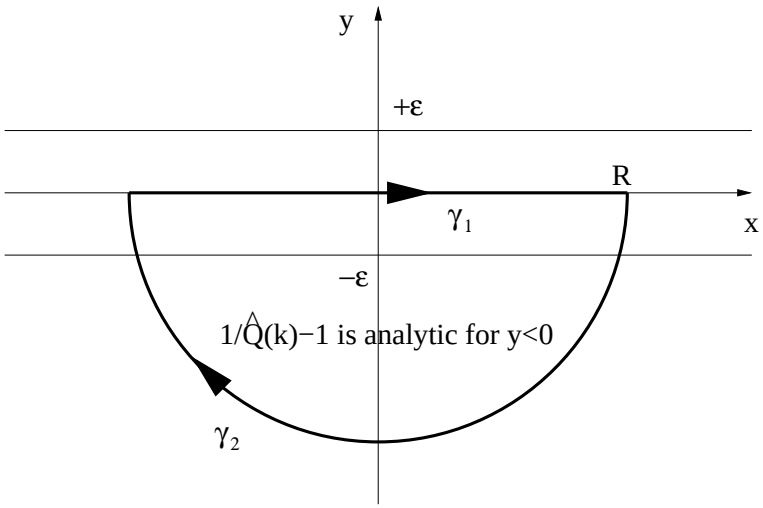

FIGURE B.4: Path of integration.

$\oint_{\gamma_2}\ldots\to 0$ as $R\to\infty$ since $1/\hat{Q}(-k)-1\to 0$ as $y\to-\infty$. From property (1) we know that $1/\hat{Q}(-k)-1$ is analytic for $y<0$, then by Cauchy' s theorem we must have $I(r)=0$ for $r>0$. We can then write

$$\int_{-\infty}^{\infty} e^{-ikr}\left\{\left[1-2\pi\rho\int_0^d e^{iks}Q(s)ds\right]\left[1+2\pi\rho\int_{-\infty}^{\infty}e^{ikt}J(t)dt\right]-1\right\}dk=0. \tag{B.:40}$$

From which follows

$$-Q(r)+J(r)-2\pi\rho\int_0^d ds\int_{-\infty}^{\infty}dt\,\delta(t+s-r)Q(s)J(t)=0 \quad , \tag{B.:41}$$

or

$$J(r)=Q(r)+2\pi\rho\int_0^d ds\,Q(s)J(r-s) \quad . \tag{B.:42}$$

Since $J(r)$ is even we can rewrite

$$J(r)=Q(r)+2\pi\rho\int_0^d ds\,Q(s)J(|r-s|) \qquad r>0 \quad . \tag{B.:43}$$

Let us now take the derivative with respect to r of the expressions found for $S(r)$ and $J(r)$. Since $dJ/dr = -rh(r)$ from equation (B.:43) we find

$$rh(r) = -Q'(r) + 2\pi\rho \int_0^d (r-s)h(|r-s|)Q(s)\,ds \quad r > 0 \quad , \tag{B.:44}$$

where the prime denotes differentiation. Since $dS/dr = -rc(r)$ from equation (B.:36) we find

$$\begin{aligned} rc(r) &= -Q'(r) + 2\pi\rho \left[-Q(r)Q(0) - \int_r^d Q(s) \frac{dQ(s-r)}{ds}\, ds \right] \\ &= -Q'(r) + 2\pi\rho \left\{ -Q(r)Q(0) - [Q(s)Q(s-r)]_r^d + \int_r^d Q'(s)Q(s-r)\,ds \right\} \\ &= -Q'(r) + 2\pi\rho \left[-Q(d)Q(d-r) + \int_r^d Q'(s)Q(s-r)\,ds \right] \quad . \end{aligned} \tag{B.:45}$$

Since $Q(d) = 0$ (see equation (B.:30)) we have that

$$rc(r) = -Q'(r) + 2\pi\rho \int_r^d Q'(s)Q(s-r)\,ds \quad 0 < r < d \quad . \tag{B.:46}$$

We want to stress that the two expressions just found for $h(r)$ (B.:44) and for $c(r)$ (B.:46) have been derived from:

- the OZ equation,
- $c(r) = 0$ for $r > d$,
- the static structure factor is finite at all wave vectors.

It should also be noticed how this technique:

- must reduce the problem to a set of algebraic equations, in order to be succesful;
- has been generalized to multicomponent systems by R. J. Baxter [44] (PY solution of a mixture of additive hard spheres) and by L. Blum [46] (MSA solution of the primitive model of charged hard spheres). In these cases one have to make an ansatz for the matricial factorization to be verified a posteriori;
- has some defects as the non unicity of the $\hat{Q}(k)$ or the non unicity of the solutions of the algebraic equations.

Appendix C

The PY solution for Hard spheres

The simplest model of a fluid is a system of hard spheres, i.e. a system of particles whose pair potential is given by

$$v(r) = \begin{cases} \infty & r < d \quad , \\ 0 & r > d \quad , \end{cases} \tag{C.:1}$$

where d is the diameter of the spheres.

The configuration in which the volume occupied by the spheres is the maximum is called close-packed (see figure C.1). Let us calculate the close-packed density ρ_0. The volume of an

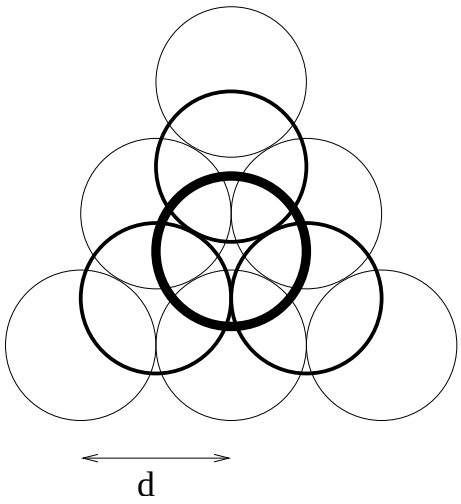

FIGURE C.1: Close-packed configuration of 10 spheres seen from above.

equilateral prism of side l is $V_l = l^3/(6\sqrt{2})$. Let a_n be the number of spheres in a close-packed configuration with n spheres per side. We will then have $a_1 = 1$ and $a_n = a_{n-1} + n(n+1)/2$, or

$$\begin{aligned} a_k &= \frac{1}{2}\sum_{n=1}^{k} n(n+1) = \frac{1}{2}\left[\sum_{n=1}^{k} n^2 + \sum_{n=1}^{k} n\right] \\ &= \frac{1}{2}\left\{\frac{1}{6}[2k^3 + 3k^2 + k] + \frac{1}{2}[k^2 + k]\right\} \quad . \end{aligned} \tag{C.:2}$$

We then find

$$\rho_0 = \lim_{k\to\infty} \frac{a_k}{V_{d(k-1)}} = \frac{1/6}{d^3/(6\sqrt{2})} = \sqrt{2}/d^3 \quad . \tag{C.:3}$$

The hard spheres fluid undergoes a freezing transition at $\rho_f = 0.67\rho_0$ but the absence of attractive forces means that there is only a single fluid phase [136].

In [12] section 4.6 one can find a detailed account on virial coefficients and the equation of state of the hard spheres fluid. Here we want to show how it is possible to find an analytic solution to the PY approximation. The PY closure rewritten in terms of the function $y(r) = \exp[\beta v(r)]g(r)$ and of the Mayer function $f(r) = \exp[-\beta v(r)] - 1$ is

$$c(r) = y(r)f(r) \quad . \tag{C.:4}$$

For hard spheres of diameter d this equation is equivalent to

$$c(r) = \begin{cases} -y(r) & r < d \quad , \\ 0 & r > d \quad , \end{cases} \tag{C.:5}$$

and there is a further exact restriction on the solution, namely

$$g(r) = 0 \qquad r < d \quad . \tag{C.:6}$$

It is then possible to use the Wiener-Hopf factorization (see section B). From equation (B.:44) we find for the auxiliary function Q

$$Q'(r) = ar + b \quad , \tag{C.:7}$$

with

$$a = 1 - \frac{12\eta}{d^3}\int_0^d Q(s)\,ds \quad , \tag{C.:8}$$

$$b = \frac{12\eta}{d^3}\int_0^d sQ(s)\,ds \quad , \tag{C.:9}$$

where we introduced the *packing fraction* $\eta = \rho\pi d^3/6$. Substituting $Q(r) = ar^2/2 + br - \gamma$ into (C.:8), (C.:9), and in $Q(d) = 0$ we find three equations in the three unknown a, b, and γ. The solution of the linear system of equations is

$$a = \frac{1+2\eta}{(1-\eta)^2} \quad , \tag{C.:10}$$

$$b = \frac{-3d\eta}{2(1-\eta)^2} \quad , \tag{C.:11}$$

$$\gamma = \frac{1}{2}ad^2 + bd \quad . \tag{C.:12}$$

Knowing $Q(r)$ we can calculate $c(r)$ from equation (B.:46). It is found that

$$c(x) = \begin{cases} -\lambda_1 - 6\eta\lambda_2\, x - \frac{1}{2}\eta\lambda_1\, x^3 & x < 1 \quad , \\ 0 & x > 1 \quad , \end{cases} \tag{C.:13}$$

where $x = r/d$ and

$$\lambda_1 = a^2 = \frac{(1+2\eta)^2}{(1-\eta)^4} \quad , \tag{C.:14}$$

$$\lambda_2 = -\frac{(1+\eta/2)^2}{(1-\eta)^4} \quad . \tag{C.:15}$$

i Compressibility pressure

From the definition of isothermal compressibility we have

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_{T,N} \quad , \tag{C.i:1}$$

Integrating over the density we find

$$\beta P = \int_0^\rho \frac{\beta}{\rho' \chi_T} d\rho' \quad . \tag{C.i:2}$$

From the compressibility equation we know that

$$\frac{\beta}{\rho \chi_T} = \frac{1}{S(k=0)} = \frac{1}{1+\rho\hat{h}(0)} = 1 - \rho\hat{c}(0) \quad . \tag{C.i:3}$$

Substituting (C.i:3) into (C.i:2) and changing variable of integration we find

$$\beta P = \rho - \frac{1}{v_0^2}\int_0^\eta \hat{c}(0)\eta\, d\eta \quad , \tag{C.i:4}$$

where $v_0 = \pi d^3/6$ is the volume of a sphere. From equation (C.:13) we find

$$\hat{c}(0) = 4\pi \int_0^d c(r) r^2\, dr \tag{C.i:5}$$

$$= -v_0 \frac{8 - 2\eta + 4\eta^2 - \eta^3}{(1-\eta)^4} \quad . \tag{C.i:6}$$

Substituting this result into equation (C.i:4) we find

$$\frac{\beta P}{\rho} = \frac{1 + \eta + \eta^2}{(1-\eta)^3} \quad . \tag{C.i:7}$$

which is the equation of state looked for.

ii Virial pressure

From the virial theorem we have

$$\frac{\beta P}{\rho} = 1 - \frac{2}{3}\pi\beta\rho \int_0^\infty v'(r) g(r) r^3\, dr \quad . \tag{C.ii:1}$$

Rewriting this expression in terms of the y function which is everywhere continuous [12] we find

$$\frac{\beta P}{\rho} = 1 + \frac{2}{3}\pi\rho \int_0^\infty r^3 y(r) \frac{de^{-\beta v(r)}}{dr}\, dr \quad . \tag{C.ii:2}$$

Since

$$\frac{de^{-\beta v(r)}}{dr} = \delta(r-d) \quad , \tag{C.ii:3}$$

we have

$$\begin{aligned}\frac{\beta P}{\rho} &= 1+\frac{2}{3}\pi\rho d^3 y(d) \\ &= 1-\frac{2}{3}\pi\rho d^3 \lim_{r\to d^-} c(r) \\ &= \frac{1+2\eta+3\eta^2}{(1-\eta)^2} \quad , \end{aligned} \tag{C.ii:4}$$

where in the second equality we used equation (C.:5) and in the last equality expression (C.:13).

In figure C.2 we plot the compressibility and virial equations of state and compare them with the Carnahan-Starling [137] formula. The latter can be recovered by adding together the expressions (C.i:7) and (C.ii:4) with weights of 2/3 and 1/3 respectively

$$\frac{\beta P_{cs}}{\rho} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \quad . \tag{C.ii:5}$$

This formula gives results that are almost indistinguishable from those of molecular dynamics and Monte Carlo calculations.

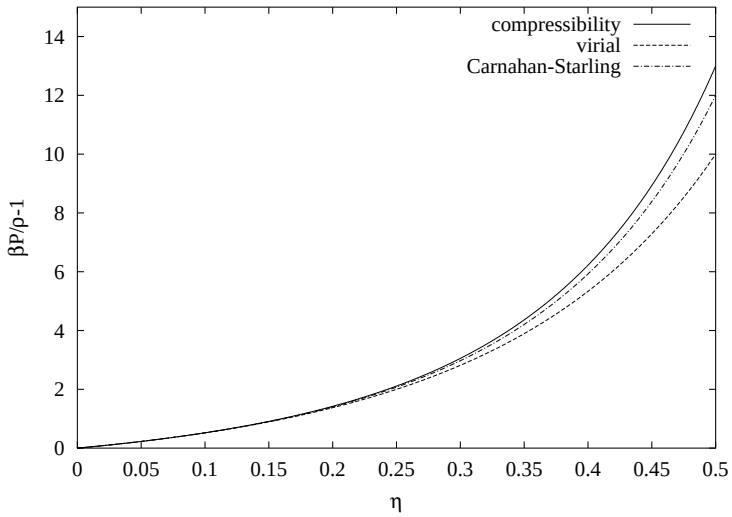

FIGURE C.2: We plot the equation of state obtained from the PY approximation via the compressibility route (C.i:7) and the virial route (C.ii:4) and we compare them with the Carnahan-Starling formula (C.ii:5).

iii Hard rods

In this subsection we will calculate the direct correlation function of a system of hard spheres in one dimension (hard rods) in the PY approximation, using the Wiener-Hopf factorization described in appendix B.

In one dimension equations (B.:12) and (B.:13) become,

$$\hat{A}(k) = 1-\rho\int_{-\infty}^{\infty} e^{ikr}c(r)\,dr \quad , \tag{C.iii:1}$$

$$\hat{h}(k) = \int_{-\infty}^{\infty} e^{ikr}h(r)\,dr \quad . \tag{C.iii:2}$$

where $h(r)$ and $c(r)$ are even functions of r.

We define the auxiliary function $Q(r)$ in equation (B.:31), without the prefactor 2π

$$\hat{Q}(k) = 1 - \rho \int_0^d e^{ikr} Q(r)\, dr \quad . \tag{C.iii:3}$$

Then equations (B.:36) and (B.:43) become,

$$c(r) = Q(r) - \rho \int_r^d Q(x)Q(x-r)\, dx \quad 0 < r < d \quad , \tag{C.iii:4}$$

$$h(r) = Q(r) + \rho \int_0^d ds\, Q(s)h(|r-s|) \quad 0 < r < d \quad . \tag{C.iii:5}$$

Since $h(r)$ is involved in equation (C.iii:5) only over the interval $0 < r < d$ we can replace it with -1. We then find from that equation that $Q(r)$ must be a constant in $0 < r < d$

$$Q(r) = -1 + \rho \int_0^d Q(s)\, ds = a \quad , \tag{C.iii:6}$$

from which we can easily find the constant a

$$a = \frac{1}{\rho d - 1} \quad . \tag{C.iii:7}$$

When we substitute this result in (C.iii:4) we find for the direct correlation function

$$c(r) = a - \rho a^2 (d - r) = \frac{\rho r - 1}{(\rho d - 1)^2} \quad , \tag{C.iii:8}$$

this is the result already obtained by Wertheim [29] following a different calculation. The PY approximation for an hard sphere fluid in odd dimensions has been solved analytically by Leutheusser [47].

Appendix D

Mixtures

The discussion until now has been limited to one component systems. We consider now an n-component system in which N_ν particles, labeled by $i_\nu = 1, 2, \ldots, N_\nu$, are of specie ν with $\nu = 1, 2, \ldots, n$. The total number of particles is $N = \sum_{\nu=1}^{n} N_\nu$ and the concentration number for specie ν is $x_\nu = N_\nu / N$.

The microscopic partial densities are defined as

$$\rho_\nu(\mathbf{r}) = \sum_{i_\nu=1}^{N_\nu} \delta(\mathbf{r} - \mathbf{r}_{i_\nu}) \quad , \tag{D.:1}$$

and their Fourier transform is

$$\rho_\nu(\mathbf{k}) = \int \rho_\nu(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}}\, d\mathbf{r} = \sum_{i_\nu=1}^{N_\nu} e^{-i\mathbf{k}\mathbf{r}_{i_\nu}} \quad . \tag{D.:2}$$

i The static structure factor

The partial static structure factors are defined as

$$\begin{aligned} S_{\nu\mu}(\mathbf{k}) &= \frac{1}{N}\langle \rho_\nu(\mathbf{k})\rho_\mu(-\mathbf{k})\rangle \\ &= x_\nu \delta_{\nu\mu} + \frac{1}{N}\langle {\sum_{i_\nu=1}^{N_\nu}}' {\sum_{i_\mu=1}^{N_\mu}}' e^{-i\mathbf{k}(\mathbf{r}_{i_\nu} - \mathbf{r}_{i_\mu})}\rangle \quad , \end{aligned} \tag{D.i:1}$$

where we used $\langle \ldots \rangle$ to denote a canonical average and the prime over the double sum means that $i_\mu \neq i_\nu$ when $\mu = \nu$. We can further write

$$\begin{aligned} S_{\nu\mu}(\mathbf{k}) &= x_\nu \delta_{\nu\mu} + \frac{1}{N}\int e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')} \langle {\sum_{i_\nu=1}^{N_\nu}}' {\sum_{i_\mu=1}^{N_\mu}}' \delta(\mathbf{r} - \mathbf{r}_{i_\nu})\delta(\mathbf{r}' - \mathbf{r}_{i_\mu})\rangle \, d\mathbf{r}\, d\mathbf{r}' \\ &= x_\nu \delta_{\nu\mu} + \frac{1}{N}\int e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')} \rho^{(2)}_{N,\nu\mu}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \quad , \end{aligned} \tag{D.i:2}$$

where we introduced the two particles correlation function $\rho^{(2)}_{N,\nu\mu}(\mathbf{r}, \mathbf{r}')$. It represents the probability of finding a particle of specie ν in $\mathbf{r}$ and one of specie μ in $\mathbf{r}'$. The partial pair distribution

function is then defined as

$$g_{\nu\mu}(\mathbf{r},\mathbf{r}') = \frac{\rho^{(2)}_{N,\nu\mu}(\mathbf{r},\mathbf{r}')}{\rho^{(1)}_{N,\nu}(\mathbf{r})\rho^{(1)}_{N,\mu}(\mathbf{r}')} \quad , \tag{D.i:3}$$

where the partial single particle correlation function is defined as

$$\rho^{(1)}_{N,\nu}(\mathbf{r}) = \langle \sum_{i_\nu=1}^{N_\nu} \delta(\mathbf{r}-\mathbf{r}_{i_\nu})\rangle \quad . \tag{D.i:4}$$

If the system is homogeneous we have

$$\rho^{(1)}_{N,\nu}(\mathbf{r}) = \frac{N_\nu}{V} = x_\nu \rho \quad , \tag{D.i:5}$$

where $\rho = N/V$ is the usual density of the system. And

$$\rho^{(2)}_{N,\nu\mu}(\mathbf{r},\mathbf{r}') = \rho^{(2)}_{N,\nu\mu}(\mathbf{r}-\mathbf{r}') = \rho^2 x_\nu x_\mu g_{\nu\mu}(\mathbf{r}-\mathbf{r}') \quad . \tag{D.i:6}$$

Then equation (D.i:2) becomes

$$S_{\nu\mu}(\mathbf{k}) = x_\nu\delta_{\nu\mu} + \rho x_\nu x_\mu \int e^{-i\mathbf{kr}} g_{\nu\mu}(\mathbf{r})\, d\mathbf{r} \quad . \tag{D.i:7}$$

If we define the partial total correlation function as

$$h_{\nu\mu}(\mathbf{r}) = g_{\nu\mu}(\mathbf{r}) - 1 \overset{r\to\infty}{\longrightarrow} 0 \quad , \tag{D.i:8}$$

we find, neglecting the forward scattering,

$$S_{\nu\mu}(\mathbf{k}) = x_\nu\delta_{\nu\mu} + \rho x_\nu x_\mu \hat{h}_{\nu\mu}(\mathbf{k}) \quad , \tag{D.i:9}$$

where the hat stands for Fourier transformed.

If the system is homogeneous and isotropic we must have

$$\rho^{(2)}_{\nu\mu}(r) = \rho^{(2)}_{\mu\nu}(r) \quad . \tag{D.i:10}$$

We will then have $n(n+1)/2$ distinct partial pair distribution functions.

ii The OZ equation

The partial direct correlation function $c_{\nu\mu}(\mathbf{r}_1,\mathbf{r}_2)$ is defined from the OZ equation as follows

$$h_{\mu\nu}(\mathbf{r}_1,\mathbf{r}_2) = c_{\mu\nu}(\mathbf{r}_1,\mathbf{r}_2) + \sum_{\gamma=1}^{n} \int \rho^{(1)}_\gamma(\mathbf{r}_3) c_{\mu\gamma}(\mathbf{r}_1,\mathbf{r}_3) h_{\gamma\nu}(\mathbf{r}_3,\mathbf{r}_2)\, d\mathbf{r}_3 \quad . \tag{D.ii:1}$$

If the system is homogeneous taking the Fourier transform of D.ii:1 and multiplying both sides by $\sqrt{x_\mu x_\nu}$ we find

$$\sqrt{x_\mu x_\nu}\hat{h}_{\mu\nu}(\mathbf{k}) = \sqrt{x_\mu x_\nu}\hat{c}_{\mu\nu}(\mathbf{k}) + \rho \sum_{\gamma=1}^{n} [\sqrt{x_\mu x_\gamma}\hat{c}_{\mu\gamma}(\mathbf{k})\sqrt{x_\gamma x_\nu}\hat{h}_{\gamma\nu}(\mathbf{k})] \quad , \tag{D.ii:2}$$

or in matricial form

$$H = C[1+\rho H] \quad , \tag{D.ii:3}$$

where $H_{\mu\nu} = \sqrt{x_\mu x_\nu}\hat{h}_{\mu\nu}(\mathbf{k})$ and $C_{\mu\nu} = \sqrt{x_\mu x_\nu}\hat{c}_{\mu\nu}(\mathbf{k})$.

If the system is isotropic then H is symmetric, $[1+\rho H]$ is symmetric, $[1+\rho H]^{-1}$ is symmetric, and since H and $[1+\rho H]^{-1}$ commute, C is also symmetric.

iii The grand canonical formalism

Let $\{\mu_\nu\}$ be the chemical potentials of the n species. The grand canonical partition function of the mixture is

$$\begin{aligned}\Theta(\{\mu_\nu\},V,T) &= \sum_{\{N_\nu\}=0}^{\infty}\left(\prod_{\nu=1}^{n}\frac{e^{\beta N_\nu\mu_\nu}}{\Lambda^{3N_\nu}N_\nu!}\right)\int e^{-\beta W(r^N)}\,dr^N \\ &= \sum_{\{N_\nu\}=0}^{\infty}\left(\prod_{\nu=1}^{n}\frac{\zeta_\nu^{N_\nu}}{N_\nu!}\right)Z_N(V,T) \quad , \end{aligned} \tag{D.iii:1}$$

where $r^N=(\{\mathbf{r}_{i_1}\},\{\mathbf{r}_{i_2}\},\ldots,\{\mathbf{r}_{i_n}\})$, $\zeta_\nu=\Lambda^{-3}e^{\beta\mu_\nu}$ are the fugacities, and Z_N is the configuration integral. The probability that the system contains N_1 particles of specie 1, N_2 particles of specie 2, ..., N_n particles of specie n is

$$P(\{N_\nu\})=\frac{1}{\Theta}\left(\prod_{\nu=1}^{n}\frac{\zeta_\nu^{N_\nu}}{N_\nu!}\right)Z_N \quad . \tag{D.iii:2}$$

The one particle density for specie ν is then

$$\rho_\nu^{(1)}(\mathbf{r})=\sum_{N_\nu=1}^{\infty}\sum_{\{N_\mu\}_{\mu\neq\nu}=0}^{\infty}P(\{N_\gamma\})\rho_{N,\nu}^{(1)}(\mathbf{r}) \quad , \tag{D.iii:3}$$

the two particles density for species ν and μ is

$$\rho_{\mu\nu}^{(2)}(\mathbf{r},\mathbf{r}')=\begin{cases}\displaystyle\sum_{N_\mu,N_\nu=1}^{\infty}\sum_{\{N_\delta\}_{\delta\neq\mu,\nu}=0}^{\infty}P(\{N_\gamma\})\rho_{N,\mu\nu}^{(2)}(\mathbf{r},\mathbf{r}') & \mu\neq\nu \quad , \\ \displaystyle\sum_{N_\mu=2}^{\infty}\sum_{\{N_\delta\}_{\delta\neq\mu}=0}^{\infty}P(\{N_\gamma\})\rho_{N,\mu\mu}^{(2)}(\mathbf{r},\mathbf{r}') & \mu=\nu \quad . \end{cases} \tag{D.iii:4}$$

Their normalization is

$$\int\rho_\nu^{(1)}(\mathbf{r})\,d\mathbf{r} = \langle N_\nu\rangle \quad , \tag{D.iii:5}$$

$$\int\int\rho_{\mu\nu}^{(2)}(\mathbf{r},\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' = \langle N_\mu N_\nu-\delta_{\mu\nu}N_\mu\rangle \quad . \tag{D.iii:6}$$

iv The Kirkwood and Buff equation

Let us consider the following combination

$$\int\int[\rho_{\mu\nu}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)-\rho_\mu^{(1)}(\mathbf{r}_1)\rho_\nu^{(1)}(\mathbf{r}_2)]\,d\mathbf{r}_1\,d\mathbf{r}_2=\langle N_\mu N_\nu\rangle-\delta_{\mu\nu}\langle N_\mu\rangle-\langle N_\mu\rangle\langle N_\nu\rangle \; . \tag{D.iv:1}$$

If the system is homogeneous we find

$$V\rho^2x_\mu x_\nu\int[g_{\mu\nu}(\mathbf{r})-1]\,d\mathbf{r}=\langle N_\mu N_\nu\rangle-\langle N_\mu\rangle\langle N_\nu\rangle-\delta_{\mu\nu}\langle N_\mu\rangle \quad , \tag{D.iv:2}$$

where in the grand canonical ensemble the concentration numbers are ratios of average numbers of particles, i.e. $x_\nu = \langle N_\nu \rangle / \langle N \rangle$. We call

$$\begin{aligned} A_{\mu\nu} &= x_\mu [\rho x_\nu \hat{h}_{\mu\nu}(0) + \delta_{\mu\nu}] \\ &= x_\mu \left(\frac{\langle N_\mu N_\nu \rangle - \langle N_\mu \rangle \langle N_\nu \rangle}{\langle N_\mu \rangle} \right) \quad . \end{aligned} \tag{D.iv:3}$$

From the OZ equation we have

$$\hat{h}_{\mu\nu}(0) = \hat{c}_{\mu\nu}(0) + \rho \sum_\gamma x_\gamma \hat{c}_{\mu\gamma}(0) \hat{h}_{\gamma\nu}(0) \quad . \tag{D.iv:4}$$

Multiplying both sides by $\rho x_\mu x_\nu$ we find

$$A_{\mu\nu} - \delta_{\mu\nu} x_\mu = \sum_\gamma B_{\mu\gamma} A_{\gamma\nu} \quad , \tag{D.iv:5}$$

where $B_{\mu\nu} = \rho x_\mu \hat{c}_{\mu\nu}(0)$. If we know the inverse of A we can then determine B

$$B_{\mu\delta} = \delta_{\mu\delta} - [A^{-1}]_{\mu\delta} x_\mu \quad , \tag{D.iv:6}$$

or, using $\sum_\nu x_\nu = 1$

$$\sum_{\mu\nu} x_\nu B_{\mu\nu} = \rho \sum_{\mu\nu} x_\mu x_\nu \hat{c}_{\mu\nu}(0) = 1 - \sum_{\mu\nu} x_\mu x_\nu [A^{-1}]_{\mu\nu} \quad . \tag{D.iv:7}$$

We want now to show Kirkwood and Buff formula [138]

$$\sum_{\mu\nu} x_\mu x_\nu [A^{-1}]_{\mu\nu} = \chi_T^0 / \chi_T \quad . \tag{D.iv:8}$$

where $\chi_T^0 = \beta/\rho$ is the isothermal compressibility of the ideal gas and χ_T the one of the interacting mixture.

From the definition of the partition function follows that

$$\langle N_\nu \rangle = \frac{1}{\Theta} \left[\frac{\partial \Theta}{\partial(\beta \mu_\nu)} \right]_{T,V} \quad . \tag{D.iv:9}$$

Taking one more derivative we find

$$\begin{aligned} \left[\frac{\partial \langle N_\nu \rangle}{\partial(\beta \mu_\gamma)} \right]_{T,V} &= \frac{1}{\Theta} \left[\frac{\partial^2 \Theta}{\partial(\beta\mu_\gamma)\partial(\beta\mu_\nu)} \right]_{T,V} - \frac{1}{\Theta^2} \left[\frac{\partial \Theta}{\partial(\beta\mu_\gamma)} \right]_{T,V} \left[\frac{\partial \Theta}{\partial(\beta\mu_\nu)} \right]_{T,V} \\ &= \langle N_\gamma N_\nu \rangle - \langle N_\gamma \rangle \langle N_\nu \rangle \quad . \end{aligned} \tag{D.iv:10}$$

Omitting the average symbol for the number of particles we find for A the following thermodynamic expression

$$A_{\nu\gamma} = \frac{1}{N\beta} \left(\frac{\partial N_\nu}{\partial \mu_\gamma} \right)_{T,V,\{\mu_\alpha\}'} \quad , \tag{D.iv:11}$$

where $\{\mu_\alpha\}' = \{\mu_\alpha\}_{\alpha \neq \nu}$. We are choosing as independent variables T, V, and $\{\mu_\alpha\}$. At constant T and V the chemical potentials $\{\mu_\alpha\}$ are just functions of $\{N_\alpha\}$. From the Jacobian identity

$$\frac{\partial(\mu_1, \ldots, \mu_n)}{\partial(N_1, \ldots, N_n)} \frac{\partial(N_1, \ldots, N_n)}{\partial(\mu_1, \ldots, \mu_n)} = 1 \quad , \tag{D.iv:12}$$

follows that

$$[A^{-1}]_{\nu\gamma} = N\beta \left(\frac{\partial \mu_\nu}{\partial N_\gamma}\right)_{T,V,\{N_\alpha\}'} \quad . \tag{D.iv:13}$$

Moreover from the infinitesimal change in the grand thermodynamic potential $\Omega = -PV$

$$-d\Omega = S\,dT + P\,dV + \sum_\nu N_\nu\,d\mu_\nu = P\,dV + V\,dP \quad , \tag{D.iv:14}$$

follows at constant T and V

$$\sum_\nu N_\nu \sum_\gamma \left(\frac{\partial \mu_\nu}{\partial N_\gamma}\right)_{T,V,\{N_\alpha\}'} dN_\gamma = V \sum_\gamma \left(\frac{\partial P}{\partial N_\gamma}\right)_{T,V,\{N_\alpha\}'} dN_\gamma \quad , \tag{D.iv:15}$$

from which we find

$$\sum_\nu N_\nu \left(\frac{\partial \mu_\nu}{\partial N_\gamma}\right)_{T,V,\{N_\alpha\}'} = V \left(\frac{\partial P}{\partial N_\gamma}\right)_{T,V,\{N_\alpha\}'} \quad . \tag{D.iv:16}$$

Upon multiplying both sides by βx_γ, summing over γ, and using equation (D.iv:13) we reach the following expression

$$\sum_{\nu\gamma} x_\gamma x_\nu [A^{-1}]_{\nu\gamma} = \chi_T^0 \sum_\gamma N_\gamma \left(\frac{\partial P}{\partial N_\gamma}\right)_{T,V,\{N_\alpha\}'} \quad . \tag{D.iv:17}$$

We now use the following identity

$$\left(\frac{\partial V}{\partial N}\right)_{T,P} \left(\frac{\partial P}{\partial V}\right)_{T,N} = \frac{\partial(V,P)}{\partial(N,P)} \frac{\partial(P,N)}{\partial(V,N)} = -\frac{\partial(V,P)}{\partial(V,N)} = -\left(\frac{\partial P}{\partial N}\right)_{T,V} \quad , \tag{D.iv:18}$$

to rewrite

$$\sum_{\nu\gamma} x_\gamma x_\nu [A^{-1}]_{\nu\gamma} = -\chi_T^0 \left(\frac{\partial P}{\partial V}\right)_{T,\{N_\alpha\}} \sum_\gamma N_\gamma \left(\frac{\partial V}{\partial N_\gamma}\right)_{T,P,\{N_\alpha\}'} \quad . \tag{D.iv:19}$$

Since the volume is an homogeneous function of order one over $\{N_\alpha\}$ then

$$V = \sum_\gamma N_\gamma \left(\frac{\partial V}{\partial N_\gamma}\right)_{T,P,\{N_\alpha\}'} \quad , \tag{D.iv:20}$$

which upon insertion into (D.iv:19) gives formula (D.iv:8).

Appendix E

Very tedious algebra for the MSA solution

In this appendix we will use Roman indices for the species. We will start with the determination of $Q_{ij}(r)$ which will allow us to find the relationship between the a_j and the J_{ij}.

Plugging (4.i:57) into (4.i:56) we find

$$Q_{ij}(r) = a_{ij} + b_{ij}r + c_{ij}r^2 + d_{ij}r^3 \quad , \tag{E.:1}$$

where

$$\begin{aligned} a_{ij} &= J_{ij} - \frac{1}{2}A_{ij} - \sum_k \rho_k \left[J_{ik} \int_{\lambda_{jk}}^{\sigma_{jk}} dr\, Q_{kj}(r) + \pi \int_{\lambda_{jk}}^{\sigma_{jk}} dr\, Q_{kj}(r) r^2 \right. \\ &\quad \left. + J_{ik}A_{kj}\sigma_{jk} + \frac{\pi}{3}A_{kj}\sigma_{jk}^3 \right] \quad , \end{aligned} \tag{E.:2}$$

$$b_{ij} = \sum_k \rho_k \left[2\pi \int_{\lambda_{jk}}^{\sigma_{jk}} dr\, Q_{kj}(r) r + J_{ik}A_{kj} + \pi A_{kj}\sigma_{jk}^2 \right] \quad , \tag{E.:3}$$

$$c_{ij} = \pi - \sum_k \rho_k \left[\pi \int_{\lambda_{jk}}^{\sigma_{jk}} dr\, Q_{kj}(r) + \pi A_{kj}\sigma_{jk} \right] \quad , \tag{E.:4}$$

$$d_{ij} = \frac{\pi}{3} \sum_k \rho_k A_{kj} \quad . \tag{E.:5}$$

From the neutrality condition (4.i:2) we find that $d_{ij} = 0$. $Q_{ij}(r)$ must then be a second degree polynomial. We now define the following constants

$$\alpha_{kj}^0 = \int_{\lambda_{jk}}^{\sigma_{jk}} dr\, Q_{kj}(r) = a_{kj}\delta_{kj}^1 + b_{kj}\frac{1}{2}\delta_{jk}^2 + c_{kj}\frac{1}{3}\delta_{jk}^3 \quad , \tag{E.:6}$$

$$\alpha_{kj}^1 = \int_{\lambda_{jk}}^{\sigma_{jk}} dr\, Q_{kj}(r) r = a_{kj}\frac{1}{2}\delta_{kj}^2 + b_{kj}\frac{1}{3}\delta_{jk}^3 + c_{kj}\frac{1}{4}\delta_{jk}^4 \quad , \tag{E.:7}$$

$$\alpha_{kj}^0 = \int_{\lambda_{jk}}^{\sigma_{jk}} dr\, Q_{kj}(r) r^2 = a_{kj}\frac{1}{3}\delta_{kj}^3 + b_{kj}\frac{1}{4}\delta_{jk}^4 + c_{kj}\frac{1}{5}\delta_{jk}^5 \quad , \tag{E.:8}$$

where $\delta_{jk}^n = \sigma_{jk}^n - \lambda_{jk}^n$. Using this constants and taking into account equation (4.i:34) we can

rewrite the coefficients of $Q_{ij}(r)$ as follows

$$a_{ij} = J_{ij} - \frac{1}{2} z_i a_j - \sum_k \rho_k (J_{ik}\alpha^0_{kj} + \pi\alpha^2_{kj} + J_{ik} z_k a_j \sigma_{jk} + \frac{\pi}{3} z_k a_j \sigma^3_{jk}) \quad , \tag{E.:9}$$

$$b_{ij} = \sum_k \rho_k (2\pi\alpha^1_{kj} + \pi z_k a_j \sigma^2_{jk} + J_{ik} z_k a_j) \quad , \tag{E.:10}$$

$$c_{ij} = \pi - \sum_k \rho_k (\pi\alpha^0_{kj} + \pi z_k a_j \sigma_{jk}) \quad , \tag{E.:11}$$

From the boundary condition (4.i:38) follows that

$$a_{ij} = -b_{ij}\sigma_{ij} - c_{ij}\sigma^2_{ij} - z_i a_j \quad . \tag{E.:12}$$

We can then solve for c_{ij} and b_{ij} in terms of a_j and J_{ij} and later use expression (E.:12) to determine the relationship between the a_j and the J_{ij}.

Let us begin calculating the δ^n in terms of the diameters

$$\delta^1_{jk} = \sigma_k \quad , \tag{E.:13}$$

$$\delta^2_{jk} = \sigma_j\sigma_k \quad , \tag{E.:14}$$

$$\delta^3_{jk} = \frac{3}{4}\sigma^2_j\sigma_k + \frac{1}{4}\sigma^3_k \quad , \tag{E.:15}$$

$$\delta^4_{jk} = \frac{1}{2}\sigma^3_j\sigma_k + \frac{1}{2}\sigma_j\sigma^3_k \quad , \tag{E.:16}$$

$$\delta^5_{jk} = \frac{5}{16}\sigma^4_j\sigma_k + \frac{5}{8}\sigma^2_j\sigma^3_k + \frac{1}{16}\sigma^5_k \quad . \tag{E.:17}$$

Then we rewrite the α in terms of c and b only

$$\begin{aligned}\alpha^0_{kj} &= b_{kj}\left(\frac{1}{2}\delta^2_{jk} - \sigma_{kj}\delta^1_{jk}\right) + c_{kj}\left(\frac{1}{3}\delta^3_{jk} - \sigma^2_{kj}\delta^1_{jk}\right) - z_k a_j \delta^1_{jk} \\ &= b_{kj}B^0_{jk} + c_{kj}C^0_{jk} - z_k a_j \delta^1_{jk} \quad , \end{aligned} \tag{E.:18}$$

$$\begin{aligned}\alpha^1_{kj} &= b_{kj}\left(\frac{1}{3}\delta^3_{jk} - \sigma_{kj}\frac{1}{2}\delta^2_{jk}\right) + c_{kj}\left(\frac{1}{4}\delta^4_{jk} - \sigma^2_{kj}\frac{1}{2}\delta^2_{jk}\right) - z_k a_j \frac{1}{2}\delta^2_{jk} \\ &= b_{kj}B^1_{jk} + c_{kj}C^1_{jk} - z_k a_j \frac{1}{2}\delta^2_{jk} \quad , \end{aligned} \tag{E.:19}$$

$$\begin{aligned}\alpha^2_{kj} &= b_{kj}\left(\frac{1}{4}\delta^4_{jk} - \sigma_{kj}\frac{1}{3}\delta^3_{jk}\right) + c_{kj}\left(\frac{1}{5}\delta^5_{jk} - \sigma^2_{kj}\frac{1}{3}\delta^3_{jk}\right) - z_k a_j \frac{1}{3}\delta^3_{jk} \\ &= b_{kj}B^2_{jk} + c_{kj}C^2_{jk} - z_k a_j \frac{1}{3}\delta^3_{jk} \quad . \end{aligned} \tag{E.:20}$$

We calculate the B^n, C^n defined in the previous equations in terms of the diameters

$$\begin{cases} B^0_{jk} = -\frac{1}{2}\sigma^2_k \quad , \\ C^0_{jk} = -\frac{1}{6}\sigma^3_k - \frac{1}{2}\sigma^2_k\sigma_j \quad , \end{cases} \tag{E.:21}$$

$$\begin{cases} B^1_{jk} = \frac{1}{12}\sigma^3_k - \frac{1}{4}\sigma_j\sigma^2_k \quad , \\ C^1_{jk} = -\frac{1}{4}\sigma^2_k\sigma^2_j \quad , \end{cases} \tag{E.:22}$$

$$\begin{cases} B^2_{jk} = -\frac{1}{24}\sigma^4_k + \frac{1}{12}\sigma_j\sigma^3_k - \frac{1}{8}\sigma^2_j\sigma^2_k \quad , \\ C^2_{jk} = -\frac{1}{120}\sigma^5_k + \frac{1}{24}\sigma^2_j\sigma^3_k - \frac{1}{24}\sigma_j\sigma^4_k - \frac{1}{8}\sigma^3_j\sigma^2_k \quad , \end{cases} \tag{E.:23}$$

we will see that we will not have to use B^2 and C^2. We now have for the coefficients b_{ij} and c_{ij}

$$\begin{aligned} b_{ij} &= \left[2\pi \sum_k \rho_k (b_{kj} B^1_{jk} + c_{kj} C^1_{jk})\right] + \left[\sum_k \rho_k (-\pi z_k a_j \delta^2_{jk} + \pi z_k a_j \sigma^2_{jk} + J_{ik} z_k a_j)\right] \\ &\equiv D^b_j + \gamma^b_{ij} \quad , \end{aligned} \tag{E.:24}$$

$$\begin{aligned} c_{ij} &= \left[-\pi \sum_k \rho_k (b_{kj} B^0_{jk} + c_{kj} C^0_{jk})\right] + \left[\pi - \sum_k \rho_k (-\pi z_k a_j \delta^1_{jk} + \pi z_k a_j \sigma_{jk})\right] \\ &\equiv D^c_j + \gamma^c_{ij} \quad , \end{aligned} \tag{E.:25}$$

where we defined D^b, D^c and γ^b, γ^c. We now define

$$S_{zR} = \sum_k \rho_k z_k \sigma_k \quad , \tag{E.:26}$$

$$S_{zR^2} = \sum_k \rho_k z_k \sigma^2_k \quad , \tag{E.:27}$$

$$S^i_{zJ} = \sum_k \rho_k z_k J_{ik} \quad . \tag{E.:28}$$

Using the neutrality condition (4.i:2) the γ' s can be rewritten as follows

$$\gamma^b_{ij} = a_j \left(S^i_{zJ} + \frac{\pi}{4} S_{zR^2} - \frac{\pi}{2} S_{zR} \sigma_j\right) \quad , \tag{E.:29}$$

$$\gamma^c_{ij} = \pi + \frac{\pi}{2} S_{zR} a_j \quad . \tag{E.:30}$$

i Calculation of D^b and D^c

Let us now determine D^b and D^c. From their definition follows

$$\begin{aligned} D^b_j &= 2\pi \sum_k \rho_k [(D^b_j + \gamma^b_{kj}) B^1_{jk} + (D^c_j + \gamma^c_{kj}) C^1_{jk}] \\ &= D^b_j \left[2\pi \sum_k \rho_k B^1_{jk}\right] + D^c_j \left[2\pi \sum_k \rho_k C^1_{jk}\right] + \left[2\pi \sum_k \rho_k (\gamma^b_{kj} B^1_{jk} + \gamma^c_{kj} C^1_{jk})\right] \\ &\equiv D^b_j X^b_j + D^c_j Y^b_j + Z^b_j \quad , \end{aligned} \tag{E.i:1}$$

$$\begin{aligned} D^c_j &= -\pi \sum_k \rho_k [(D^b_j + \gamma^b_{kj}) B^0_{jk} + (D^c_j + \gamma^c_{kj}) C^0_{jk}] \\ &= D^b_j \left[-\pi \sum_k \rho_k B^0_{jk}\right] + D^c_j \left[-\pi \sum_k \rho_k C^0_{jk}\right] + \left[-\pi \sum_k \rho_k (\gamma^b_{kj} B^0_{jk} + \gamma^c_{kj} C^0_{jk})\right] \\ &\equiv D^b_j X^c_j + D^c_j Y^c_j + Z^c_j \quad , \end{aligned} \tag{E.i:2}$$

where we defined X^b, Y^b, Z^b and X^c, Y^c, Z^c. We find then

$$\begin{pmatrix} 1 - X^b & -Y^b \\ -X^c & 1 - Y^c \end{pmatrix} \begin{pmatrix} D^b \\ D^c \end{pmatrix} = \begin{pmatrix} Z^b \\ Z^c \end{pmatrix} \tag{E.i:3}$$

The determinant of the coefficients matrix is

$$det = 1 - (X^b + Y^c) + X^b Y^c - X^c Y^b \quad , \tag{E.i:4}$$

then we have

$$D^b = \frac{Z^b(1-Y^c)+Z^cY^b}{det} \quad , \tag{E.i:5}$$

$$D^c = \frac{Z^c(1-X^b)+Z^bX^c}{det} \quad . \tag{E.i:6}$$

In terms of the following two constants

$$S_{R^2} = \sum_k \rho_k \sigma_k^2 \quad , \tag{E.i:7}$$

$$S_{R^3} = \sum_k \rho_k \sigma_k^3 \quad , \tag{E.i:8}$$

$$\tag{E.i:9}$$

the X' s and Y' s can be rewritten as follows

$$X_j^b = \pi\left(\frac{1}{6}S_{R^3} - \frac{1}{2}S_{R^2}\sigma_j\right) \quad , \tag{E.i:10}$$

$$X_j^c = \pi\left(\frac{1}{2}S_{R^2}\right) \quad , \tag{E.i:11}$$

$$Y_j^b = \pi\left(-\frac{1}{2}S_{R^2}\sigma_j^2\right) \quad , \tag{E.i:12}$$

$$Y_j^c = \pi\left(\frac{1}{6}S_{R^3} + \frac{1}{2}S_{R^2}\sigma_j\right) \quad . \tag{E.i:13}$$

Then the determinant (E.i:4) is

$$det = \left(1 - \frac{\pi}{6}S_{R^3}\right)^2 \equiv \Delta^2 \quad , \tag{E.i:14}$$

where we have defined

$$\Delta = 1 - \frac{\pi}{6}S_{R^3} \quad . \tag{E.i:15}$$

Let us now rewrite the Z' s. We introduce the two constants

$$S_{zJR^2}^2 = \sum_{ij} \rho_i \rho_j z_j J_{ij} \sigma_i^2 \quad , \tag{E.i:16}$$

$$S_{zJR^3}^2 = \sum_{ij} \rho_i \rho_j z_j J_{ij} \sigma_i^3 \quad , \tag{E.i:17}$$

then the Z' s can be rewritten as follows

$$\begin{aligned} Z_j^b = {} & \pi\left[a_j\sigma_j\left(-\frac{1}{2}S_{zJR^2}^2 - \frac{\pi}{8}S_{zR^2}S_{R^2} - \frac{\pi}{12}S_{zR}S_{R^3}\right)\right. \\ & \left. + a_j\left(\frac{1}{6}S_{zJR^3}^2 + \frac{\pi}{24}S_{zR^2}S_{R^3}\right) + \sigma_j^2\left(-\frac{\pi}{2}S_{R^2}\right)\right] \quad , \end{aligned} \tag{E.i:18}$$

$$\begin{aligned} Z_j^b = {} & -\pi\left[a_j\left(-\frac{1}{2}S_{zJR^2}^2 - \frac{\pi}{8}S_{zR^2}S_{R^2} - \frac{\pi}{12}S_{zR}S_{R^3}\right)\right. \\ & \left. + 1\left(-\frac{\pi}{6}S_{R^3}\right) + \sigma_j\left(-\frac{\pi}{2}S_{R^2}\right)\right] \quad . \end{aligned} \tag{E.i:19}$$

We find for the D' s the following expressions

$$\frac{\Delta^2}{\pi}D_j^b = -\phi_1 a_j\sigma_j + \phi_2 a_j - \phi_3\sigma_j^2 \quad , \tag{E.i:20}$$

$$\frac{\Delta^2}{\pi}D_j^c = -\phi_1 a_j\sigma_j + \phi_3\sigma_j + \Delta(1-\Delta) \quad , \tag{E.i:21}$$

where

$$\phi_1 = \Delta\left(\frac{1}{2}S^2_{zJR^2} + \frac{\pi}{8}S_{zR^2}S_{R^2} + \frac{\pi}{12}S_{zR}S_{R^3}\right) + \frac{\pi}{2}S_{R^2}\left(\frac{\phi_2}{\Delta}\right) \quad , \tag{E.i:22}$$

$$\phi_2 = \Delta\left(\frac{1}{6}S^2_{zJR^3} + \frac{\pi}{24}S_{zR^2}S_{R^3}\right) \quad , \tag{E.i:23}$$

$$\phi_3 = \frac{\pi}{2}S_{R^2} \quad . \tag{E.i:24}$$

The coefficients b_{ij} (E.:24) and c_{ij} (E.:25), taking into account equations (E.:29) and (E.:30) for the γ' s, can be rewritten as follows

$$b_{ij} = b_j + S^i_{zJ}a_j \quad , \tag{E.i:25}$$

$$c_{ij} = c_j \quad , \tag{E.i:26}$$

where

$$b_j = \frac{1}{\Delta^2}(-\psi_1 a_j\sigma_j + \psi_2 a_j - \psi_3\sigma_j^2) \quad , \tag{E.i:27}$$

$$c_j = \frac{1}{\Delta^2}(\psi_1 a_j + \psi_3\sigma_j) + \frac{\pi}{\Delta} \quad , \tag{E.i:28}$$

with

$$\psi_1 = \pi\left(\phi_1 + \Delta^2\frac{1}{2}S_{zR}\right) \quad , \tag{E.i:29}$$

$$\psi_2 = \pi\left(\phi_2 + \Delta^2\frac{1}{4}S_{zR^2}\right) \quad , \tag{E.i:30}$$

$$\psi_3 = \pi\phi_3 \quad . \tag{E.i:31}$$

ii Relationship between a_j and J_{ij}

Multiplying equation (E.:9) by $\rho_i z_i$, taking the sum over i and taking into account the neutrality condition (4.i:2) we find

$$\sum_i \rho_i z_i a_{ij} = \sum_i \rho_i z_i\left[J_{ij} - \frac{1}{2}z_i a_j - \sum_k \rho_k(J_{ik}\alpha^0_{kj} + J_{ik}z_k a_j\sigma_{jk})\right] \quad . \tag{E.ii:1}$$

We substitute a_{ij} and α^0_{kj} with their expressions in terms of the coefficients c_{ij} and b_{ij} (see equations (E.:12) and (E.:18)-(E.:20)). We find

$$\sum_i \rho_i(-b_{ij}\sigma_{ij} - c_{ij}\sigma^2_{ij} - z_i a_j) =$$

$$\sum_i \rho_i a_i\left[J_{ij} - \frac{1}{2}z_i a_j - \sum_k \rho_k(J_{ik}b_{kj}B^0_{jk} + J_{ik}c_{kj}C^0_{jk} - J_{ik}z_k a_j\lambda_{jk})\right] \quad . \tag{E.ii:2}$$

Substituting B^0 and C^0 with their expressions in terms of the diameters (see equations (E.:21)) we have

$$\sum_i \rho_i z_i (b_{ij}\sigma_{ij} + c_{ij}\sigma_{ij}^2) = -S_{zJ}^j - \left(\frac{1}{2}\sum_i \rho_i z_i^2\right) a_j + \sum_{ik} \rho_k \rho_i z_i J_{ik} \left[\left(-\frac{1}{2}\sigma_k^2\right) b_{kj} + \left(-\frac{1}{6}\sigma_k^3 - \frac{1}{2}\sigma_k^2\sigma_j\right) c_{kj}\right] + \left[\sum_{ik} \rho_k \rho_i z_i z_k J_{ik} \frac{1}{2}(\sigma_j - \sigma_k)\right] a_j \quad . \tag{E.ii:3}$$

We define new constants

$$S_{z^2} = \sum_i \rho_i z_i^2 \quad , \tag{E.ii:4}$$

$$S_{z^2J}^2 = \sum_{ik} \rho_k \rho_i z_i z_k J_{ik} \quad , \tag{E.ii:5}$$

$$S_{z^2JR}^2 = \sum_{ik} \rho_k \rho_i z_i z_k J_{ik} \sigma_k \quad . \tag{E.ii:6}$$

In terms of these new constants equation (E.ii:3) can be rewritten as follows

$$\sum_i \rho_i z_i (b_{ij}\sigma_{ij} + c_{ij}\sigma_{ij}^2) = -S_{zJ}^j - \frac{1}{2} S_{z^2} a_j + \sum_{ik} \rho_k \rho_i z_i J_{ik} \left[\left(-\frac{1}{2}\sigma_k^2\right) b_{kj} + \left(-\frac{1}{6}\sigma_k^3 - \frac{1}{2}\sigma_k^2\sigma_j\right) c_{kj}\right] + \frac{1}{2} S_{z^2J}^2 a_j \sigma_j - \frac{1}{2} S_{z^2JR}^2 a_j \quad . \tag{E.ii:7}$$

Let us now rewrite the terms containing the coefficients b_{ij} and c_{ij} using equations (E.i:25) and (E.i:26). In order of appearance in equation (E.ii:7) from left to right we have

- first term

$$\sum_i \rho_i z_i b_{ij} \sigma_{ij} = \frac{1}{2} S_{zR} b_j + \frac{1}{2} S_{z^2JR}^2 a_j + \frac{1}{2} S_{z^2J}^2 a_j \sigma_j \quad , \tag{E.ii:8}$$

- second term

$$\sum_i \rho_i z_i c_{ij} \sigma_{ij}^2 = \frac{1}{4} S_{zR^2} c_j + \frac{1}{2} S_{zR} c_j \sigma_j \quad , \tag{E.ii:9}$$

- third term

$$\sum_{ik} \rho_k \rho_i z_i J_{ik} \left(-\frac{1}{2}\sigma_k^2\right) b_{kj} = -\frac{1}{2} S_{zJR^2}^2 b_j - \frac{1}{2} \sum_k \rho_k (\sigma_k S_{zJ}^k)^2 a_j \quad , \tag{E.ii:10}$$

- fourth term

$$\sum_{ik} \rho_k \rho_i z_i J_{ik} \left(-\frac{1}{6}\sigma_k^3 - \frac{1}{2}\sigma_k^2\sigma_j\right) c_{kj} = -\frac{1}{6} S_{zJR^3}^2 c_j - \frac{1}{2} S_{zJR^2}^2 c_j \sigma_j \quad . \tag{E.ii:11}$$

Upon substitution of these terms back in equation (E.ii:7) we find

$$\frac{1}{2}S_{zR}b_j + S^2_{z^2JR}a_j + \frac{1}{4}S_{zR^2}c_j + \frac{1}{2}S_{zR}c_j\sigma_j = -S^j_{zJ} - \frac{1}{2}S_{z^2}a_j - \frac{1}{2}S^2_{zJR^2}b_j$$
$$-\frac{1}{2}\sum_k \rho_k(\sigma_k S^k_{zJ})^2 a_j - \frac{1}{6}S^2_{zJR^3}c_j - \frac{1}{2}S^2_{zJR^2}c_j\sigma_j \quad ,$$

Multiplying both members by 2 and reordering terms we find

$$a_j\left[\sum_k \rho_k(z_k + \sigma_k S^k_{zJ})^2\right] + (b_j + c_j\sigma_j)[S_{zR} + S^2_{zJR^2}] + c_j\left[\frac{1}{2}S_{zR^2} + \frac{1}{3}S^2_{zJR^3}\right]$$
$$= -2S^j_{zJ} \quad . \qquad \text{(E.ii:12)}$$

We now rewrite the sum of the second and third term on the left hand side of (E.ii:12) substituting for b_j and c_j the expressions found in (E.i:27) and (E.i:28). We find

$$(b_j + c_j\sigma_j)[S_{zR} + S^2_{zJR^2}] + c_j\left[\frac{1}{2}S_{zR^2} + \frac{1}{3}S^2_{zJR^3}\right] =$$
$$a_j\left\{\frac{1}{\Delta^2}\left[\psi_2(S_{zR} + S^2_{zJR^2}) + \psi_1\left(\frac{1}{2}S_{zR^2} + \frac{1}{3}S^2_{zJR^3}\right)\right]\right\} +$$
$$\sigma_j\left[\frac{\pi}{\Delta}(S_{zR} + S^2_{zJR^2}) + \frac{\psi_3}{\Delta^2}\left(\frac{1}{2}S_{zR^2} + \frac{1}{3}S^2_{zJR^3}\right)\right] +$$
$$\frac{\pi}{\Delta}\left(\frac{1}{2}S_{zR^2} + \frac{1}{3}S^2_{zJR^3}\right) \quad . \qquad \text{(E.ii:13)}$$

In terms of the following quantity

$$N_j = \sum_k \rho_k z_k\left[J_{kj} + \frac{\pi}{4\Delta}\left(\sigma_k^2 + \frac{2}{3}\sum_l \rho_l\sigma_l^3 J_{kl}\right)\right]$$
$$= S^j_{zJ} + \frac{\pi}{2\Delta}\left(\frac{1}{2}S_{zR^2} + \frac{1}{3}S^2_{zJR^3}\right) \quad , \qquad \text{(E.ii:14)}$$

the coefficient of σ_j in equation (E.ii:13) can be rewritten (recalling the value of ψ_3) as

$$\frac{\pi}{\Delta}(S_{zR} + S^2_{zJR^2}) + \frac{\pi^2}{2\Delta^2}S_{R^2}\left(\frac{1}{2}S_{zR^2} + \frac{1}{3}S^2_{zJR^3}\right) =$$
$$\frac{\pi}{\Delta}\sum_k \rho_k\sigma_k(z_k + N_k\sigma_k) \quad . \qquad \text{(E.ii:15)}$$

At least we find for a_j

$$a_j = -\frac{2}{D_a}\left\{N_j + \left[\frac{\pi}{2\Delta}\sum_k \rho_k\sigma_k(z_k + N_k\sigma_k)\right]\sigma_j\right\} \quad , \qquad \text{(E.ii:16)}$$

where

$$D_a = \sum_k \rho_k(z_k + \sigma_k S^k_{zJ})^2 +$$
$$\frac{1}{\Delta^2}\left[\psi_2(S_{zR} + S^2_{zJR^2}) + \psi_1\left(\frac{1}{2}S_{zR^2} + \frac{1}{3}S^2_{zJR^3}\right)\right] \quad . \qquad \text{(E.ii:17)}$$

We still have to simplify this expression for D_a. In particular we want to express it in terms of N_j.

Let us rewrite the second term in (E.ii:17) in terms of the ϕ' s

$$\begin{aligned}\frac{1}{\Delta^2}\left[\psi_2(S_{zR}+S^2_{zJR^2})+\psi_1\left(\frac{1}{2}S_{zR^2}+\frac{1}{3}S^2_{zJR^3}\right)\right]= \\ \frac{\pi}{\Delta^2}\left[\phi_1\left(\frac{1}{2}S_{zR^2}+\frac{1}{3}S^2_{zJR^3}\right)+\phi_2(S_{zR}+S^2_{zJR^2})\right. \\ \left.\Delta^2\left(\frac{1}{2}S_{zR^2}S_{zR}+\frac{1}{4}S_{zR^2}S^2_{zJR^2}+\frac{1}{6}S_{zR}S^2_{zJR^3}\right)\right] \quad . \end{aligned} \tag{E.ii:18}$$

Recalling the ϕ' s

$$\begin{aligned}\phi_1 &= \Delta\left[\frac{1}{2}S^2_{zJR^2}+\frac{\pi}{8}S_{zR^2}S_{R^2}+\frac{1}{2}S_{zR}(1-\Delta)\right]+\frac{\pi}{2}S_{R^2}\frac{\phi_2}{\Delta} \quad , \\ \phi_2 &= \Delta\left[\frac{1}{6}S^2_{zJR^3}+\frac{1}{4}S_{zR^2}(1-\Delta)\right] \quad ,\end{aligned}$$

we see that the terms in Δ^2 in the square braces of equation (E.ii:18) vanish. We are then left with

$$\begin{aligned}\frac{\pi}{\Delta^2}\left[\frac{\pi}{4}S_{R^2}\Sigma^2+\Delta(S^2_{zJR^2}\Sigma+S_{zR}\Sigma)\right]= \\ \sum_k \rho_k\left[\sigma_k^2\left(\frac{\pi}{\Delta}S^k_{zJ}\Sigma+\frac{\pi^2}{4\Delta^2}\Sigma^2\right)+z_k\sigma_k\left(\frac{\pi}{\Delta}\Sigma\right)\right] \quad ,\end{aligned} \tag{E.ii:19}$$

where

$$\Sigma=\frac{1}{2}S_{zR^2}+\frac{1}{3}S^2_{zJR^3} \quad . \tag{E.ii:20}$$

Inserting equation (E.ii:19) into equation (E.ii:17) for D_a and recalling the definition of N_j (E.ii:14) we find the following expression for D_a

$$D_a=\sum_k \rho_k(z_k+N_k\sigma_k)^2 \quad . \tag{E.ii:21}$$

iii Calculation of $Q_{ij}(\lambda_{ji})$

Let us now calculate $Q_{jk}(r)$ in $r=\lambda_{kj}$

$$\begin{aligned}Q_{jk}(\lambda_{kj}) &= a_{jk}+b_{jk}\lambda_{kj}+c_{jk}\lambda^2_{kj} \\ &= b_{jk}(-\delta^1_{kj})+c_{jk}(-\delta^2_{kj})-z_ja_k \\ &= b_{jk}(-\sigma_j)+c_{jk}(-\sigma_j\sigma_k)-z_ja_k \\ &= -[\sigma_j(b_k+c_k\sigma_k)+S^j_{zJ}a_k\sigma_j+z_ja_k] \\ &= -\left[\sigma_j\left(\frac{1}{\Delta^2}\psi_2a_k+\frac{\pi}{\Delta}\sigma_k\right)+a_k(z_j+S^j_{zJ}\sigma_j)\right] \\ &= -\frac{\pi}{\Delta}\sigma_j\sigma_k-a_k\left[z_j+\left(\frac{\psi_2}{\Delta^2}+S^j_{zJ}\right)\sigma_j\right] \quad ,\end{aligned}$$

where in the second equality we used equation (E.:12) for a_{ij}, in the third equality we used the definitions of the δ^n (E.:13)-(E.:17), in the fourth equality we used the expressions (E.i:25) and (E.i:26) for the coefficients b_{ij} and c_{ij}, and in the fifth equality we used equations (E.i:27) and (E.i:28) for b_i and c_i. Recalling that $\psi_2 = \pi\Delta\Sigma/2$ we find

$$Q_{jk}(\lambda_{kj}) = -\frac{\pi}{\Delta}\sigma_j\sigma_k - a_k(z_j + N_j\sigma_j) \quad , \tag{E.iii:1}$$

where we used the definition of N_j (E.ii:14).

From equation (4.i:39) we now that it must be $Q_{ij}(\lambda_{ji}) = Q_{ji}(\lambda_{ij})$ or

$$a_j(z_i + N_i\sigma_i) = a_i(z_j + N_j\sigma_j) \quad . \tag{E.iii:2}$$

From which follows that

$$\frac{z_i + N_i\sigma_i}{a_i} = \text{constant} \equiv \frac{D_a}{2\Gamma} \quad , \tag{E.iii:3}$$

where we have defined the *separation* constant Γ. Equation (E.iii:3) allows to determine the a_j independently from the J_{ij}:

(1) From the expression (E.ii:16) for the a_j we find

$$-\Gamma(z_i + N_i\sigma_i) = N_i + \left[\frac{\pi}{2\Delta}\sum_k \rho_k(z_k + N_k\sigma_k)\right]\sigma_j \quad , \tag{E.iii:4}$$

from which we determine the N_i as functions of Γ, $N_i(\Gamma)$;

(2) from equation (4.i:35) we find

$$\alpha^2 = \left(\frac{2\Gamma}{D_a}\right)^2 \sum_k \rho_k a_k^2 \frac{(z_k + N_k\sigma_k)^2}{a_k^2} = \frac{4\Gamma^2}{D_a} \quad , \tag{E.iii:5}$$

where we used expression (E.ii:21) for D_a. We then find $D_a = 4\Gamma^2/\alpha^2$;

(3) From the algebraic equation

$$D_a = \sum_k \rho_k(z_k + N_k(\Gamma)\sigma_k)^2 = \frac{4\Gamma^2}{\alpha^2} \quad , \tag{E.iii:6}$$

we find Γ choosing the solution with the right asymptotic behavior at small concentrations;

(4) the a_i are then determined by

$$a_i = \frac{\alpha^2}{2\Gamma}(z_i + N_i(\Gamma)\sigma_i) \quad . \tag{E.iii:7}$$

Note that at small concentrations ρ_k the equations (E.iii:4) for the $N_i(\Gamma)$ decouple

$$-\Gamma(z_i + N_i\sigma_i) \simeq N_i \quad . \tag{E.iii:8}$$

Moreover from equation (E.iii:6) follows that at small concentrations $\gamma \to 0$.

iv The equimolar binary mixture

Let us now consider the particular case of a binary mixture with same concentrations of the two species ($\rho_1 = \rho_2 = \rho/2$), equal diameters ($\sigma_1 = \sigma_2 = \sigma$), and opposite charges ($z_1 = -z_2 = 1$). From the symmetry of the system we now know that $h_{11}(r) = h_{22}(r)$ so that we must have $J_{11} = J_{22}$. Equation (E.iii:4) then reduces to

$$-\Gamma(z_i + N_i\sigma_i) \simeq N_i \quad . \tag{E.iv:1}$$

From which we determine the $N_i(\Gamma)$

$$N_i(\Gamma) = -\frac{\Gamma z_i}{1+\Gamma\sigma_i} = \frac{\rho}{2}(J_{1i} - J_{2i}) \quad , \tag{E.iv:2}$$

where $N_1 = -N_2$. The equation for Γ (E.iii:6) reduces to

$$\pm\alpha\sqrt{\sum_i \rho_i z_i^2} = 2\Gamma(1+\Gamma\sigma) \quad . \tag{E.iv:3}$$

We call $x \equiv \sigma k_D = \sigma\alpha\sqrt{\sum_i \rho_i z_i^2} = \sigma\alpha\sqrt{\rho} > 0$, where we have defined the Debye wavenumber k_D. We then find for $\Gamma\sigma$

$$\Gamma\sigma = \frac{-1 \pm \sqrt{1\pm 2x}}{2} \quad . \tag{E.iv:4}$$

Since Γ has to be real for all concentrations and it has to go to 0 when $x \to 0$ we choose

$$\Gamma\sigma = \frac{-1+\sqrt{1+2x}}{2} > 0 \quad . \tag{E.iv:5}$$

Next we define $B = N_1\sigma$

$$B = \frac{-1-x+\sqrt{1+2x}}{x} < 0 \quad . \tag{E.iv:6}$$

From equation (E.iii:7) we find for the a_j

$$a_1 = \frac{\alpha^2}{2\Gamma}(1+B) = -a_2 \quad . \tag{E.iv:7}$$

Let us now rewrite the coefficients of $Q_{ij}(r)$. We notice that

$$\begin{aligned} S_{zR} &= 0 \quad , \\ S_{zR^2} &= 0 \quad , \\ S^2_{zJR^2} &= 0 \quad , \\ S^2_{zJR^3} &= 0 \quad , \\ S_{R^2} &= \sigma^2\rho \quad , \\ S_{R^3} &= \sigma^3\rho \quad , \end{aligned}$$

then

$$\Delta = 1 - \frac{\pi}{6}\sigma^3\rho \quad , \tag{E.iv:8}$$

$$\psi_1 = 0 \quad , \tag{E.iv:9}$$

$$\psi_2 = 0 \quad , \tag{E.iv:10}$$

$$\psi_3 = \frac{\pi^2}{2}\sigma^2\rho \quad , \tag{E.iv:11}$$

so that

$$b_j = b = -\left(\frac{\sigma}{\Delta}\right)^2 \psi_3 \quad , \tag{E.iv:12}$$

$$c_j = c = \frac{\sigma}{\Delta^2}\psi_3 + \frac{\pi}{\Delta} \quad , \tag{E.iv:13}$$

and

$$b_{ij} = b + S^i_{zJ} a_j \quad , \tag{E.iv:14}$$

$$c_{ij} = c \quad , \tag{E.iv:15}$$

$$a_{ij} = -b\sigma - c\sigma^2 - (\sigma S^i_{zJ} + z_i)a_j \quad , \tag{E.iv:16}$$

where

$$S^1_{zJ} = \frac{\rho}{2}(J_{11} - J_{12}) = \frac{B}{\sigma} = -S^2_{zJ} \quad . \tag{E.iv:17}$$

v Calculation of the charge density direct correlation function

Our last task is to determine the partial direct correlation function

$$\begin{aligned} c_{\alpha\beta}(r) &= c^0_{\alpha\beta}(r) - \beta v^c_{\alpha\beta}(r) \\ &= c^0_{\alpha\beta}(r) - \frac{\alpha^2}{4\pi} z_\alpha z_\beta \frac{1}{r} \quad . \end{aligned}$$

In particular we want to calculate the charge density direct correlation function

$$\begin{aligned} c_d(r) &= \sum_\beta z_\beta c_{1\beta}(r) \\ &= c^0_d(r) - \frac{\alpha^2}{2\pi}\frac{1}{r} \quad . \end{aligned}$$

From the Wiener-Hopf factorization (4.i:43) we find

$$2\pi r c^0_d(r) = -\sum_\beta z_\beta Q'_{1\beta}(r) + \frac{\rho}{2}\int_r^\sigma \sum_{\gamma\beta} z_\beta Q_{\beta\gamma}(s-r) Q'_{1\gamma}(s)\, ds \quad . \tag{E.v:1}$$

The first term in the right hand side is

$$\begin{aligned} \sum_\beta z_\beta Q'_{1\beta}(r) &= \sum_\beta z_\beta b_{1\beta} + \sum_\beta z_\beta (2c_{1\beta}) r \\ &= \sum_\beta z_\beta b_{1\beta} \\ &= 2a_1 S^1_{zJ} \\ &= -\alpha^2 (1+B)^2 \quad , \end{aligned} \tag{E.v:2}$$

where we used for a_1 the following expression in terms of B

$$a_1 = -\sigma \frac{\alpha^2}{2}\frac{(1+B)^2}{B} \quad . \tag{E.v:3}$$

The second term in the right hand side of (E.v:1) is

$$\frac{\rho}{2}I = \frac{\rho}{2}\int_r^\sigma \sum_\gamma \left\{ \left[\sum_\beta z_\beta Q_{\beta\gamma}(s-r) \right] Q'_{1\gamma}(s) \right\} ds \quad , \tag{E.v:4}$$

where

$$\begin{aligned} Q'_{1\gamma}(s) &= b_{1\gamma} + 2c_{1\gamma}s \\ &\equiv C_\gamma + D_\gamma s \quad , \end{aligned} \tag{E.v:5}$$

$$\begin{aligned} \sum_\beta z_\beta Q_{\beta\gamma}(t) &= \sum_\beta a_{\beta\gamma}z_\beta + \left(\sum_\beta b_{\beta\gamma}z_\beta\right)t + \left(\sum_\beta c_{\beta\gamma}z_\beta\right)t^2 \\ &= -a_\gamma \sum_\beta (\sigma S^\beta_{zJ} + z_\beta)z_\beta + (a_\gamma \sum_\beta S^\beta_{zJ} z_\beta)t \\ &= -2(\sigma S^1_{zJ} + 1)a_\gamma + (2S^1_{zJ}a_\gamma)t \\ &\equiv A_\gamma + B_\gamma t \quad , \end{aligned} \tag{E.v:6}$$

where we defined the constants $A_\gamma, B_\gamma, C_\gamma$, and D_γ,. Omitting the γ indexes we find for I

$$\begin{aligned} I &= \left(AC\sigma + \frac{1}{2}AD\sigma^2 + \frac{1}{2}BC\sigma^2 + \frac{1}{3}BD\sigma^3 \right) + \\ &\quad \left(-AC - BC\sigma - \frac{1}{2}BD\sigma^2 \right) r + \qquad (E.v:7) \\ &\quad \left(BC - \frac{1}{2}AD - \frac{1}{2}BC \right) r^2 + \qquad (E.v:8) \\ &\quad \left(\frac{1}{2}BD - \frac{1}{3}BD \right) r^3 \quad . \qquad (E.v:9) \end{aligned}$$

We calculate next the three contractions

$$\begin{aligned} BD &= \sum_\gamma (2S^1_{zJ}a_\gamma)(2c_{1\gamma}) = 0 \quad , \\ AD &= \sum_\gamma [-2(\sigma S^1_{zJ} + 1)a_\gamma](2c_{1\gamma}) = 0 \quad , \\ BC &= \sum_\gamma (2S^1_{zJ}a_\gamma)(b_{1\gamma}) = 2S^1_{zJ}\sum_\gamma a_\gamma S^1_{zJ}a_\gamma = (2S^1_{zJ}a_1)^2 \quad , \\ AC &= \sum_\gamma [-2(\sigma S^1_{zJ} + 1)a_\gamma](b_{1\gamma}) = -2(\sigma S^1_{zJ} + 1)\sum_\gamma a_\gamma S^1_{zJ}a_\gamma \\ &= -\sigma(2S^1_{zJ}a_1)^2 - 4S^1_{zJ}a_1^2 \quad , \end{aligned}$$

which rewritten in terms of B becomes

$$BD = AD = 0 \quad , \tag{E.v:10}$$

$$BC = \alpha^4(1+B)^4 \quad , \tag{E.v:11}$$

$$AC = -\sigma\alpha^4(1+B)^4 - \sigma\alpha^4\frac{(1+B)^4}{B} \quad . \tag{E.v:12}$$

Then I becomes

$$\begin{aligned} I &= \left(AC\sigma + \frac{1}{2}BC\sigma^2\right) + (-AC - BC\sigma)r + \left(\frac{1}{2}BC\right)r^2 \\ &= \left[\sigma^2\alpha^4(1+B)^4(-\frac{1}{2} - \frac{1}{B})\right] + \\ &\quad \left[\sigma^2\alpha^4(1+B)^4\frac{1}{B}\right]\left(\frac{r}{\sigma}\right) + \\ &\quad \left[\sigma^2\alpha^4(1+B)^4\frac{1}{2}\right]\left(\frac{r}{\sigma}\right)^2 \quad . \end{aligned}$$

For c_d^0 we find

$$\begin{aligned} 2\pi r c_d^0(r) &= \left[\alpha^2(1+B)^2 + \frac{\rho}{2}\sigma^2\alpha^4(1+B)^4(-\frac{1}{2} - \frac{1}{B})\right] + \\ &\quad \left[\frac{\rho}{2}\sigma^2\alpha^4(1+B)^4\frac{1}{B}\right]\left(\frac{r}{\sigma}\right) + \\ &\quad \left[\frac{\rho}{2}\sigma^2\alpha^4(1+B)^4\frac{1}{2}\right]\left(\frac{r}{\sigma}\right)^2 \quad . \end{aligned} \tag{E.v:13}$$

We now recall that

$$x = \sqrt{\rho}\sigma\alpha = 2\Gamma\sigma(1+\Gamma\sigma) = -2\frac{B}{(1+B)^2} \quad , \tag{E.v:14}$$

from which follows

$$\frac{\rho}{2}\sigma^2\alpha^2 = 2\frac{B^2}{(1+B)^4} \quad , \tag{E.v:15}$$

which when inserted into equation (E.v:13) gives

$$c_d^0(r) = \frac{\alpha}{2\pi r}\left[1 + 2B\left(\frac{r}{\sigma}\right) + B^2\left(\frac{r}{\sigma}\right)^2\right] \quad . \tag{E.v:16}$$

At least we find for the charge density direct correlation function in the interval $0 < r < \sigma$

$$c_d(r) = \frac{\alpha}{2\pi r}\left[2B\left(\frac{r}{\sigma}\right) + B^2\left(\frac{r}{\sigma}\right)^2\right] \quad . \tag{E.v:17}$$

Appendix F

Thermodynamic consistency

For a homogeneous liquid interacting through a pair potential $\phi(r)$, the Helmholtz free energy per particle f can be considered a functional of ϕ. Indeed, in the canonical ensemble, one has

$$\beta f[\phi] = \beta f_0 - \frac{1}{N} \ln \left(\frac{1}{V^N} \int e^{-\beta \frac{1}{2} \sum_{i \neq j} \phi(\mathbf{r}_{ij})} d\mathbf{r}_1 \cdots d\mathbf{r}_N \right) \quad , \tag{F.:1}$$

where f_0 is the free energy per particle of the ideal gas ($\phi = 0$) and V is the volume of the liquid. Taking the functional derivative with respect to $\beta\phi(r)$ one finds

$$\frac{\delta \beta f[\phi]}{\delta \beta \phi(r)} = \frac{\rho}{2} g(r) \quad , \tag{F.:2}$$

where $g(r) = h(r) + 1$ is the pair distribution function.

Imagine that we found a functional $\mathcal{A}([h], [\phi], \rho, \beta)$ that has an extremum for those correlation functions that solve the OZ and the closure system of equations. Suppose further that such functional has the following property

$$\frac{\delta \beta \mathcal{A}}{\delta \beta \phi(r)} = \frac{\rho}{2} g(r) \quad , \tag{F.:3}$$

which can be rewritten more explicitly as follows

$$\left. \frac{\delta \beta \mathcal{A}}{\delta \beta \phi(r)} \right|_{[h],\rho,\beta} + \int d\mathbf{r}' \left. \frac{\delta \beta \mathcal{A}}{\delta h(r')} \right|_{[\phi],\rho,\beta} \frac{\delta h(r')}{\delta \beta \phi(r)} = \frac{\rho}{2} g(r) \quad . \tag{F.:4}$$

Evaluating this expression on the correlation function $\bar{h}$ solution of the OZ plus closure system of equations, which is an extremum for $\mathcal{A}$, we find

$$\left. \frac{\delta \beta \mathcal{A}}{\delta \beta \phi(r)} \right|_{[\bar{h}],\rho,\beta} = \frac{\rho}{2} \bar{g}(r) \quad . \tag{F.:5}$$

Then we can write

$$\beta \mathcal{A}([\bar{h}], [\phi], \rho, \beta) = \int d\mathbf{r} \left. \frac{\delta \beta \mathcal{A}}{\delta \beta \phi(r)} \right|_{[\bar{h}],\rho,\beta} \beta\phi(r) + \mathcal{D}([\bar{h}], \rho, \beta) \quad , \tag{F.:6}$$

with $\mathcal{D}$ a functional independent of ϕ. Changing variables to adimensional ones, $\mathbf{r} = \mathbf{r}^\star \rho^{-1/3}$ and using equation (F.:5) we find

$$\beta \mathcal{A}([\bar{h}^\star], [\phi], \rho, \beta) = \frac{1}{2} \int d\mathbf{r}^\star \, \bar{g}^\star(r^\star) \beta\phi(r^\star \rho^{-1/3}) + \mathcal{D}([\bar{h}^\star], \rho, \beta) \quad , \tag{F.:7}$$

where we defined new distribution functions $g^\star(r^\star) = g(r^\star\rho^{-1/3})$. If $\mathcal{D}$ has no explicit dependence on ρ then one readily finds

$$\begin{aligned}\rho\frac{\partial\beta\mathcal{A}([\bar{h}^\star],[\phi],\rho,\beta)}{\partial\rho} &= -\frac{\rho}{6}\int d\mathbf{r}^\star\,\bar{g}^\star(r^\star)\beta\phi'(r^\star\rho^{-1/3})r^\star\rho^{-4/3}\\ &= -\frac{\rho}{6}\int d\mathbf{r}\,\bar{g}(r)\,\beta\phi'(r)\,r\\ &= \beta P^{exc}/\rho \quad , \end{aligned} \tag{F.:8}$$

where again we used the fact that $\mathcal{A}$ has an extremum for $h = \bar{h}$. We used a prime to denote a derivative with respect to the argument and P^{exc} is the excess pressure of the liquid.

If $\mathcal{D}$ has no explicit dependence on β we also find

$$\begin{aligned}\frac{\partial\beta\mathcal{A}([\bar{h}^\star],[\phi],\rho,\beta)}{\partial\beta} &= \frac{\rho}{2}\int d\mathbf{r}\,\bar{g}(r)\phi(r)\\ &= U^{exc}/N \quad , \end{aligned} \tag{F.:9}$$

where U^{exc} is the excess internal energy.

If $\mathcal{D}$ has no explicit dependence on both β and ρ, $\mathcal{D}([\bar{h}^\star],\rho,\beta) = \mathcal{D}([\bar{h}^\star])$, we conclude from equations (F.:8) and (F.:9) that

$$\mathcal{A}([\bar{h}^\star],[\phi],\rho,\beta) = f^{exc}(\rho,\beta) + \text{constant} \quad , \tag{F.:10}$$

where f^{exc} is the excess free energy per particle of the fluid. Under these circumstances we see from equation (F.:8) that we have thermodynamic consistency between the route to the pressure going through the partial derivative of the free energy and the route to the pressure going through the virial theorem.

Appendix G

Strict convexity of $\mathcal{F}_{OZ}[h]$

It can be proven that the functional

$$\mathcal{F}_{OZ}[h] = \int \frac{d\mathbf{k}}{(2\pi)^3}\{\rho\hat{h}(k) - \ln[1+\rho\hat{h}(k)]\} \quad , \tag{G.:1}$$

defined on the convex set

$$D_c = \{h(r)|S(k) > 0 \quad \forall k\} \quad , \tag{G.:2}$$

is a strictly convex functional. The strict convexity is a trivial consequence of the strict convexity of the integrand in equation (G.:1).

It remains to prove that D_c is a convex set. Given two elements of this set h' and h'', we need to show that $h = \lambda h' + (1-\lambda)h''$ is an element of D_c for all $\lambda \in [0,1]$. Since

$$\begin{aligned} S(k) &= 1 + \rho\hat{h}(k) \\ &= 1 + \rho[\lambda\hat{h}'(k) + (1-\lambda)\hat{h}''(k)] \\ &= 1 + \lambda[S'(k) - 1] + (1-\lambda)[S''(k) - 1] \\ &= \lambda S'(k) + (1-\lambda)S''(k) > 0 \quad \forall\lambda \in [0,1] \quad , \end{aligned} \tag{G.:3}$$

then D_c is a convex set.

Appendix H

Green function of Helmholtz equation

In this appendix we give the Green function G, of Helmholtz equation,

$$
\begin{aligned}
&(-\Delta_1 + \alpha^2) G(d_{01}) = \epsilon_d \delta^{(d)}(d_{01}) \quad , \\
&d_{01} = \text{geodesic distance between the origin and } \vec{q}_1 \quad , \\
&\Delta_1 = \text{Laplace-Beltrami operator acting on } \vec{q}_1 \quad , \\
&\delta^{(d)}(d_{01}) = \delta(\vec{q}_0 - \vec{q}_1)/\sqrt{g} \quad , \\
&\epsilon_d = \begin{cases} 2 & d = 1 \\ 2\pi & d = 2 \\ 4\pi & d = 3 \end{cases} \quad .
\end{aligned}
\tag{H.:1}
$$

on various manifolds $\mathcal{R}$ of dimension $d \leq 3$.

(i) $\mathcal{R} = \mathbb{R}^1$

$$
\begin{aligned}
d_{01} &= r = |x| \quad , \\
G(r) &= \frac{e^{-\alpha r}}{\alpha} \quad .
\end{aligned}
$$

(ii) $\mathcal{R} = \mathbb{R}^2$

$$
\begin{aligned}
d_{01} &= r = \sqrt{x^2 + y^2} \quad , \\
G(r) &= K_0(\alpha r) \quad ,
\end{aligned}
$$

where K_0 is a modified Bessel function.

(iii) $\mathcal{R} = \mathbb{R}^3$

$$
\begin{aligned}
d_{01} &= r = \sqrt{x^2 + y^2 + z^2} \quad , \\
G(r) &= \frac{e^{-\alpha r}}{r} \quad .
\end{aligned}
$$

(iv) $\mathcal{R} = S^3$ the three dimensional hypersphere of radius R [139]

$$
\begin{aligned}
d_{01} &= R\psi \quad , \\
G(\psi) &= \begin{cases} \dfrac{\sinh \omega(\pi - \psi)}{R \sin\psi \sinh \omega\pi} & \alpha R > 1 \\ \dfrac{\sin \omega(\pi - \psi)}{R \sin\psi \sin \omega\pi} & \alpha R < 1 \end{cases} \quad ,
\end{aligned}
$$

where $\omega = \sqrt{|(\alpha R)^2 - 1|}$.

(v) $\mathcal{R} = S^2$ the sphere of radius R

$$\begin{aligned} d_{01} &= R\theta \quad , \\ G(\theta) &= -\frac{\pi P_\nu(-\cos\theta)}{2\sin\nu\pi} \quad , \end{aligned}$$

where P_ν is the Legendre function with $\mu = 0$ and $\nu = \frac{1}{2}[-1 + \sqrt{1 - 4(\alpha R)^2}]$. The green function is regular at $\theta = \pi$ and diverges as [140] $-\ln\theta$ as $\theta \to 0$.

(vi) $\mathcal{R} = \mathcal{S}$ the pseudosphere of "radius" a

$$\begin{aligned} d_{01} &= a\tau \quad , \\ G(\tau) &= Q_\nu(\cosh\tau) \quad , \end{aligned}$$

where P_ν is the Legendre function of the second kind with $\mu = 0$ and $\nu = \frac{1}{2}[-1 + \sqrt{1 + 4(\alpha a)^2}]$. The green function vanishes as $\tau \to \infty$ and diverges as [140] $-\ln\tau$ as $\tau \to 0$.

Appendix I

Density near the wall

In this appendix we want to find which condition the one particle correlation function $\rho_\Omega^{(1)}(\tau)$ has to satisfy, in order to be possible to replace it with the bulk density n when calculating the thermodynamic limit of (8.iii:10) and of the first term on the right hand side of (8.iii:14). In both these terms the integrand is made up of $\rho_\Omega^{(1)}(\tau)$ times a factor that increases very fast near the upper bound of integration τ_0. Then we cannot in general neglect the fact that $\rho_\Omega^{(1)}(\tau)$ may have oscillations about n in a neighborhood of τ_0.

Without any loss of generality we can write,

$$\rho_\Omega^{(1)}(\tau) = n + f_{\tau_0}(\tau_0 - \tau) \quad , \tag{I.:1}$$

with f_{τ_0} non zero only in the neighborhood of τ_0 (for $\tau_0 > \tau > \tau_0 - \lambda$, where $a\lambda$ is a screening length). Since $\int \rho_\Omega^{(1)}(\tau)\, dS = \langle N \rangle$, we must have,

$$\int_0^\lambda f_{\tau_0}(\sigma) \sinh(\tau_0 - \sigma)\, d\sigma = 0 \quad , \tag{I.:2}$$

where $\sigma = \tau_0 - \tau$.

Now let us calculate, for example, (8.iii:10),

$$\begin{aligned} \frac{1}{\beta}\int_\Omega \rho_\Omega^{(1)}(\tau)\frac{\tau}{\tanh\tau}\, dS &= \frac{n}{\beta}\int_0^{\tau_0} \frac{\tau}{\tanh\tau}\, dS + \\ &\quad \frac{2\pi a^2}{\beta}\int_0^\lambda f_{\tau_0}(\sigma)(\tau_0 - \sigma)\cosh(\tau_0 - \sigma)\, d\sigma \ . \end{aligned} \tag{I.:3}$$

We want to establish whether or not we can neglect the second term in the right hand side of this equation when calculating the thermodynamic limit of $P_\Omega^{(v)}$. Now in the limit $\tau_0 \to \infty$ and using (I.:2) we find that such term has the following asymptotic behavior,

$$e^{\tau_0}\left(-\frac{\pi a^2}{\beta}\int_0^\lambda f_{\tau_0}(\sigma)\sigma e^{-\sigma}\, d\sigma\right) \quad . \tag{I.:4}$$

After comparing this with the asymptotic behavior of $\tau_0 \lll (\partial\Omega)$ we reach the conclusion that if

$$\int_0^\lambda f_{\tau_0}(\sigma)\sigma e^{-\sigma}\, d\sigma \quad , \tag{I.:5}$$

diverges less rapidly than τ_0, then we are allowed to neglect the second term on the right hand side of equation (I.:3). In other words when calculating the thermodynamic limit of $P_\Omega^{(v)}$ we are allowed to replace the one particle correlation function by n from the start in equation (8.iii:10), neglecting its behavior near the wall. Either from the exact calculation at $\beta q^2 = 2$ or from numerical calculations of the one particle density we expect expression (I.:5) to go to a constant as $\tau_0 \to \infty$.

Appendix J

Electrostatic potential of the background

In this appendix we give the expression for the electrostatic potential of the background,

$$w(\vec{q}_1) = \int \rho_b \, v(d_{10}) \, dS_0 = -nq \int_\Omega v(d_{10}) \, dS_0 \quad . \tag{J.:1}$$

The electric potential of the background satisfies equation (8.i:21). Using the coordinates (r, φ) we have,

$$w''(r) + \frac{1}{r} w'(r) = \alpha \frac{4a^2}{(1-r^2)^2} \quad , \tag{J.:2}$$

where $\alpha = -2\pi\rho_b$ and we denote with a prime a derivative with respect to r. This differential equation admits the following solution for w',

$$\begin{aligned} w'(r) &= e^{\int_{r_1}^r -\frac{1}{r} dr} \left[w'(r_1) + \int_{r_1}^r \frac{4a^2\alpha}{(1-r^2)^2} \, e^{\int_{r_1}^r \frac{1}{r} dr} \right] \\ &= \frac{r_1 w'(r_1)}{r} + \frac{4a^2}{r} \int_{r_1}^r \alpha \frac{r}{(1-r^2)^2} dr \quad . \end{aligned} \tag{J.:3}$$

Choosing $r_1 = 0$ we find,

$$\begin{aligned} w'(r) &= \frac{4a^2}{r} \int_0^r \alpha \frac{r}{(1-r^2)^2} dr \\ &= 2a^2\alpha \begin{cases} \dfrac{r}{1-r^2} & r \le r_0 \\ \dfrac{r_0^2}{1-r_0^2} \dfrac{1}{r} & r > r_0 \end{cases} \quad , \end{aligned} \tag{J.:4}$$

where $r_0 = \tanh(\tau_0/2)$. The potential has to be chosen continuous at r_0. For the potential inside $\Omega_{a\tau_0}$ we find,

$$w(r) = -\alpha a^2 \ln(1-r^2) + \text{constant} \quad , \tag{J.:5}$$

or using the coordinates (τ, φ),

$$w(\tau) = -\alpha a^2 \ln[1 - \tanh^2(\tau/2)] + \text{constant} \quad . \tag{J.:6}$$

We need to adjust the additive constant in such a way that this potential at $\tau = \tau_0$ has the correct value corresponding to the total background charge. We then have,

$$\begin{aligned} \text{constant} &= w(0) = -qn \int_{\Omega_{a\tau_0}} v(\tau a)\, dS \\ &= 2\pi a^2 qn \int_0^{\tau_0} \ln[\tanh(\tau/2)] \sinh\tau\, d\tau \\ &= \alpha a^2 [\ln[1-\tanh^2(\tau_0/2)] + \sinh^2(\tau_0/2) \ln[\tanh^2(\tau_0/2)]] \quad . \end{aligned} \tag{J.:7}$$

We reach then the following expression for the potential inside $\Omega_{a\tau_0}$,

$$w(\tau) = \alpha a^2 \left\{ \ln\left[\frac{1-\tanh^2(\tau_0/2)}{1-\tanh^2(\tau/2)}\right] + \sinh^2(\tau_0/2) \ln[\tanh^2(\tau_0/2)] \right\} \quad . \tag{J.:8}$$

The self energy of the background is,

$$v_0 = \frac{1}{2} \int_{\mathcal{S}} \rho_b\, w\, dS \tag{J.:9}$$

$$\begin{aligned} &= \frac{1}{2} \rho_b \alpha a^2 2\pi a^2 \left\{ \int_0^{\tau_0} \ln\left[\frac{1-\tanh^2(\tau_0/2)}{1-\tanh^2(\tau/2)}\right] \sinh\tau\, d\tau + \right. \\ &\qquad \left. \sinh^2(\tau_0/2) \ln[\tanh^2(\tau_0/2)] \int_0^{\tau_0} \sinh\tau\, d\tau \right\} \\ &= -2a^4(\pi\rho_b)^2 \{1 - \cosh\tau_0 + 4\, \ln[\cosh(\tau_0/2)] + 2\sinh^4(\tau_0/2) \ln[\tanh^2(\tau_0/2)]\}. \end{aligned}$$

Notice that if we drop the last term on the right hand side of this equation, i.e. if we adjust the additive constant so that the potential of the background vanishes on the boundary $\partial\Omega_{a\tau_0}$, then in the limit $a \to \infty$ we recover the self energy of the flat system $N^2q^2/8$.

Appendix K

The flat limit

In this Appendix we study the flat limit $a \to \infty$ of the expressions found for the density in section v. We shall study the limit $a \to \infty$ for a finite system and then take the thermodynamic limit and compare to the result of taking first the thermodynamic limit and then the flat limit $a \to \infty$. Since for a large system on the pseudosphere boundary effects are of the same order as bulk effects it is not clear a priori whether computing these two limits in different order would give the same results. We shall show that, indeed, the same results are obtained.

For a finite disk of radius $d = a\tau_0$, we have in the flat limit $a \to \infty$, $d \sim r_0$. In equation (8.v:32), in the limit $a \to \infty$, the term e^C given by (8.v:3) becomes

$$e^C \sim \left(\frac{r_0^2}{4a^2}\right)^{-N_b} e^{N_b} \tag{K.:1}$$

where $N_b = \pi n_b r_0^2$ is the number of particles in the background in the flat limit. Since for large a, $t_0 = r_0^2/(4a^2)$ is small, the incomplete beta function in equation (8.v:32) is

$$B_{t_0}(\ell+1,\alpha) = \int_0^{t_0} e^{(\alpha-1)\ln(1-t)}\, t^\ell\, dt \sim \int_0^{t_0} e^{-(\alpha-1)t}\, t^\ell\, dt \sim \frac{\gamma(\ell+1,N_b)}{\alpha^{\ell+1}} \tag{K.:2}$$

Expanding $(1-(r^2/4a^2))^{4\pi n_b a^2} \sim \exp(-\pi n_b r^2)$ in equation (8.v:32) we finally find the density as a function of the distance r from the center

$$n^{(1)}(r) = n_b e^{-\pi n_b r^2} \sum_{\ell=0}^{\infty} \frac{(\pi n_b r^2)^\ell}{\alpha^{\ell-N_b} N_b^{N_b} e^{-N_b}(n_b/\zeta) + \gamma(\ell+1,N_b)} \tag{K.:3}$$

When $\alpha \to \infty$ the terms for $\ell > N_b$ in the sum vanish because $\alpha^{\ell-N_b} \to \infty$. Then

$$n^{(1)}(r) = n_b e^{-\pi n_b r^2} \sum_{\ell=0}^{E(N_b)-1} \frac{(\pi n_b r^2)^\ell}{\gamma(\ell+1,N_b)} + \Delta n^{(1)}(r) \tag{K.:4}$$

The first term is the density for a flat OCP in the canonical ensemble with a background with $E(N_b)$ elementary charges ($E(N_b)$ is the integer part of N_b). The second term is a correction due to the inequivalence of the ensembles for finite systems and it depends on whether N_b is an integer or not. If N_b is not an integer

$$\Delta n^{(1)}(r) = n_b \frac{(\pi n_b r^2)^{E(N_b)} e^{-\pi n_b r^2}}{\gamma(E(N_b)+1,N_b)} \tag{K.:5}$$

and if N_b is an integer

$$\Delta n^{(1)}(r) = n_b \frac{(\pi n_b r^2)^{N_b} e^{-\pi n_b r^2}}{N_b^{N_b} e^{-N_b}(n_b/\zeta) + \gamma(N_b+1, N_b)} \tag{K.:6}$$

In any case in the thermodynamic limit $r_0 \to \infty$, $N_b \to \infty$, this term $\Delta n^{(1)}(r)$ vanishes giving the known results for the OCP in a flat space in the canonical ensemble [4, 104]. Integrating the profile density (K.:4) one finds the average number of particles. For a finite system it is interesting to notice that the average total number of particles N is

$$N = E(N_b) + 1 \tag{K.:7}$$

for N_b not an integer and

$$N = N_b + \frac{1}{1 + \dfrac{N_b^{N_b} e^{-N_b} n_b}{\zeta \gamma(N_b+1, N_b)}} \tag{K.:8}$$

for N_b an integer. In both cases the departure from the neutral case $N = N_b$ is at most of one elementary charge as it was noticed before [129, 130].

Let us now consider the other order of the limits. We start with the expression (8.v:51) for the contact density in the thermodynamic limit in the pseudosphere and show that in the limit $a \to \infty$ the value of the contact density reduces to the known expression for a neutral OCP in a flat space at a hard wall [104]. We also show that in that limit the average density is independent of the fugacity and equal to the background density $n = n_b$.

Equation (8.v:51) can be rewritten as

$$\frac{n_{\text{contact}}}{n_b} = \int_0^\infty \frac{x^\alpha e^{-x}\, dx}{\frac{n_b}{\zeta} x^\alpha e^{-\alpha} + \alpha \Gamma(\alpha, x)} \tag{K.:9}$$

For large α, the numerator of the integrand in (K.:9) has a sharp peak at $x = \alpha$ and can be expanded as

$$x^\alpha e^{-x} \sim e^{\alpha \ln \alpha - \alpha - \left(\frac{x-\alpha}{\sqrt{2\alpha}}\right)^2} \tag{K.:10}$$

In the denominator, using the large α expansion of the incomplete gamma function [140], and neglecting 1 with respect to α, we obtain

$$\alpha \Gamma(\alpha, x) \sim \alpha^\alpha e^{-\alpha} \sqrt{\frac{\pi\alpha}{2}} \left[1 - \operatorname{erf}\left(\frac{x - \alpha + 1}{\sqrt{2\alpha}}\right)\right] \tag{K.:11}$$

where

$$\operatorname{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-u^2}\, du \tag{K.:12}$$

is the error function. Using (K.:10) and (K.:11) in (K.:9) gives

$$\frac{n_{\text{contact}}}{n_b} \sim \int_0^\infty \frac{e^{-\left(\frac{x-\alpha}{\sqrt{2\alpha}}\right)^2} dx}{\frac{n_b}{\zeta}\left(\frac{x}{\alpha}\right)^\alpha + \sqrt{\frac{\pi\alpha}{2}}\left[1 - \operatorname{erf}\left(\frac{x-\alpha+1}{\sqrt{2\alpha}}\right)\right]} \tag{K.:13}$$

For $x > \alpha$, the first term in the denominator goes to infinity for large α and the integrand goes to zero. On the other hand, when $x < \alpha$, this same first term goes to zero, thus, after the change of variable $t = (x - \alpha)/\sqrt{2\alpha}$,

$$\frac{n_{\text{contact}}}{n_b} \sim \frac{2}{\sqrt{\pi}} \int_{-\sqrt{\alpha/2}}^0 \frac{e^{-t^2}\, dy}{1 - \operatorname{erf}\left(t + \frac{1}{\sqrt{2\alpha}}\right)} \tag{K.:14}$$

Finally, as $\alpha \to \infty$,

$$\frac{n_{\text{contact}}}{n_b} \to \int_{-\infty}^{0} \frac{\frac{d\ \text{erf}(t)}{dt}}{1-\text{erf}(t)} dt = \ln 2 \tag{K.:15}$$

This is the known value [104] for the contact density at a hard plain wall for a neutral OCP.

Following the same lines, equation (8.v:56) for the average density becomes in the limit $\alpha \to \infty$

$$\frac{n}{n_b} \sim \sqrt{\frac{2}{\alpha}} \int_{-\sqrt{\alpha/2}}^{0} \frac{[1-\text{erf}(t)]\ dt}{1-\text{erf}(t)} = 1 \tag{K.:16}$$

The average density is equal to the background density and it is independent of the fugacity. Whatever value the fugacity has, the system cannot be charged in the flat case in the thermodynamic limit.

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