

Replica Ornstein–Zernike Equations and Simulations of the Structure of a Simple Fluid in Disordered Porous Media. Application to Monomolecular Adsorption

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A two-dimensional (2D) model for a simple fluid adsorbed in a disordered porous medium is investigated by means of the replica Ornstein–Zernike (ROZ) equations with the hypernetted chain (HNC) and Percus–Yevick (PY) approximations. In addition, Monte Carlo simulations for this model are presented. The structural properties of adsorbed monolayer resulting from the theory agree well with the computer simulation data. Also we obtain the fluid compressibility from the ROZ equations and the adsorption isotherms. Besides the hard core repulsion, a long-range interaction between the fluid species in the form of an attractive square well is included. The contribution of this long-range term is considered using a mean-field approximation. This permits us to analyze the qualitative dependence of the behavior of the critical density and temperature on the matrix parameters. We find that the critical temperature of the hard discs with a square well attraction decreases with an increasing density of the quenched component. The critical density is less sensitive to these changes.

1. Introduction

There has been considerable research in quenched–annealed systems during the last years. Different groups have investigated this subject using computer simulations and an extension of liquid-state statistical mechanics. The quenched–annealed, or partly quenched, system represents a fluid equilibrated in a matrix of obstacles that has been quenched in a disordered or random configuration.

Experimental studies of partly quenched systems have revealed their unusual thermodynamic properties. It has been shown that the liquid–vapor transition and liquid–liquid separation are different in annealed and partly quenched systems.^{1–4} The theoretical study of quenched–annealed systems has been initiated by Madden and Glandt;^{5,6} almost simultaneously Given and Stell have performed a detailed analysis of the cluster expansion for the partition function and have derived the exact replica Ornstein–Zernike (ROZ) equations.^{7,8} A set of approximations also have been proposed for the ROZ equations.^{8,9} It has been pointed out^{7,8} that the theoretical methods that have been developed are appropriate for the problem of random sequential adsorption. However, so far this option has not been exploited extensively. Many recent studies have focused on the description of the bulk, homogeneous quenched–annealed systems.^{9–17} Very recently, the study of inhomogeneous partly quenched models has been initiated in our laboratory.^{18,19}

In this work we are interested in another important aspect of the problem that is closely related to the phenomena of monomolecular adsorption. Imagine the following physical situation. A fluid is adsorbed (deposited) onto a surface such

that a monolayer of particles with a homogeneous density, on average, has been formed. The monolayer can be quenched at certain conditions. Those can be chosen such that the in-plane configuration of the matrix species formed after quench corresponds to an equilibrium distribution. On the other hand, one can imagine that the adsorption occurs via a chemisorption mechanism so that the particles have formed a rigid, disordered structure on the surface. For simplicity, we assume that the matrix has been deposited on an ideal surface neglecting possible effects of surface roughness. Usually, a two-dimensional approximation is sufficiently well suited for the description of monolayer adsorption. Thus, a two-dimensional distribution of the matrix particles is characterized by a pair distribution function, whereas its density profile is homogeneous.

At the next step we suppose that another fluid (that will be considered as an annealed component) has been adsorbed onto the surface with a matrix monolayer in a given configuration. We assume that the adsorption of this fluid has been performed so carefully that only a monolayer consisting of a matrix and annealed species has been formed. Our aim is to apply powerful statistical mechanical methods, including simulations, for such a two-dimensional (2D) system.

Despite this idealization, we are convinced that the adlayer model described above will be helpful for a future study of multilayer adsorption and of thin fluid films in the presence of a quenched component. In particular, we expect that the model and the results obtained will provide a basis for investigating two-dimensional phase transitions, a subject of great interest. To our very best knowledge, there has been only one attempt to apply a 2D approximation for a composed quenched–annealed monolayer.²⁰ However, the main emphasis in that recent work was the theoretical description of dimerization in a monolayer.

We would like to note also that in the present work the matrix is taken to be disordered. The case of random matrixes,^{7,9} i.e.

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when matrix species are permitted to overlap each other arbitrarily, will be studied elsewhere.

2. Model for a Partly Quenched Monomolecular Adlayer and Theoretical Procedure

We consider a 2D model for a simple fluid in a disordered quenched environment. It consists of a hard disc fluid and a hard disc matrix. Similarly to previous studies of partly quenched systems,⁷⁻⁹ we introduce, for the sake of convenience, the species index “0” for the matrix component and the species index “1” for the fluid component. The matrix and fluid particles are at the densities ρ^0 and ρ^1 , respectively. The diameters of the matrix and fluid particles are σ_0 (σ_m) and σ_1 (σ_f), respectively. Actually, the monolayer deposition of the matrix species can be considered to be at a given chemical potential. However, as the matrix is quenched, it is sufficient for our purposes to fix its density. The chemical potential of the adsorbed fluid is obtained afterward, from the solution of the ROZ equations.

The model for the matrix and fluid species is defined by

$$U^{ij}(R) = \begin{cases} \infty, & R < (\sigma_i + \sigma_j)/2 \\ 0, & R > (\sigma_i + \sigma_j)/2 \end{cases} \quad (1)$$

where i and j take the values 0 and 1. In the final part of our work we will add a square well attraction between fluid species. However, it will be defined below. All the distances introduced are two-dimensional.

We assume that the matrix distribution can be prepared so as to correspond to an equilibrium distribution of discs. Let us proceed to the ROZ equations:⁷⁻⁹

$$h^{00} - c^{00} = c^{00} \otimes \rho^0 h^{00} \quad (2)$$

for the matrix subsystem,

$$h^{10} - c^{10} = c^{10} \otimes \rho^0 h^{00} + c^{11(1)} \otimes \rho^1 h^{10} \quad (3)$$

for the fluid–matrix correlations, and

$$h^{11} - c^{11} = c^{10} \otimes \rho^0 h^{10} + c^{11(1)} \otimes \rho^1 h^{11} + c^{11(2)} \otimes \rho^1 h^{11(1)} \quad (4)$$

$$h^{11(1)} - c^{11(1)} = c^{11(1)} \otimes \rho^1 h^{11(1)}$$

for fluid–fluid correlations.

Here \otimes denotes a 2D convolution; R dependencies are omitted for brevity. In eqs 3 and 4 we have used standard decomposition of the pair and direct fluid–fluid correlation functions into connected, $\phi^{11(1)}$, and blocking, $\phi^{11(2)}$, parts (ϕ stands for h and c , as appropriate) such that each function consists of two terms: $\phi^{11} = \phi^{11(1)} + \phi^{11(2)}$.

Consider the closure relations for the ROZ equations. For the sake of convenience, we introduce the notation $\gamma = h - c$. In this work, the replica hypernetted chain approximation (HNC) and the Percus–Yevick approximation are used. The HNC closure is used to evaluate the matrix structure:

$$c^{00}(R) = \exp[-\beta U^{00}(R)] \exp[\gamma^{00}(R)] - 1 - \gamma^{00}(R) \quad (5)$$

The HNC closure for the fluid–matrix and fluid–fluid correlation functions is

$$c^{1i}(R) = \exp[-\beta U^{1i}(R)] \exp[\gamma^{1i}(R)] - 1 - \gamma^{1i}(R) \quad (6)$$

where $i = 0, 1$. However, in the case of ROZ equations, we also must use a closure for the blocking parts of the direct

correlation function, in addition to the above closures. The HNC closure for this function does not contain the interparticle interaction because particles belonging to different replicas do not interact. Thus,

$$c^{11(2)}(R) = \exp[\gamma^{11(2)}(R)] - 1 - \gamma^{11(2)}(R) \quad (7)$$

Equations 2–4 together with 5–7 represent a complete ROZ–HNC problem for the numerical solution. The PY closure also will be used, but only for the fluid–matrix and fluid–fluid correlations (the matrix structure is formally irrelevant). The PY approximation for the problem at hand is usual:

$$c^{1i}(R) = \{\exp[-\beta U^{1i}(R)] - 1\}\{1 + \gamma^{1i}(R)\} \quad (8)$$

$i = 1, 2$, whereas the blocking term is neglected; $c^{11(2)}(R) = 0$. A set of equations, complemented by the relevant closure, can be solved straightforwardly by direct iteration. Only for high fluid densities need one take care about the convergence of the numerical scheme. In contrast to the 3D case, which requires the Fourier transformation of the correlation functions, our procedure is performed similarly to Lado²¹ and involves Hankel transforms.

However, structural properties are not the only objective of our study. We intend to obtain thermodynamic properties as well. The adsorbed fluid compressibility for the partly quenched systems is obtained easily. This is a well-established route, in contrast to the virial route. The compressibility equation is^{10,16}

$$\beta^{-1}(\partial \rho^1 / \partial P)_T = \{1 + \rho^1 \int d\mathbf{R} h^{11(1)}(R)\} \quad (9)$$

where $h^{11(1)}(R)$ is the connected part of the pair correlation function; it is obtained in the numerical solution (the vector \mathbf{R} is two-dimensional and the integral in eq 9 is the Hankel transform).

Let us proceed now with the evaluation of the adsorption isotherms for which we need density dependence of $\mu^1(\rho^1)$. We apply an algorithm similar to that proposed for 3D simple fluids by Ford and Glandt.¹⁶ The chemical potential of a simple fluid adsorbed in a disordered matrix is written as

$$\beta \mu^1(\rho^1) = \beta \mu_{\text{id}}^1(\rho^1) + \beta \mu_{\text{ex}}^1(\rho^1) \quad (10)$$

where the ideal gas contribution is written as $\beta \mu_{\text{id}}^1(\rho^1) = \ln(\rho^1 \sigma_1^2)$. The excess term $\beta \mu_{\text{ex}}^1(\rho^1)$ is taken in the form

$$\beta \mu_{\text{ex}}^1(\rho^1) = \beta \mu_{\text{ex}}^1(\rho^0, \rho^1 = 0) - \int_0^{\rho^1} d\rho' \int d\mathbf{R} c^{11(1)}(R, \rho') \quad (11)$$

The first term in the excess chemical potential, $\beta \mu_{\text{id}}^1(\rho^0, \rho^1 = 0)$ is the excess chemical potential of the fluid component at infinite dilution in the mixture composed of matrix and fluid particles. The second term comes from the ROZ equation. It is an integral along the density path of the Hankel-transformed connected part of the fluid–fluid direct correlation function (at $k = 0$). The first term of the excess chemical potential, $\beta \mu_{\text{ex}}^1(\rho^0, \sigma^1 = 0)$, is approximated using the theoretical equation of state of Boublik for a mixture of hard discs,²²

$$\beta P/\rho = 1/(1 - \eta) + \gamma_s \eta/(1 - \eta)^2 \quad (12)$$

where η is the packing fraction of a hard disc fluid (or a mixture) and $\gamma_s = \pi(\sum x_i R_i)^2 / \sum x_i A_i$ is the factor that characterizes the composition of a mixture (x_i , R_i , and A_i are the concentration of discs of the component i , the radius, and area of discs

belonging to this component, respectively). Integrating this equation with respect to the density yields the free energy of a mixture of hard discs with arbitrary diameters of the discs. Then, the chemical potential of fluid species is easily obtained.

Recent studies have shown²³ that, in three dimensions, Boublik type approximations are somewhat in error when there is a small concentration of the large spheres. No doubt this is true in two dimensions also. For the moment, we ignore this point.

In the region of phase coexistence (at least that obtained from the solution of integral equations) it is impossible to use eq 11. Similarly to Ford and Glandt,¹⁶ we use this equation only for the reference system, i.e. for hard discs in a hard disc matrix, that does not possess a liquid–vapor phase transition; the effect of attractive interaction included below will be considered in a mean-field approximation.

To evaluate the accuracy of the applied theoretical methods for hard discs adsorbed in a disordered hard disc matrix, we have performed computer simulations. It would be preferable to use the grand canonical Monte Carlo method (GCMC) for the evaluation of the structure and thermodynamics of the system. However, at this initial stage of our investigation of 2D partly quenched systems we have decided, similarly to Fanti et al.,¹¹ to perform a comparison of the theory and simulations at the level of the structural properties. We have performed canonical Monte Carlo simulations to obtain the fluid–matrix and fluid–fluid pair distribution functions for the matrix and fluid densities that have been used as parameters for the solution of ROZ integral equations.

The usual NVT technique²⁴ has been used. However, similarly to ref 11, the collected averages that provide the pair distribution functions have been averaged over independent configurations of matrix species. This averaging has been performed over not less than 10 independent matrix configurations.

3. Results and Discussion

Let us proceed with a description of the results that we have obtained. First compare the fluid–fluid, $g^{11}(R)$, i.e. $g_{ff}(R)$, and fluid–matrix, $g^{10}(R) = g^{01}(R)$, i.e. $g_{mf}(R)$, pair distribution functions obtained from the HNC and PY approximations with the MC simulation data.

In Figures 1 and 2 we present these functions for the model with equal diameters of matrix and fluid particles ($\sigma_0 = \sigma_1$). The model is considered at the densities $\rho^0\sigma_0^2 = 0.3$ and $\rho^1\sigma_1^2 = 0.4$ (Figure 1). At these densities, the HNC approximation is worse than the PY approximation for both functions. In particular, the HNC approximation overestimates the contact values of $g_{ff}(R)$ and $g_{mf}(R)$, as is common for hard particles. The PY approximation is more successful; it agrees better with the MC data close to the contact distance between particles and for larger interparticle separations. It is evident that some inaccuracies are present. Similar trends are observed at a higher matrix density $\rho^0\sigma_0^2 = 0.535$ and at a fluid density $\rho^1\sigma_1^2 = 0.25$ (Figure 2). Both the HNC and PY approximations overestimate the magnitude of the oscillations of the fluid–fluid pdf $g_{ff}(R)$. The PY closure is more adequate for this function at small interparticle separations. The observed trends are similar to those obtained for the three-dimensional hard sphere model of Lomba et al.,⁹ who concluded that the PY closure is more successful for the model with equal diameters of matrix and fluid species despite the fact that the PY approximation does not include the blocking effects of the matrix species on the fluid particle correlations. It seems that more

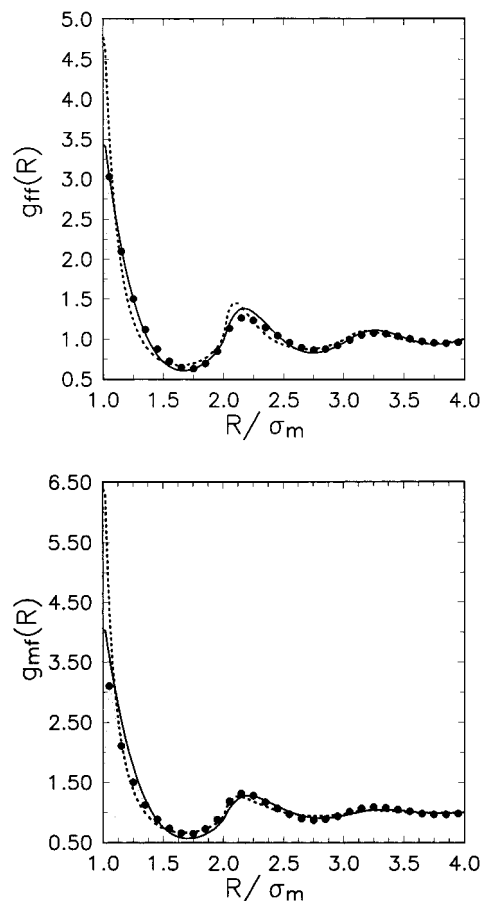


Figure 1. Fluid–fluid, $g_{ff}(r)$, (part a) and matrix–fluid, $g_{mf}(r)$, (part b) pair distribution functions of disks obtained from the ROZ–HNC and ROZ–PY theories and from Monte Carlo simulations at $\rho^0\sigma_0^2 = 0.3$ and $\rho^1\sigma_1^2 = 0.4$. The matrix and fluid particles are of equal diameter, $\sigma_0 = \sigma_1$. Here and in all following figures the HNC and the PY results are shown by dashed and solid curves, respectively.

sophisticated closures, consistent with the ROZ equations and probably with the inclusion of the bridge function, are required. It was shown by Meroni et al.¹² that the HNC closure, complemented by a parametrized contribution of the bridge function, has a high accuracy in the case of three-dimensional hard sphere models. However, the determination of such an approximation for this model requires intensive numerical work. We hope to probe some such new approximations in a separate study.

It is of interest to mention that the approximations applied here seem to be more successful for models with unequal diameters of the matrix and fluid particles, Figures 3 and 4. Now we consider a model in which the fluid particles are half the size of the matrix particles, $\sigma_f = 0.5\sigma_m$. As was seen previously for the model with equal diameters, the PY approximation is better than the HNC approximation for both the functions $g_{ff}(R)$ and $g_{mf}(R)$. The PY reproduces the contact value of both functions and their oscillations quite well for two states studied, $\rho^0\sigma_0^2 = 0.45$ and $\rho^1\sigma_1^2 = 0.1125$ (low-density fluid in a matrix of intermediate density, Figure 3) and for $\rho^0\sigma_0^2 = 0.45$ and $\rho^1\sigma_1^2 = 0.275$ (intermediate-density fluid in a matrix of intermediate density, Figure 4). The HNC overestimates the contact values. However, at larger distances it is qualitatively correct. One may ask the question, why is the PY more accurate in this case despite neglecting the blocking term of the fluid–fluid correlations? It would appear that the diagrams that are neglected by the PY approximation may cancel to some extent the diagrams corresponding to the blocking effect of the matrix.

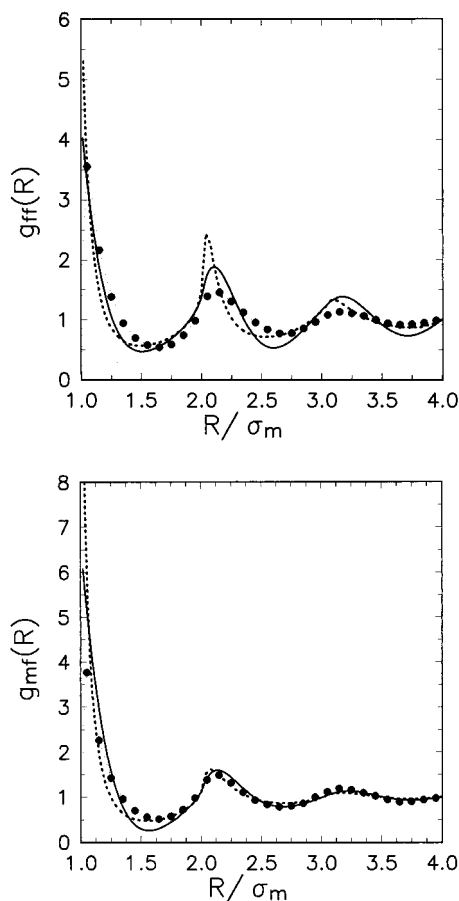


Figure 2. Same as in Figure 1 but for $\rho^0\sigma_0^2 = 0.535$ and $\rho^1\sigma_1^2 = 0.25$; $\sigma_0 = \sigma_1$.

It would be important to include a bridge function supplement to the HNC closure (the HNC is a natural approximation for the ROZ equations) in further work, because the ROZ equations intrinsically require an approximation that involves many-body hard core correlations via matrix species.

Now we turn our attention to the results obtained for the adsorbed fluid compressibility, Figure 5a. The fluid compressibility decreases with increasing density, as expected. The presence of the matrix species in the form of a rigid network results in lower values for fluid compressibility. Both approximations involved yield a qualitatively similar picture. However, the difference between the HNC and PY results becomes larger for a high-density matrix. The most important quantities that the theory yields are the adsorption isotherms (Figure 5b). They have been evaluated as described above, using both the HNC and the PY approximations for the fluid–fluid direct correlation function. Both closures give similar results for the adsorption isotherms. At a given value of the chemical potential, the fluid density is smaller in a high-density matrix than in a low-density matrix. This conclusion is easy to understand physically. It has been shown by Ford and Glandt¹⁶ that the adsorption isotherms, obtained in the HNC and PY approximations, agree quite well with the grand canonical MC data. We have not yet obtained the GCMC results for the adsorption isotherms. However, we expect that the accuracy of applied approximations is sufficient for at least a qualitatively correct description of this property. In part c of Figure 5 we present the adsorption isotherms for the model of hard discs in a hard disc matrix but for the following choice of diameters, $\sigma_1 = 0.5\sigma_0$. From a comparison of parts b and c of Figure 5 it follows that the density of a fluid consisting of twice

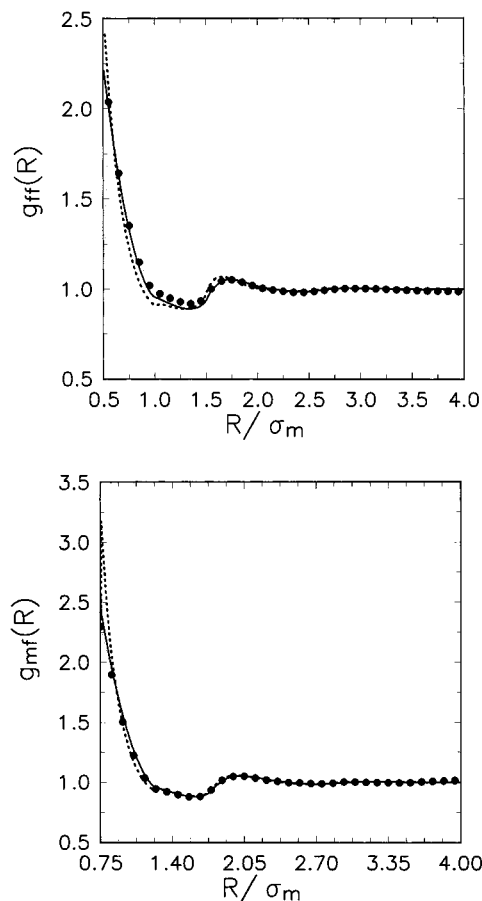


Figure 3. Same as in Figure 1 but for $\rho^0\sigma_0^2 = 0.45$ and $\rho^1\sigma_1^2 = 0.1125$; $\sigma_1 = 0.5\sigma_0$.

smaller particles, $\sigma_1 = 0.5\sigma_0$, in a matrix with given density is much higher than the density of a fluid in a model with $\sigma_1 = \sigma_0$ in the same matrix. This comparison is made at a certain value of the chemical potential for adsorbed fluid.

With the adsorption isotherms available, we make a comparison of the structure of the adsorbed fluid at a given value of the chemical potential, Figure 6. One can see that for the model with equal diameters of fluid and matrix particles the correlations between fluid particles in a matrix with a high density are much stronger compared with the correlations at a low matrix density. In particular, the contact value for the pair distribution function of fluid species is much higher and the oscillations of this function are of a larger magnitude in a high-density matrix in comparison with a low-density matrix. This effect of steric restriction, due to the presence of matrix species, could be anticipated in the absence of specific adsorption of fluid particles on the matrix.

Our final goal is to get a qualitative description of the liquid–vapor coexistence curves for an adsorbed fluid in a disordered matrix in a simple model with an interparticle attraction of the fluid species. Therefore, we modify the model for the fluid species by assuming the following interaction between them:

$$U^{11}(R) = \begin{cases} \infty, & R < \sigma_1 \\ -\epsilon_{sw}, & \sigma_1 + w < R < \sigma_1 \\ 0, & R > \sigma_1 + w \end{cases} \quad (13)$$

where ϵ_{sw} and w are the depth and width of the attractive square well. We have chosen the width of the well to be $w = 0.148$ in the following calculations. The annealed fluid model, chosen in this simple way, possesses liquid–vapor phase transition. Our intention is to obtain the effect of the matrix on the critical

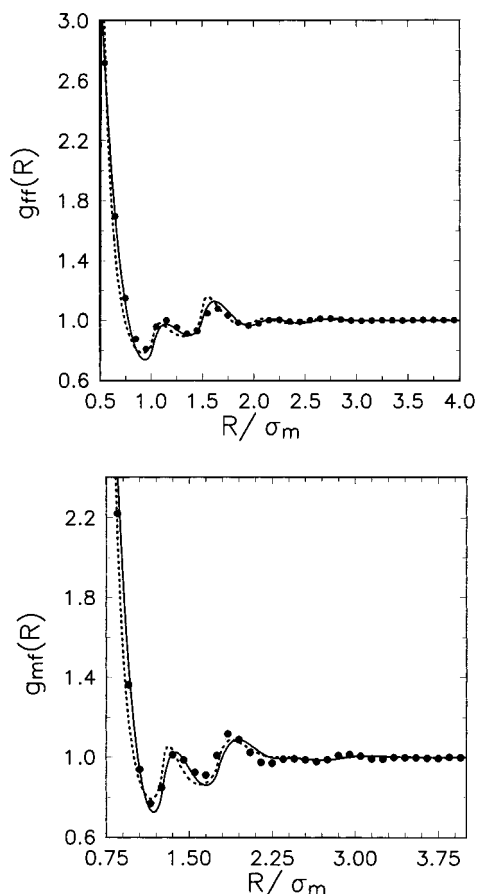


Figure 4. Same as in Figure 1 but for $\rho^0\sigma_0^2 = 0.45$ and $\rho^1\sigma_1^2 = 0.275$; $\sigma_1 = 0.5\sigma_0$.

temperature and density using the simplest of theoretical techniques. Therefore, a mean-field approximation is used for the contribution of the fluid–fluid attractive forces to the chemical potential. The additional term necessary to be included in the right-hand side of eq 11. $\beta\mu_{at}(\rho^0, \rho^1)$, is

$$\beta\mu_{at}(\rho^0, \rho^1) = -\beta\epsilon_{att}2\pi w(w+2)(\rho^0 + \rho^1) \quad (14)$$

The coexistence curves, obtained by using the Maxwell construction, are presented in Figure 7. We have observed that with an increasing matrix density the critical temperature of adsorbed fluid decreases. However, the critical density is less sensitive to disordered matrix density. Our conclusions agree well with the results obtained by Ford and Glandt¹⁶ and by Kierlik et al.¹⁷ for three-dimensional models. A quantitative assessment of the accuracy of the results for critical parameters for 2D systems must await the computer simulation data. Moreover, one can see from the results obtained that the critical temperature and critical density depend on the ratio of matrix and fluid disc diameters. Even a small difference of the diameters of species yields changes of the critical temperature and density, in contrast with the model of equal diameters.

4. Conclusions

We have found, by comparison with simulations, that the ROZ equations, with the PY closure, describe rather well the correlation functions of an adsorbed fluid of hard particles in a disordered porous medium of hard particles. The situation is even more favorable when the fluid particles are smaller than those of the porous medium; in this case, both the PY and HNC

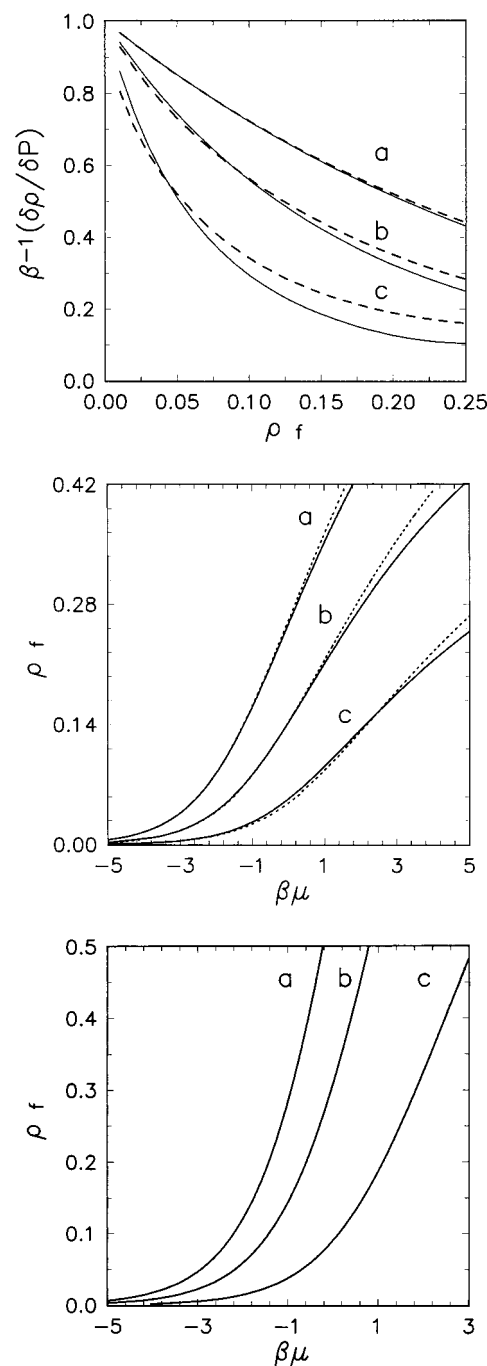


Figure 5. Compressibility of an adsorbed hard disk fluid for different matrix disk densities $\rho^0\sigma_0^2 = 10^{-2}$; $\rho^0\sigma_0^2 = 0.3$, and $\rho^0\sigma_0^2 = 0.6$ (the curves labeled as a, b, and c, respectively); $\sigma_0 = \sigma_1$ (part a). The adsorption isotherms for the model with $\sigma_1 = \sigma_0$ and with $\sigma_1 = 0.5\sigma_0$ are given in parts b and c, respectively. In both parts: $\rho^0\sigma_0^2 = 5 \times 10^{-2}$; $\rho^0\sigma_0^2 = 0.25$, and $\rho^0\sigma_0^2 = 0.45$ (the curves labeled a, b, and c, respectively).

closures seem quite reliable. Also, we have calculated the thermodynamics, including the adsorption isotherms, of such systems.

Finally, using a simple mean-field argument, we have examined the dependence of the critical temperature and density on the density of the porous material. We find that the critical temperature decreases as the density of the porous material increases. Presumably, the porous material separates the fluid particles and has the effect of weakening the effective strength of the attractive interaction. In contrast, the critical density is largely unaffected by the density of the porous material. This

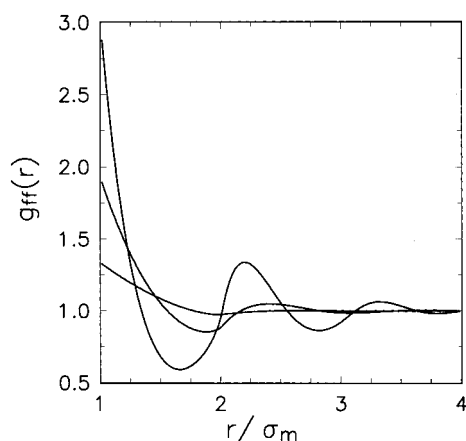


Figure 6. Comparison of the adsorbed fluid structure in the PY approximation at a chemical potential $\beta\mu_1 = 1.0$ in matrixes at different density, $\rho^0\sigma_0^2 = 0.05$, $\rho^0\sigma_0^2 = 0.25$, and $\rho^0\sigma_0^2 = 0.45$ from bottom to top at a contact distance $R = 1$. The matrix and fluid particles are of equal diameter, $\sigma_0 = \sigma_1$.

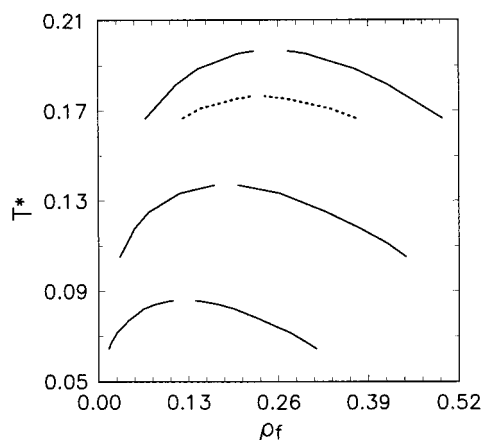


Figure 7. Liquid–vapor coexistence curves for adsorbed fluid in matrixes at the densities $\rho^0\sigma_0^2 = 0.05$, $\rho^0\sigma_0^2 = 0.25$, and $\rho^0\sigma_0^2 = 0.45$, in sequence from top to bottom. The width of the attractive potential is $w = 0.148$ and $T^* = 1/\beta\epsilon_{attr}$. These results are for the model $\sigma_0 = \sigma_1$. The dotted line shows the coexistence curve for the model $\sigma_1 = 0.9\sigma_0$ with the same square well attraction as in the previous case but with the matrix density $\rho^0\sigma_0^2 = 0.25$.

is not unexpected. It occurs in other systems such as hard spheres with a variable range for the attractive interaction. This same effect occurs in the correlation functions of the hard disc fluid. Increasing the density of the porous material weakens

the correlations between the hard discs. Since the critical density must lie between the liquid and vapor densities, it does not have much scope for change. The location of the critical point is affected by the size ratio of the matrix and fluid particles.

We plan to extend these calculations through the use of more sophisticated closures and incorporating from the start the attractive part of the potential into the calculation.

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