Adsorption of Dimerizing and Dimer Fluids in Disordered Porous Media

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The pair distribution functions and the adsorption isotherms for a hard-core dimerizing fluid in disordered hard-sphere matrices have been determined using the associative extension of replica Ornstein−Zernike equations. Some grand canonical Monte Carlo simulation results for tangent hard-sphere dumbbells adsorbed in hard-sphere matrices are presented. Theoretical predictions for the structure from the solutions of integral equations with the associative hypernetted chain (HNC) and Percus−Yevick (PY) approximation agree with those from the simulations. However, the HNC closure has been found to work better than the PY one.

1. Introduction

Recently much attention has been focused on the extension of liquid-state statistical mechanics for quenched-annealed (partly quenched) systems. They consist of a fluid thermally equilibrated in a matrix of particles quenched in a disordered configuration.

Experimental studies of partly quenched systems have discovered their unusual structural and thermodynamic properties. In particular, phase transitions, such as liquid−vapor transition and liquid−liquid separation, are different in annealed and partly quenched systems.[1−3] Theoretical studies of quenched-annealed systems have been initiated by Madden and Glandt;[4,5] more recently 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.[6−8] Also a set of approximations has been proposed for the ROZ integral equations.[8,9]

The ROZ theory has been applied extensively in many recent studies, see, for example, refs 10−14. However, most attention has been paid to simple fluids in the framework of hard-sphere and Lennard-Jones models. Complex fluids have been investigated less frequently.[15] Obtained theoretical results for simple fluids have been tested versus computer simulations in many aspects. Moreover, some simulation data, for liquid−vapor and liquid−liquid equilibria in partly quenched systems,[16,17] have become a challenge for the development of perturbational approaches based on the ROZ equations.[14,18] First results of the theoretical studies of inhomogeneous fluids adsorbed in an inhomogeneous matrix have appeared recently.[19,20]

Some experimental studies have being dealing with chemical association phenomena in fluids adsorbed in disordered porous media.[21] This is an important area for several practical applications, such as, for example, gel-exclusion chromatography, separation science, and heterogeneous catalysis.

On the other hand, a systematic theoretical investigation of chemical association in fluids adsorbed in disordered porous media has been initiated recently.[22−25] In particular, the associative ROZ (AROZ) equations and closures for them have been proposed. This approach has been used first for the model of methane adsorbed in xerosilica gel developed by Kaminsky and Monson.[26] The model is characterized by the strong fluid-matrix attraction, which can be formally treated using the association concept. The results for the structural properties following from integral equations have been shown[24] to agree very well with simulation data of Vega et al.[27] The AROZ theory also has been implemented for a dimerizing fluid model of Wertheim.[28] The results for the correlation functions seem to be qualitatively correct. However, they have not been tested versus computer simulation data.

In this work we apply the associative ROZ equations for a simple, hard-sphere model that permits dimerization of particles due to the associative site−site interaction. For the moment, the model does not include nonassociative attractive interactions such that liquid−vapor transition is out of question. Our main concern is, however, to evaluate the accuracy of theoretical results obtained with the associative hypernetted chain (HNC) approximation and Percus−Yevick (PY) approximation versus computer simulations. Therefore, we have performed computer simulations for diatomic fluids as well as for diatomic-hard-sphere mixture adsorbed in a disordered hard-sphere matrix.

We expect that our results for a hard-core dimerizing model will provide reference fluid data for investigating thermodynamic properties for an associating model with attractive interactions. This problem will be studied in our future work.

2. Model for Partly Quenched Chemically Associating Fluid

In this work, we consider a simple model for chemically associating fluid in a disordered quenched environment. It consists of a dimerizing fluid and a hard-sphere matrix.

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Similarly to previous studies of partly quenched systems,[6−9] we introduce, for the sake of convenience, species index "0" for the matrix component and species index "1" for the fluid component. We use superscripts to denote species and reserve subscripts to classify the bonding states in the theory of Wertheim for chemical association.[23−31] We consider the matrix and fluid particles at density ρ^0 and ρ^1, respectively. The diameter of matrix and fluid particles is denoted by σ_0 and σ_1, respectively.

The model for a dimerizing fluid is defined by the following potentials

$$U^{11}(12) = U^{11}_{\text{non}}(r) + U^{11}_{\text{as}}(x_{12}) \tag{1}$$

where the first and the second term denote the nonassociative and associative contribution to the fluid−fluid interaction, respectively. The nonassociative term is taken in the form

$$U^{11}_{\text{non}}(r) = \begin{cases} \infty, & r < \sigma_1 \\ 0, & r > \sigma_1 \end{cases} \tag{2}$$

The associative term in the fluid−fluid interaction has the form[28]

$$U^{11}_{\text{as}}(x) = \begin{cases} -\epsilon_{\text{as}}, & x < a \\ 0, & x > a \end{cases} \tag{3}$$

where ϵ_{as} is the associative energy and a denotes the range of associative interaction; $x_{12} = |\mathbf{r}_{12} + \mathbf{d}(\vartheta_1) - \mathbf{d}(\vartheta_2)|$, where $\mathbf{d}(\vartheta_1)$ denotes the position and orientation of the attractive site on the surface of the repulsive core of molecule 1.

The geometric parameters of associative interaction, d, a, for a dimerizing model, must satisfy steric saturation conditions, namely, $\sigma_1 < 2d + a < \sigma_1 + (2 - \sqrt{3})d$.[28] In our theoretical treatment we have chosen a slightly smaller bonding length than the diameter of hard spheres such that the outer shell of the association site coincides with the surface of a hard sphere; then two spheres can form dimers while touching and also with negligible degree of overlap.

The matrix−matrix and fluid matrix interactions are chosen using the model of additive hard spheres, i.e.

$$U^{00}(r) = \begin{cases} \infty, & r < \sigma_0 \\ 0, & r > \sigma_0 \end{cases} \tag{4}$$

and

$$U^{10}(r) = \begin{cases} \infty, & r < (\sigma_0 + \sigma_1)/2 \\ 0, & r > (\sigma_0 + \sigma_1)/2 \end{cases} \tag{5}$$

respectively. Let us define now the Mayer functions

$$\begin{aligned} f^{00}(r) &= \exp[-\beta U^{00}(r)] - 1 \\ f^{10}(r) &= \exp[-\beta U^{10}(r)] - 1 \\ f^{11}_{\text{non}}(r) &= \exp[-\beta U^{11}_{\text{non}}(r)] - 1 \end{aligned} \tag{6}$$

and the associative "Mayer" function[28]

$$F_{\text{as}}(12) = \exp[-\beta U^{11}_{\text{non}}(r_{12})]\{\exp[-U^{11}_{\text{as}}(x_{12})] - 1\} \tag{7}$$

In the theory of Wertheim only its orientation-averaged form is needed

$$F_{\text{as}}(r_{12}) = \int \mathrm{d}\vartheta_1 \mathrm{d}\vartheta_2\, F^{11}_{\text{as}}(12) = \begin{cases} 0, & r_{12} < \sigma_1 \\ 0, & r_{12} > 2d + a \\ {}^1\!/_{24} \exp(\beta\epsilon_{\text{as}})(a + 2d - r_{12})^2 \times \\ \quad (a - d + 0.5 r_{12})/d^2 r_{12}, & \sigma_1 < r_{12} < 2d + a \end{cases} \tag{8}$$

These ingredients are necessary for the application of the associative ROZ equations.

3. Associative Replica Ornstein−Zernike Equations and Closure Relations

Let us assume that the matrix distribution corresponds to an equilibrium distribution of nonassociating hard spheres. Extending then the ROZ equations for nonassociating system to the case of associating fluid, we obtain the associative ROZ equations. They read[23−25]

$$h^{00} - c^{00} = c^{00} \otimes \rho^0 h^{00} \tag{9}$$

for the matrix subsystem

$$h^{10}_{\alpha} - c^{10}_{\alpha} = c^{10}_{\alpha} \otimes \rho^0 h^{00} + \sum_{\mu\nu} c^{11(1)}_{\alpha\mu} \otimes \rho^1_{\mu\nu}\, h^{10}_{\nu} \tag{10}$$

for the fluid−matrix correlations, and

$$\begin{aligned} h^{11}_{\alpha\beta} - c^{11}_{\alpha\beta} = c^{10}_{\alpha} \otimes \rho^0 h^{00} + \sum_{\mu\nu} c^{11(1)}_{\alpha\mu} \otimes \rho^1_{\mu\nu}\, h^{11}_{\nu\beta} + \\ \sum_{\mu\nu} c^{11(2)}_{\alpha\mu} \otimes \rho^1_{\mu\nu}\, h^{11}_{\nu\beta} \\ h^{11(1)}_{\alpha\beta} - c^{11(1)}_{\alpha\beta} = \sum_{\mu\nu} c^{11(1)}_{\alpha\mu} \otimes \rho^1_{\mu\nu}\, h^{11(1)}_{\nu} \end{aligned} \tag{11}$$

for fluid−fluid correlations. Here ⊗ denotes convolution and r-dependencies are omitted for brevity. In eqs 10 and 11 we have used standard decomposition of the pair and direct fluid−fluid correlation functions into connected, $\phi^{11(1)}_{\alpha\beta}$, and blocking, $\phi^{11(2)}_{\alpha\beta}$, parts ($\phi$ stands for h and c, as appropriate) such that each function consists of two terms: $\phi^{11}_{\alpha\beta} = \phi^{11(1)}_{\alpha\beta} + \phi^{11(2)}_{\alpha\beta}$. The correlation functions that are solved in eqs 10 and 11 are the *partial* correlation functions, similar to those in the theory of Wertheim for chemical association.[28−31]

In the case of dimerization, which we consider in the present work, lower indices in the correlation functions take the values 0 and 1, dependent on the bonding state of a fluid particle (it can be either free or participate in a dimer). The symmetry relations for the correlation functions imply $\phi^{11}_{10} = \phi^{11}_{01}$; $\phi^{10}_{\alpha} = \phi^{01}_{\alpha}$. The matrix of fluid density in the case of dimerization has the following form

$$\rho^1 = \begin{pmatrix} \rho^1 & \rho^1_0 \\ \rho^1_0 & 0 \end{pmatrix} \tag{12}$$

where ρ^1_0 is the density of unbounded fluid particles.

The partial pair correlation functions, $h^{11}_{\alpha\beta}$, yield the usual total pair correlation function (pcf) for fluid species via the following relation[28]

$$h^{11}(r) = h^{11}_{00}(r) + 2\chi^1 h^{11}_{10}(r) + (\chi^1)^2 h^{11}_{11}(r) \tag{13}$$

where $\chi^1 = \rho^1_0/\rho^1$ is the fraction of unbonded fluid particles. In the similar manner, the total fluid−matrix correlation function is defined as

$$h^{10}(r) = h_0^{10}(r) + (\chi^1)h_1^{10}(r) \tag{14}$$

The AROZ equation must be supplemented by the self-consistency relation for the density of adsorbed fluid. It reads[28]

$$\rho^1 = \rho_0^1 + (\rho_0^1)^2 \int \mathrm{d}\mathbf{r}\, F_{\mathrm{as}}(r)\, y_{00}^{11}(r) \tag{15}$$

where $y_{00}^{11}(R)$ is the partial cavity distribution function for unbounded fluid species.

Let us now consider the closure relations for AROZ equations. For the sake of convenience, introduce the notation $\gamma = h - c$. In this work the associative hypernetted chain approximation (HNC) is used. In the absence of associative interactions it reduces to the HNC closure, and this is used to evaluate the matrix structure

$$c^{00}(r) = [1 + f^{00}(r)]\exp[\gamma^{00}(r)] - 1 - \gamma^{00}(r) \tag{16}$$

The HNC closures for fluid−matrix and fluid−fluid correlation functions are

$$c_\alpha^{10}(r) = [1 + f^{10}(r)]\exp[\gamma_0^{00}(r)][\delta_{\alpha,0} + \delta_{\alpha,1}\gamma_\alpha^{10}(r)] - \delta_{\alpha,0} - \gamma_\alpha^{10}(r) \tag{17}$$

where $\delta_{\mu,\nu}$ is the Kronecker symbol, and

$$c_{\alpha\beta}^{11}(r) = [1 + f_{\mathrm{non}}^{11}(r)]\exp[\gamma_{00}^{11}(r)]\{\delta_{\alpha,0}\delta_{\beta,0} + \delta_{\alpha,1}\delta_{\beta,0}\gamma_{\alpha\beta}^{11}(r) + \delta_{\alpha,1}\delta_{\beta,1}[(\gamma_{00}^{11}(r))^2 + \gamma_{\alpha\beta}^{11}(r)]\} - \delta_{\alpha,0}\delta_{\beta,0} - \gamma_{\alpha\beta}^{11}(r) + \delta_{\alpha,1}\delta_{\beta,1}\exp[\gamma_{00}^{11}(r)]F_{\mathrm{as}}(r) \tag{18}$$

However, in the case of ROZ equations, in addition to these closures, we also must use the closure for the blocking parts of the partial dcfs. The associative HNC closure for these functions reads

$$c_{\alpha\beta}^{11(2)}(r) = \exp[\gamma_{00}^{11(2)}(r)]\{\delta_{\alpha,0}\delta_{\beta,0} + \delta_{\alpha,1}\delta_{\beta,0}\gamma_{\alpha\beta}^{11(2)}(r) + \delta_{\alpha,1}\delta_{\beta,1}[(\gamma_{00}^{11(2)}(r))^2 + \gamma_{\alpha\beta}^{11}(r)]\} - \delta_{\alpha,0}\delta_{\beta,0} - \gamma_{\alpha\beta}^{11(2)}(r) \tag{19}$$

Finally the cavity distribution function in eq 15 following from the associative HNC closure is

$$y_{00}^{11}(r) = \exp\{h_{00}^{11}(r) - c^{11}{}_{00}(r)\} \tag{20}$$

Equations 9−11 together with 15−20 represent a complete associative ROZ−HNC problem for numerical solution. In previous studies of nonassociating and associating fluids in disordered porous media the Percus−Yevick closure also has been applied, and it has been successful in many cases. Therefore, we also apply the associative Percus−Yevick closure for the system in question, however, only for the fluid−fluid and fluid−matrix correlations, because matrix structure is irrelevant. The associative Percus−Yevick closure reads

$$c_\alpha^{10}(r) = f^{10}(r)\, y_\alpha^{10}(r)$$

$$c_{\alpha\beta}^{11}(r) = f_{\mathrm{non}}^{11}(r)\, y_{\alpha\beta}^{11}(r) + (1 - \delta_{\alpha,0})(1 - \delta_{\beta,0})y_{00}^{11}(r)\, F_{\mathrm{as}}(r) \tag{21}$$

$$c_{\alpha\beta}^{11(2)}(r) = 0$$

where $y_\alpha^{10}(r) = \delta_{\alpha0} + h_\alpha^{10}(r) - c_\alpha^{10}(r)$; $y_{\alpha\beta}^{11}(r) = \delta_{\alpha0}\delta_{\beta0} + h_{\alpha\beta}^{11}(r) - c_{\alpha\beta}^{11}(r)$.

The problem, either with the HNC or with the PY closure, has been solved numerically by direct iterations, only for high fluid densities one needs to take care about the convergence of the numerical scheme.

4. Computer Simulation Procedure

Let us proceed with the description of the simulation procedure that is applied for a dimer, i.e., a diatomic made of rigidly bonded atoms, adsorption in a disordered porous media. The simulation results will be compared with the theory for the complete dimerization limit. In the simulated model the interaction between diatomics is taken in the form of hard-sphere atom−atom potentials

$$u^{11}(ij) = \sum_{m=1,2}\sum_{n=1,2} u_{i,j}^{\mathrm{hs}}(r_{mn}) \tag{22}$$

where the indexes m, n run over atoms of the diatomic molecules i and j, and the superscript hs denote a hard-sphere interaction. Everywhere in our simulations the diatomics are made of tangent hard spheres. The interaction between matrix hard spheres and a diatomic is

$$u^{10}(ij) = \sum_{m=1,2} u_{i,j}^{\mathrm{hs}}(r_{mj}) \tag{23}$$

The quenched-annealed system (consisting of matrix hard spheres and diatomics) will be studied by grand canonical MC (GCMC) simulations[32,33] and MC NVT simulations. First, a MC NVT simulation of a one-component fluid made up of hard spheres is performed. One of the equilibrium configurations is quenched; i.e., it remains fixed during the rest of GCMC run for adsorbed diatomic molecules calculations.

The input data in GCMC simulations are the chemical potential for diatomics, volume of the system simulated in the NVT ensemble, and the configuration of the matrix particles. We have performed several GCMC simulations at a given chemical potential of fluid species, but for “independent” configurations of matrix species chosen from the productive part of the NVT run. By independent we understand that these configurations are distanced from each other for at least 10^5 steps.

Details concerning GCMC simulations can be found in refs 32 and 33. In the GCMC runs we have performed 2×10^5 MC steps for equilibration of a diatomic fluid and 10^6 MC steps for the collection of ensemble averages. A MC step consists of attempts to displace and rotate (independently) all the diatomics in the system, as well as of attempt to insert or delete a diatomic molecule. During the course of the simulations, the average density of the diatomic molecules, the matrix sphere−diatomic atom, and the fluid atom−atom distribution functions will be determined. In some cases, the results obtained from each GCMC simulation have been averaged over three matrix configurations. In fact, we have observed that the results do not differ even if we take them for only one of chosen matrix configurations. Similar conclusion has been already obtained by Page and Monson in the simulation study of liquid-vapor phase transition in a fluid confined to disordered matrix.

The simulations for a partially dimerized fluid, i.e., for a thermodynamically equivalent mixture of hard spheres and diatomics, have been performed using the MC NVT simulations. We quench equilibrium configurations for the one-component hard-sphere fluid as mentioned above. Then we insert hard

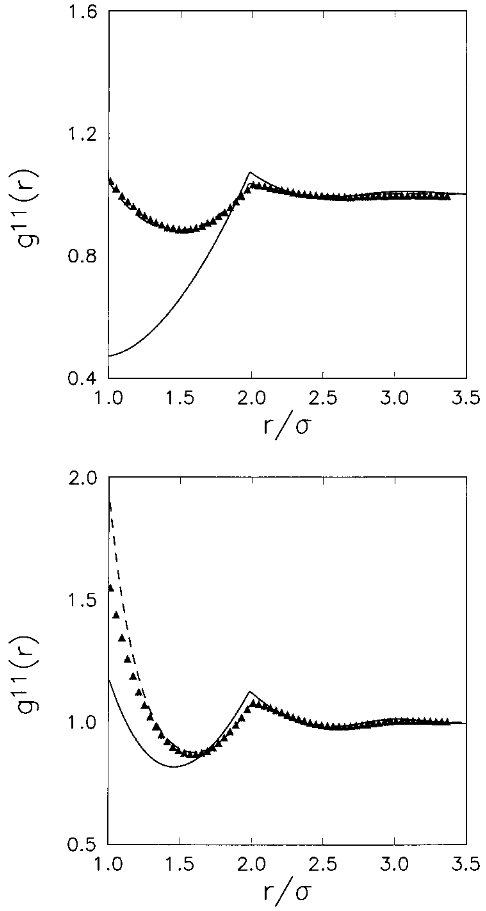

Figure 1. Fluid−fluid pair distribution functions, $g^{11}(r)$, for a dimerizing fluid in a state close to a complete association limit from the associative ROZ equations with PY (solid line) and HNC (dashed line) closures, and from the GCMC simulations for adsorbed diatomic molecules (triangles). In (a, top) the chemical potential of diatomic molecules fixed in GCMC is $\beta\mu_d = 1.715$, whereas in (b, bottom) $\beta\mu_d = 6.483$. The corresponding densities, $\rho^1 = 0.190\,986$ and $\rho^1 = 0.381\,972$, are taken as an input for theoretical evaluation of the structure. The disordered matrix density is $\rho^0 = 0.190\,986$.

spheres and hard dumbbells until we obtain the desired density and composition (we restrict ourselves to the case of equimolecular mixture of monomers and dimers) of the confined fluid. Then we perform a MC NVT simulation where we have evaluated the chemical potential using the method of Widom. Actually in these simulations we do not focus on the value of association energy that results in certain composition of adsorbed fluid. Let us proceed now with the description of the results obtained.

5. Results

We would like to discuss first the results obtained in the theory and simulations for states close to complete dimerization versus simulation data for adsorbed diatomic fluid.

In Figure 1 we present the fluid−fluid pair distribution functions, $g^{11}(r)$, obtained from the solution of the associative ROZ equations with HNC and PY closure. While solving the equations we have used the values for fluid density from simulations. The simulation data for the distribution functions of atoms belonging to different diatomics also are given in Figure 1. In Figure 1a, the results are for adsorbed diatomic fluid at the density of diatomics $\rho_d = 0.095\,493$, which corresponds to the chemical potential of diatomics, $\beta\mu_d = 1.715$. In Figure 1b the density of diatomic molecules is $\rho_d = 0.190\,986$ corresponding to $\beta\mu_d = 6.483$. A comparison between the theory and simulations has been performed as follows. We have taken the value of adsorbed diatomic fluid density from the simulations and choose the association energy in the theory, such that at this density ($\rho^1 = 2\rho_d$) the fraction of monomers (resulting from eq 15) is very small. A small difference between theoretical and simulated models may yield some discrepancies between the results of both approaches; we are convinced, however, that this effect is negligible.

We would like to make the following comment. In fact, it is impossible to reach a complete dimerization regime while solving integral equations numerically for the model with an association site of finite diameter. One has to have in mind that in analytical solutions of associating models involving the PY closure, the complete dimerization regime must be introduced *by hand* in the early stage of the treatment, see, for example, ref 34. The equations for adsorption of simple and associating fluids in disordered porous media do not possess analytical solutions, however.

We conclude, from the results given in Figure 1, that the HNC theory is very successful in the description of the pair distribution functions of fluid particles for a low value of the chemical potential of fluid species. For high values of the chemical potential the HNC approximation overestimates the contact value of $g^{11}(r)$, i.e., at $r = 1$, while the PY approximation underestimates it, in comparison with simulation data. At low values of the chemical potential, the PY approximation yields poor results at small interparticle separations. For larger distances between particles, the results of both approximations become closer to each other, and the HNC is more successful anyway. However, the PY closure overestimates the value of the cusp at $r = 2$ for both chemical potentials in question. Very similar trends to those described by us at $\beta\mu_d = 6.483$, in the description of the contact value of $g^{11}(r)$, have been observed in comparison of simulation and theoretical data for adsorbed hard-sphere fluid at high density.[9] Evidently the PY closure neglects the blocking effects, due to the presence of matrix species, in $c^{11}(r)$. However, it seems that the HNC closure overestimates the blocking effect of the matrix for high values of the chemical potential. Very recently Meroni et al.[12] have shown that the performance of the HNC can be essentially improved for high densities of adsorbed fluid, if the bridge function contribution would be included into the closure. This issue for associating fluids is difficult and requires special study; we hope to gain some progress in solving this problem in a future work.

The fluid−matrix distribution function, $g^{10}(r)$, from the theory and simulations is shown in Figure 2 for the same states as in Figure 1. For both values of the chemical potential we observe that the HNC approximation slightly overestimates the values for the distribution function $g^{10}(r)$ for small distances while the PY closure underestimates this function. The discrepancy between the PY result and the simulation data is larger for the lowest value of $\beta\mu_d$, i.e., $\beta\mu_d = 1.715$. The HNC is more successful in the description of a characteristic cusp at $r = 2$ for both values of the chemical potential. We would like to conclude that for the states close to complete dimerization, the HNC approximation is sufficiently accurate to describe correlation in adsorbed fluid as well as between fluid particles and matrix species for different values of the chemical potential, at least for intermediate density matrix, $\rho^0 = 0.190\,986$.

Let us proceed with the examination of the results corresponding to states of incomplete dimerization. In Figure 3 we present the results for $g^{11}(r)$, for adsorbed dimerizing fluid in

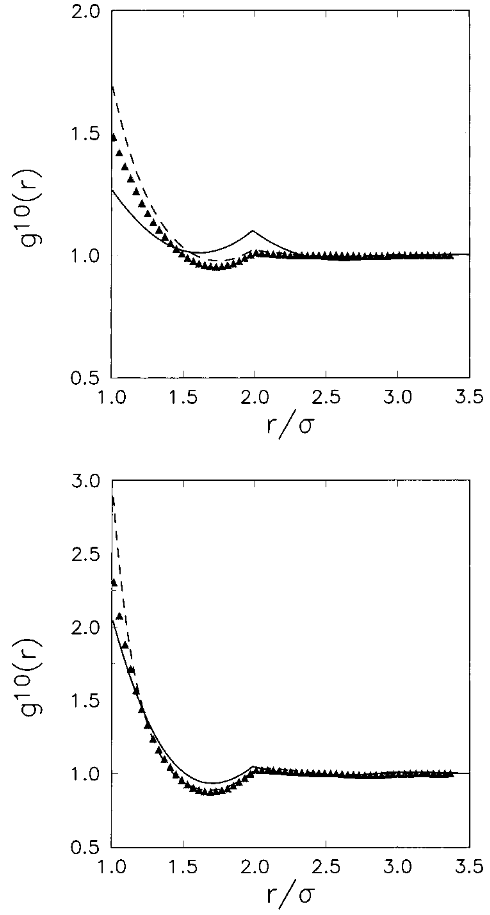

Figure 2. The matrix−fluid pair distribution functions, $g^{10}(r)$, for the same system as in Figure 1. The nomenclature of lines and symbols is as in Figure 1. In (a, top) and (b, bottom) the results for low and high value of the chemical potential of adsorbed diatomic molecules, $\beta\mu_d = 1.715$ and $\beta\mu_d = 6.483$ are shown, respectively.

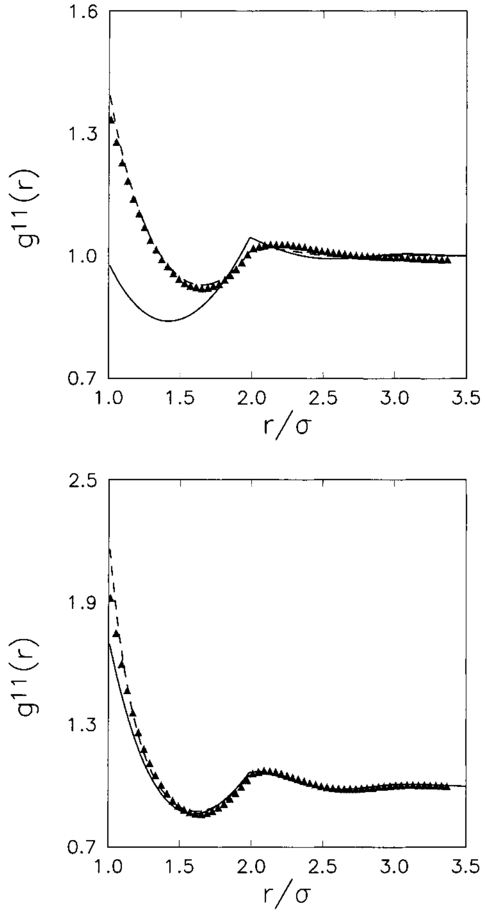

Figure 3. The fluid−fluid pair distribution functions, $g^{11}(r)$, for a dimerizing fluid in partially dimerized state from the associative ROZ equations with PY (solid line) and HNC (dashed line) closures, and from MC simulations for adsorbed diatomic molecules (triangles). In (a, top) the chemical potential of diatomic molecules in adsorbed fluid, which is evaluated from MC simulations, is $\beta\mu_d = 0.08$, whereas in (b, bottom) $\beta\mu_d = 3.10$. The corresponding fluid densities: $\rho^1 = 0.191$ and $\rho^1 = 0.382$ are taken as an input for theoretical evaluation of the structure. The disordered matrix density is $\rho^0 = 0.190\,986$.

which the number of unbounded hard spheres and diatomics is equal, 50% each. There is a large discrepancy between the PY result and simulation data for $g^{11}(r)$ for small distances between particles if the chemical potential of adsorbed diatomic fluid is low, $\beta\mu_d = 0.08$. On the other hand, the HNC result is of much better quality, as it follows from our comparison with simulations. For the highest value of the chemical potential, $\beta\mu_d = 3.10$, the quality the PY approximation improves. Nevertheless, the HNC theory is more accurate.

Figure 4 contains our results for $g^{10}(r)$ for the same system as in Figure 3. It can be seen that for low values of the chemical potential of diatomic molecules, $\beta\mu_d = 0.08$ (Figure 4a), the HNC reproduces the simulation data almost exactly. The PY result is of poor quality for this case. For a higher value of the chemical potential, $\beta\mu_d = 3.10$ (Figure 4b), both theories almost agree with computer simulation results for small matrix−fluid distances. The HNC overestimates the contact value, i.e., overestimates adsorption of fluid species on the matrix, while the PY underestimates contact value of $g^{10}(r)$.

We would like to summarize at this point our opinion about the structure of adsorbed fluid from the theory and simulations. Evidently, we have restricted ourselves to a single matrix density that lies somewhere in between low and intermediate densities. This makes GCMC simulations less difficult in comparison to a high-density matrix case. It follows from our results that the HNC approximation works better than the PY one; the latter approach neglects blocking effects of matrix species on the correlations between fluid particles and probably is not too accurate in describing association in the region of parameters studied. Computer simulations of the blocking contribution require sophisticated efforts. However, it seems that blocking term contribution is important, if adsorbed fluid is characterized by a low value of the chemical potential. For higher values of the chemical potential, the blocking term contribution becomes less important at this matrix density, and the PY and the HNC closures work almost with similar accuracy. We are convinced, however, that at a higher matrix density in the region of chemical potentials studied in this work the blocking term contributions will become more important.

6. Conclusions

In this work we have investigated the structure of dimerizing and dimer fluids in random porous media. We have compared the predictions of the associative replica Ornstein−Zernike (AROZ) equations for a hard-sphere model that permits dimerization due to associative site−site interactions with structure data from computer simulations. Two closures have been used to solve the AROZ equations, namely, the associative HNC and the associative PY approximation. From our results we conclude that the HNC closure is superior to the PY for all cases studied in this work.

In future theoretical work and simulations of models with a more sophisticated form of the nonassociative interparticle

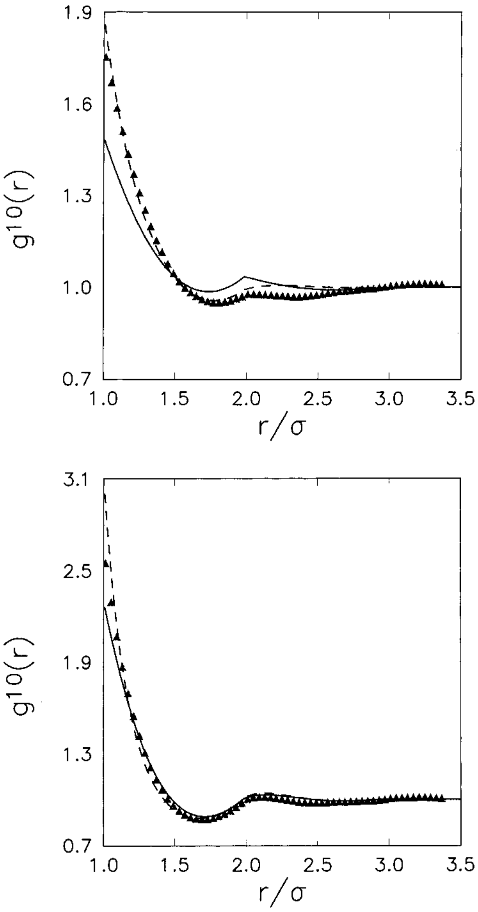

Figure 4. Matrix−fluid pair distribution functions, $g^{10}(r)$, for the same system as in Figure 3. The nomenclature of lines and symbols is as in Figure 3. In (a, top) and (b, bottom) the results for low and high value of the chemical potential of adsorbed diatomic molecules, $\beta\mu_d = 0.08$ and $\beta\mu_d = 3.10$, are shown, respectively.

interactions, we plan to use these closures for the description of the structural and thermodynamic properties. The adsorption isotherms for models with associative interactions and attractive forces have not been obtained from computer simulations so far. Moreover, a closed form expressions for the chemical potential of associating fluids adsorbed in disordered porous media, similar to the development of Kierlik et al.[14], is unavailable at the moment. Therefore it is difficult to evaluate validity of theoretical approaches based on thermodynamic perturbation theory[35] for a dimerizing model, as well as for more sophisticated four-site model,[36] at present. A comparison of the theory with simulations for adsorption isotherms will become a subject of our future work.

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