DIPLOMARBEIT

Structural and thermodynamic properties of liquids in porous media

ausgeführt am Institut für

Theoretische Physik

der Technischen Universität Wien

unter der Anleitung von
ao. Univ. Prof. Dr. Gerhard Kahl
durch

Elisabeth Maria Paschinger

Bürgerspitalgasse 29/24
1060 Wien

Datum: 4.12.1998 Unterschrift:

meiner Großmutter Maria Andres

Abstract

In an effort to describe the structural and thermodynamic properties of a liquid adsorbed in a disordered porous matrix we have used in the present study the Madden-Glandt approach [W. G. Madden and E. G. Glandt, J. Stat. Phys., **Vol.** 51, 537 (1988)]. Here the system is treated as a special partly quenched binary mixture, i.e., a system where the matrix particles are frozen in place (quenched), and the fluid particles are annealed, or allowed to equilibrate in the rigid matrix structure. Using the replica method introduced by Given and Stell [J. A. Given and G. Stell, J. Chem. Phys., **Vol.** 97, 4573 (1992)], which allows to replace the study of the partly quenched system by that of a fully equilibrated system we can treat the system with methods of standard liquid state theory, and are able to derive integral equations for the correlation functions of a fluid mixture confined in a matrix. We also present derivations of the Gibbs-Duhem relation, the energy equation, the virial equation, and the compressibility equation for a binary fluid in equilibrium with a quenched matrix. Furthermore, the optimised random phase approximation has been extended to the case of a two-component fluid in a matrix. We present results for the correlation functions obtained from integral equation and perturbation theory calculations and compare them with Monte Carlo simulations. The perturbation theory approach has been applied to a single-component square-well fluid in a matrix: we have determined the liquid-vapour phase diagram and have investigated the effects of the matrix density on the shape of coexistence curves.

Contents

Chapter 1

Introduction

In recent years the behaviour of fluids confined in disordered porous materials has been a subject of great interest both from an experimental and theoretical point of view.

A porous material (or matrix) can be considered as a mixture of disordered voids and solid regions. The detailed shapes of the pores depend on the shape of the solid particles, their size distribution and their mode of packing. The overall structure, however, can be considered as statistically homogeneous and isotropic at length scales larger than the dimensions of the constituent particles. This means that the material can be characterised by statistical quantities such as an average density and a specific void volume (or porosity).

Due to the importance of porous materials in many technological applications such as catalysis, gas separation and purification, a large amount of experimental data on gas adsorption on porous substrates have been accumulated over the years [1]. Another point of interest in experimental research has been the study of liquids adsorbed in porous media. Investigations have been focussed on the influence of the properties of the porous media on the critical behaviour and on the process of phase separation of a liquid adsorbed in this material. This research was motivated by de Gennes [2] who suggested that binary mixtures adsorbed in porous media near the critical point may be thought as experimental realisations of the random field Ising model (RFIM) [3] – a spin model of random magnets. In this model the random field describes the spatially varying preference of the pore network for the adsorption of one of the fluid components. However, this model does not take account of the confinement of the fluid in the pore network.

Some of the results of experimental studies of the phase behaviour of binary mixtures [4] in porous glasses and single-component fluids or fluid mixtures in dilute silica gels (porous materials with high porosity where the porosity can be as high as 99.9%) were interpreted by this model. The liquid-vapour phase transition of pure ^{4}He in a silica aerogel was studied by Wong and Chan [5]. They discovered that the coexistence curve of the confined fluid was strikingly different from that of the bulk fluid: the critical point is shifted to a lower temperature and a higher density and the coexistence curve is narrower. What is remarkable is that even a small amount of impurity can alter the phase diagram drastically.

On the other hand, it has been argued that the experiments in Vycor (which is a glass with a fairly low porosity) can be interpreted in terms of wetting phenomena in a confined geometry with no randomness [6]. Theoretical studies of confined fluids have generally been limited to 'single pore' models with idealised pore geometries, (e.g. fluids confined to narrowly spaced plane walls, cylindrical or spherical pores [7]) which lack the ability to represent a truly disordered structure. In reality, however, porous solids are often disordered, containing an interconnected network of pores of various sizes and shapes. On the other hand, confinement in the pores plays no role in the RFIM. Hence, both approaches do not seem sufficient to describe the vast variety of phase behaviour observed. Consequently, a more realistic continuum description for the fluid/solid system was required which is able to comprise randomness, confinement and connectivity between the pores.

Such an approach was first proposed by Madden and Glandt [8, 9]. These authors modelled such a system as a special binary mixture: the solid is treated as an ensemble of particles in some predefined micro-structure which is assumed to be rigid, i.e., which is not affected by the introduction of the liquid. Therefore, the solid is simply viewed as a disordered matrix of quenched (or frozen in place) obstacles in with which the fluid establishes itself in a state of thermal equilibrium. The configuration of the quenched matrix of immobile particles is assumed to have been formed by an instantaneous thermal quench of a fluid in equilibrium at a higher temperature. Any restructuring of the matrix during quenching is neglected; that is, the quenched particles are distributed according to an equilibrium ensemble corresponding to some specified potential in the absence of the fluid. Madden [9] subsequently generalised the formalism to the case in which the distribution of the quenched particles is essentially arbitrary.

The field acting on each fluid particle depends on the local structure of the rigid obstacles. However, it is clear that observable quantities, such as the free energy of the adsorbed fluid, its density and its structural properties, etc. should only depend on some averaged characteristics of the porous material. Thus, one has to perform two successive averages, first a thermal average over the fluid configurations in a given matrix realisation, and then a second average over all possible matrix configurations, a procedure that is, for instance, realised in computer simulations of porous materials [10]. A major consequence of this average over disorder is that translational invariance is recovered in the statistical mechanical treatment. This allows an extension of the conventional methods of liquid state theory to quenched-annealed systems.

Similar as in conventional liquid state theory, the structure of the mixture is described through so-called correlation functions. Madden and Glandt derived cluster expansions for these functions by exploiting the similarity of this system with a fully equilibrated binary mixture and omitting those graphs that are not compatible with the fact that there is no structural response of the matrix to the presence of the fluid. In addition, they derived integral equations for such systems as counterparts to the standard Ornstein Zernike (OZ) equations relating the total pair correlation functions to the direct correlation functions.

However, later Given and Stell [11] showed that these integral equations derived by Madden and Glandt are only an approximation in which a certain class of terms was neglected in the cluster expansion of the direct correlation function for the fluid particles. They derived the *exact* so-called replica OZ equations (ROZ) making use of the replica trick [12, 13], originally developed in the context of the theory of spin glasses [14, 15]. This method allows us, to replace the study of the original quenched-annealed mixture by that of a limiting case of a special, fully equilibrated $(s+1)$-component mixture – called the replicated system. This system consists of s noninteracting identical copies (replicas) of the original fluid, each interacting with the matrix particles. As an application of the replica formalism, closed expressions for the structural and thermodynamic properties of the systems were developed [16, 17, 18].

The simplest example of such a quenched-annealed mixture, where only excluded-volume interactions are taken into account, is a hard-sphere fluid inside a matrix of hard spheres arranged in an equilibrium structure or a hard-sphere fluid which is contained in the interstices of a bed of randomly placed spherical obstacles (i.e., a quenched 'ideal gas') [19, 10, 20]. Integral equation theories which use approximate closures to the ROZ equations have been applied to the calculation of pair distribution functions [19, 10, 20, 21]. Comparison with results from Monte Carlo simulations [10, 20] indicates that the approach has an accuracy comparable to that of bulk liquid state theory.

Recently, theoretical research has focused on the phase behaviour of fluids in disordered porous materials, since experiments indicate deviations from the phase behaviour of bulk fluids. Page and Monson [22] observed in their Monte Carlo simulation of a Lennard-Jones fluid that is confined in a rigid matrix of spherical obstacles a significant narrowing of the liquid-vapour coexistence curve as well as the evidence of a second fluid-fluid phase transition at low temperature. Kaminsky and Monson [23] and Ford and Glandt [24] applied a mean-field theory to model systems and showed that both the critical temperature and the critical density decrease with increasing matrix concentration. Kierlik *et al.* [25] have applied an improved perturbation theory – the optimised cluster theory – to describe phase diagrams of Lennard-Jones fluids. They observed that the liquid-vapour coexistence curve was similar to that of a bulk fluid, although displaced and narrowed. Additionally, the theory predicted the appearance of a second fluid-fluid transition at low temperatures.

So far, theoretical research was mainly restricted to atomic single-component classical fluids. Generalisation of the theory to ionic fluids has partly been done [26, 27].

This study presents the formal theory generalised to the case of a two-component fluid inside a porous matrix. We make use of the replica trick to derive both structural as well as thermodynamic relations. The ROZ equations for a binary fluid in a matrix are derived and formulated in a compact matrix notation. The Gibbs-Duhem relation, the compressibility equation, the virial equation, and the energy equation are presented for the case of a two-component fluid in a matrix. The optimised cluster theory (OCT) and optimised random phase approximation (ORPA) introduced by Weeks, Andersen, and Chandler [36] is extended to the case of a binary fluid in a matrix. The ROZ equations for the one-component fluid were solved numerically in different approximations for various kinds of model systems (pure hard-sphere system and hard-sphere system with attractive square-well or Lennard-Jones tail) and the results of the two latter ones compared with the solutions obtained within the perturbation theory and are presented with results from Monte Carlo simulations. A phase diagram was calculated for a one-component fluid in a matrix in the case of a hard-sphere interaction with attractive square-well tail.

The report is organised as follows: In chapter 2 we give a brief introduction into the structural properties of fluids adsorbed in disordered porous media. The ROZ equations for a two-component fluid in a matrix are derived and the generalisation to a k-component fluid is presented. In addition, we rewrite these equations in a compact matrix notation. In chapter 3 the numerical algorithm is presented which was used to solve the integral equations together with some approximate closure relation. In chapter 4 we develop the thermodynamics of a two-component fluid in a matrix. In particular, we present an alternative derivation of the compressibility equation. In chapter 5 the perturbation theory (the optimised random phase approximation) which was used in this work is presented and generalised to the case of a two-component fluid in the matrix. Numerical results, including a phase diagram are presented in chapter 6.

Chapter 2

Structure of fluids in porous media

2.1 Model and basic notations for fluids in porous media

In the present study we will investigate the properties of continuum systems with quenched disorder. Examples for such systems are porous materials, gels, amorphous materials and spin glasses. In a theoretical model such materials are treated as being constructed in layers: each layer is added to those already in place, allowed to equilibrate at some temperature, then frozen in place without structural relaxation before the next layer is added and starting to interpenetrate the previous ones. Such materials are distinguished from fully equilibrated mixtures in that they are formed by a step-by-step annealing or equilibration process.

We now concentrate on the simplest of such systems consisting just of two layers. The first one is quenched or frozen in place, the second one is annealed or allowed to equilibrate. The particles in the quenched layer constitute a matrix through which the particles in the annealed layer move. This model describes a one-component fluid in a porous medium as a special two-component mixture: in contrast to a 'standard' two-component equilibrium mixture, there is no structural response of the matrix to the particles in the fluid. The particles of the matrix form a rigid structure that is not affected by the mobile phase. It can be regarded as a field of obstacles through which the fluid particles move.

Physical quantities describing such systems are therefore formulated as double averages. First, one averages over all degrees of freedom of the fluid particles, keeping the matrix particles fixed, then one performs a matrix average over all degrees of freedom associated with the matrix.

Consider the two-component system in a volume V. The matrix particles which are fixed in place are denoted as species 0 particles, the fluid particles as species 1 particles. The latter ones are allowed to equilibrate with some inverse temperature $\beta_1 = \frac{1}{k_B T_1}$. We assume now that the N_0 matrix particles are distributed according to a canonical equilibrium distribution at some inverse temperature $\beta_0 = \frac{1}{k_B T_0}$. In a particular realisation they will be located at positions $\mathbf{q}^{N_0} := \{\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_{N_0}\}$. The matrix particles are thus distributed with the probability density

$$p_0(\mathbf{q}^{N_0}) = \frac{1}{Z_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})}, \tag{2.1}$$

where H_{00} is the potential energy of the N_0 particles and

$$Z_0 = \frac{1}{N_0!} \int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})}$$

is the canonical partition function (to be more precise, it is the configurational integral, but in the following we stick to the convention found in the literature of fluids in porous media). Furthermore, we write $\mathbf{dq}^{N_0}$ to represent integration over all the positions of particles of species 0.

For a specified realisation of the matrix $\mathbf{q}^{N_0}$ we assume that the conditional probability density that the system contains N_1 fluid particles at positions $\mathbf{r}^{N_1} := \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_1}\}$ is given by a grand canonical distribution

$$p_1(\mathbf{r}^{N_1}|\mathbf{q}^{N_0}) = \frac{1}{\Xi_1(\mathbf{q}^{N_0})} z_1^{N_1} e^{-\beta_1\left[H_{01}(\mathbf{q}^{N_0},\mathbf{r}^{N_1}) + H_{11}(\mathbf{r}^{N_1})\right]}, \tag{2.2}$$

where z_1 is the specific activity of the fluid particles, $H_{01}+H_{11}$ is the potential energy of the N_1 fluid particles in the presence of the N_0 matrix particles and

$$\Xi_1(\mathbf{q}^{N_0}) = \sum_{N_1} \frac{1}{N_1!} z_1^{N_1} \int \mathbf{dr}^{N_1} e^{-\beta_1\left[H_{01}(\mathbf{q}^{N_0},\mathbf{r}^{N_1}) + H_{11}(\mathbf{r}^{N_1})\right]} \tag{2.3}$$

is the matrix configuration dependent grand partition function.

This choice of ensemble distributions corresponds to the experimental situation where the fluid is in contact with a reservoir fixing its chemical potential and temperature and penetrates a matrix characterised by its average density $\rho_0 = \frac{N_0}{V}$. In the literature also other choices of ensembles can be found. In [13] for instance, both fluid and matrix particles are treated in the canonical ensemble. This approach will be used in the case of a two-component fluid in a matrix (see subsection 2.7.1). On the other hand, Madden and Glandt [8] and Given [12] have used the grand canonical ensemble for both fluid and matrix particles. Both this and the aforementioned models relax the constraint that the number of annealed particles belonging to each replica must be exactly equal. It was shown in [17], that methods based on different choices of ensembles become equivalent in the thermodynamic limit.

2.2 Dual ensemble formalism

For a specified matrix realisation $\mathbf{q}^{N_0}$ the thermal average of any mechanical variable $X(\mathbf{r}^{N_1}; \mathbf{q}^{N_0})$ over the fluid variables is

$$\langle X \rangle (z_1, T_1, V; \mathbf{q}^{N_0}) = \sum_{N_1} \frac{1}{N_1!} \int \mathbf{dr}^{N_1} X(\mathbf{r}^{N_1}; \mathbf{q}^{N_0}) p_1(\mathbf{r}^{N_1} | \mathbf{q}^{N_0}), \tag{2.4}$$

where the angular brackets indicate an average over the annealed degrees of freedom at a given temperature T_1, chemical activity z_1 and volume V. So the resulting quantity is a function of $\mathbf{q}^{N_0}$ and may further be averaged over the ensemble of matrix particles to give

$$\begin{aligned} X(z_1, T_1, \rho_0, T_0, V) &= \overline{\langle X \rangle (z_1, T_1, V; \mathbf{q}^{N_0})} \\ &= \frac{1}{N_0!} \int \mathbf{dq}^{N_0} \langle X \rangle (z_1, T_1, V; \mathbf{q}^{N_0}) p_0(\mathbf{q}^{N_0}), \end{aligned} \tag{2.5}$$

where the over-bar denotes an average over matrix configurations. Inserting eqs. 2.1, 2.2 and 2.4 in eq. 2.5 we obtain

$$\begin{aligned} X(z_1, T_1, \rho_0, T_0, V) &= \frac{1}{Z_0 N_0!} \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int \mathbf{dq}^{N_0} \frac{1}{\Xi_1(\mathbf{q}^{N_0})} \int \mathbf{dr}^{N_1} X(\mathbf{r}^{N_1}; \mathbf{q}^{N_0}) \times \\ & \qquad e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} e^{-\beta_1 \left[H_{01}(\mathbf{q}^{N_0}, \mathbf{r}^{N_1}) + H_{11}(\mathbf{r}^{N_1}) \right]}. \end{aligned} \tag{2.6}$$

It is worthwhile to compare eq. 2.6 with the corresponding expression for a binary mixture in complete thermodynamic equilibrium, characterised by a single inverse temperature β where one component is distributed according to a canonical ensemble, and the other one according to a grand canonical ensemble, i.e.,

$$\begin{aligned} X_{mix}(z_1, \rho_0, T, V) = & \frac{1}{\Xi}\frac{1}{N_0!}\sum_{N_1}\frac{z_1^{N_1}}{N_1!}\int \mathbf{dq}^{N_0}\int \mathbf{dr}^{N_1} X(\mathbf{r}^{N_1};\mathbf{q}^{N_0}) \times \\ & e^{-\beta\left[H_{00}(\mathbf{q}^{N_0})+H_{01}(\mathbf{q}^{N_0},\mathbf{r}^{N_1})+H_{11}(\mathbf{r}^{N_1})\right]}, \end{aligned} \tag{2.7}$$

where

$$\Xi = \frac{1}{N_0!}\sum_{N_1}\frac{z_1^{N_1}}{N_1!}\int \mathbf{dq}^{N_0}\int \mathbf{dr}^{N_1} e^{-\beta\left[H_{00}(\mathbf{q}^{N_0})+H_{01}(\mathbf{q}^{N_0},\mathbf{r}^{N_1})+H_{11}(\mathbf{r}^{N_1})\right]}$$

is the corresponding partition function.

The essential difference between eq. 2.6 and 2.7 is not the appearance of two different temperatures in eq. 2.6 which is only of quantitative interest, but the presence of the partition function $\Xi_1(\mathbf{q}^{N_0})$ (eq. 2.3) within the integral over matrix positions.

2.3 The replicated system

Following Given [12], we will use the replica trick to show that the partly quenched system is isomorphic to a limiting case of a corresponding equilibrium system, called the replicated system. This system is an equilibrium mixture of a one-component fluid (composed of matrix particles that are now mobile) with an s-component fluid, given by s identical copies (or replicas) of the annealed species. Each pair of particles has the same pairwise interaction in the replicated system as in the original system except that a pair of annealed particles from different replicas do not interact. Exploiting this isomorphism we will be able to replace the study of the partly quenched system by that of the replicated system. For example, the correlation functions of the quenched system are obtained by taking the $s \to 0$ limit of the correlation functions of the replicated system. In particular, we can use the standard

OZ equations for the replicated system and then take the $s \to 0$ limit to obtain the integral equations for the original system, called the replica Ornstein Zernike (ROZ) equations. All thermodynamic relations of the system can be obtained in a straightforward manner.

To demonstrate the replica trick we start with the average value of the grand potential of the system (see eq. 2.3)

$$-\beta_1 \Omega_1(z_1, T_1, V; \mathbf{q}^{N_0}) = \ln \Xi_1(\mathbf{q}^{N_0}), \tag{2.8}$$

which is given as

$$-\beta_1 \overline{\Omega}_1(z_1, T_1, \rho_0, T_0, V) = \frac{1}{Z_0 N_0!} \int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} \ln \Xi_1(\mathbf{q}^{N_0}). \tag{2.9}$$

The average is difficult to treat because of the presence of the logarithm under the integral. We thus make use of the replica trick [14, 15] which consists of replacing the logarithm by an exponential, using the identity

$$\ln x = \lim_{s\to 0} \frac{x^s - 1}{s} = \lim_{s \to 0} \frac{d}{ds} x^s. \tag{2.10}$$

Inserting eq. 2.10 in eq. 2.9 yields

$$\begin{aligned} -\beta_1 \overline{\Omega}_1 &= \frac{1}{Z_0} \lim_{s\to 0} \frac{d}{ds} \Bigg\{ \frac{1}{N_0!} \int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} \times \\ &\qquad \Bigg(\sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int \mathbf{dr}^{N_1} e^{-\beta_1 \left[H_{01}(\mathbf{q}^{N_0}, \mathbf{r}^{N_1}) + H_{11}(\mathbf{r}^{N_1}) \right]} \Bigg)^s \Bigg\} \\ &= \frac{1}{Z_0} \lim_{s \to 0} \frac{d}{ds} \Xi^{rep}(s), \end{aligned} \tag{2.11}$$

where $\Xi^{rep}(s)$ can be written – if s is an integer – as

$$\begin{aligned} \Xi^{rep}(s) &= \frac{1}{N_0!} \sum_{N_1 \dots N_s} \frac{z_1^{N_1} \cdots z_1^{N_s}}{N_1! \cdots N_s!} \int \mathbf{dq}^{N_0} \mathbf{dr}^{N_1} \cdots \mathbf{dr}^{N_s} \\ &\qquad e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} e^{-\beta_1 \sum_{\alpha=1}^{s} \left[H_{0\alpha}(\mathbf{q}^{N_0}, \mathbf{r}^{N_\alpha}) + H_{\alpha\alpha}(\mathbf{r}^{N_\alpha}) \right]}, \end{aligned}$$

where $\mathbf{r}^{N_\alpha}$ denotes the positions of the N_α fluid particles in replica α ($\alpha = 1, \dots, s$), $H_{0\alpha}$ the potential energy of interaction between matrix particles and fluid particles of replica α and $H_{\alpha\alpha}$ the energy of interaction between fluid particles of replica α.

The fluid particles have been replicated and now appear in s copies. For integer values of s, $\Xi^{rep}(s)$ is the equilibrium partition function of an $(s+1)$-component fluid (if we neglect the appearance of two different temperatures) in which there is no interaction between particles of components α and β $(1 \leq \alpha \neq \beta \leq s)$. More precisely, we are considering a grand canonical ensemble for the replicas and a canonical ensemble for the matrix.

Furthermore, the $s \to 0$ limit of $\Xi^{rep}(s)$

$$\lim_{s\to 0} \Xi^{rep}(s) = \frac{1}{N_0!}\int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} = Z_0\,,$$

is the partition function of the matrix.

Thus if we assume equal temperatures $(\beta_0 = \beta_1 = \beta)$, which is not a restriction in the following, since we will only consider random or hard-sphere matrices for which β_0 can be equally well replaced by β_1, eq. 2.11 can be simplified to

$$-\beta\overline{\Omega}_1 = \lim_{s\to 0}\frac{d}{ds}\ln \Xi^{rep}(s) = -\beta \lim_{s\to 0}\frac{d}{ds}\Omega^{rep}(s), \qquad (2.12)$$

where

$$\Omega^{rep}(s) = -k_B T \ln \Xi^{rep}(s).$$

If we introduce the pairwise interaction potentials ϕ_{00} (between a pair of quenched particles), ϕ_{11} (between a pair of annealed particles) and ϕ_{01} (between a quenched and an annealed particle), the interaction potential of the replicated system can be written as

$$\begin{aligned} H = & \sum_{\substack{i<j \\ i,j\in\{1,\ldots,N_0\}}} \phi_{00}(\mathbf{q}_i,\mathbf{q}_j) + \sum_{\alpha=1}^{s} \sum_{\substack{i,j \\ i\,\in\,\{1,\ldots,N_0\} \\ j\,\in\,\{1,\ldots,N_\alpha\}}} \phi_{01}^{\alpha}(\mathbf{q}_i,\mathbf{r}_{\alpha,j}) \\ & + \sum_{\alpha=1}^{s}\sum_{\beta=1}^{s} \sum_{\substack{i<j \\ i\,\in\,\{1,\ldots,N_\alpha\} \\ j\,\in\,\{1,\ldots,N_\beta\}}} \phi_{11}^{\alpha\beta}(\mathbf{r}_{\alpha,i},\mathbf{r}_{\beta,j}) \end{aligned}$$

with

$$\begin{aligned} \phi_{11}^{\alpha\beta} &\equiv \phi_{11}\delta_{\alpha\beta} \\ \phi_{01}^{\alpha} &\equiv \phi_{01}, \end{aligned} \qquad (2.13)$$

where $\phi_{11}^{\alpha\beta}$ is the pairwise interaction potential between fluid particles of the replicas α and β, ϕ_{01}^{α} is the pairwise interaction potential between matrix particles and particles of replica α, $\mathbf{r}_{\alpha,j}$ is the position of particle j in replica α, etc.

The Kronecker delta on the right hand side of eq. 2.13 indicates that pairs of replica particles only interact if they belong to the same copy. Thus the component of the species 0 particles can be thought of as a 'solvent' which mediates interactions between species 1 particles of different replicas.

Note that the limiting case $s \to 0$ cannot be interpreted physically. Firstly, a physical interpretation of the replicated system as an equilibrium mixture of $(s+1)$ components is only valid if s is an integer. Furthermore, although in the limit $s \to 0$ the replica system becomes an equilibrium system containing only the quenched particles, we still have nontrivial correlation functions $h_{11}(r)$ and $h_{12}(r)$ describing the correlations between a pair of annealed particles in the same replica and a pair of particles in different replicas. Instead, one must envision the replica method merely as a mathematical tool which tells us how to relate the thermodynamic potential of a partly quenched system to that of a fully equilibrated system

$$\overline{\Omega}_1 = \lim_{s \to 0} \frac{d}{ds} \Omega^{rep}(s).$$

Starting from this point, one is able to relate all thermodynamic properties of the partly quenched system to those of the replicated system which can be found by methods of standard liquid state theory.

2.4 Derivation of the ROZ equations

The structure of the partly quenched system is described by correlation functions similar to those used in equilibrium liquid state theory. The pair distribution functions $g_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ give the probability density for simultaneously finding a particle of species i within the infinitesimal volume $\mathbf{dr}$ at $\mathbf{r}_1$ and a particle of species j within $\mathbf{dr}$ at $\mathbf{r}_2$. We now pose the question how these correlation functions are obtained from those of the replicated system.

By definition, the pair density $\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ for the mobile phase is the average of $\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0})$ – the two-particle density of the fluid in a particular matrix realisation – over all matrix configurations. We introduce the pair distribution function as in standard liquid state theory (see eq. A.1)

$$g_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_1^{(1)}(\mathbf{r}_1)\rho_1^{(1)}(\mathbf{r}_2)},$$

where $\rho_1^{(1)}(\mathbf{r})$ is the one-particle density of the fluid component. Thus the total correlation function $h_{11}^{(2)} = g_{11}^{(2)} - 1$ (see eq. A.2) is given by

$$\rho_1^{(1)}(\mathbf{r}_1)\rho_1^{(1)}(\mathbf{r}_2)h_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho_1^{(1)}(\mathbf{r}_1)\rho_1^{(1)}(\mathbf{r}_2).$$

For further investigations we only consider homogeneous systems. In addition we restrict our considerations to systems with spherically symmetric interaction potentials. Under such conditions, the simplifications

$$\rho_1^{(1)}(\mathbf{r}) = \rho_1 \quad \text{and} \quad h_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = h_{11}^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|) = h_{11}(r_{12})$$

can be made. Assuming that the fluid-fluid interaction potential is a sum of pairwise interactions $\phi_{11}(\mathbf{r}_i, \mathbf{r}_j)$, one can use $\Xi_1(\mathbf{q}^{N_0})$ as a generating functional for the densities and perform a functional derivative with respect to $\phi_{11}(\mathbf{r}_1, \mathbf{r}_2)$ to obtain

$$\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) = -2k_B T \frac{\delta \ln \Xi_1(\mathbf{q}^{N_0})}{\delta \phi_{11}(\mathbf{r}_1, \mathbf{r}_2)}$$

(see [28, 29]). Thus we find, using eqs. 2.8 and 2.12,

$$\begin{aligned}
\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \overline{\rho_{11}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0})} = -2k_B T \frac{\delta \overline{\ln \Xi_1(\mathbf{q}^{N_0})}}{\delta \phi_{11}(\mathbf{r}_1, \mathbf{r}_2)} \\
&= 2 \frac{\delta \overline{\Omega}_1}{\delta \phi_{11}(\mathbf{r}_1, \mathbf{r}_2)} = 2 \lim_{s \to 0} \frac{d}{ds} \left(\frac{\delta \Omega^{rep}(s)}{\delta \phi_{11}(\mathbf{r}_1, \mathbf{r}_2)} \right) \\
&= 2 \lim_{s \to 0} \frac{d}{ds} \left(\frac{\delta \Omega^{rep}(s)}{\delta \phi_{11}^{11}(\mathbf{r}_1, \mathbf{r}_2)} + \frac{\delta \Omega^{rep}(s)}{\delta \phi_{11}^{22}(\mathbf{r}_1, \mathbf{r}_2)} + \cdots + \frac{\delta \Omega^{rep}(s)}{\delta \phi_{11}^{ss}(\mathbf{r}_1, \mathbf{r}_2)} \right) \\
&= \lim_{s \to 0} \frac{d}{ds} \left(s \rho_{11}^{(2),rep}(r_{12}; s) \right) = \lim_{s \to 0} \rho_{11}^{(2),rep}(r_{12}; s),
\end{aligned}$$

where we have considered the fact that there are s identical replicas which do not interact to obtain the symmetry properties of the functional $\Omega^{rep}(s)$

which lead to the last equalities. Thus

$$h_{11}(r_{12}) = \lim_{s\to 0} h_{11}^{rep}(r_{12}; s). \tag{2.14}$$

h_{00}, h_{01} and h_{12} are related to their counterparts in the replicated system by similar equations

$$\begin{aligned} h_{00}(q_{12}) &= \lim_{s\to 0} h_{00}^{rep}(q_{12}; s) \\ h_{01}(|\mathbf{r}_1 - \mathbf{q}_2|) &= \lim_{s\to 0} h_{01}^{rep}(|\mathbf{r}_1 - \mathbf{q}_2|; s) \\ h_{12}(r_{12}) &= \lim_{s\to 0} h_{12}^{rep}(r_{12}; s). \end{aligned} \tag{2.15}$$

The replica system has the following symmetry properties which we assume to be also valid for non-integers such that there is no breaking of the replica symmetry when performing the analytic continuation to $s=0$:

$$\begin{array}{lll} c_{0i}^{rep} = c_{01}^{rep}; \quad h_{0i}^{rep} = h_{01}^{rep} & \text{for} & i = 1, \ldots, s \\ c_{ii}^{rep} = c_{11}^{rep}; \quad h_{ii}^{rep} = h_{11}^{rep} & \text{for} & i = 1, \ldots, s \\ c_{ij}^{rep} = c_{12}^{rep}; \quad h_{ij}^{rep} = h_{12}^{rep} & \text{for} & i, j = 1, \ldots, s \text{ and } i \neq j \\ \rho_i = \rho_1 & \text{for} & i = 1, \ldots, s, \end{array} \tag{2.16}$$

where $h_{12}^{rep}(s), c_{12}^{rep}(s)$ denote the correlation functions between two different replicas, and $h_{11}^{rep}(s), c_{11}^{rep}(s)$ between the same replicas.

Furthermore, we have the usual symmetry relation

$$c_{ij}^{rep} = c_{ji}^{rep}; \quad h_{ij}^{rep} = h_{ji}^{rep} \quad \text{for} \quad i, j = 0, \ldots, s. \tag{2.17}$$

Now we write down the standard OZ equations (see eq. A.5) for the replicated system and isolate the s-dependence of these equations by grouping together identical terms (for notational simplicity we drop out the explicit r dependence):

$$h_{00}^{rep}(s) = c_{00}^{rep}(s) + \rho_0 c_{00}^{rep}(s) \otimes h_{00}^{rep}(s) + s\rho_1 c_{01}^{rep}(s) \otimes h_{01}^{rep}(s) \tag{2.18}$$

$$\begin{aligned} h_{01}^{rep}(s) &= c_{01}^{rep}(s) + \rho_0 c_{00}^{rep}(s) \otimes h_{01}^{rep}(s) + \rho_1 c_{01}^{rep}(s) \otimes h_{11}^{rep}(s) \\ &\quad + (s-1)\rho_1 c_{01}^{rep}(s) \otimes h_{12}^{rep}(s) \end{aligned} \tag{2.19}$$

$$\begin{aligned} h_{11}^{rep}(s) &= c_{11}^{rep}(s) + \rho_0 c_{01}^{rep}(s) \otimes h_{01}^{rep}(s) + \rho_1 c_{11}^{rep}(s) \otimes h_{11}^{rep}(s) \\ &\quad + (s-1)\rho_1 c_{12}^{rep}(s) \otimes h_{12}^{rep}(s) \end{aligned} \tag{2.20}$$

$$\begin{aligned} h_{12}^{rep}(s) &= c_{12}^{rep}(s) + \rho_0 c_{01}^{rep}(s) \otimes h_{01}^{rep}(s) + \rho_1 c_{11}^{rep}(s) \otimes h_{12}^{rep}(s) \\ &\quad + \rho_1 c_{12}^{rep}(s) \otimes h_{11}^{rep}(s) + (s-2)\rho_1 c_{12}^{rep}(s) \otimes h_{12}^{rep}(s), \end{aligned} \tag{2.21}$$

where the symbol $\otimes$ denotes a convolution integral.

Exploiting the symmetry relations 2.17 and using the equation for $h_{10}^{rep}(s)$ an alternative equation for $h_{01}^{rep}(s)$ is

$$\begin{aligned} h_{01}^{rep}(s) &= c_{01}^{rep}(s) + \rho_0 c_{01}^{rep}(s) \otimes h_{00}^{rep}(s) + \rho_1 c_{11}^{rep}(s) \otimes h_{01}^{rep}(s) \\ &\quad + (s-1)\rho_1 c_{12}^{rep}(s) \otimes h_{01}^{rep}(s), \end{aligned}$$

which can also be derived from above equations.

We now take the $s \to 0$ limit of eqs. 2.18 - 2.21 and use eqs. 2.14 and 2.15 to obtain the ROZ equations:

$$\begin{aligned} h_{00} &= c_{00} + \rho_0 c_{00} \otimes h_{00} && (2.22) \\ h_{01} &= c_{01} + \rho_0 c_{00} \otimes h_{01} + \rho_1 c_{01} \otimes h_{11} - \rho_1 c_{01} \otimes h_{12} && (2.23) \\ h_{11} &= c_{11} + \rho_0 c_{01} \otimes h_{01} + \rho_1 c_{11} \otimes h_{11} - \rho_1 c_{12} \otimes h_{12} && (2.24) \\ h_{12} &= c_{12} + \rho_0 c_{01} \otimes h_{01} + \rho_1 c_{11} \otimes h_{12} + \rho_1 c_{12} \otimes h_{11} \\ &\qquad - 2\rho_1 c_{12} \otimes h_{12} && (2.25) \end{aligned}$$

An alternative equation for h_{01} is

$$h_{01} = c_{01} + \rho_0 c_{01} \otimes h_{00} + \rho_1 c_{11} \otimes h_{01} - \rho_1 c_{12} \otimes h_{01}.$$

Note that the equation for the matrix decouples from the others because the matrix configurations are not influenced by the fluid.

2.5 Reformulation of the ROZ equations

We now introduce (for reasons outlined below)

$$\begin{aligned} h_b &= h_{12}; \quad h_c = h_{11} - h_{12} \\ c_b &= c_{12}; \quad c_c = c_{11} - c_{12}, \end{aligned}$$

the so called <u>b</u>locking (or disconnected) parts and <u>c</u>onnected parts of h_{11} and c_{11}. With these definitions eqs. 2.22 - 2.25 become

$$h_{00} = c_{00} + \rho_0 c_{00} \otimes h_{00} \qquad (2.26)$$

$$\begin{aligned} h_{01} &= c_{01} + \rho_0 c_{00} \otimes h_{01} + \rho_1 c_{01} \otimes h_c && (2.27) \\ h_{11} &= c_{11} + \rho_0 c_{01} \otimes h_{01} + \rho_1 c_{11} \otimes h_c + \rho_1 c_c \otimes h_b && \\ &= c_{11} + \rho_0 c_{01} \otimes h_{01} + \rho_1 c_c \otimes h_{11} + \rho_1 c_b \otimes h_c && (2.28) \\ h_c &= c_c + \rho_1 c_c \otimes h_c && (2.29) \end{aligned}$$

or, alternatively,

$$h_{01} = c_{01} + \rho_0 c_{01} \otimes h_{00} + \rho_1 c_c \otimes h_{01}.$$

Given and Stell [13] introduced the two correlation functions h_c and h_b by their diagrammatic expansion. It should be borne in mind that h_{12} describes the correlation between particles of different replicas which do not interact directly. They only interact indirectly through the mediation of the quenched particles. Therefore $h_b = h_{12}$ consists precisely of those graphs contributing to the function h_{11} that contain at least one ρ_0-field point in all paths between the fluid root points, i.e., they do not have an annealed path connecting their root points (for a brief introduction in graph theory see [29]). The connected function h_c describes correlations between a pair of fluid particles that are transmitted through successive layers of fluid particles whereas the blocking function h_b describes correlations between fluid particles blocked or separated from each other by matrix particles. Note that, though the matrix particles are immobile, they tend to order the fluid particles on either side of them and thus are capable of mediating correlations through a layer of matrix particles. At very low matrix porosities, i.e. very high densities of the matrix, the volume accessible to fluid particles is divided into small cavities. In this limit the function h_c describes correlations between fluid particles in the same cavity, whereas h_b describes correlations between fluid particles in different cavities.

In [17] another way was presented to introduce these functions. By defining the connected pair density as

$$\rho^{(2)}_{11,c}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) = \rho^{(2)}_{11}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0}) - \rho^{(1)}_1(\mathbf{r}_1; \mathbf{q}^{N_0}) \rho^{(1)}_1(\mathbf{r}_2; \mathbf{q}^{N_0}),$$

where $\rho^{(1)}_1(\mathbf{r}; \mathbf{q}^{N_0})$ is the matrix dependent one-particle density, we can define the following correlation functions h_c and h_b by

$$\rho_1^2 h_c(r_{12}) = \overline{\rho^{(2)}_{11,c}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{q}^{N_0})} = \rho_{11}(r_{12}) - \overline{\rho^{(1)}_1(\mathbf{r}_1; \mathbf{q}^{N_0}) \rho^{(1)}_1(\mathbf{r}_2; \mathbf{q}^{N_0})}$$

and

$$\rho_1^2 h_b(r_{12}) = \overline{\rho_1^{(1)}(\mathbf{r}_1;\mathbf{q}^{N_0})\rho_1^{(1)}(\mathbf{r}_2;\mathbf{q}^{N_0})} - \rho_1^2,$$

hence

$$h_{11}(r_{12}) = h_c(r_{12}) + h_b(r_{12}).$$

In [17] it is shown that these functions satisfy the relation

$$h_c(r_{12}) = \lim_{s\to 0} h_{11}^{rep}(r_{12};s) - \lim_{s\to 0} h_{12}^{rep}(r_{12};s)$$

which is precisely the definition of the connected correlation function introduced by Given and Stell.

2.6 Closure relations

The ROZ equations do not represent a closed set of equations for the correlation functions, therefore – as in standard liquid state theory – additional relations, the so-called closure relations, have to be provided. To obtain approximate closures for porous systems we start from standard approximations (see [29] and eqs. A.8, A.9) for the equilibrium replicated system and then take the $s \to 0$ limit. Since particles belonging to different replicas do not interact, the replicated system is characterised by highly non-additive interactions. Thus far the standard closure relations have only been investigated in additive systems; therefore, the validity of these approximations can be judged only by the resulting predictions for some specific systems [10, 20].

2.7 Structure of a binary fluid in a porous medium

The generalisation of the formalism presented in the previous sections to the case of a binary fluid in a porous media is straightforward. As a first step we will generalise the replica method to the case of the two-component fluid. Then, using this formalism we will be able to present the corresponding

ROZ equations which will be rewritten in terms of blocking and connecting parts of the correlation functions. Finally, we suggest how to generalise the formalism to a k-component fluid in a matrix.

2.7.1 The replicated system

As before, we use the subscript 0 for quantities concerning the matrix particles. The particles of one of the fluid components are denoted as species 1, those of the other component as species 2 particles. The subscript 12 will be used for properties of the whole binary mixture. We use the formalism of a canonical ensemble both for the matrix and the fluid mixture. Thus we obtain the following probability densities

$$p_0(\mathbf{q}^{N_0}) = \frac{1}{Z_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})}$$

and

$$p_{12}(\mathbf{r}^{N_1}, \mathbf{s}^{N_2}|\mathbf{q}^{N_0}) = \frac{1}{Z_{12}(\mathbf{q}^{N_0})} \times \\ e^{-\beta_{12}\left[H_{01}(\mathbf{q}^{N_0},\mathbf{r}^{N_1})+H_{02}(\mathbf{q}^{N_0},\mathbf{s}^{N_2})+H_{11}(\mathbf{r}^{N_1})+H_{12}(\mathbf{r}^{N_1},\mathbf{s}^{N_2})+H_{22}(\mathbf{s}^{N_2})\right]},$$

where $\mathbf{r}^{N_1} = \{\mathbf{r}_1, \ldots, \mathbf{r}_{N_1}\}$ denote the positions of the N_1 particles of component 1 and $\mathbf{s}^{N_2} = \{\mathbf{s}_1, \ldots, \mathbf{s}_{N_2}\}$ denote the positions of the N_2 particles of component 2, H_{ij} is the interaction potential between particles of species i and j,

$$Z_{12}(\mathbf{q}^{N_0}) = \frac{1}{N_1!N_2!} \int \mathbf{dr}^{N_1} \mathbf{ds}^{N_2} e^{-\beta_{12}[H_{01}+H_{02}+H_{11}+H_{12}+H_{22}]} \tag{2.30}$$

is the matrix dependent partition function and $\beta_{12} = \frac{1}{k_B T_{12}}$ the inverse temperature of the fluid mixture.

Again, we obtain the thermodynamic quantities of this system via quenched averages. In particular, the Helmholtz free energy of the fluid mixture for a given matrix configuration,

$$-\beta_{12} F_{12}(N_1, N_2, V, T_{12}; \mathbf{q}^{N_0}) = \ln Z_{12}(\mathbf{q}^{N_0})$$

must be averaged over the matrix realisations to yield

$$\begin{aligned}
&-\beta_{12}\overline{F}_{12}(N_0, N_1, N_2, V, T_{12}, T_0) \\
&= \overline{\ln Z_{12}(\mathbf{q}^{N_0})} = \frac{1}{N_0! Z_0} \int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} \ln Z_{12}(\mathbf{q}^{N_0}). \qquad (2.31)
\end{aligned}$$

Using the replica trick 2.10 and inserting eq. 2.30 into 2.31 we obtain

$$\begin{aligned}
-\beta_{12}\overline{F}_{12} &= \frac{1}{Z_0} \lim_{s\to 0} \frac{d}{ds} \frac{1}{N_0!} \int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} Z_{12}^{s}(\mathbf{q}^{N_0}) \\
&= \frac{1}{Z_0} \lim_{s\to 0} \frac{d}{ds} Z^{rep}(s). \qquad (2.32)
\end{aligned}$$

Using the fact that

$$\lim_{s\to 0} Z^{rep}(s) = Z_0$$

eq. 2.32 simplifies to

$$-\beta_{12}\overline{F}_{12} = \lim_{s\to 0} \frac{d}{ds} \ln Z^{rep}(s). \qquad (2.33)$$

For integer s

$$\begin{aligned}
Z^{rep}(s) \;=\; & \frac{1}{N_0!\,(N_1!)^s\,(N_2!)^s} \int \mathbf{dq}^{N_0} \mathbf{dr}_1^{N_1} \cdots \mathbf{dr}_s^{N_1} \mathbf{ds}_1^{N_2} \cdots \mathbf{ds}_s^{N_2} \times \\
& e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} e^{-\beta_{12} \sum_{\alpha=1}^{s} \left[H_{01}^{\alpha}(\mathbf{q}^{N_0}, \mathbf{r}_\alpha^{N_1}) + H_{02}^{\alpha}(\mathbf{q}^{N_0}, \mathbf{s}_\alpha^{N_2}) \right]} \times \\
& \qquad e^{-\beta_{12} \sum_{\alpha=1}^{s} \left[H_{11}^{\alpha}(\mathbf{r}_\alpha^{N_1}) + H_{12}^{\alpha}(\mathbf{r}_\alpha^{N_1}, \mathbf{s}_\alpha^{N_2}) + H_{22}^{\alpha}(\mathbf{s}_\alpha^{N_2}) \right]}, \qquad (2.34)
\end{aligned}$$

where H_{01}^{α} is the potential energy of interaction between matrix particles and fluid particles of component 1 in replica α, $\mathbf{r}_\alpha^{N_1}$ denotes the positions of the N_1 fluid particles of component 1 in replica α, etc. If we assume that the system can be described through pairwise interaction potentials ϕ_{00}, ϕ_{01}, ϕ_{02}, ϕ_{11}, ϕ_{12}, ϕ_{22}, then eq. 2.34 is the equilibrium partition function of a system with the interaction potential

$$\begin{aligned}
H = & \sum_{\substack{i<j \\ i,j\in\{1,\ldots,N_0\}}} \phi_{00}(\mathbf{q}_i, \mathbf{q}_j) + \sum_{\alpha=1}^{s} \sum_{\substack{i,j \\ i\in\{1,\ldots,N_0\} \\ j\in\{1,\ldots,N_1\}}} \phi_{01}^{\alpha}(\mathbf{q}_i, \mathbf{r}_{\alpha,j}) \\
& + \sum_{\alpha=1}^{s} \sum_{\substack{i,j \\ i\in\{1,\ldots,N_0\} \\ j\in\{1,\ldots,N_2\}}} \phi_{02}^{\alpha}(\mathbf{q}_i, \mathbf{s}_{\alpha,j}) + \sum_{\alpha=1}^{s} \sum_{\beta=1}^{s} \sum_{\substack{i<j \\ i,j\in\{1,\ldots,N_1\}}} \phi_{11}^{\alpha\beta}(\mathbf{r}_{\alpha,i}, \mathbf{r}_{\beta,j}) \\
& + \sum_{\alpha=1}^{s} \sum_{\beta=1}^{s} \sum_{\substack{i,j \\ i\in\{1,\ldots,N_1\} \\ j\in\{1,\ldots,N_2\}}} \phi_{12}^{\alpha\beta}(\mathbf{r}_{\alpha,i}, \mathbf{s}_{\beta,j}) + \sum_{\alpha=1}^{s} \sum_{\beta=1}^{s} \sum_{\substack{i<j \\ i,j\in\{1,\ldots,N_2\}}} \phi_{22}^{\alpha\beta}(\mathbf{s}_{\alpha,i}, \mathbf{s}_{\beta,j})
\end{aligned}$$

with

$$\begin{aligned} \phi_{11}^{\alpha\beta} &\equiv \phi_{11}\delta_{\alpha\beta} \\ \phi_{12}^{\alpha\beta} &\equiv \phi_{12}\delta_{\alpha\beta} \\ \phi_{22}^{\alpha\beta} &\equiv \phi_{22}\delta_{\alpha\beta} \\ \phi_{01}^{\alpha} &\equiv \phi_{01} \\ \phi_{02}^{\alpha} &\equiv \phi_{02}. \end{aligned}$$

$\phi_{12}^{\alpha\beta}$ denotes the pairwise interaction potential between particles of the two different fluid components belonging to the copies α and β, $\mathbf{r}_{\alpha,j}$ is the position of particle number j of fluid component 1 in replica α, etc.

The binary mixture now appears in s identical copies. For integer values of s, $Z^{rep}(s)$ is the equilibrium canonical partition function of a $(2s+1)$-component mixture (if we neglect that the temperatures are different) with the same interactions as in the original system, except that fluid particles from different replicas do not interact.

2.7.2 Derivation of the ROZ equations

In order to obtain the ROZ equations for the partly quenched system we first write down the standard OZ equations for the $(2s+1)$-component mixture, exploiting the symmetries of the replica system and grouping together identical terms. For this purpose we introduce the following convention to number the $(2s+1)$ fluid components in the equilibrium mixture:

0	for the matrix
$1, 3, \ldots, 2s-1$	for fluid component 1 in replica number $1, \ldots, s$
$2, 4, \ldots, 2s$	for fluid component 2 in replica number $1, \ldots, s$.

If we define the following sets, which contain the $\underline{\text{o}}$dd and $\underline{\text{e}}$ven numbers of the fluid components

$$\begin{aligned} O &= \{1, 3, \ldots, 2s-1\} \\ E &= \{2, 4, \ldots, 2s\}, \end{aligned}$$

we obtain the following symmetry relations in the replica system for integer values of s:

$$\begin{aligned}
c_{0i}^{rep} &= c_{01}^{rep}; \quad h_{0i}^{rep} = h_{01}^{rep} \quad \text{for} \quad i \in O \\
c_{0i}^{rep} &= c_{02}^{rep}; \quad h_{0i}^{rep} = h_{02}^{rep} \quad \text{for} \quad i \in E \\
c_{ii}^{rep} &= c_{11}^{rep}; \quad h_{ii}^{rep} = h_{11}^{rep} \quad \text{for} \quad i \in O \\
c_{ij}^{rep} &= c_{12}^{rep}; \quad h_{ij}^{rep} = h_{12}^{rep} \quad \text{for} \quad i \in O,\ j = i+1 \\
c_{ii}^{rep} &= c_{22}^{rep}; \quad h_{ii}^{rep} = h_{22}^{rep} \quad \text{for} \quad i \in E \\
c_{ij}^{rep} &= c_{13}^{rep}; \quad h_{ij}^{rep} = h_{13}^{rep} \quad \text{for} \quad i, j \in O,\ i \neq j \\
c_{ij}^{rep} &= c_{14}^{rep}; \quad h_{ij}^{rep} = h_{14}^{rep} \quad \text{for} \quad i \in O,\ j \in E,\ j \neq i+1 \\
c_{ij}^{rep} &= c_{24}^{rep}; \quad h_{ij}^{rep} = h_{24}^{rep} \quad \text{for} \quad i, j \in E,\ i \neq j \\
\rho_i &= \rho_1 \quad \text{for} \quad i \in O \\
\rho_i &= \rho_2 \quad \text{for} \quad i \in E
\end{aligned} \tag{2.35}$$

in addition to the usual symmetry relations which are valid in mixtures

$$c_{ij}^{rep} = c_{ji}^{rep}; \quad h_{ij}^{rep} = h_{ji}^{rep} \quad \text{for} \quad i, j = 0, \ldots, 2s. \tag{2.36}$$

The correlation functions h_{13}, h_{14} and h_{24} describe correlations between particles from different replicas and are therefore equivalent to the blocked parts of the correlation functions h_{11}, h_{12} and h_{22} (see section 2.5).

Using the symmetry relations 2.35, 2.36 for the equilibrium system we obtain the OZ equations for the mixture

$$\begin{aligned}
h_{00}^{rep}(s) &= c_{00}^{rep}(s) + \rho_0 c_{00}^{rep}(s) \otimes h_{00}^{rep}(s) + s\rho_1 c_{01}^{rep}(s) \otimes h_{01}^{rep}(s) \\
&\quad + s\rho_2 c_{02}^{rep}(s) \otimes h_{02}^{rep}(s) \qquad (2.37) \\
h_{01}^{rep}(s) &= c_{01}^{rep}(s) + \rho_0 c_{00}^{rep}(s) \otimes h_{01}^{rep}(s) + \rho_1 c_{01}^{rep}(s) \otimes h_{11}^{rep}(s) \\
&\quad + \rho_2 c_{02}^{rep}(s) \otimes h_{12}^{rep}(s) + (s-1)\rho_1 c_{01}^{rep}(s) \otimes h_{13}^{rep}(s) \qquad (2.38) \\
&\quad + (s-1)\rho_2 c_{02}^{rep}(s) \otimes h_{14}^{rep}(s) \\
h_{02}^{rep}(s) &= c_{02}^{rep}(s) + \rho_0 c_{00}^{rep}(s) \otimes h_{02}^{rep}(s) + \rho_1 c_{01}^{rep}(s) \otimes h_{12}^{rep}(s) \\
&\quad + \rho_2 c_{02}^{rep}(s) \otimes h_{22}^{rep}(s) + (s-1)\rho_1 c_{01}^{rep}(s) \otimes h_{14}^{rep}(s) \qquad (2.39) \\
&\quad + (s-1)\rho_2 c_{02}^{rep}(s) \otimes h_{24}^{rep}(s) \\
h_{11}^{rep}(s) &= c_{11}^{rep}(s) + \rho_0 c_{01}^{rep}(s) \otimes h_{01}^{rep}(s) + \rho_1 c_{11}^{rep}(s) \otimes h_{11}^{rep}(s)
\end{aligned}$$

$$
\begin{aligned}
& + \rho_2 c_{12}^{rep}(s) \otimes h_{12}^{rep}(s) + (s-1)\rho_1 c_{13}^{rep}(s) \otimes h_{13}^{rep}(s) \qquad (2.40)\\
& + (s-1)\rho_2 c_{14}^{rep}(s) \otimes h_{14}^{rep}(s)
\end{aligned}
$$

$$
\begin{aligned}
h_{12}^{rep}(s) &= c_{12}^{rep}(s) + \rho_0 c_{01}^{rep}(s) \otimes h_{02}^{rep}(s) + \rho_1 c_{11}^{rep}(s) \otimes h_{12}^{rep}(s)\\
& + \rho_2 c_{12}^{rep}(s) \otimes h_{22}^{rep}(s) + (s-1)\rho_1 c_{13}^{rep}(s) \otimes h_{14}^{rep}(s)\\
& + (s-1)\rho_2 c_{14}^{rep}(s) \otimes h_{24}^{rep}(s)
\end{aligned} \tag{2.41}
$$

$$
\begin{aligned}
h_{22}^{rep}(s) &= c_{22}^{rep}(s) + \rho_0 c_{02}^{rep}(s) \otimes h_{02}^{rep}(s) + \rho_1 c_{12}^{rep}(s) \otimes h_{12}^{rep}(s)\\
& + \rho_2 c_{22}^{rep}(s) \otimes h_{22}^{rep}(s) + (s-1)\rho_1 c_{14}^{rep}(s) \otimes h_{14}^{rep}(s)\\
& + (s-1)\rho_2 c_{24}^{rep}(s) \otimes h_{24}^{rep}(s)
\end{aligned} \tag{2.42}
$$

$$
\begin{aligned}
h_{13}^{rep}(s) &= c_{13}^{rep}(s) + \rho_0 c_{01}^{rep}(s) \otimes h_{01}^{rep}(s) + \rho_1 c_{11}^{rep}(s) \otimes h_{13}^{rep}(s)\\
& + \rho_2 c_{12}^{rep}(s) \otimes h_{14}^{rep}(s) + \rho_1 c_{13}^{rep}(s) \otimes h_{11}^{rep}(s)\\
& + \rho_2 c_{14}^{rep}(s) \otimes h_{12}^{rep}(s) + (s-2)\rho_1 c_{13}^{rep}(s) \otimes h_{13}^{rep}(s)\\
& + (s-2)\rho_2 c_{14}^{rep}(s) \otimes h_{14}^{rep}(s)
\end{aligned} \tag{2.43}
$$

$$
\begin{aligned}
h_{14}^{rep}(s) &= c_{14}^{rep}(s) + \rho_0 c_{01}^{rep}(s) \otimes h_{02}^{rep}(s) + \rho_1 c_{11}^{rep}(s) \otimes h_{14}^{rep}(s)\\
& + \rho_2 c_{12}^{rep}(s) \otimes h_{24}^{rep}(s) + \rho_1 c_{13}^{rep}(s) \otimes h_{12}^{rep}(s)\\
& + \rho_2 c_{14}^{rep}(s) \otimes h_{22}^{rep}(s) + (s-2)\rho_1 c_{13}^{rep}(s) \otimes h_{14}^{rep}(s)\\
& + (s-2)\rho_2 c_{14}^{rep}(s) \otimes h_{24}^{rep}(s)
\end{aligned} \tag{2.44}
$$

$$
\begin{aligned}
h_{24}^{rep}(s) &= c_{24}^{rep}(s) + \rho_0 c_{02}^{rep}(s) \otimes h_{02}^{rep}(s) + \rho_1 c_{12}^{rep}(s) \otimes h_{14}^{rep}(s)\\
& + \rho_2 c_{22}^{rep}(s) \otimes h_{24}^{rep}(s) + \rho_1 c_{14}^{rep}(s) \otimes h_{12}^{rep}(s)\\
& + \rho_2 c_{24}^{rep}(s) \otimes h_{22}^{rep}(s) + (s-2)\rho_1 c_{14}^{rep}(s) \otimes h_{14}^{rep}(s)\\
& + (s-2)\rho_2 c_{24}^{rep}(s) \otimes h_{24}^{rep}(s).
\end{aligned} \tag{2.45}
$$

Alternative equations for h_{01}^{rep}, h_{02}^{rep}, h_{12}^{rep} and h_{14}^{rep}, which can be derived from eqs. 2.37 - 2.45 or by exploiting the symmetry relations 2.35, 2.36 in the OZ equations for h_{10}^{rep}, h_{20}^{rep}, h_{21}^{rep} and h_{41}^{rep}, are

$$
\begin{aligned}
h_{01}^{rep}(s) &= c_{01}^{rep}(s) + \rho_0 c_{01}^{rep}(s) \otimes h_{00}^{rep}(s) + \rho_1 c_{11}^{rep}(s) \otimes h_{01}^{rep}(s)\\
& + \rho_2 c_{12}^{rep}(s) \otimes h_{02}^{rep}(s) + (s-1)\rho_1 c_{13}^{rep}(s) \otimes h_{01}^{rep}(s)\\
& + (s-1)\rho_2 c_{14}^{rep}(s) \otimes h_{02}^{rep}(s)\\
h_{02}^{rep}(s) &= c_{02}^{rep}(s) + \rho_0 c_{02}^{rep}(s) \otimes h_{00}^{rep}(s) + \rho_1 c_{12}^{rep}(s) \otimes h_{01}^{rep}(s)\\
& + \rho_2 c_{22}^{rep}(s) \otimes h_{02}^{rep}(s) + (s-1)\rho_1 c_{14}^{rep}(s) \otimes h_{01}^{rep}(s)\\
& + (s-1)\rho_2 c_{24}^{rep}(s) \otimes h_{02}^{rep}(s)
\end{aligned}
$$

$$\begin{aligned}
h_{12}^{rep}(s) &= c_{12}^{rep}(s) + \rho_0 c_{02}^{rep}(s) \otimes h_{01}^{rep}(s) + \rho_1 c_{12}^{rep}(s) \otimes h_{11}^{rep}(s) \\
&\quad + \rho_2 c_{22}^{rep}(s) \otimes h_{12}^{rep}(s) + (s-1)\rho_1 c_{14}^{rep}(s) \otimes h_{13}^{rep}(s) \\
&\quad + (s-1)\rho_2 c_{24}^{rep}(s) \otimes h_{14}^{rep}(s) \\
h_{14}^{rep}(s) &= c_{14}^{rep}(s) + \rho_0 c_{02}^{rep}(s) \otimes h_{01}^{rep}(s) + \rho_1 c_{14}^{rep}(s) \otimes h_{11}^{rep}(s) \\
&\quad + \rho_2 c_{24}^{rep}(s) \otimes h_{12}^{rep}(s) + \rho_1 c_{12}^{rep}(s) \otimes h_{13}^{rep}(s) \\
&\quad + \rho_2 c_{22}^{rep}(s) \otimes h_{14}^{rep}(s) + (s-2)\rho_1 c_{14}^{rep}(s) \otimes h_{13}^{rep}(s) \\
&\quad + (s-2)\rho_2 c_{24}^{rep}(s) \otimes h_{14}^{rep}(s).
\end{aligned}$$

Similar as in the one-component case, the correlation functions h_{00}, h_{01}, h_{02}, h_{11}, h_{12}, h_{22}, h_{13}, h_{14}, h_{24} describing the structure of the partly quenched system are related to the corresponding functions in the replicated system by equations similar to 2.14, 2.15. For example, we find

$$\begin{aligned}
&\rho_{12}^{(2)}(\mathbf{r}_1, \mathbf{s}_2) = \overline{\rho_{12}^{(2)}(\mathbf{r}_1, \mathbf{s}_2; \mathbf{q}^{N_0})} \\
&= 2\frac{\delta\overline{\Omega}_{12}}{\delta\phi_{12}(\mathbf{r}_1, \mathbf{s}_2)} = 2\lim_{s\to 0}\frac{d}{ds}\left[\frac{\delta\Omega^{rep}(s)}{\delta\phi_{12}(\mathbf{r}_1, \mathbf{s}_2)}\right] \\
&= 2\lim_{s\to 0}\frac{d}{ds}\left(\frac{\delta\Omega^{rep}(s)}{\delta\phi_{12}^{12}(\mathbf{r}_1, \mathbf{s}_2)} + \frac{\delta\Omega^{rep}(s)}{\delta\phi_{12}^{34}(\mathbf{r}_1, \mathbf{s}_2)} + \cdots + \frac{\delta\Omega^{rep}(s)}{\delta\phi_{12}^{2s-1,2s}(\mathbf{r}_1, \mathbf{s}_2)}\right) \\
&= \lim_{s\to 0}\frac{d}{ds}s\rho_{12}^{(2),rep}(|\mathbf{r}_1 - \mathbf{s}_2|; s) = \lim_{s\to 0}\rho_{12}^{(2),rep}(|\mathbf{r}_1 - \mathbf{s}_2|; s),
\end{aligned}$$

which yields

$$h_{12}(|\mathbf{r}_1 - \mathbf{s}_2|) = \lim_{s\to 0} h_{12}^{rep}(|\mathbf{r}_1 - \mathbf{s}_2|; s).$$

Therefore we take the $s \to 0$ limit of eqs. 2.37 - 2.45 to obtain

$$h_{00} = c_{00} + \rho_0 c_{00} \otimes h_{00} \tag{2.46}$$

$$\begin{aligned}
h_{01} &= c_{01} + \rho_0 c_{00} \otimes h_{01} + \rho_1 c_{01} \otimes h_{11} + \rho_2 c_{02} \otimes h_{12} - \rho_1 c_{01} \otimes h_{13} \\
&\quad - \rho_2 c_{02} \otimes h_{14}
\end{aligned} \tag{2.47}$$

$$\begin{aligned}
h_{02} &= c_{02} + \rho_0 c_{00} \otimes h_{02} + \rho_1 c_{01} \otimes h_{12} + \rho_2 c_{02} \otimes h_{22} - \rho_1 c_{01} \otimes h_{14} \\
&\quad - \rho_2 c_{02} \otimes h_{24}
\end{aligned} \tag{2.48}$$

$$\begin{aligned}
h_{11} &= c_{11} + \rho_0 c_{01} \otimes h_{01} + \rho_1 c_{11} \otimes h_{11} + \rho_2 c_{12} \otimes h_{12} - \rho_1 c_{13} \otimes h_{13} \\
&\quad - \rho_2 c_{14} \otimes h_{14}
\end{aligned} \tag{2.49}$$

$$\begin{aligned}
h_{12} &= c_{12} + \rho_0 c_{01} \otimes h_{02} + \rho_1 c_{11} \otimes h_{12} + \rho_2 c_{12} \otimes h_{22} - \rho_1 c_{13} \otimes h_{14} \\
&\quad - \rho_2 c_{14} \otimes h_{24}
\end{aligned} \tag{2.50}$$

$$\begin{aligned} h_{22} = {} & c_{22} + \rho_0 c_{02} \otimes h_{02} + \rho_1 c_{12} \otimes h_{12} + \rho_2 c_{22} \otimes h_{22} - \rho_1 c_{14} \otimes h_{14} \\ & - \rho_2 c_{24} \otimes h_{24} \end{aligned} \tag{2.51}$$

$$\begin{aligned} h_{13} = {} & c_{13} + \rho_0 c_{01} \otimes h_{01} + \rho_1 c_{11} \otimes h_{13} + \rho_2 c_{12} \otimes h_{14} + \rho_1 c_{13} \otimes h_{11} \\ & + \rho_2 c_{14} \otimes h_{12} - 2\rho_1 c_{13} \otimes h_{13} - 2\rho_2 c_{14} \otimes h_{14} \end{aligned} \tag{2.52}$$

$$\begin{aligned} h_{14} = {} & c_{14} + \rho_0 c_{01} \otimes h_{02} + \rho_1 c_{11} \otimes h_{14} + \rho_2 c_{12} \otimes h_{24} + \rho_1 c_{13} \otimes h_{12} \\ & + \rho_2 c_{14} \otimes h_{22} - 2\rho_1 c_{13} \otimes h_{14} - 2\rho_2 c_{14} \otimes h_{24} \end{aligned} \tag{2.53}$$

$$\begin{aligned} h_{24} = {} & c_{24} + \rho_0 c_{02} \otimes h_{02} + \rho_1 c_{12} \otimes h_{14} + \rho_2 c_{22} \otimes h_{24} + \rho_1 c_{14} \otimes h_{12} \\ & + \rho_2 c_{24} \otimes h_{22} - 2\rho_1 c_{14} \otimes h_{14} - 2\rho_2 c_{24} \otimes h_{24} \end{aligned} \tag{2.54}$$

or alternatively,

$$\begin{aligned} h_{01} = {} & c_{01} + \rho_0 c_{01} \otimes h_{00} + \rho_1 c_{11} \otimes h_{01} + \rho_2 c_{12} \otimes h_{02} - \rho_1 c_{13} \otimes h_{01} \\ & - \rho_2 c_{14} \otimes h_{02} \end{aligned} \tag{2.55}$$

$$\begin{aligned} h_{02} = {} & c_{02} + \rho_0 c_{02} \otimes h_{00} + \rho_1 c_{12} \otimes h_{01} + \rho_2 c_{22} \otimes h_{02} - \rho_1 c_{14} \otimes h_{01} \\ & - \rho_2 c_{24} \otimes h_{02} \end{aligned} \tag{2.56}$$

$$\begin{aligned} h_{12} = {} & c_{12} + \rho_0 c_{02} \otimes h_{01} + \rho_1 c_{12} \otimes h_{11} + \rho_2 c_{22} \otimes h_{12} - \rho_1 c_{14} \otimes h_{13} \\ & - \rho_2 c_{24} \otimes h_{14} \end{aligned} \tag{2.57}$$

$$\begin{aligned} h_{14} = {} & c_{14} + \rho_0 c_{02} \otimes h_{01} + \rho_1 c_{14} \otimes h_{11} + \rho_2 c_{24} \otimes h_{12} + \rho_1 c_{12} \otimes h_{13} \\ & + \rho_2 c_{22} \otimes h_{14} - 2\rho_1 c_{14} \otimes h_{13} - 2\rho_2 c_{24} \otimes h_{14}. \end{aligned} \tag{2.58}$$

Note that again the equation for h_{00} is decoupled from the others since the matrix particles are unaffected by the fluid. Furthermore, it can easily be shown that the above equations satisfy necessary symmetry relations. By exchanging

$$\begin{array}{ccc} & \rho_1 \leftrightarrow \rho_2 & \\ h_{01} \leftrightarrow h_{02} & & c_{01} \leftrightarrow c_{02} \\ h_{11} \leftrightarrow h_{22} & & c_{11} \leftrightarrow c_{22} \\ h_{13} \leftrightarrow h_{24} & & c_{13} \leftrightarrow c_{24} \end{array}$$

while keeping h_{14}, c_{14}, h_{12} and c_{12} fixed, the equations for h_{01}, h_{11}, h_{13} become those for h_{02}, h_{22}, h_{24} and vice versa. The equations for h_{14} and h_{12} turn into the alternative ones.

2.7.3 Reduction to the one-component fluid

Eqs. 2.46 - 2.54 simplify to the ROZ equations of the one-component system if we assume that the two fluid components become identical, i.e.

$$\phi_{01} = \phi_{02}, \quad \phi_{11} = \phi_{12} = \phi_{22}.$$

In this case we have to replace

$$\begin{aligned} \rho_1 + \rho_2 &\rightarrow \rho_1 \\ c_{02} &\rightarrow c_{01} \\ c_{12}, c_{22} &\rightarrow c_{11} \\ c_{14}, c_{24} &\rightarrow c_{13} \end{aligned}$$

in eqs. 2.46 - 2.54 and obtain

$$\begin{aligned} h_{01} &= h_{02} \\ h_{11} &= h_{12} = h_{22} \\ h_{13} &= h_{14} = h_{24} \end{aligned}$$

The remaining equations correspond to the eqs. 2.22 - 2.25.

In fact, we will use this limiting case to calculate an initial estimate for the numerical solution of the ROZ equations in the case of the two-component fluid. Another possibility in order to approach the case of a one-component fluid is to set the density of one fluid component equal to zero. For $\rho_2 = 0$ the ROZ eqs. 2.46 - 2.54 are satisfied if

$$h_{02} = h_{12} = h_{22} = h_{14} = h_{24} = c_{02} = c_{12} = c_{22} = c_{14} = c_{24} = 0$$

The nontrivial remaining equations are equivalent to eqs. 2.22 - 2.25.

2.7.4 Matrix formulation of the ROZ equations

In this section we introduce a compact matrix formulation of the ROZ equations for a binary liquid in a matrix. This notation has the following advantages: It is a compact notation, in which the ROZ equations have the same structure as in the one-component case. Furthermore, it helps us to extend the formulation of the ROZ equations to a k-component fluid in a matrix.

If we define the following vectors and matrices

$$\mathbf{h}_{01} = \begin{pmatrix} h_{01} \\ h_{02} \end{pmatrix} \qquad \mathbf{c}_{01} = \begin{pmatrix} c_{01} \\ c_{02} \end{pmatrix}$$

$$\mathbf{h}_{11} = \begin{pmatrix} h_{11} & h_{12} \\ h_{12} & h_{22} \end{pmatrix} \quad \mathbf{c}_{11} = \begin{pmatrix} c_{11} & c_{12} \\ c_{12} & c_{22} \end{pmatrix}$$

$$\mathbf{h}_{12} = \begin{pmatrix} h_{13} & h_{14} \\ h_{14} & h_{24} \end{pmatrix} \quad \mathbf{c}_{12} = \begin{pmatrix} c_{13} & c_{14} \\ c_{14} & c_{24} \end{pmatrix}$$

$$\boldsymbol{\rho}_1 = \begin{pmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{pmatrix}$$

then eqs. 2.46 - 2.58 take the form

$$\begin{aligned} h_{00} &= c_{00} + \rho_0 c_{00} \otimes h_{00} && (2.59)\\ \mathbf{h}_{01} &= \mathbf{c}_{01} + \mathbf{h}_{01} \otimes \rho_0 c_{00} + \boldsymbol{\rho}_1 \mathbf{h}_{11} \otimes \mathbf{c}_{01} - \boldsymbol{\rho}_1 \mathbf{h}_{12} \otimes \mathbf{c}_{01} && (2.60)\\ \mathbf{h}_{11} &= \mathbf{c}_{11} + \mathbf{h}_{01} \otimes \rho_0 \mathbf{c}_{01}^T + \boldsymbol{\rho}_1 \mathbf{h}_{11} \otimes \mathbf{c}_{11} - \boldsymbol{\rho}_1 \mathbf{h}_{12} \otimes \mathbf{c}_{12} && (2.61)\\ \mathbf{h}_{12} &= \mathbf{c}_{12} + \mathbf{h}_{01} \otimes \rho_0 \mathbf{c}_{01}^T + \boldsymbol{\rho}_1 \mathbf{h}_{12} \otimes \mathbf{c}_{11} + \boldsymbol{\rho}_1 \mathbf{h}_{11} \otimes \mathbf{c}_{12} \\ &\qquad - 2\boldsymbol{\rho}_1 \mathbf{h}_{12} \otimes \mathbf{c}_{12}, && (2.62) \end{aligned}$$

which are formally equivalent to the ROZ equations of the one-component case 2.22 - 2.25.

2.7.5 Reformulation of the ROZ equations

Similar to section 2.5 we introduce the blocking and connecting parts of the correlation functions

$$\begin{aligned} h_{11} &= h_{11}^c + h_{11}^b \quad \text{with} \quad h_{11}^b = h_{13}\\ h_{12} &= h_{12}^c + h_{12}^b \quad \text{with} \quad h_{12}^b = h_{14}\\ h_{22} &= h_{22}^c + h_{22}^b \quad \text{with} \quad h_{22}^b = h_{24}. \end{aligned}$$

Again, h^b_{ij} describes correlations between fluid particles of species i and j which are mediated through matrix particles and h^c_{ij} describes correlations transmitted through successive layers of fluid particles. The ROZ equations thus simplify to

$$h_{00} = c_{00} + \rho_0 c_{00} \otimes h_{00} \tag{2.63}$$

$$h_{01} = c_{01} + \rho_0 c_{00} \otimes h_{01} + \rho_1 c_{01} \otimes h^c_{11} + \rho_2 c_{02} \otimes h^c_{12} \tag{2.64}$$

$$h_{02} = c_{02} + \rho_0 c_{00} \otimes h_{02} + \rho_1 c_{01} \otimes h^c_{12} + \rho_2 c_{02} \otimes h^c_{22} \tag{2.65}$$

$$\begin{aligned} h_{11} = {} & c_{11} + \rho_0 c_{01} \otimes h_{01} + \rho_1 c_{11} \otimes h^c_{11} + \rho_2 c_{12} \otimes h^c_{12} + \rho_1 c^c_{11} \otimes h^b_{11} \\ & + \rho_2 c^c_{12} \otimes h^b_{12} \end{aligned} \tag{2.66}$$

$$\begin{aligned} h_{12} = {} & c_{12} + \rho_0 c_{01} \otimes h_{02} + \rho_1 c^c_{11} \otimes h_{12} + \rho_2 c^c_{12} \otimes h_{22} + \rho_1 c^b_{11} \otimes h^c_{12} \\ & + \rho_2 c^b_{12} \otimes h^c_{22} \end{aligned} \tag{2.67}$$

$$\begin{aligned} h_{22} = {} & c_{22} + \rho_0 c_{02} \otimes h_{02} + \rho_1 c_{12} \otimes h^c_{12} + \rho_2 c_{22} \otimes h^c_{22} + \rho_1 c^c_{12} \otimes h^b_{12} \\ & + \rho_2 c^c_{22} \otimes h^b_{22} \end{aligned} \tag{2.68}$$

$$h^c_{11} = c^c_{11} + \rho_1 c^c_{11} \otimes h^c_{11} + \rho_2 c^c_{12} \otimes h^c_{12} \tag{2.69}$$

$$h^c_{12} = c^c_{12} + \rho_1 c^c_{12} \otimes h^c_{11} + \rho_2 c^c_{22} \otimes h^c_{12} \tag{2.70}$$

$$h^c_{22} = c^c_{22} + \rho_1 c^c_{12} \otimes h^c_{12} + \rho_2 c^c_{22} \otimes h^c_{22}, \tag{2.71}$$

or, alternatively

$$\begin{aligned} h_{01} &= c_{01} + \rho_0 c_{01} \otimes h_{00} + \rho_1 c^c_{11} \otimes h_{01} + \rho_2 c^c_{12} \otimes h_{02} \\ h_{02} &= c_{02} + \rho_0 c_{02} \otimes h_{00} + \rho_1 c^c_{12} \otimes h_{01} + \rho_2 c^c_{22} \otimes h_{02} \\ h_{12} &= c_{12} + \rho_0 c_{02} \otimes h_{01} + \rho_1 c_{12} \otimes h^c_{11} + \rho_2 c_{22} \otimes h^c_{12} + \rho_1 c^c_{12} \otimes h^b_{11} \\ & \quad + \rho_2 c^c_{22} \otimes h^b_{12} \\ h^c_{12} &= c^c_{12} + \rho_1 c^c_{11} \otimes h^c_{12} + \rho_2 c^c_{12} \otimes h^c_{22}. \end{aligned}$$

2.7.6 Generalisation to a k-component fluid

The formulae introduced in section 2.7 for a two-component fluid in a matrix can easily be generalised to a k-component fluid in a matrix. Using the replica trick one finds that the partly quenched system is isomorphic to a limiting case of a $(ks+1)$-component equilibrium mixture. We choose the following convention to number the fluid components in the $(ks+1)$-component mixture of the replica system:

0	for the matrix
$1, k+1, 2k+1, \ldots, (s-1)k+1$	for fluid 1 in replica number $1, 2, \ldots, s$
$2, k+2, 2k+2, \ldots, (s-1)k+2$	for fluid 2 in replica number $1, 2, \ldots, s$
$\vdots$	$\vdots$
$k, 2k, 3k, \ldots, sk$	for fluid k in replica number $1, 2, \ldots, s$

If we define the following partition of the set $\{1, 2, \ldots, sk\}$

$$\begin{aligned} P_1 &= \{1, k+1, 2k+1, \ldots, (s-1)k+1\} \\ P_2 &= \{2, k+2, 2k+2, \ldots, (s-1)k+2\} \\ &\vdots \\ P_k &= \{k, 2k, 3k, \ldots, sk\} \end{aligned}$$

we obtain the following symmetry relations in the replica system where the number to the right of the curly brackets gives the number of symmetry relations:

$$\left.\begin{array}{lll}
c_{0i}^{rep}=c_{01}^{rep} & h_{0i}^{rep}=h_{01}^{rep} & \text{for } i\in P_1 \\
c_{0i}^{rep}=c_{02}^{rep} & h_{0i}^{rep}=h_{02}^{rep} & \text{for } i\in P_2 \\
\vdots & \vdots & \vdots \\
c_{0i}^{rep}=c_{0k}^{rep} & h_{0i}^{rep}=h_{0k}^{rep} & \text{for } i\in P_k
\end{array}\right\} k$$

$$\left.\begin{array}{lll}
c_{ij}^{rep}=c_{11}^{rep} & h_{ij}^{rep}=h_{11}^{rep} & \text{for } i\in P_1,\ j=i \\
c_{ij}^{rep}=c_{12}^{rep} & h_{ij}^{rep}=h_{12}^{rep} & \text{for } i\in P_1,\ j=i+1 \\
c_{ij}^{rep}=c_{13}^{rep} & h_{ij}^{rep}=h_{13}^{rep} & \text{for } i\in P_1,\ j=i+2 \\
\vdots & \vdots & \vdots \\
c_{ij}^{rep}=c_{k-1,k}^{rep} & h_{ij}^{rep}=h_{k-1,k}^{rep} & \text{for } i\in P_{k-1},\ j=i+1 \\
c_{ij}^{rep}=c_{kk}^{rep} & h_{ij}^{rep}=h_{kk}^{rep} & \text{for } i\in P_k,\ j=i
\end{array}\right\} \tbinom{k+1}{2}$$

$$\left.\begin{array}{lll}
c_{ij}^{rep}=c_{1,k+1}^{rep} & h_{ij}^{rep}=h_{1,k+1}^{rep} & \text{for } i\in P_1,\ j\neq i \\
c_{ij}^{rep}=c_{1,k+2}^{rep} & h_{ij}^{rep}=h_{1,k+2}^{rep} & \text{for } i\in P_1,\ j\neq i+1 \\
c_{ij}^{rep}=c_{1,k+3}^{rep} & h_{ij}^{rep}=h_{1,k+3}^{rep} & \text{for } i\in P_1,\ j\neq i+2 \\
\vdots & \vdots & \vdots \\
c_{ij}^{rep}=c_{k-1,2k}^{rep} & h_{ij}^{rep}=h_{k-1,2k}^{rep} & \text{for } i\in P_{k-1},\ j\neq i+1 \\
c_{ij}^{rep}=c_{k,2k}^{rep} & h_{ij}^{rep}=h_{k,2k}^{rep} & \text{for } i\in P_k,\ j\neq i
\end{array}\right\} \tbinom{k+1}{2}$$

Again, the last block of lines denotes correlation functions between fluid components of different replicas. Furthermore we see that the number of ROZ equations, i.e.

$$1+k+\binom{k+1}{2}+\binom{k+1}{2}=(k+1)^2$$

is rapidly increasing with increasing number of fluid components.

If we define the following vectors and symmetric matrices

$$\mathbf{h}_{01} = \begin{pmatrix} h_{01} \\ h_{02} \\ \vdots \\ h_{0k} \end{pmatrix} \qquad \mathbf{c}_{01} = \begin{pmatrix} c_{01} \\ c_{02} \\ \vdots \\ c_{0k} \end{pmatrix}$$

$$\mathbf{h}_{11} = \begin{pmatrix} h_{11} & h_{12} & \cdots & h_{1k} \\ & h_{22} & \cdots & h_{2k} \\ & & \ddots & \vdots \\ & & & h_{kk} \end{pmatrix} \qquad \mathbf{c}_{11} = \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1k} \\ & c_{22} & \cdots & h_{2k} \\ & & \ddots & \vdots \\ & & & c_{kk} \end{pmatrix}$$

$$\mathbf{h}_{12} = \begin{pmatrix} h_{1,k+1} & h_{1,k+2} & \cdots & h_{1,2k} \\ & h_{2,k+2} & \cdots & h_{2,2k} \\ & & \ddots & \vdots \\ & & & h_{k,2k} \end{pmatrix} \quad \mathbf{c}_{12} = \begin{pmatrix} c_{1,k+1} & c_{1,k+2} & \cdots & c_{1,2k} \\ & c_{2,k+2} & \cdots & h_{2,2k} \\ & & \ddots & \vdots \\ & & & c_{k,2k} \end{pmatrix}$$

$$\boldsymbol{\rho}_1 = \mathrm{diag}(\rho_1, \rho_2, \cdots, \rho_k)$$

then eqs. 2.59 - 2.62 represent also the ROZ equations for a k-component fluid in a matrix.

Chapter 3

Numerical solution of the ROZ equations

In this chapter an algorithm for the numerical solution of the ROZ integral equations for a one and two-component fluid in a quenched matrix is presented. The method used here is a hybrid of the iterative Picard scheme and the Newton-Raphson technique which was developed by Gillan [30]. The numerical solution of the ROZ equations is based on an algorithm introduced by Labik, Malijevsky and Vonka (LMV algorithm [31]), an extension of Gillan's work, which was originally proposed for solving numerically the OZ equations for homogeneous liquids (and mixtures) and extended by Lomba [10] to the case of the ROZ equations.

In section 3.1 a brief overview is given over those numerical algorithms for solving the OZ integral equations which are necessary to understand the LMV algorithm. A detailed description of the LMV algorithm for solving the ROZ equations will be presented in section 3.2 for the one-component case. In section 3.3 those modifications are presented which are necessary to adopt the algorithm for the two-component fluid. In the last section we describe the model potentials for the fluid and the matrix which were used in our calculations.

3.1 Introduction to numerical algorithms for solving integral equations

In many frameworks of liquid state theory we search for numerical solutions of integral equations which contain convolution integrals such as the OZ or ROZ equations and which are supplemented with some closure relations. To demonstrate the following considerations we consider here for simplicity the one-component OZ equation for a homogeneous, radially symmetric liquid, i.e.

$$\gamma(r) = \rho \int \mathbf{dr}'\, h(r')c(|\mathbf{r} - \mathbf{r}\,'|), \text{ where } \quad \gamma(r) = h(r) - c(r). \tag{3.1}$$

The simplest method of solving this equation numerically together with a closure relation of the form

$$c(r) = f(\gamma(r), \phi(r)) \tag{3.2}$$

is one of direct iterations: an initial estimate for $\gamma(r)$ is used in eq. 3.2 to obtain $c(r)$ and $h(r) = \gamma(r) + c(r)$. These functions are inserted in the right hand side of eq. 3.1 to obtain a new estimate for $\gamma(r)$. This cycle, which is called the Picard cycle, is repeated until numerical convergence is achieved, i.e., the procedure is repeated until the difference between the input- and output-$\gamma(r)$ is smaller then a certain value. Except in the weak-coupling limit (i.e., at low densities or high temperature) this method is divergent. The divergence can be cured by Broyles mixing procedure. It is usually sufficient to mix the output of two previous iterations to construct the subsequent input according to the rule

$$\gamma^{(i+1)}(r) = (1 - \alpha)\gamma^{(i)}(r) + \alpha\gamma^{(i-1)}(r),$$

where the mixing parameter α ($0 < \alpha < 1$) is adjusted empirically. In subsection 3.2.4 a modified Broyles mixing-iterates method is presented which was proposed by Lomba [32]. But still a very accurate initial estimate is necessary and convergence remains slow.

A more attractive approach is to evaluate the convolution integral by the Fourier transform method rather than by direct integration since less operations are required. On taking the Fourier transform of eq. 3.1 we obtain an algebraic relation between $\tilde{\gamma}(k)$ and $\tilde{c}(k)$

$$\tilde{\gamma}(k) = \frac{\rho \tilde{c}^2(k)}{1 - \rho \tilde{c}(k)}. \tag{3.3}$$

Here the tilde on top of a function denotes its Fourier transform. An initial estimate for $\gamma(r)$ is inserted in eq. 3.2 to yield $c(r)$. $c(r)$ is Fourier transformed and inserted into eq. 3.3 to give the Fourier transform $\tilde{\gamma}(k)$ of the new approximation $\gamma(r)$. This is the Picard cycle which will be used in the LMV algorithm.

An alternative to the Picard method is to use eqs. 3.1 and 3.2 in discrete form. The range of r is divided by N equally spaced grid points r_i. The functions $\gamma(r)$ and $c(r)$ may then be regarded as vectors $\boldsymbol{\gamma}$ and $\mathbf{c}$, with components $\gamma_i = \gamma(r_i)$ and $c_i = c(r_i)$, $i = 1, \ldots, N$. The OZ relation, together with some approximate closure relation, yields a set of N nonlinear, simultaneous equations for the components of $\boldsymbol{\gamma}$. Sets of equations of this type are usually solved by the Newton-Raphson method (see Appendix B for the NR-method or [33]). The power of the NR-method lies in its property of an extremely rapid convergence. On the other side, however, the method requires considerable computational effort: in each iteration a matrix of dimension N (the Jacobi-matrix), with N typically of the order 10^3, has to be calculated and inverted.

We therefore come to the conclusion that the Picard method is slow and instable while the NR-method is not convenient when applied to large sets of equations. Gillan therefore proposed an effective combination of the two methods which overcomes the slowness of the Picard iteration while retaining the power of the NR-method [30].

In this approach, the solution $\gamma(r)$ is decomposed into a coarse part, written as an expansion in terms of functions $P_j(r)$, $j = 1, \ldots, M$, and a fine part $\Delta\gamma(r)$ whose length scale is much smaller than the scale characterising the solution $\gamma(r)$ (i.e. its Fourier components are mainly at large wave vectors):

$$\gamma(r) = \sum_{j=1}^{M} a_j P_j(r) + \Delta\gamma(r).$$

The instability of the Picard method stems from coarse displacements of $\gamma(r)$ from the solution which change the overall shape and magnitude of $\gamma(r)$ whereas displacements in the fine part are rapidly reduced by direct iterations. Therefore, the coarse part of $\gamma(r)$ is determined by the NR-method, leaving the fine part to be dealt with to the Picard method. The basis functions $P_j(r)$ must be chosen in such a way that only a few of these functions is necessary to give an adequate representation of the overall shape of $\gamma(r)$. Thus the problem of large matrices, which troubles the NR-method, will be removed. In his work, Gillan used roof functions as basis functions. At this point it becomes clear why the smooth function $\gamma(r)$ was introduced in eq. 3.1 and why the OZ equation was solved for $\gamma(r)$: this function is more easily represented in terms of a few basis functions $P_j(r)$, the fine part will be small so that more weight will be given to the efficient NR-method. The functions $c(r)$ and $h(r)$ are less suitable for this purpose, since they are rapidly varying in the region of the core diameter.

Labik, Malijevsky and Vonka [31] proposed a quite similar procedure whose main advantage lies in the use of a sine function basis instead of Gillan's roof functions. The coarse part is decomposed into sine functions with small wave vectors giving a representation of the general shape while higher terms give a detailed description. Let us have a look at figure 3.1 where the blocked function $\tilde{\gamma}_b(k)$ as a function of k is shown for a partly quenched system with pure hard-sphere interactions. The figure shows that $\tilde{\gamma}_b$ is a non-negative oscillating function that decays rapidly with increasing k. Thus the sine functions with small wave vectors give already a good representation of the function.

Furthermore, in contrast to the Gillan algorithm, the calculation of the Jacobi-matrix for the NR-iteration is very rapid since no additional Fourier transformations are involved in the NR-iteration. This is achieved by a Fourier transformation of the linearised closure relations and applying the NR-scheme directly in the Fourier space.

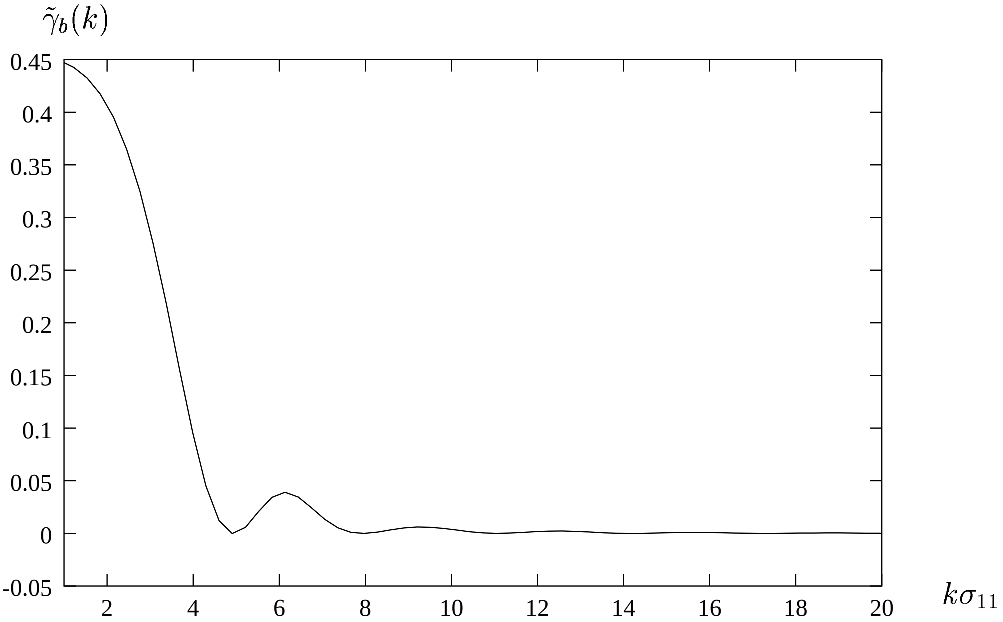

Figure 3.1: Fourier transform of $\gamma_b(r)$ for a partly quenched system with pure hard-sphere interactions and parameters $\sigma_{00} = \sigma_{01} = \sigma_{11} = 1,\ \rho_0 = 0.1$ and $\rho_1 = 0.25$ in the HNC approximation.

3.2 LMV Algorithm for the one-component case

In this section the LMV algorithm is presented for solving the ROZ equations for a one-component liquid in a porous medium. As a first step for the solution of the set of eqs. 2.27 - 2.29

$$\begin{aligned} h_{01} &= c_{01} + \rho_0 c_{00} \otimes h_{01} + \rho_1 c_{01} \otimes h_c && (3.4) \\ h_{11} &= c_{11} + \rho_0 c_{01} \otimes h_{01} + \rho_1 c_{11} \otimes h_c + \rho_1 c_c \otimes h_b && (3.5) \\ h_c &= c_c + \rho_1 c_c \otimes h_c && (3.6) \end{aligned}$$

we introduce smooth functions

$$\gamma_{\alpha\beta}(r) = h_{\alpha\beta}(r) - c_{\alpha\beta}(r), \tag{3.7}$$

where $\alpha\beta$ is 01, 11 or 12. Eqs. 3.4 - 3.6 are now Fourier transformed, yielding algebraic equations which are solved for $h_{\alpha\beta}$; using eq. 3.7 one obtains

$$\begin{aligned}\tilde{\gamma}_{01} &= -\tilde{c}_{01} + \frac{\tilde{c}_{01}(1+\rho_0\tilde{h}_{00})}{1-\rho_1\tilde{c}_{11}+\rho_1\tilde{c}_{12}} && (3.8)\\ \tilde{\gamma}_{11} &= -\tilde{c}_{11} + \frac{\tilde{c}_{11}+\rho_0\tilde{c}_{01}^2\left(1+\rho_0\tilde{h}_{00}\right)-\rho_1\left(\tilde{c}_{11}-\tilde{c}_{12}\right)^2}{\left(1-\rho_1\tilde{c}_{11}+\rho_1\tilde{c}_{12}\right)^2} && (3.9)\\ \tilde{\gamma}_{12} &= -\tilde{c}_{12} + \frac{\tilde{c}_{12}+\rho_0\tilde{c}_{01}^2\left(1+\rho_0\tilde{h}_{00}\right)}{\left(1-\rho_1\tilde{c}_{11}+\rho_1\tilde{c}_{12}\right)^2}. && (3.10)\end{aligned}$$

3.2.1 Fourier transformation

Exploiting the spherical symmetry of the functions, the three-dimensional Fourier transform of e.g. $\gamma(r)$,

$$\tilde{\gamma}(k) = \int \mathbf{dk} e^{i\mathbf{kr}}\gamma(r)$$

can be simplified to a one dimensional integral

$$\begin{aligned}\tilde{\gamma}(k) &= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} drr^2 e^{ikr\cos\theta}\gamma(r)\\ &= 4\pi\int_0^{\infty} drr\gamma(r)\frac{\sin(kr)}{k}.\end{aligned}$$

Similarly, the inverse three-dimensional Fourier transform

$$\gamma(r) = \frac{1}{(2\pi)^3}\int \mathbf{dk} e^{-i\mathbf{kr}}\tilde{\gamma}(k)$$

becomes

$$\gamma(r) = \frac{1}{2\pi^2}\int_0^{\infty} dkk\tilde{\gamma}(k)\frac{\sin(kr)}{r}.$$

If we adopt the notation that capitalised quantities are related to the corresponding uncapitalised quantities by a factor k in Fourier space and a factor r in real space, e.g.

$$\begin{aligned}\Gamma(r) &= r\gamma(r) && (3.11)\\ \tilde{\Gamma}(k) &= k\tilde{\gamma}(k) && (3.12)\end{aligned}$$

the Fourier transforms can be written as

$$\tilde{\Gamma}(k) = 4\pi \int_0^\infty dr\, \Gamma(r) \sin(kr) \tag{3.13}$$

and

$$\Gamma(r) = \frac{1}{2\pi^2} \int_0^\infty dk\, \tilde{\Gamma}(k) \sin(kr). \tag{3.14}$$

For the numerical solution of the ROZ equations, the range of r is divided into a set of N equal mesh points $r_i = i\Delta r$, $i = 1, \ldots, N$, where N is assumed to be a power of 2, a feature which is recommended if a fast Fourier transform method is used; the functions $\gamma(r)$ etc. are represented by their values $\gamma_i = \gamma(r_i)$ etc. on these grid points. In a similar way one proceeds in the Fourier space where the range of k is divided into N equal mesh points $k_i = i\Delta k$. In a fast Fourier approach Δr and Δk are related via

$$\Delta r \Delta k = \frac{\pi}{N}.$$

In a discrete form eqs. 3.13 and 3.14 now read

$$\begin{aligned} \tilde{\Gamma}(k_j) &= 4\pi\Delta r \sum_{i=1}^{N-1} \Gamma(r_i) \sin\frac{ij\pi}{N} \quad \text{for} \quad j = 1, 2, \ldots, N-1 \qquad (3.15) \\ \Gamma(r_i) &= \frac{\Delta k}{2\pi^2} \sum_{j=1}^{N-1} \tilde{\Gamma}(k_j) \sin\frac{ij\pi}{N} \quad \text{for} \quad i = 1, 2, \ldots, N-1. \qquad (3.16) \end{aligned}$$

Eqs. 3.8 - 3.10 then become

$$\begin{aligned} \tilde{\Gamma}_{01}(k_j) &= -\tilde{C}_{01}(k_j) + \frac{\tilde{C}_{01}(k_j)\chi(k_j)}{k_j - \rho_1\tilde{C}_{11}(k_j) + \rho_1\tilde{C}_{12}(k_j)} \qquad (3.17) \\ \tilde{\Gamma}_{11}(k_j) &= -\tilde{C}_{11}(k_j) \qquad (3.18) \\ &\quad + \frac{k_j^2\tilde{C}_{11}(k_j) + \rho_0\tilde{C}_{01}(k_j)^2\chi(k_j) - k_j\rho_1\left(\tilde{C}_{11}(k_j) - \tilde{C}_{12}(k_j)\right)^2}{\left(k_j - \rho_1\tilde{C}_{11}(k_j) + \rho_1\tilde{C}_{12}(k_j)\right)^2} \\ \tilde{\Gamma}_{12}(k_j) &= -\tilde{C}_{12}(k_j) + \frac{k_j^2\tilde{C}_{12}(k_j) + \rho_0\tilde{C}_{01}(k_j)^2\chi(k_j)}{\left(k_j - \rho_1\tilde{C}_{11}(k_j) + \rho_1\tilde{C}_{12}(k_j)\right)^2} \qquad (3.19) \end{aligned}$$

with $\chi(k_j) = k_j + \rho_0\tilde{H}_{00}(k_j)$.

3.2.2 Linearised Fourier transformed closure relations

The ROZ equations are supplemented by providing additional functional relations between $\Gamma_{\alpha\beta}$ and $C_{\alpha\beta}$, i.e., by

$$C_{\alpha\beta}(r) = f(\Gamma_{\alpha\beta}(r)) \quad \text{for} \quad \alpha\beta = 01, 11, 12; \tag{3.20}$$

for instance, in the case of the HNC approximation eq. 3.20 reads

$$C_{\alpha\beta}(r) = re^{\Gamma_{\alpha\beta}(r)/r - \beta\phi_{\alpha\beta}(r)} - r - \Gamma_{\alpha\beta}(r) \quad \text{for} \quad \alpha\beta = 01, 11$$

and

$$C_{12}(r) = re^{\Gamma_{12}(r)/r} - r - \Gamma_{12}(r),$$

while in the PY approximation eq. 3.20 reads

$$C_{\alpha\beta}(r) = \left(e^{-\beta\phi_{\alpha\beta}(r)} - 1\right)(\Gamma_{\alpha\beta}(r) + r) \quad \text{for} \quad \alpha\beta = 01, 11$$

and

$$C_{12}(r) = 0.$$

In the NR-cycle we will need the closure relation in Fourier space. Therefore we perform a first order Taylor expansion of $C_{\alpha\beta}(r)$ in eq. 3.20 around the point $\Gamma^0_{\alpha\beta}(r)$ and obtain

$$C_{\alpha\beta}(r) \cong C^0_{\alpha\beta}(r) + \phi^0_{\alpha\beta}(r)\left(\Gamma_{\alpha\beta}(r) - \Gamma^0_{\alpha\beta}(r)\right), \tag{3.21}$$

where

$$\phi^0_{\alpha\beta}(r) = \left(\frac{df}{d\Gamma_{\alpha\beta}(r)}\right)_{\Gamma_{\alpha\beta}(r) = \Gamma^0_{\alpha\beta}(r)} \tag{3.22}$$

and

$$C^0_{\alpha\beta} = f(\Gamma^0_{\alpha\beta}(r)).$$

The derivative 3.22 depends of course on the closure relation to be used. For instance, the HNC closure yields

$$\phi^0_{\alpha\beta}(r) = h_{\alpha\beta}(r)$$

while in the PY approximation we find

$$\phi^0_{\alpha\beta}(r) = e^{-\beta\phi_{\alpha\beta}(r)} - 1.$$

Eq. 3.21 is discretised and Fourier transformed to give

$$\tilde{C}_{\alpha\beta}(k_j) \cong \tilde{C}^0_{\alpha\beta}(k_j) + 4\pi\Delta r \sum_{i=1}^{N-1} \phi^0_{\alpha\beta}(r_i)\left(\Gamma_{\alpha\beta}(r_i) - \Gamma^0_{\alpha\beta}(r_i)\right)\sin\frac{ij\pi}{N}.$$

Substituting for $\Gamma_{\alpha\beta}(r_i)$ and $\Gamma^0_{\alpha\beta}(r_i)$ (eq. 3.16) we obtain

$$\tilde{C}_{\alpha\beta}(k_j) \cong \tilde{C}^0_{\alpha\beta}(k_j) + \frac{2}{N}\sum_{l=1}^{N-1}\sum_{i=1}^{N-1} \phi^0_{\alpha\beta}(r_i)\left(\tilde{\Gamma}_{\alpha\beta}(k_l) - \tilde{\Gamma}^0_{\alpha\beta}(k_l)\right)\sin\frac{il\pi}{N}\sin\frac{ij\pi}{N}.$$

Using the identity

$$\sin\frac{il\pi}{N}\sin\frac{ij\pi}{N} = \frac{1}{2}\left(\cos\frac{i(l-j)\pi}{N} - \cos\frac{i(l+j)\pi}{N}\right)$$

yields

$$\tilde{C}_{\alpha\beta}(k_j) \cong \tilde{C}^0_{\alpha\beta}(k_j) + \sum_{l=1}^{N-1} C_{\alpha\beta;jl}\left(\tilde{\Gamma}_{\alpha\beta}(k_l) - \tilde{\Gamma}^0_{\alpha\beta}(k_l)\right), \tag{3.23}$$

where

$$C_{\alpha\beta;jl} = D_{\alpha\beta}(|j-l|) - D_{\alpha\beta}(j+l) \tag{3.24}$$

and

$$D_{\alpha\beta}(l) = \frac{1}{N}\sum_{i=1}^{N-1} \phi^0_{\alpha\beta}(r_i)\cos\frac{il\pi}{N}. \tag{3.25}$$

Expression 3.25 can easily be evaluated by means of fast Fourier transforms.

3.2.3 Calculation of the Jacobian

Inserting eqs. 3.23 - 3.25 in eqs. 3.17 - 3.19 we arrive at a set of $3(N-1)$ non-linear equations for the unknown $\tilde{\Gamma}_{\alpha\beta}(k_i)$. The problem now reduces to determine the zeros of the $3(N-1)$ functions

$$\Psi_{01}(k_j) = \tilde{\Gamma}_{01}(k_j) - F_{01}(\tilde{C}_{\mu\nu}(k_j)) \quad \text{for} \quad j = 1, \ldots, N-1 \tag{3.26}$$

$$\Psi_{11}(k_j) = \tilde{\Gamma}_{11}(k_j) - F_{11}(\tilde{C}_{\mu\nu}(k_j)) \quad \text{for} \quad j = 1, \ldots, N-1 \tag{3.27}$$

$$\Psi_{12}(k_j) = \tilde{\Gamma}_{12}(k_j) - F_{12}(\tilde{C}_{\mu\nu}(k_j)) \quad \text{for} \quad j = 1, \ldots, N-1, \tag{3.28}$$

where by $F_{\alpha\beta}$ we denote the algebraic expressions on the right hand side of eqs. 3.17 - 3.19 and the $\tilde{C}_{\mu\nu}(k_j)$ required in the $F_{\alpha\beta}$ are calculated from the linearised closure relations 3.23 - 3.25.

The Jacobian of these equations

$$\begin{aligned}
J_{\alpha\beta\mu\nu;jl} &= \frac{d\Psi_{\alpha\beta}(k_j)}{d\tilde{\Gamma}_{\mu\nu}(k_l)} = \delta_{\alpha\mu}\delta_{\beta\nu}\delta_{jl} - \frac{dF_{\alpha\beta}\left[\tilde{C}_{\mu\nu}(\tilde{\Gamma}_{\mu\nu}(k_j))\right]}{d\tilde{\Gamma}_{\mu\nu}(k_l)} \\
&= \delta_{\alpha\mu}\delta_{\beta\nu}\delta_{jl} - \sum_m \underbrace{\frac{dF_{\alpha\beta}(k_j)}{d\tilde{C}_{\mu\nu}(k_m)}}_{\frac{dF_{\alpha\beta}(k_j)}{d\tilde{C}_{\mu\nu}(k_j)}\delta_{jm}} \underbrace{\frac{d\tilde{C}_{\mu\nu}(k_m)}{d\tilde{\Gamma}_{\mu\nu}(k_l)}}_{C_{\mu\nu;ml}} \\
&= \delta_{\alpha\mu}\delta_{\beta\nu}\delta_{jl} - \frac{dF_{\alpha\beta}(k_j)}{d\tilde{C}_{\mu\nu}(k_j)} C_{\mu\nu;jl}
\end{aligned}$$

is a $3(N-1)$-dimensional matrix. Explicit expressions for the Jacobian elements can be found in the Appendix of [10].

Again we have a look at figure 3.1 which shows $\tilde{\gamma}_b(k)$. The plot shows that $\tilde{\gamma}_b(k)$ is rapidly decreasing with increasing k. The solution of the set of non-linear equations 3.26 - 3.28 will therefore primarily depend on $\tilde{\Gamma}_{\alpha\beta}(k)$ at small k. Thus the following procedure will be efficient: we calculate the coarse part $\tilde{\Gamma}(k_j)$, $j \leq M$, using the NR-method. When convergence is obtained the values $\tilde{\Gamma}(k_j)$, $j > M$, are determined by direct iteration. Thus we obtain an algorithm as outlined in the subsequent subsection.

3.2.4 The Labik-Malijevsky-Vonka Algorithm

1. The matrix contribution is calculated e.g. using the analytic solution of the OZ equation (we only assume hard-sphere or randomly centred matrix particles)

   $$h_{00} = c_{00} + \rho_0 h_{00} \otimes c_{00}$$

   in the PY approximation.

2. Given a first estimate of $\Gamma_{\alpha\beta}$, i.e.,

   $$\Gamma^0_{\alpha\beta}(r_i), \quad i = 1, \ldots, N; \quad \alpha\beta = 01, 11, 12$$

   and its Fourier transform

   $$\tilde{\Gamma}^0_{\alpha\beta}(k_j), \quad j = 1, \ldots, N-1; \quad \alpha\beta = 01, 11, 12$$

3. one gets $C^0_{\alpha\beta}$ from the chosen closure relation

   $$C^0_{\alpha\beta}(r_i) = f(\Gamma^0_{\alpha\beta}(r_i)) \quad i = 1, \ldots, N-1.$$

   $\Phi^0_{\alpha\beta}(r_i)$ is calculated via eq. 3.22 for the chosen theory.

4. $C^0_{\alpha\beta}(r_i)$ and $\Phi^0_{\alpha\beta}(r_i)$ are Fourier transformed to obtain

   $$\tilde{C}^0_{\alpha\beta}(k_j), D_{\alpha\beta}(k_j) \quad j = 1, \ldots, N-1.$$

5. For a chosen M, $C_{\alpha\beta;jl}$ is calculated for $j, l = 1, \ldots, M$ from eq. 3.24.

6. The initial estimate for the NR-iterations is

   $$\tilde{\Gamma}_{\alpha\beta}(k_j) = \tilde{\Gamma}^0_{\alpha\beta}(k_j) \quad j = 1, \ldots, M.$$

7. $\tilde{C}_{\alpha\beta}(k_j)$ are calculated from

   $$\tilde{C}_{\alpha\beta}(k_j) = \tilde{C}^0_{\alpha\beta}(k_j) + \sum_{l=1}^{M} C_{\alpha\beta;jl} \left(\tilde{\Gamma}_{\alpha\beta}(k_l) - \tilde{\Gamma}^0_{\alpha\beta}(k_l)\right)$$

   and inserted in

   $$J_{\alpha\beta\mu\nu;jl} = \delta_{\alpha\mu}\delta_{\beta\nu}\delta_{jl} - \frac{dF_{\alpha\beta}(k_j)}{d\tilde{C}_{\mu\nu}(k_j)} C_{\mu\nu;jl} \quad j, l = 1, \ldots M$$

   to calculate the elements of the Jacobian.

8. The Jacobian is inverted.

9. By means of the NR-method the

   $$\Delta\tilde{\Gamma}_{\alpha\beta}(k_j) = -\sum_{\mu\nu}\sum_{l=1}^{M} \left(J^{-1}\right)_{\alpha\beta\mu\nu;jl} \phi_{\mu\nu}(k_l) \quad j = 1, \ldots, M$$

   are calculated and a new estimate is obtained via

   $$\tilde{\Gamma}_{\alpha\beta}(k_j) + \Delta\tilde{\Gamma}_{\alpha\beta}(k_j) \rightarrow \tilde{\Gamma}_{\alpha\beta}(k_j) \quad j = 1, \ldots, M.$$

10. If

    $$\left(\sum_{\alpha\beta}\sum_{j=1}^{M} \left(\Delta\tilde{\Gamma}_{\alpha\beta}(k_j)\right)^2\right)^{1/2} > 10^{-5}$$

    a new NR-cycle is started by returning to operation (7).

11. Once a converged solution from the NR-method is obtained for $\tilde{\Gamma}_{\alpha\beta}(k_j)$, $j = 1, \ldots, M$, one performs a direct iteration for the remaining grid points, i.e.

$$\tilde{\Gamma}_{\alpha\beta}(k_j) = F_{\alpha\beta}(\tilde{C}_{\mu\nu}(k_j)) \quad j = M+1, \ldots, N-1$$

(the $F_{\alpha\beta}$ are defined in eqs. 3.26 - 3.28) and the result is combined with the output of the NR-method to yield a complete new estimate for $\tilde{\Gamma}_{\alpha\beta}(k_j)$.

12. $\tilde{\Gamma}_{\alpha\beta}(k_j)$ are transformed back to r-space to obtain $\Gamma_{\alpha\beta}(r_i)$. If

$$\xi = \left(\sum_{\alpha\beta} \sum_{i=1}^{N-1} \left(\Gamma_{\alpha\beta}(r_i) - \Gamma^0_{\alpha\beta}(r_i) \right)^2 \Delta r \right)^{1/2} > 10^{-5}$$

we set

$$\Gamma_{\alpha\beta}(r_i) \to \Gamma^0_{\alpha\beta}(r_i) \quad \text{and} \quad \tilde{\Gamma}_{\alpha\beta}(k_j) \to \tilde{\Gamma}^0_{\alpha\beta}(k_j) \quad i, j = 1, \ldots, N-1$$

and return to operation (3). In order to improve the convergence of the direct iterations we make use of the Broyles mixing iterates method. The new $\Gamma^0_{\alpha\beta}(r_i)$ and $\tilde{\Gamma}^0_{\alpha\beta}(k_j)$ are obtained from

$$\begin{aligned} (1-\alpha)\Gamma^0_{\alpha\beta}(r_i) + \alpha\Gamma_{\alpha\beta}(r_i) &\to \Gamma^0_{\alpha\beta}(r_i) \quad i = 1, \ldots, N-1 \\ (1-\alpha)\tilde{\Gamma}^0_{\alpha\beta}(k_j) + \alpha\tilde{\Gamma}_{\alpha\beta}(k_j) &\to \tilde{\Gamma}^0_{\alpha\beta}(k_j) \quad j = 1, \ldots, N-1 \end{aligned}$$

with the mixing parameter being determined by

$$\alpha = \begin{cases} \alpha_i & \text{if} \quad \xi > \xi_m \\ 1 - (1-\alpha_i)\left(\frac{\xi}{\xi_m}\right)^2 & \text{if} \quad \xi < \xi_m \end{cases},$$

where α_i is the initial variable and ξ_m is the threshold of the error at which we start to decrease the mixing parameter. This choice of the variable α ensures that the direct iteration will also converge for large displacements from the final solution. Furthermore when approaching the final solution, α tends towards 1 and the convergence is considerably speeded up. In our calculations α_i was chosen to be 0.5.

3.3 LMV algorithm for the two-component case

The generalisation of the LMV algorithm to the case of a two-component fluid in the matrix is complicated, but straightforward. Now eqs. 2.63 - 2.71 are Fourier transformed and the resulting algebraic equations solved for the $\tilde{h}_{\alpha\beta}(k)$ ($\alpha\beta$ = 01, 02, 11, 12, 22, 13, 14 and 24). Replacing $\tilde{h}_{\alpha\beta}(k)$ by eq. 3.7 we obtain the explicit formulae for the $\tilde{\gamma}_{\alpha\beta}(k)$ which are compiled in Appendix C.

Again we introduce the capitalised quantities as in eqs. 3.11 and 3.12. The Jacobian of the $8M$ functions

$$\Psi_{\alpha\beta}(k_j) = \tilde{\Gamma}_{\alpha\beta}(k_j) - F_{\alpha\beta}(k_j) \qquad j = 1, \ldots, M$$
$$\alpha\beta = 01, 02, \ldots, 24,$$

where the $F_{\alpha\beta}$ are the algebraic expressions on the right hand side of eqs. C.1 - C.5 with the capitalised quantities, is now a $8M \times 8M$-matrix, which means that we had to calculate 64 expressions similar to those in the Appendix of [10].

For a numerical solution of the eqs. C.1 - C.5 the algorithm presented in subsection 3.2.4 can be adopted with the following modifications:

1. Whenever the pair of indices $\alpha\beta$ appears, it now represents 01, 02, 11, 12, 22, 13, 14 and 24.
2. The $F_{\alpha\beta}$ in operation (10) are replaced by the algebraic expressions of Appendix C.
3. The Jacobian is now a $8M \times 8M$-matrix.

3.4 Model system

The model systems investigated in this work consist of a fluid with spherically symmetric pair potentials which is confined in a matrix of particles formed either by equilibrium hard-sphere ($\sigma_{00} > 0$) or randomly centred sphere configurations ($\sigma_{00} = 0$). The following matrix-fluid and fluid-fluid interactions were considered:

1. pure hard-sphere interactions

$$\phi_{ij}(r) = \begin{cases} +\infty & r < \sigma_{ij} \\ 0 & r > \sigma_{ij} \end{cases}$$

2. hard-sphere interactions with square-well attraction

$$\phi_{ij}(r) = \begin{cases} +\infty & r < \sigma_{ij} \\ -\epsilon_{ij} & \sigma_{ij} < r < \gamma_{ij}\sigma_{ij} \\ 0 & \gamma_{ij}\sigma_{ij} < r \end{cases}$$

3. hard-sphere interactions with Lennard-Jones tail

$$\phi_{ij}(r) = \begin{cases} +\infty & r < \sigma_{ij} \\ -\epsilon_{ij} & \sigma_{ij} < r < \sqrt[6]{2}\,\sigma_{ij} \\ 4\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right) & \sqrt[6]{2}\,\sigma_{ij} < r < 2.5\,\sigma_{ij} \\ 0 & 2.5\,\sigma_{ij} < r \end{cases}$$

The parameters are explained in figure 3.2.

The last two models comprise already many features of a realistic intermolecular potential: the harsh, short range repulsion is modelled by the infinitely repulsion of the hard-sphere potential and the smoothly varying, long-range attraction is modelled either by an attractive potential well or by a Lennard-Jones tail which is truncated at $r = 2.5\,\sigma_{ij}$. In principle this truncation is not required for integral equation approaches. It is done in order to facilitate direct comparisons to computer simulations where the Lennard-Jones tail is (usually) truncated at $2.5\,\sigma_{ij}$.

The first model of the hard-sphere (HS) fluid plays a central role in liquid state theory. This is because the structure of a simple liquid, at least at high density, is largely determined by geometric factors, associated with the packing of the hard cores. So the structure of the HS fluid can be used as

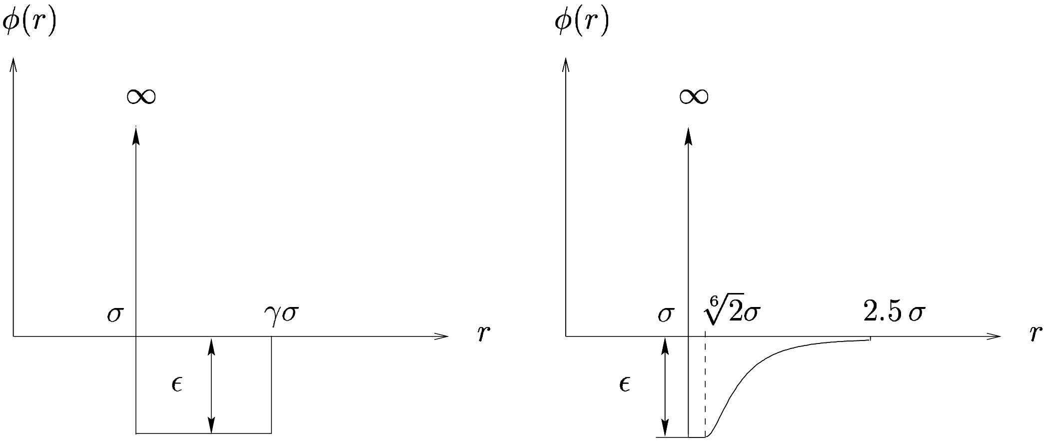

Figure 3.2: Hard-sphere potential with attractive square-well and Lennard-Jones tail

a zeroth order approximation to that of real liquids. This observation is the starting point of the successful perturbation theories presented in chapter 5 where the properties of a given liquid can be related to those of a HS reference system, the attractive part of the potential being treated as a perturbation.

The case of a one-component system in a matrix is described through the following parameters:

$\rho_0^\star = \rho_0\sigma_{11}^3,\ \rho_1^\star = \rho_1\sigma_{11}^3$	matrix and fluid density
$\sigma_{00},\ \sigma_{01},\ \sigma_{11}$	hard-sphere diameters
$T^\star = \frac{kT}{\epsilon_{11}}$	reduced temperature
$y = \frac{\epsilon_{01}}{\epsilon_{11}}$	interaction ratio

For these pair potentials the ROZ equations were solved with the LMV-algorithm in the HNC and PY-approximation which take in the case of pure hard-sphere systems the form (see [10])

$$\begin{aligned}
c_{ij}(r) &= \begin{cases} -1-\gamma_{ij}(r) & \text{if} \quad r<\sigma_{ij} \\ e^{\gamma_{ij}(r)}-1-\gamma_{ij}(r) & \text{if} \quad r>\sigma_{ij} \end{cases} \\
c_b(r) &= e^{\gamma_b(r)}-1-\gamma_b(r).
\end{aligned}$$

and

$$c_{ij}(r) = \begin{cases} -1-\gamma_{ij}(r) & \text{if} \quad r<\sigma_{ij} \\ 0 & \text{if} \quad r>\sigma_{ij} \end{cases}$$

$$c_b(r) = 0.$$

For the initial estimate of the $\gamma_{\alpha\beta}$ a PY solution for two noninteracting fluids with pure hard-sphere interactions is sufficient in a large region of the system parameters. However, at higher densities ρ_0 and ρ_1, in systems with quite different hard-sphere diameters and at low temperatures a more accurate initial estimate is necessary. Solutions at higher densities can be obtained by switching on the densities and convergence at lower temperatures can be achieved by switching on the attraction parameter. However the method still remains divergent at lower temperatures and higher densities which are required in the calculation of the phase diagrams. This problem can be overcome by treating the attractive potential as a perturbation and using the ORPA (see chapter 5).

The two-component fluid in the matrix is described through the following parameters:

$\rho_0,\ \rho_1,\ \rho_2$	matrix and fluid densities
$\sigma_{00},\ \sigma_{01},\ \sigma_{02},\ \sigma_{11},\ \sigma_{12},\ \sigma_{22}$	hard-sphere diameters
$\frac{kT}{\epsilon_{01}},\ \frac{kT}{\epsilon_{02}},\ \frac{kT}{\epsilon_{11}},\ \frac{kT}{\epsilon_{12}},\ \frac{kT}{\epsilon_{22}}$	reduced temperatures

For the two-component fluid the initial estimate of a PY solution for non interacting fluids is not sufficient except in the case, where the hard-sphere diameters σ_{01}, σ_{02} and σ_{11}, σ_{12}, σ_{22} are equal. By exploiting the limiting case of the ROZ equations presented in subsection 2.7.3 a more accurate initial estimate can be obtained in the following way:

1. Choose the fluid component with the higher density (let us assume the first one).
2. Set the hard-sphere diameter of the other component equal to the chosen one, i.e. $\sigma_{02} = \sigma_{01}$ and $\sigma_{12} = \sigma_{22} = \sigma_{11}$.
3. Solve the one-component ROZ equations for a system with fluid density $\rho_1 + \rho_2$ and hard-sphere diameters σ_{01} and σ_{11} for pure hard-sphere interactions.

4. Take this solution as initial estimate and switch on the differing hard-sphere diameters and afterwards the attractive tail of the potential (if one is existing).

In most of the calculations we used a grid size of $\Delta r = 0.01\sigma_{11}$ and $N = 1024$ points. The efficiency of the LMV algorithm depends on the number of equations $3M$ and $8M$ involved in the NR iterations. When M is chosen to be too small, the convergence is slow because too much is left to direct iterations. For large M, inverting the Jacobian requires a large amount of computer time. A reasonable compromise is to choose $M \approx 20$ in the one-component case and $M \approx 10$ in the two-component case.

Chapter 4

Thermodynamic properties of fluids in quenched disordered matrices

Using the replica method we derive thermodynamic relations for a binary fluid that is in equilibrium with a quenched porous matrix: The Gibbs-Duhem equation, the virial equation and the expression of the configurational free energy are obtained as straightforward generalisations of the results derived by Rosinberg *et al.* [17] for a one-component fluid. Further we present an alternative derivation of the compressibility equation which was derived by Rosinberg *et al.* [17] using the replica trick and, independently, by Ford and Glandt from a graphical analysis [34]. The derivation presented here is based on density functional formalism and has the advantage that it can easily be generalised to a two-component fluid in a matrix.

4.1 Gibbs-Duhem relation

In order to derive the Gibbs-Duhem relation we return to subsection 2.7.1. There it was proven that the partly quenched system is a limiting case of the replicated system, a fully equilibrated system in which the fluid particles have been replicated in s identical copies. In these derivations we used a canonical ensemble to describe both the replicas and the matrix. Equivalently, we could have considered a grand canonical ensemble for the replicas and a canonical ensemble for the matrix; we will use this formalism to derive the thermodynamic relations of a binary fluid in a matrix.

In this ensemble the corresponding expression to eq. 2.33 is

$$\overline{\Omega}_{12} = \lim_{s\to 0} \frac{d}{ds}\Omega^{rep}(s). \tag{4.1}$$

The change in $\Omega^{rep}(s)$ associated with any infinitesimal change in a thermodynamic state is given by

$$\begin{aligned} d\Omega^{rep}(s) &= -P^{rep}(s)dV - S^{rep}(s)dT \\ &\qquad - sN_1^{rep}(s)d\mu_1 - sN_2^{rep}(s)d\mu_2 + \mu_0^{rep}(s)dN_0 \\ &= \left[-P^{rep}(s) + \rho_0\mu_0^{rep}(s)\right]dV - S^{rep}(s)dT \\ &\qquad - sN_1^{rep}(s)d\mu_1 - sN_2^{rep}(s)d\mu_2 + \mu_0^{rep}(s)Vd\rho_0, \end{aligned}$$

where we have explicitly indicated that the pressure P^{rep}, the entropy S^{rep}, the number of particles N_1^{rep} and N_2^{rep} in the respective replica, and the chemical potential μ_0^{rep} of the matrix depend on the number of replicas.

Using eq. 4.1, we obtain the corresponding equation for the original quenched-annealed mixture

$$\begin{aligned} d\overline{\Omega}_{12} &= -\lim_{s\to 0}\frac{d}{ds}[P^{rep}(s) - \rho_0\mu_0^{rep}(s)]dV - \lim_{s\to 0}\frac{dS^{rep}(s)}{ds}dT \\ &\quad - \lim_{s\to 0} N_1^{rep}(s)d\mu_1 - \lim_{s\to 0} N_2^{rep}(s)d\mu_2 + \lim_{s\to 0}\frac{d\mu_0^{rep}(s)}{ds}Vd\rho_0 \\ &= -P_{12}dV - S_{12}dT - N_1d\mu_1 - N_2d\mu_2 + X_{12}Vd\rho_0 \end{aligned} \tag{4.2}$$

from which we get

$$P_{12} = -\left(\frac{\partial\overline{\Omega}_{12}}{\partial V}\right)_{T,\mu_1,\mu_2,\rho_0} = \lim_{s\to 0}\frac{d}{ds}[P^{rep}(s) - \rho_0\mu_0^{rep}(s)] \tag{4.3}$$

$$S_{12} = -\left(\frac{\partial\overline{\Omega}_{12}}{\partial T}\right)_{V,\mu_1,\mu_2,\rho_0} = \lim_{s\to 0}\frac{dS^{rep}(s)}{ds} \tag{4.4}$$

$$N_1 = -\left(\frac{\partial\overline{\Omega}_{12}}{\partial \mu_1}\right)_{V,T,\mu_2,\rho_0} = \lim_{s\to 0} N_1^{rep}(s) \tag{4.5}$$

$$N_2 = -\left(\frac{\partial\overline{\Omega}_{12}}{\partial \mu_2}\right)_{V,T,\mu_1,\rho_0} = \lim_{s\to 0} N_2^{rep}(s) \tag{4.6}$$

and

$$X_{12} = \frac{1}{V}\left(\frac{\partial\overline{\Omega}_{12}}{\partial\rho_0}\right)_{V,T,\mu_1,\mu_2} = \lim_{s\to 0}\frac{d\mu_0^{rep}(s)}{ds}. \tag{4.7}$$

Note that the thermodynamic quantities P_{12}, S_{12}, N_1, and N_2 for a fluid inside a matrix are defined at constant density of the matrix. Indeed, this is the correct definition: for instance, in order to calculate the pressure of the fluid by changing the volume, one is not allowed to modify the density of the matrix.

From the Gibbs-Duhem equation for the $(2s+1)$-component mixture

$$\begin{aligned} 0 &= -VdP^{rep}(s) + S^{rep}(s)dT + sN_1^{rep}(s)d\mu_1 + sN_2^{rep}(s)d\mu_2 + N_0 d\mu_0^{rep}(s) \\ &= -Vd[P^{rep}(s) - \rho_0\mu_0^{rep}(s)] + S^{rep}(s)dT \\ &\qquad + sN_1^{rep}(s)d\mu_1 + sN_2^{rep}(s)d\mu_2 - V\mu_0^{rep}(s)d\rho_0 \end{aligned}$$

we get with eqs. 4.3 - 4.7 the Gibbs-Duhem equation for a fluid inside a matrix

$$0 = -VdP_{12} + S_{12}dT + N_1 d\mu_1 + N_2 d\mu_2 - VX_{12}d\rho_0 \tag{4.8}$$

and thus by using eq. 4.2

$$d\overline{\Omega}_{12} = -P_{12}dV - VdP_{12}$$

and, after integrating $d\overline{\Omega}_{12}$,

$$\overline{\Omega}_{12} = -P_{12}V, \tag{4.9}$$

which shows that this standard thermodynamic relation is also valid for a fluid inside a matrix.

Furthermore, we find that X_{12}, defined by eq. 4.7, is

$$X_{12} = -\left(\frac{\partial P_{12}}{\partial\rho_0}\right)_{V,T,\mu_1,\mu_2}. \tag{4.10}$$

The Helmholtz free energy of the replicated system is

$$\begin{aligned} F^{rep}(s) &= -P^{rep}(s)V + \mu_0^{rep}(s)N_0 + s\mu_1 N_1^{rep}(s) + s\mu_2 N_2^{rep}(s) \\ &= -[P^{rep}(s) - \mu_0^{rep}(s)\rho_0]V + s\mu_1 N_1^{rep}(s) + s\mu_2 N_2^{rep}(s) \end{aligned}$$

from which we obtain the Helmholtz free energy of the binary fluid in the matrix

$$\overline{F}_{12} = \lim_{s\to 0} \frac{d}{ds} F^{rep}(s) = -P_{12}V + \mu_1 N_1 + \mu_2 N_2.$$

Taking the limiting case $N_2 \to 0$ we obtain the corresponding quantity for a one-component fluid (see [17])

$$\overline{F}_1 = -P_1 V + \mu_1 N_1. \tag{4.11}$$

4.2 Compressibility equation

The isothermal compressibility of a one-component fluid inside a matrix is defined via

$$\chi_1 = -\frac{1}{V}\left(\frac{\partial V}{\partial P_1}\right)_{N_1,T,\rho_0}.$$

The Gibbs-Duhem relation eq. 4.8 for a one-component fluid in a matrix (N_2=0)

$$0 = -VdP_1 + S_1 dT + N_1 d\mu_1 - VX_1 d\rho_0$$

for an infinitesimal isothermal ($dT = 0$) change at constant matrix density ($d\rho_0 = 0$) takes the form

$$VdP_1 = N_1 d\mu_1.$$

If the change also takes place at constant volume, both dP_1 and $d\mu_1$ are proportional to dN_1:

$$\begin{aligned} dP_1 &= \left(\frac{\partial P_1}{\partial N_1}\right)_{V,T,\rho_0} dN_1 \\ d\mu_1 &= \left(\frac{\partial \mu_1}{\partial N_1}\right)_{V,T,\rho_0} dN_1 \end{aligned}$$

and therefore

$$\begin{aligned} \rho_1\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{V,T,\rho_0} &= N_1\left(\frac{\partial \mu_1}{\partial N_1}\right)_{V,T,\rho_0} = V\left(\frac{\partial P_1}{\partial N_1}\right)_{V,T,\rho_0} \\ &= \left(\frac{\partial P_1}{\partial \rho_1}\right)_{V,T,\rho_0} = -\frac{V}{\rho_1}\left(\frac{\partial P_1}{\partial V}\right)_{N_1,T,\rho_0} = \frac{1}{\rho_1 \chi_1}. \end{aligned}$$

Using eq. 4.9 we obtain the partial derivative of the pressure of the fluid with respect to the one-particle density

$$\frac{V}{kT}\left(\frac{\partial P_1}{\partial \rho_1}\right)_{V,T,\rho_0} = -\frac{1}{kT}\left(\frac{\partial \overline{\Omega}_1}{\partial \rho_1}\right)_{V,T,\rho_0}.$$

Using the replica trick (eq. 4.1) we find

$$\begin{aligned}
\left(\frac{\partial \overline{\Omega}_1}{\partial \rho_1}\right)_{V,T,\rho_0} d\rho_1 &= d\overline{\Omega}_1\Big|_{V,T,\rho_0} = \lim_{s\to 0}\frac{d}{ds}\left[d\Omega^{rep}(s)\Big|_{V,T,\rho_0}\right] \\
&= \lim_{s\to 0}\frac{d}{ds}\left[\left(\frac{\partial \Omega^{rep}(s)}{\partial \rho_1^{rep}(s)}\right)_{V,T,\rho_0} d\rho_1^{rep}(s)\right] \\
= \lim_{s\to 0}\frac{d}{ds}&\left(\frac{\partial \Omega^{rep}(s)}{\partial \rho_1^{rep}(s)}\right)_{V,T,\rho_0} d\rho_1 + \lim_{s\to 0}\left[\left(\frac{\partial \Omega^{rep}(s)}{\partial \rho_1^{rep}(s)}\right)_{V,T,\rho_0}\frac{d}{ds}d\rho_1^{rep}(s)\right].
\end{aligned}$$

We will see below that

$$\lim_{s\to 0}\left(\frac{\partial \Omega^{rep}(s)}{\partial \rho_1^{rep}(s)}\right)_{V,T,\rho_0} = 0 \tag{4.12}$$

and therefore

$$\left(\frac{\partial \overline{\Omega}_1}{\partial \rho_1}\right)_{V,T,\rho_0} = \lim_{s\to 0}\frac{d}{ds}\left(\frac{\partial \Omega^{rep}(s)}{\partial \rho_1^{rep}(s)}\right)_{V,T,\rho_0}.$$

Thus

$$\begin{aligned}
\frac{V}{kT}\left(\frac{\partial P_1}{\partial \rho_1}\right)_{V,T,\rho_0} &= \lim_{s\to 0}\frac{d}{ds}\left(-\frac{1}{kT}\frac{\partial \Omega^{rep}(s)}{\partial \rho_1^{rep}(s)}\right)_{V,T,\rho_0} \\
&= \lim_{s\to 0}\frac{d}{ds}\left(\frac{\partial \ln \Xi^{rep}(s)}{\partial \rho_1^{rep}(s)}\right)_{V,T,\rho_0}.
\end{aligned} \tag{4.13}$$

Now we introduce an external potential $u_1(\mathbf{r})$ which is acting only on the fluid particles. Thus $\Xi^{rep}(s)$ becomes a functional of the non-uniform one-particle density $\rho_1^{(1)}(\mathbf{r})$ and we have to replace eq. 4.13 through the corresponding density-functional formulation

$$\begin{aligned}
\frac{V}{kT}\left(\frac{\partial P_1}{\partial \rho_1}\right)_{V,T,\rho_0} &= \lim_{s\to 0}\frac{d}{ds}\int \mathbf{dr}_2\left[\frac{\delta \ln \Xi^{rep}(s)}{\delta \rho_1^{(1),rep}(\mathbf{r}_2; s)}\right]_{u_1=0} \\
= \lim_{s\to 0}\frac{d}{ds}\sum_{i=1}^{s}&\iint \mathbf{dr}_1\mathbf{dr}_2\left[\frac{\delta \ln \Xi^{rep}(s)}{\delta\left(\beta\left[\mu_i - u_1(\mathbf{r}_1)\right]\right)}\frac{\delta(\beta\left[\mu_i - u_1(\mathbf{r}_1)\right])}{\delta \rho_1^{(1),rep}(\mathbf{r}_2; s)}\right]_{u_1=0}.
\end{aligned}$$

We now use the functional relation (see [28])

$$\frac{\delta \ln \Xi^{rep}(s)}{\delta(\beta\,[\mu_i - u_1(\mathbf{r}_1)])} = \rho_i^{(1),rep}(\mathbf{r}_1; s) = \rho_1^{(1),rep}(\mathbf{r_1}; s) \quad \text{for } i = 1, \ldots, s.$$

Due to the symmetry relations of the replica system, we can write

$$\begin{aligned}
\frac{\delta(\beta\,[\mu_i - u_1(\mathbf{r}_1)])}{\delta\rho_1^{(1),rep}(\mathbf{r}_2; s)} &= \sum_{j=1}^{s} \int \mathbf{dr}_3 \frac{\delta(\beta\,[\mu_i - u_1(\mathbf{r}_1)])}{\delta\rho_j^{(1),rep}(\mathbf{r}_3; s)} \underbrace{\frac{\delta\rho_j^{(1),rep}(\mathbf{r}_3; s)}{\delta\rho_1^{(1),rep}(\mathbf{r}_2; s)}}_{\delta(\mathbf{r}_2 - \mathbf{r}_3)} \\
&= \sum_{j=1}^{s} \frac{\delta(\beta\,[\mu_i - u_1(\mathbf{r}_1)])}{\delta\rho_j^{(1),rep}(\mathbf{r}_2; s)} \\
&= \sum_{j=1}^{s} \Big(\frac{\delta_{ij}\delta(\mathbf{r}_1, \mathbf{r}_2)}{\rho_j^{(1),rep}(\mathbf{r}_2; s)} - c_{ij}^{(2),rep}(\mathbf{r}_1, \mathbf{r}_2; s) \Big).
\end{aligned}$$

Gathering these results we obtain from eq. 4.13

$$\begin{aligned}
&\frac{V}{kT}\left(\frac{\partial P_1}{\partial \rho_1}\right)_{V,T,\rho_0} = \qquad\qquad (4.14) \\
&= \lim_{s\to 0} \frac{d}{ds} \sum_{i=1}^{s} \iint \mathbf{dr}_1 \mathbf{dr}_2 \left[\rho_i^{(1),rep}(\mathbf{r}_1; s) \sum_{j=1}^{s} \left(\frac{\delta_{ij}\delta(\mathbf{r}_1, \mathbf{r}_2)}{\rho_j^{(1),rep}(\mathbf{r}_2; s)} - c_{ij}^{(2),rep}(\mathbf{r}_1, \mathbf{r}_2; s) \right) \right]_{u_1=0} \\
&= \lim_{s\to 0} \frac{d}{ds} s \iint \mathbf{dr}_1 \mathbf{dr}_2 \Big[\delta(\mathbf{r}_1, \mathbf{r}_2) - \rho_1^{(1),rep}(\mathbf{r}_1; s) c_{11}^{(2),rep}(\mathbf{r}_1, \mathbf{r}_2; s) \\
&\qquad\qquad - (s-1)\rho_1^{(1),rep}(\mathbf{r}_1; s) c_{12}^{(2),rep}(\mathbf{r}_1, \mathbf{r}_2; s) \Big]_{u_1=0}.
\end{aligned}$$

Due to the factor s in front of the integral the limit $s \to 0$ of this expression tends towards 0 and thus the validity of eq. 4.12 is explicitly checked.

If we set the external potential equal to zero we obtain a homogeneous system; dropping the index (2) in the direct correlation functions and integrating over the particle coordinates, eq. 4.14 becomes

$$\begin{aligned}
&\frac{V}{kT}\left(\frac{\partial P_1}{\partial \rho_1}\right)_{V,T,\rho_0} = \\
&= \lim_{s\to 0} \frac{d}{ds} \Big\{ V\Big(s - s\rho_1^{rep}(s)\tilde{c}_{11}^{rep}(k{=}0; s) - s(s-1)\rho_1^{rep}(s)\tilde{c}_{12}^{rep}(k{=}0; s) \Big) \Big\} \\
&= V\Big(1 - \rho_1\tilde{c}_{11}(k{=}0) + \rho_1\tilde{c}_{12}(k{=}0) \Big)
\end{aligned}$$

and therefore

$$\left(\frac{\partial \beta P_1}{\partial \rho_1}\right)_{V,T,\rho_0} = 1 - \rho_1\tilde{c}_c(k{=}0) \qquad (4.15)$$

or,

$$\rho_1\left(\frac{\partial\beta\mu_1}{\partial\rho_1}\right)_{V,T,\rho_0} = 1-\rho_1\tilde{c}_c(k{=}0), \tag{4.16}$$

which is the compressibility equation derived by Ford and Glandt [34] and independently by Rosinberg *et al.* [17].

We now proceed to a binary fluid inside a matrix and also use the density functional formalism to derive the partial derivatives of the pressure with respect to the partial densities.

If we proceed as above we find

$$\begin{aligned}\frac{V}{kT}\left(\frac{\partial P_{12}}{\partial\rho_1}\right)_{V,T,N_2,\rho_0} &= -\frac{1}{kT}\left(\frac{\partial\overline{\Omega}_{12}}{\partial\rho_1}\right)_{V,T,N_2,\rho_0} = \lim_{s\to0}\frac{d}{ds}\left(-\frac{1}{kT}\frac{\partial\Omega^{rep}(s)}{\partial\rho_1^{rep}(s)}\right)_{V,T,N_2,\rho_0}\\ &= \lim_{s\to0}\frac{d}{ds}\sum_{i=1}^{2s}\iint \mathbf{dr}_1\mathbf{dr}_2\left[\frac{\delta\ln\Xi^{rep}(s)}{\delta(\beta[\mu_i-u_{12}(\mathbf{r}_1)])}\,\frac{\delta(\beta[\mu_i-u_{12}(\mathbf{r}_1)])}{\delta\rho_1^{(1),rep}(\mathbf{r}_2;s)}\right]_{u_{12}=0},\end{aligned} \tag{4.17}$$

where u_{12} is an external potential acting only on the fluid particles; the functional derivatives are now

$$\frac{\delta\ln\Xi^{rep}(s)}{\delta(\beta\left[\mu_i-u_{12}(\mathbf{r}_1)\right])} = \rho_i^{(1),rep}(\mathbf{r}_1;s) = \begin{cases}\rho_1^{(1),rep}(\mathbf{r}_1;s) & \text{for } i=1,3,\dots,2s-1\\ \rho_2^{(1),rep}(\mathbf{r}_1;s) & \text{for } i=2,4,\dots,2s\end{cases}$$

and

$$\begin{aligned}\frac{\delta(\beta\left[\mu_i-u_{12}(\mathbf{r}_1)\right])}{\delta\rho_1^{(1),rep}(\mathbf{r}_2;s)} &= \sum_{j=1}^{2s-1\;\prime}\frac{\delta(\beta\left[\mu_i-u_{12}(\mathbf{r}_1)\right])}{\delta\rho_j^{(1),rep}(r_2;s)}\\ &= \sum_{j=1}^{2s-1\;\prime}\left(\frac{\delta_{ij}\delta(\mathbf{r}_1,\mathbf{r}_2)}{\rho_j^{(1),rep}(\mathbf{r}_2;s)}-c_{ij}^{(2),rep}(\mathbf{r}_1,\mathbf{r}_2;s)\right),\end{aligned} \tag{4.18}$$

where the prime denotes that the sum runs only over odd j-values.

Thus

$$\begin{aligned}&\frac{V}{kT}\left(\frac{\partial P_{12}}{\partial\rho_1}\right)_{V,T,N_2,\rho_0} =\\ &=\lim_{s\to0}\frac{d}{ds}\sum_{i=1}^{2s}\iint\mathbf{dr}_1\mathbf{dr}_2\left[\rho_i^{(1),rep}(\mathbf{r}_1;s)\sum_{j=1}^{2s-1\;\prime}\left(\frac{\delta_{ij}\delta(\mathbf{r}_1,\mathbf{r}_2)}{\rho_j^{(1),rep}(\mathbf{r}_2;s)}-c_{ij}^{(2),rep}(\mathbf{r}_1,\mathbf{r}_2;s)\right)\right]_{u_{12}=0}\end{aligned}$$

$$=\lim_{s\to 0}\frac{d}{ds}\Big\{V\Big(s-s\rho_1^{rep}(s)\tilde{c}_{11}^{rep}(k=0;s)-s(s-1)\rho_1^{rep}(s)\tilde{c}_{13}^{rep}(k=0;s)$$
$$-s\rho_2^{rep}(s)\tilde{c}_{12}^{rep}(k=0;s)-s(s-1)\rho_2^{rep}(s)\tilde{c}_{14}^{rep}(k=0;s)\Big)\Big\}$$

which yields

$$\left(\frac{\partial\beta P_{12}}{\partial\rho_1}\right)_{V,T,N_2,\rho_0}=1-\rho_1\tilde{c}_{11}^{c}(k=0)-\rho_2\tilde{c}_{12}^{c}(k=0).$$

In a similar way, starting from $\frac{V}{kT}\left(\frac{\partial P_{12}}{\partial\rho_2}\right)_{V,T,N_1,\rho_0}$ in eq. 4.17 we obtain

$$\left(\frac{\partial\beta P_{12}}{\partial\rho_2}\right)_{V,T,N_2,\rho_0}=1-\rho_1\tilde{c}_{12}^{c}(k=0)-\rho_2\tilde{c}_{22}^{c}(k=0).$$

In order to obtain the partial derivatives of the chemical potentials with respect to the fluid densities, we first have to establish the correct relation between the chemical potential of the partly quenched system and that of the replica system. For this purpose we consider a replicated system in which both the fluid particles and the matrix particles are treated in a canonical ensemble. The change in the thermodynamic potential due to an infinitesimal change of the thermodynamic state is therefore

$$\begin{aligned}dF^{rep}(s) &= -P^{rep}(s)dV-S^{rep}(s)dT-s\mu_1^{rep}(s)dN_1\\ &\qquad -s\mu_2^{rep}(s)dN_2+\mu_0^{rep}(s)dN_0\\ &= \left[-P^{rep}(s)+\rho_0\mu_0^{rep}(s)\right]dV-S^{rep}(s)dT-s\mu_1^{rep}(s)dN_1\\ &\qquad -s\mu_2^{rep}(s)dN_2+\mu_0^{rep}(s)Vd\rho_0,\end{aligned}$$

and thus

$$\mu_1=-\left(\frac{\partial\overline{F}_{12}}{\partial N_1}\right)_{V,T,N_2,\rho_0}=-\lim_{s\to 0}\frac{d}{ds}\left(\frac{\partial F^{rep}(s)}{\partial N_1}\right)_{V,T,N_2,\rho_0}=\lim_{s\to 0}\mu_1^{rep}(s). \tag{4.19}$$

Therefore

$$\begin{aligned}\rho_1\frac{\partial\beta\mu_1}{\partial\rho_1} &= \lim_{s\to 0}\left[\rho_1^{rep}(s)\frac{\partial\beta\mu_1^{rep}(s)}{\partial\rho_1^{rep}(s)}\right]\\ &= \lim_{s\to 0}\int d\mathbf{r}_2\left[\rho_1^{(1),rep}(\mathbf{r}_2;s)\frac{\delta(\beta\left[\mu_1^{rep}(s)-u_{12}(\mathbf{r}_1)\right])}{\delta\rho_1^{(1),rep}(\mathbf{r}_2;s)}\right]_{u_{12}=0};\end{aligned}$$

with eq. 4.18 this yields

$$\begin{aligned}
\rho_1 \frac{\partial \beta\mu_1}{\partial \rho_1} &= \lim_{s\to 0} \left\{ (1 - \rho_1^{rep}(s)\tilde{c}_{11}^{rep}(k\!=\!0;s) - (s-1)\rho_1^{rep}(s)\tilde{c}_{13}^{rep}(k\!=\!0;s)) \right\} \\
&= 1 - \rho_1 \tilde{c}_{11}^{c}(k\!=\!0).
\end{aligned}$$

In a similar way one obtains (the double prime denotes a sum over even numbers only)

$$\begin{aligned}
\rho_1 \frac{\partial \beta\mu_1}{\partial \rho_2} &= \lim_{s\to 0} \rho_1^{rep}(s) \frac{\partial \beta\mu_1^{rep}(s)}{\partial \rho_2^{rep}(s)} \\
&= \lim_{s\to 0} \int \mathbf{dr}_2 \left[\frac{\delta(\beta\left[\mu_1 - u_{12}(\mathbf{r}_1)\right])}{\delta \rho_2^{(1),rep}(\mathbf{r}_2;s)} \rho_1^{(1),rep}(\mathbf{r}_2;s) \right]_{u_{12}=0} \\
&= \lim_{s\to 0} \int \mathbf{dr}_2 \left[{\sum_{i=2}^{2s}}'' \frac{\delta(\beta\left[\mu_1 - u_{12}(\mathbf{r}_1)\right])}{\delta \rho_i^{(1),rep}(\mathbf{r}_2;s)} \rho_1^{(1),rep}(\mathbf{r}_2;s) \right]_{u_{12}=0} \\
&= \lim_{s\to 0} \left\{ (-\rho_1^{rep}(s)\tilde{c}_{12}^{rep}(k\!=\!0;s) - (s-1)\rho_1^{rep}(s)\tilde{c}_{14}^{rep}(k\!=\!0;s)) \right\} \\
&= -\rho_1 \tilde{c}_{12}^{c}(k\!=\!0).
\end{aligned}$$

Similarly, one finds

$$\rho_2 \frac{\partial \beta\mu_2}{\partial \rho_2} = 1 - \rho_2 \tilde{c}_{22}^{c}(k\!=\!0)$$

and

$$\rho_2 \frac{\partial \beta\mu_2}{\partial \rho_1} = -\rho_2 \tilde{c}_{12}^{c}(k\!=\!0).$$

It can be explicitly checked that these expressions fulfill the thermodynamic relations

$$\left(\frac{\partial \beta P_{12}}{\partial \rho_1}\right)_{V,T,N_2,\rho_0} = \rho_1 \left(\frac{\partial \beta\mu_1}{\partial \rho_1}\right)_{T,V,N_2,\rho_0} + \rho_2 \left(\frac{\partial \beta\mu_2}{\partial \rho_1}\right)_{T,V,N_2,\rho_0}$$

and

$$\left(\frac{\partial \beta P_{12}}{\partial \rho_2}\right)_{V,T,N_1,\rho_0} = \rho_1 \left(\frac{\partial \beta\mu_1}{\partial \rho_2}\right)_{T,V,N_1,\rho_0} + \rho_2 \left(\frac{\partial \beta\mu_2}{\partial \rho_2}\right)_{T,V,N_1,\rho_0},$$

which follow from the Gibbs-Duhem relation eq. 4.8.

4.3 Virial equation

We apply the virial equation of a mixture [35]

$$\beta P = \sum_i \rho_i - \frac{1}{6}\beta \sum_{i,j} \rho_i \rho_j \int \mathbf{dr} r g_{ij}(r)\phi'_{ij}(r),$$

where $\phi'_{ij}(r) = \frac{d\phi_{ij}(r)}{dr}$, to the replicated system and obtain

$$\begin{aligned}\beta P^{rep}(s) \;&=\; \rho_0 + s\rho_1^{rep}(s) + s\rho_2^{rep}(s) - \frac{\beta}{6}\int \mathbf{dr} r\Big[(\rho_0^{rep}(s))^2 g_{00}^{rep}(r;s)\phi'_{00}(r) \\ &+ s(\rho_1^{rep}(s))^2 g_{11}^{rep}(r;s)\phi'_{11}(r) + s(\rho_2^{rep}(s))^2 g_{22}^{rep}(r;s)\phi'_{22}(r) \\ &+ 2s\rho_0\rho_1^{rep}(s) g_{01}^{rep}(r;s)\phi'_{01}(r) + 2s\rho_0\rho_2^{rep}(s) g_{02}^{rep}(r;s)\phi'_{02}(r) \\ &+ 2s\rho_1^{rep}(s)\rho_2^{rep}(s) g_{12}^{rep}(r;s)\phi'_{12}(r)\Big].\end{aligned}$$

The pressure of the fluid inside a matrix (eq. 4.3) is, using eq. 4.7 and eq. 4.10

$$\beta P_{12} = \beta \lim_{s\to 0} \frac{dP^{rep}(s)}{ds} + \rho_0 \left(\frac{\partial \beta P_{12}}{\partial \rho_0}\right)_{V,T,\mu_1,\mu_2}$$

and therefore

$$\begin{aligned}\beta P_{12} \;-\; \rho_0 \left(\frac{\partial \beta P_{12}}{\partial \rho_0}\right)_{V,T,\mu_1,\mu_2} &= \rho_1 + \rho_2 - \frac{\beta}{6}\int \mathbf{dr} r \left[\rho_0^2 \frac{d g_{00}^{rep}(r;s)}{ds}\phi'_{00}(r)\right. \\ &+ \rho_1^2 g_{11}(r)\phi'_{11}(r) + \rho_2^2 g_{22}(r)\phi'_{22}(r) + 2\rho_0\rho_1 g_{01}(r)\phi'_{01}(r) \\ &\left. + 2\rho_0\rho_2 g_{02}(r)\phi'_{02}(r) + 2\rho_1\rho_2 g_{12}(r)\phi'_{12}(r)\right].\end{aligned}$$

In particular, for hard-sphere interactions characterised by the diameters σ_{00}, σ_{01}, σ_{02}, σ_{11}, σ_{12} and σ_{22} this equation reduces to

$$\begin{aligned}\beta P_{12} \;-\; \rho_0 \left(\frac{\partial \beta P_{12}}{\partial \rho_0}\right)_{V,T,\mu_1,\mu_2} &= \rho_1 + \rho_2 + \frac{2\pi}{3}\left[\rho_0^2\sigma_{00}^3 \lim_{s\to 0}\frac{d g_{00}^{rep}(\sigma_{00};s)}{ds}\right. \\ &+ \rho_1^2\sigma_{11}^3 g_{11}(\sigma_{11}) + \rho_2^2\sigma_{22}^3 g_{22}(\sigma_{22}) + 2\rho_0\rho_1\sigma_{01}^3 g_{01}(\sigma_{01}) \\ &\left. + 2\rho_0\rho_2\sigma_{02}^3 g_{02}(\sigma_{02}) + 2\rho_1\rho_2\sigma_{12}^3 g_{12}(\sigma_{12})\right].\end{aligned}$$

Taking one of the limiting cases introduced in subsection 2.7.3 to recover the one-component case we obtain the virial equation for a one-component fluid in a matrix (see [17, 18])

$$
\begin{aligned}
&\beta P_1 - \rho_0 \left(\frac{\partial \beta P_1}{\partial \rho_0} \right)_{V,T,\mu_1} \\
&= \rho_1 - \frac{\beta}{6} \int \mathbf{dr} r \left[\rho_0^2 \frac{d g_{00}^{rep}(r;s)}{ds} \phi_{00}'(r) + \rho_1^2 g_{11}(r) \phi_{11}'(r) + 2\rho_0 \rho_1 g_{01}(r) \phi_{01}'(r) \right].
\end{aligned}
$$

4.4 Energy equation

The excess energy of a fluid inside a matrix is obtained from the quenched average of the potential energy (in the following we use the notation introduced in section 2.2)

$$
\overline{U}^{ex} = \overline{\langle H_{01} + H_{11} \rangle} = \overline{\langle H_{01} \rangle} + \overline{\langle H_{11} \rangle}.
$$

To simplify the derivation we consider a canonical ensemble both for the fluid (at temperature β_1) and the matrix (at temperature β_0). Furthermore, we restrict ourselves to a system where particles interact through pairwise-additive forces. Thus the total potential energy can be written as a sum of pair terms.

$$
\begin{aligned}
H_{01} &= \sum_{i=1}^{N_0} \sum_{j=1}^{N_1} \phi_{01}(\mathbf{q}_i, \mathbf{r}_j) \\
H_{11} &= \sum_{i<j}^{N_1} \phi_{11}(\mathbf{r}_i, \mathbf{r}_j).
\end{aligned}
$$

We then obtain expressions for the particle densities in terms of averages over delta functions of the particle positions (see [29])

$$
\begin{aligned}
\rho_{01}^{(2)}(\mathbf{q}, \mathbf{r}) &= \overline{\left\langle \sum_{i=1}^{N_0} \sum_{j=1}^{N_1} \delta(\mathbf{q} - \mathbf{q}_i) \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle} \\
&= \frac{1}{Z_0 N_0!} \int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} \sum_{i=1}^{N_0} \delta(\mathbf{q} - \mathbf{q}_i) \times \\
&\quad \frac{1}{Z_1(\mathbf{q}^{N_0}) N_1!} \int \mathbf{dr}^{N_1} e^{-\beta_1 \left[H_{01}(\mathbf{q}^{N_0}, \mathbf{r}^{N_1}) + H_{11}(\mathbf{r}^{N_1}) \right]} \sum_{j=1}^{N_1} \delta(\mathbf{r} - \mathbf{r}_j).
\end{aligned}
$$

The sum over all particle coordinates can be written as $N_0 N_1$ times the contribution from any two particles; therefore

$$\begin{aligned}\rho_{01}^{(2)}(\mathbf{q},\mathbf{r}) \;=\; & \frac{N_0}{Z_0 N_0!}\int \mathbf{dq}^{N_0-1} e^{-\beta_0 H_{00}(\mathbf{q},\mathbf{q}^{N_0-1})} \times \\ & \frac{N_1}{Z_1(\mathbf{q},\mathbf{q}^{N_0-1})N_1!}\int \mathbf{dr}^{N_1-1} e^{-\beta_1\left[H_{01}(\mathbf{q},\mathbf{q}^{N_0-1},\mathbf{r},\mathbf{r}^{N_1-1})+H_{11}(\mathbf{r},\mathbf{r}^{N_1-1})\right]},\end{aligned} \tag{4.20}$$

where $\mathbf{q}^{N_0-1} = \{\mathbf{q}_2, \mathbf{q}_3, \ldots, \mathbf{q}_{N_0}\}$, etc.

The first contribution to $\overline{U}^{ex}$ can be written as

$$\begin{aligned}\overline{\langle H_{01}\rangle} \;=\; & \frac{1}{Z_0 N_0!}\int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} \times \\ & \frac{1}{Z_1(\mathbf{q}^{N_0})N_1!}\int \mathbf{dr}^{N_1} e^{-\beta_1\left[H_{01}(\mathbf{r}^{N_1};\mathbf{q}^{N_0})+H_{11}(\mathbf{r}^{N_1})\right]} \sum_{i=1}^{N_0}\sum_{j=1}^{N_1}\phi_{01}(\mathbf{q}_i,\mathbf{r}_j).\end{aligned}$$

The double sum on i and j contains $N_0 N_1$ terms, each yielding the same result after integration,

$$\begin{aligned}\overline{\langle H_{01}\rangle} \;=\; & \frac{N_0}{Z_0 N_0!}\int \mathbf{dq}^{N_0} e^{-\beta_0 H_{00}(\mathbf{q}^{N_0})} \times \\ & \frac{N_1}{Z_1(\mathbf{q}^{N_0})N_1!}\int \mathbf{dr}^{N_1} e^{-\beta_1\left[H_{01}(\mathbf{r}^{N_1};\mathbf{q}^{N_0})+H_{11}(\mathbf{r}^{N_1})\right]}\phi_{01}(\mathbf{q}_1,\mathbf{r}_1);\end{aligned}$$

with the expression of the two particle density eq. 4.20 we obtain

$$\begin{aligned}\overline{\langle H_{01}\rangle} &= \int \mathbf{dq}_1 \int \mathbf{dr}_1 \rho_{01}^{(2)}(\mathbf{q}_1,\mathbf{r}_1)\phi_{01}(\mathbf{q}_1,\mathbf{r}_1) \\ &= \rho_0\rho_1 \int \mathbf{dq}_1 \int \mathbf{dr}_1 g_{01}^{(2)}(\mathbf{q}_1,\mathbf{r}_1)\phi_{01}(\mathbf{q}_1,\mathbf{r}_1)\end{aligned}$$

which for a homogeneous system becomes

$$\overline{\langle H_{01}\rangle} = \rho_0\rho_1 V \int \mathbf{dr} g_{01}(r)\phi_{01}(r).$$

The fluid-fluid two particle density can also be expressed as a quenched average over delta functions, i.e.,

$$\begin{aligned}\rho_{11}^{(2)}(\mathbf{r},\mathbf{r}') \;=\; & \overline{\left\langle \sum_{i\neq j}^{N_1} \delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)\right\rangle} = \overline{\rho_{11}^{(2)}(\mathbf{r},\mathbf{r}';\mathbf{q}^{N_0})} \\ =\; & \overline{\frac{1}{Z_1(\mathbf{q}^{N_0})}\frac{N_1(N_1-1)}{N_1!}\int \mathbf{dr}^{N_1-2} e^{-\beta_1\left[H_{01}(\mathbf{q}^{N_0},\mathbf{r},\mathbf{r}',\mathbf{r}^{N_1-2})+H_{11}(\mathbf{r},\mathbf{r}',\mathbf{r}^{N_1-2})\right]}}\end{aligned}$$

and hence, following a similar line,

$$\begin{aligned}
\overline{\langle H_{11}\rangle} &= \overline{\sum_{i<j}^{N_1} \frac{1}{Z_1(\mathbf{q}^{N_0})N_1!} \int \mathbf{dr}^{N_1} e^{-\beta_1\left[H_{01}(\mathbf{r}^{N_1},\mathbf{q}^{N_0})+H_{11}(\mathbf{r}^{N_1})\right]} \phi_{11}(\mathbf{r}_i,\mathbf{r}_j)} \\
&= \overline{\frac{1}{2}\int \mathbf{dr}_1 \int \mathbf{dr}_2 \rho_{11}^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{q}^{N_0})\phi_{11}(\mathbf{r}_1,\mathbf{r}_2)} \\
&= \frac{1}{2}\int \mathbf{dr}_1 \int \mathbf{dr}_2 \rho_{11}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\phi_{11}(\mathbf{r}_1,\mathbf{r}_2) \\
&= \frac{1}{2} V \rho_1^2 \int \mathbf{dr} g_{11}(r)\phi_{11}(r).
\end{aligned}$$

Collecting these results we obtain

$$\frac{\overline{U}^{ex}}{V} = \rho_0\rho_1 \int \mathbf{dr} g_{01}(r)\phi_{01}(r) + \frac{1}{2}\rho_1^2 \int \mathbf{dr} g_{11}(r)\phi_{11}(r). \tag{4.21}$$

With this result we are now able to present an alternative derivation of the energy equation 4.21. Applying the formula of the excess internal energy for mixtures

$$\frac{U^{ex}}{V} = \frac{1}{2}\sum_i\sum_j \rho_i\rho_j \int \mathbf{dr} g_{ij}(r)\phi_{ij}(r)$$

to the replicated system (where we must omit the matrix configurational internal energy) yields

$$\begin{aligned}
\frac{U^{ex,rep}(s)}{V} &= \frac{1}{2}\Big[2s\rho_0\rho_1^{rep}(s)\int \mathbf{dr} g_{01}^{rep}(r;s)\phi_{01}(r) \\
&\qquad + s(\rho_1^{rep}(s))^2 \int \mathbf{dr} g_{11}^{rep}(r;s)\phi_{11}(r)\Big].
\end{aligned} \tag{4.22}$$

If we compare the expressions 4.21 and 4.22 we can check explicitly that the corresponding quantity for the quenched system is obtained by the limiting case

$$\overline{U}^{ex} = \lim_{s\to 0}\frac{d}{ds}U^{ex,rep}(s). \tag{4.23}$$

Now we are able to prove that the configurational internal energy satisfies the Gibbs-Helmholtz equation

$$\overline{U}^{ex} = \frac{\partial\beta\overline{F}_1}{\partial\beta}$$

since

$$\overline{U}^{ex} = \lim_{s\to 0}\frac{d}{ds}U^{ex,rep}(s) = \lim_{s\to 0}\frac{d}{ds}\frac{\partial\beta F^{rep}(s)}{\partial\beta} = \frac{\partial\beta\overline{F}_1}{\partial\beta}.$$

Finally, to derive the corresponding expression for a binary fluid inside a matrix we write down the energy equation of the replicated system

$$\begin{aligned}\frac{U^{ex,rep}(s)}{V} = \frac{1}{2}\Big[&2s\rho_0\rho_1^{rep}(s)\int \mathbf{dr}g_{01}^{rep}(r;s)\phi_{01}(r)\\ &+2s\rho_0\rho_2^{rep}(s)\int \mathbf{dr}g_{02}^{rep}(r;s)\phi_{02}(r) + 2s\rho_1^{rep}(s)\rho_2^{rep}(s)\int \mathbf{dr}g_{12}^{rep}(r;s)\phi_{12}(r)\\ &+s(\rho_1^{rep}(s))^2\int \mathbf{dr}g_{11}^{rep}(r;s)\phi_{11}(r) + s(\rho_2^{rep}(s))^2\int \mathbf{dr}g_{22}^{rep}(r;s)\phi_{22}(r)\Big].\end{aligned}$$

Taking the limiting case as in eq. 4.23 we obtain

$$\begin{aligned}\frac{\overline{U}^{ex}}{V} &= \rho_0\rho_1\int \mathbf{dr}g_{01}(r)\phi_{01}(r) + \rho_0\rho_2\int \mathbf{dr}g_{02}(r)\phi_{02}(r)\\ &+\frac{1}{2}\rho_1^2\int \mathbf{dr}g_{11}(r)\phi_{11}(r) + \frac{1}{2}\rho_2^2\int \mathbf{dr}g_{22}(r)\phi_{22}(r)\\ &+\frac{1}{2}\rho_1\rho_2\int \mathbf{dr}g_{12}(r)\phi_{12}(r).\end{aligned}$$

Chapter 5

Optimised random phase approximation

The solution of the ROZ equations within the PY and HNC approximation gives a good prediction for the pair distribution functions at high temperature, but the predictions deteriorate at lower temperatures and it becomes increasingly difficult to obtain a solution of the ROZ equations at low temperature. Thus there are regions of state space where integral equation approaches to calculate the correlation functions fail either due to numerical or physical reasons. This motivates to develop a complementary method, such as, for example, perturbation theories. In this chapter we will present the perturbation theory which was used in this work, i.e. the optimised random phase approximation (ORPA): we first present the ORPA for homogeneous liquids, then specialise it to the case of the replicated equilibrium system and take a limiting case in order to obtain the ORPA for a fluid in a porous matrix. Finally, we present the ORPA for a two-component mixture in a matrix.

5.1 ORPA for a homogeneous liquid

The ORPA [36, 37] is applicable to fluid mixtures at equilibrium in which the interactions between particles are pairwise additive. The pair potential

ϕ_{ij} between particles of species i and j is separated into

$$\phi_{ij}(r) = \phi_{ij}^R(r) + \Delta\phi_{ij}(r), \tag{5.1}$$

where $\phi_{ij}^R(r)$ is the pair potential of the reference system which is in general chosen to be a hard-sphere mixture and $\Delta\phi_{ij}(r)$ is the attractive perturbation. In the case where $\phi_{ij}^R(r)$ is not a hard-sphere potential, the softness of the potential can be taken into account via the Weeks-Chandler-Andersen 'blip'-function expansion. The choice of the hard-sphere equilibrium mixture as a reference system is obvious since its thermodynamic and structural properties are well known. The division of the potential leads naturally to the decomposition of all the correlation functions

$$h_{ij}(r) = h_{ij}^R(r) + \Delta h_{ij}(r)$$

and

$$c_{ij}(r) = c_{ij}^R(r) + \Delta c_{ij}(r),$$

where $h_{ij}^R(r)$ and $c_{ij}^R(r)$ are the correlation functions of the reference fluid and $\Delta h_{ij}(r)$ and $\Delta c_{ij}(r)$ the corrections to the reference correlation functions due to the attractive interaction.

We write down the OZ equations for the fluid mixture and the reference system, using the matrix formalism introduced in Appendix A (eq. A.6), i.e.,

$$\begin{aligned} \mathcal{H}^R + \Delta\mathcal{H} &= \mathcal{C}^R + \Delta\mathcal{C} + (\mathcal{C}^R + \Delta\mathcal{C})(\mathcal{H}^R + \Delta\mathcal{H}) \\ \mathcal{H}^R &= \mathcal{C}^R + \mathcal{C}^R\mathcal{H}^R \end{aligned}$$

and calculate the difference of these equations to obtain the so called residual OZ-equations

$$\Delta\mathcal{H} = \Delta\mathcal{C} + \mathcal{C}^R\Delta\mathcal{H} + \Delta\mathcal{C}\mathcal{H}^R + \Delta\mathcal{C}\Delta\mathcal{H}. \tag{5.2}$$

It is known that the direct correlation function asymptotically approaches the negative (dimensionless) potential. Thus, in the <u>r</u>andom <u>p</u>hase <u>a</u>pproximation (RPA) one assumes that

$$\Delta c_{ij}(r) = -\beta\Delta\phi_{ij}(r) \tag{5.3}$$

for *all* r values.

In an exact theory $g_{ij}(r)$ necessarily vanishes for $r < \sigma_{ij}$, where σ_{ij} is the distance of closest approach between particle i and j. However, in the approximation presented by eq. 5.3, there is no guarantee that this requirement will be fulfilled. This means that geometrical exclusion effects are not treated correctly. On the other hand, in this framework, there is a flexibility in the choice of $\Delta\phi_{ij}(r)$ that can usefully be exploited. It is clear that eq. 5.1 does not define the perturbation uniquely for $r < \sigma_{ij}$. For this physically inaccessible region, the perturbation can be chosen to have any finite functional form. Thus the perturbing potential $\Delta\phi_{ij}(r)$ inside the hard core ($r < \sigma_{ij}$) can be varied without changing the properties of the fluid to obtain the so called optimised potential. We thus obtain the o̲ptimised r̲andom p̲hase a̲pproximation (ORPA) which takes the following form:

$$\Delta c_{ij}(r) = -\beta \Delta\phi_{ij}(r) \quad \text{for} \quad r > \sigma_{ij}$$

and the perturbation potentials inside the cores are chosen so that

$$g_{ij}(r) = h_{ij}(r) + 1 = 0 \quad \text{for} \quad r < \sigma_{ij}$$

or equivalently

$$h_{ij}(r) = \underbrace{h_{ij}^R(r)}_{-1} + \Delta h_{ij}(r) = -1 \quad \text{for} \quad r < \sigma_{ij}$$

so that

$$\Delta h_{ij}(r) = 0 \quad \text{for} \quad r < \sigma_{ij}.$$

In the following we give a proof that the second condition is equivalent to the stationarity of a functional of the direct correlation functions with respect to variations of the perturbative potential inside the core region:

The functional is given as

$$\mathcal{F}\left[\Delta\tilde{\mathcal{C}}\right] = -\frac{1}{2(2\pi)^3} \int \mathbf{dk} \Big(\operatorname{tr}\left(\Delta\tilde{\mathcal{C}}\mathcal{S}^R\right) + \ln\det\left(\mathcal{I} - \Delta\tilde{\mathcal{C}}\mathcal{S}^R\right) \Big), \qquad (5.4)$$

where tr and det denote the matrix trace and determinant and the matrix $\mathcal{S}^R$ consists of the partial structure factors of the reference system defined in Appendix A (eq. A.7). We claim that the functional derivative of $\mathcal{F}$ with respect to $\Delta\tilde{c}_{ij}(k)$ is proportional to $\Delta\tilde{h}_{ij}(k)$

$$\frac{\delta\mathcal{F}}{\delta\Delta\tilde{c}_{ij}(k)} = \begin{cases} \frac{1}{2(2\pi)^3} 2\rho_i\rho_j\Delta\tilde{h}_{ij}(k) & \text{for } i \neq j \\ \frac{1}{2(2\pi)^3} \rho_i\rho_j\Delta\tilde{h}_{ij}(k) & \text{for } i = j \end{cases} . \tag{5.5}$$

Taking the inverse Fourier transform of eq. 5.5 we find that

$$\frac{\delta\mathcal{F}}{\delta\Delta c_{ij}(r)} \propto \Delta h_{ij}(r)$$

and thus the hard core conditions $\Delta h_{ij}(r) = 0$ for $r < \sigma_{ij}$ are satisfied if the functional derivatives with respect to $\Delta c_{ij}(r)$ vanish for $r < \sigma_{ij}$ which is a necessary condition for the existence of an extremum with respect to variations of the perturbing potentials inside the hard cores. Andersen and Chandler [36] argue that $\mathcal{F}$ is positive definite and therefore it has some minimum value. Thus, all that remains is to prove eq. 5.5.

Proof:

$$2(2\pi)^3 \frac{\delta\mathcal{F}}{\delta\Delta\tilde{c}_{ij}(k)} = -\frac{\partial}{\partial\Delta\tilde{c}_{ij}(k)}\Big(\mathrm{tr}\big(\Delta\tilde{\mathcal{C}}\mathcal{S}^R\big) + \ln\det\big(\mathcal{I} - \Delta\tilde{\mathcal{C}}\mathcal{S}^R\big)\Big)$$

Using the OZ equations for the reference system, the structure factors become

$$\mathcal{S}^R = \mathcal{I} + \widetilde{\mathcal{H}}^R = \big(\mathcal{I} - \tilde{\mathcal{C}}^R\big)^{-1}$$

and thus we find

$$\begin{aligned} \mathcal{I} - \Delta\tilde{\mathcal{C}}\mathcal{S}^R &= \mathcal{I} - \Delta\tilde{\mathcal{C}}\big(\mathcal{I} - \tilde{\mathcal{C}}^R\big)^{-1} \\ &= \big(\mathcal{I} - \tilde{\mathcal{C}}^R - \Delta\tilde{\mathcal{C}}\big)\big(\mathcal{I} - \tilde{\mathcal{C}}^R\big)^{-1} \\ &= \big(\mathcal{I} - \tilde{\mathcal{C}}\big)\big(\mathcal{I} - \tilde{\mathcal{C}}^R\big)^{-1} \end{aligned}$$

and therefore

$$\ln\det\big(\mathcal{I} - \Delta\tilde{\mathcal{C}}\mathcal{S}^R\big) = \ln\det\big(\mathcal{I} - \tilde{\mathcal{C}}\big) - \ln\det\big(\mathcal{I} - \tilde{\mathcal{C}}^R\big). \tag{5.6}$$

Taking the partial derivatives yields

$$\frac{\partial}{\partial\Delta\tilde{c}_{ij}(k)}\mathrm{tr}\big(\Delta\tilde{\mathcal{C}}\mathcal{S}^R\big) = \sqrt{\rho_i\rho_j}\,\mathcal{S}^R_{ij}$$

and

$$\begin{aligned}\frac{\partial}{\partial\Delta\tilde{c}_{ij}(k)}\ln\det\left(\mathcal{I}-\Delta\tilde{\mathcal{C}}\mathcal{S}^R\right) &= \frac{1}{\det(\mathcal{I}-\tilde{\mathcal{C}})}\frac{\partial\det(\mathcal{I}-\tilde{\mathcal{C}})}{\partial\Delta\tilde{c}_{ij}(k)}\\ &= \frac{1}{\det(\mathcal{I}-\tilde{\mathcal{C}})}\frac{\partial\det(\delta_{kl}-\sqrt{\rho_k\rho_l}\,\tilde{c}_{kl})}{\partial\Delta\tilde{c}_{ij}(k)}.\end{aligned}$$

We evaluate the determinant by expansion by cofactors[1] with respect to the i^{th} row

$$\begin{aligned}\frac{1}{\det(\mathcal{I}-\tilde{C})}\frac{\partial}{\partial\Delta\tilde{c}_{ij}(k)}\Big(\,&(\delta_{i1}-\sqrt{\rho_1\rho_i}\,\tilde{c}_{i1})(\delta_{1i}-\sqrt{\rho_1\rho_i}\,\tilde{c}_{1i})^{\wedge}+\\ &+(\delta_{i2}-\sqrt{\rho_2\rho_i}\,\tilde{c}_{i2})(\delta_{2i}-\sqrt{\rho_2\rho_i}\,\tilde{c}_{2i})^{\wedge}+\cdots\\ &\cdots+(\delta_{in}-\sqrt{\rho_n\rho_i}\,\tilde{c}_{in})(\delta_{ni}-\sqrt{\rho_n\rho_i}\,\tilde{c}_{ni})^{\wedge}\Big),\end{aligned}$$

where $(\ldots)^{\wedge}$ denotes the cofactor.

Since the cofactors appearing in this formula are obtained by deleting the i^{th} row of the matrix, $\Delta\tilde{c}_{ij}$ does not occur in these factors, we only have to perform the differentiation in the preceding factor and obtain

$$\frac{\partial}{\partial\Delta\tilde{c}_{ij}(k)}\ln\det\left(\mathcal{I}-\Delta\tilde{\mathcal{C}}\mathcal{S}^R\right)=\frac{1}{\det(\mathcal{I}-\tilde{\mathcal{C}})}\Big(-\sqrt{\rho_i\rho_j}\,(\delta_{ji}-\sqrt{\rho_i\rho_j}\,\tilde{c}_{ji})^{\wedge}\Big).$$

If we use the fact that the inverse of a matrix can be calculated via

$$\left(A^{-1}\right)_{lk}=\frac{\hat{a}_{lk}}{\det A}$$

this yields

$$\frac{\partial}{\partial\Delta\tilde{c}_{ij}(k)}\ln\det\left(\mathcal{I}-\Delta\tilde{\mathcal{C}}\mathcal{S}^R\right)=-\sqrt{\rho_i\rho_j}\left((\mathcal{I}-\tilde{\mathcal{C}})^{-1}\right)_{ij}.$$

---

[1] Laplace expansion formula with respect to the i^{th} row: The determinant of an $n\times n$ matrix $A=(a_{ij})$ is

$$\det A=a_{i1}\widehat{a}_{1i}+a_{i2}\widehat{a}_{2i}+\cdots+a_{in}\widehat{a}_{ni}.$$

The cofactor $\widehat{a}_{kl}$ is defined as

$$\widehat{a}_{kl}=(-1)^{k+l}\det S_{lk}$$

where for each pair (l,k), $l,k=1,\ldots,n$ the matrix S_{lk} denotes a $(n-1)\times(n-1)$ matrix which is obtained from A by deleting the l^{th} row and k^{th} column.

Collecting these results and using the OZ equations we obtain

$$\begin{aligned} 2(2\pi)^3 \frac{\delta \mathcal{F}}{\delta \Delta \tilde{c}_{ij}(k)} &= \sqrt{\rho_i \rho_j} \Big(\underbrace{-\mathcal{S}^R}_{-\mathcal{I}-\widetilde{\mathcal{H}}^R} + \underbrace{(\mathcal{I}-\widetilde{\mathcal{C}})^{-1}}_{\mathcal{I}+\widetilde{\mathcal{H}}} \Big)_{ij} \\ &= \sqrt{\rho_i \rho_j}\, \Delta \widetilde{\mathcal{H}}_{ij} = \rho_i \rho_j \Delta \tilde{h}_{ij}. \end{aligned}$$

The factor 2 in the case $i \neq j$ of formula 5.5 can be understood from the following argument: Due to the symmetry relation $\mathcal{C} = \mathcal{C}^T$

$$\frac{\delta \mathcal{F}}{\delta \Delta \tilde{c}_{ij}(k)} = \frac{\delta \mathcal{F}}{\delta \Delta \tilde{c}_{ij}(k)} + \frac{\delta \mathcal{F}}{\delta \Delta \tilde{c}_{ji}(k)} = \frac{1}{2(2\pi)^3} 2 \rho_i \rho_j \Delta \tilde{h}_{ij}(k).$$

q.e.d.

Thermodynamic properties of the system can be obtained from the approximation of the excess Helmholtz free energy density which is given by

$$\mathcal{F}^{\text{ORPA}} = -\frac{\beta F_{\text{ex}}}{V} = \mathcal{F}^R + f_{\text{HTA}} + \mathcal{F},$$

where $\mathcal{F}^R$ is the excess free energy density of the reference system, and f_{HTA} is the high-temperature approximation correction,

$$f_{\text{HTA}} = \frac{1}{2} \sum_{ij} \rho_i \rho_j \int \mathbf{dr} g_{ij}^R(r) \Delta c_{ij}(r).$$

We can rewrite the ORPA free energy in terms of the direct correlation functions only by using eq. 5.6 in the second term of $\mathcal{F}$, eq. 5.4, and by collecting the HTA term and the first term of $\mathcal{F}$

$$\begin{aligned} &\frac{1}{2} \sum_{ij} \int \mathbf{dr} \rho_i \rho_j g_{ij}^R(r) \Delta c_{ij}(r) - \frac{1}{2(2\pi)^3} \sum_{ij} \int \mathbf{dk} \sqrt{\rho_i \rho_j} \Delta \tilde{c}_{ij}(k) \left(\delta_{ij} + \sqrt{\rho_i \rho_j} \tilde{h}_{ij}^R(k) \right) \\ &= \frac{1}{2} \sum_{ij} \rho_i \rho_j \Delta \tilde{c}_{ij}(k) \Big|_{k=0} - \frac{1}{2} \sum_i \rho_i \Delta c_{ii}(r) \Big|_{r=0} \\ &\qquad + \frac{1}{2} \sum_{i,j} \rho_i \rho_j \int \mathbf{dr}\, h_{ij}^R(r) \Delta c_{ij}(r) - \frac{1}{2} \sum_{i,j} \frac{\rho_i \rho_j}{(2\pi)^3} \int \mathbf{dk}\, \tilde{h}_{ij}^R(k) \Delta \tilde{c}_{ij}(k) \\ &\qquad = \frac{1}{2} \sum_{i,j} \rho_i \rho_j \Delta \tilde{c}_{ij}(k) \Big|_{k=0} - \frac{1}{2} \sum_i \rho_i \Delta c_{ii}(r) \Big|_{r=0}, \end{aligned}$$

where we have used the Parseval theorem[2] to see that the last two integrals cancel.

We finally obtain

$$\mathcal{F}^{\mathrm{ORPA}} = \mathcal{F}^{R} + \frac{1}{2}\sum_{i,j} \rho_i \rho_j \Delta\tilde{c}_{ij}(k)\Big|_{k=0} - \frac{1}{2}\sum_{i} \rho_i \Delta c_{ii}(r)\Big|_{r=0}$$
$$-\frac{1}{2(2\pi)^3}\int \mathbf{dk}\left(\ln\det\big(\mathcal{I}-\tilde{\mathcal{C}}(k)\big) - \ln\det\big(\mathcal{I}-\tilde{\mathcal{C}}^{R}(k)\big)\right). \qquad (5.7)$$

5.2 ORPA for the replicated system

We now apply these equations to the replicated system (see [25]). The ORPA free energy of the replicated system, which is an equilibrium mixture of $(s{+}1)$-components with the symmetry relations 2.16 is obtained from 5.7 to be

$$\begin{aligned}
&\mathcal{F}^{\mathrm{ORPA},rep}(s)\\
&= \mathcal{F}^{R,rep}(s) + \frac{1}{2}\Big[\rho_0^2\, \Delta\tilde{c}_{00}^{rep}(k;s) + 2s\rho_0\rho_1\Delta\tilde{c}_{01}^{rep}(k;s)\\
&\qquad\qquad + s\rho_1^2\Delta\tilde{c}_{11}^{rep}(k;s) + s(s-1)\rho_1^2\Delta\tilde{c}_{12}^{rep}(k;s)\Big]_{k=0}\\
&\quad -\frac{1}{2}\Big[\rho_0\Delta c_{00}^{rep}(r;s) + s\rho_1\Delta c_{11}^{rep}(r;s)\Big]_{r=0} \qquad (5.8)\\
&\quad -\frac{1}{2(2\pi)^3}\int \mathbf{dk}\Big[\ln\det\big(\mathcal{I}-\tilde{\mathcal{C}}^{rep}(k;s)\big) - \ln\det\big(\mathcal{I}-\tilde{\mathcal{C}}^{R,rep}(k;s)\big)\Big]
\end{aligned}$$

where the symmetric matrix $\big(\mathcal{I}-\tilde{\mathcal{C}}^{rep}(k;s)\big)$ has the following special form (for notational simplicity we omit the s and k dependence and the index ‘rep’ indicating that quantities belong to the replicated system)

---

[2] The Parseval theorem states that, if for a function $f(t)$ and $|f(t)|^2$ the integral over the interval $(-\infty,+\infty)$ exists then

$$\int_{-\infty}^{+\infty} |f(t)|^2\, dt = \frac{1}{2\pi}\int_{-\infty}^{+\infty} |\tilde{f}(k)|^2\, dk;$$

for a function $g(t)$ which satisfies the same conditions as $f(t)$ we therefore obtain

$$\int_{-\infty}^{+\infty} f(t) g^{\star}(t)\, dt = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \tilde{f}(k)\tilde{g}^{\star}(k)\, dk.$$

$$\begin{pmatrix} 1-\rho_0\tilde{c}_{00} & -\sqrt{\rho_0\rho_1}\,\tilde{c}_{01} & -\sqrt{\rho_0\rho_1}\,\tilde{c}_{01} & \cdots & -\sqrt{\rho_0\rho_1}\,\tilde{c}_{01} \\ & 1-\rho_1\tilde{c}_{11} & -\rho_1\tilde{c}_{12} & \cdots & -\rho_1\tilde{c}_{12} \\ & & 1-\rho_1\tilde{c}_{11} & \ddots & \vdots \\ & & & \ddots & -\rho_1\tilde{c}_{12} \\ & & & & 1-\rho_1\tilde{c}_{11} \end{pmatrix}.$$

By exploiting the symmetry properties of this matrix, computation of the determinant gives

$$\begin{aligned} \ln\det\Big(\mathcal{I}-\tilde{\mathcal{C}}^{rep}(k;s)\Big) &= (s-1)\ln\Big[1-\rho_1\Big(\tilde{c}_{11}^{rep}(s)-\tilde{c}_{12}^{rep}(s)\Big)\Big] \\ &+ \ln\Big[1-\rho_0\tilde{c}_{00}^{rep}(s)\Big]\Big[1-\rho_1\tilde{c}_{11}^{rep}(s)-\rho_1(s-1)\tilde{c}_{12}^{rep}(s)-s\rho_0\rho_1(\tilde{c}_{01}^{rep})^2(s)\Big]. \end{aligned}$$

5.3 ORPA for the quenched system

We now have to find the correct limiting case to obtain the ORPA free energy for the quenched system (see [25]). Since we study only the case of hard-sphere or randomly centred matrix particles where $\Delta\phi_{00}=0$ we obtain

$$\begin{aligned} c_{00}(r) &= c_{00}^{R}(r) \\ c_{01}(r) &= c_{01}^{R}(r)+\Delta c_{01}(r) \\ c_{11}(r) &= c_{11}^{R}(r)+\Delta c_{11}(r) \\ c_{12}(r) &= c_{12}^{R}(r), \end{aligned} \tag{5.9}$$

where we have used the fact that particles belonging to different replicas do not interact ($\phi_{12}(r)=0$) to obtain the last equation. From eq. 5.9 it follows that

$$c_c(r)=c_c^R(r)+\Delta c_{11}(r).$$

The core conditions are

$$\begin{aligned} \Delta h_{01}(r) &= 0 \\ \Delta h_{11}(r) &= 0. \end{aligned}$$

Using

$$\bar{F}_1 = \lim_{s\to 0} \frac{d}{ds} F^{rep}(s)$$

the ORPA free energy is obtained from

$$\mathcal{F}^{\text{ORPA}} = \lim_{s\to 0} \frac{d}{ds} \mathcal{F}^{\text{ORPA},rep}(s). \tag{5.10}$$

This result can also be obtained from the following considerations. Generalising eq. 5.5 to the replicated system and using its symmetry properties we obtain

$$\frac{\delta \mathcal{F}^{rep}}{\delta \Delta \tilde{c}_{ij}^{rep}(k;s)} = \frac{2-\delta_{ij}}{2(2\pi)^3} \rho_i \rho_j s \Delta \tilde{h}_{ij}^{rep}(k;s), \quad ij = 01, 11.$$

With eqs. 2.14 and 2.15 we find

$$\begin{aligned} \frac{2-\delta_{ij}}{2(2\pi)^3} \rho_i \rho_j \Delta \tilde{h}_{ij}(k) &= \frac{2-\delta_{ij}}{2(2\pi)^3} \rho_i \rho_j \lim_{s\to 0} \frac{d}{ds} s \Delta \tilde{h}_{ij}^{rep}(k;s) \\ &= \lim_{s\to 0} \frac{d}{ds} \frac{\delta \mathcal{F}^{rep}}{\delta \Delta \tilde{c}_{ij}^{rep}(k;s)} \\ &= \frac{\delta}{\delta \Delta \tilde{c}_{ij}(k)} \lim_{s\to 0} \frac{d}{ds} \mathcal{F}^{rep}(s), \quad ij = 01, 11 \end{aligned}$$

and in order to obtain the relation

$$\frac{\delta \mathcal{F}}{\delta \Delta \tilde{c}_{ij}(k)} = \frac{2-\delta_{ij}}{2(2\pi)^3} \rho_i \rho_j \Delta \tilde{h}_{ij}(k), \quad ij = 01, 11$$

we have to set

$$\mathcal{F} = \lim_{s\to 0} \frac{d}{ds} \mathcal{F}^{rep}(s).$$

Taking the limiting case 5.10 of eq. 5.8 yields

$$\begin{aligned} \mathcal{F}^{\text{ORPA}}\left[\Delta\tilde{c}\right] = \mathcal{F}^{R} &+ \frac{1}{2}\left[\rho_1^2 \Delta\tilde{c}_{11}(k) + 2\rho_0\rho_1\Delta\tilde{c}_{01}(k)\right]_{k=0} - \frac{1}{2}\rho_1 \Delta c_{11}(r)\Big|_{r=0} \\ &- \frac{1}{2(2\pi)^3} \int \mathbf{dk} \left[\ln\Big(1 - \rho_1 \tilde{c}_c(k)\Big) - \frac{\rho_1}{1-\rho_1\tilde{c}_c(k)} \Big(\tilde{c}_b^R(k) + \rho_0 \tilde{c}_{01}^2(k)\chi(k)\Big) \right. \\ &\left. - \ln\Big(1 - \rho_1 \tilde{c}_c^R(k)\Big) + \frac{\rho_1}{1-\rho_1\tilde{c}_c^R(k)} \Big(\tilde{c}_b^R(k) + \rho_0 \left(\tilde{c}_{01}^R(k)\right)^2 \chi(k)\Big) \right], \end{aligned} \tag{5.11}$$

where $\chi(k) = \Big(1 + \rho_0 \tilde{h}_{00}(k)\Big)$.

As it can be shown, this functional satisfies

$$\frac{\delta \mathcal{F}^{\mathrm{ORPA}}}{\delta \Delta c_{01}(r)} = \rho_0 \rho_1 \left(g_{01}^R(r) + \Delta h_{01}(r) \right) \tag{5.12}$$

$$\frac{\delta \mathcal{F}^{\mathrm{ORPA}}}{\delta \Delta c_{11}(r)} = \frac{1}{2} \rho_1^2 \left(g_{11}^R(r) + \Delta h_{11}(r) \right) . \tag{5.13}$$

Note that $\mathcal{F}^{\mathrm{ORPA}}$ also contains the HTA-approximation which yields the terms $g_{01}^R(r)$ and $g_{11}^R(r)$. Since $g_{01}^R(r)$ and $g_{11}^R(r)$ are equal to zero in the core region one can equivalently minimise $\mathcal{F}^{\mathrm{ORPA}}$ instead of $\mathcal{F}$.

5.4 ORPA for the binary fluid in a porous medium

The generalisation of the ORPA presented in the previous sections to the case of a binary fluid is straightforward. We start with the calculation of the free energy for the replicated system within the ORPA, and then we take the correct limiting case to obtain the free energy of the quenched system.

5.4.1 ORPA for the replicated system

We apply eq. 5.7 to a $(2s + 1)$-component equilibrium mixture with the symmetry relations 2.35 and obtain

$$\begin{aligned}
&\mathcal{F}^{\mathrm{ORPA},rep}(s) \\
&= \mathcal{F}^{R,rep}(s) + \frac{1}{2} \Big[\rho_0^2 \Delta \tilde{c}_{00}^{rep}(k;s) + s\rho_1^2 \Delta \tilde{c}_{11}^{rep}(k;s) + s\rho_2^2 \Delta \tilde{c}_{22}^{rep}(k;s) \\
&\quad + s(s-1) \left(\rho_1^2 \Delta \tilde{c}_{13}^{rep}(k;s) + \rho_1 \rho_2 \Delta \tilde{c}_{14}^{rep}(k;s) + \rho_2^2 \Delta \tilde{c}_{24}^{rep}(k;s) \right) \\
&\quad + 2s\rho_0\rho_1 \Delta \tilde{c}_{01}^{rep}(k;s) + 2s\rho_0\rho_2 \Delta \tilde{c}_{02}^{rep}(k;s) + 2s\rho_1\rho_2 \Delta \tilde{c}_{12}^{rep}(k;s) \Big]_{k=0} \\
&\quad - \frac{1}{2} \Big[\rho_0 \Delta c_{00}^{rep}(r;s) + s\rho_1 \Delta c_{11}^{rep}(r;s) + s\rho_2 \Delta c_{22}^{rep}(r;s) \Big]_{r=0} \\
&\quad - \frac{1}{2(2\pi)^3} \int dk \left[\ln \det\left(\mathcal{I} - \tilde{\mathcal{C}}^{rep}(k;s) \right) - \ln \det\left(\mathcal{I} - \tilde{\mathcal{C}}^{R,rep}(k;s) \right) \right]
\end{aligned}$$

where the symmetric matrix $\mathcal{I} - \widetilde{\mathcal{C}}^{rep}(k; s)$ has the following special form (for notational simplicity we omit the k and s dependence and the index 'rep' indicating that quantities belong to the replicated system)

$$\mathcal{I} - \tilde{\mathcal{C}}^{rep}(k;s) =$$

$$\begin{pmatrix}
1-\rho_0\tilde{c}_{00} & -\sqrt{\rho_0\rho_1}\,\tilde{c}_{01} & -\sqrt{\rho_0\rho_2}\,\tilde{c}_{02} & -\sqrt{\rho_0\rho_1}\,\tilde{c}_{01} & -\sqrt{\rho_0\rho_2}\,\tilde{c}_{02} & -\sqrt{\rho_0\rho_1}\,\tilde{c}_{01} & \cdots & -\sqrt{\rho_0\rho_1}\,\tilde{c}_{01} & -\sqrt{\rho_0\rho_2}\,\tilde{c}_{02} \\
 & 1-\rho_1\tilde{c}_{11} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{12} & -\rho_1\tilde{c}_{13} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} & -\rho_1\tilde{c}_{13} & \cdots & -\rho_1\tilde{c}_{13} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} \\
 & & 1-\rho_2\tilde{c}_{22} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} & -\rho_2\tilde{c}_{24} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} & \cdots & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} & -\rho_2\tilde{c}_{24} \\
 & & & 1-\rho_1\tilde{c}_{11} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{12} & -\rho_1\tilde{c}_{13} & \cdots & -\rho_1\tilde{c}_{13} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} \\
 & & & & 1-\rho_2\tilde{c}_{22} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} & \cdots & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} & -\rho_2\tilde{c}_{24} \\
 & & & & & \ddots & \ddots & \vdots & \vdots \\
 & & & & & & 1-\rho_2\tilde{c}_{22} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{14} & -\rho_2\tilde{c}_{24} \\
 & & & & & & & 1-\rho_1\tilde{c}_{11} & -\sqrt{\rho_1\rho_2}\,\tilde{c}_{12} \\
 & & & & & & & & 1-\rho_2\tilde{c}_{22}
\end{pmatrix}$$

By using the symmetry properties of the matrix, we obtain for the determinant

$$\begin{aligned}
&\ln\det\Big(\mathcal{I}-\tilde{\mathcal{C}}^{rep}(k;s)\Big)\\
&=(s-1)\ln\Bigg[\Big(1-\rho_1\big(\tilde{c}^{rep}_{11}(s)-\tilde{c}^{rep}_{13}(s)\big)\Big)\Big(1-\rho_2\big(\tilde{c}^{rep}_{22}(s)-\tilde{c}^{rep}_{24}(s)\big)\Big)\\
&\qquad\qquad\qquad\qquad-\rho_1\rho_2\Big(\tilde{c}^{rep}_{12}(s)-\tilde{c}^{rep}_{22}(s)\Big)^2\Bigg]\\
&\quad+\ln\Bigg\{\Big(1-\rho_0\tilde{c}^{rep}_{00}(s)\Big)\Bigg[\Big(1-\rho_1\tilde{c}^{rep}_{11}(s)-\rho_1(s-1)\tilde{c}^{rep}_{13}(s)\Big)\times\\
&\qquad\Big(1-\rho_2\tilde{c}^{rep}_{22}(s)-\rho_2(s-1)\tilde{c}^{rep}_{24}(s)\Big)-\rho_1\rho_2\Big(\tilde{c}^{rep}_{12}(s)+(s-1)\tilde{c}^{rep}_{14}(s)\Big)^2\Bigg]\\
&\quad-s\rho_0\rho_1\Big(\tilde{c}^{rep}_{01}(s)\Big)^2\Big(1-\rho_2\tilde{c}^{rep}_{22}(s)-(s-1)\tilde{c}^{rep}_{24}(s)\Big)^2\\
&\quad-2s\rho_0\rho_1\rho_2\tilde{c}^{rep}_{01}(s)\tilde{c}^{rep}_{02}(s)\Big(\tilde{c}^{rep}_{12}(s)+(s-1)\tilde{c}^{rep}_{14}(s)\Big)\\
&\quad-s\rho_0\rho_2\Big(\tilde{c}^{rep}_{02}(s)\Big)^2\Big(1-\rho_1\tilde{c}^{rep}_{11}(s)-(s-1)\tilde{c}^{rep}_{13}(s)\Big)^2\Bigg\}\,.
\end{aligned}$$

5.4.2 ORPA for the quenched system

Also in the case of a binary fluid we restrict our considerations to systems with hard-sphere or randomly centred matrix particles, which brings along that $\Delta c_{00}(r)=0$. Most importantly, since the particles belonging to different replicas do not interact, one has $\phi_{13}=\phi_{14}=\phi_{24}=0$ and therefore

$$\begin{aligned}
c_{00}(r)&=c^R_{00}(r)\\
c_{ij}(r)&=c^R_{ij}(r)+\Delta c_{ij}(r) &&\text{for } i,j=01,02,11,12,22\\
c_{ij}(r)&=c^R_{ij}(r) &&\text{for } i,j=13,14,24\ .
\end{aligned}$$

Using eq. 5.10, one finally obtains

$$\begin{aligned}
\mathcal{F}^{\mathrm{ORPA}}\left[\Delta\tilde{c}\right]=\mathcal{F}^R+\frac{1}{2}\Big[&\rho_1^2\Delta\tilde{c}_{11}(k)+\rho_2^2\Delta\tilde{c}_{22}(k)\\
&+2\rho_0\rho_1\Delta\tilde{c}_{01}(k)+2\rho_0\rho_2\Delta\tilde{c}_{02}(k)+2\rho_1\rho_2\Delta\tilde{c}_{12}(k)\Big]_{k=0}\\
&-\frac{1}{2}\Big[\rho_1\Delta c_{11}(r)+\rho_2\Delta c_{22}(r)\Big]_{r=0}-\\
\frac{1}{2(2\pi)^3}\int\mathbf{dk}\Bigg\{\ln\Big[&\Big(1-\rho_1(\tilde{c}_{11}-\tilde{c}_{13})\Big)\Big(1-\rho_1(\tilde{c}_{22}-\tilde{c}_{24})\Big)-\rho_1\rho_2\Big(\tilde{c}_{12}-\tilde{c}_{14})\Big)^2\Big]
\end{aligned}$$

$$
\begin{aligned}
&-\frac{1}{\Big(1-\rho_1(\tilde{c}_{11}-\tilde{c}_{13})\Big)\Big(1-\rho_2(\tilde{c}_{22}-\tilde{c}_{24})\Big)-\rho_1\rho_2\Big(\tilde{c}_{12}-\tilde{c}_{14}\Big)^2}\times\\
&\Bigg[\rho_1\tilde{c}_{13}\Big(1-\rho_2(\tilde{c}_{22}-\tilde{c}_{24})\Big)+\rho_2\tilde{c}_{24}\Big(1-\rho_1(\tilde{c}_{11}-\tilde{c}_{13})\Big)+2\rho_1\rho_2\tilde{c}_{14}(\tilde{c}_{12}-\tilde{c}_{14})\\
&\qquad+\frac{\rho_0}{1-\rho_0\tilde{c}_{00}}\Big(\rho_1\tilde{c}_{01}^2\Big(1-\rho_2(\tilde{c}_{22}-\tilde{c}_{24})\Big)+\rho_2\tilde{c}_{02}^2\Big(1-\rho_1(\tilde{c}_{11}-\tilde{c}_{13})\Big)\\
&\qquad\qquad+2\rho_1\rho_2\tilde{c}_{01}\tilde{c}_{02}(\tilde{c}_{12}-\tilde{c}_{14})\Big)\Bigg]\Bigg\}+\\
&\frac{1}{2(2\pi)^3}\int\mathbf{dk}\Bigg\{\ln\Bigg[\Big(1-\rho_1(\tilde{c}_{11}^R-\tilde{c}_{13}^R)\Big)\Big(1-\rho_1(\tilde{c}_{22}^R-\tilde{c}_{24}^R)\Big)-\rho_1\rho_2\Big(\tilde{c}_{12}^R-\tilde{c}_{14}^R\Big)^2\Bigg]\\
&-\frac{1}{\Big(1-\rho_1(\tilde{c}_{11}^R-\tilde{c}_{13}^R)\Big)\Big(1-\rho_2(\tilde{c}_{22}^R-\tilde{c}_{24}^R)\Big)-\rho_1\rho_2\Big(\tilde{c}_{12}^R-\tilde{c}_{14}^R\Big)^2}\times\\
&\Bigg[\rho_1\tilde{c}_{13}^R\Big(1-\rho_2(\tilde{c}_{22}^R-\tilde{c}_{24}^R)\Big)+\rho_2\tilde{c}_{24}^R\Big(1-\rho_1(\tilde{c}_{11}^R-\tilde{c}_{13}^R)\Big)+2\rho_1\rho_2\tilde{c}_{14}^R(\tilde{c}_{12}^R-\tilde{c}_{14}^R)\\
&\qquad+\frac{\rho_0}{1-\rho_0\tilde{c}_{00}^R}\Big(\rho_1(\tilde{c}_{01}^R)^2\Big(1-\rho_2(\tilde{c}_{22}^R-\tilde{c}_{24}^R)\Big)+\rho_2(\tilde{c}_{02}^R)^2\Big(1-\rho_1(\tilde{c}_{11}^R-\tilde{c}_{13}^R)\Big)\\
&\qquad\qquad+2\rho_1\rho_2\tilde{c}_{01}^R\tilde{c}_{02}^R(\tilde{c}_{12}^R-\tilde{c}_{14}^R)\Big)\Bigg]\Bigg\}
\end{aligned}
$$

It can be checked explicitly that this functional reduces to the one of the one-component case by using the two limiting cases introduced in subsection 2.7.3. Further it can be shown that

$$
\frac{\delta\mathcal{F}^{\mathrm{ORPA}}}{\delta\Delta c_{ij}(r)}=\frac{2-\delta_{ij}}{2}\rho_i\rho_j\left(g_{ij}^R(r)+\Delta h_{ij}(r)\right).
$$

5.5 Numerical method

We present the numerical method to solve the ORPA for the one-component fluid in a matrix. The generalisation to the two-component fluid should be clear.

5.5.1 Deepest descent method

In order to solve the ORPA, we have to find the minimum of $\mathcal{F}$ (or $\mathcal{F}^{\mathrm{ORPA}}$) with respect to variations of the perturbative potentials $\Delta c_{01}(r)$ and $\Delta c_{11}(r)$ inside the core regions. This can be done for instance with the deepest descent method (see [33]). We start the iteration at a point $\left(\Delta c_{01}^{(0)}(r), \Delta c_{11}^{(0)}(r)\right)$. In the i^{th} step of the iteration we move from point $\left(\Delta c_{01}^{(i)}(r), \Delta c_{11}^{(i)}(r)\right)$ to $\left(\Delta c_{01}^{(i+1)}(r), \Delta c_{11}^{(i+1)}(r)\right)$ in the negative direction of the local gradient, which is given by $-\left(\frac{\delta\mathcal{F}}{\delta\Delta c_{01}(r)}, \frac{\delta\mathcal{F}}{\delta\Delta c_{11}(r)}\right)$, until we have reached the minimum within a certain accuracy. Thus in each iteration we correct the perturbative potentials $\Delta c_{01}(r)$ and $\Delta c_{11}(r)$ inside the hard cores according to

$$\begin{aligned}
\Delta c_{01}^{(i+1)}(r) &= \Delta c_{01}^{(i)}(r) - \lambda_{01}\Delta h_{01}(r) \quad \text{for} \quad r < \sigma_{01} \\
\Delta c_{11}^{(i+1)}(r) &= \Delta c_{11}^{(i)}(r) - \lambda_{11}\Delta h_{11}(r) \quad \text{for} \quad r < \sigma_{11},
\end{aligned}$$

where the parameters λ_{01} and λ_{11} have to be chosen in such a way that the numerical method is both stable and rapid. This can be achieved by changing the parameters according to the error

$$\xi = \left(\int_{r<\sigma_{01}} dr\, r^2 \Delta h_{01}^2(r) + \int_{r<\sigma_{11}} dr\, r^2 \Delta h_{11}^2(r)\right)^{1/2}.$$

We start with a small value of $(\lambda_{01}, \lambda_{11})$ to be on the safe side. As the error decreases we increase the parameters $(\lambda_{01}, \lambda_{11})$ to speed up convergence.

Note that the deepest descent method does not require the calculation of the functional itself but only of its derivatives $\Delta h_{01}(r)$ and $\Delta h_{11}(r)$ (see eqs. 5.12 and 5.13) which can be obtained directly from the residual ROZ equations 5.2. The explicit calculation of the functional is only necessary when determining thermodynamic properties.

5.5.2 Numerical algorithm

1. The reference correlation functions are obtained by solving the ROZ integral equations in the HNC or PY approximation using the LMV algorithm. For a chosen number of grid points N and a grid size Δr

we calculate the reference functions and its Fourier transforms on a set of equally spaced discrete points r_i and k_j.

2. We choose first estimates $\Delta C_{01}^{(0)}$ and $\Delta C_{11}^{(0)}$ inside the cores and set

$$\Delta C_{\alpha\beta}(r_i) = \Delta C_{\alpha\beta}^{(0)}(r_i) \ \text{for}\, i : r_i < \sigma_{\alpha\beta}, \quad \alpha\beta = 01, 11$$

while the ORPA fixes the corrections of the direct correlations outside the core region

$$\Delta C_{\alpha\beta}(r_i) = -\beta r_i \phi_{\alpha\beta}(r_i) \ \text{for}\, i : r_i > \sigma_{\alpha\beta}, \quad \alpha\beta = 01, 11.$$

3. We insert the Fourier transforms of the direct correlation functions $\Delta\tilde{C}_{01}(k_j)$ and $\Delta\tilde{C}_{11}(k_j)$ in the residual ROZ equations 5.2, i.e.

$$\begin{aligned}
\Delta\tilde{S}_{01}(k_j) &= \Delta\widetilde{H}_{01}(k_j) - \Delta\tilde{C}_{01}(k_j) \\
&= \widetilde{H}_{01}(k_j) - \widetilde{H}_{01}^R(k_j) - \Delta\tilde{C}_{01}(k_j) \\
&= \frac{\tilde{C}_{01}(k_j)\chi(k_j)}{k_j - \rho_1\tilde{C}_{11}(k_j) + \rho_1\tilde{C}_{12}(k_j)} - \widetilde{H}_{01}^R(k_j) - \Delta\tilde{C}_{01}(k_j) \\
\Delta\tilde{S}_{11}(k_j) &= \Delta\widetilde{H}_{11}(k_j) - \Delta\tilde{C}_{11}(k_j) \\
&= \widetilde{H}_{11}(k_j) - \widetilde{H}_{11}^R(k_j) - \Delta\tilde{C}_{11}(k_j) \\
&= \frac{k_j^2\tilde{C}_{11}(k_j) + \rho_0\tilde{C}_{01}(k_j)^2\chi(k_j) - k_j\rho_1\left(\tilde{C}_{11}(k_j) - \tilde{C}_{12}(k_j)\right)^2}{\left(k_j - \rho_1\tilde{C}_{11}(k_j) + \rho_1\tilde{C}_{12}(k_j)\right)^2} \\
&\qquad -\widetilde{H}_{11}^R(k_j) - \Delta\tilde{C}_{11}(k_j).
\end{aligned}$$

4. We take the inverse Fourier transforms of $\Delta\tilde{S}_{01}(k_j)$ and $\Delta\tilde{S}_{11}(k_j)$ to calculate the local gradient of the functional via

$$\begin{aligned}
\Delta H_{01}(r_i) &= \Delta S_{01}(r_i) + \Delta C_{01}(r_i) \\
\Delta H_{11}(r_i) &= \Delta S_{11}(r_i) + \Delta C_{11}(r_i).
\end{aligned}$$

5. A new estimate for $\Delta C_{\alpha\beta}(r_i)$ is obtained by means of the deepest descent method

$$\Delta C_{\alpha\beta}(r_i) - \lambda_{\alpha\beta}\Delta H_{\alpha\beta}(r_i) \to \Delta C_{\alpha\beta}(r_i) \quad \text{for} \quad i : r_i < \sigma_{\alpha\beta}, \quad \alpha\beta = 01, 11.$$

6. If the error

$$\xi = \left(\left(\sum_{i:r_i<\sigma_{01}} \left(\Delta H_{01}(r_i) \right)^2 + \sum_{i:r_i<\sigma_{11}} \left(\Delta H_{11}(r_i) \right)^2 \right) \Delta r \right)^{1/2} > 10^{-5}$$

   we return to operation 3.

7. The result is combined with the reference functions to give the direct correlation functions of the perturbed system

$$\left.\begin{aligned} C_{01} &= C_{01}^R(r_i) + \Delta C_{01}(r_i) \\ C_{11} &= C_{11}^R(r_i) + \Delta C_{11}(r_i) \\ C_{12} &= C_{12}^R(r_i) \end{aligned}\right\} i = 1, \ldots, N-1$$

   and the ROZ equations 3.17 - 3.19 finally yield the pair correlation functions

$$h_{01}(r_i),\ h_{11}(r_i) \text{ and } h_{12}(r_i), \quad i = 1, \cdots, N-1.$$

Note that both in the LMV algorithm and in the deepest method we only calculate the inverse Fourier transform of the functions $\widetilde{S}_{\alpha\beta}(k)$ which are continuous functions since they can be written as convolution integrals.

5.6 Thermodynamic properties within the ORPA

5.6.1 Chemical potential

From eq. 4.11 we obtain the chemical potential for the fluid inside the matrix via

$$\beta\mu_1 = \left(\frac{\partial \left(\beta \overline{F}_1 \right)}{\partial N_1} \right)_{V,T,\rho_0} .$$

If we separate the free energy into an <u>id</u>eal and an <u>ex</u>ess part – where the excess part contains all contributions to $\overline{F}_1$ which arise from interactions between the particles – we obtain the corresponding division for the chemical potential

$$\beta\mu_1 = \beta\mu_1^{id} + \beta\mu_1^{ex}.$$

The ideal part is (see e.g. [29])

$$\beta\mu_1^{id} = \ln\rho_1 + 3\ln\Lambda_1,$$

where

$$\Lambda_1 = \left(\frac{2\pi\beta\hbar^2}{m_1}\right)^{1/2}$$

is the de Broglie thermal wavelength of the fluid without any restriction. We choose the mass m_1 of the fluid particles so that the ideal contribution to the chemical potential of the fluid reduces to

$$\beta\mu_1^{id} = \ln\rho_1.$$

The excess part can be obtained via integration of the compressibility equation 4.16

$$\beta\mu_1^{ex}(\rho_1) = \beta\mu_1^{ex}(\rho_1\!=\!0) - \int_0^{\rho_1} \tilde{c}_c(k\!=\!0;\rho_1')d\rho_1'. \tag{5.14}$$

The knowledge of the integration constant is irrelevant for the phase diagram. However, if we want to compare the prediction for the chemical potential for a given theory with results from simulations an expression for $\beta\mu_1^{ex}(\rho_1\!=\!0)$, i.e. the chemical potential of the fluid at infinite dilution in the matrix, is required.

Due to

$$\mu_1^{ex}(\rho_1) = \left(\frac{\partial\left(\beta\overline{F}_1^{ex}\right)}{\partial N_1}\right)_{V,T,\rho_0} = \overline{F}_1^{ex}(N_1+1,T,V,\rho_0) - \overline{F}_1^{ex}(N_1,T,V,\rho_0)$$

$\mu_1^{ex}(\rho_1 = 0)$ is just the change in the excess part of the free energy if we introduce a single fluid particle into a matrix of density ρ_0 [34].

If we consider a system with pure hard-sphere interactions, and the fluid and matrix particles are of equal size ($\sigma_{00} = \sigma_{01} = \sigma_{11}$), $\mu_1^{ex}(\rho_1 = 0)$ is thus equal to the excess part of the chemical potential of an equilibrium system of hard spheres with density ρ_0. We can therefore use the Carnahan-Starling expression for the chemical potential:

Integration of the Carnahan-Starling equation of state for a system of hard spheres [38]

$$\frac{\beta P}{\rho} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3},$$

where η is the packing fraction

$$\eta = \frac{1}{6}\pi\rho\sigma^3,$$

yields an expression for the excess Helmholtz free energy

$$\frac{\beta F^{ex}}{N} = \int_0^{\eta}\left(\frac{\beta P}{\rho}-1\right)\frac{d\eta'}{\eta'} = \frac{\eta\,(4-3\eta)}{(1-\eta)^2}.$$

Using the Gibbs-Duhem relation we obtain the excess part of the chemical potential

$$\beta\mu^{ex} = \frac{\beta F^{ex}}{N} + \frac{\beta P^{ex}}{\rho} = \frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3}$$

and thus

$$\beta\mu_1^{ex}(\rho_1=0) = \frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3},$$

where

$$\eta = \frac{1}{6}\pi\rho_0\sigma_{00}^3$$

is the packing fraction of the matrix particles.

For randomly centred matrix particles ($\sigma_{00}=0, \sigma_{01}=\sigma_{11}$) Kaminsky and Monson [39] derived

$$\beta\mu_1^{ex}(\rho_1=0) = \frac{4\pi\rho_0\sigma_{01}^3}{3}.$$

In the ORPA the chemical potential separates into three contributions

$$\beta\mu_1 = \beta\mu_1^{id} + \beta\mu_1^{ex,R} + \left(\beta\mu_1^{ex} - \beta\mu_1^{ex,R}\right),$$

where $\mu_1^{ex,R}$ is the excess part of the chemical potential of the reference system, which can be calculated via integration of the compressibility equation of state, and $\left(\beta\mu_1^{ex} - \beta\mu_1^{ex,R}\right)$ is the correction due to the perturbing potential.

In the mean spherical approximation (MSA), which is obtained from the ORPA by replacing the exact reference functions by their Percus Yevick counterparts, we obtain a closed expression for the excess chemical potential of the fluid, which can be derived by differentiating the excess free energy density with respect to ρ_1

$$\begin{aligned}\left(\beta\mu_1^{ex} - \beta\mu_1^{ex,R}\right) &= -\frac{\partial\left(\mathcal{F}^{\text{ORPA}} - \mathcal{F}^{R}\right)}{\partial\rho_1} \\ &= -\left[\rho_1\Delta\tilde{c}_{11}(k) + \rho_0\Delta\tilde{c}_{01}(k)\right]_{k=0} + \frac{1}{2}\left[\Delta c_{11}(r)\right]_{r=0}.\end{aligned} \tag{5.15}$$

This expression can also be obtained by applying the general expression for fully equilibrated fluid mixtures derived by Høye and Stell [40] to the replicated system

$$\begin{aligned}-\beta\rho_1\Delta\mu_1^{ex,rep}(s) = &\left[\rho_0\rho_1\Delta\tilde{c}_{01}^{rep}(k;s) + \rho_1^2\Delta\tilde{c}_{11}^{rep}(k;s) + (s-1)\rho_1^2\underbrace{\Delta\tilde{c}_{12}^{rep}(k;s)}_{=0}\right]_{k=0} \\ &+\left[\frac{1}{2}\rho_1\underbrace{\Delta h_{11}(r)}_{=0} - \frac{1}{2}\rho_1\Delta c_{11}(r)\right]_{r=0}.\end{aligned}$$

Taking the limit $s \to 0$ (see eq. 4.19) of this expression yields eq. 5.15.

In a similar way we obtain the chemical potential for the case of a two-component fluid in a porous matrix in the MSA

$$\begin{aligned}-\beta\rho_1\Delta\mu_1^{ex,rep}(s) = &\Big[\rho_0\rho_1\Delta\tilde{c}_{01}^{rep}(k;s) + \rho_1^2\Delta\tilde{c}_{11}^{rep}(k;s) + \rho_1\rho_2\Delta\tilde{c}_{12}^{rep}(k;s) \\ &+ (s-1)\rho_1^2\underbrace{\Delta\tilde{c}_{13}^{rep}(k;s)}_{=0} + (s-1)\rho_1\rho_2\underbrace{\Delta\tilde{c}_{14}^{rep}(k;s)}_{=0}\Big]_{k=0} \\ &+ \frac{1}{2}\Big[\rho_1\underbrace{\Delta h_{11}(r)}_{=0} - \rho_1\Delta c_{11}(r)\Big]_{r=0} \\ -\beta\rho_2\Delta\mu_2^{ex,rep}(s) = &\Big[\rho_0\rho_2\Delta\tilde{c}_{02}^{rep}(k;s) + \rho_2^2\Delta\tilde{c}_{22}^{rep}(k;s) + \rho_1\rho_2\Delta\tilde{c}_{12}^{rep}(k;s) \\ &+ (s-1)\rho_2^2\underbrace{\Delta\tilde{c}_{24}^{rep}(k;s)}_{=0} + (s-1)\rho_1\rho_2\underbrace{\Delta\tilde{c}_{14}^{rep}(k;s)}_{=0}\Big]_{k=0} \\ &+ \frac{1}{2}\Big[\rho_1\underbrace{\Delta h_{22}(r)}_{=0} - \rho_2\Delta c_{22}(r)\Big]_{r=0}.\end{aligned}$$

Taking the limit $s \to 0$ yields

$$\beta\Delta\mu_1^{ex,rep} = -\left[\rho_0\Delta\tilde{c}_{01}^{rep}(k) + \rho_1\Delta\tilde{c}_{11}^{rep}(k) + \rho_2\Delta\tilde{c}_{12}^{rep}(k)\right]_{k=0}$$

$$\begin{aligned} &+\frac{1}{2}\Big[\rho_1 \Delta c_{11}(r)\Big]_{r=0} \\ \beta\Delta\mu_2^{ex,rep} &= -\Big[\rho_0 \Delta\tilde{c}_{02}^{rep}(k) + \rho_2 \Delta\tilde{c}_{22}^{rep}(k) + \rho_1 \Delta\tilde{c}_{12}^{rep}(k)\Big]_{k=0} \\ &+\frac{1}{2}\Big[\rho_2 \Delta c_{22}(r)\Big]_{r=0}. \end{aligned}$$

5.6.2 Pressure

From eq. 4.11 we obtain the thermodynamic pressure of the fluid via

$$P_1 = -\left(\frac{\partial \overline{F}_1}{\partial V}\right)_{T,N_1,\rho_0}.$$

Again, we separate the pressure P_1 into an ideal and excess part

$$P_1 = P_1^{id} + P_1^{ex},$$

where the ideal part is

$$\beta P_1^{id} = \rho_1,$$

and the excess part can be obtained by integration of the compressibility equation 4.15

$$\beta P^{ex}(\rho_1) = \beta P^{ex}(\rho_1 \!=\! 0) - \int_0^{\rho_1} \rho_1' \tilde{c}_c(k\!=\!0; \rho_1') d\rho_1'. \tag{5.16}$$

In the ORPA the pressure can be split (similar to the case of the chemical potential) into three contributions

$$P_1^{ex,R} + \left(\beta P_1^{ex} - \beta P_1^{ex,R}\right).$$

The contribution due to the perturbation potential $\left(\beta P_1^{ex} - \beta P_1^{ex,R}\right)$ is obtained from the Gibbs-Duhem relation using eqs. 5.11 and 5.15

$$\begin{aligned} &\beta P_1^{ex} - \beta P_1^{ex,R} = \mathcal{F}^{\text{ORPA}} - \mathcal{F}^R + \rho_1\left(\beta\mu_1^{ex} - \beta\mu_1^{ex,R}\right) \\ &= -\frac{\rho_1^2}{2}\left[\tilde{c}_{11}(k\!=\!0) - \tilde{c}_{11}^R(k\!=\!0)\right] \\ &\quad -\frac{1}{2(2\pi)^3}\int \mathbf{dk}\left[\ln\left(1-\rho_1\tilde{c}_c(k)\right) - \frac{\rho_1}{1-\rho_1\tilde{c}_c(k)}\left(\tilde{c}_b^R(k) + \rho_0\tilde{c}_{01}^2(k)\chi(k)\right)\right. \\ &\qquad\qquad \left. - \ln\left(1-\rho_1\tilde{c}_c^R(k)\right) + \frac{\rho_1}{1-\rho_1\tilde{c}_c^R(k)}\left(\tilde{c}_b^R(k) + \rho_0\left(\tilde{c}_{01}^R(k)\right)^2\chi(k)\right)\right]. \end{aligned}$$

Chapter 6

Numerical Results

In this chapter we present some results obtained from the numerical solution of the ROZ equations in the various approximations presented in the preceding sections. The correlation functions obtained within the ORPA and those obtained from integral equation theory for a Lennard-Jones system are compared with results from Monte Carlo (MC) simulations [41]. Furthermore, we apply the ORPA to a hard-sphere system with square-well interaction to obtain vapour-liquid coexistence curves.

6.1 Correlation functions

In the following examples we consider a completely repulsive hard-sphere interaction between the matrix and the fluid particles (y=0). The fluid-fluid interactions decompose into a hard-sphere part and a Lennard-Jones tail (see section 3.4) with $\sigma_{00}=\sigma_{01}=\sigma_{11}=\sigma$. In figure 6.1 we compare the results for the fluid-fluid pair distribution function obtained from a solution of the ROZ equations in the HNC approximation with the results from MC simulations [41] for densities $\rho_0^\star=0.05$ and $\rho_1^\star=0.465$ at a temperature $T^\star=1.5$. We see that the HNC approximation overestimates the correlation functions near the contact. Results obtained within other approximations are shown in figures 6.2 and 6.3, where the MC simulations are compared with results obtained within the ORPA. The ROZ equations of the reference system were solved in the PY (figure 6.2) and in the HNC (figure 6.3) approximation. Figure 6.2 shows that the MSA underestimates the correlation function near the contact. Furthermore, the oscillations are slightly out of phase compared with the Monte Carlo results. Better agreement with simulation results are obtained within the ORPA, where the reference correlation functions are calculated in the HNC approximation (see figure 6.3).

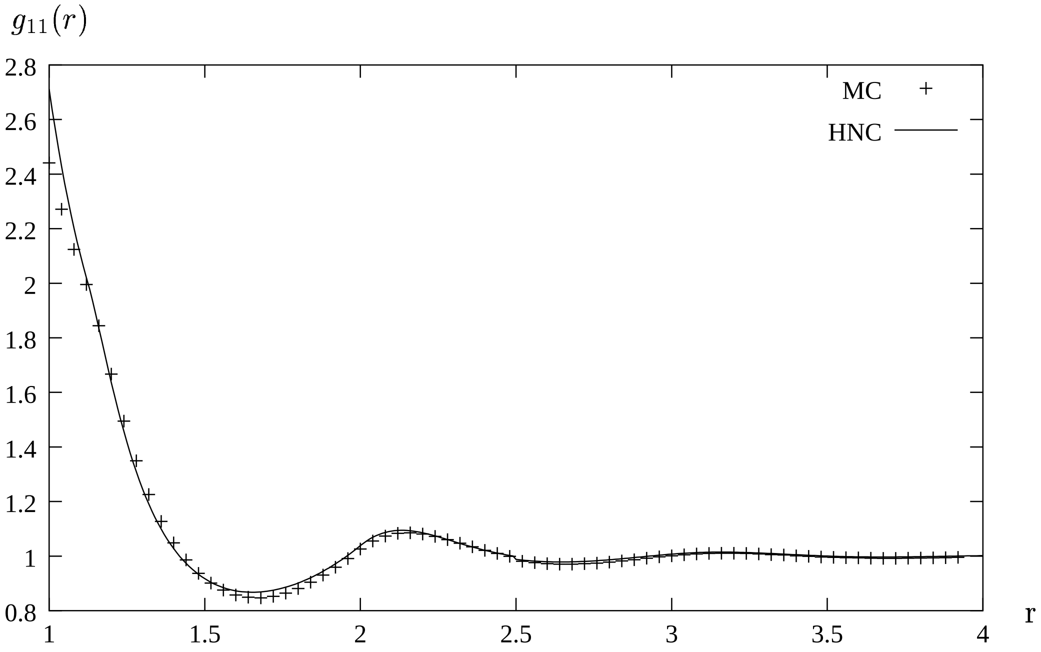

Figure 6.1: Fluid-fluid pair distribution function $g_{11}(r)$ for a hard-sphere fluid with attractive Lennard-Jones tail in a hard-sphere equilibrium matrix. The system is characterised by $\sigma_{00}=\sigma_{01}=\sigma_{11}=\sigma$, $y=0$, $\rho_0\sigma^3=0.05$, $\rho_1\sigma^3=0.465$ and $T^\star = 1.5$. The line represents HNC integral equation results and the crosses the results from MC simulations [41].

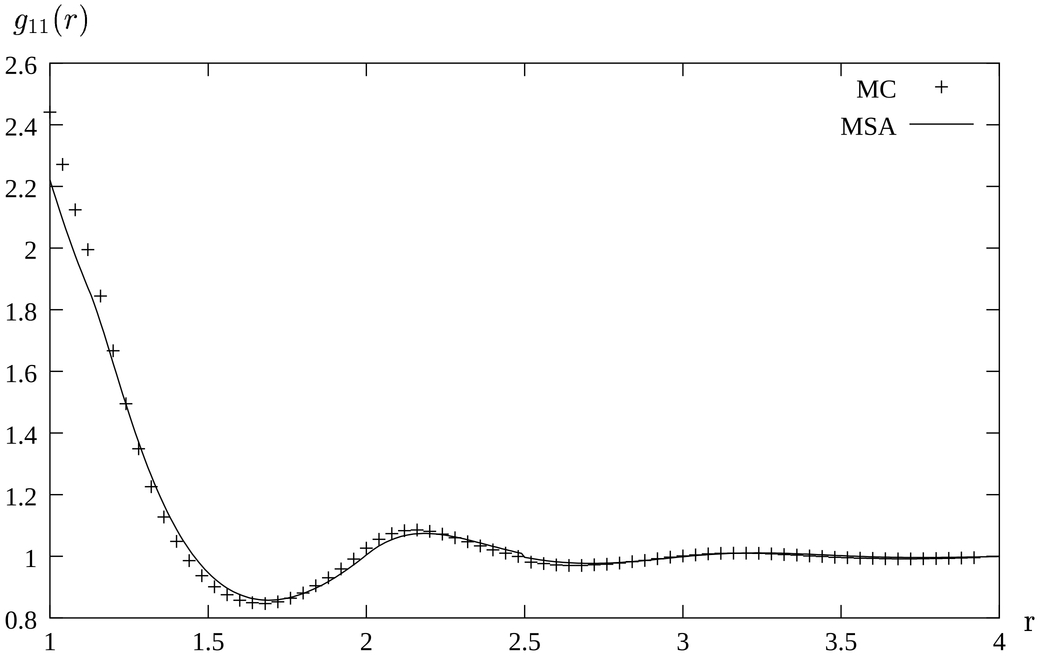

Figure 6.2: Same as in figure 6.1, but now the MC simulations results are compared with $g_{11}(r)$ obtained within the ORPA, the structure of the hard-sphere reference system is calculated within the PY-approximation.

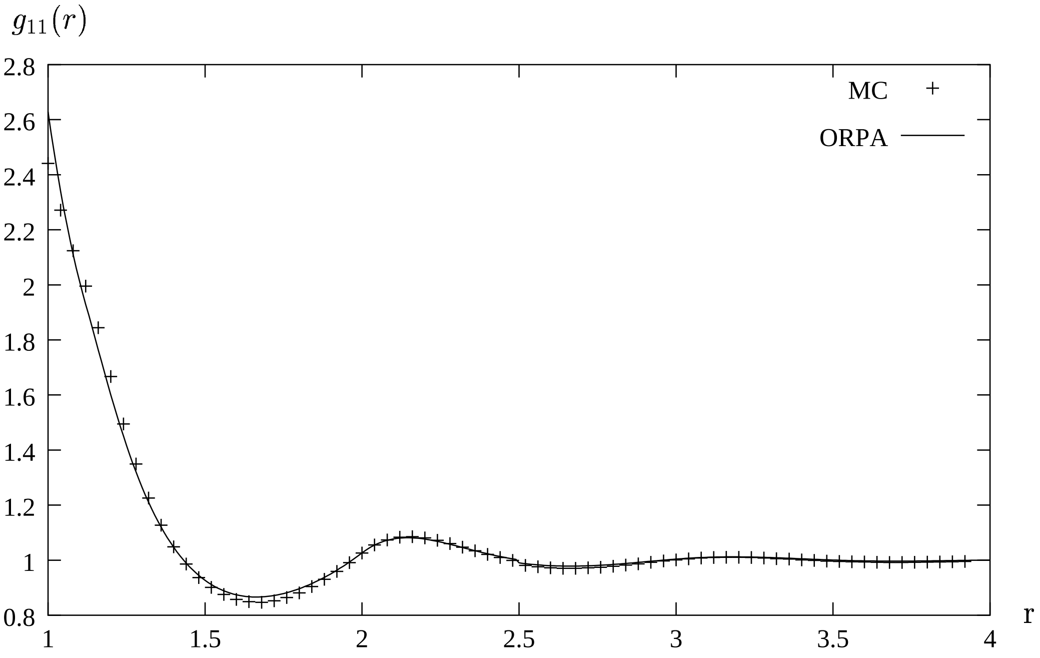

Figure 6.3: Same as in figure 6.1, but now the MC simulations results are compared with $g_{11}(r)$ obtained within the ORPA, the structure of the hard-sphere reference system is calculated within the HNC-approximation.

6.2 Phase diagrams

At a given temperature $T^\star = \frac{kT}{\epsilon_{11}}$, the densities ρ_1' and ρ_1'' of two coexisting phases of a single-component fluid are determined from the solution of the following system of equations

$$\begin{aligned} P_1(\rho_1') &= P_1(\rho_1'') \qquad (6.1)\\ \mu_1(\rho_1') &= \mu_1(\rho_1''). \end{aligned}$$

Therefore, if we want to determine the phase diagram we have to calculate the pressure and chemical potential of the fluid as functions of the density (see subsections 5.6.1 and 5.6.2). In our calculations, the reference-system correlation functions were obtained from a PY-solution of the ROZ equations using the LMV algorithm (see section 3.2). A grid size in r-space of $0.01\sigma_{11}$ and 1024 points were used in the calculations. Pressure and chemical potential of the reference system were obtained by integration of the compressibility equation of state (see eqs. 5.14 and 5.16). The trapezoidal rule was used to perform the numerical integration of eqs. 5.14 and 5.16 and the spacing in ρ_1 was $\Delta\rho_1\sigma_{11}^3 = 0.005$. Once the correlation functions of the reference system were obtained, we minimised the free energy with respect to variations of the perturbative potentials inside the core regions using the deepest descent method (see subsection 5.5.1) to compute the corrections of the correlation functions; furthermore we calculate the correction terms due to the perturbation of the chemical potential and the pressure. To perform the numerical integration which was required in the calculation of the pressure and to evaluate the correlation functions and their Fourier transforms at $r = 0$ and $k = 0$ we used the Simpson rule. Finally, the coupled set of equations 6.1 was solved with the NR-technique (see Appendix B).

The system which we consider now consists of an equilibrium hard-sphere matrix. Fluid-matrix and fluid-fluid interactions decompose in a hard-sphere part and an attractive square-well tail ($y=1, \sigma_{00}=\sigma_{01}=\sigma_{11}=\sigma$). A series of isotherms, i.e., $\mu_1^\star = \frac{\mu_1}{kT}$ versus $\rho_1\sigma^3$, for a matrix density $\rho_0\sigma^3 = 0.2$ is shown in figure 6.4. Note that the curves have a loop similar to those observed in the van der Waals theory of equilibrium fluids, indicating liquid-vapour coexistence. This loop is replaced in the instable region by a horizontal line joining the two values of $\rho_1^\star$ at coexistence [42]. For $T^\star = 0.76$ no phase equilibrium could be observed, indicating that we are already above the critical temperature.

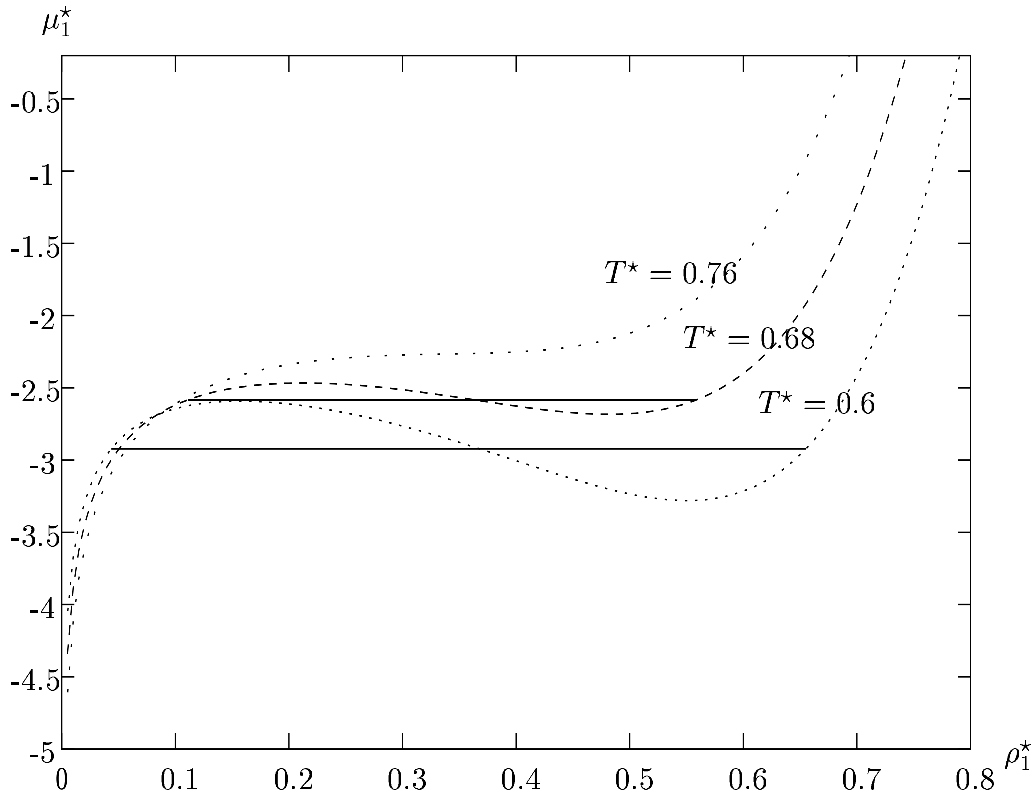

Figure 6.4: A series of isotherms of $\mu_1^\star = \frac{\mu_1}{kT}$ versus $\rho_1^\star$ at $\rho_0^\star = 0.2$ and $y = 1$ in an equilibrium hard-sphere matrix ($\sigma_{00} = \sigma_{01} = \sigma_{11} = \sigma$). Each curve is labelled with the corresponding values of $T^\star = \frac{kT}{\epsilon_{11}}$. The intersection points of these curves with the solid lines indicate the loci of the coexistence densities.

Figure 6.5 shows the phase diagram of a square-well fluid with $\gamma_{01} = \gamma_{11} = 1.25$ and $y = 1$ for different matrix densities in the $(T^\star, \rho_1^\star/(1 - \eta_0))$ plane. $\phi = 1 - \eta_0$ is the matrix porosity, i.e., the fraction of space not occupied by the matrix particles. The parameters of this example are exactly those as the ones used in a mean field theory approach by Ford and Glandt [24] for a square-well system. The figure shows that the critical point is shifted to lower densities and lower temperatures as the matrix density increases. Furthermore, we see that the liquid-vapour coexistence curves become narrower. From a qualitative point of view these results are in agreement with previous theoretical studies on square-well [24] and Lennard-Jones systems [25]. However, in a quantitative comparison with the results of Ford and Glandt we find that the values of the critical point differ substantially between the two methods.

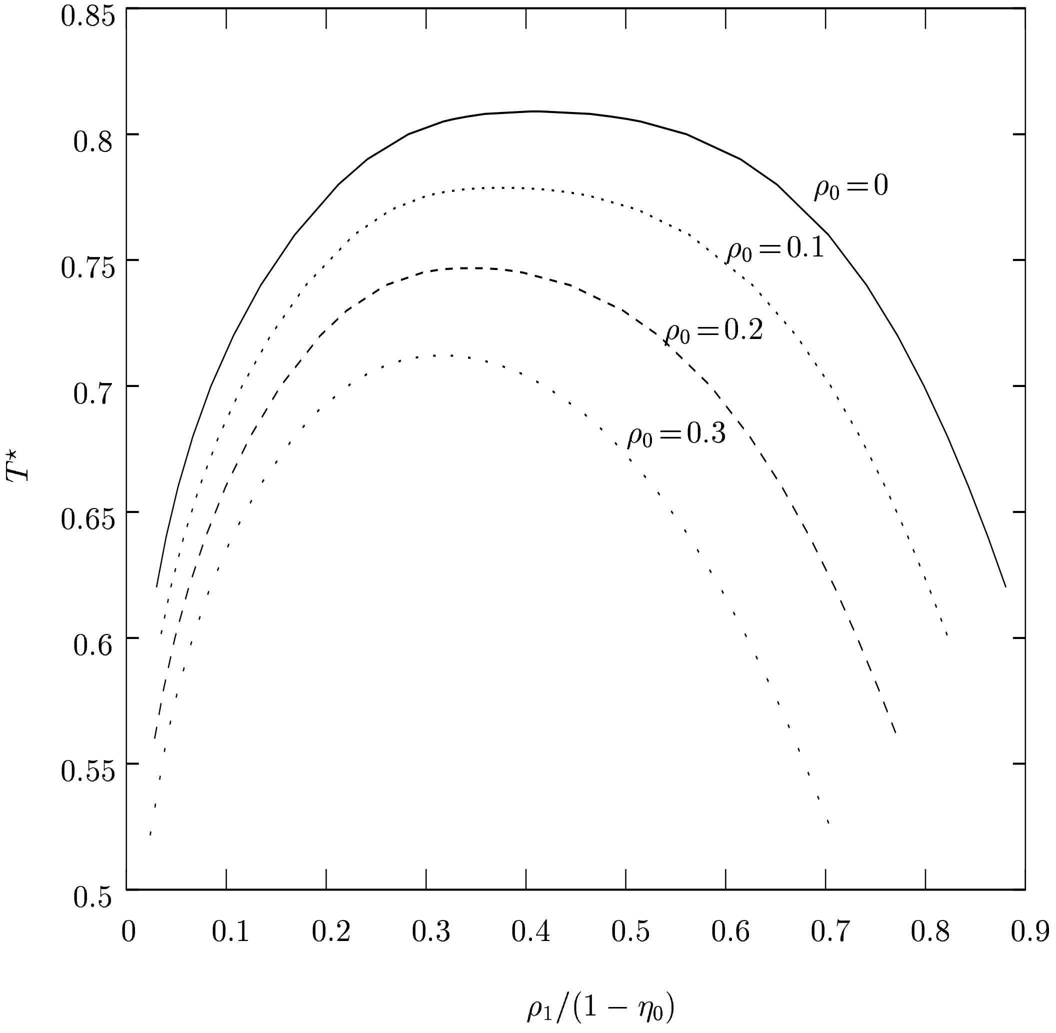

Figure 6.5: MSA predictions for the coexistence curves of a fluid in a hard-sphere matrix. The fluid-fluid and matrix-fluid interactions are assumed to be hard-sphere interactions with attractive square-well tails ($y = 1$, $\gamma_{01} = \gamma_{11} = 1.25$). Each curve is labelled with the corresponding value of ρ_0. The upper curve ($\rho_0 = 0$) represents the bulk fluid.

Chapter 7

Summary and conclusions

In this report we have discussed the physical properties of fluids adsorbed in porous media. Using the replica trick and the related formalism we have derived both structural and thermodynamic properties of fluid particles immersed in a disordered rigid matrix. So far, theoretical research has mainly been restricted to atomic, single-component fluids. In this study we have generalised the formalism to the case of a two-component fluid in a matrix. The replica method, combined with standard liquid state theory, allowed the development of integral equations for the correlation functions – the replica Ornstein Zernike equations – for a multicomponent fluid in a matrix. Furthermore, we have rewritten these equations in a compact matrix notation in which we were able to recover the structure of the one-component ROZ equations. Using the replica trick, we have also developed thermodynamic relations for a two-component fluid in a matrix: the Gibbs-Duhem relation, the virial equation, and the energy equation were derived. In addition, we presented a derivation of the compressibility equation which is based on density functional formalism.

In the present investigation of the phase behaviour of fluids adsorbed in a matrix we considered partly quenched systems where matrix-fluid and fluid-fluid interactions contain a hard-sphere part and an attractive tail which is treated as a perturbation. For such systems we have generalised a perturbation theory for a two-component fluid in a matrix: the optimised random phase approximation (ORPA) was extended to a two-component mixture in a quenched system. The perturbation theory approach has been applied to a single-component fluid in a matrix. The interparticle potential between fluid-fluid and fluid-matrix particles was assumed to consist of a hard-sphere part and an attractive square-well or a truncated Lennard-Jones tail.

For the Lennard-Jones fluid results for the fluid-fluid pair distribution functions in different approximations were compared with Monte Carlo simulations.

For the square-well fluid confined in a matrix liquid-vapour coexistence curves were obtained. In qualitative agreement with previous theoretical studies and experimental results of the phase behaviour of fluids confined in a disordered matrix it was found that the critical temperature, the critical density and the width of the coexistence curves decrease with increasing matrix density.

The approaches developed in this contribution allow widespread studies in this field which will be dealt with in the future: a systematic investigation of the phase behaviour of a square-well liquid with different ranges in a porous medium, or the determination of phase diagrams of binary liquids in a matrix obtained from a perturbative approach.

Danksagung

Meiner Familie möchte ich für die Unterstützung während des Studiums herzlich danken.

Gerhard Kahl bin ich zu großem Dank verpflichtet für die fachliche Betreuung meiner Diplomarbeit und sein Interesse an ihr, für seine Bereitschaft zur Beantwortung meiner Fragen, für die Ermöglichung des Auslandsaufenthaltes, und nicht zuletzt für das gute Arbeitsklima, das sehr zum Gelingen dieser Arbeit beigetragen hat.

Et puis je veux remercier Dominique Levesque, Jean-Jacques Weis et sa femme Elisabeth ainsique Martha Alvarez Fernandez qui ont fait mon séjour à Paris très agréable. Par leur savoir étendu ils ont augmenté ma comprehension de la physique des fluides et des musées de Paris.

Further I would like to thank Enrique Lomba who was so kind to put a Fortran program for the numerical solution of the ROZ equations at my disposal.

Nicht zuletzt möchte ich noch Joachim Schöll für wertvolle Hinweise, Hilfestellungen und seine Geduld danken.

Der Aufenthalt am Laboratoire de Physique Théorique et Hautes Energies an der Université de Paris-Sud wurde durch ein großzügiges Förderungsstipendium der technisch-naturwissenschaftlichen Fakultät der TU Wien ermöglicht.

Appendix A

Definitions and formulae of standard fluid theory

The replica trick relates thermodynamic quantities of the quenched system to those of an equilibrium mixture by taking a special limiting case. The advantage of this approach is the fact that the equilibrium mixture can be described with standard liquid state theories. Thus in the following we give a brief overview over those formulae and definitions of standard liquid state theory to which we refer in the text.

n-particle distribution function

The n-particle distribution function $g_N^{(n)}(\mathbf{r}^n)$ of a fluid consisting of N particles is defined in terms of the corresponding n-particle density by

$$g_N^{(n)}(\mathbf{r}^n) = \frac{\rho_N^{(n)}(\mathbf{r}^n)}{\prod\limits_{i=1}^{n} \rho_N^{(1)}(\mathbf{r}_i)}, \tag{A.1}$$

where $\rho_N^{(n)}(\mathbf{r}^n)$ is the probability density of finding a set of n particles at positions $\mathbf{r}^n = \{\mathbf{r}_1, \ldots, \mathbf{r}_n\}$ regardless of the positions of the remaining particles.

Pair distribution function and radial distribution function

If we consider formula A.1 for $n = 2$ we obtain the so called pair distribution function. Thus $\rho_1^{(1)}(\mathbf{r}_1)\rho_2^{(1)}(\mathbf{r}_2)g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\mathbf{dr}_1\mathbf{dr}_2$ is the probability of finding a particle in the infinitesimal volume $\mathbf{dr}_1$ at $\mathbf{r}_1$ and another one in $\mathbf{dr}_2$ at $\mathbf{r}_2$. If the system is isotropic and homogeneous, the pair distribution function $g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ is a function of the separation $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ only - called the radial distribution function and simply written as $g(r)$. $g(r)$ is the factor by which the mean density $\rho g(r)$ at a distance r from a reference particle situated in the origin deviates from the bulk density due to interactions between the particles. Since the repulsion between two particles is very large at small distances, $g \to 0$ as $r \to 0$. Further, at large distances, where particles are no longer influenced by the reference particle, $g \to 1$ as $r \to \infty$. In a typical simple liquid $g(r)$ is an oscillating function around 1 and shows a series of peaks (see e.g. fig. 6.1) which correspond to first neighbours, second neighbours distances, etc. and express the short range order that exists in a liquid. For two reasons the radial distribution function is of fundamental importance in fluid theory: Firstly thermodynamic functions of the fluid can be expressed in terms of it; secondly it is directly measurable by radiation scattering experiments.

Correlation functions and the OZ equation

The pair correlation or total correlation function is defined as

$$h^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = g^{(2)}(\mathbf{r}_1,\mathbf{r}_2) - 1 \tag{A.2}$$

It vanishes in the limit $r_{12} \to \infty$.

The direct correlation function $c^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ is related to the total correlation function via the OZ relation which has the form

$$h^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = c^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + \int \mathbf{dr_3}\, \rho^{(1)}(\mathbf{r}_3)c^{(2)}(\mathbf{r}_1,\mathbf{r}_3)h^{(2)}(\mathbf{r}_3,\mathbf{r}_2). \tag{A.3}$$

Iterative solution of eq. A.3 shows that the total correlation between particles 1 and 2 is due in part to the direct correlation between 1 and 2 but also to the indirect correlation propagated via increasingly large numbers of intermediate particles. If the system is homogeneous and isotropic the OZ equation simplifies to

$$h(r) = c(r) + \rho \int \mathbf{dr}' c(|\mathbf{r} - \mathbf{r}'|) h(r'). \tag{A.4}$$

Multicomponent OZ equations

The multicomponent generalisation of A.4 is

$$h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int \mathbf{dr}' c_{ik}(|\mathbf{r} - \mathbf{r}'|) h_{kj}(r') \tag{A.5}$$

where the sum on k runs over all components in the fluid.

In a matrix formulation eq. A.5 can be written as

$$\mathcal{H} = \mathcal{C} + \mathcal{C}\mathcal{H} \quad \text{with} \quad \mathcal{C} := (\hat{c}_{ij}) \quad \text{and} \quad \mathcal{H} := \left(\hat{h}_{ij}\right), \tag{A.6}$$

where $\hat{c}_{ij} := \sqrt{\rho_i \rho_j}\, c_{ij}$ and $\hat{h}_{ij} := \sqrt{\rho_i \rho_j}\, h_{ij}$ and the multiplications of the direct and total correlation functions have to be interpreted as convolution integrals. The matrices $\mathcal{H}$ and $\mathcal{C}$ satisfy the symmetry relations

$$\mathcal{H}^T = \mathcal{H} \quad \text{and} \quad \mathcal{C}^T = \mathcal{C}$$

which take into account the fact that the probability of finding a particle of species i at a distance r, given that a particle of species j is in the origin, is equal to the probability of observing a particle of species j at a distance r, given that a particle of species i is in the origin.

Structure factor

The structure factor of a fluid, which is related to the cross-sections for scattering of radiation, can be written as the Fourier transform of $h(r)$

$$S(k) = 1 + \rho \tilde{h}(k).$$

The partial structure factors of a system of more than one-component are defined as

$$S_{ij}(k) = \delta_{ij} + \sqrt{\rho_i \rho_j}\, \tilde{h}_{ij}(k). \tag{A.7}$$

or, in the simpler matrix formulation, as

$$\mathcal{S}(k) = \mathcal{I} + \widetilde{\mathcal{H}}(k).$$

Closure relations

In addition to the OZ equation an approximate closure relation, relating the total and direct correlation function, has to be provided, which can be derived either using graphical expansion or Taylor expansions of thermodynamic functionals (see [29]). It can be written in the general form

$$c(r) = f(\gamma(r), \phi(r)) \quad \text{with} \quad \gamma(r) = h(r) - c(r),$$

where f is the chosen approximate function and ϕ the pair potential.

For instance, in the Percus-Yevick (PY) approximation

$$f\left(\gamma(r)\right) = \left(e^{-\beta\phi(r)} - 1\right)\left(\gamma(r) + 1\right) \tag{A.8}$$

while in the hypernetted-chain (HNC) approximation

$$f\left(\gamma(r)\right) = e^{-\beta\phi(r) + \gamma(r)} - \gamma(r) - 1. \tag{A.9}$$

Appendix B

The NR-method

In order to find a root $x^\star$ of a single function $f(x)$, we start with an initial estimate $x^{(1)}$ and thereby can obtain an improved estimate $x^{(2)}$ by linearising the function $f(x)$ at the point $x^{(1)}$

$$t(x) = f\left(x^{(1)}\right) + \left(\frac{df}{dx}\right)_{x=x^{(1)}} \left(x - x^{(1)}\right);$$

we find the point $x^{(2)}$ where this tangent has its zero

$$x^{(2)} = x^{(1)} - \left(\frac{df}{dx}\right)^{-1}_{x=x^{(1)}} f\left(x^{(1)}\right).$$

We now generalise this algorithm to a set of N functions $\{f_i\}$ of N variables $\mathbf{x} = \{x_1, \ldots, x_N\}$; we wish to find a value $\mathbf{x}^\star$ at which the $\{f_i\}$ are zero:

$$\mathbf{f}\left(\mathbf{x}^\star\right) = \mathbf{0}.$$

From the initial estimate $\mathbf{x}^{(1)}$ one finds the improved estimate $\mathbf{x}^{(2)}$ according to

$$\mathbf{x}^{(2)} = \mathbf{x}^{(1)} - J^{-1}\Big|_{\mathbf{x}=\mathbf{x}^{(1)}} \mathbf{f}\left(\mathbf{x}^{(1)}\right)$$

where J is the Jacobian matrix

$$J = (J_{ij}) = \left(\frac{\partial f_i}{\partial x_j}\right). \tag{B.1}$$

One then iterates eq. B.1 to obtain successive approximations $\mathbf{x}^{(j)}$ with $\mathbf{x}^{(j)} \to \mathbf{x}^\star$. It is not necessary that the sequence $x^{(j)}$ tends towards $x^\star$. This is only the case if the initial estimate was chosen in the attractive region of $x^\star$.

Appendix C

ROZ equations for a two-component fluid

If we define

$$N := \Big[1 - \rho_1(\tilde{c}_{11} - \tilde{c}^b_{11}))(1 - \rho_2(\tilde{c}_{22} - \tilde{c}^b_{22})) - \rho_1\rho_2(\tilde{c}_{12} - \tilde{c}^b_{12})^2\Big]^{-1}$$

and use the convention

$$i, j \in \{1, 2\} \text{ and } j \neq i$$

the ROZ equations for the two-component fluid are

$$\tilde{\gamma}_{0i} = -\tilde{c}_{0i} + (1 + \rho_0 h_{00})\Big[\Big(1 - \rho_j(\tilde{c}_{jj} - \tilde{c}^b_{jj})\Big)\tilde{c}_{0i} + \rho_j(\tilde{c}_{ij} - \tilde{c}^b_{ij})\tilde{c}_{0j}\Big] \cdot N \tag{C.1}$$

$$\begin{aligned}\tilde{\gamma}_{ii} = -\tilde{c}_{ii} + \Big\{&\tilde{c}_{ii} - \rho_j\Big[2\tilde{c}_{ii}(\tilde{c}_{jj} - \tilde{c}^b_{jj}) - 2\tilde{c}_{ij}(\tilde{c}_{ij} - \tilde{c}^b_{ij}) + (\tilde{c}_{ij} - \tilde{c}^b_{ij})^2\Big]\\ &+\rho_j^2\Big[\tilde{c}_{ii}(\tilde{c}_{jj} - \tilde{c}^b_{jj})^2 - 2\tilde{c}_{ij}(\tilde{c}_{ij} - \tilde{c}^b_{ij})(\tilde{c}_{jj} - \tilde{c}^b_{jj}) + \tilde{c}_{jj}(\tilde{c}_{ij} - \tilde{c}^b_{ij})^2\Big]\\ &-\rho_i\Big[\tilde{c}_{ii} - \tilde{c}^b_{ii} - \rho_j(\tilde{c}_{ii} - \tilde{c}^b_{ii})(\tilde{c}_{jj} - \tilde{c}^b_{jj}) + \rho_j(\tilde{c}_{ij} - \tilde{c}^b_{ij})^2\Big]^2\\ &+\rho_0(1 + \rho_0 h_{00})\Big[\tilde{c}_{0i} - \rho_j\tilde{c}_{0i}(\tilde{c}_{jj} - \tilde{c}^b_{jj}) + \rho_j\tilde{c}_{0j}(\tilde{c}_{ij} - \tilde{c}^b_{ij})\Big]^2\Big\} \cdot N^2\end{aligned} \tag{C.2}$$

$$\begin{aligned}\tilde{\gamma}_{ij} = -\tilde{c}_{ij} + \Big\{&\rho_0(1 + \rho_0 h_{00})\Big[\tilde{c}_{0i} + \rho_j\tilde{c}_{0j}(\tilde{c}_{ij} - \tilde{c}^b_{ij}) - \rho_j\tilde{c}_{0i}(\tilde{c}_{jj} - \tilde{c}^b_{jj})\Big]\\ &\Big[\tilde{c}_{0j} + \rho_i\tilde{c}_{0i}(\tilde{c}_{ij} - \tilde{c}^b_{ij}) - \rho_i\tilde{c}_{0j}(\tilde{c}_{ii} - \tilde{c}^b_{ii})\Big]\end{aligned}$$

$$
\begin{aligned}
&+\rho_i\rho_j\Big[\tilde{c}_{ij}(\tilde{c}_{ij}-\tilde{c}^b_{ij})^2-2(\tilde{c}_{ij}-\tilde{c}^b_{ij})^3\Big]\\
&+\rho_i\tilde{c}^b_{ii}(\tilde{c}_{ij}-\tilde{c}^b_{ij})\Big[1-\rho_j(\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big]\\
&+\rho_j\tilde{c}^b_{jj}(\tilde{c}_{ij}-\tilde{c}^b_{ij})\Big[1-\rho_i(\tilde{c}_{ii}-\tilde{c}^b_{ii})\Big]\\
&+\tilde{c}_{ij}\Big[1-\rho_i(\tilde{c}_{ii}-\tilde{c}^b_{ii})\Big]\Big[1-\rho_2(\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big]\Bigg\}\cdot N^2
\end{aligned}
\tag{C.3}
$$

$$
\begin{aligned}
\tilde{\gamma}^b_{ii} = {} & -\tilde{c}^b_{ii}+\Bigg\{\Big[1-\rho_j(\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big]^2\tilde{c}^b_{ii}\\
&+2\rho_j(\tilde{c}_{ij}-\tilde{c}^b_{ij})\tilde{c}_{ij}\Big[1-\rho_j(\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big]\\
&+\rho_j(\tilde{c}_{ij}-\tilde{c}^b_{ij})^2\Big[-2+\rho_j(2\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big]\\
&+\rho_0(1+\rho_0 h_{00})\Big[\tilde{c}_{0i}-\rho_j\tilde{c}_{0i}(\tilde{c}_{jj}-\tilde{c}^b_{jj})+\rho_j\tilde{c}_{0j}(\tilde{c}_{ij}-\tilde{c}^b_{ij})\Big]^2\Bigg\}\cdot N^2
\end{aligned}
\tag{C.4}
$$

$$
\begin{aligned}
\tilde{\gamma}^b_{ij} = {} & -\tilde{c}^b_{ij}+\Bigg\{\rho_0(1+\rho_0 h_{00})\Big[\tilde{c}_{0j}+\rho_i\tilde{c}_{0i}(\tilde{c}_{ij}-\tilde{c}^b_{ij})-\rho_i\tilde{c}_{0j}(\tilde{c}_{ii}-\tilde{c}^b_{ii})\Big]\\
&\times\Big[\tilde{c}_{0i}+\rho_j\tilde{c}_{0j}(\tilde{c}_{ij}-\tilde{c}^b_{ij})-\rho_j\tilde{c}_{0i}(\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big]\\
&+\rho_i\Big[(\tilde{c}_{ij}-\tilde{c}^b_{ij})\tilde{c}_{ii}-\tilde{c}_{ij}(\tilde{c}_{ii}-\tilde{c}^b_{ii})\Big]\Big[1-\rho_j(\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big]\\
&+\rho_j\Big[(\tilde{c}_{ij}-\tilde{c}^b_{ij})\tilde{c}_{jj}-\tilde{c}_{ij}(\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big]\Big[1-\rho_i(\tilde{c}_{ii}-\tilde{c}^b_{ii})\Big]\\
&+\tilde{c}^b_{ij}\Big(1+\rho_i\rho_j(\tilde{c}_{ij}-\tilde{c}^b_{ij})^2-\rho_i\rho_j(\tilde{c}_{ii}-\tilde{c}^b_{ii})(\tilde{c}_{jj}-\tilde{c}^b_{jj})\Big)\Bigg\}\cdot N^2.
\end{aligned}
\tag{C.5}
$$

Bibliography

[1] S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity* (London: Academic Press, 1982)

[2] F. Brochard and P.G. de Gennes, J. Phys. (Paris) Lett., **Vol.** 44, 785 (1983)

[3] E. Pitard, M. L. Rosinberg, G. Stell, and G. Tarjus, Phys. Rev. Lett., **Vol.** 74, 4361 (1995)

[4] M. C. Goh, W. I. Goldburg, and C. M. Knobler Phys. Rev. Lett., **Vol.** 58, 1008 (1987)
S. B. Dierker and P. Wiltzius, Phys. Rev. Lett., **Vol.** 58, 1865 (1987)
P. Wiltzius, S. B. Dierker, and B. S. Dennis, Phys. Rev. Lett., **Vol.** 62, 804 (1989)
B. J. Frisken and D. S. Canell, Phys. Rev. Lett., **Vol.** 69, 632 (1992)

[5] A. P. Y. Wong and M. H. W. Chan, Phys. Rev. Lett., **Vol.** 65, 2567 (1990)

[6] L. Monette, A. Liu, and G. S. Grest, Phys. Rev. A, **Vol.** 46, 7664 (1992)

[7] R. Evans, J. Phys.: Condens. Matter, **Vol.** 2, 8989 (1990)

[8] W. G. Madden and E. G. Glandt, J. Stat. Phys., **Vol.** 51, 537 (1988)

[9] W. G. Madden, J. Chem. Phys., **Vol.** 96, 5422 (1992)

[10] E. Lomba, J. A. Given, G. Stell, J. J. Weis, and D. Levesque, Phys. Rev. E, **Vol.** 48, 233 (1993)

[11] J. A. Given and G. Stell, J. Chem. Phys., **Vol.** 97, 4573 (1992)

[12] J. A. Given, Phys. Rev. A **Vol.** 45, 816 (1992)
J. A. Given, J. Chem. Phys., **Vol.** 96, 2287 (1992)

[13] J. A. Given and G. Stell, Physica A, **Vol.** 209, 495 (1994)

[14] S. F. Edwards and P. W. Anderson, J. Phys. F, **Vol.** 5, 965 (1975)

[15] S. F. Edwards and C. Jones, J. Phys. A, **Vol.** 9, 1595 (1976)

[16] J. A. Given, J. Chem. Phys., **Vol.** 102, 2934 (1995)

[17] M. L. Rosinberg, G. Tarjus, and G. Stell, J. Chem. Phys., **Vol.** 100, 5172 (1995)

[18] E. Kierlik, M. L. Rosinberg, G. Tarjus, and P. Monson, J. Chem. Phys., **Vol.** 103, 4256 (1995)

[19] L. A. Fanti, E. D. Glandt, and W. G. Madden, J. Chem. Phys., **Vol.** 93, 5945 (1990)

[20] A. Meroni, D. Levesque, and J. J. Weis, J. Chem. Phys., **Vol.** 105, 1101 (1996)

[21] C. Vega, R. D. Kaminsky, and P. A. Monson, J. Chem. Phys., **Vol.** 99, 3003 (1993)

[22] K. S. Page and P. A. Monson, Phys. Rev. E, **Vol.** 54, R29 (1996)

[23] R. D. Kaminisky and P. A. Monson, Phys. Rev. E54, R29 (1996) Phys., **Vol.** 95, 2936 (1991)

[24] D. M. Ford and E. D. Glandt, J. Chem. Phys., **Vol.** 100, 2391 (1994)

[25] E. Kierlik, M. L. Rosinberg, G. Tarjus, and P. A. Monson, J. Chem. Phys., **Vol.** 106, 264 (1997)

[26] D. Bratko and A.K. Chakraborty, J. Chem. Phys., **Vol.** 104, 7700 (1996)

[27] B. Hribar, O. Pizio, A. Trokhymchuk, and V. Vlachy, J. Chem. Phys., **Vol.** 109, 2480 (1998)

[28] R. Evans, Adv. Phys., **Vol.** 28, 143 (1979)

[29] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (New York: Academic Press, 1986, 2^{nd} edition)

[30] M. J. Gillan, Molec. Phys., **Vol.** 38, 1781 (1979)

[31] S. Labik, A. Malijevsky, and P. Vonka, Molec. Phys., **Vol.** 56, 709 (1985)

[32] E. Lomba, J. Chem. Phys., **Vol.** 68, 87 (1989)

[33] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, 1988)

[34] D. M. Ford and E. D. Glandt, Phys. Rev. E, **Vol.** 50, 1280 (1994)

[35] B. D'Aguanno and R. Klein, J. Chem. Soc. Faraday Trans., **Vol.** 87, 379 (1991)

[36] H. C. Andersen and D. Chandler, J. Chem. Phys., **Vol.** 57, 1918 (1972)

[37] H. C. Andersen, D. Chandler and J. D. Weeks, J. Chem. Phys., **Vol.** 56, 3812 (1972)

[38] N. F. Carnahan and K.E. Starling, J. Chem. Phys., **Vol.** 51, 635 (1969)

[39] R. D. Kaminisky and P. A. Monson, J. Chem. Phys., **Vol.** 95, 2936 (1991)

[40] J. S. Høye and G. Stell, J. Chem. Phys., **Vol.** 67, 439 (1977)

[41] J. J. Weis, private communication

[42] T. L. Hill, *Statistical Thermodynamics* (Massachusetts: Addison-Wesley Publishing Company, 1960)