Structure and thermodynamic properties of a binary liquid in a porous matrix: The formalism

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Using the replica trick we derive a formalism to describe the structure and the thermodynamic properties of a binary liquid in equilibrium with a porous medium. We present the replica Ornstein-Zernike equations for the general case of a k-component liquid inside a porous matrix; besides the usual liquid-state closure relations, we consider in particular the optimized random phase approximation (ORPA) restricting ourselves at present to hard-core potentials exclusively. We present furthermore several thermodynamic relations: the Gibbs-Duhem equation, the compressibility, and the virial equation. Within the framework of the ORPA (mean spherical approximation), closed expressions for the perturbation contribution to the free energy and the chemical potentials can be presented. Finally, we offer suggestions for numerical implementations.

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I. INTRODUCTION

In recent years, considerable effort has been dedicated to developing theoretical tools that allow the investigation of structural and thermodynamic properties of liquids that are in equilibrium with a quenched porous medium. The increased activity in this field is certainly due to the following reasons: on the one hand, in many experiments the phase behavior of liquids and liquid mixtures inside porous matrices has been studied (for an overview see, for instance, [1,2]) and many interesting effects were discovered; on the other hand, these complex systems are of technological interest, with application in catalysis, gas separation, or purification.

From the theoretical point of view, the main problem in the description of such systems lies in the double average required for the calculation of thermodynamic and structural properties: one average is taken over the configurations of the liquid, keeping the matrix particles in fixed positions, and the second average is then taken over different matrix configurations. The first steps to solving this complex problem were proposed by Madden and Glandt [3], who derived cluster expansions for the distribution functions; integral equations for the correlation functions, which are similar to the Ornstein-Zernike equations in standard liquid state theory, have been presented. In subsequent work, Given and Stell have applied the replica method (introduced originally in the theory of spin glasses [4]) to this problem [5–7] and have thus provided a powerful tool on which many of the present-day approaches in this field are based. The replica trick exploits a mathematical isomorphism between a partly quenched system and a limiting case of a corresponding equilibrium system, which consists of the now mobile matrix particles and of s noninteracting identical copies of the liquid: the properties of the quenched system are obtained by considering the limit $s \rightarrow 0$ of the properties of the equilibrium system, which, in turn, can be treated by standard liquid state theories. Given and Stell presented in their work the (now correct) formulation of the so-called replica Ornstein-Zernike (ROZ) equations, the counterpart of the Ornstein-Zernike equations in standard liquid state theory: they relate the liquid-liquid, the liquid-matrix, and the matrix-matrix

correlation functions. Finally, thermodynamic relations for such systems have been presented by Rosinberg, Stell, and co-workers [8,9]. Using the ROZ equations, the phase diagrams of simple liquids inside a porous matrix have been calculated in combination with different closure relations (see, for instance, [1,2]); recently, a formalism to treat systems containing partly quenched mixtures with electrostatic interactions between various species has also been presented [10]. To conclude this overview, one should mention that several of these numerical calculations were complemented by computer simulations (for instance, [11–13]).

Similar to the *homogeneous* case, the step from a one-component to a binary liquid offers—due to the increased number of parameters—a much richer variety of phase diagrams and phenomena: the concentrations of the species and the differences in the particle size and in the interatomic potentials can now be varied and can lead to interesting effects. While the case of a one-component liquid in a porous medium has been considered thoroughly during the past years by several groups, practically no attention has been paid to describe binary liquids inside a porous matrix. A further and important motivation to proceed to liquid mixtures is the fact that several experiments have been made for such systems. In the present study, we present the generalization of the formalism to binary liquids: using the replica trick we have proceeded along similar lines to the one-component case; we derive the ROZ equations, which now consist of one decoupled equation for the matrix correlation functions h_{00} and c_{00} (as in the case of a one-component liquid) and a set of eight coupled integral equations for the set of the remaining correlation functions (versus three coupled equations in the case of a simple liquid). These equations can be solved along with one of the standard liquid state closures (such as Percus-Yevick or hypernetted chain approximation) using efficient numerical algorithms, like the one proposed by Lomba *et al.* [11] for the simple one-component case. As a further closure relation, we have also considered the random-phase approximation (RPA)—as already done by Kierlik and co-workers [2] in the one-component case—along with an optimization criterion in the closure relation (ORPA [14,15]), which guarantees that the

pair distribution functions vanish inside the core region. We should also note that the present version of the ORPA is equivalent to the MSA. We show that the solution of the ROZ equations together with the MSA closure relation can be mapped on the solution of a variational problem: a suitably defined functional (which turns out to be a second-order contribution to the free energy) is minimized with respect to variations of the direct correlation functions inside the core region. We give numerical hints for the solution of the integral equations and of the variational problem which leads to the determination of the correlation functions and hence to the structure of the system. We present thermodynamic relations, some of which can be used to calculate phase diagrams: the Gibbs-Duhem equation, the compressibility, the energy, and the virial equation. Furthermore, the ORPA/ MSA allows us to derive closed expressions for the perturbation contribution of the free energy and the chemical potentials. The presentation of numerical results will be postponed to a future contribution: currently we are investigating a symmetric liquid inside a porous matrix [16]; we show that the increase of the matrix density leads to variations of the phase diagram similar to those observed for a binary symmetric liquid when modifying the strength of the unlike interaction [17].

In the subsequent section, we present the formalism, we derive the ROZ equations, and present different closure relations; in particular, we concentrate on the ORPA and discuss possibilities for its numerical implementation. We then present the relations for the thermodynamic quantities. The paper is closed with concluding remarks.

II. FORMALISM

A binary liquid inside a porous (one-component) matrix can be considered as a very special three-component liquid, where the particles of the matrix are fixed in place and are not affected by the mobile particles of the liquid. Physical quantities are hence obtained by two successive averages: one average is taken over the degrees of freedom of the fluid particles (where the positions of the matrix particles are kept fixed) and the other average is performed over all possible degrees of freedom of the matrix particles. The actual calculation of such averages turns out to be very difficult; to circumvent these problems, Given and Stell have applied the replica method (introduced originally in [4]) to liquid-state systems [5–7]: this method exploits a mathematical isomorphism between a partly quenched system and a limiting case of a corresponding equilibrium system, which is usually denoted as the replicated system. We briefly demonstrate this trick for the case of a binary liquid, using a canonical ensemble for both the matrix and the binary liquids. For a given matrix configuration (the positions of the N_0 matrix particles are denoted by $\mathbf{q}^{N_0} = \{\mathbf{q}_i\}$), and a given temperature T_1 ($\beta_1 = 1/k_B T_1$), the free energy A is given by

$$-\beta_1 A(N_1, N_2, V, T_1; \mathbf{q}^{N_0}) = \ln Z(\mathbf{q}^{N_0}), \qquad (1)$$

$Z(\mathbf{q}^{N_0})$ being the usual canonical partition function, i.e.,

$$Z(\mathbf{q}^{N_0}) = \frac{1}{N_1! N_2!} \int d\mathbf{r}^{N_1} d\mathbf{s}^{N_2} \exp[-\beta_1(H_{01} + H_{02} + H_{11}$$
$$+ H_{12} + H_{22})]. \qquad (2)$$

The H_{ij} are the configurational parts of the Hamilton functions describing the interactions between matrix particles (index 0) and particles of the liquid (indices 1 and 2). The positions of the N_1 (N_2) fluid particles of component 1 (component 2) are denoted by $\mathbf{r}^{N_1} = \{\mathbf{r}_i\}$ ($\mathbf{s}^{N_2} = \{\mathbf{s}_i\}$). The free energy of the quenched system, $\bar{A}$, where the matrix particles are distributed according to a canonical ensemble at a temperature T_0 ($\beta_0 = 1/k_B T_0$), is obtained via averaging over the $\mathbf{q}^{N_0}$, i.e.,

$$-\beta_1 \bar{A} = -\beta_1 \bar{A}(N_0, N_1, N_2, V, T_1, T_0)$$
$$= \frac{1}{N_0! Z_0} \int d\mathbf{q}^{N_0} \exp[-\beta_0 H_{00}(\mathbf{q}^{N_0})] \ln Z(\mathbf{q}^{N_0}), \qquad (3)$$

where Z_0 is a normalizing factor. The logarithm in the above expression makes the calculation of the average very difficult. However, using the identity $\ln x = \lim_{s \to 0} dx^s/dx$, one obtains

$$-\beta_1 \bar{A} = \frac{1}{Z_0} \lim_{s \to 0} \frac{d}{ds} \left[\frac{1}{N_0!} \int d\mathbf{q}^{N_0} \exp[-\beta_0 H_{00}(\mathbf{q}^{N_0})] \right.$$
$$\left. \times [Z(\mathbf{q}^{N_0})]^s \right]. \qquad (4)$$

The bracketed term in the above equation is denoted by $Z^{\text{rep}}(s)$ and can be explicitly written for integer values of s as an iterated integral,

$$Z^{\text{rep}}(s) = \frac{1}{N_0! (N_1!)^s (N_2!)^s}$$
$$\times \int d\mathbf{q}^{N_0} \, d\mathbf{r}_1^{N_1} \cdots d\mathbf{r}_s^{N_1} \, d\mathbf{s}_1^{N_2} \cdots d\mathbf{s}_s^{N_2}$$
$$\times \exp[-\beta_0 H_{00}(\mathbf{q}^{N_0})]$$
$$\times \exp\left[-\beta_1 \sum_{\alpha=1}^{s} [H_{01}^\alpha(\mathbf{q}^{N_0}, \mathbf{r}_\alpha^{N_1}) + H_{02}^\alpha(\mathbf{q}^{N_0}, \mathbf{s}_\alpha^{N_2})] \right]$$
$$\times \exp\left[-\beta_1 \sum_{\alpha=1}^{s} [H_{11}^\alpha(\mathbf{r}_\alpha^{N_1}) + H_{12}^\alpha(\mathbf{r}_\alpha^{N_1}, \mathbf{s}_\alpha^{N_2}) \right.$$
$$\left. + H_{22}^\alpha(\mathbf{s}_\alpha^{N_2})] \right]. \qquad (5)$$

If we assume that the interactions between the particles of the system can be described via pair potentials Φ_{ij}, then Eq. (5) is the equilibrium partition function of a system with the following configurational part of the Hamilton function:

$$H = \sum_{\substack{i<j \\ i,j\in\{1,\ldots,N_0\}}} \Phi_{00}(\mathbf{q}_i,\mathbf{q}_j) + \sum_{\alpha=1}^{s} \sum_{\substack{i,j \\ i\in\{1,\ldots,N_0\} \\ j\in\{1,\ldots,N_1\}}} \Phi_{01}^{\alpha}(\mathbf{q}_i,\mathbf{r}_{\alpha,j})$$

$$+ \sum_{\alpha=1}^{s} \sum_{\substack{i,j \\ i\in\{1,\ldots,N_0\} \\ j\in\{1,\ldots,N_2\}}} \Phi_{02}^{\alpha}(\mathbf{q}_i,\mathbf{s}_{\alpha,j})$$

$$+ \sum_{\alpha=1}^{s} \sum_{\beta=1}^{s} \sum_{\substack{i<j \\ i,j\in\{1,\ldots,N_1\}}} \Phi_{11}^{\alpha\beta}(\mathbf{r}_{\alpha,i},\mathbf{r}_{\beta,j})$$

$$+ \sum_{\alpha=1}^{s} \sum_{\beta=1}^{s} \sum_{\substack{i,j \\ i\in\{1,\ldots,N_1\} \\ j\in\{1,\ldots,N_2\}}} \Phi_{12}^{\alpha\beta}(\mathbf{r}_{\alpha,i},\mathbf{s}_{\beta,j})$$

$$+ \sum_{\alpha=1}^{s} \sum_{\beta=1}^{s} \sum_{\substack{i<j \\ i,j\in\{1,\ldots,N_2\}}} \Phi_{22}^{\alpha\beta}(\mathbf{s}_{\alpha,i},\mathbf{s}_{\beta,j})$$

$$= H_{00}(\mathbf{q}^{N_0}) + \sum_{\alpha=1}^{s} \left[H_{01}^{\alpha}(\mathbf{q}^{N_0},\mathbf{r}_{\alpha}^{N_1}) + H_{02}^{\alpha}(\mathbf{q}^{N_0},\mathbf{s}_{\alpha}^{N_2}) \right.$$

$$\left. + H_{11}^{\alpha}(\mathbf{r}_{\alpha}^{N_1}) + H_{12}^{\alpha}(\mathbf{r}_{\alpha}^{N_1},\mathbf{s}_{\alpha}^{N_2}) + H_{22}^{\alpha}(\mathbf{s}_{\alpha}^{N_2}) \right]. \quad (6)$$

$\Phi_{ij}^{\alpha\beta}$ denotes the pair interaction between a fluid particle of component i in replica α with a particle of component j in replica β, etc., and the system is characterized by the following pair potentials:

$$\Phi_{01}^{\alpha}(\mathbf{q}_i,\mathbf{r}_{\alpha,j}) = \Phi_{01}(\mathbf{q}_i,\mathbf{r}_{\alpha,j}), \quad \Phi_{02}^{\alpha}(\mathbf{q}_i,\mathbf{s}_{\alpha,j}) = \Phi_{02}(\mathbf{q}_i,\mathbf{s}_{\alpha,j}), \quad (7)$$

$$\Phi_{11}^{\alpha\beta}(\mathbf{r}_{\alpha,i},\mathbf{r}_{\beta,j}) = \delta_{\alpha\beta}\Phi_{11}(\mathbf{r}_{\alpha,i},\mathbf{r}_{\beta,j}), \quad \Phi_{12}^{\alpha\beta}(\mathbf{r}_{\alpha,i},\mathbf{s}_{\beta,j})$$
$$= \delta_{\alpha\beta}\Phi_{12}(\mathbf{r}_{\alpha,i},\mathbf{s}_{\beta,j}), \quad (8)$$

$$\Phi_{22}^{\alpha\beta}(\mathbf{s}_{\alpha,i},\mathbf{s}_{\beta,j}) = \delta_{\alpha\beta}\Phi_{22}(\mathbf{s}_{\alpha,i},\mathbf{s}_{\beta,j}).$$

Equation (5) represents the canonical partition function of a fully equilibrated $(2s+1)$-component system, consisting of the matrix and of s identical copies (replicas, denoted by the Greek index) of the liquid mixture where the interaction of the liquid particles has a very special feature: pairs of liquid particles interact only if they belong to the same replica.

In the following we assume $T_0 = T_1 \equiv T$, hence

$$-\beta\bar{A} = \frac{1}{Z_0}\lim_{s\to 0}\frac{d}{ds}Z^{\text{rep}}(s) = \lim_{s\to 0}\frac{d}{ds}[-\beta A^{\text{rep}}(s)]. \quad (9)$$

Thus we have related the thermodynamic potential of the partly quenched system to the limiting case of the thermodynamic potential of a fully equilibrated system. Structure functions and further thermodynamic properties of the partly quenched system can now be obtained from the corresponding quantities of the fully equilibrated replicated system by special prescriptions, involving throughout limits $s\to 0$: a complete set of these rules is compiled in Ref. [8].

A. The structure

1. The replica Ornstein-Zernike equation

The structure of a binary liquid inside a porous matrix can be most readily determined via the replica Ornstein-Zernike (ROZ) equations. Following similar lines to the one-component case, these relations are derived from the standard Ornstein-Zernike (OZ) equations for the fully equilibrated $(2s+1)$-component system, relating correlation functions $h_{ij}^{\text{rep}}(s) = h_{ij}^{\text{rep}}(r;s)$ and $c_{ij}^{\text{rep}}(s) = c_{ij}^{\text{rep}}(r;s)$. Since there is no risk of ambiguity, we can suppress in the following the arguments r and q of the functions; the arguments are obvious from the following notation: functions in q space carry a tilde, while all other functions are in r space. The densities of the matrix is denoted by ρ_0, the partial densities of the two liquid components by ρ_1 and ρ_2. Introducing O (E) as the set of odd (even) numbers less equal than $2s$ and using the symmetry relations

$$c_{0i}^{\text{rep}}(s) = c_{01}^{\text{rep}}(s) \quad i\in O; \quad c_{0i}^{\text{rep}}(s) = c_{02}^{\text{rep}}(s) \quad i\in E; \quad (10)$$

$$c_{ii}^{\text{rep}}(s) = c_{11}^{\text{rep}}(s) \quad i\in O; \quad c_{ii}^{\text{rep}}(s) = c_{22}^{\text{rep}}(s) \quad i\in E;$$

$$c_{ij}^{\text{rep}}(s) = c_{12}^{\text{rep}}(s) \quad i\in O, \ j=i+1; \quad (11)$$

$$c_{ij}^{\text{rep}}(s) = c_{13}^{\text{rep}}(s) \quad i,j\in O, \ i\neq j;$$

$$c_{ij}^{\text{rep}}(s) = c_{14}^{\text{rep}}(s) \quad i\in O, \ j\in E, \ j\neq i+1; \quad (12)$$

$$c_{ij}^{\text{rep}}(s) = c_{24}^{\text{rep}}(s) \quad i,j\in E, \ i\neq j \quad (13)$$

(and similar relations for the h's) and finally taking the limit $s\to 0$, one finally arrives at the following set of integral equations where $\otimes$ represents a convolution:

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

$$h_{01} = c_{01} + \rho_0 c_{00}\otimes h_{01} + \rho_1 c_{01}\otimes h_{11} + \rho_2 c_{02}\otimes h_{12} - \rho_1 c_{01}\otimes h_{13}$$
$$- \rho_2 c_{02}\otimes h_{14},$$

$$h_{02} = c_{02} + \rho_0 c_{00}\otimes h_{02} + \rho_1 c_{01}\otimes h_{12} + \rho_2 c_{02}\otimes h_{22} - \rho_1 c_{01}\otimes h_{14}$$
$$- \rho_2 c_{02}\otimes h_{24},$$

$$h_{11} = c_{11} + \rho_0 c_{01}\otimes h_{01} + \rho_1 c_{11}\otimes h_{11} + \rho_2 c_{12}\otimes h_{12} - \rho_1 c_{13}\otimes h_{13}$$
$$- \rho_2 c_{14}\otimes h_{14},$$

$$h_{12} = c_{12} + \rho_0 c_{01}\otimes h_{02} + \rho_1 c_{11}\otimes h_{12} + \rho_2 c_{12}\otimes h_{22} - \rho_1 c_{13}\otimes h_{14}$$
$$- \rho_2 c_{14}\otimes h_{24}, \quad (14)$$

$$h_{22} = c_{22} + \rho_0 c_{02}\otimes h_{02} + \rho_1 c_{12}\otimes h_{12} + \rho_2 c_{22}\otimes h_{22} - \rho_1 c_{14}\otimes h_{14}$$
$$- \rho_2 c_{24}\otimes h_{24},$$

$$h_{13} = c_{13} + \rho_0 c_{01}\otimes h_{01} + \rho_1 c_{11}\otimes h_{13} + \rho_2 c_{12}\otimes h_{14} + \rho_1 c_{13}\otimes h_{11}$$
$$+ \rho_2 c_{14}\otimes h_{12} - 2\rho_1 c_{13}\otimes h_{13} - 2\rho_2 c_{14}\otimes h_{14},$$

$$h_{14} = c_{14} + \rho_0 c_{01}\otimes h_{02} + \rho_1 c_{11}\otimes h_{14} + \rho_2 c_{12}\otimes h_{24} + \rho_1 c_{13}\otimes h_{12}$$
$$+ \rho_2 c_{14}\otimes h_{22} - 2\rho_1 c_{13}\otimes h_{14} - 2\rho_2 c_{14}\otimes h_{24},$$

$$h_{24} = c_{24} + \rho_0 c_{02}\otimes h_{02} + \rho_1 c_{12}\otimes h_{14} + \rho_2 c_{22}\otimes h_{24} + \rho_1 c_{14}\otimes h_{12}$$
$$+ \rho_2 c_{24}\otimes h_{22} - 2\rho_1 c_{14}\otimes h_{14} - 2\rho_2 c_{24}\otimes h_{24}.$$

To some of the above relations, alternative equations can be derived:

$$h_{01} = c_{01} + \rho_0 c_{01} \otimes h_{00} + \rho_1 c_{11} \otimes h_{01} + \rho_2 c_{12} \otimes h_{02} - \rho_1 c_{13} \otimes h_{01}$$
$$- \rho_2 c_{14} \otimes h_{02},$$

$$h_{02} = c_{02} + \rho_0 c_{02} \otimes h_{00} + \rho_1 c_{12} \otimes h_{01} + \rho_2 c_{22} \otimes h_{02} - \rho_1 c_{14} \otimes h_{01}$$
$$- \rho_2 c_{24} \otimes h_{02},$$

$$\text{(15)}$$

$$h_{12} = c_{12} + \rho_0 c_{02} \otimes h_{01} + \rho_1 c_{12} \otimes h_{11} + \rho_2 c_{22} \otimes h_{12} - \rho_1 c_{14} \otimes h_{13}$$
$$- \rho_2 c_{24} \otimes h_{14},$$

$$h_{14} = c_{14} + \rho_0 c_{02} \otimes h_{01} + \rho_1 c_{14} \otimes h_{11} + \rho_2 c_{24} \otimes h_{12} + \rho_1 c_{12} \otimes h_{13}$$
$$+ \rho_2 c_{22} \otimes h_{14} - 2\rho_1 c_{14} \otimes h_{13} - 2\rho_2 c_{24} \otimes h_{14}.$$

Similarly to the one-component case, we can introduce the blocking (disconnected) parts of the correlation functions, i.e., $h_{11}^b = \lim_{s \to 0} h_{13}^{\text{rep}}(s)$, $h_{12}^b = \lim_{s \to 0} h_{14}^{\text{rep}}(s)$, and $h_{22}^b = \lim_{s \to 0} h_{24}^{\text{rep}}(s)$ and the corresponding connected parts, defined as

$$h_{11}^c = h_{11} - h_{13}, \quad h_{12}^c = h_{12} - h_{14}, \quad h_{22}^c = h_{22} - h_{24}. \quad \text{(16)}$$

Similar relations hold for the c_{ij}. For the definition of the blocked and the connected parts of the correlation functions see, for instance, [7]. Introducing finally the matrix-notation

$$\boldsymbol{\rho}_1 = \begin{pmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{pmatrix}, \quad \mathbf{h}_{01} = \begin{pmatrix} h_{01} \\ h_{02} \end{pmatrix}, \quad \mathbf{c}_{01} = \begin{pmatrix} c_{01} \\ c_{02} \end{pmatrix},$$

$$\text{(17)}$$

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

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

the ROZ equations (14) can be written in the following compact form (''T'' denotes the transpose of a vector):

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

$$\mathbf{h}_{01} = \mathbf{c}_{01} + \mathbf{h}_{01} \otimes \rho_0 c_{00} + \boldsymbol{\rho}_1 \mathbf{h}_{11} \otimes \mathbf{c}_{01} - \boldsymbol{\rho}_1 \mathbf{h}_{12} \otimes \mathbf{c}_{01},$$

$$\text{(18)}$$

$$\mathbf{h}_{11} = \mathbf{c}_{11} + \mathbf{h}_{01} \otimes \rho_0 \mathbf{c}_{01}^{\text{T}} + \boldsymbol{\rho}_1 \mathbf{h}_{11} \otimes \mathbf{c}_{11} - \boldsymbol{\rho}_1 \mathbf{h}_{12} \otimes \mathbf{c}_{12},$$

$$\mathbf{h}_{12} = \mathbf{c}_{12} + \mathbf{h}_{01} \otimes \rho_0 \mathbf{c}_{01}^{\text{T}} + \boldsymbol{\rho}_1 \mathbf{h}_{12} \otimes \mathbf{c}_{11} + \boldsymbol{\rho}_1 \mathbf{h}_{11} \otimes \mathbf{c}_{12}$$
$$- 2\boldsymbol{\rho}_1 \mathbf{h}_{12} \otimes \mathbf{c}_{12}.$$

These equations are formally equivalent to the ROZ equations of the one-component case. In addition, one can show [18] that by extending the definitions (17) in a straightfor-

ward way, the above equations are also valid for the general case of a k-component liquid inside a porous (one-component) matrix.

2. Integral-equation closure relations

The ROZ equations can now be solved with one of the standard closure relations of liquid-state theory [19], such as the Percus-Yevick (PY) or the hypernetted chain (HNC) approximation. Our program package is based on Lomba's implementation to solve the ROZ equations for the one-component case, using a hybrid Newton-Raphson procedure to solve integral equations in liquid-state physics; the original numerical concept stems from Gillan [20] and was refined in subsequent work by Labik, Malijevsky, and Vonka (LMV) [21] and by Høye, Lomba, and Stell [22]. Our implementation follows closely the one outlined in Ref. [11]; in particular, the Newton-Raphson part of the algorithm requires the inversion of the Jacobian of the system of integral equations; this matrix is built up by quantities $F_{\alpha\beta\mu\nu}$ which are defined as

$$F_{\alpha\beta\mu\nu}(q) = \frac{d\tilde{\Gamma}_{\alpha\beta}(q)}{d\tilde{C}_{\mu\nu}(q)}. \quad \text{(19)}$$

The capitalized quantities stand for $\tilde{C}_{\mu\nu}(q) = q\tilde{c}_{\mu\nu}(q)$, etc., and $\gamma_{\mu\nu} = h_{\mu\nu} - c_{\mu\nu}$. The pairs of indices (α, β) and (μ, ν) now run over (0,1), (0,2), (1,1), (1,2), (2,2), (1,3), (1,4), and (2,4) and the 64 $F_{\alpha\beta\mu\nu}$ are of course considerably more complex than in the one-component case. In principle, they can be derived in a straightforward manner by using symbolic languages, such as MAPLE; they can be provided upon request.

3. The optimized random phase approximation

Another closure relation to the ROZ equations is the optimized random-phase approximation (ORPA), which can also be obtained from a perturbative approach [14]. The formalism of the ORPA can be extended to porous systems and again it is most convenient to use the replica trick: we formulate the ORPA for the replicated system and then take the limiting case.

In the ORPA one assumes that all the pair potentials between the different particles can be split up into a reference part (index ''r'') and a perturbation part (index ''p''), i.e.,

$$\Phi_{ij}(r) = \Phi_{\text{r};ij}(r) + \Phi_{\text{p};ij}(r). \quad \text{(20)}$$

Since in the present contribution we consider exclusively hard-core interactions, it is most obvious that the $\Phi_{\text{r};ij}(r)$ are represented throughout by hard-sphere potentials, characterized by hard-sphere diameters σ_{ij}. This defines $\Phi_{\text{p};ij}(r)$ apart from finite variations inside the core. In a similar way, the correlation functions are split up into reference and perturbation parts. In the following, it is convenient to introduce matrices C and H, which collect these correlation functions via $\mathsf{C}_{ij} = \sqrt{\rho_i \rho_j} c_{ij}$, etc.

The RPA closure relation assumes that

$$c_{\mathrm{p};ij}(r) = -\beta\Phi_{\mathrm{p};ij}(r), \quad r > \sigma_{ij} \tag{21}$$

and—for instance—$c_{\mathrm{p};ij}(r) = 0$ for $r < \sigma_{ij}$, which leads to a violation of the core condition, i.e., $g_{ij}(r) \neq 0$ inside the core region. This deficiency is compensated by the additional (optimized) closure relation: $c_{\mathrm{p};ij}(r)$ is chosen inside the core so that

$$g_{ij}(r) = 0 \text{ for } r < \sigma_{ij} \iff h_{\mathrm{p};ij}(r) = 0 \text{ for } r < \sigma_{ij}. \tag{22}$$

For completeness, we would like to point out that in the case of soft interactions, the reference part of the potentials can be mapped back onto a set of suitably chosen hard-sphere potentials using the prescription of Weeks, Chandler, and Andersen [15,23].

It can now be shown that the reduced (dimensionless) excess free energy of the system (over the ideal gas) is given by [14]

$$A^* = -\frac{\beta A^{\mathrm{ex}}}{V} = A_{\mathrm{r}}^* + A_{\mathrm{HTA}}^* + A_{\mathrm{ORPA}}^*, \tag{23}$$

where A_{r}^* is the excess free energy of the (hard-sphere) reference system, A_{HTA}^* is the high-temperature correction, given by

$$A_{\mathrm{HTA}}^* = \frac{1}{2}\sum_{ij}\rho_i\rho_j\int d\mathbf{r}\, g_{\mathrm{r};ij}(r)c_{\mathrm{p};ij}(r), \tag{24}$$

and A_{ORPA}^* is the sum of composite ring diagrams, which is found to be

$$A_{\mathrm{ORPA}}^* = A_{\mathrm{ORPA}}^*[\tilde{\mathsf{C}}_{\mathrm{p}}] = -\frac{1}{2(2\pi)^3}\int d\mathbf{q}\,\{\mathrm{Tr}[\tilde{\mathsf{C}}_{\mathrm{p}}(q)\mathsf{S}_{\mathrm{r}}(q)]$$

$$+ \ln\mathrm{Det}[\mathsf{I} - \tilde{\mathsf{C}}_{\mathrm{p}}(q)\mathsf{S}_{\mathrm{r}}(q)]\}. \tag{25}$$

"Tr" and "Det" denote the trace and the determinant of a matrix, I is the unit matrix, and $\mathsf{S}_{\mathrm{r}}(q)$ is the matrix of the partial structure factors of the hard-sphere reference system. The ORPA contribution to the free energy is now a functional of the perturbation part of the direct correlation functions $c_{\mathrm{p};ij}$. It is straightforward to show that

$$\left[\frac{\delta A_{\mathrm{ORPA}}^*}{\delta c_{\mathrm{p};ij}}\right](r) \propto h_{\mathrm{p};ij}(r). \tag{26}$$

This relation points out that the solution of the OZ equations along with the ORPA closure relations (21) and (22) is equivalent to a minimization problem of the functional $A_{\mathrm{ORPA}}^*[\tilde{\mathsf{C}}_{\mathrm{p}}]$ with respect to variations of the direct correlation functions $c_{\mathrm{p};ij}(r)$ inside the core region as the minimization condition (26) is equivalent to the optimization condition (22). This fact is particularly useful for the *numerical* solution of the ORPA: although, of course, the numerical solutions of integral equations and of the minimization of the functional should lead to the same results, we found that—

from the numerical point of view—in some cases it can be more convenient to solve the minimization problem.

As shown in [2,18], the expression for the free energy (23) can be rewritten with the help of the OZ equations and Parseval's theorem as follows:

$$A^* = A_{\mathrm{r}}^* + \frac{1}{2}\sum_{i,j}\rho_i\rho_j\tilde{c}_{\mathrm{p};ij}\bigg|_{q=0} - \frac{1}{2}\sum_i\rho_i c_{\mathrm{p};ii}\bigg|_{r=0}$$

$$- \frac{1}{2(2\pi)^3}\int d\mathbf{q}\,\{\ln\mathrm{Det}[1 - \tilde{\mathsf{C}}(q)] - \ln\mathrm{Det}[1$$

$$- \tilde{\mathsf{C}}_{\mathrm{r}}(q)]\}. \tag{27}$$

The replicated system is now a $(2s+1)$-component system with a very special set of interatomic potentials $\Phi_{ij}(r)$. We assume that the matrix particles are pure hard spheres; then the RPA closure relations read

$$c_{00}^{\mathrm{rep}}(s) = c_{\mathrm{r};00}^{\mathrm{rep}}(s),$$

$$c_{ij}^{\mathrm{rep}}(s) = c_{\mathrm{r};ij}^{\mathrm{rep}}(s) + c_{\mathrm{p};ij}^{\mathrm{rep}}(s) \text{ for } i,j = 01,02,11,12,22,$$
$$\tag{28}$$

$$c_{ij}^{\mathrm{rep}}(s) = c_{\mathrm{r};ij}^{\mathrm{rep}}(s) \quad \text{for } i,j = 13,14,24$$

with $c_{\mathrm{p};ij}^{\mathrm{rep}} = -\beta\Phi_{\mathrm{p};ij}(r)$, while the core conditions now read $h_{\mathrm{p};ij}(r) = 0$ for $r < \sigma_{ij}$. Using the symmetry properties of the replicated system, the expression for the free energy in the replicated system, $(A^{\mathrm{rep}})^*$, is given by

$$(A^{\mathrm{rep}})^*(s) = (A_{\mathrm{r}}^{\mathrm{rep}})^*(s) + \frac{1}{2}\left[s\sum_{i=1,2}\rho_i^2\tilde{c}_{\mathrm{p};ii}^{\mathrm{rep}}(s)\right.$$

$$\left. + 2s\sum_{\substack{i<j\\i=0,1}}\rho_i\rho_j\tilde{c}_{\mathrm{p};ij}^{\mathrm{rep}}(s)\right]_{q=0}$$

$$- \frac{1}{2}\left[s\sum_{i=1,2}\rho_i c_{\mathrm{p};ii}^{\mathrm{rep}}(s)\right]_{r=0}$$

$$- \frac{1}{2(2\pi)^3}\int d\mathbf{q}\,\{\ln\mathrm{Det}[1 - \tilde{\mathsf{C}}^{\mathrm{rep}}(s)]$$

$$- \ln\mathrm{Det}[1 - \tilde{\mathsf{C}}_{\mathrm{r}}^{\mathrm{rep}}(s)]\}. \tag{29}$$

Again, closer investigation of the symmetry of the two matrices appearing in the above equation allows us to derive the following identity, which can be applied to both contributions to the above integral:

$$\ln \mathrm{Det}[1-\tilde{\mathbf{C}}^{\mathrm{rep}}(s)]=(s-1)\ln(\{1-\rho_1(\tilde{c}_{11}^{\mathrm{rep}}(s)-\tilde{c}_{13}^{\mathrm{rep}}(s)]\}\{1-\rho_2[\tilde{c}_{22}^{\mathrm{rep}}(s)-\tilde{c}_{24}^{\mathrm{rep}}(s)]\}$$

$$-\rho_1\rho_2[\tilde{c}_{12}^{\mathrm{rep}}(s)-\tilde{c}_{14}^{\mathrm{rep}}(s)]^2)+\ln([1-\rho_0\tilde{c}_{00}^{\mathrm{rep}}(s)]\{[1-\rho_1\tilde{c}_{11}^{\mathrm{rep}}(s)-\rho_1(s-1)\tilde{c}_{13}^{\mathrm{rep}}(s)]$$

$$\times[1-\rho_2\tilde{c}_{22}^{\mathrm{rep}}(s)-\rho_2(s-1)\tilde{c}_{24}^{\mathrm{rep}}(s)]-\rho_1\rho_2[\tilde{c}_{12}^{\mathrm{rep}}(s)+(s-1)\tilde{c}_{14}^{\mathrm{rep}}(s)]^2\}$$

$$-s\rho_0\rho_1[\tilde{c}_{01}^{\mathrm{rep}}(s)]^2[1-\rho_2\tilde{c}_{22}^{\mathrm{rep}}(s)-\rho_2(s-1)\tilde{c}_{24}^{\mathrm{rep}}(s)]^2-2s\rho_0\rho_1\rho_2\tilde{c}_{01}^{\mathrm{rep}}(s)\tilde{c}_{02}^{\mathrm{rep}}(s)$$

$$\times[\tilde{c}_{12}^{\mathrm{rep}}(s)+(s-1)\tilde{c}_{14}^{\mathrm{rep}}(s)]-s\rho_0\rho_2[\tilde{c}_{02}^{\mathrm{rep}}(s)]^2[1-\rho_1\tilde{c}_{11}^{\mathrm{rep}}(s)-\rho_1(s-1)\tilde{c}_{13}^{\mathrm{rep}}(s)]^2). \qquad (30)$$

The free energy of the quenched system, $\bar{A}$, is now obtained via $\bar{A}=\lim_{s\to 0}(d/ds)A^{\mathrm{rep}}(s)$ [8,2],

$$\bar{A}^*=A_{\mathrm{r}}^*-\mathcal{A}[\mathsf{C}]+\mathcal{A}[\mathsf{C}_{\mathrm{r}}]+\frac{1}{2}[\rho_1^2\tilde{c}_{\mathrm{p};11}+\rho_2^2\tilde{c}_{\mathrm{p};22}+2\rho_0\rho_1\tilde{c}_{\mathrm{p};01}$$

$$+2\rho_0\rho_2\tilde{c}_{\mathrm{p};02}+2\rho_1\rho_2\tilde{c}_{\mathrm{p};12}]_{q=0}$$

$$-\frac{1}{2}[\rho_1 c_{\mathrm{p};11}+\rho_2 c_{\mathrm{p};22}]_{r=0}, \qquad (31)$$

where the functional $\mathcal{A}[\mathsf{C}]$ is defined as follows:

$$\mathcal{A}[\mathsf{C}]=\frac{1}{2(2\pi)^3}\int d\mathbf{q}\left\{\ln\{(1-\rho_1\tilde{c}_{11}^c)(1-\rho_1\tilde{c}_{22}^c)\right.$$

$$-\rho_1\rho_2[\tilde{c}_{12}^c]^2\}-\frac{1}{[1-\rho_1\tilde{c}_{11}^c][1-\rho_2\tilde{c}_{22}^c]-\rho_1\rho_2[\tilde{c}_{12}^c]^2}$$

$$\times\left\{\rho_1\tilde{c}_{13}(1-\rho_2\tilde{c}_{22}^c)+\rho_2\tilde{c}_{24}(1-\rho_1\tilde{c}_{11}^c)\right.$$

$$+2\rho_1\rho_2\tilde{c}_{14}\tilde{c}_{12}^c(q)+\frac{\rho_0}{1-\rho_0\tilde{c}_{00}}[\rho_1\tilde{c}_{01}^2(1-\rho_2\tilde{c}_{22}^c)$$

$$\left.\left.+\rho_2\tilde{c}_{02}^2(1-\rho_1\tilde{c}_{11}^c)+2\rho_1\rho_2\tilde{c}_{01}\tilde{c}_{02}\tilde{c}_{12}^c]\right\}\right\}. \qquad (32)$$

Finally, one can show that for the above expression of the free energy the following relation holds:

$$\left(\frac{\delta\bar{A}^*}{\delta c_{\mathrm{p};ij}}\right)(r)=\frac{2-\delta_{ij}}{2}\rho_i\rho_j[g_{\mathrm{r};ij}(r)+h_{\mathrm{p};ij}(r)], \qquad (33)$$

which means that the minimization of the functional $\bar{A}^*[\mathsf{C}_{\mathrm{p}}]$ with respect to variations of the $c_{\mathrm{p};ij}(r)$ inside the core region is equivalent to the optimization requirement (22).

The numerical solution of the ORPA leads to the correlation functions; to this end we have discretized these functions both in r and in q space, using typically 1024 grid points and a mesh-size of $\Delta r=0.01\sigma_{11}$ (σ_{11} being the diameter of species 1 of the binary liquid; furthermore, we assume $\sigma_{11}<\sigma_{22}$). Given the system, we first calculate the correlation functions $h_{r;ij}$ and $c_{r;ij}$ of the reference system by solving the ROZ equations (14) along with the PY closure using the LMV algorithm adapted to the present problem [11]. Then we solve the ORPA by minimizing the functional

$\mathcal{A}[\mathsf{C}]$ (32) using the steepest-descent method. The advantage of this minimization algorithm lies in the fact that the explicit calculation of the functional is not required; we only need its derivatives, i.e., $h_{\mathrm{p};ij}$, which we easily obtain from the so-called residual ROZ equations [18]. Starting from an initial guess for the direct correlation functions inside the core region (for instance, the simple RPA expression), we create with these gradients a sequence of new, improved direct correlation functions until we obtain a minimum in the functional within a sufficient accuracy. The step size in the sequence of these estimates is triggered by a parameter ξ, which measures the degree of violation of the core condition by the resulting perturbation parts of the total correlation functions, $h_{\mathrm{p};ij}$,

$$\xi=\left\{\left[\sum_{j=1,2}\sum_{k:r_k<\sigma_{0j}}[H_{\mathrm{p};0j}(r_k)]^2\right.\right.$$

$$\left.\left.+\sum_{i,j=1,2;i\leqslant j}\sum_{k:r_k<\sigma_{ij}}[H_{\mathrm{p};ij}(r_k)]^2\right]\Delta r\right\}^{1/2}. \qquad (34)$$

B. The thermodynamic properties

1. General expressions

Using the replica trick we derive—as a straightforward generalization of the one-component case [8]—in a first step the Gibbs-Duhem relation and the virial equation. If we use a grand-canonical ensemble for the replicas and a canonical ensemble for the matrix, one can easily derive an expression between the grand potential of the replicated system, $\Omega^{\mathrm{rep}}(s)$, and the quenched system, $\bar{\Omega}$, i.e., $\bar{\Omega}=\lim_{s\to 0}(d/ds)\Omega^{\mathrm{rep}}(s)$. $d\Omega^{\mathrm{rep}}(s)$ now contains—with respect to the one-component case— an additional term due to changes $d\mu_2$ and we can proceed along similar lines: the expression for $d\bar{\Omega}$ can be integrated to give

$$\bar{\Omega}=-PV, \qquad (35)$$

P, the pressure of the partly quenched system, being given by

$$P=-\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu_1,\mu_2,\rho_0}. \qquad (36)$$

In a similar way we find for the free energy, $\bar{A}$,

$$\bar{A}=-PV+\mu_1 N_1+\mu_2 N_2. \qquad (37)$$

To derive the virial equation, we start again from the expression for the pressure in the replicated system, $P^{\text{rep}}(s)$. As in the one-component system, the pressure in the partly quenched system, P, is given by

$$\beta P = \beta \lim_{s \to 0} \frac{dP^{\text{rep}}(s)}{ds} + \rho_0 \left(\frac{\partial \beta P}{\partial \rho_0} \right)_{V,T,\mu_1,\mu_2}. \tag{38}$$

Inserting the virial equation for the replicated system, one therefore obtains

$$\beta P - \rho_0 \left(\frac{\partial \beta P}{\partial \rho_0} \right)_{V,T,\mu_1,\mu_2}$$

$$= \sum_i \rho_i - \frac{\beta}{6} \int d\mathbf{r} r \left[\rho_0^2 \lim_{s \to 0} \frac{dg_{00}^{\text{rep}}(s)}{ds} \Phi_{00}' + \sum_{i=1,2} \rho_i^2 g_{ii} \Phi_{ii}' \right.$$

$$\left. + 2 \sum_{i=1,2} \rho_0 \rho_i g_{0i} \Phi_{0i}' + 2\rho_1 \rho_2 g_{12} \Phi_{12}' \right], \tag{39}$$

which reduces for hard-core interactions to

$$\beta P - \rho_0 \left(\frac{\partial \beta P}{\partial \rho_0} \right)_{V,T,\mu_1,\mu_2}$$

$$= \sum_i \rho_i - \frac{2\pi}{3} \left[\rho_0^2 \sigma_{00}^3 \lim_{s \to 0} \frac{dg_{00}^{\text{rep}}(\sigma_{00};s)}{ds} + \sum_{i=1,2} \rho_i^2 \sigma_{ii}^3 g_{ii}(\sigma_{ii}) \right.$$

$$\left. + 2 \sum_{i=1,2} \rho_0 \rho_i \sigma_{0i}^3 g_{0i}(\sigma_{0i}) + 2\rho_1 \rho_2 \sigma_{12}^3 g_{12}(\sigma_{12}) \right]. \tag{40}$$

To derive the compressibility equation we proceed as follows. From Eq. (35) one finds

$$\frac{V}{kT} \left(\frac{\partial P}{\partial \rho_1} \right)_{V,T,N_2,\rho_0} = -\frac{1}{kT} \left(\frac{\partial \bar{\Omega}}{\partial \rho_1} \right)_{V,T,N_2,\rho_0}$$

$$= \lim_{s \to 0} \frac{d}{ds} \left[-\frac{1}{kT} \frac{\partial \Omega^{\text{rep}}(s)}{\partial \rho_1^{\text{rep}}(s)} \right]_{V,T,N_2,\rho_0}. \tag{41}$$

Introducing an external potential $u(\mathbf{r})$ in the replicated system that acts on the liquid particles only, we can use the standard relation of classical density-functional theory [24] to rewrite the bracketed term of the above equation as follows:

$$\left[-\frac{1}{kT} \frac{\partial \Omega^{\text{rep}}(s)}{\partial \rho_1^{\text{rep}}(s)} \right]_{V,T,N_2,\rho_0}$$

$$= \sum_{i=1}^{2s} \int \int d\mathbf{r}_1 d\mathbf{r}_2$$

$$\times \left[\frac{\delta \ln \Xi^{\text{rep}}(s)}{\delta(\beta[\mu_i - u(\mathbf{r}_1)])} \frac{\delta(\beta[\mu_i - u(\mathbf{r}_1)])}{\delta \rho_1^{(1),\text{rep}}(\mathbf{r}_2;s)} \right]_{u=0}, \tag{42}$$

where $\rho_1^{(1),\text{rep}}(\mathbf{r};s)$ is the inhomogeneous one-particle density of species 1 in the replicated system. The two functional derivatives of the right-hand side of the above relation can easily be calculated and yield

$$\frac{\delta \ln \Xi^{\text{rep}}(s)}{\delta(\beta[\mu_i - u(\mathbf{r}_1)])} = \rho_i^{(1),\text{rep}}(\mathbf{r}_1;s)$$

$$= \begin{cases} \rho_1^{(1),\text{rep}}(\mathbf{r}_1;s) & \text{for } i=1,3,\ldots,2s-1 \\ \rho_2^{(1),\text{rep}}(\mathbf{r}_1;s) & \text{for } i=2,4,\ldots,2s \end{cases}$$

and

$$\frac{\delta(\beta[\mu_i - u(\mathbf{r}_1)])}{\delta \rho_1^{(1),\text{rep}}(\mathbf{r}_2;s)} = \sum_{j=1}^{2s-1}{}' \left(\delta_{ij} \frac{\delta(\mathbf{r}_1,\mathbf{r}_2)}{\rho_j^{(1),\text{rep}}(\mathbf{r}_2;s)} \right.$$

$$\left. - c_{ij}^{(2),\text{rep}}(\mathbf{r}_1,\mathbf{r}_2;s) \right), \tag{43}$$

where summation is taken only over odd j values. Inserting this into Eq. (42) and setting $u(\mathbf{r})=0$, we find

$$\frac{V}{kT} \left(\frac{\partial P}{\partial \rho_1} \right)_{V,T,N_2,\rho_0} = V \lim_{s \to 0} \frac{d}{ds} \{ s - s\rho_1^{\text{rep}}(s) \tilde{c}_{11}^{\text{rep}}(q=0;s)$$

$$- s(s-1)\rho_1^{\text{rep}}(s) \tilde{c}_{13}^{\text{rep}}(q=0;s)$$

$$- s\rho_2^{\text{rep}}(s) \tilde{c}_{12}^{\text{rep}}(q=0;s)$$

$$- s(s-1)\rho_2^{\text{rep}}(s) \tilde{c}_{14}^{\text{rep}}(q=0;s) \}, \tag{44}$$

which finally yields

$$\left(\frac{\partial \beta P}{\partial \rho_1} \right)_{V,T,N_2,\rho_0} = 1 - \rho_1 \tilde{c}_{11}^c(q=0) - \rho_2 \tilde{c}_{12}^c(q=0). \tag{45}$$

In a similar way we obtain

$$\left(\frac{\partial \beta P}{\partial \rho_2} \right)_{V,T,N_1,\rho_0} = 1 - \rho_1 \tilde{c}_{12}^c(q=0) - \rho_2 \tilde{c}_{22}^c(q=0). \tag{46}$$

One can furthermore relate the above equations to the chemical potentials μ_i. To this end we start from the relation $\mu_1 = -(\partial \bar{A}/\partial N_1)_{V,T,N_2,\rho_0} = \lim_{s \to 0} \mu_1^{\text{rep}}(s)$ and a similar relation for μ_2. Using again the density-functional formalism and Eq. (43), one finds

$$\rho_1\left(\frac{\partial\beta\mu_1}{\partial\rho_1}\right)_{V,T,N_2,\rho_0}$$

$$=\lim_{s\to0}\left[\rho_1^{\mathrm{rep}}(s)\frac{\partial\beta\mu_1^{\mathrm{rep}}(s)}{\partial\rho_1^{\mathrm{rep}}(s)}\right]$$

$$=\lim_{s\to0}\int d\mathbf{r}_2\left[\rho_1^{(1),\mathrm{rep}}(\mathbf{r}_2;s)\frac{\delta(\beta[\mu_1^{\mathrm{rep}}(s)-u_{12}(\mathbf{r}_1)])}{\delta\rho_1^{(1),\mathrm{rep}}(\mathbf{r}_2;s)}\right]_{u=0}$$

$$=\lim_{s\to0}\{(1-\rho_1^{\mathrm{rep}}(s)\tilde{c}_{11}^{\mathrm{rep}}(q=0;s)$$

$$-(s-1)\rho_1^{\mathrm{rep}}(s)\tilde{c}_{13}^{\mathrm{rep}}(q=0;s))\}$$

$$=1-\rho_1\tilde{c}_{11}^c(q=0). \tag{47}$$

Following similar lines one derives also

$$\rho_1\left(\frac{\partial\beta\mu_1}{\partial\rho_2}\right)_{V,T,N_1,\rho_0}=-\rho_1\tilde{c}_{12}^c(q=0), \tag{48}$$

$$\rho_2\left(\frac{\partial\beta\mu_2}{\partial\rho_2}\right)_{V,T,N_1,\rho_0}=1-\rho_2\tilde{c}_{22}^c(q=0),\quad\rho_2\left(\frac{\partial\beta\mu_2}{\partial\rho_1}\right)_{V,T,N_2,\rho_0}$$

$$=-\rho_2\tilde{c}_{12}^c(q=0). \tag{49}$$

Consistent with the Gibbs-Duhem relation, one finds that

$$\left(\frac{\partial\beta P}{\partial\rho_j}\right)_{V,T,N_{j'},\rho_0}=\sum_{i=1,2}\rho_i\left(\frac{\partial\beta\mu_i}{\partial\rho_j}\right)_{V,T,N_{j'},\rho_0}, \tag{50}$$

where $j'=1$ for $j=2$ and vice versa.

Finally, to derive the expression for the excess internal energy of the quenched system, $\bar{U}^{\mathrm{ex}}$, we start again from the corresponding expression for the replicated system,

$$\frac{U^{\mathrm{ex;\,rep}}(s)}{V}=\frac{1}{2}\left\{\sum_{i=1,2}2s\rho_0\rho_i^{\mathrm{rep}}(s)\int d\mathbf{r}\,g_{0i}^{\mathrm{rep}}(s)\Phi_{0i}\right.$$

$$+2s\rho_1^{\mathrm{rep}}(s)\rho_2^{\mathrm{rep}}(s)\int d\mathbf{r}\,g_{12}^{\mathrm{rep}}(s)\Phi_{12}$$

$$\left.+\sum_{i=1,2}s[\rho_i^{\mathrm{rep}}(s)]^2\int d\mathbf{r}\,g_{ii}^{\mathrm{rep}}(s)\Phi_{ii}\right\} \tag{51}$$

and using the relation $\bar{U}^{\mathrm{ex}}=\lim_{s\to0}(d/ds)U^{\mathrm{ex;\,rep}}(s)$, hence,

$$\frac{\bar{U}^{\mathrm{ex}}}{V}=\sum_{i=1,2}\rho_0\rho_i\int d\mathbf{r}\,g_{0i}\Phi_{0i}+\frac{1}{2}\sum_{i=1,2}\rho_i^2\int d\mathbf{r}\,g_{ii}\Phi_{ii}$$

$$+\rho_1\rho_2\int d\mathbf{r}\,g_{12}\Phi_{12}. \tag{52}$$

It should be noted that the same relation can be obtained by using the definition that $\bar{U}^{\mathrm{ex}}$ is given by a double average of the Hamilton function: one over the degrees of freedom of the liquid for a fixed matrix and then over all possible matrix configurations. Furthermore, it is straightforward to show that the following Gibbs-Helmholtz relation holds:

$$\bar{U}^{\mathrm{ex}}=\frac{\partial}{\partial\beta}(\beta\bar{A}). \tag{53}$$

2. MSA and ORPA expressions

As shown in the preceding section, in the ORPA one can derive closed expressions for the free energy $\bar{A}$ [Eq. (31)]. In addition, in the version of the ORPA used in this contribution (which is equivalent to the MSA) one is able to derive closed expressions for the perturbation contribution to the chemical potentials, $\mu_{\mathrm{p};i}$,

$$\beta\mu_{\mathrm{p};1}=\beta\mu_1-\beta\mu_{\mathrm{r};1}=-[\rho_1\tilde{c}_{\mathrm{p};11}+\rho_0\tilde{c}_{\mathrm{p};01}+\rho_2\tilde{c}_{\mathrm{p};12}]_{q=0}$$

$$+\frac{1}{2}[c_{\mathrm{p};11}]_{r=0}, \tag{54}$$

$$\beta\mu_{\mathrm{p};2}=\beta\mu_2-\beta\mu_{\mathrm{r};2}=-[\rho_2\tilde{c}_{\mathrm{p};22}+\rho_0\tilde{c}_{\mathrm{p};02}+\rho_1\tilde{c}_{\mathrm{p};12}]_{q=0}$$

$$+\frac{1}{2}[c_{\mathrm{p};22}]_{r=0}. \tag{55}$$

The $\mu_{\mathrm{r};i}$ are the chemical potentials of the reference system. Above expressions can equally well be derived from the general MSA expressions for the replicated system [25] and taking the limit $s\to0$.

Using the results for $\bar{A}$ and the chemical potentials, one can obtain the pressure directly from the Gibbs-Duhem relation (37).

III. CONCLUSIONS

In this contribution we have presented the formalism to describe the structural and the thermodynamic properties of a binary liquid in equilibrium with a porous matrix. Following a similar approach to that in the one-component case, we used the replica trick, which establishes an isomorphism between the partly quenched system and a fully equilibrated system, consisting of the matrix and s identical, noninteracting copies of the binary liquid. In particular, we focus on hard-core systems. The formalism is based on the replica Ornstein-Zernike equations which have been presented for the general case of a k-component liquid in equilibrium with a porous matrix. These coupled integral equations can be complemented by standard liquid state closure relations, such as the Percus-Yevick or the hypernetted chain approximation. In particular, we have considered the optimized random-phase approximation (ORPA), an MSA-type closure relation that fully takes into account the core condition for the hard-sphere pair distribution functions. We have shown that the solution of the ORPA is equivalent to minimizing a suitably defined functional with respect to variations of the direct correlation functions inside the core region. General expressions for thermodynamic quantities and relations have been presented; for some of these (such as the perturbation

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