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Structure and thermodynamic properties of a polydisperse fluid in contact with a polydisperse matrix

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We present expressions that allow the determination of the structural and thermodynamic properties of a polydisperse liquid mixture in contact with a polydisperse matrix; polydispersity of the fluid and of the matrix are described by distribution functions $f_{\mathrm{f}}(\sigma)$ and $f_{\underline{\mathrm{m}}}(\underline{\sigma})$, where σ and $\underline{\sigma}$ characterize the size of the fluid and of the matrix particles. The formalism is based on the replica trick (to describe the properties of a fluid in contact with a matrix) and on the expansion of size-dependent functions in terms of orthogonal polynomials associated with the distribution functions $f_{\mathrm{f}}(\sigma)$ and $f_{\underline{\mathrm{m}}}(\underline{\sigma})$. In our expressions structural and thermodynamic properties are calculated from coefficient functions (of these expansions) which are obtained from a numerical solution of the generalized replica Ornstein–Zernike equations, solved along with a suitable closure relation.

1. Introduction

Over the past years considerable effort has been dedicated both experimentally and theoretically to the study of the structural and thermodynamic properties of fluids that are in contact with a porous matrix (for a recent overview see [1]). In qualitative (and sometimes even in quantitative) agreement between theoretical and experimental investigations it has been found that a matrix which occupies only a minute amount of volume can change the properties of the system drastically; this holds in particular for the phase behaviour of the fluid. Most of the (continuum) systems that have been studied up to now in theoretical investigations were simple fluids or binary mixtures, characterized by spherically symmetric potentials; in general, the fluid is in contact with a matrix, which is usually realized by a frozen configuration of a simple fluid or binary mixture. Only recently the theoretical concepts were generalized to systems where the particles are characterized by orientational potentials [2, 3]; although this generalization is expensive both with respect to conceptual efforts as well as to numerical costs, it represents an important step forward to a more realistic description of problems that are of technological relevance, such as catalysis, gas separation or purification.

The models based on simple fluids are certainly appropriate when describing atomic systems. However, when proceeding to mesoscopic systems, such as colloids, one has to take into account (size-) polydispersity of the particles as a characteristic feature of these systems. In this contribution we present a formalism that allows the description of the structural and thermodynamic properties of a polydisperse fluid mixture which is in contact with a polydisperse matrix.

This formalism is based on two successful concepts which have been proposed in recent years: the replica method and the orthogonal decomposition technique. The replica trick, on the one hand, was introduced by Given and Stell to liquid state physics to describe fluids in contact with a porous matrix [4–6]: it allows one to calculate the structural and thermodynamic properties of a fluid in contact with a porous matrix (partly quenched system) from those of an (artificial) fully annealed system (replicated system). In the most simple case, i.e. a one-component fluid in contact with a one-component matrix, the replicated system is a $(s+1)$-component system: it consists of the now mobile particles of the matrix and of s copies of the fluid; particles of different copies (replicas) are not allowed to interact with each other. Then, by taking the limit $s \to 0$ the structural and thermodynamic properties of the partly quenched system can be related to those of the replicated system, which, in turn, can be described by standard liquid state methods. This replica method has become undoubtedly *the* preferred theoretical tool to

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describe fluids in contact with a porous matrix and has been applied to a large variety of systems (see [1, 7]). The orthogonal decomposition technique, on the other hand, was introduced by Lado [8] to describe the structural and thermodynamic properties of a polydisperse system. Such a system can most conveniently be viewed as a mixture with an infinite number of components, characterized, for instance, by their diameter σ, which is now a continuous rather than a discrete variable. The mathematically rigorous concept which underlies our access to polydisperse systems was developed by Salacuse and Stell [9] and by Briano and Glandt [10]. In these formulations, σ is the realization of some random variable Σ, distributed according to a probability distribution $f_\Sigma(\sigma) = f(\sigma)$, which replaces the finite set of concentrations of the discrete components of a mixture; being a probability distribution function, $f(\sigma)$ is positive and normalized to one. Several numerical techniques that date back to the 1980s and 1990s were based on this formalism (for an overview see [11]). The orthogonal decomposition technique represents a very elegant and, at the same time, a numerically very efficient method to deal with polydispersity in liquid systems: in this concept, all σ-dependent functions (in particular the distribution functions and the interatomic potentials) are expanded in orthogonal polynomials $p_i(\sigma)$ associated with the weight function $f(\sigma)$. It should be pointed out that the same technique can further be applied to a much wider range of problems dealing both with internal and external degrees of freedom in fluid systems [12].

In this contribution we merge these two successful concepts and present expressions that allow the calculation of the structural and thermodynamic properties of a polydisperse fluid mixture in contact with a polydisperse matrix; we have restricted ourselves to particles with spherically symmetric interactions. It should be noted that for the special case of a *monodisperse* fluid of hard spheres in contact with a *polydisperse* hard sphere matrix, the structural properties have already been studied in [13, 14]. Here we present the general formalism that can be applied to systems with arbitrary spherically symmetric interactions. We focus in particular on the thermodynamic properties which are required when calculating phase diagrams.

The paper is organized as follows: at the beginning of the subsequent section we present the notation and specify our system. We then derive the integral equations which allow the determination of the structure of a polydisperse fluid in contact with a polydisperse matrix; using these results we present closed expressions for the thermodynamic properties (equations of state) of such a system. The paper is concluded with a discussion and an outlook.

2. The method

In an effort to distinguish between (discrete and continuous) indices related to fluid and matrix particles, we introduce the following notation: liquid particles—i and σ; matrix particles—$\underline{i}$ and $\underline{\sigma}$. To derive expressions for the structural and thermodynamic properties of a polydisperse fluid in contact with a polydisperse matrix we shall proceed as follows: we first consider a fluid mixture with n_{f} components in contact with an $n_{\underline{\mathrm{m}}}$-component matrix. For this system we derive—via the replica trick—the replica Ornstein–Zernike (ROZ) equations, relating the correlation functions of the partly quenched system, and the relevant expressions for the thermodynamic properties; then by letting n_{f} and $n_{\underline{\mathrm{m}}}$ tend towards infinity we introduce the distribution functions $f_{\mathrm{f}}(\sigma)$ and $f_{\underline{\mathrm{m}}}(\underline{\sigma})$ which characterize the size distribution of the fluid and matrix particles. We then apply the orthogonal decomposition technique by expanding the σ- and $\underline{\sigma}$-dependent functions in terms of orthogonal polynomials $p_i(\sigma)$ and $p_{\underline{i}}(\underline{\sigma})$ associated with the weight functions $f_{\mathrm{f}}(\sigma)$ and $f_{\underline{\mathrm{m}}}(\underline{\sigma})$.

2.1. *The system*

The interatomic potentials of the system are denoted by $\Phi_{ij}(r)$ or $\Phi(r; \sigma_1, \sigma_2)$ where the (discrete) indices i and j and the (continuous) diameters σ_1 and σ_2 can characterize now both fluid and matrix particles. Further we introduce a temperature T, $\beta = (k_{\mathrm{B}}T)^{-1}$ (k_{B} being the Boltzmann constant), and number densities ρ_{f} and $\rho_{\underline{\mathrm{m}}}$ of the fluid and of the matrix. Partial number densities ρ_i and $\rho_{\underline{i}}$ are calculated in the discrete case via $\rho_i = c_i\rho_{\mathrm{f}}$ and $\rho_{\underline{i}} = c_{\underline{i}}\rho_{\underline{\mathrm{m}}}$, the c_i and $c_{\underline{i}}$ being the concentrations $\left(\sum_{i=1}^{n_{\mathrm{f}}} c_i = 1 \text{ and } \sum_{\underline{i}=1}^{n_{\underline{\mathrm{m}}}} c_{\underline{i}} = 1\right)$.

2.2. *Structural properties*

We start from the discrete case of an n_{f}-component fluid in contact with an $n_{\underline{\mathrm{m}}}$-component matrix. Structural properties are most readily expressed in liquid state theory via correlation functions [15]: we use the direct correlation functions $c_{ij}(r)$ and the total correlation functions $h_{ij}(r)$, written down here for the discrete case of fluid–fluid correlations; extension of this notation for the other correlation functions (including the matrix particles) and for the polydisperse case is straightforward. Further, we shall introduce the pair distribution functions $g_{ij}(r)$, calculated from the $h_{ij}(r)$ via $g_{ij}(r) = h_{ij}(r) + 1$. The direct and the total correlation functions are related in equilibrium liquid state theory via the Ornstein–Zernike (OZ) equations [16].

We start from the replicated system, which is a fully equilibrated mixture of the now mobile matrix particles and s copies of the fluid; this system is hence an $(s \times n_{\mathrm{f}} + n_{\underline{\mathrm{m}}})$-component mixture. Particles of different replicas are not allowed to interact with each other.

Writing down the OZ equations for the replicated system and taking the limit $s \to 0$ we arrive at the ROZ equations that relate the correlation functions of the partly quenched system (for simplicity we omit the argument of the correlation functions, r, and denote convolutions by $\otimes$)

$$\begin{aligned}
h_{\underline{i}\underline{j}} &= c_{\underline{i}\underline{j}} + \sum_{\underline{k}=1}^{n_{\underline{\mathrm{m}}}} \rho_{\underline{k}} c_{\underline{i}\underline{k}} \otimes h_{\underline{k}\underline{j}}, \\
h_{\underline{i}j} &= c_{\underline{i}j} + \sum_{\underline{k}=1}^{n_{\underline{\mathrm{m}}}} \rho_{\underline{k}} c_{\underline{i}\underline{k}} \otimes h_{\underline{k}j} + \sum_{l=1}^{n_{\mathrm{f}}} \rho_l c_{\underline{i}l} \otimes h_{lj} \\
&\quad - \sum_{l=1}^{n_{\mathrm{f}}} \rho_l c_{\underline{i}l} \otimes h_{l'j}, \\
h_{ij} &= c_{ij} + \sum_{\underline{k}=1}^{n_{\underline{\mathrm{m}}}} \rho_{\underline{k}} c_{i\underline{k}} \otimes h_{\underline{k}j} + \sum_{l=1}^{n_{\mathrm{f}}} \rho_l c_{il} \otimes h_{lj} \\
&\quad - \sum_{l=1}^{n_{\mathrm{f}}} \rho_l c_{il'} \otimes h_{l'j}, \\
h_{ij'} &= c_{ij'} + \sum_{\underline{k}=1}^{n_{\underline{\mathrm{m}}}} \rho_{\underline{k}} c_{i\underline{k}} \otimes h_{\underline{k}j} + \sum_{l=1}^{n_{\mathrm{f}}} \rho_l c_{il} \otimes h_{lj'} \\
&\quad + \sum_{l=1}^{n_{\mathrm{f}}} \rho_l c_{il'} \otimes h_{lj} - 2\sum_{l=1}^{n_{\mathrm{f}}} \rho_l c_{il'} \otimes h_{lj'}.
\end{aligned} \tag{1}$$

i' denotes the replica of component i and the following symmetry relations hold for the system

$$h_{ij} = h_{ji}; \quad h_{ij'} = h_{j'i}; \quad h_{ij'} = h_{ji'}, \quad \text{for all } i > j; \tag{2}$$

$$h_{\underline{i}\underline{j}} = h_{\underline{j}\underline{i}}; \quad h_{\underline{i}j} = h_{j\underline{i}}; \quad h_{\underline{i}j'} = h_{\underline{i}j}; \quad h_{i'j'} = h_{ij}. \tag{3}$$

Sometimes it is convenient to introduce the connected parts of the correlation functions (upper index 'c'), defined as $h^{\mathrm{c}}_{ij}(r) = h_{ij}(r) - h_{ij'}(r)$ and generalized in a straightforward way to the other correlation functions. Using this function, and with the help of the equation for h_{ij} in (1), the last of equations (1) can be reduced to

$$h^{\mathrm{c}}_{ij} = c^{\mathrm{c}}_{ij} + \sum_{l=1}^{n_{\mathrm{f}}} \rho_l c^{\mathrm{c}}_{il} \otimes h^{\mathrm{c}}_{lj}. \tag{4}$$

We now define matrices for the densities and for the correlation functions

$$\boldsymbol{\rho}_{\underline{\mathrm{m}}} = \begin{pmatrix} \rho_{\underline{1}} & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \rho_{n_{\underline{\mathrm{m}}}} \end{pmatrix}, \tag{5}$$

$$\boldsymbol{\rho}_{\mathrm{f}} = \begin{pmatrix} \rho_1 & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \rho_{n_{\mathrm{f}}} \end{pmatrix}, \tag{6}$$

$$(\mathsf{h}_{\underline{\mathrm{mm}}})_{ij} = h_{\underline{i}\underline{j}}, \quad (\mathsf{h}_{\mathrm{f}\underline{\mathrm{m}}})_{ij} = h_{i\underline{j}}, \quad (\mathsf{h}_{\mathrm{ff}})_{ij} = h_{ij}, \quad (\mathsf{h}_{\mathrm{fr}})_{ij} = h_{ij'}, \tag{7}$$

where '$\underline{\mathrm{m}}$' stands for the matrix, 'f' for the fluid and 'r' for the replica, and similar matrices for the direct correlation functions. Note that all matrices defined above are symmetric except for $\mathsf{h}_{\mathrm{f}\underline{\mathrm{m}}}$ and $\mathsf{c}_{\mathrm{f}\underline{\mathrm{m}}}$; for these matrices the following relations hold: $\mathsf{h}_{\mathrm{f}\underline{\mathrm{m}}} = \mathsf{h}^{\mathrm{T}}_{\underline{\mathrm{m}}\mathrm{f}}$ and $\mathsf{c}_{\mathrm{f}\underline{\mathrm{m}}} = \mathsf{c}^{\mathrm{T}}_{\underline{\mathrm{m}}\mathrm{f}}$, where the upper index 'T' denotes the transpose of a matrix. One can then rewrite the OZ relations as follows

$$\begin{aligned}
\mathsf{h}_{\underline{\mathrm{mm}}} &= \mathsf{c}_{\underline{\mathrm{mm}}} + \mathsf{h}_{\underline{\mathrm{mm}}} \otimes \boldsymbol{\rho}_{\underline{\mathrm{m}}} \mathsf{c}_{\underline{\mathrm{mm}}}, \\
\mathsf{h}_{\mathrm{f}\underline{\mathrm{m}}} &= \mathsf{c}_{\mathrm{f}\underline{\mathrm{m}}} + \mathsf{h}_{\mathrm{f}\underline{\mathrm{m}}} \otimes \boldsymbol{\rho}_{\underline{\mathrm{m}}} c_{\underline{\mathrm{mm}}} + \mathsf{h}_{\mathrm{ff}} \otimes \boldsymbol{\rho}_{\mathrm{f}} \mathsf{c}_{\mathrm{f}\underline{\mathrm{m}}} \\
&\quad - \mathsf{h}_{\mathrm{fr}} \otimes \boldsymbol{\rho}_{\mathrm{f}} \mathsf{c}_{\mathrm{f}\underline{\mathrm{m}}}, \\
\mathsf{h}_{\mathrm{ff}} &= \mathsf{c}_{\mathrm{ff}} + \mathsf{h}_{\mathrm{f}\underline{\mathrm{m}}} \otimes \boldsymbol{\rho}_{\underline{\mathrm{m}}} \mathsf{c}^{\mathrm{T}}_{\mathrm{f}\underline{\mathrm{m}}} + \mathsf{h}_{\mathrm{ff}} \otimes \boldsymbol{\rho}_{\mathrm{f}} \mathsf{c}_{\mathrm{ff}} \\
&\quad - \mathsf{h}_{\mathrm{fr}} \otimes \boldsymbol{\rho}_{\mathrm{f}} \mathsf{c}_{\mathrm{fr}}, \\
\mathsf{h}_{\mathrm{fr}} &= \mathsf{c}_{\mathrm{fr}} + \mathsf{h}_{\mathrm{f}\underline{\mathrm{m}}} \otimes \boldsymbol{\rho}_{\underline{\mathrm{m}}} \mathsf{c}^{\mathrm{T}}_{\mathrm{f}\underline{\mathrm{m}}} + \mathsf{h}_{\mathrm{fr}} \otimes \boldsymbol{\rho}_{\mathrm{f}} \mathsf{c}_{\mathrm{ff}} \\
&\quad + \mathsf{h}_{\mathrm{ff}} \otimes \boldsymbol{\rho}_{\mathrm{f}} \mathsf{c}_{\mathrm{fr}} - 2\mathsf{h}_{\mathrm{fr}} \otimes \boldsymbol{\rho}_{\mathrm{f}} \mathsf{c}_{\mathrm{fr}}.
\end{aligned} \tag{8}$$

We now proceed to the polydisperse case and switch from discrete indices i and $\underline{i}$ to continuous indices σ_i and $\underline{\sigma}_i$; then, e.g. the direct correlation function $c_{ij}(r)$ is replaced by $c(r; \sigma_i, \underline{\sigma}_j)$. For a polydisperse fluid with total density ρ_{f} in contact with a polydisperse matrix of total density $\rho_{\underline{\mathrm{m}}}$, the ROZ equations (8) read

$$\begin{aligned}
&h(r_{12}; \underline{\sigma}_1, \underline{\sigma}_2) \\
&\quad = c(r_{12}; \underline{\sigma}_1, \underline{\sigma}_2) \\
&\qquad + \rho_{\underline{\mathrm{m}}} \int \mathrm{d}\mathbf{r}_3 \int \mathrm{d}\underline{\sigma}_3\, f_{\underline{\mathrm{m}}}(\underline{\sigma}_3) c(r_{13}; \underline{\sigma}_1, \underline{\sigma}_3) h(r_{32}; \underline{\sigma}_3, \underline{\sigma}_2), \\
&h(r_{12}; \sigma_1, \underline{\sigma}_2) \\
&\quad = c(r_{12}; \sigma_1, \underline{\sigma}_2) \\
&\qquad + \rho_{\underline{\mathrm{m}}} \int \mathrm{d}\mathbf{r}_3 \int \mathrm{d}\underline{\sigma}_3\, f_{\underline{\mathrm{m}}}(\underline{\sigma}_3) h(r_{13}; \sigma_1, \underline{\sigma}_3) c(r_{32}; \underline{\sigma}_3, \underline{\sigma}_2) \\
&\qquad + \rho_{\mathrm{f}} \int \mathrm{d}\mathbf{r}_3 \int \mathrm{d}\sigma_3\, f_{\mathrm{f}}(\sigma_3) h(r_{13}; \sigma_1, \sigma_3) c(r_{32}; \sigma_3, \underline{\sigma}_2) \\
&\qquad - \rho_{\mathrm{f}} \int \mathrm{d}\mathbf{r}_3 \int \mathrm{d}\sigma_3\, f_{\mathrm{f}}(\sigma_3) h(r_{13}; \sigma_1, \sigma'_3) c(r_{32}; \sigma_3, \underline{\sigma}_2), \\
&h(r_{12}; \sigma_1, \sigma_2) \\
&\quad = c(r_{12}; \sigma_1, \sigma_2) \\
&\qquad + \rho_{\underline{\mathrm{m}}} \int \mathrm{d}\mathbf{r}_3 \int \mathrm{d}\underline{\sigma}_3\, f_{\underline{\mathrm{m}}}(\underline{\sigma}_3) h(r_{13}; \sigma_1, \underline{\sigma}_3) c(r_{32}; \underline{\sigma}_3, \sigma_2)
\end{aligned}$$

$$+\rho_{\mathrm{f}}\int \mathrm{d}\mathbf{r}_3\int \mathrm{d}\sigma_3\, f_{\mathrm{f}}(\sigma_3)h(r_{13};\sigma_1,\sigma_3)c(r_{32};\sigma_3,\sigma_2)$$
$$-\rho_{\mathrm{f}}\int \mathrm{d}\mathbf{r}_3\int \mathrm{d}\sigma_3\, f_{\mathrm{f}}(\sigma_3)h(r_{13};\sigma_1,\sigma_3')c(r_{32};\sigma_3',\sigma_2)\,,$$
$$h(r_{12};\sigma_1,\sigma_2')$$
$$=c(r_{12};\sigma_1,\sigma_2')$$
$$+\rho_{\underline{\mathrm{m}}}\int \mathrm{d}\mathbf{r}_3\int \mathrm{d}\underline{\sigma}_3\, f_{\underline{\mathrm{m}}}(\underline{\sigma}_3)h(r_{13};\sigma_1,\underline{\sigma}_3)c(r_{32};\underline{\sigma}_3,\sigma_2)$$
$$+\rho_{\mathrm{f}}\int \mathrm{d}\mathbf{r}_3\int \mathrm{d}\sigma_3\, f_{\mathrm{f}}(\sigma_3)h(r_{13};\sigma_1,\sigma_3)c(r_{32};\sigma_3,\sigma_2')$$
$$+\rho_{\mathrm{f}}\int \mathrm{d}\mathbf{r}_3\int \mathrm{d}\sigma_3\, f_{\mathrm{f}}(\sigma_3)h(r_{13};\sigma_1,\sigma_3')c(r_{32};\sigma_3,\sigma_2)$$
$$-2\rho_{\mathrm{f}}\int \mathrm{d}\mathbf{r}_3\int \mathrm{d}\sigma_3\, f_{\mathrm{f}}(\sigma_3)h(r_{13};\sigma_1,\sigma_3')c(r_{32};\sigma_3,\sigma_2') \quad (9)$$

and equation (4) becomes

$$h^{\mathrm{c}}(r_{12};\sigma_1,\sigma_2)$$
$$=c^{\mathrm{c}}(r_{12};\sigma_1,\sigma_2)+\rho_{\mathrm{f}}\int \mathrm{d}\mathbf{r}_3$$
$$\times\int \mathrm{d}\sigma_3\, f_{\mathrm{f}}(\sigma_3)c^{\mathrm{c}}(r_{13};\sigma_1,\sigma_3)h^{\mathrm{c}}(r_{32};\sigma_3,\sigma_2). \quad (10)$$

Again the prime on the σ's denotes the size parameter of the replica particles, and now the continuous version of the symmetry rules (2) and (3) hold for this system.

We now expand all σ- and $\underline{\sigma}$-dependent functions in terms of the orthonormal polynomials $p_i(\sigma)$ and $p_{\underline{i}}(\underline{\sigma})$ ($i, \underline{i} = 0, 1, 2, \ldots$) associated with the distribution functions $f_{\mathrm{f}}(\sigma)$ and $f_{\underline{\mathrm{m}}}(\underline{\sigma})$; they are defined via

$$\int_0^\infty \mathrm{d}\sigma f_{\mathrm{f}}(\sigma)p_i(\sigma)p_j(\sigma)=\delta_{ij} \quad (11)$$

and a similar relation for the polynomials associated with $f_{\underline{\mathrm{m}}}(\underline{\sigma})$. Thus, given some σ-dependent functions $x(r;\sigma)$ and $y(r;\sigma_1,\sigma_2)$, their expansions read

$$x(r;\sigma)=\sum_{i=0}^{\infty}x_i(r)p_i(\sigma), \quad (12)$$

$$y(r;\sigma_1,\sigma_2)=\sum_{i,j=0}^{\infty}y_{ij}(r)p_i(\sigma_1)p_j(\sigma_2), \quad (13)$$

where the coefficient functions are given by

$$x_i(r)=\int_0^\infty \mathrm{d}\sigma f_{\mathrm{f}}(\sigma)x(r;\sigma)p_i(\sigma), \quad (14)$$

$$y_{ij}(r)=\int_0^\infty \mathrm{d}\sigma_1\,\mathrm{d}\sigma_2\, f_{\mathrm{f}}(\sigma_1)\,f_{\mathrm{f}}(\sigma_2)y(r;\sigma_1,\sigma_2)p_i(\sigma_1)p_j(\sigma_2). \quad (15)$$

Similar relations hold for functions depending on the $\underline{\sigma}$ only. For the 'mixed' case above relations read

$$y(r;\sigma_1,\underline{\sigma}_2)=\sum_{i,\underline{j}=0}^{\infty}y_{i\underline{j}}(r)p_i(\sigma_1)p_{\underline{j}}(\underline{\sigma}_2) \quad (16)$$

with

$$y_{i\underline{j}}(r)=\int_0^\infty \mathrm{d}\sigma_1\,\mathrm{d}\underline{\sigma}_2\, f_{\mathrm{f}}(\sigma_1)\,f_{\underline{\mathrm{m}}}(\underline{\sigma}_2)y(r;\sigma_1,\underline{\sigma}_2)p_i(\sigma_1)p_{\underline{j}}(\underline{\sigma}_2)\,. \quad (17)$$

However, in practical applications any of the above expansions have to be truncated at some finite upper summation index (n_{num}) which has to be chosen according to different aspects; for the choice of this parameter one of the most crucial criteria is certainly the width of the distribution functions $f_{\mathrm{f}}(\sigma)$ and $f_{\underline{\mathrm{m}}}(\underline{\sigma})$. For details we refer the reader to [11,17]. Having chosen n_{num}, the above integrations used to calculate the coefficient functions $x_i(r)$, $y_{ij}(r)$, etc., are most conveniently realized by a Gaussian quadrature algorithm (see [8] for details).

Denoting the expansion coefficients for the orthogonal polynomial expansions of the direct and the total correlation functions by $c_{ij}(r)$, $c_{\underline{i}\,\underline{j}}(r)$, $h_{ij}(r)$ and $h_{\underline{i}\,\underline{j}}(r)$, and similarly for their Fourier transforms which we characterize by a tilde, and collecting these in matrices $\tilde{\mathsf{C}}_{\alpha\beta}$ and $\tilde{\mathsf{H}}_{\alpha\beta}$ (α and β standing for $\underline{\mathrm{m}}$, f or r), the ROZ (9) in k-space now read

$$\begin{aligned}
\tilde{\mathsf{H}}_{\underline{\mathrm{m}}\underline{\mathrm{m}}} &= \tilde{\mathsf{C}}_{\underline{\mathrm{m}}\underline{\mathrm{m}}}+\rho_{\underline{\mathrm{m}}}\tilde{\mathsf{C}}_{\underline{\mathrm{m}}\underline{\mathrm{m}}}\tilde{\mathsf{H}}_{\underline{\mathrm{m}}\underline{\mathrm{m}}},\\
\tilde{\mathsf{H}}_{\mathrm{f}\underline{\mathrm{m}}} &= \tilde{\mathsf{C}}_{\mathrm{f}\underline{\mathrm{m}}}+\rho_{\underline{\mathrm{m}}}\tilde{\mathsf{H}}_{\mathrm{f}\underline{\mathrm{m}}}\tilde{\mathsf{C}}_{\underline{\mathrm{m}}\underline{\mathrm{m}}}+\rho_{\mathrm{f}}\tilde{\mathsf{H}}_{\mathrm{ff}}\tilde{\mathsf{C}}_{\mathrm{f}\underline{\mathrm{m}}}\\
&\quad -\rho_{\mathrm{f}}\tilde{\mathsf{H}}_{\mathrm{fr}}\tilde{\mathsf{C}}_{\mathrm{f}\underline{\mathrm{m}}},\\
\tilde{\mathsf{H}}_{\mathrm{ff}} &= \tilde{\mathsf{C}}_{\mathrm{ff}}+\rho_{\underline{\mathrm{m}}}\tilde{\mathsf{H}}_{\mathrm{f}\underline{\mathrm{m}}}\tilde{\mathsf{C}}^{\mathrm{T}}_{\mathrm{f}\underline{\mathrm{m}}}+\rho_{\mathrm{f}}\tilde{\mathsf{H}}_{\mathrm{ff}}\tilde{\mathsf{C}}_{\mathrm{ff}}-\rho_{\mathrm{f}}\tilde{\mathsf{H}}_{\mathrm{fr}}\tilde{\mathsf{C}}_{\mathrm{fr}},\\
\tilde{\mathsf{H}}_{\mathrm{fr}} &= \tilde{\mathsf{C}}_{\mathrm{fr}}+\rho_{\underline{\mathrm{m}}}\tilde{\mathsf{H}}_{\mathrm{f}\underline{\mathrm{m}}}\tilde{\mathsf{C}}^{\mathrm{T}}_{\mathrm{f}\underline{\mathrm{m}}}+\rho_{\mathrm{f}}\tilde{\mathsf{H}}_{\mathrm{fr}}\tilde{\mathsf{C}}_{\mathrm{ff}}+\rho_{\mathrm{f}}\tilde{\mathsf{H}}_{\mathrm{ff}}\tilde{\mathsf{C}}_{\mathrm{fr}}\\
&\quad -2\rho_{\mathrm{f}}\tilde{\mathsf{H}}_{\mathrm{fr}}\tilde{\mathsf{C}}_{\mathrm{fr}}.
\end{aligned} \quad (18)$$

In the above equations, the matrices $\tilde{\mathsf{C}}_{\alpha\beta}$ and $\tilde{\mathsf{H}}_{\alpha\beta}$ are $n_{\mathrm{num}}\times n_{\mathrm{num}}$ matrices, n_{num} being defined above.

The ROZ equations for the expansion functions have now to be solved along with a suitable closure relation (see [15]) leading to the structure of the system in terms of the correlation functions. From these functions one can then calculate the thermodynamic properties; the corresponding expressions are given in the subsequent subsection.

2.3. *Thermodynamic properties*

Using the replica trick we first derive the Gibbs–Duhem relation for the partly quenched system,

following similar lines as in the one-component case [18] and in the binary case [19]. Again we use a grand-canonical ensemble for the replicas and a canonical ensemble for the matrix. Then the grand potential of the quenched system, $\bar{\Omega}$, and the grand potential of the replicated system, $\Omega^{\mathrm{rep}}(s)$, are related via [18]

$$\bar{\Omega} = \lim_{s\to 0} \frac{\mathrm{d}}{\mathrm{d}s} \Omega^{\mathrm{rep}}(s) \,. \tag{19}$$

In $\mathrm{d}\Omega^{\mathrm{rep}}(s)$ additional terms (including $\mathrm{d}\mu_i$ and $\mathrm{d}\rho_{\underline{i}}$) have now to be taken into account as a consequence of the multi-component nature of the matrix and of the fluid. Following similar lines as in the above quoted papers, an expression for $\mathrm{d}\bar{\Omega}$ for the partly quenched system is found to be

$$\mathrm{d}\bar{\Omega} = -P\,\mathrm{d}V - S\,\mathrm{d}T - \sum_{i=1}^{n_{\mathrm{f}}} N_i\,\mathrm{d}\mu_i + V \sum_{\underline{i}=1}^{n_{\underline{\mathrm{m}}}} \mu_{\underline{i}}\,\mathrm{d}\rho_{\underline{i}} \,. \tag{20}$$

P and S are the pressure and the entropy of the partly quenched system and the N_i are the number of particles of component i of the liquid. From this equation we can extract the following relations that will be required below

$$\begin{aligned} P &= -\left(\frac{\partial \bar{\Omega}}{\partial V}\right)_{T,\{\mu_i\},\{\rho_{\underline{k}}\}} \\ &= \lim_{s\to 0} \frac{\mathrm{d}}{\mathrm{d}s} \left[P^{\mathrm{rep}}(s) - \sum_{\underline{k}=1}^{n_{\underline{\mathrm{m}}}} \rho_{\underline{k}} \mu_{\underline{k}}^{\mathrm{rep}}(s) \right] \end{aligned} \tag{21}$$

and

$$\frac{1}{V}\left(\frac{\partial \bar{\Omega}}{\partial \rho_{\underline{k}}}\right)_{V,T,\{\mu_l\},\{\rho_{\underline{i}}\}_{\underline{k}}} = \lim_{s\to 0} \frac{\mathrm{d}}{\mathrm{d}s} \mu_{\underline{k}}^{\mathrm{rep}}(s). \tag{22}$$

Here and in the following we use the notation $\{\rho_{\underline{i}}\}_{\underline{k}} = \{\rho_{\underline{i}}, \underline{i} \neq \underline{k}\}$ and $\{N_i\}_k = \{N_i, i \neq k\}$.

Using the Gibbs–Duhem relation for the replicated system, $\mathrm{d}\bar{\Omega}$ can be integrated (as in the one-component case [18]) to give

$$\bar{\Omega} = -PV. \tag{23}$$

Further, writing down the explicit expression for the Helmholtz free energy of the replicated system, $A^{\mathrm{rep}}(s)$, one can easily derive via $\bar{A} = \lim_{s\to 0}(\mathrm{d}/\mathrm{d}s)A^{\mathrm{rep}}(s)$ an expression for $\bar{A}$

$$\bar{A} = -PV + \sum_{i=1}^{n_{\mathrm{f}}} \mu_i N_i. \tag{24}$$

The starting point to derive the compressibility equation is to write down the partial density derivative of the pressure using equation (23). Then, with the help of the replica trick (19) one can easily show

$$\begin{aligned} V\left(\frac{\partial \beta P}{\partial \rho_i}\right)_{V,T,\{N_j\}_i,\{\rho_{\underline{k}}\}} &= -\beta\left(\frac{\partial \bar{\Omega}}{\partial \rho_i}\right)_{V,T,\{N_j\}_i,\{\rho_{\underline{k}}\}} \\ &= \lim_{s\to 0} \frac{\mathrm{d}}{\mathrm{d}s}\left[-\beta \frac{\partial \Omega^{\mathrm{rep}}(s)}{\partial \rho_i^{\mathrm{rep}}(s)}\right]_{V,T,\{N_j\}_i,\{\rho_{\underline{k}}\}} \end{aligned} \tag{25}$$

Following similar ideas to those presented in [19] we now introduce an external potential $u(\mathbf{r})$ in the replicated system which acts on the liquid particles *only*. Using in addition standard relations of classical density functional theory [20] one arrives at the compressibility equation

$$\left(\frac{\partial \beta P}{\partial \rho_i}\right)_{V,T,\{N_j\}_i,\{\rho_{\underline{k}}\}} = 1 - \sum_{l=1}^{n_{\mathrm{f}}} \rho_l \tilde{c}_{li}^{\mathrm{c}}(q=0) \,, \tag{26}$$

which has been written here in terms of the connected part of the direct correlation function.

One can derive a similar expression relating now the chemical potential instead of the pressure to the direct correlation functions: in a first step we relate the chemical potential of a fluid particle of species i of the partly quenched system, μ_i, and the corresponding chemical potential of the replicated system using the relation $\bar{A} = \lim_{s\to 0}(\mathrm{d}/\mathrm{d}s)A^{\mathrm{rep}}(s)$

$$\begin{aligned} \mu_i &= \left(\frac{\partial \bar{A}}{\partial N_i}\right)_{V,T,\{N_j\}_i,\{\rho_{\underline{k}}\}} \\ &= \lim_{s\to 0} \frac{\mathrm{d}}{\mathrm{d}s}\left(\frac{\partial A^{\mathrm{rep}}(s)}{\partial N_i}\right)_{V,T,\{N_j\}_i,\{\rho_{\underline{k}}\}} \\ &= \lim_{s\to 0} \mu_i^{\mathrm{rep}}(s). \end{aligned} \tag{27}$$

Using again density functional formalism one can derive in a straightforward way the relations

$$\rho_i\left(\frac{\partial \beta \mu_i}{\partial \rho_j}\right)_{V,T,\{N_k\}_j,\{\rho_{\underline{k}}\}} = \delta_{ij} - \rho_i \tilde{c}_{ij}^{\mathrm{c}}(q=0). \tag{28}$$

Additionally, combining (26) and (27) one finds

$$\left(\frac{\partial \beta P}{\partial \rho_j}\right)_{V,T,\{N_k\}_j,\{\rho_{\underline{k}}\}} = \sum_{i=1}^{n_{\mathrm{f}}} \rho_i \left(\frac{\partial \beta \mu_i}{\partial \rho_j}\right)_{V,T,\{N_k\}_j,\{\rho_{\underline{k}}\}} . \tag{29}$$

To derive the virial pressure we start from (21); using (22) and (23) we arrive at

$$\beta P = \beta \lim_{s\to 0} \frac{\mathrm{d}P^{\mathrm{rep}}(s)}{\mathrm{d}s} + \sum_{\underline{k}=1}^{n_{\underline{\mathrm{m}}}} \rho_{\underline{k}} \left(\frac{\partial \beta P}{\partial \rho_{\underline{k}}}\right)_{V,T,\{\mu_l\},\{\rho_{\underline{i}}\}_{\underline{k}}} . \tag{30}$$

Inserting in the above relation the expression for the pressure of the replicated system, $P^{\mathrm{rep}}(s)$, we obtain

$$\beta P - \sum_{\underline{k}=1}^{n_{\underline{\mathrm{m}}}} \rho_{\underline{k}} \left(\frac{\partial \beta P}{\partial \rho_{\underline{k}}}\right)_{V,T,\{\mu_l\},\{\rho_{\underline{i}}\}_{\underline{k}}}$$
$$= \sum_{i=1}^{n_{\mathrm{f}}} \rho_i - \frac{\beta}{6}\int \mathrm{d}^3 r r \left\{ \sum_{\underline{i},\underline{j}=1}^{n_{\underline{\mathrm{m}}}} \rho_{\underline{i}}\rho_{\underline{j}} \left[\lim_{s\to 0} \frac{\mathrm{d}g_{\underline{ij}}(r;s)}{\mathrm{d}s}\right] \Phi'_{\underline{ij}}(r) \right.$$
$$\left. + \sum_{i,j=1}^{n_{\mathrm{f}}} \rho_i\rho_j g_{ij}(r)\Phi'_{ij}(r) + 2\sum_{i=1}^{n_{\mathrm{f}}}\sum_{\underline{j}=1}^{n_{\underline{\mathrm{m}}}} \rho_i\rho_{\underline{j}} g_{i\underline{j}}(r)\Phi'_{i\underline{j}}(r) \right\}, \quad (31)$$

where the prime denotes derivative with respect to r.

We finally turn towards the energy equation. An expression for the excess (over ideal gas) internal energy, $\bar{U}^{\mathrm{ex}}$ of the quenched system can easily be derived from an ensemble average over the Hamiltonian characterizing the system or from the corresponding expression for the replicated system, $\bar{U}^{\mathrm{ex}} = \lim_{s\to 0}(\mathrm{d}/\mathrm{d}s)U^{\mathrm{ex,rep}}(s)$. Choosing the second route and following similar lines as in [19], we arrive at the following expression

$$\frac{\bar{U}^{\mathrm{ex}}}{V} = \sum_{\underline{i}=1}^{n_{\underline{\mathrm{m}}}}\sum_{j=1}^{n_{\mathrm{f}}} \rho_{\underline{i}}\rho_j \int \mathrm{d}^3 r g_{\underline{i}j}(r)\Phi_{\underline{i}j}(r) + \frac{1}{2}\sum_{i,j=1}^{n_{\mathrm{f}}} \rho_i\rho_j \int \mathrm{d}^3 r g_{ij}(r)\Phi_{ij}(r). \quad (32)$$

We now turn towards the polydisperse case. Here one should bear in mind that partial derivatives with respect to ρ_i or $\rho_{\underline{i}}$ in the discrete case now become functional derivatives with respect to $[\rho_{\mathrm{f}} f_{\mathrm{f}}(\sigma_i)]$ and $[\rho_{\underline{\mathrm{m}}} f_{\underline{\mathrm{m}}}(\underline{\sigma}_i)]$. For the free energy, the pressure and the excess internal energy one thus obtains from (24), (31) and (32)

$$\bar{A} = -PV + V\rho_{\mathrm{f}} \int_0^\infty \mathrm{d}\sigma f_{\mathrm{f}}(\sigma)\mu(\sigma). \quad (33)$$

$$\beta P - \int_0^\infty \mathrm{d}\underline{\sigma}\, f_{\underline{\mathrm{m}}}(\underline{\sigma}) \left(\frac{\delta \beta P}{\delta[f_{\underline{\mathrm{m}}}(\underline{\sigma})]}\right)_{V,T,\mu(\sigma)}$$
$$= \rho_{\mathrm{f}} - \frac{\beta}{6}\int \mathrm{d}^3 r r \left\{ \rho_{\underline{\mathrm{m}}}^2 \int_0^\infty \mathrm{d}\underline{\sigma}_1\, \mathrm{d}\underline{\sigma}_2 f_{\underline{\mathrm{m}}}(\underline{\sigma}_1) f_{\underline{\mathrm{m}}}(\underline{\sigma}_2) \right.$$
$$\times \left[\lim_{s\to 0} \frac{\mathrm{d}g(r;\underline{\sigma}_1,\underline{\sigma}_2;s)}{\mathrm{d}s}\right] \Phi'(r;\underline{\sigma}_1,\underline{\sigma}_2)$$
$$+ \rho_{\mathrm{f}}^2 \int_0^\infty \mathrm{d}\sigma_1 d\sigma_2 f_{\mathrm{f}}(\sigma_1) f_{\mathrm{f}}(\sigma_2) g(r;\sigma_1,\sigma_2)\Phi'(r;\sigma_1,\sigma_2)$$
$$\left. + 2\rho_{\mathrm{f}}\rho_{\underline{\mathrm{m}}} \int_0^\infty \mathrm{d}\sigma_1\, \mathrm{d}\underline{\sigma}_2 f_{\mathrm{f}}(\sigma_1) f_{\underline{\mathrm{m}}}(\underline{\sigma}_2) g(r;\sigma_1,\underline{\sigma}_2)\Phi'(r;\sigma_1,\underline{\sigma}_2) \right\} \quad (34)$$

and

$$\frac{\bar{U}^{\mathrm{ex}}}{V} = \rho_{\underline{\mathrm{m}}}\rho_{\mathrm{f}} \int \mathrm{d}^3 r \int_0^\infty \mathrm{d}\underline{\sigma}_1\, \mathrm{d}\sigma_2 f_{\underline{\mathrm{m}}}(\underline{\sigma}_1) f_{\mathrm{f}}(\sigma_2)$$
$$\times g(r;\underline{\sigma}_1,\sigma_2)\Phi(r;\underline{\sigma}_1,\sigma_2)$$
$$+ \frac{\rho_{\mathrm{f}}^2}{2}\int \mathrm{d}^3 r \int_0^\infty \mathrm{d}\sigma_1\, \mathrm{d}\sigma_2 f_{\mathrm{f}}(\sigma_1) f_{\mathrm{f}}(\sigma_2)$$
$$\times g(r;\sigma_1,\sigma_2)\Phi(r;\sigma_1,\sigma_2). \quad (35)$$

For the chemical potential of the fluid particles, $\mu(\sigma)$, which are now functions of σ we obtain from (27)

$$\mu(\sigma) = \frac{1}{V\rho_{\mathrm{f}}} \left(\frac{\delta \bar{A}}{\delta[f_{\mathrm{f}}(\sigma)]}\right)_{V,T,f_{\underline{\mathrm{m}}}}, \quad (36)$$

a relation which is also evident from (33).

Differential relations derived above for the case of mixtures with a finite number of components, (26), (28) and (29) become in the polydisperse case

$$\frac{1}{\rho_{\mathrm{f}}} \left(\frac{\delta \beta P}{\delta[f_{\mathrm{f}}(\sigma_1)]}\right)_{V,T,f_{\underline{\mathrm{m}}}}$$
$$= 1 - \rho_{\mathrm{f}} \int_0^\infty \mathrm{d}\sigma_2 f_{\mathrm{f}}(\sigma_2)\tilde{c}^{\mathrm{c}}(q=0;\sigma_1,\sigma_2), \quad (37)$$

$$f_{\mathrm{f}}(\sigma_1) \left(\frac{\delta \beta \mu(\sigma_1)}{\delta[f_{\mathrm{f}}(\sigma_2)]}\right)_{V,T,f_{\underline{\mathrm{m}}}}$$
$$= \delta(\sigma_1 - \sigma_2) - \rho_{\mathrm{f}} f_{\mathrm{f}}(\sigma_1)\tilde{c}^{\mathrm{c}}(q=0;\sigma_1,\sigma_2), \quad (38)$$

and

$$\frac{1}{\rho_{\mathrm{f}}} \left(\frac{\delta \beta P}{\delta[f_{\mathrm{f}}(\sigma_1)]}\right)_{V,T,f_{\underline{m}}} = \int_0^\infty \mathrm{d}\sigma_2 f_{\mathrm{f}}(\sigma_2) \left(\frac{\delta \beta \mu(\sigma_2)}{\delta[f_{\mathrm{f}}(\sigma_1)]}\right)_{V,T,f_{\underline{m}}}. \quad (39)$$

Introducing finally the coefficient functions of the expansions of the correlation functions and of the interatomic potentials in terms of the orthogonal polynomials, the above expressions for the pressure and the internal energy become

$$\beta P - \int_0^\infty \mathrm{d}\underline{\sigma}\, f_{\underline{\mathrm{m}}}(\underline{\sigma}) \left(\frac{\delta \beta P}{\delta[f_{\underline{\mathrm{m}}}(\underline{\sigma})]}\right)_{V,T,\mu(\sigma)}$$
$$= \rho_{\mathrm{f}} - \frac{\beta}{6}\int \mathrm{d}^3 r r \left\{ \rho_{\underline{\mathrm{m}}}^2 \sum_{\underline{ij}} \left[\lim_{s\to 0} \frac{\mathrm{d}g_{\underline{ij}}(r;s)}{\mathrm{d}s}\right] \frac{\mathrm{d}\Phi_{\underline{ij}}(r)}{\mathrm{d}r} \right.$$
$$\left. + \rho_{\mathrm{f}}^2 \sum_{ij} g_{ij}(r)\frac{\mathrm{d}\Phi_{ij}}{\mathrm{d}r}(r) + 2\rho_{\mathrm{f}}\rho_{\underline{\mathrm{m}}} \sum_{\underline{ij}} g_{i\underline{j}}(r)\frac{\mathrm{d}\Phi_{i\underline{j}}(r)}{\mathrm{d}r} \right\} \quad (40)$$

and

$$\frac{\bar{U}^{\mathrm{ex}}}{V} = \rho_{\underline{\mathrm{m}}}\rho_{\mathrm{f}} \sum_{i\underline{j}} \int \mathrm{d}^3 r g_{i\underline{j}}(r)\Phi_{i\underline{j}}(r) + \frac{\rho_{\mathrm{f}}^2}{2} \sum_{ij} \int \mathrm{d}^3 r g_{ij}(r)\Phi_{ij}(r). \tag{41}$$

Again, in practical applications the above summations are truncated at a suitable upper index n_{num}.

3. Discussion and outlook

In practical applications the ROZ equations for the coefficient functions (18) have to be solved along with a suitable closure relation, i.e. a relation between the interatomic potentials and the correlation functions [15]. The choice for the closure depends—among others—on the character of the interatomic potentials; the Percus–Yevick or the hypernetted chain approximations are, for instance, suitable candidates. In addition we would like to point out the attractive features of another closure relation, the optimized random phase approximation (ORPA) [21]; it has proven to be both reliable as well as very attractive (from the conceptual and from the numerical point of view) in describing the properties of polydisperse systems [11, 17] and of simple (one- and two-component) fluids in contact with a porous matrix [19, 22]. Guidelines for an appropriate truncation level of the expansion in terms of orthogonal polynomials (via n_{num}) can be found in [8, 11, 17]. Using the solution of the ROZ equations in terms of the coefficient functions, one can then proceed to calculate the thermodynamic properties of the polydisperse fluid in contact with the polydisperse porous matrix. Expressions for the most commonly used thermodynamic quantities are summarized in § 2.3. It should be mentioned that the present contribution also contains the expressions for the structure and the thermodynamic properties, which are required to describe a fluid in contact with a porous matrix, where both the fluid and the matrix are mixtures with *finite* numbers of components.

Using the expressions for the thermodynamic quantities we can then proceed to the next step, the calculation of the phase diagram. A brief summary on what has been done up to now in determining the phase diagram of *equilibrium* polydisperse fluids is in order (in particular we refer to a review article [23]). The determination of the full phase diagram of a polydisperse fluid mixture (i.e. including the localization of cloud and shadow curves and describing on a quantitative level interesting effects such as fractionation) is indeed a formidable task. Although several sophisticated methods have been proposed during the past years (again see [23]), the actual determination of the phase diagram of such a system has not exceeded the level of a van der Waals approximation (see for instance [24]). On the level of more sophisticated and more reliable liquid state theories (such as the ORPA mentioned above), the determination of the full phase diagram as well as an accurate description of fractionation effects remains—as a consequence of the complexity of the coexistence conditions and the related numerical problems—at present out of reach.

For the case considered here this means that the determination of the *full* phase behaviour of a polydisperse liquid mixture in contact with a polydisperse porous matrix is at present out of reach. Nevertheless, special cases might be considered. One of them (which seems to us to be the most promising one) is a simple one-component fluid which is in contact with a polydisperse matrix. Here we are faced with a simplified problem in the sense that only the coexistence conditions for the simple fluid have to be fulfilled to describe phase coexistence; the properties of the polydisperse matrix enter only via the coefficient functions of the matrix, which are fixed from the beginning and are left unaffected by the phase separation processes of the fluid. Since it is well known that a matrix is able to influence the phase behaviour of the fluid drastically, the step from a simple to a polydisperse matrix might be an interesting case to consider.

Despite the fact that the solution of the full problem seems at present out of reach, we would like to encourage our colleagues to dedicate efforts to its solution since such a system might be appropriate for describing realistic systems of technological interest.

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References

[1] Rosinberg, M. L., 1999, *New Approaches to Problems in Liquid State Theory*, *NATO Science Series*, edited by C. Caccamo, J.-P. Hansen and G. Stell (Dordrecht: Kluwer).
[2] Spöler, C., and Knapp, S., 2003, *J. chem. Phys.*, **118,** 3628.
[3] Fernaud, M. J., Lomba, E., Weis, J. J., and Levesque, D., 2003, *Molec. Phys.*, **101,** 1721.
[4] Given, J. A., 1992, *Phys. Rev.* A, **45,** 816.
[5] Given, J. A., 1992, *J. chem. Phys.*, **96,** 2287.
[6] Given, J. A., and Stell, G., 1994, *Physica* A, **209,** 495.
[7] Schöll-Paschinger, E., 2002, PhD thesis, Technische Universität Wien, Austria, unpublished (thesis available

from the homepage: http://tph.tuwien.ac.at/~paschinger/ and download 'PhD').

[8] LADO, F., 1996, *Phys. Rev.* E, **54,** 4411.

[9] SALACUSE, J. J., and STELL, G., 1982, *J. chem. Phys.*, **77,** 3714; SALACUSE, J. J., 1984, *J. chem. Phys.*, **81,** 2468; SALACUSE, J. J., 1987, PhD thesis, Department of Applied Mathematics, State University of New York at Stony Brook, USA.

[10] BRIANO, J. G., and GLANDT, E. D., 1984, *J. chem. Phys.*, **80,** 3336.

[11] LEROCH, S., KAHL, G., and LADO, F., 1999, *Phys. Rev.* E, **59,** 6937.

[12] LADO, F., 1997, *Phys. Rev.* E, **55,** 426; LADO, F., LOMBA, E., and LOMBARDERO, M., 1998, *J. chem. Phys.*, **108,** 4530; LADO, F., and LOMBA, E., 1998, *Phys. Rev. Lett.*, **80,** 3535.

[13] ILNYTSKY, JA., PATRYKIEJEW, A., SKOŁOWSKI, S., and PIZIO, D., 1999, *J. phys. Chem.* B, **103,** 868.

[14] RZYSKO, W., SKOŁOWSKI, S., and PIZIO, O., 2002, *J. chem. Phys.*, **116,** 4286.

[15] HANSEN, J. P., and MCDONALD, I. R., 1986, *Theory of Simple Liquids*, 2nd Edn (New York: Academic Press).

[16] ORNSTEIN, L. S., and ZERNIKE, F., 1914, *Proc. Acad. Sci.* (Amsterdam), **17,** 1452.

[17] LEROCH, S., 2002, PhD thesis, Technische Universität Wien, Austria, unpublished.

[18] ROSINBERG, M. L., TARJUS, G., and STELL, G., 1994, *J. chem. Phys.*, **100,** 5172.

[19] PASCHINGER, E., and KAHL, G., 2000, *Phys. Rev.* E, **61,** 5330.

[20] EVANS, R., 1979, *Adv. Phys.*, **28,** 143; EVANS, R., 1992, *Fundamentals of Inhomogeneous Fluids*, edited by D. HENDERSON (Dekker, New York), Chap. 3.

[21] ANDERSEN, H. C., and CHANDLER, D., 1972, *J. chem. Phys.*, **57,** 1918; ANDERSEN, H. C., CHANDLER, D., and WEEKS, J. D., 1972, *J. chem. Phys.*, **56,** 3812.

[22] SCHÖLL-PASCHINGER, E., LEVESQUE, D., KAHL, G., and WEIS, J.-J., 2001, *Europhys. Lett.*, **55,** 178; SCHÖLL-PASCHINGER, E., LEVESQUE, D., WEIS, J.-J., and KAHL, G., 2001, *Phys. Rev.* E, **64,** 11502.

[23] SOLLICH, P., 2002, *J. Phys. condens. Matter*, **14,** R79.

[24] BELLIER-CASTELLA, L.., XU, H., and BAUS, M., 2000, *J. chem. Phys.*, **113,** 8337; BELLIER-CASTELLA, L., BAUS, M., and XU, H., 2001, *J. chem. Phys.*, **115,** 3381.