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The structure and adsorption of diatomic fluids in disordered porous media. A Monte Carlo simulation study

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The adsorption isotherms for diatomic fluids in disordered porous media have been obtained from grand canonical Monte Carlo computer simulation. A disordered porous medium, or matrix, is prepared by quenching an equilibrium configuration of spherical hard core molecules. In addition, canonical Monte Carlo simulations have been performed for equilibrium binary mixtures that represent counterparts of quenched–annealed systems in question. For the same chemical potential of diatomic molecules at a fixed density of matrix species, the structure and the density of the diatomic fluid in the binary mixture and in the quenched medium are very similar. This behaviour holds also for systems with attractive interactions in the region of high temperatures. Observed similarity of the structural and thermodynamic properties of the mixture and the corresponding annealed fluid–quenched matrix system permits the use of the thermodynamics of the mixture to evaluate some properties of quenched–annealed fluids. Calculations were made of the adsorption isotherm of the diatomic fluid in a disordered hard sphere matrix using a successful theoretical equation of state for mixtures, agreement with computer simulation data was excellent.

1. Introduction

During the last decade the study of adsorption of fluids in pores of well defined geometry (slit-like and cylindrical pores, spherical cavities) has received considerable attention, such that at present we have quite a good understanding of these systems [1]. However, in recent years interest in the problem of adsorption in disordered porous materials has grown considerably [2–17]. In these systems, the adsorbent is disordered even on a molecular length scale. One example of microporous material is silica gel, commonly used in experimental studies of adsorption. Madden and Glandt [2] were the first to realize that the study of adsorption in disordered porous materials could benefit from the advances of liquid state theory. In their seminal work [2], Madden and Glandt considered a fluid–microporous adsorbent system as a binary mixture with one quenched component (called the matrix) and an annealed component representing a fluid. From an analysis of the Mayer cluster expansions for this system, a set of Ornstein–Zernike-like (OZ) equations, denominated commonly as the Madden and Glandt (MG) equations, has been derived. However, Given and Stell [3, 4] have shown, more recently, that certain graphs were missing in the original derivation, and proposed the correct version of the OZ-like equations, known as the Replica Ornstein–Zernike (ROZ) equations.

Thermodynamic equations for adsorption isotherms and other properties from the results of the ROZ equations have been obtained also [5–7]. Since then, several theoretical and simulation studies of the adsorption of simple and complex fluids in disordered microporous media have appeared [8–17].

Equilibrium fluid mixtures and fluids confined in porous media evidently are different types of system that are described by different OZ equations and require different routes for the thermodynamics. Surprisingly, it appeared that some properties of quenched–annealed

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fluids and usual mixtures in the case of a large difference in diameters of matrix and fluid particles are very similar [8]. A reasonable explanation of this similarity has been provided in [8]. Very recently, Vega has performed a cluster expansion analysis and shown that a mixture of hard spheres and point-like particles and its quenched–annealed counterpart (with hard spheres quenched) are characterized by identical structural properties [18]. In this work we will present computer simulation results for this particular model which give further evidence of the similarity of properties of the two systems. It seems, however, that a similarity of properties of a fluid mixture and the annealed fluid–quenched matrix system is not restricted only to the case of a large difference in diameters of particles. Evidence for similarity between the two systems composed of particles of similar size has been obtained by Ford, Thompson and Glandt [13], and for flexible hard molecules in disordered porous media by two of us [14].

At present, the similarity between properties of a mixture and their quenched–annealed counterparts is not fully understood even for simple models. However, it may have some important practical consequences. To study mixtures is simpler than fluids in microporous environment. The similarity between both systems means that one can apply successful theoretical approaches for mixtures, available for a number of systems, to study adsorption of fluids in random porous materials.

In this work we shall focus on the study of a molecular fluid (a diatomic molecule) in a disordered porous medium prepared by the quench of spherical particles. We have many goals. First, we would like to analyse in detail whether a similarity between mixtures and quenched-annealed systems holds in the case of molecular fluids. Second, since very good equations of state for mixtures of hard spheres and diatomics are available [19–24], the possibility of obtaining the adsorption isotherms for molecular fluids in a quenched microporous environment from the theory of mixtures will be considered. Since the diatomic molecule can be considered as a product of infinitely strong association between monomers, the results presented in this work may be of interest for the study of association within porous materials. This area has received increasing attention recently [17, 25–27]. Moreover, we shall consider hard core models and a model with attractive interactions to see how our conclusions depend on the presence of interparticle attraction.

The structure of this work is the following. In Section 2 we present the molecular models and details of the simulations. Section 3 describes briefly a theoretical equation of state for mixtures of hard spheres and hard diatomic molecules. In Section 4 the results of our study are presented. In the final section a discussion and conclusions are given.

2. Models and simulation details

In this section the potential models used in this work and the details of the simulations are described. The models in question contain two components. Component 1 is a fluid of hard spheres of diameter D, and component 2 is a fluid of hard dumbbells (HD). The HD consists of two tangent hard spheres of diameter σ. Therefore, the reduced bond length of the dumbbell is $L^* = L/\sigma = 1$ where L is the bond length.

The interaction between two molecules of component 1 (spheres) u_{mm} is given by:

$$u^{\mathrm{H}}_{\mathrm{mm}}(r) = \begin{cases} 0, & r > D \\ \infty, & r < D. \end{cases} \tag{1}$$

where r is the distance between centres of spheres. The interaction between two diatomic molecules is

$$u^{\mathrm{H}}_{\mathrm{ff}} = \sum_{i=1}^{i=2}\sum_{j=1}^{j=2} u^{\mathrm{H}}(r_{ij}), \tag{2}$$

where

$$u^{\mathrm{H}}(r_{ij}) = \begin{cases} 0, & r_{ij} > \sigma, \\ \infty, & r_{ij} < \sigma. \end{cases} \tag{3}$$

The summation in equation (2) runs over the two interaction sites of the diatomic molecule and r_{ij} is the distance between the sites i and j of two diatomic molecules. Finally, the interaction between the diatomic molecule and the sphere is given by

$$u^{\mathrm{H}}_{\mathrm{mf}} = \sum_{i=1}^{i=2} u^{\mathrm{H}}(r_i), \tag{4}$$

with

$$u^{\mathrm{H}}(r_i) = \begin{cases} 0, & r_i > (D+\sigma)/2, \\ \infty, & r_i < (D+\sigma)/2, \end{cases} \tag{5}$$

where r_i is the distance from site i of the diatomic molecule to the centre of the sphere. In the equations above the superscript H denotes a hard core interaction. The origin of the subscripts mm, ff and mf, used to label the sphere–sphere, diatomic–diatomic and sphere–diatomic interactions, respectively, will be clarified below. Three types of hard core model will be considered in this work. In model 1 (M1) $D = \sigma$ such that the sphere and the two beads which constitute the diatomic molecule are of the same diameter. In model 2 (M2) we choose $D = 7\sigma$, such that the diameter of the sphere is seven times larger than the diameter of the beads of the diatomic. In model 3 (M3) we have assumed $\sigma = 0$, such that component 1

Table 1. Models considered in this work (H denotes hard body interaction and LJ indicates Lennard-Jones interactions). In models M1, M2, and M3 component 1 is a hard sphere of diameter D, whereas component 2 is a hard diatomic molecule formed by two tangent hard spheres of diameter σ. Obviously when $\sigma = 0$ the diatomic molecule reduces to a point. In model M4 the sphere–sphere, sphere–site and site–site interactions are of LJ type with the same value of σ and ϵ.

Model	Interaction	D	σ
M1	H	1	1
M2	H	7	1
M3	H	1	0
M4	LJ	1	1

represents a fluid of hard spheres with diameter D, and component 2 represents point-like particles which cannot penetrate spheres.

The last model considered in this study is denoted M4. It is a modification of M1 in which hard core interactions are replaced by Lennard-Jones (LJ) ones. The sphere–sphere, sphere–site and site–site interactions become

$$u^{\mathrm{LJ}} = 4\varepsilon_{\mathrm{LJ}}\left[\left(\frac{\sigma_{\mathrm{LJ}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{LJ}}}{r}\right)^{6}\right]. \tag{6}$$

The values of $\varepsilon_{\mathrm{LJ}}$ and σ_{LJ} used for the sphere–sphere, sphere–diatomic site, and diatomic site–diatomic site interactions are chosen to be equal. For this model the reduced bond length of the diatomic molecule also is unity ($L^* = L/\sigma_{\mathrm{LJ}} = 1$) where σ_{LJ} is the parameter defining the LJ interaction. To avoid problems with long range corrections to thermodynamic properties, the LJ interactions were truncated and shifted at $r = 2.5\sigma_{\mathrm{LJ}}$.

The characteristics of the models studied in this work are summarized in table 1.

Reduced densities will be defined as $\rho_1^* = \rho_1\sigma^3$ for component 1 and $\rho_2^* = \rho_2\sigma^3$ for the diatomic molecules (component 2), where ρ_1 and ρ_2 are the number densities of spheres and diatomic molecules, respectively, and σ is either the size of beads of the HD or the LJ size parameter in the model M4. In the system with attractive forces (M4) the reduced temperature will be defined as $T^* = kT/\varepsilon$.

Two physically different types of system will be considered. The first is an equilibrium binary mixture. In the simulations of an equilibrium binary mixture the molecules of both components move within the simulation box. The second consists of a quenched matrix made up of spherical molecules (then the spheres are not moved during simulations) in which the diatomic molecules adsorb and equilibrate.

The equilibrium binary mixture was studied by canonical NVT Monte Carlo (MC) simulation [28]. In the course of simulation, the intermolecular structure has been calculated. Also, the residual part of the chemical potential of the diatomic molecule was evaluated by using Widom's test particle method [29]. Therefore, the total chemical potential of the diatomic molecule was obtained using the relation

$$\frac{\mu_2}{kT} = \ln(\rho_2^*) - \ln\langle \exp(-\beta U^{\mathrm{test}})\rangle \tag{7}$$

where $\langle\ldots\rangle$ denotes thermal average. Equation (7) can be implemented readily. During the NVT MC simulation a diatomic test particle has been inserted randomly into the mixture from time to time. The interaction energy of the test particle with the rest of the particles of the system has been computed. In this way $\langle \exp(-\beta U^{\mathrm{test}})\rangle$ was evaluated. In the NVT simulations of the systems denoted as M1, M2, M3 we always used 128 molecules of component 1 (the spheres). For M4 system, 256 molecules of the component 1 were used instead. The number of diatomic molecules was chosen to provide for molar fractions $x_2 = 1/3$ and $x_2 = 1/2$. We performed 2×10^5 MC steps for equilibration and 10^6 MC steps for obtaining averages. Each MC step consists of an attempt to displace all the particles of the system. The sphere–sphere, sphere–site, and site–site correlation functions were obtained during the run. By site we mean the interaction site of the diatomic molecule. The pressure of the system was computed using the virial theorem. For the LJ system the internal energy also was computed during the simulations. After each 10 MC steps we performed 5000 attempts to inserting a test diatomic particle to compute the residual chemical potential.

Now let us describe the grand canonical Monte Carlo (GCMC) simulations carried out for diatomic molecules confined in a matrix of quenched spheres. First, an NVT MC simulation of a system containing only spheres is performed (for the M1, M2, M3 models these are hard spheres whereas for M4 system they are spherical LJ particles). Five different equilibrium configurations of spheres have been selected from these simulations. The spheres preserve their positions, i.e., they remain fixed, during the rest of the calculations. Each configuration of spheres defines a random porous medium (matrix) in which the adsorption of diatomic molecules (fluid) takes place. Hence, the labelling mm (matrix–matrix), ff (fluid–fluid) and mf (matrix–fluid) has been used in equations (1)–(8) to denote the sphere–sphere, diatomic–diatomic and sphere–diatomic interactions. For each configuration of the spheres we perform GCMC

[30], such that the adsorption isotherm for a particular configuration of matrix particles is obtained. The adsorption isotherm gives the density of the diatomic molecules confined in the random medium as a function of the chemical potential, at a fixed temperature. A GCMC simulation is performed for each of the five independent configurations of matrix particles. Therefore, for each thermodynamic state, the results reported (concerning the structure and thermodynamics) correspond to the average of simulations over five independent configurations of the matrix particles. The input data in GCMC simulations are temperature, volume, and chemical potential, and in our case the configuration of the matrix particles. General details concerning GCMC simulations can be found in [28, 30]. In each of the GCMC simulations we performed 2×10^5 MC steps for equilibration and 10^6 MC steps to collect the ensemble averages. In the simulations an MC step consists of attempts to displace and rotate (independently) all the diatomic molecules in the system, and of attempts to insert or delete a diatomic molecule approximately every 100 trials of displacing the molecules. During the simulations, the average density of the diatomic molecules, the sphere–site and the site–site correlation functions have been determined. In the case of the LJ system the internal energy of the diatomic molecule in the porous media has been determined.

There are two main questions which we would like to answer using the simulations. The first is: are the structures of the diatomic molecular fluid in the binary mixture and in the microporous medium similar when the chemical potential of the diatomic molecule is the same in both systems? The second question is: are the densities of diatomic molecules in the binary mixture and in the microporous medium similar when both systems present the same chemical potential for the diatomic molecule? If the answer to this second question would be affirmative, then a route to determine the adsorption isotherm may involve an equation of state (EOS) for the corresponding mixture. In the next section such an EOS for the hard sphere–hard diatomic mixture is presented.

3. Theoretical EOS for hard sphere–hard diatomic mixture

Wertheim [19] and Chapman *et al.* [20] have proposed an EOS for a multicomponent system of chains of tangent hard spheres of the same diameter. Later, Jackson *et al.* [21–24] extended this equation for heteronuclear chains (each chain is formed by tangent hard spheres with different diameters) and mixtures of chains. This extension is usually referred to as bonded hard sphere (BHS) theory and will be used in this work. We shall describe this theory only briefly, referring the reader to [21–24] for a more detailed presentation. The Helmholtz free energy A, and the compressibility factor of the system Z, for a mixture of hard spheres of diameter D and hard dumbbells with $L^* = L/\sigma = 1$, and diameter σ, given by BHS theory can be expressed as

$$m_{\text{mixture}} = 1 \times x_1 + 2 \times x_2, \tag{8}$$

$$Z = \frac{p}{\rho kT} = (m_{\text{mixture}}) Z_{\text{CS}} - x_2 \left(1 + \rho \frac{\mathrm{d} \ln (g_{22}(\sigma))}{\mathrm{d}\rho} \right), \tag{9}$$

$$A/NkT = A^{\text{ideal}}/NkT + A^{\text{res}}/NkT, \tag{10}$$

$$A^{\text{ideal}}/NkT = \ln(\rho\sigma^3) - 1 + x_1 \ln(x_1) + x_2 \ln(x_2), \tag{11}$$

$$A^{\text{res}}/NkT = m_{\text{mixture}} A^{\text{res}}_{\text{CS}}/(N_s kT) - x_2 \ln(g_{22}(\sigma)), \tag{12}$$

where x_1 and x_2 are the molar fractions of component 1 (hard spheres) and the component 2 (hard dumbbells), respectively, ρ is the total number density of molecules, and m_{mixture} is the average length of the molecules in the mixture. By $Z_{\text{CS}} = pV/(N_s kT)$ we denote the compressibility factor following from Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) [31, 32] EOS of the 'unbonded' mixture consisting of N_s spheres. The unbonded mixture is obtained by breaking (deleting) bonds of the chains of the mixture (in our case the hard dumbbell bonds must be deleted). The free energy $A^{\text{res}}_{\text{CS}}/(N_s kT)$ is the residual free energy per site of the unbonded mixture given by the BMCSL EOS, and $g_{22}(\sigma)$ is the contact value of the radial distribution function between the monomers forming the dumbbell, however, in the unbonded mixture. The expressions for Z_{CS}, $A^{\text{res}}_{\text{CS}}$ and g_{22} needed to implement equations (9)–(12) can be found elsewhere [21–24].

For a particular case, in which the diameter D of particles of component 1 is equal to σ, the compressibility factor and the residual part of the free energy can be rewritten in a simpler manner:

$$Z = \frac{p}{\rho kT} = (m_{\text{mixture}}) \frac{1 + y + y^2 - y^3}{(1-y)^3} - (m_{\text{mixture}} - 1) \frac{1 + y - y^2/2}{(1-y)(1-y/2)} \tag{13}$$

$$\frac{A^{\text{res}}}{NkT} = (m_{\text{mixture}} - 1) \ln\left(\frac{2(1-y)^2}{(2-y)} \right) - \frac{(m_{\text{mixture}})(2y-3)}{(1-y)^2} - 3(m_{\text{mixture}} - 1) \tag{14}$$

where the volume fraction y, and the average volume of

Table 2. MC results for the equilibrium binary mixtures denoted as M1 and M4 in table I. The reduced number densities of spherical ρ_1^* and diatomic ρ_2^* molecules are presented. For M4 model simulations were performed for the reduced temperature $T^* = 2.5$. For each state, results are presented for the compressibility factor Z, the residual chemical potential μ^{res} of the diatomic particles and the interaction energy U_2 of the diatomic particles with the rest of molecules in the system. N_2 stands for the number of diatomic molecules.

Model	ρ_1^*	ρ_2^*	μ_2^{res}/kT	$Z = p/(\rho kT)$	$U_2/(N_2\epsilon)$
M1	0.190 986	0.095 493	4.064(1)	2.72	0
M1	0.190 986	0.190 986	8.139(9)	4.95	0
M4	0.190 986	0.095 493	0.275(1)	1.229	− 5.270(3)
M4	0.190 986	0.190 986	1.494(1)	2.006	− 6.988(2)

Table 3. Comparison between theory and simulation (MC) for the compressibility factor and residual chemical potential of the diatomic molecule, in the hard sphere (1)–hard diatomic (2) mixture denoted as M1 in table I.

Model	ρ_1^*	ρ_2^*	Z^{MC}	Z^{theory}	$\mu_2^{\mathrm{res,MC}}/kT$	$\mu_2^{\mathrm{res,theory}}/kT$
M1	0.190 986	0.095 493	2.72	2.66	4.064	4.05
M1	0.190 986	0.190 986	4.95	4.91	8.139	8.10

the molecules of the mixture, V_{mixture} are determined by

$$V_{\mathrm{mixture}} = x_1 V_1 + x_2 V_2, \tag{15}$$

$$y = \rho V_{\mathrm{mixture}}. \tag{16}$$

In equation (15), V_1, V_2 stand for the molecular volume of components 1, 2, respectively. The residual chemical potential of component 2 (dumbbells), μ_2^{res}, can obtained from the thermodynamic relation

$$\mu_2^{\mathrm{res}}/kT = \left(\frac{\partial A^{\mathrm{res}}/kT}{\partial N_2}\right)_{T,V,N_1}, \tag{17}$$

where N_1 and N_2 are the number of spherical and diatomic molecules, respectively. In the case when $D = \sigma$, equation (14) has been used for A^{res}, whereas when $D \neq \sigma$, equation (12) has been applied.

4. Simulation results

In this section we will present the results obtained for the model systems described in the previous section. First we shall comment briefly on the conditions chosen for our computer experiments. The packing fraction (density) of spheres is the same in all cases, $\eta = 0.1$. Thus, when the spheres are quenched they form a matrix which can represent a porous material of high porosity as, for instance, silica aerogel, which has a porosity of 95% [33]. Nevertheless, the purpose of this investigation is not to mimic a specific experimental situation but rather to explore the similarities between a diatomic fluid confined in a random medium and the corresponding binary mixture. The densities chosen for the diatomic fluid also are low. The effect of density on the similarities between the confined fluid and mixture will be commented upon later.

In table 2, computer simulation results for the binary mixtures M1 and M4 are presented. For a given number density of spheres and diatomic molecules simulation results for the compressibility factor, the residual chemical potential, and the interaction energy of the diatomic molecule are given.

In table 3, simulation results for M1 mixture are compared with the predictions of BHS theory. As can be seen, agreement is quite good, both for the compressibility factor and for the residual chemical potential. This is not surprising since it has been shown previously that BHS theory describes well the compressibility factor of the M1 mixture [23]. Here we observe that this agreement also is excellent for the chemical potential.

With the properties of binary mixtures M1 and M4 presented, let us now look for the properties of the diatomic fluid in a disordered porous medium, from the GCMC simulations. We shall start with the results for a hard core system denoted as M1. As the input value for the chemical potential in the GCMC simulations we have used the values of μ_2 given in the first column of table 4. This value of the chemical potential is obtained by adding the ideal term ($\ln(\rho_2^*)$) to the residual chemical potential of the diatomic molecule (sixth column of table 3). Now, the output of the simulation is the average density of the diatomic molecules confined in a disordered porous medium. This result is presented in the second column of table 4. The last column of table 4 gives the number density of dumbbells in an

Table 4. Average reduced density of the diatomic particles in the quenched medium, $\rho^*_{2,\rm quenched}$, as obtained from GCMC simulations for model M1. The chemical potential used for the diatomic in GCMC simulations was obtained by adding to the residual part presented in table 2 the ideal contribution to the chemical potential. The reduced number density of the spherical particles constituting the matrix is $\rho^*_1 = 0.190\,986$. The last column is the number density of the diatomic molecule, $\rho^*_{2,\rm mixture}$, in the binary equilibrium mixture with the same chemical potential as the diatomic.

μ_2/kT	$\rho^*_{2,\rm quenched}$	$\rho^*_{2,\rm mixture}$
1.715	0.0935(5)	0.095 493
6.483	0.190(2)	0.190 986

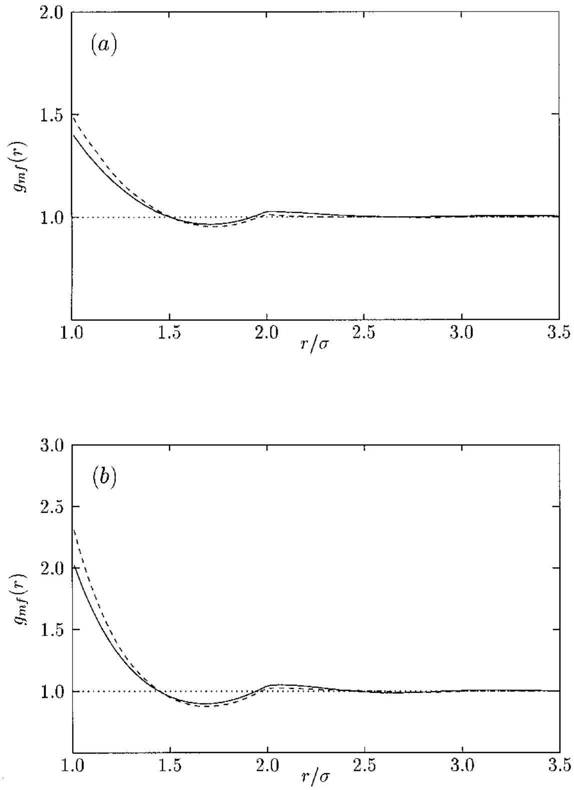

Figure 1. Sphere–site $g_{\rm mf}$ correlation functions for the M1 model: solid line, binary mixture; and dashed line, quenched media. Results for (*a*) a low and (*b*) a high chemical potential of the diatomic molecule (see table 4).

equilibrium mixture having the same number density of spheres and the same chemical potential for the dumbbell as the quenched system. By comparing the last two columns of table 4 we observe that, at the same chemical potential, the number densities of diatomic particles in the binary mixture and confined in the porous medium are equal within the uncertainty of the GCMC simulation results (the number density of spherical particles is the same in both systems). The closeness between the densities of the diatomic particles in the porous medium and in the mixture, at the same chemical potential, is the central result of this work. It proves that the adsorption isotherms of diatomic molecules in disordered microporous media can be obtained from the theoretical developments for binary equilibrium mixtures. Of course this is only an approximation, but the results collected in table 4 show that it is a fairly good approximation. Moreover, the results of table 4 give further evidence of the fact that, for certain properties, the confined diatomic particles in the quenched medium and the binary mixture show a resemblance. The first indication of that was obtained in [8] for mixtures of spherical hard particles. Further evidence was obtained in [13], again for mixtures of spherical hard particles, and in [14] for flexible molecules in microporous media. Now, in this work, we show that this is again true for a sphere–diatomic mixture. The message of table 4 is is that for the same number density of the matrix particles and chemical potential of the diatomic molecules the number densities of the diatomic particles in the mixture and in the porous medium are very close.

The results presented so far emphasize the similarities between the binary mixture and the quenched medium. Does this similarity extent also to structural properties? To analyse this point, figures 1 and 2 present the results for site–site correlations functions. We have defined two site-site correlation functions, namely the sphere–site, $g_{\rm mf}(r)$, and the site–site, $g_{\rm ff}(r)$, i.e.

$$g_{\rm mf}(r) = \frac{1}{2}\sum_{i=1,2} g^{i}_{\rm mf}(r), \tag{18}$$

$$g_{\rm ff}(r) = \frac{1}{4}\sum_{i=1,2}\sum_{j=1,2} g^{ij}_{\rm ff}(r), \tag{19}$$

where the indexes i and j run over the interaction sites of the diatomic molecule and $g^{i}_{\rm mf}$ and $g^{ij}_{\rm ff}$ are the correlation functions between a sphere and the site i of the diatomic molecule, and between sites i and j of different diatomic molecules, respectively.

Figure 1 gives the results for the sphere–site correlation function $g_{\rm mf}(r)$ in the binary mixture and in the porous medium. The results shown in figure 1(*a*) correspond to the lowest value of the chemical potential (i.e., to the lowest density of diatomic molecules). It can be seen that the sphere–site correlations are similar in the two systems. Figure 1(*b*) shows the results for the highest chemical potential (i.e., for the highest diatomic

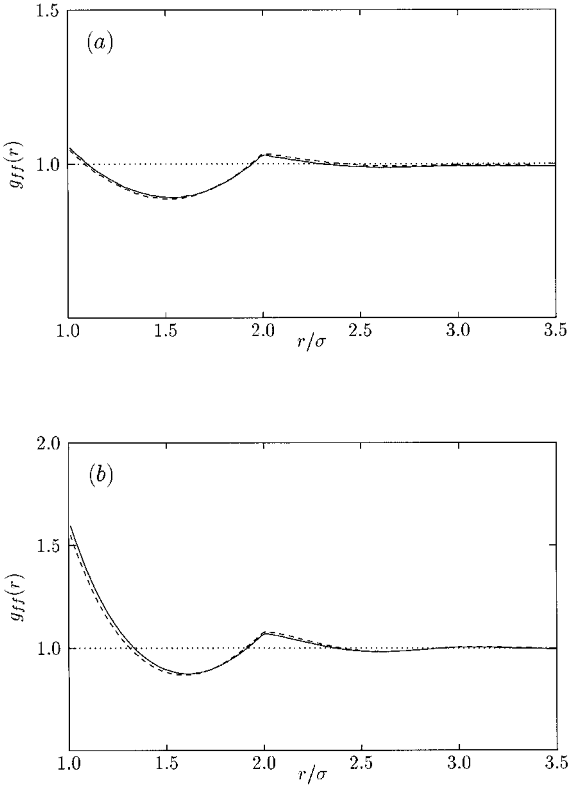

Figure 2. Site–site g_{ff} correlation functions for M1 model: solid line, binary mixture; and dashed line, quenched media. Results for (a) a low and (b) a high chemical potential of the diatomic molecule (see table 4).

density). The differences between the quenched system and the binary mixture are clear: the contact values are higher in the case of a partly quenched system; i.e. the diatomic molecules tend to be closer to the spherical obstacles in the quenched system rather than in the binary mixture.

Figure 2 presents the results for the site–site correlation functions $g_{\mathrm{ff}}(r)$ in the binary mixture and in the porous medium and includes the results for (a) the lowest chemical potential (i.e., for the lowest density of diatomic molecules) and (b) for the highest chemical potential. It can be seen that the resemblance of the site–site correlations in the two systems is stronger than for the sphere–site correlation functions.

The conclusions so far obtained from a study of the hard core systems are:

(i) thermodynamic properties are quite similar in the binary mixture and in the random media for the same number density of matrix particles and for the same chemical potential of the fluid (diatomic) particles.
(ii) the fluid–fluid correlation functions in the random medium are quite close to those in the binary mixture; and
(iii) the largest differences between the two systems (a diatomic fluid confined in a random porous medium and in a binary mixture) are in the shapes of the fluid–matrix correlation functions.

By analysing points (i)–(iii), an obvious conclusion is that thermodynamic properties of fluids in confined media depend mainly on the fluid–fluid correlations and, to a minor extent, on the fluid–matrix correlations. Only in this way can points (i)–(iii) be consistent. An interesting observation in this context is that the compressibility route to the thermodynamic properties of the fluid in the porous media includes fluid–fluid correlations only [5, 7, 8].

Let us now analyse whether the analogy between the mixture and the fluid confined in a random porous material holds when attractive forces are present. For that purpose we have performed simulations of an LJ system, denoted as M4 (table 1). The simulations are performed at $T^* = 2.5$ to avoid the vapour–liquid coexistence curve of the mixture. Table 2 presents the results for the binary M4 mixture. Table 5 results from GCMC simulations for the number density and internal energy of the diatomic molecules are presented. The input chemical potentials used in GCMC simulations are those of the diatomic molecule in the binary mixtures presented in table 2 (by adding the ideal term to the residual part). Again, it is clear that, for a given chemical potential, the values of the densities of the diatomic molecule in the binary mixture and in the quenched medium are close. The density of the diatomic molecules is higher in the mixture than in the porous medium. Differences between the mixture and the random porous media are slightly larger than for the M1 system which means that attractive forces increase somewhat the differences between both systems. Nevertheless, these differences are not large.

As mentioned above, the densities considered in this work are low: as density increases and correlations become stronger we expect that the similarity between the binary mixture and the confined system will diminish for the hard body system and for the LJ system.

Additionally, we have performed GCMC simulations where the matrix was an equilibrium configuration of an HD system, but where the fluid–matrix and fluid–fluid interactions were LJ. The results for this case are denoted by M4* in table 5. The reason for performing this calculation is that it is expected that the properties of confined fluid systems with attractive forces will depend on the prequenching conditions of the matrix. Our results show that the values of the density of the

Table 5. Average density of the diatomic molecule in the quenched medium, $\rho^*_{2,\mathrm{quenched}}$, obtained from GCMC simulations for the LJ sphere–LJ diatomic model M4. Model M4* means that the matrix was an equilibrium configuration of HS; nevertheless fm and ff interactions were LJ. The reduced number density of the spherical particles constituting the matrix is $\rho^*_1 = 0.190\,986$. The chemical potential of the diatomic particles used in the GCMC simulations was obtained by adding the ideal contribution to the residual part presented in table 2. The number density of the diatomic molecule, $\rho^*_{2,\mathrm{mixture}}$, in the binary equilibrium mixture with the same chemical potential as the diatomic is presented. Interaction energies of the diatomic molecule in the quenched medium, $U_{2,\mathrm{quenched}}$ and in the binary mixture $U_{2,\mathrm{mixture}}$ as obtained from simulation are shown also.

Model	μ_2/kT	$\rho^*_{2,\mathrm{quenched}}$	$\rho^*_{2,\mathrm{mixture}}$	$U_{2,\mathrm{quenched}}/(N_2\epsilon)$	$U_{2,\mathrm{mixture}}/(N_2\epsilon)$
M4	− 2.073	0.0933(14)	0.095 493	− 5.25(6)	− 5.270(3)
M4	− 0.162	0.187(2)	0.190 986	− 6.94(3)	− 6.988(2)
M4*	− 2.073	0.0920(10)	0.095 493	− 5.18(2)	− 5.270(3)
M4*	− 0.162	0.185(2)	0.190 986	− 6.88(2)	− 6.988(2)

diatomics (adsorption isotherm) are not significantly different from the results for model M4; nevertheless, the internal energy appears to be slightly lower than for model M4. Even in this case the adsorption isotherms could be estimated successfully from theories of mixtures.

Let us now analyse the structural results for the LJ potential. In figure 3(*a*) the results for g_{mf} in the mixture and in the random media are presented. Figure 3(*a*) corresponds to the state with the low chemical potential of the diatomic molecule and figure 3(*b*) to the state with the high chemical potential. In figure 4 the g_{ff} functions are presented for both systems (*a*) low and (*b*) high chemical potential. As in the systems of hard bodies we again find that fluid–fluid correlations g_{ff} are the same in the binary mixture and in the porous material, but that the differences between the two systems are larger in the g_{mf} functions. Hence, this study of the M4 system illustrates that conclusions (i)–(iii) also are valid for systems with attractive forces.

It is important to emphasize at this point that the binary mixture and the random porous medium are different systems in a number of ways. The thermodynamic routes to be used in the two systems and the Ornstein–Zernike equations to be solved to determine the structure are different. The message of our results is that even though the two systems are different and cannot be identified, in a number of cases some properties are similar; therefore, one can use the theory of mixtures with success to obtain a good approximation to the properties of the adsorbed system.

There is one particular system where the binary mixture and the random porous material are identical in many respects. This is the system constituted by spheres and points which was denoted as M3 in table 1. For this system it has been shown by graph theory that the structure is identical in both systems [18]. To show further evidence of this we have performed simulations of the sphere–point system. We have considered an equimolar mixture of spheres and points. The volume fraction of the system is $y = 0.25$. First we perform NVT MC simulations of the mixture. The residual chemical potential of the points which can be obtained from the Widom test particle method obviously is $\mu_2^{\mathrm{res}}/kT = -\ln(1-y)$. Using this value of the chemical potential as input, a second GCMC simulation of confined points in a

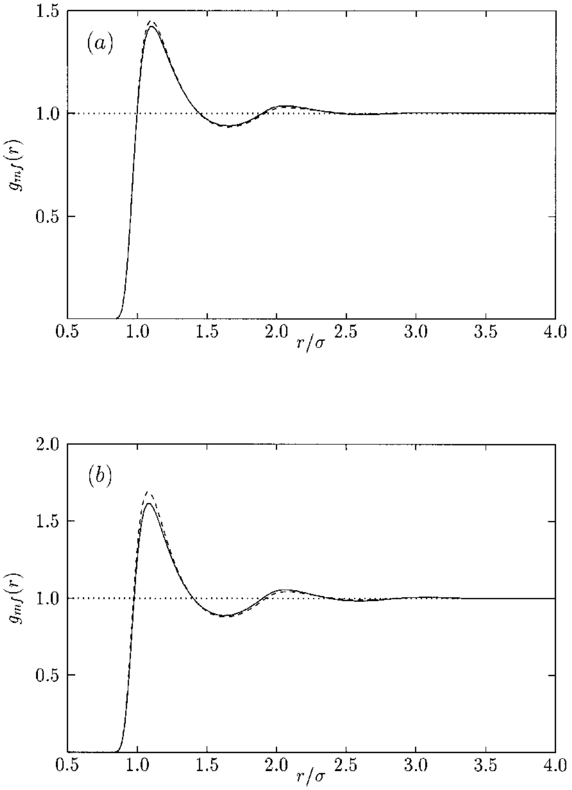

Figure 3. Sphere–site g_{mf} correlation functions for M4 system: solid line, binary mixture; and dashed line, quenched media. Results for (*a*) a low and (*b*) chemical potential of the diatomic molecule (see table 5).

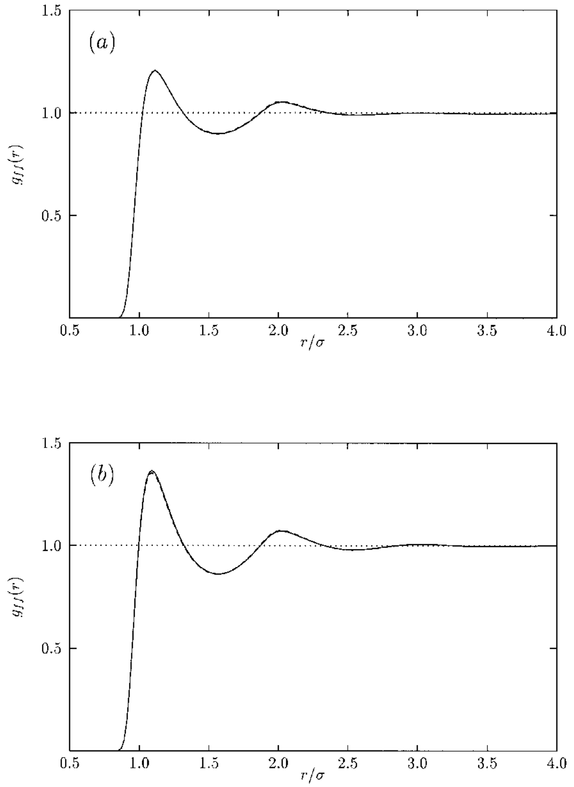

Figure 4. Site–site g_{ff} correlation functions for M4 system: solid line, binary mixture; and dashed line, quenched media. Results for (*a*) a low and (*b*) a high chemical potential of the diatomic molecule (see table 5).

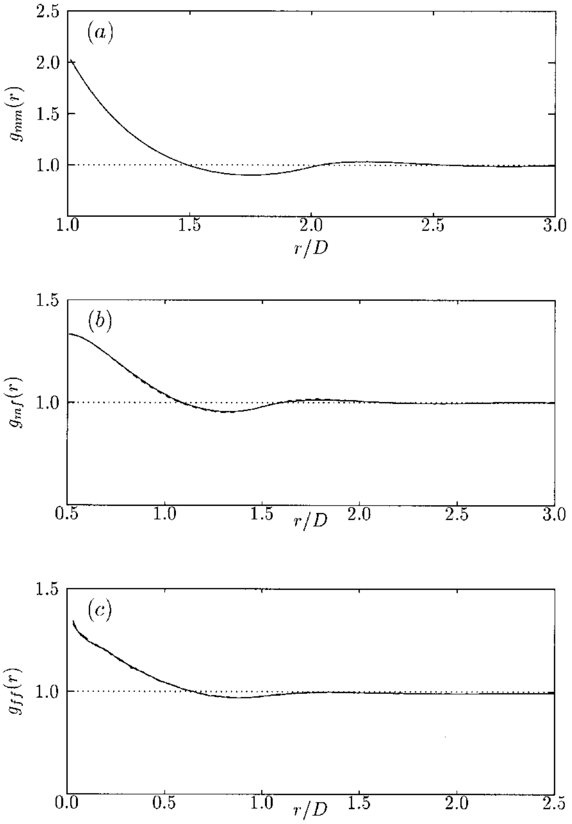

Figure 5. Structure for the M3 model (sphere–point system), volume fraction $y = 0.25$. The system contains the same number of spheres and points. Results of the binary mixture are given by the solid line whereas those of the random media are given by the dashed line: (*a*) matrix–matrix correlation function g_{mm}; (*b*) matrix–fluid correlation function g_{mf}; and (*c*) fluid–fluid correlation function g_{ff}.

matrix of hard spheres was carried out. Figure 5 presents the results for g_{mf}, g_{ff} and g_{mm} in the binary mixture and in the porous media. Obviously, the g_{mm} of the porous media correspond to the radial distribution function of pure hard spheres. As can be seen, the structure in the two systems is identical. The sphere–point case is one example of a system where the identification between mixture and porous media is exact.

Finally, we shall give an example of how the statistical mechanical theory of mixtures can be used successfully to predict adsorption isotherms. Let us consider an M2 model consisting of hard spheres of diameter $D = 7\sigma$ and a diatomic molecule composed of two beads of diameter σ, and let us consider the problem of the adsorption of the diatomic fluid in the random porous medium of spheres. Porous materials have been modelled in the past as randomly distributed spheres [34, 35]. For instance, a few years ago Kaminsky and Monson [35] proposed a simple model for the adsorption of methane in silica gel. Methane molecules were described as spherical particles and the silica gel was modelled as a random configuration of spheres of diameter seven times larger. Therefore an M2 model can be considered as a very naïve approximation to the problem of the adsorption of a linear molecule, as for instance ethane in silica gel [35, 36]. However, our intention was not to study ethane adsorbed in silica gel, since for such a goal a more accurate study of the shape of the intermolecular forces must be carried out. Rather we wish to perform a theoretical approximation to the problem of predicting an adsorption isotherm. To determine the adsorption isotherm one needs to know the chemical potential for a given density of adsorbed molecules. We shall approximate the chemical potential of the diatomic adsorbed molecules in the random porous media from that of the diatomic particle in the binary mixture, and to describe the mixture we shall use BHS theory. We have also performed GCMC simulations of an M2 model. The results from these simulations are presented in table 6, and figure 6 presents the adsorption isotherms for the M2 model as obtained from BHS theory and from GCMC simulations. As can be seen, agreement between theory and simulation is excellent. The complicated problem of getting the adsorption iso-

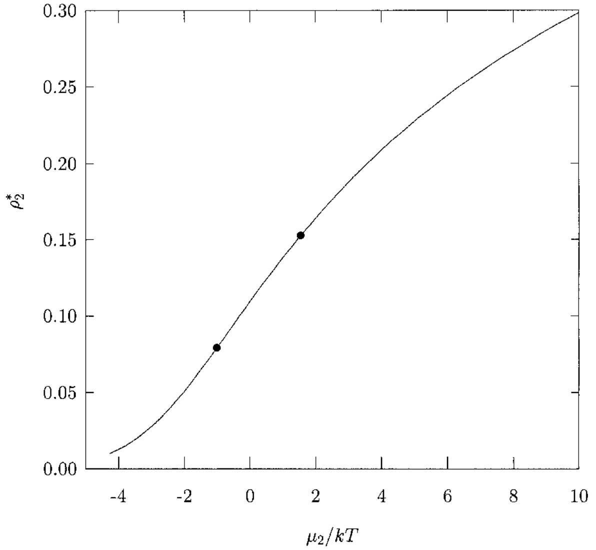

Figure 6. Adsorption isotherm for the M2 model. The number density of spheres of the matrix is $\rho_1^* = 0.000\,556\,8$, which corresponds to a volume fraction of $y = 0.1$. For each value of the chemical potential the average reduced density of the diatomic molecule in the porous material ρ_2^* is given. The solid line is the results from BHS theory, and the symbols are the results for the GCMC simulations.

Table 6. GCMC results for adsorption of diatomic molecules in a matrix of hard spheres (model M2, see table 1): μ is the input chemical potential of the diatomic molecules used in the simulations, ρ_1^* is the reduced number density of matrix molecules, and ρ_2^* is the average reduced density of diatomic molecules as obtained from the simulation results.

Model	μ_2/kT	ρ_1^*	ρ_2^*
M2	- 1.01	0.000 556 8	0.0795(1)
M2	1.54	0.000 556 8	0.1526(6)

therm for a diatomic fluid in a matrix of hard spheres is reduced to the simpler problem of getting the chemical potential from a reliable analytical EOS of the mixture. Figure 6 illustrates the main message of this work: adsorption isotherms can be determined in an approximate way from the EOS of binary mixtures. Finally, figure 7 shows the g_{mf} and g_{ff} functions obtained from GCMC simulations.

5. Conclusions

We have performed computer simulations for mixtures of spherical and diatomic molecules. By using the Widom test particle method, the chemical potential of the diatomic molecule in the mixture was computed. Then, by using this value of the chemical potential as input, GCMC simulations of a confined diatomic fluid in a medium of quenched spheres were performed. The output of these simulations is the average density of diatomic molecules. It was found that fluid–fluid correlation functions (site–site) are quite similar in the binary mixture and in the quenched media. However, larger differences between the two systems were found for the matrix–fluid correlation functions. Thermodynamic properties of the diatomic fluid in the binary mixture and confined in the porous material are quite similar, which suggests that the thermodynamic properties of the fluid in the porous material depend mainly on fluid–fluid correlation functions. Nevertheless, we expect that the similarity mentioned above will diminish as the density increases. All these conclusions are valid both for hard body models and models including attractive forces. Here, we want to stress that the results for systems with attractive forces were obtained for relatively high temperatures in order to avoid the region of coexistence of phases. Since the phase equilibria for mixtures and for confined fluids in disordered porous media are very

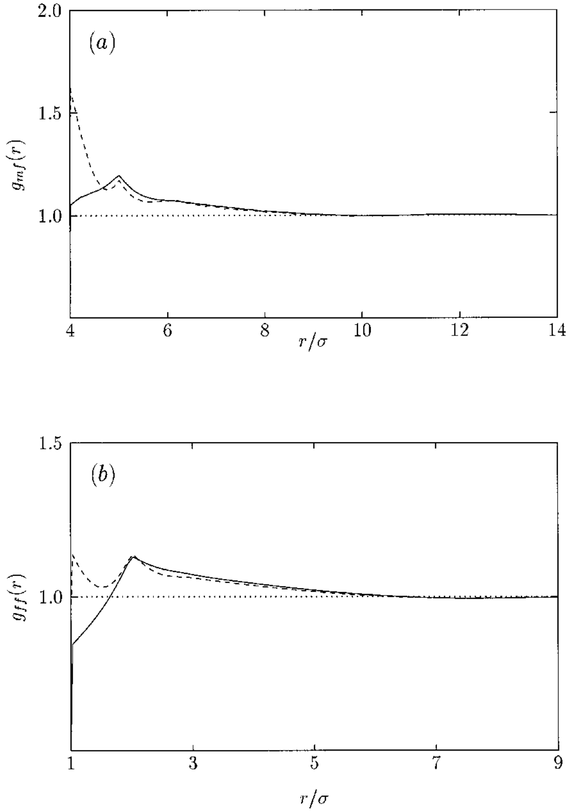

Figure 7. Structural results as obtained from GCMC simulations for the adsorption of a diatomic fluid in a matrix of hard spheres (results correspond to M2 model and the densities are those reported in table 6): solid line, low chemical potential and dashed line, high chemical potential of the diatomic. (a) Results for the matrix–fluid correlations and (b) results for the fluid–fluid correlations.

different, it is in the regions near these phase transitions where one expects that the similarity between a fluid in a mixture and a fluid confined in disordered porous medium will disappear.

The extension of Wertheim's theory of association performed by Jackson *et al.* [21–24], (bonded hard sphere, BHS, theory) provides a fairly good description of the EOS and chemical potential of the hard sphere–hard diatomic particle mixture. This is true for several size ratios between the sphere and the beads which constitute the diatomic molecule. Moreover, our finding concerning the similarity in the thermodynamic properties of the mixture and the fluid confined in a quenched medium allows us to go one step further. We simply assume that the chemical potential of the diatomic molecule in the quenched medium is the same as in the binary mixture. In this way, adsorption isotherms for hard models of diatomic molecules in hard sphere matrices were computed. The agreement with simulation was found to be excellent. The importance of this result is that a complicated problem has been mapped into a simpler one. The diatomic molecule within the porous material can be regarded as the limiting case of infinitely strong association between monomers within a solid material. The case of partial association could be treated on the same basis. We could imagine that the system is a ternary mixture of monomers, dimers and the spherical particles of the matrix. Wertheim's theory of association could be used to obtain the degree of association in this ternary mixture. By identifying the mixture with the random porous material an approximate adsorption isotherm for the associating fluid within the porous material could be obtained.

Again it is important to stress that the mixture and the annealed fluid are different systems. Only in the case of infinite difference in size do the two systems become identical [18]. This was suggested in a previous work and it has been confirmed here by computer simulations of the hard sphere–point mixture. However, this paper plus previous work show that this similarity holds, even when differences in size are small. At this stage we do not have an explanation. Further theoretical work is required, exploring the conditions under which mixtures and fluids confined in quenched media differ significantly. Nevertheless, since it seems that, for many systems, differences are small, one can take advantage of that and use the equilibrium theory of mixtures for determining adsorption isotherms. In this work it has been shown that this approach yields excellent results for the adsorption of diatomic molecules within porous media. In fact with an analytical and simple EOS of the mixture a quite good description of the adsorption isotherm of the diatomic molecules is obtained.

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