

Replica Ornstein–Zernike Equations for Polydisperse Quenched-Annealed Fluids. Hard Spheres in a Polydisperse Disordered Hard Sphere Matrix

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An extension of the replica Ornstein–Zernike (ROZ) equations for partly quenched *polydisperse* systems is presented. Explicit calculations have been performed for a hard sphere fluid confined by a polydisperse hard sphere disordered matrix. A numerical solution of the ROZ equations makes use of the orthonormal polynomials with the weight function corresponding to the distribution function of the diameters of matrix species.

The study of the behavior of fluids and mixtures in microporous solid adsorbents has received much interest recently, see e.g. refs 1–12. Theoretical tools to investigate the structural properties of these partly quenched (quenched-annealed) fluids have been based on the exact replica Ornstein–Zernike (ROZ) equations of Given and Stell^{1,2} and on Madden–Glandt approximation (MGOZ) for these equations.^{3,4} Several models have been developed in order to interpret the effects of confinement of fluids by real microporous adsorbents. In particular, the models of MacElroy and Raghavan,¹³ and of Kaminsky and Monson,¹⁴ have been designed for the methane–silica gel system. Both these models are restricted to the monodisperse gel particles. However, in many experimental situations, and in some systems of practical importance, the microporous adsorbents consist of particles of different diameters or may be characterized by a continuous distribution of diameters of species.^{15–17} In order to model such systems, an extension of the ROZ equations that takes into account polydispersity of the matrix particles is necessary. More generally, an extension of the ROZ equations is required to deal with the problem of adsorption and of structural properties of polydisperse fluids in either monodisperse or polydisperse matrices.

A polydisperse fluid mixture can be characterized by a continuous probability density of one or more parameters, such as the diameter of particles, for example. The effects of polydispersity in molecular mixtures has received much attention recently.^{18–26} In particular, in very recent works of Lado,^{25,26} the Ornstein–Zernike equation has been proposed and solved for a polydisperse mixture by using a novel algorithm. This theory is of much interest to extend for quenched–annealed systems of various kinds. In the present paper our principal goal is to reformulate the ROZ equations for a polydisperse partly quenched fluids and, for demonstrative purposes, to solve them for the most simple model.

We assume that a microporous adsorbent (matrix) has been prepared by quenching of an equilibrium polydisperse hard sphere fluid at density $\rho_0 = N_0/V$, where N_0 is the number of

hard spheres with different diameters and V is the volume of the system. The average density of particles with the diameter σ_{0i} is given by

$$\rho(\sigma_{0i}) = \rho_0 f_0(\sigma_{0i}) \quad (1)$$

where $f_0(\sigma_0)$ is the normalized distribution function of diameters,

$$\int f_0(\sigma_0) d\sigma_0 = 1 \quad (2)$$

The structure of a polydisperse quenched disordered matrix is characterized by the total, $h_{00}(r, \sigma_{0i}, \sigma_{0j})$, and the direct, $c_{00}(r, \sigma_{0i}, \sigma_{0j})$, correlation function (dcf), both being the functions of the particles' diameters. These functions are related each other via the Ornstein–Zernike equation (cf. refs 25, 26),

$$\begin{aligned} \gamma_{00}(r_{12}, \sigma_{0i}, \sigma_{0j}) &\equiv h_{00}(r_{12}, \sigma_{0i}, \sigma_{0j}) - c_{00}(r_{12}, \sigma_{0i}, \sigma_{0j}) \\ &= \rho_0 \int d\mathbf{r}_3 \int d\sigma_0 f_0(\sigma_0) h_{00}(r_{13}, \sigma_{0i}, \sigma_0) c_{00}(r_{32}, \sigma_0, \sigma_{0j}) \end{aligned} \quad (3)$$

Now, we would like to focus on another polydisperse fluid, described by the species index 1. It is considered at density $\rho_1 = N_1/V$. The average density of particles with the diameter σ_{1j} is determined similar to eq 1, $\rho(\sigma_{1j}) = \rho_1 f_1(\sigma_{1j})$, where $f_1(\sigma_{1j})$ is the normalized (cf. eq 2) distribution function of the diameters of particles belonging to species 1. The fluid of species 1 is assumed to be confined by the prepared already, rigidly fixed microporous medium of matrix particles of species 0. The structure of the adsorbed fluid (1) is characterized by the fluid–fluid and fluid–matrix total and direct correlation functions, $\varphi_{11}(r, \sigma_{1i}, \sigma_{1j})$ and $\varphi_{10}(r, \sigma_{1i}, \sigma_{0j})$, where φ stands for h and c , as appropriate.

An extension of the ROZ equations (cf. refs 1, 2) for a polydisperse partly quenched system is straightforward. The equation for the fluid–matrix correlations is

$$\begin{aligned} \gamma_{10}(r_{12}, \sigma_{1i}, \sigma_{0j}) &\equiv h_{10}(r_{12}, \sigma_{1i}, \sigma_{0j}) - c_{10}(r_{12}, \sigma_{1i}, \sigma_{0j}) \\ &= \rho_0 \int d\mathbf{r}_3 \int d\sigma_0 f_0(\sigma_0) c_{10}(r_{13}, \sigma_{1i}, \sigma_0) h_{00}(r_{31}, \sigma_0, \sigma_{0j}) + \\ &\quad \rho_1 \int d\mathbf{r}_3 \int d\sigma_1 f_1(\sigma_1) c_{c,11}(r_{13}, \sigma_{1i}, \sigma_1) h_{10}(r_{32}, \sigma_1, \sigma_{0j}) \end{aligned} \quad (4)$$

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whereas for the fluid–fluid correlations we have two equations

$$\begin{aligned} \gamma_{11}(r_{12}, \sigma_{1i}, \sigma_{1j}) &\equiv h_{11}(r_{12}, \sigma_{1i}, \sigma_{1j}) - c_{11}(r_{12}, \sigma_{1i}, \sigma_{1j}) \\ &= \rho_0 \int d\mathbf{r}_3 \int d\sigma_0 f_0(\sigma_0) c_{10}(r_{13}, \sigma_{1i}, \sigma_0) h_{10}(r_{23}, \sigma_{1j}, \sigma_0) + \\ &\quad \rho_1 \int d\mathbf{r}_3 \int d\sigma_1 f_1(\sigma_1) c_{c,11}(r_{13}, \sigma_{1i}, \sigma_1) h_{11}(r_{32}, \sigma_{1j}, \sigma_1) + \\ &\quad \rho_1 \int d\mathbf{r}_3 \int d\sigma_1 f_1(\sigma_1) c_{b,11}(r_{13}, \sigma_{1i}, \sigma_1) h_{c,11}(r_{32}, \sigma_{1j}, \sigma_1) \quad (5) \\ \gamma_{c,11}(r_{12}, \sigma_{1i}, \sigma_{1j}) &\equiv h_{c,11}(r_{12}, \sigma_{1i}, \sigma_{1j}) - c_{c,11}(r_{12}, \sigma_{1i}, \sigma_{1j}) \\ &= \rho_1 \int d\mathbf{r}_3 \int d\sigma_1 f_1(\sigma_1) c_{c,11}(r_{13}, \sigma_{1i}, \sigma_1) h_{c,11}(r_{32}, \sigma_{1j}, \sigma_1) \quad (6) \end{aligned}$$

The fluid–fluid total (h) and direct (c) correlation functions consist of the blocking and connected part,^{1,2} $\varphi_{11}(1,2) = \varphi_{b,11}(1,2) + \varphi_{c,11}(1,2)$.

There is an additional integration with respect to the particles diameters in eqs 3–6, in comparison with the original ROZ equations, that makes the polydisperse ROZ (PROZ) equations more difficult to solve. However, before proceeding with that integration, we would like to comment on the application of the closure relations. They must be tested for polydisperse systems in more detail. At this initial stage of the systematic investigations of the effects of polydispersity, we restrict ourselves to the Percus–Yevick (PY) closure that belongs to the class of approximations reducing the ROZ equations to the MGOZ approximate form.^{1–4} If the PY closure is used, the direct correlation functions (dcfs) are

$$c_{\alpha\beta}(r, \sigma_{\alpha i}, \sigma_{\beta j}) = [\gamma_{\alpha\beta}(r, \sigma_{\alpha i}, \sigma_{\beta j}) + 1] f_{M,\alpha\beta}(r, \sigma_{\alpha i}, \sigma_{\beta j}) \quad (7)$$

where α, β 00, 10 and 11, and $f_{M,\alpha\beta}(r, \sigma_{\alpha i}, \sigma_{\beta j})$ denotes the Mayer function

$$f_{M,\alpha\beta}(r, \sigma_{\alpha i}, \sigma_{\beta j}) = [-u_{\alpha\beta}(r, \sigma_{\alpha i}, \sigma_{\beta j})/k_B T] - 1 \quad (8)$$

with $u_{\alpha\beta}(r, \sigma_{\alpha i}, \sigma_{\beta j})$ denoting the interparticle potential. The PY approximation implies that the blocking term of the fluid–fluid direct correlation function, $c_{b,11}(r, \sigma_{1i}, \sigma_{1j})$, vanishes, i.e., $c_{b,11}(r, \sigma_{1i}, \sigma_{1j}) = 0$, because fluid particles belonging to different replicas do not interact between themselves. Then, eq 6 for the connected parts of the correlation functions becomes unnecessary; eqs 3–5 form a closed set in which the equation for the matrix correlations is decoupled as usual.^{1–4}

The PROZ equations have been presented in a general form appropriate for the case of arbitrary polydispersity of diameters of matrix and fluid species. However, to proceed further and present the procedure for elimination of the additional integration over particle's diameters, we restrict ourselves to the model in which a monodispersed fluid is confined in a polydisperse matrix, i.e., we assume that

$$f_i(\sigma) = \delta(\sigma - \sigma_1) \quad (9)$$

The method for performing integration of the PROZ equations according to a given distribution of diameters of species (only matrix species remain polydisperse for the model at hand) is similar to that proposed by Lado.^{25,26} We expand the σ_0 -dependent functions by using a set of orthogonal polynomials $P_j(\sigma_0)$, $j = 0, 1, 2, \dots$, defined as follows:

$$\int d\sigma_0 f(\sigma_0) P_i(\sigma_0) P_j(\sigma_0) = \delta_{ij} \quad (10)$$

where δ_{ij} is the Kronecker delta. Any function $\varphi(x, \sigma_{0i}, \sigma_{0j})$ can be thus represented by

$$\varphi(x, \sigma_{0i}, \sigma_{0j}) = \sum_{k,l} \varphi_{kl}(x) P_k(\sigma_{0i}) P_l(\sigma_{0j}) \quad (11)$$

A similar expansion of a function $\varphi(x, \sigma_1, \sigma_{0i})$ reads

$$\varphi(x, \sigma_1, \sigma_{0i}) = \sum_k \varphi_k(x, \sigma_1) P_k(\sigma_{0i}) \quad (12)$$

The expansion coefficients entering the two last equations are given by

$$\varphi_{kl}(x) = d\sigma_{0i} d\sigma_{0j} f(\sigma_{0i}) f(\sigma_{0j}) \varphi(x, \sigma_{0i}, \sigma_{0j}) P_k(\sigma_{0i}) P_l(\sigma_{0j}) \quad (13)$$

$$\varphi_k(x, \sigma_1) = d\sigma_{0i} f(\sigma_{0i}) \varphi(x, \sigma_1, \sigma_{0i}) P_k(\sigma_{0i}) \quad (14)$$

respectively.

The orthonormality of the polynomials $P_i(\sigma_{0i})$ permits to rewrite eq 3 in the following form

$$\tilde{\gamma}_{00,nm}(t) = \rho_0 \sum_l [\tilde{c}_{00,nl}(t) + \gamma_{00,nl}(t)] \tilde{c}_{00,lm}(t) \quad (15)$$

where $\tilde{\gamma}_{00,nm}(t)$ and $\tilde{c}_{00,nm}(t)$ stand for the Fourier transforms of the coefficients $\gamma_{00,nm}(r)$ and $c_{00,nm}(r)$, respectively. Similar procedure is applied to eqs 4 and 5. We then obtain

$$\begin{aligned} \tilde{\gamma}_{10,n}(t, \sigma_1) &= \rho_0 \sum_l \tilde{c}_{10,l}(t, \sigma_1) [\tilde{c}_{00,nl}(k) + \tilde{\gamma}_{00,nl}(k)] + \\ &\quad \rho_1 \tilde{c}_{11}(t, \sigma_1, \sigma_1) [\tilde{c}_{10,n}(t, \sigma_1) + \tilde{\gamma}_{10,n}(t, \sigma_1)] \quad (16) \end{aligned}$$

$$\begin{aligned} \tilde{\gamma}_{11}(t, \sigma_1, \sigma_1) &= \rho_0 \sum_l [\tilde{c}_{10,l}(t, \sigma_1) + \tilde{\gamma}_{10,l}(t, \sigma_1)] \tilde{c}_{10}(t, \sigma_1) + \\ &\quad \rho_1 \tilde{c}_{11}(t, \sigma_1, \sigma_1) [\tilde{c}_{11}(t, \sigma_1, \sigma_1) + \tilde{\gamma}_{11}(t, \sigma_1, \sigma_1)] \quad (17) \end{aligned}$$

Further development requires specification of the distribution function for the diameters of matrix species. We assume that the matrix has been formed of polydisperse hard spheres with additive diameters, i.e.

$$u_{00}(r, \sigma_{0i}, \sigma_{0j}) = \begin{cases} \infty & r < (\sigma_{0i} + \sigma_{0j})/2 \\ 0 & r > (\sigma_{0i} + \sigma_{0j})/2 \end{cases} \quad (18)$$

The distribution function of diameters of matrix species is chosen for simplicity to be stepwise

$$f(\sigma_0) = \begin{cases} 1/(\sigma_u - \sigma_l) & \sigma_l < \sigma_0 < \sigma_u \\ 0 & \text{otherwise} \end{cases} \quad (19)$$

The interactions between fluid particles and between fluid and matrix are also of hard sphere type with the hard sphere diameters equal to σ_1 and $(\sigma_{0i} + \sigma_1)/2$, respectively. Without loss of generality we assume that $\sigma_1 \equiv 1$. The orthonormal polynomials appropriate for the distribution (19) are the normalized Lagrange polynomials.

The distribution function given by eq 19 is simple; it provides restriction for the maximum size heterogeneity of matrix particles with respect to the average diameter $\langle \sigma_0 \rangle$. The size of matrix spheres is cut abruptly at σ_l and σ_u ; neither very large nor very small particles exist in the matrix subsystem. On the other hand, Lado^{25,26} in his studies of polydisperse fluids has used the Schulz distribution.²⁷ This distribution is Gaussian-like and requires the associated Laguerre polynomials for the solution of the OZ or PROZ equations. One can consider arbitrary distribution of diameters, $f(\sigma_0)$, dependent on desired

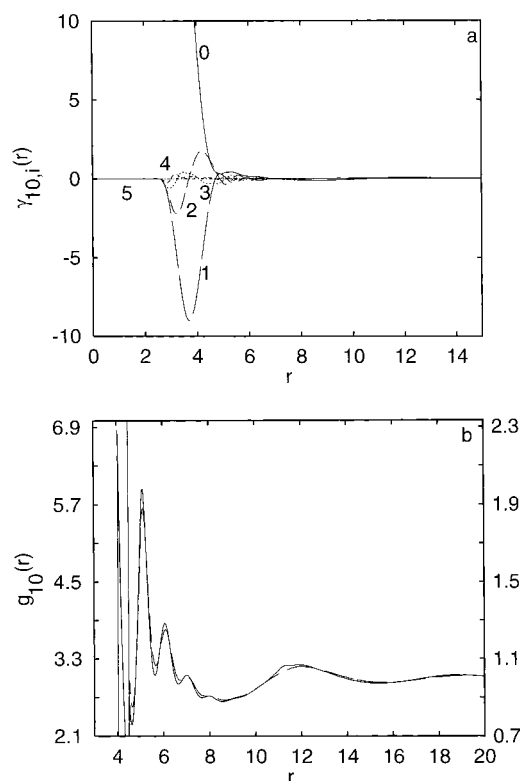


Figure 1. (a) Expansion coefficients of the function $\gamma_{10,i}(r)$, $i = 0, 1, \dots, 5$ (according to the labels). (b) Fluid-matrix distribution function for a monodisperse matrix $g_{10}(r; \sigma_0 = 7.055)$ (solid line), and for polydisperse matrix $g_{10}(r; f_0(\sigma_0))$ (dashed line); $\sigma_1 = 6.055$, $\sigma_u = 8.055$. The fluid density is $\rho_1^* = 0.4$, and the matrix packing fraction is $\eta = 0.386$. The left axis in part b is for the first peak of the distribution function whereas the right axis is for the remaining part.

modeling, and then construct a relevant set of orthonormal polynomials using a numerical algorithm of Press and Teukolsky.²⁸

A monodisperse disordered matrix of particles of the diameter σ_0 can be characterized conveniently by the parameter of porosity, $p = 1 - \eta$, where η is the matrix packing fraction, $\eta = \rho_0 \pi \sigma_0^3 / 6$. For a polydisperse matrix the porosity can be defined as

$$\chi = 1 - (\pi/6) \rho_0 \int \sigma_0^3 f(\sigma_0) d\sigma_0 \quad (20)$$

For the model in question, the porosity is thus given by $p = \pi \rho_0 \langle \sigma_0 \rangle (\sigma_u^2 + \sigma_l^2) / 12$, where $\langle \sigma_0 \rangle$ is the average matrix particle diameter $(\sigma_u + \sigma_l) / 2$.

The method for the solution of the PROZ equations is similar to that used by Lado.^{25,26} We have found that the expansions with the first six (0–5) normalized Lagrange polynomials provide a reasonable accuracy of the calculations. Our model calculations have been carried out for a single distribution of the matrix particles, $\sigma_u = 8.055$, $\sigma_l = 6.055$, such that the average diameter of the matrix particles is $\langle \sigma_0 \rangle = 7.055$. A monodisperse matrix formed of particles of the diameter 7.055 was used by Vega et al.⁵ in their model denoted by M2. The packing fraction of the matrix, $\eta = 1 - \chi$, was chosen equal to 0.386, exactly like in the model M2 of Vega et al.⁵ It has been shown by comparison with the simulation data, cf. Figure 5 of ref 5, that the PY approximation in the framework of the MGOZ equations provides excellent description of the pair distribution functions of an adsorbed hard sphere fluid at density $\rho_1^* = \rho_1 \sigma_1^3 = 0.2336$ in the monodisperse matrix at $\eta = 0.386$.

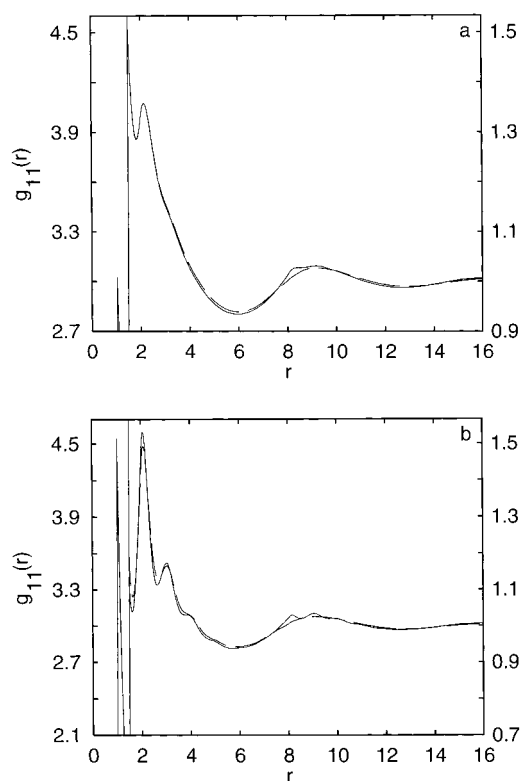


Figure 2. Fluid-fluid pair distribution functions in a monodisperse and a polydisperse adsorbent, as in Figure 1. The fluid density is $\rho_1^* = 0.2336$ (a) and $\rho_1^* = 0.4$ (b), $\eta = 0.386$. The nomenclature of the axes is as in Figure 1b.

However, before investigating this particular state, we would like to demonstrate convergence of the expansions used in the solutions of the PROZ equations.

In Figure 1a we have shown the expansion coefficients of the fluid-matrix function, $\gamma_{10,i}(r)$, defined according to eq 14, for a monodisperse fluid ($f_1(\sigma) = \delta(\sigma - \sigma_1)$) at moderate density, $\rho_1^* = 0.4$, in the polydisperse matrix at $\eta = 0.386$. One can see that the expansion involving six terms is sufficient to provide an accurate description of the function $\gamma_{10}(r; \sigma_1; f_0(\sigma_0))$. The highest order expansion coefficient, $\gamma_{10,5}(r)$ is almost vanishing in the entire range of distances.

In Figure 1b we present the fluid-matrix pair distribution function for a polydisperse system, $g_{10}(r; \sigma_1; f_0(\sigma_0))$ and the corresponding monodisperse system $g_{10}(r; \sigma_1; \sigma_0 = 7.055)$ at fluid density $\rho_1^* = 0.4$. We observe that the difference between the case of a polydisperse and monodisperse matrix is not large. Due to the presence of matrix particles in the range from $\sigma_0 = 6.055$ to $\sigma_0 = 8.055$, the first maximum of the function $g_{10}(r)$ becomes somewhat lower in the case of a polydisperse matrix compared to the monodisperse one. Also, the oscillations of the distribution function become slightly smoother. The overall structure of the pair distribution function $g_{10}(r)$ following from the case of a monodisperse matrix remains similar in a polydisperse case.

In Figure 2, a and b, we have shown the results for the fluid-fluid pair distribution function, $g_{11}(r)$, at fluid density $\rho_1^* = 0.2336$ and at $\rho_1^* = 0.4$, respectively. In each part of Figure 2 the results for a polydisperse and monodisperse matrix are compared. At lower density, $\rho_1^* = 0.2336$, the smoothing effect of polydispersity is observed at distances corresponding to the correlations between fluid particles separated by a matrix sphere. At a higher fluid density, $\rho_1^* = 0.4$, smoothing of the oscillations of the function $g_{11}(r)$ is well seen even at smaller

interparticle separations. These trends may be interpreted due to the influence of matrix species of different diameter on the correlations between fluid particles that are close to the matrix surface. One must have in mind, however, that a more detailed comparison of the results for the structural properties in a polydisperse and monodisperse adsorbents requires the development of reliable tools to obtain the chemical potential for both cases. This nontrivial issue will be analyzed in more detail in the following studies.

To summarize, in this work we have extended the ROZ equations for partly quenched fluids of monodisperse particles to account for the effects of polydispersity. Explicit calculations, at this preliminary stage of investigation of the polydisperse quenched—annealed fluids, have been performed for a hard sphere fluid in a polydisperse hard sphere disordered quenched matrix. However, the model and the theory permit several extensions of interest for basic and applied research. In particular, a more sophisticated model for the interactions between fluid species would permit the study of phase transitions in fluids adsorbed in microporous media and investigate the influence of the polydispersity effects. The role of polydispersity effects on fluid—matrix correlations must be clarified. On the other hand, it is of much interest to investigate the compositional changes in the adsorbed polydisperse mixture with respect to its bulk. Theoretical results must be with necessity tested versus computer simulation data, unavailable at the moment. Some of these problems, however, are under study in our laboratory at present.

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