

**Adsorption of a diatomic molecular fluid into random porous media**

M. J. Fernaund and E. Lomba

*Instituto de Química Física Rocasolano, CSIC, Serrano 119, E-28006 Madrid, Spain*

J. J. Weis

*Laboratoire de Physique Théorique, UMR 8627, Bâtiment 211, Université de Paris–Sud, 91405 Orsay Cedex, France*

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Structural and thermodynamic properties of a homonuclear hard dumbbell fluid adsorbed into a disordered hard sphere matrix are studied by means of integral equation techniques and computer simulation. In particular, we have rewritten the replica Ornstein-Zernike equations to deal with orientational degrees of freedom and we have solved them in two different approaches: the hypernetted chain equation and a semiempirical extension of Verlet's approximation. We have also derived direct expressions to calculate the chemical potential in these approximations. Comparison with grand canonical Monte Carlo results shows that both theoretical treatments describe adequately the physical behavior of the system, Verlet's approach being, however, clearly superior in accordance with previous findings for equilibrated hard core mixtures.

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**I. INTRODUCTION**

The behavior of a fluid confined in a porous material has been since long a problem of interest both from the theoretical and experimental standpoint. In particular, the phase diagram of confined fluids can present peculiarities due to the effects of the disorder, the finite pore size and pore geometry, and obviously adsorption phenomena will also play a significant role in the physics of these systems. Phase separations, wetting transitions, and the shift in the location of the phase boundaries are key aspects to be considered.

A variety of experiments have been carried out to study these phenomena using different techniques. For instance, the phase transitions in CO<sub>2</sub> confined in Vycor glass [1], or the capillary condensation of N<sub>2</sub> in the same substrate [2] have been successfully studied through positron/positronium annihilation. Recently, adsorbed N<sub>2</sub> has also been used as a probe to determine the pore structure of highly ordered porous materials [3]. The samples of these materials exhibit a narrow pore size distribution, but the determination of the pore geometry and size and the pore wall thickness are remarkably difficult problems. It has been shown that the use of nitrogen as an adsorption probe combined with x-ray diffraction provides relevant information for the structural characterization of these type of materials.

From a statistical mechanical standpoint, the problem posed by the adsorption of a fluid into a disordered matrix, or equivalently a gas inclusion in a quenched random substrate, can be mapped onto that of a general quenched-annealed mixture, a multicomponent system in which one of its constituents has its translational degrees-of-freedom frozen. In this connection, the pioneering work of Madden and Glandt [4] and the theoretically sound reformulation made by Given and Stell [5], set a firm basis from which these problems can be tackled with the standard tools of equilibrium statistical mechanics. Following Given and Stell [5], it is possible to make use of Edward's replica trick [6], and thus transform our non-equilibrium mixture into a fully annealed multicomponent system, in which, together with the matrix particles,

one has  $n$  noninteracting replicas of the fluid. This equivalence is only fulfilled in the limit of vanishing number of replicas, i.e.,  $n \rightarrow 0$ . It is then possible to write down Ornstein-Zernike equations for this new annealed  $(n+1)$ -component system and, once the limit  $n \rightarrow 0$  is taken, a new set of equations denoted by replica Ornstein-Zernike (ROZ) is obtained. Thus, ROZ equations coupled with a variety of closure relations constructed via similar procedures, will describe the correlation functions (and hence the thermodynamics) of our quenched-annealed mixture. Simulations of quenched hard sphere matrices with hard sphere fluids adsorbed [7], have shown that simple approximations like the hypernetted chain (HNC) and Percus-Yevick (PY) equations are already remarkably accurate. Recently, a more sophisticated closure implementing thermodynamic and structural consistencies—zero separation (ZSEP) closure—has also been applied to the same system [8] obtaining more accurate results and minimizing at the same time the inconsistency problems of PY and HNC.

More realistic systems have also been considered using soft potentials. Thus, for instance, through grand canonical simulations a system of repulsive  $n$  alkanes confined in a porous medium was studied by Padilla and Vega [9]. Theoretically, Padilla *et al.* [10] also extended the ROZ equations to associating fluids using Wertheim's statistical associating fluid theory [11] to calculate structural properties and the adsorption isotherm of a dimerizing fluid inside a hard sphere matrix. They solve the associative ROZ equations in the HNC and PY approximations that compare well with grand canonical Monte Carlo (GCMC) simulations. Also phase separations have been studied by means of GCMC simulations by Page and Monson [12] and Alvarez, Levesque, and Weis [13]. A theoretical approach devised by Rosinberg *et al.* [14] was also put to test in this type of problems with relative success.

In this work we introduce an extension of ROZ equations to study the adsorption of a molecular fluid inside a porous medium somewhat different in scope to the treatment of Padilla *et al.* [10]. Here we propose the treatment of the molecular fluid, in this case a homonuclear hard diatomic, using

the standard spherical harmonic expansion. This approach has proved to be extremely successful in describing the structure of linear molecular fluids in the framework of the molecular Ornstein-Zernike equation [15,16]. The extension of the ROZ equations to molecular fluids is conceptually straightforward and its practical implementation using the spherical harmonic technique will be seen to be rather simple. The equations thus developed have been solved with two different closures, the HNC and an appropriate extension of the Verlet's modified (VM) [17,18] approach.

As to thermodynamics, the calculation of the isothermal compressibility is straightforward, and for the chemical potential we have derived direct formulas both in the HNC and in the VM approximations. Other quantities would have to be evaluated using appropriate reformulations of the expressions proposed by Rosinberg and co-workers [14,19], but their explicit calculation is somewhat cumbersome and is not considered here. In this work, a variety of systems with different fluid and matrix densities and two different relative fluid-matrix size ratios have been studied and both structural and thermodynamic results have been compared with extensive GCMC simulation data. Our aim here is to investigate the ability of the molecular version of the ROZ equations to provide an adequate description of the adsorption behavior of a standard model molecular fluid, namely, the diatomic hard dumbbell. It will be shown how this approach furnishes a correct description of the structure and thermodynamics of this type of systems and in particular how the influence of the molecular shape can be elucidated from the results.

The rest of the paper is sketched as follows. In Secs. II–IV, we introduce the ROZ equations for the present instance, the corresponding closure relations and the expressions derived for the calculation of the thermodynamic properties. Finally, in Sec. V, integral equation results are presented and compared with simulation data. The most significant conclusions are also commented upon therein.

## II. THE ROZ EQUATIONS FOR A MOLECULAR FLUID

As mentioned before, we have extended the ROZ equations to the case of a molecular fluid adsorbed into a disordered atomic matrix. Following the replica method guidelines [5], one first considers a completely equilibrated system of  $s+1$  species. Now  $s$  of them are replicated molecular species and the other remaining species is atomic. Then, the Ornstein-Zernike equation for such a system reads

$$\begin{aligned} \gamma^{\alpha\beta}(\mathbf{r}_{12}, \omega_1, \omega_2) &= \sum_{\lambda} \rho_{\lambda} \int c^{\alpha\lambda}(\mathbf{r}_{13}, \omega_1, \omega_3) [\gamma^{\lambda\beta}(\mathbf{r}_{32}, \omega_3, \omega_2) \\ &\quad + c^{\lambda\beta}(\mathbf{r}_{32}, \omega_3, \omega_2)] d\mathbf{r}_3 d\omega_3, \end{aligned} \quad (1)$$

where  $\rho_{\lambda}$  is the number density of species  $\lambda$ , and  $\omega_i$  designates the orientation of particle  $i$ ,  $c^{\alpha\beta}$  is the direct correlation function, and  $\gamma^{\alpha\beta}$  the indirect correlation function defined by  $\gamma^{\alpha\beta} = g^{\alpha\beta} - 1 - c^{\alpha\beta}$ , with  $g^{\alpha\beta}$  being the pair distribution function between particles of type  $\alpha$  and  $\beta$ . Hereafter, we

will label the matrix particles by 0, the fluid particles by 1, and each of its  $s-1$  noninteracting replicas as 2.

To deal with the orientational degrees of freedom of the molecular species, we make the usual spherical harmonic expansion of the correlation functions. One explicitly has

$$f^{00}(\mathbf{r}_{12}) = f^{00}(r_{12}),$$

$$f^{01}(\mathbf{r}_{12}, \omega_2) = \sqrt{4\pi} \sum_{l_2, m} f_0^{01}{}_{l_2 m}(r_{12}) Y_{l_2 m}(\omega_2),$$

$$f^{10}(\mathbf{r}_{12}, \omega_1) = \sqrt{4\pi} \sum_{l_1, m} f_{l_1 0}^{10}(r_{12}) Y_{l_1 m}(\omega_1),$$

$$f^{11}(\mathbf{r}_{12}, \omega_1, \omega_2)$$

$$= 4\pi \sum_{l_1, l_2, m} f_{l_1 l_2}^{11}(r_{12}) Y_{l_1 m}(\omega_1) Y_{l_2 \bar{m}}(\omega_2),$$

$$f^{12}(\mathbf{r}_{12}, \omega_1, \omega_2)$$

$$= 4\pi \sum_{l_1, l_2, m} f_{l_1 l_2}^{12}(r_{12}) Y_{l_1 m}(\omega_1) Y_{l_2 \bar{m}}(\omega_2),$$

where  $f$  is an arbitrary correlation function. As usual, we will express our ROZ equations in Fourier space, denoting the transformed functions by  $\tilde{f}$ . The OZ equation for the equilibrated  $s+1$  mixture after the expansion of the correlation functions and the use of the orthogonality properties of the spherical harmonics, transforms into

$$\begin{aligned} \tilde{\gamma}_{l_1 l_2}^{\alpha\beta}(k) &= (-1)^m \sum_{\lambda} \rho_{\lambda} \sum_{l_3} \tilde{c}_{l_1 l_3}^{\alpha\lambda}(k) [\tilde{\gamma}_{l_3 l_2}^{\lambda\beta}(k) \\ &\quad + \tilde{c}_{l_3 l_2}^{\lambda\beta}(k)]. \end{aligned} \quad (2)$$

This equation can be rewritten in matrix form defining the elements  $[\tilde{\mathbf{F}}_m^{\alpha\beta}]_{l_1 l_2} = \tilde{f}_{l_1 l_2}^{\alpha\beta}$ . Note that Eq. (2) is the general OZ equation for a molecular mixture. Now, once the limit  $s \rightarrow 0$  is taken, one finally gets the ROZ equations for the molecular fluid

$$\tilde{h}^{00} = \tilde{c}^{00} + \rho_0 \tilde{c}^{00} \tilde{h}^{00},$$

$$\tilde{\mathbf{H}}_m^{10} = \tilde{S}^{00} \tilde{\mathbf{G}}_m \tilde{\mathbf{C}}_m^{10},$$

$$\begin{aligned} \tilde{\mathbf{H}}_m^{11} &= \tilde{\mathbf{G}}_m [\tilde{\mathbf{C}}_m^{11} \tilde{\mathbf{G}}_m + (-1)^m \rho_0 \tilde{S}^{00} \tilde{\mathbf{C}}_m^{10} \tilde{\mathbf{C}}_m^{01} \tilde{\mathbf{G}}_m \\ &\quad - (-1)^m \rho_1 \tilde{\mathbf{C}}_m^c \tilde{\mathbf{G}}_m \tilde{\mathbf{C}}_m^c], \end{aligned}$$

$$\tilde{\mathbf{H}}_m^c = \tilde{\mathbf{C}}_m^c + (-1)^m \rho_1 \tilde{\mathbf{G}}_m (\tilde{\mathbf{C}}_m^c)^2, \quad (3)$$

where

$$\tilde{\mathbf{G}}_m = [\mathbf{I} - (-1)^m \rho_1 \tilde{\mathbf{C}}_m^c]^{-1} \quad (4)$$

$$\tilde{S}^{00} = 1 + \rho_0 \tilde{h}^{00} \quad (5)$$

The connected part of the correlation functions is defined by  $f^c = f^{11} - f^{12}$ . Obviously, the matrix-matrix equation is completely decoupled and can be solved independently, while the remaining coupled equations have to be solved simultaneously in conjunction with their corresponding closure relations.

### III. THE CLOSURE RELATION

For the closure relation we have the usual expression

$$\begin{aligned} h^{\alpha\beta}(12) = & \exp[-\beta u^{\alpha\beta}(12) + h^{\alpha\beta}(12) - c^{\alpha\beta}(12) \\ & + b^{\alpha\beta}(12)] - 1, \end{aligned} \quad (6)$$

where  $(12) = (\mathbf{r}_{12}, \omega_1, \omega_2)$ ,  $b^{\alpha\beta}(12)$  is the bridge function, and  $u^{\alpha\beta}(12)$  is the interaction potential between the species  $\alpha$  and  $\beta$ . In our case, we will be dealing with hard sphere matrix species  $u^{00}(r_{12}) = u_{HS}(r_{12})$  and hard diatomic fluid,  $u^{11}(\mathbf{r}_{12}, \omega_1, \omega_2) = \sum_{st} u_{st}^{HS}(r_{12}^{st})$ , where  $st$  denote the sites  $s$  and  $t$  in particles 1 and 2, respectively. Similarly, we will have a fluid-matrix interaction  $u^{10}(\mathbf{r}_{12}, \omega_1) = \sum_s u_s^{HS}(r_{12}^s)$  and following the replica definitions,  $u^{12} = 0$ . Note that the fluid-fluid, fluid-matrix, and replica-replica terms in Eq. (6) have to be expanded in spherical harmonics and consequently one has

$$\begin{aligned} h_{l_1 l_2 m}^{\alpha\beta}(r_{12}) = & \langle \exp[-\beta u^{\alpha\beta}(12) + h^{\alpha\beta}(12) - c^{\alpha\beta}(12) \\ & + b^{\alpha\beta}(12)] | l_1 l_2 m \rangle - \delta_{l_1 l_2 m, 000}, \end{aligned} \quad (7)$$

where we use  $\langle \dots | l_1 l_2 m \rangle$  to denote the projection of the exponential onto the spherical harmonics  $Y_{l_1 m}(\omega_1) Y_{l_2 \bar{m}}(\omega_2)$ . For the bridge function, we have studied two different approximations: HNC, for which  $b^{\alpha\beta}(\mathbf{r}_{12}) = 0 \forall \alpha, \beta$ , and an extension for mixtures of hard spheres of the modified Verlet's approach [20,21] made by Henderson *et al.* [17]. The latter was already used with success by Anta *et al.* [18] for a fully equilibrated mixture of hard spheres and hard dumbbells. The bridge function in this approximation has the form

$$b^{\alpha\beta}(12) = -\frac{1}{2} \frac{\gamma^{\alpha\beta}(12)^2}{1 + \eta^{\alpha\beta} \gamma^{\alpha\beta}(12)}. \quad (8)$$

The set of parameters  $\eta^{\alpha\beta}$  are calculated following Refs. [17,18] so that  $b^{\alpha\beta}(0)$  are exact at low densities. Using an appropriate notation for our system

$$\eta^{\alpha\beta} = a^{\alpha\beta} e^{2\xi} + 0.8 - 0.45\xi \quad (9)$$

and

$$\xi = \frac{\pi}{6} \rho (x_0 d_{00}^3 + x_1 d_{11}^3), \quad (10)$$

$$\begin{aligned} a_{00} = & \frac{3}{4\pi\rho(x_0 d_{00}^3 + x_1 d_{01}^3)} \\ & \times \left[ -\frac{16\pi^2(x_0 d_{00}^3 + x_1 d_{01}^3)^2}{9(x_0^2 C_{000} + 2x_0 x_1 C_{001} + x_1^2 C_{011})} - 1 \right], \\ a_{11} = & \frac{3}{4\pi\rho(x_0 d_{01}^3 + x_1 d_{11}^3)} \\ & \times \left[ -\frac{16\pi^2(x_0 d_{01}^3 + x_1 d_{11}^3)^2}{9(x_0^2 C_{001} + 2x_0 x_1 C_{011} + x_1^2 C_{111})} - 1 \right], \end{aligned} \quad (11)$$

$$a_{01} = a_{ii}$$

where  $i$  designates the species of smallest size. In Eq. (11) also

$$C_{000} = -\frac{5\pi^2}{6} d_{00}^6,$$

$$C_{001} = -\frac{\pi^2}{18} (32d_{01}^3 - 18d_{00}d_{01}^2 + d_{00}^3)d_{00}^3,$$

$$C_{011} = -\frac{\pi^2}{18} (32d_{01}^3 - 18d_{11}d_{01}^2 + d_{11}^3)d_{11}^3,$$

$$C_{111} = -\frac{5\pi^2}{6} d_{11}^6, \quad (12)$$

where  $\rho = \rho_0 + \rho_1$  is the total number density,  $x_0$  and  $x_1$  are the matrix and fluid mole fractions, respectively,  $d_{00}$  is the hard sphere diameter, and  $d_{11}$  is the equivalent sphere diameter of the molecules

$$d_{11}^3 = \frac{1}{2} d_a^3 \left[ (1 + \gamma^3) + \frac{3}{2} L^* (1 + \gamma^2) - L^{*3} + \frac{3}{16} \frac{(1 - \gamma^2)^2}{L^*} \right], \quad (13)$$

and here,  $\gamma = d_b/d_a$ ,  $d_b$  and  $d_a$  being the diameters of the spheres forming the dumbbell, and  $L^* = L/d_a$ ,  $L$  being the elongation of the molecule. For  $d_{01}$  we have assumed additive diameters, i.e.,  $d_{01} = (d_{00} + d_{11})/2$ . The above expres-

sions apply to a binary mixture and consequently account for the matrix-matrix, matrix-fluid, and fluid-fluid correlations. As to the replica-replica bridge function, in Ref. [8] it was found that it is practically negligible. Consequently we have here assumed  $b^{12}=0$ .

#### IV. THERMODYNAMIC PROPERTIES

A full account of the thermodynamics of the quenched-annealed mixtures can be found in the work of Rosinberg *et al.* [14]. Here, we have focused on two thermodynamic properties of the fluid that can be evaluated in a straightforward way in the framework of integral equation theory, namely, the isothermal compressibility and the chemical potential.

##### 1. Isothermal compressibility

The isothermal compressibility of a fluid inside a matrix is given by the expression

$$\beta \left. \frac{\partial P_1}{\partial \rho_1} \right|_T = 1 - \rho_1 \int d\mathbf{r} d\omega_1 d\omega_2 c^c(\mathbf{r}, \omega_1, \omega_2), \quad (14)$$

where  $c^c(\mathbf{r}) = c^{11}(\mathbf{r}) - c^{12}(\mathbf{r})$  is the connected part of the fluid-fluid direct correlation function. In the case of the molecular fluid, integration over the orientational degrees of freedom leads to

$$\beta \left. \frac{\partial P_1}{\partial \rho_1} \right|_T = 1 - 4\pi\rho_1 \int dr r^2 c_{000}^c(r). \quad (15)$$

##### 2. Chemical potential

Following Lee's star function method [22], we have developed a direct expression to calculate the chemical potential of the fluid that bypasses cumbersome thermodynamic integrations. It can be shown that the excess chemical potential of component 1 of a molecular mixture is given by [23],

$$\begin{aligned} \beta\mu_1' = & \sum_{\nu} \rho_{\nu} \int d\mathbf{r} d\omega_1 d\omega_2 \left[ \gamma^{1\nu}(\mathbf{r}, \omega_1, \omega_2) + b^{1\nu}(\mathbf{r}, \omega_1, \omega_2) \right. \\ & - h^{1\nu}(\mathbf{r}, \omega_1, \omega_2) + \frac{1}{2} h^{1\nu}(\mathbf{r}, \omega_1, \omega_2) \gamma^{1\nu}(\mathbf{r}, \omega_1, \omega_2) \\ & \left. + h^{1\nu}(\mathbf{r}, \omega_1, \omega_2) b^{1\nu}(\mathbf{r}, \omega_1, \omega_2) \right] - S_{1\nu}^*, \end{aligned} \quad (16)$$

where the star series  $S^*$  is given by [22]

$$S_{1\nu}^* = \rho_1 \int d\mathbf{r} \frac{h^{1\nu}(\mathbf{r}, \omega_1, \omega_2)}{\gamma^{1\nu}(\mathbf{r}, \omega_1, \omega_2)} \int_0^{\gamma^{1\nu}} d\gamma' b^{1\nu}(\mathbf{r}, \omega_1, \omega_2; \gamma'^{1\nu}). \quad (17)$$

Following again the steps of the replica method, we first consider an equilibrated  $s+1$  mixture and then take the limit  $s \rightarrow 0$  to obtain the expression for the partially quenched system. After expanding the correlation functions in a spherical harmonic basis, the final expression reads

$$\begin{aligned} \beta\mu_1' = & \rho_0 \left[ -\tilde{c}_{000}^{10}(0) + \frac{1}{2} \int d\mathbf{r} \sum_{l_1} h_{l_1 00}^{10} \gamma_{l_1 00}^{10} + \frac{1}{4\pi} \int d\mathbf{r} d\omega_1 b^{10}(\mathbf{r}, \omega_1) [h^{10}(\mathbf{r}, \omega_1) + 1] - \frac{1}{4\pi} \int d\mathbf{r} d\omega_1 \frac{h^{10}(\mathbf{r}, \omega_1)}{\gamma^{10}(\mathbf{r}, \omega_1)} \right. \\ & \times \left. \int_0^{\gamma^{10}} d\gamma' b^{10}(\mathbf{r}, \omega_1; \gamma'^{10}) \right] + \rho_1 \left[ -\tilde{c}_{000}^{11}(0) + \frac{1}{2} \int d\mathbf{r} \sum_{l_1 l_2 m} h_{l_1 l_2 m}^{11} \gamma_{l_1 l_2 m}^{11} + \frac{1}{(4\pi)^2} \int d\mathbf{r} d\omega_1 d\omega_2 b^{11}(\mathbf{r}, \omega_1, \omega_2) \right. \\ & \times \left. [h^{11}(\mathbf{r}, \omega_1, \omega_2) + 1] - \frac{1}{(4\pi)^2} \int d\mathbf{r} d\omega_1 d\omega_2 \frac{h^{11}(\mathbf{r}, \omega_1, \omega_2)}{\gamma^{11}(\mathbf{r}, \omega_1, \omega_2)} \int_0^{\gamma^{11}} d\gamma' b^{11}(\mathbf{r}, \omega_1, \omega_2; \gamma'^{11}) \right] - \rho_1 \left[ -\tilde{c}_{000}^{12}(0) + \frac{1}{2} \int d\mathbf{r} \right. \\ & \times \sum_{l_1 l_2 m} h_{l_1 l_2 m}^{12} \gamma_{l_1 l_2 m}^{12} + \frac{1}{(4\pi)^2} \int d\mathbf{r} d\omega_1 d\omega_2 b^{12}(\mathbf{r}, \omega_1, \omega_2) [h^{12}(\mathbf{r}, \omega_1, \omega_2) + 1] - \frac{1}{(4\pi)^2} \int d\mathbf{r} d\omega_1 d\omega_2 \\ & \times \left. \frac{h^{12}(\mathbf{r}, \omega_1, \omega_2)}{\gamma^{12}(\mathbf{r}, \omega_1, \omega_2)} \int_0^{\gamma^{12}} d\gamma' b^{12}(\mathbf{r}, \omega_1, \omega_2; \gamma'^{12}) \right], \end{aligned} \quad (18)$$

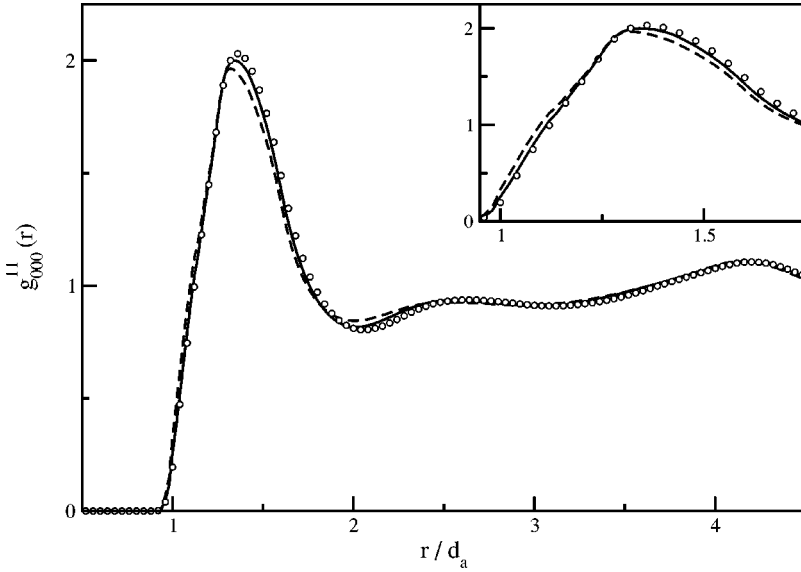


FIG. 1. Center-to-center fluid-fluid correlation functions with size ratio,  $d_{00}/d_a=3$  and densities  $\rho_0 d_a^3=0.0275$  and  $\rho_1 d_a^3=0.1605$ . Simulation results are denoted by circles, and integral equation data are represented by solid (VM) and dashed (HNC) curves.

where we have taken into account that  $\rho_2=\rho_1$ . This general expression is now to be written for the particular approximation used for the bridge function. Thus, when HNC is used, since the bridge function vanishes for all the interactions, the excess chemical potential expression is reduced to

$$\begin{aligned} \beta\mu'_1 = & \rho_0 \left[ -\tilde{c}_{000}^{10}(0) + \frac{1}{2} \int d\mathbf{r} \sum_{l_1} h_{l_1 00}^{10} \gamma_{l_1 00}^{10} \right] \\ & + \rho_1 \left[ -\tilde{c}_{000}^{11}(0) + \frac{1}{2} \int d\mathbf{r} \sum_{l_1 l_2 m} h_{l_1 l_2 m}^{11} \gamma_{l_1 l_2 m}^{11} \right] \\ & - \rho_1 \left[ -\tilde{c}_{000}^{12}(0) + \frac{1}{2} \int d\mathbf{r} \sum_{l_1 l_2 m} h_{l_1 l_2 m}^{12} \gamma_{l_1 l_2 m}^{12} \right]. \end{aligned} \quad (19)$$

In the VM approximation, the functional integration over  $\gamma$  can be explicitly performed to give

$$\begin{aligned} & \int_0^{\gamma^{\alpha\beta}} d\gamma' \alpha^{\beta} b[\gamma'^{\alpha\beta}; \mathbf{r}] \\ & = -\frac{1}{4(\eta^{\alpha\beta})^3} [(1 + \eta^{\alpha\beta} \gamma^{\alpha\beta})^2 - 4(1 + \eta^{\alpha\beta} \gamma^{\alpha\beta}) \\ & \quad + 2 \log(1 + \eta^{\alpha\beta} \gamma^{\alpha\beta}) + 3]. \end{aligned} \quad (20)$$

Additionally, the last two terms in Eq. (18) are to be dropped when the replica-replica bridge function,  $b^{12}$ , is neglected.

From a numerical standpoint, one has to recall that in Eq. (18)  $\gamma^{\alpha\beta}(\mathbf{r}_{12}, \omega_1, \omega_2)$  and  $h^{\alpha\beta}(\mathbf{r}_{12}, \omega_1, \omega_2)$  have to be reconstructed from the spherical harmonic expansion. Whereas the  $\gamma^{\alpha\beta}(\mathbf{r}_{12}, \omega_1, \omega_2)$  expansion is rapidly convergent,  $h^{\alpha\beta}(\mathbf{r}_{12}, \omega_1, \omega_2)$  must be evaluated from the closure expres-

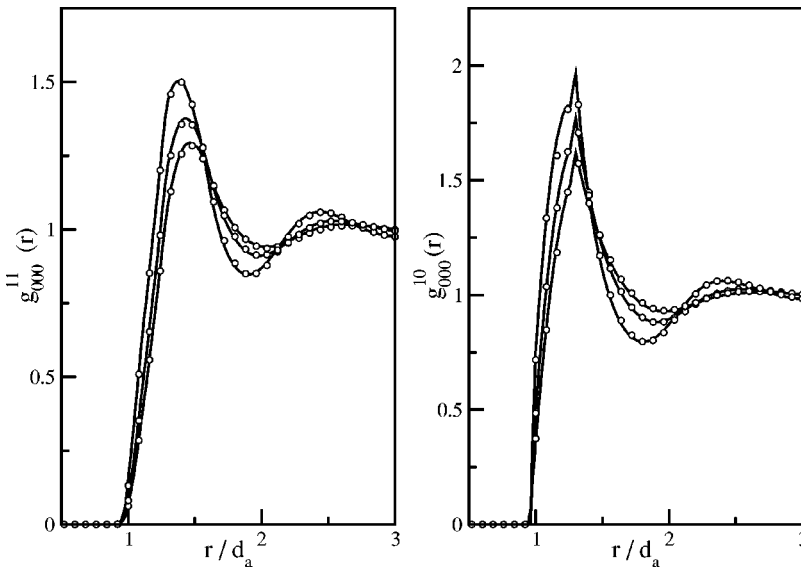


FIG. 2. Center-to-center fluid-fluid (left) and fluid-matrix (right) correlation functions for a fixed matrix density  $\rho_0 d_a^3=0.2$  and three increasing fluid densities,  $\rho_1 d_a^3=0.1289, 0.1847, 0.2696$ . The size ratio here is 1. Solid curves represent the VM solutions, and the circles stand for the simulation data.

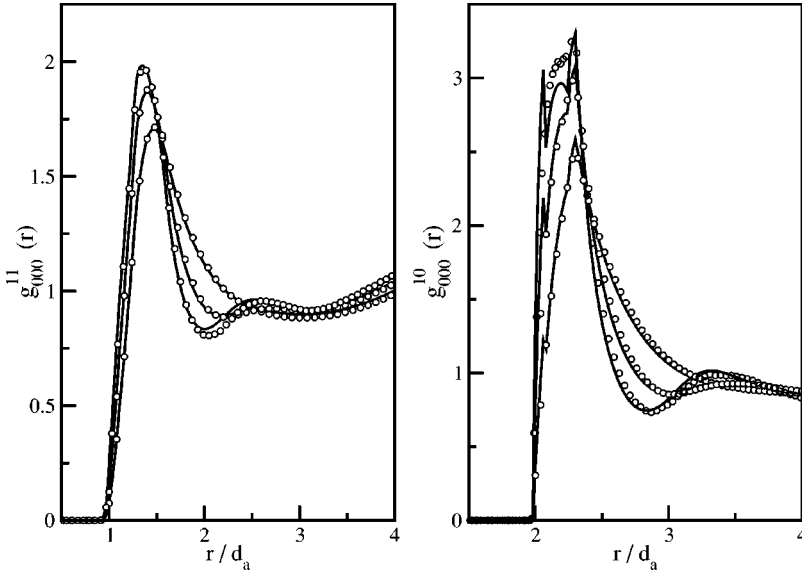


FIG. 3. Center-to-center fluid-fluid (left) and fluid-matrix (right) correlation functions for a fixed matrix density  $\rho_0 d_a^3 = 0.025$  and three increasing fluid densities,  $\rho_1 d_a^3 = 0.0478, 0.1276, 0.1824$ . The size ratio here is 3. Labels as in Fig. 2.

sions (6) and (8). Finally, the full chemical potential,  $\beta\mu_1$  is given by

$$\beta\mu_1 = \log \rho_1 + \beta\mu'_1. \quad (21)$$

## V. RESULTS AND CONCLUSIONS

The ROZ equations have been solved with the standard procedure devised by Lado [15], with  $r$  space discretized into 1024 points and a grid size of  $\Delta r = 0.02d_a$ . The expansions have been truncated at the coefficients  $f_{444}$ . A variety of fluid, matrix densities, and two different size ratios ( $d_{00}/d_a = 1$  and  $d_{00}/d_a = 3$ ) have been studied in the HNC. VM approximations and these results are compared with our GCMC simulation results. The elongation of the fluid particles has been set to  $L = 0.6d_a$ , a value characteristic of molecules like  $\text{Cl}_2$  and  $\text{Br}_2$ .

Typically a simulation run starts by selecting randomly a configuration of the matrix generated in a canonical en-

semble simulation of a hard sphere system at density  $\rho_0$  in a cube of volume  $V$  with periodic boundary conditions. The equilibrium state of the fluid at chemical potential  $\mu$  and fixed matrix configuration is then obtained via GCMC simulation [24] with the three types of trial moves were performed (displacement, creation or deletion) randomly with equal probability. Average over disorder involved between 4 and 15 matrix configurations depends on the thermodynamic state. For each matrix configuration about  $12 \times 10^6$  trial moves were performed after equilibration. The volume of the simulation box was  $V = 1000d_a^3$  for the size ratio  $d_{00}/d_a = 1$  and  $3200d_a^3$  ( $\rho_0 d_a^3 = 0.025$ ) or  $2909d_a^3$  ( $\rho_0 d_a^3 = 0.0275$ ) for size ratio 3.

In Fig. 1 we show the center-to-center correlation function (i.e.,  $g_{000}^{\alpha\beta}$ ) for the fluid-fluid correlation in the two approximations together with simulation data. This case corresponds to  $d_{00}/d_a = 3$ ,  $\rho_0 d_a^3 = 0.0275$ , and  $\rho_1 d_a^3 = 0.1605$ , a state point where the differences between both approxima-

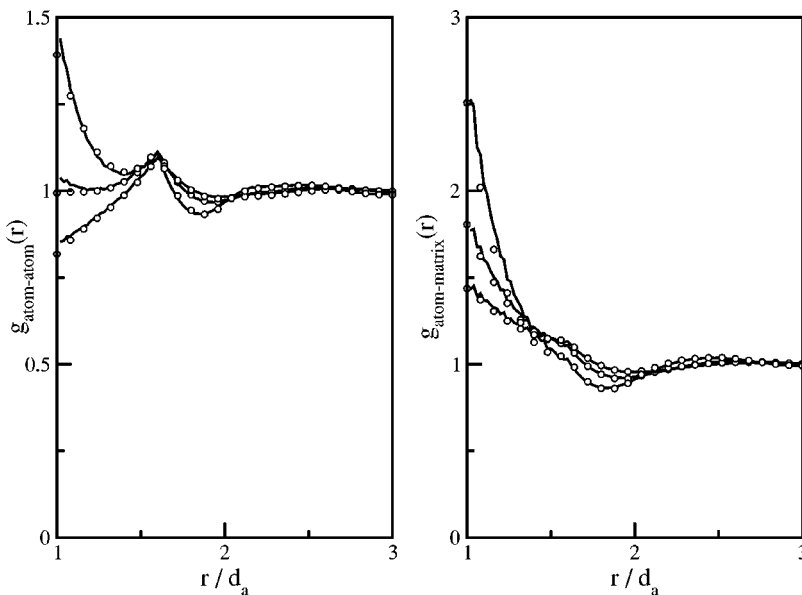


FIG. 4. Atom-atom (left) and atom-matrix (right) distribution functions for the same matrix and fluid densities as in Fig. 2. Labels as in Fig. 2.

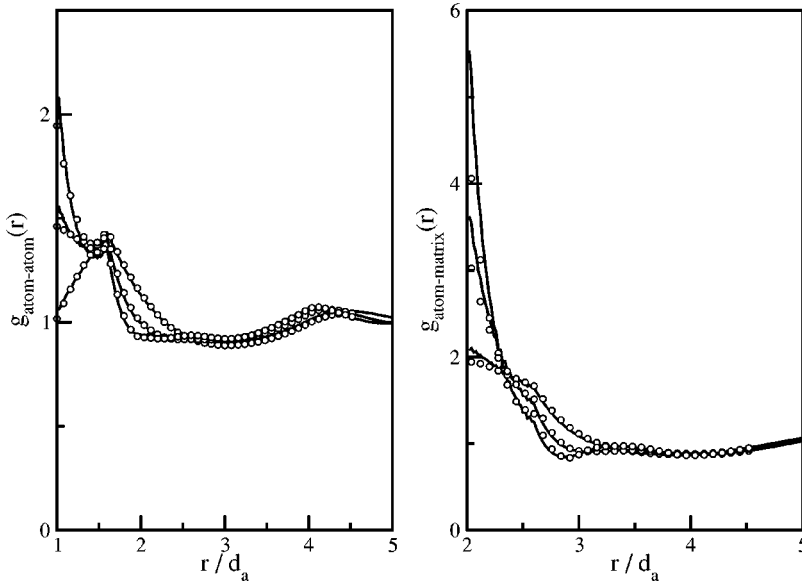


FIG. 5. Atom-atom (left) and atom-matrix (right) distribution functions for the same matrix and fluid densities as in Fig. 3. Labels as in Fig. 2.

tions are more significant. In all cases, the VM improves upon the HNC, specially as to the height of the first peak and the shift in the phase of the correlation function, which are well known to be poorly accounted for in the HNC approximation. In what follows we will present the structural properties only in the VM approach, since differences with the HNC are less appreciable.

In Figs. 2 and 3 we again depict the center-to-center distribution function, now for the fluid-fluid and fluid-matrix interactions for increasing fluid density and a fixed matrix density.

Figure 2 corresponds to the size ratio  $d_{00}/d_a=1$ ,  $\rho_0 d_a^3=0.2$ , and  $\rho_1 d_a^3=0.1289, 0.1847, 0.2696$  and, Fig. 3,  $d_{00}/d_a=3$ ,  $\rho_0 d_a^3=0.025$ , and  $\rho_1 d_a^3=0.0478, 0.1276, 0.1824$ . The VM approximation proves to be remarkably accurate, specially for the fluid-fluid correlations. The fluid-matrix distribution functions present some peculiarities for the largest size ratio. As can be seen in Fig. 3, the first coordination shell splits into two sharp peaks. This splitting increases as

the fluid density is augmented. In the simulation results there seems to be only a hint of this splitting that is perhaps over-emphasized by the integral equation.

In Figs. 4 and 5 we show results for the site-site correlation functions for the same cases as before. These functions are calculated from the molecular pair distribution functions by means of [25]

$$g_{\alpha\beta}^{\gamma\delta}(r) = \frac{1}{(4\pi)^2} \int \int \int d\mathbf{R}_{12} d\omega_1 d\omega_2 \exp[-\beta u^{\gamma\delta}(1,2) + h^{\gamma\delta}(12) - c^{\gamma\delta}(12) + b^{\gamma\delta}(12)] \delta(\mathbf{R}_{12} + \mathbf{l}_{2\beta}(\omega_2) - \mathbf{l}_{1\alpha}(\omega_1) - \mathbf{r}), \quad (22)$$

where  $\alpha$  and  $\beta$  are the atomic sites and  $\gamma$  and  $\delta$  designate the species. Also  $\mathbf{l}_{i\alpha}$  defines the location of the  $\alpha$  site in particle  $i$  and  $\mathbf{R}_{12}$ , is the center-to-center vector between the particles. In the figures, we denote these functions by  $g_{atom-atom}$

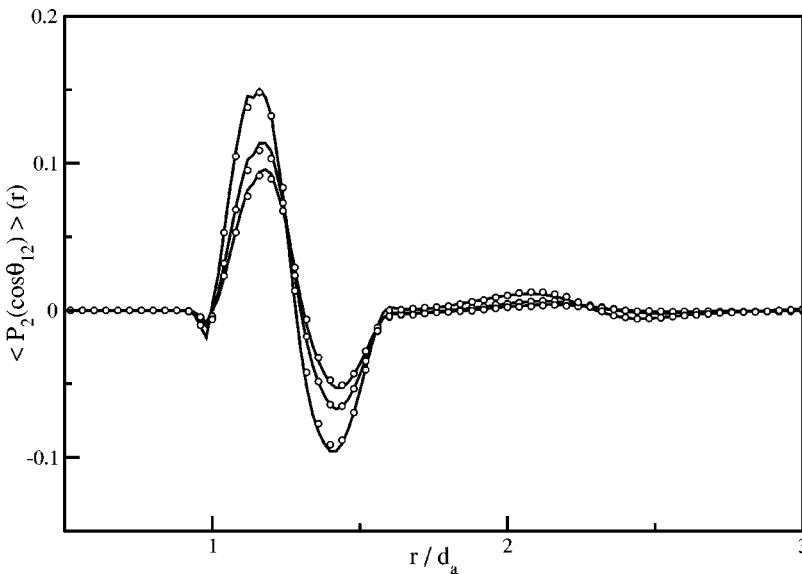


FIG. 6. Radial dependence of the orientational order function. Here,  $\rho_0 d_a^3=0.2$  and the three increasing fluid densities are  $\rho_1 d_a^3=0.1289, 0.1847, 0.2696$  with size ratio  $d_{00}/d_a=1$ . Labels as in Fig. 2.

TABLE I. Isothermal compressibility and chemical potential for HNC and VM approximations vs GCMC simulations for a hard dumbbell fluid adsorbed in a hard sphere disordered matrix. The size ratio here is  $d_{00}/d_a=1$ . Fluid densities result from the GCMC calculation and are used as input data in the theory.

$\rho_0 d_a^3$	$\rho_1 d_a^3$	$\beta \partial P_1 / \partial \rho_1$ (HNC)	$\beta \partial P_1 / \partial \rho_1$ (VM)	$\beta \mu$ (GCMC)	$\beta \mu$ (HNC)	$\beta \mu$ (VM)
0.05	0.0549±0.0001	1.641	1.651	-2	-1.992	-2.001
0.05	0.0923±0.0001	2.237	2.272	-1	-0.974	-1.002
0.05	0.1337±0.0002	3.087	3.192	0	0.066	0.001
0.05	0.1543±0.0002	3.600	3.762	0.5	0.598	0.505
0.05	0.1742±0.0001	4.164	4.400	1	1.138	1.010
0.05	0.2112±0.0001	5.423	5.857	2	2.243	2.023
0.05	0.2741±0.0002	8.374	9.413	4	4.562	4.092
0.05	0.3233±0.0004	11.694	13.562	6	6.965	6.180
0.05	0.3627±0.0004	15.285	18.145	8	9.451	8.284
0.10	0.0421±0.0002	1.537	1.547	-2	-1.978	-1.995
0.10	0.0737±0.0001	2.049	2.083	-1	-0.961	-0.997
0.10	0.1299±0.0002	3.267	3.405	0.5	0.620	0.513
0.10	0.1839±0.0003	4.935	5.310	2	2.267	2.040
0.10	0.2448±0.0002	7.667	8.577	4	4.577	4.108
0.10	0.2928±0.0002	10.758	12.398	6	6.962	6.181
0.10	0.3320±0.0002	14.164	16.652	8	9.461	8.281
0.20	0.0211±0.0002	1.343	1.354	-2	-1.957	-2.010
0.20	0.0411±0.0003	1.695	1.723	-1	-0.927	-1.004
0.20	0.0682±0.0002	2.246	2.314	0	0.126	0.005
0.20	0.1289±0.0003	3.913	4.175	2	2.297	2.031
0.20	0.1847±0.0003	6.181	6.836	4	4.594	4.100
0.20	0.2312±0.0004	8.863	10.087	6	6.998	6.197
0.20	0.2696±0.0006	11.827	13.811	8	9.475	8.346
0.30	0.078±0.001	2.932	3.104	2	2.383	2.032
0.30	0.168±0.001	6.859	7.690	6	7.042	6.170

when  $\alpha$  and  $\beta$  belong to dumbbells, and  $g_{atom-matrix}$  when  $\alpha$  belongs to a dumbbell and  $\beta$  to a matrix particle.

Again the VM approximation is remarkably accurate for most cases. Only for the highest fluid densities, deviations with respect to the simulation become significant (see Fig. 5).

In Fig. 6, we present, again for three different fluid densities and a fixed matrix density, the radial dependence of the orientational order function,

$$\langle P_2(\cos \theta_{12}) \rangle(r) = \frac{1}{(4\pi)^2} \int d\mathbf{r}_{12} d\omega_1 d\omega_2 \times g(\mathbf{r}_{12}, \omega_1, \omega_2) P_2(\cos \theta_{12}), \quad (23)$$

which can be expressed in terms of the spherical harmonic coefficients as

TABLE II. Isothermal compressibility and chemical potential for HNC and VM approximations and GCMC simulation of a hard dumbbell fluid adsorbed in a hard sphere matrix. The size ratio here is  $d_{00}/d_a=3$ . Fluid densities result from the GCMC calculation and are used as input data in the theory.

$\rho_0 d_a^3$	$\rho_1 d_a^3$	$\beta \partial P_1 / \partial \rho_1$ (HNC)	$\beta \partial P_1 / \partial \rho_1$ (VM)	$\beta \mu$ (GCMC)	$\beta \mu$ (HNC)	$\beta \mu$ (VM)
0.025	0.0478±0.0001	2.160	2.477	0	0.476	0.082
0.025	0.0895±0.0002	3.525	4.223	2	2.849	2.231
0.025	0.1276±0.0002	5.325	6.559	4	5.380	4.435
0.025	0.1594±0.0002	7.431	9.289	6	8.035	6.672
0.025	0.1824±0.0006	9.431	11.911	8	10.405	8.657
0.0275	0.0381±0.0002	2.013	2.332	0	0.605	0.105
0.0275	0.0750±0.0002	3.219	3.943	2	3.002	2.267
0.0275	0.1098±0.0002	4.877	6.092	4	5.556	4.480
0.0275	0.1391±0.0002	6.781	8.598	6	8.197	6.715
0.0275	0.1605±0.0004	8.581	10.987	8	10.527	8.674



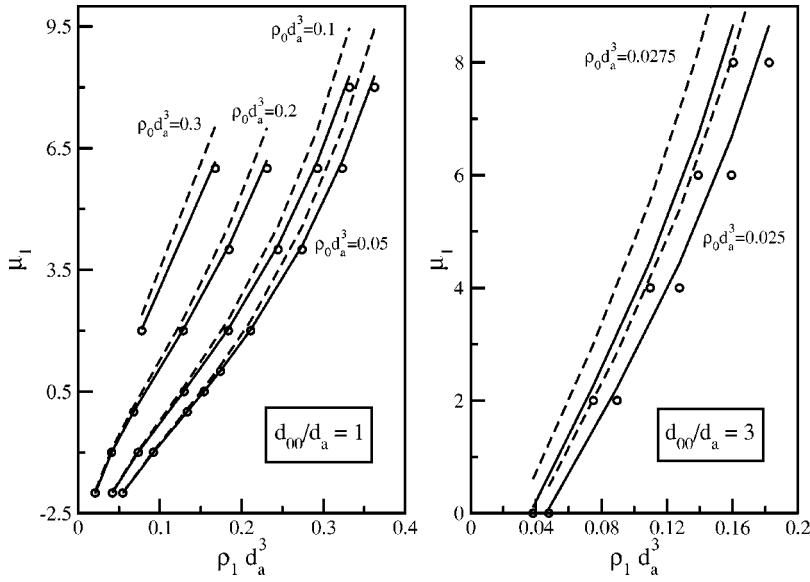


FIG. 7. Fluid chemical potential vs density for various matrix densities and size ratios. Circles correspond to GCMC data, and dashed and solid curves to HNC and VM integral equation data. Note the big discrepancies of the HNC results for the largest size ratio.

$$\begin{aligned} \langle P_2(\cos \theta_{12}) \rangle(r) &= \left\langle \frac{1}{2} (3 \cos^2 \theta_{12} - 1) \right\rangle \\ &= \frac{1}{5} [g_{220}(r_{12}) - 2g_{221}(r_{12}) + 2g_{222}(r_{12})]. \end{aligned} \quad (24)$$

As regards thermodynamics, in Tables I and II we present our results for the isothermal compressibility and chemical potential. This latter quantity is also plotted in Fig. 7, and compared with the GCMC simulation data, for which the chemical potential is an input value. Here, the improvement of the VM with respect to the HNC is much more significant than in the structural properties. The HNC approximation seems to always overestimate the chemical potential whereas the VM performs rather well for all the density range. Finally we have analyzed the effect of the

molecular shape on the adsorption isotherms. This can be seen in Fig. 8(a) where we have plotted  $\mu_1$  vs  $\rho_1 d_a^3$  for various elongations ranging from plain hard spheres to  $L = d_a$ . Simulation results are only presented for hard spheres and for  $L = 0.6d_a$ . One immediately sees that there is a considerable rise in the chemical potential as the elongation increases. To some extent this can be attributed to a simple volume effect, since the work required to insert a particle in the sample augments as the volume of the particle is increased. In order to separate more clearly volume and shape effects in Fig. 8(b) we have plotted  $\mu_1$  vs  $\rho_1 d_{11}^3$ , where  $d_{11}$  is the equivalent diameter defined in Eq. (13). Thus the quantity  $\rho_1 d_{11}^3$  is proportional to the fraction of volume occupied by the fluid particles. Again we see that the chemical potential grows as the elongation is increased (although to a lesser extent than when the plain number density is used in the abscissae). Obviously this is due to the fact that the ex-

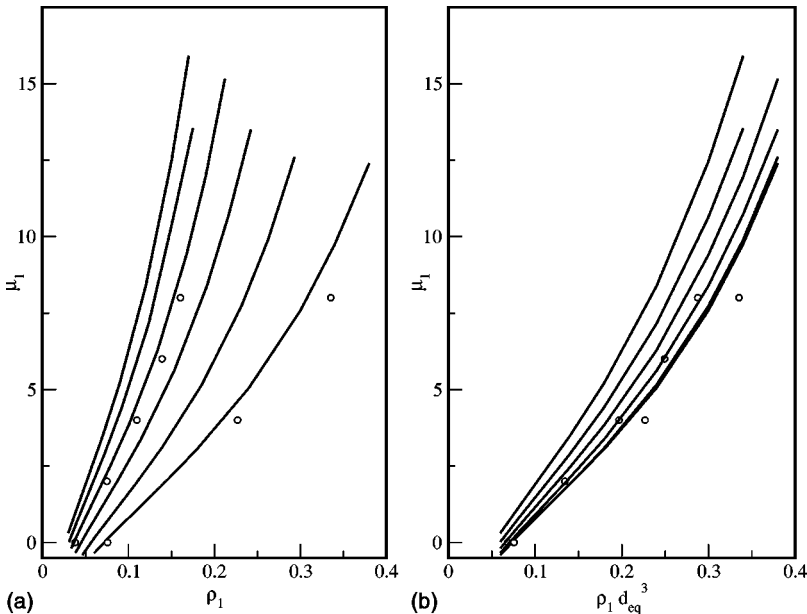


FIG. 8. (a) Fluid chemical potential vs density for elongations  $L/d_a = 0, 0.2, 0.4, 0.6, 0.8, 1.0$  (from bottom to top),  $\rho_0 d_a^3 = 0.0275$  and  $d_{00}/d_a = 3$ , calculated in the VM approximation (solid lines) and GCMC simulation (circles). (b) Same as (a) but the abscissas represent the density in terms of the diameter of the equivalent sphere, i.e., is proportional to the net fraction of volume occupied by the fluid.

cluded volume of a hard dumbbell is somewhat larger than the excluded volume of the equivalent sphere, and this is an evident shape effect. It should be mentioned here that in agreement with the findings of Ford, Thompson, and Glandt [26] very similar results are obtained for a fully annealed system. This we have checked performing HNC and VM calculations for equilibrium mixtures of both size ratios, obtaining results hardly distinguishable from those of the quenched systems. When the matrix particles are much bigger than the fluid particles this is a consequence of the similarity of the correlation functions as found in Ref. [27], but even when correlations are different thermodynamic properties remain very similar [26]. This seems to be a general feature in this type of adsorption problems, although the presence of attractive forces tends to make the quenched and annealed systems more dissimilar [28].

In summary, we find here that the extension of the VM approximation that proved successful for mixtures of molecular and atomic fluids, is equally able to provide an accu-

rate description of the behavior of molecular fluids adsorbed in quenched atomic random matrices. Moreover, the fact that direct expressions can be derived for the chemical potential in this approach make it amenable to introduce self-consistent approaches like the one proposed by Fernaud, Lomba, and Lee [8].

Future work will focus on the implementation of self-consistent closures as well as the description of more realistic systems, incorporating Lennard-Jones interactions. In this latter case, one of the most relevant aspect is the gas-liquid transitions, whose location by computer simulation remains a formidable task [12,13] and consequently, an accurate integral equation theory may well prove to be a valid alternative.

#### ACKNOWLEDGMENT

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