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Adsorption of a hard sphere fluid into a quenched matrix of permeable species

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We have studied a model of a hard sphere fluid adsorbed in a quenched matrix of disordered spheres, such that fluid species are able to penetrate into the interior of obstacles. The surface of matrix particles is represented by the Gaussian barrier of the finite height and width. The model has been studied using replica Ornstein-Zernike equations with the Percus-Yevick closure. We have discussed the structure of the system and the adsorption isotherms dependent on the surface permeability, as well as on the matrix density and the diameter of matrix particles.

Keywords: Adsorption; disordered adsorbents; permeability

Hemos estudiado un modelo de esferas duras para un fluído absorbido en una matriz congelada de esferas desordenadas, tal que las especies del fluído son capaces de penetrar en el interior de los obstáculos. La superficie de las partículas de matriz está representada por una barrera de tipo Gaussiana de altura y ancho finitos. El modelo ha sido estudiado usando ecuaciones de Ornstein-Zernike de réplicas con la cerradura de Percus-Yevick. Se ha discutido la estructura del sistema y las isotermas de absorción que dependen de la permeabilidad de la superficie de la matriz, así como de la densidad de la matriz y de los diámetros de las partículas de matriz.

Descriptores:

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1. Introduction

The structural and thermodynamic properties of fluids confined in random porous media are of interest in material science, different branches of chemical physics, and in physics and chemistry of interfaces. There has been much progress in theoretical studies of quenched-annealed systems during recent years. Computer simulations and the extension of a liquid-state integral equations to quenched-annealed fluids have been developed. Experimental studies of partly quenched systems have focused on adsorption in microporous media, on liquid-vapor and liquid-liquid separations. Theoretical research in quenched-annealed continuous systems have been initiated by Madden and Glandt [1, 2]; more recently Given and Stell have constructed exact replica Ornstein-Zernike (ROZ) integral equations [3, 4]. A set of approximations for these equations also has been proposed [4, 5].

Majority of studies performed so far, have been restricted to the description of quenched-annealed models with matrix species modelled as spheres (either impermeable or freely overlapping) [5–9]. In this note, however, we would like to consider a model which involves permeable matrix species that provide rigidly fixed disordered medium for adsorption of fluid particles. Our basic assumption is that the surface of matrix species is permeable, therefore the fluid-matrix interface can be thought as a set of membranes. We do not refer to a particular system proposing a simple model for fluid-matrix interaction. In spite of structural principles similar for many membranes, one of the most salient points to be made about membranes is their remarkable diversity. We choose the fluid-matrix potential as a finite width barrier of finite height located at a certain distance from the center of a matrix particle. The fluid-matrix interaction, together with the effect of confinement determine "encapsulating" efficiency of partially permeable objects.

Our principal focus in this note is to investigate the dependence of the fluid density on the chemical potential, *i.e.* the adsorption isotherm, and the structure of an adsorbed fluid in a microporous, rigidly fixed, medium of particles with permeable cores. We apply the ROZ integral equations for the structural properties and thermodynamics of the system in question. Previously, there have been studies of partitioning of fluids through individual (single), simple and complex, permeable barriers [10–16], but the adsorption into a quenched matrix of permeable particles, *i.e.* into a medium of multiple barriers, has not been explored so far.

In the present work we are considering a hard sphere fluid in a microporous environment corresponding to a disordered matrix of hard spheres at dimensionless density $\rho_m^* =$

$N_m\sigma_m^3/V$, where the diameter of matrix particles is denoted by σ_m. The fluid is considered at density $\rho_f^* = \rho_f\sigma_f^3$. However, without loss of generality, σ_f is picked up as a lenght unit in what follows, *i.e.*, $\sigma_f = 1$ and $\rho_f^* = \rho_f$. We assume Gaussian shape of the repulsive fluid-matrix interaction. This Gaussian finite barrier is characterized by its height $A_{\rm rep}$ and by a halfwidth ω. The barrier is located at $\sigma_m/2$. The fluid-matrix, $U_{fm}(r)/kT$, interaction has been chosen in the form

$$\frac{U_{fm}(r)}{kT} = \begin{cases} 0, & r < \dfrac{\sigma_m}{2-\omega}, \\ \left(\dfrac{A_{\rm rep}}{kT}\right)\left\{\exp\left(-\alpha\omega^2\right) - \exp\left[-\alpha\left(r - \dfrac{\sigma_m}{2}\right)^2\right]\right\}, & \dfrac{\sigma_m}{2} - \omega < r < \dfrac{\sigma_m}{2} + \omega, \\ 0, & r > \dfrac{\sigma_m}{2} + \omega \end{cases} \tag{1}$$

where α is the parameter determining decay of the Gaussian type repulsive potential. In what follows, in order to describe energetic aspects of the interaction between fluid species and each of permeable particles, we introduce the dimensionless temperature, $T^* = kT/A_{\rm rep}$ (k is the Botzmann constant and T denotes temperature). A barrier of infinite height, *i.e.* impermeable, corresponds to $T^* = 0$.

In order to describe matrix structure, we solve common Ornstein-Zernike equation

$$h_{mm} - c_{mm} = \rho_m c_{mm} \otimes h_{mm}, \tag{2}$$

(the r-dependencies here and below have been omitted for the sake of brevity and $\otimes$ denotes convolution) complemented by the Percus-Yevick (PY) closure,

$$c_{mm}(r) = \{\exp\left[-\beta U_{mm}(r)\right] - 1\} \\ [1 + h_{mm}(r) - c_{mm}(r)], \tag{3}$$

where $U_{mm}(r)$ is a hard sphere potential between matrix particles. The pair correlation function of matrix species, $h_{mm}(r)$ and the direct correlation function, $c_{mm}(r)$, become available. The ROZ equations for the fluid-matrix and fluid-fluid correlations are

$$\begin{aligned} h_{fm} - c_{fm} &= \rho_f c_{ff} \otimes h_{fm}, \\ h_{ff} - c_{ff} &= \rho_m c_{fm} \otimes h_{fm} + \rho_f c_{ff} \otimes h_{ff}. \end{aligned} \tag{4}$$

The parameter ρ_m above determines matrix density in units of fluid particles diameter. The ROZ equations have been written in the form consistent with Madden-Glandt (MG) approximation [1–4], *i.e.* the blocking part of the direct correlation function for fluid species has been assumed vanishing. The reason is that in this study we use the PY closure which belongs to a group of closures neglecting blocking term in the function $c_{ff}(r)$. We do not expect that other closures would qualitatively influence our results. The PY approximation, which is successful for hard sphere models in hard sphere matrices, reads

$$\begin{aligned} c_{ff}(r) =& \{\exp\left[-\beta U_{ff}(r)\right] - 1\}\{1 + h_{ff}(r) - c_{ff}(r)\}, \\ c_{fm}(r) =& \{\exp\left[-\beta U_{fm}(r)\right] - 1\} \\ & [1 + h_{fm}(r) - c_{fm}(r)], \end{aligned} \tag{5}$$

where $U_{ff}(r)$ is a hard sphere potential between fluid particles and $U_{fm}(r)$ has been given by Eq. (1). The ROZ Eq. (4), in conjunction with Eq. (5), have been solved numerically by direct iterations.

The structural properties in terms of the pair correlation functions (the fluid-matrix function is of much interest for the model with permeability) do not represent the only issue of this study. The equilibrium between the bulk fluid and adsorbed fluid occurs at constant chemical potential. Therefore, we need to calculate the adsorption isotherms $\rho_f(\beta\mu^f)$.The chemical potential of a fluid adsorbed in a matrix is presented as [6, 8],

$$\beta\mu^f(\rho_f, \rho_m) = \beta\mu^f_{id}(\rho_f) + \beta\mu^f_{ex}(\rho_f, \rho_m), \tag{6}$$

where the ideal gas contribution has been approximated as $\beta\mu^f_{id}(\rho_f) = \ln(\rho_f)$. The excess term is represented as a sum of two contributions

$$\beta\mu^f_{ex}(\rho_f, \rho_m) = \beta\mu^f_{ex}(\rho_f = 0, \rho_m) \\ - \int_0^{\rho_f} d\rho' \int d\mathbf{r}\, c_{ff}(r, \rho'), \tag{7}$$

where $\beta\mu^f_{ex}(\rho_f = 0, \rho_m)$ is the chemical potential of adsorbed fluid species at infinite dilution in a matrix. It corresponds to the second virial coefficient of the fluid-matrix interaction

$$\beta\mu^f_{ex}(\rho_f = 0, \rho_m) = -\rho_m \int d\mathbf{r}\, \{\exp\left[-\beta U_{fm}(r)\right] - 1\}. \tag{8}$$

The second term of Eq. (8) has been calculated by using $c_{ff}(r)$ from the solution of the ROZ equations.

Let us proceed with the description of the results obtained. We consider the models with $\sigma_m = 5$ and at $\sigma_m = 4$. The parameters of Gaussian barriers are taken the following: $\omega = 0.5$, $\alpha = 0.02$. We discuss first the adsorption isotherms for the case of a low density (highly "porous ") matrix, *i.e.* at $\rho_m^* = 0.1$ and a high density matrix (low "porous") at $\rho_m^* = 0.6$ with $\sigma_m = 5$ (Fig. 1). Worth mentioning that the

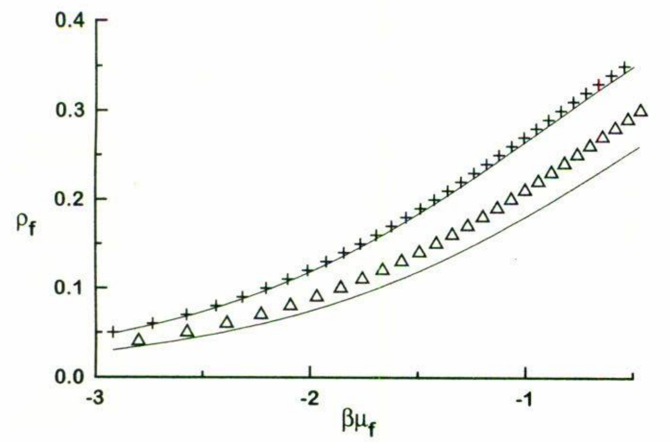
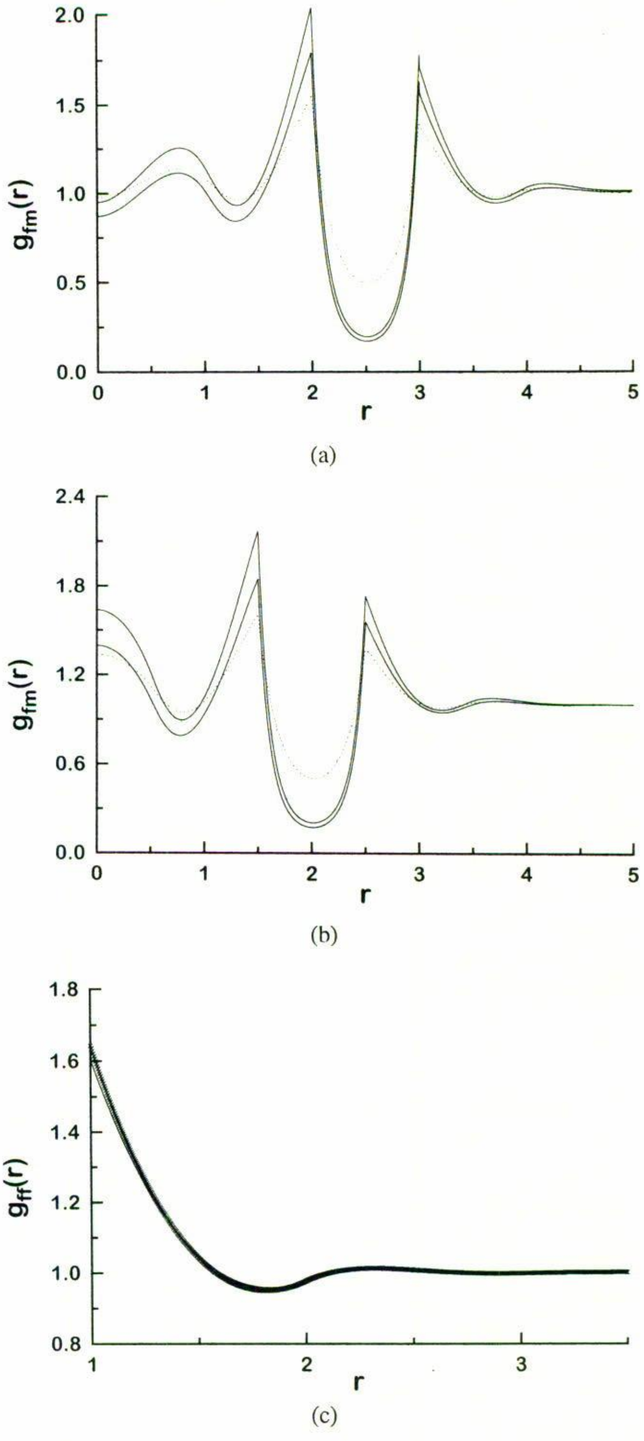


FIGURE 1. The dependencies of the fluid density, ρ_f, in a matrix of permeable disordered spheres on the fluid chemical potential $\beta\mu^f$. The matrix density is $\rho_m\sigma_m^3 = 0.1$ (upper solid line and symbols) and 0.6 (lower solid line and symbols). The solid lines correspond to $T^* = 2 \times 10^{-3}$, whereas the symbols are for $T^* = 4 \times 10^{-3}$. All the set of results is for the model with $\sigma_m = 5$.

term porosity is used in parentheses, because the excluded volume in the system in fact is determined by the repulsive core of the fluid-matrix interaction. In both cases we consider a set of parameters $T^* = 4 \times 10^{-3}$ and $T^* = 2 \times 10^{-3}$. The trends of behavior of the adsorption isotherms are the following. The adsorbed density increases with increasing chemical potential of fluid species. The adsorbed density decreases with increasing density of matrix particles. However, this tendency is much less pronounced than for impermeable hard sphere matrix, due to smaller changes of "excluded" volume with increasing ρ_m^* in the model with permeable cores. Stronger fluid-matrix repulsion (*i.e.* lower T^* or higher A_{rep}) lower adsorbed fluid density. Similar trends have been also observed for smaller matrix particles ($\sigma_m = 4$).

Interesting insight into the structure of adsorbed fluid inside and close to the external surface of matrix species is provided by the fluid-matrix distribution function, $g_{fm}(r)$. This function has not symmetric shape, as one observes for a fluid in contact with a single permeable barrier, see *e.g.* Ref 17. The asymmetry of the distribution function arises due to the confinement of fluid particles in each of permeable cavities and multiplicity of permeable barriers. In Figs. 2a and 2b, we show this function at intermediate fluid density, $\rho_f = 0.35$, for the model with $\sigma_m = 5$ and $\sigma_m = 4$, respectively. The values for $g_{fm}(r)$ at the terminating points of the Gaussian fluid-matrix barrier are different in spite that the barrier is symmetric. Higher value of the $g_{fm}(r)$ at the interior of the barrier is due to the confinement effect. Strong trends for layering of adsorbed fluid in the interior of matrix species are observed both for $\sigma_m = 5$ and $\sigma_m = 4$. The value of the ratio of the diameter of matrix particles w.r.t. the diameter of fluid particles is of importance, dependent on that ratio one can observe augmenting density in the center of the permeable core ($\sigma_m = 4$) or lower density ($\sigma_m = 5$), in comparison to the fluid density outside matrix species. The behavior of the



(a)

(b)

(c)

FIGURE 2. The fluid-matrix pair distribution function, $g_{fm}(r)$, for adsorbed fluid at density $\rho_f = 0.35$ in a disordered matrix ($\sigma_m = 5$) considered at density $\rho_m\sigma_m^3 = 0.6$ (upper solid and dotted lines) and in a matrix with $\rho_m\sigma_m^3 = 0.1$ (lower solid line). The solid lines are for $T^* = 2 \times 10^{-3}$, whereas the dotted line is for $T^* = 4 \times 10^{-3}$ (part a). In part b we show $g_{fm}(r)$ at the same conditions as in part a, however, for the model with $\sigma_m = 4$. In part c the function, $g_{ff}(r)$, for adsorbed fluid at chemical potential $\beta\mu_f = -0.54$ in disordered matrices at density $\rho_m\sigma_m^3 = 0.1$ (symbols) and at 0.6 (solid line) is shown; $\sigma_m = 5$, $T^* = 2 \times 10^{-3}$.

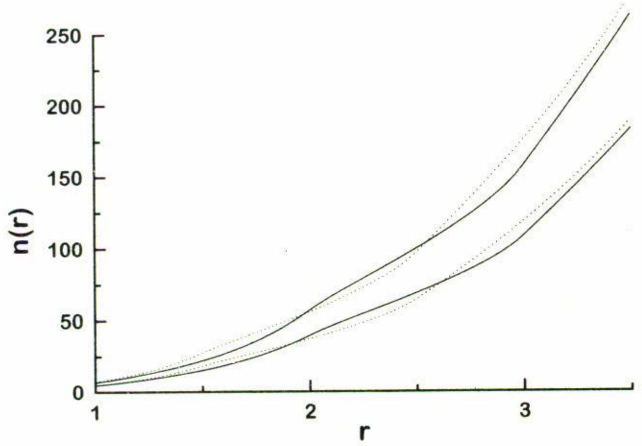


FIGURE 3. The fluid-matrix coordination number, $n_{fm}(r)$ on the distance of a fluid particle from the center of a matrix particle in the matrix at density $\rho_m \sigma_m^3 = 0.6$ (upper curves) and with the density 0.1 (lower curves); $T^* = 2 \times 10^{-3}$. The solid and dotted lines are for the model with $\sigma_m = 5$ and with $\sigma_m = 4$, respectively.

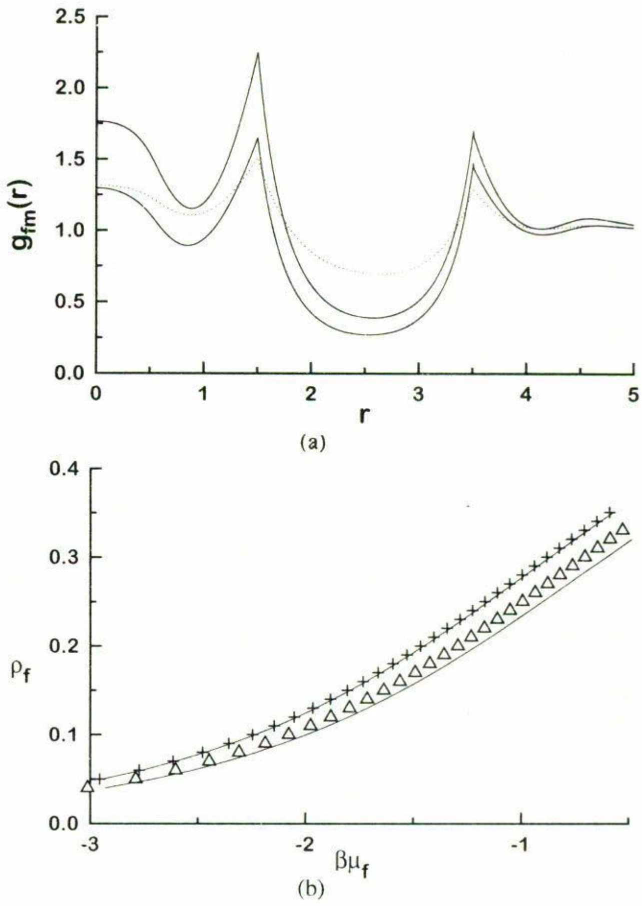
$g_{fm}(r)$ inside the barrier follows the shape of the Boltzmann multiplier, $\exp[-U_{fm}(r)/kT]$. The fluid-fluid pair distribution function is almost uninfluenced by changes of matrix density. We observe in Fig. 2c that very small changes of the contact value occur in a fluid adsorbed at a given chemical potential ($\beta\mu_f \approx -0.54$) in the permeable matrix with quite different density, $\rho_m^* = 0.1$ and $\rho_m^* = 0.6$.

It is of interest to discuss trends of the behavior of the coordination number $n_{fm}(r)$ that gives the average number of fluid particles with respect to the permeable matrix species. The coordination number is defined as

$$n_{fm}(r) = 4\pi\rho_f \int_0^r dR\, R^2 g_{fm}(R), \tag{9}$$

Due to the repulsive barrier, the dependence of the coordination number of fluid particles w.r.t. the matrix center exhibits weak trends for slowing down in the region close to $\sigma_m/2$, Fig. 3. However, due to a stronger confinement in the model with $\sigma_m = 4$, the coordination number at $1 < r < 2$ is larger than in the model with $\sigma_m = 5$. Stronger repulsive barriers would evidently influence stronger the coordination number in the region of the interface between matrix interior and exterior.

Finally, we would like to comment the effect of the width of the repulsive barrier on the surface of matrix species. In the previous studies of partitioning of simple fluids through a single permeable barrier [10–12], it has been shown that for a wide barriers of the order of one or two molecular diameters the fluid density exhibits maximum, *i.e.* the fluid layering occurs in the exterior and the interior of the barrier. We have held fixed the height of the barrier and changed the decay of the Gaussian barrier by changing the parameters α and ω. The effect of confinement on the behavior of the fluid-matrix distribution function, $g_{fm}(r)$ remains well pronounced (Fig. 4a), similar to the case of a narrower barrier (Figs. 2a and 2b). However, we have not observed trends for augmenting density in the central part of the barrier, *i.e.* in the region where the repulsion is the strongest. The explanation of this behavior is due to a smooth decay of repulsion in the model of Gaussian barrier. Strong variation of the fluid-matrix repulsive potential is necessary to provide layering in the interior of the barrier. However, the adsorption isotherms in a model of a wide Gaussian barrier, Fig. 4b, exhibit similar trends to those shown in Fig. 1. We would like to mention that at given matrix density, the adsorption becomes lower if the width of the barrier (volume of action of the fluid-matrix repulsive interaction) increases.



(a)

(b)

FIGURE 4. a) the same as in Fig. 2a but for the model of a wide Gaussian barrier, $\alpha = 0.005$ and $\omega = 1$. b) the same as in Fig. 1 but for the model of a wide barrier. The nomenclature of lines and symbols in parts a and b is like in Fig. 2a and in Fig. 1, respectively.

To conclude, this work considers the problem of adsorption of a simple fluid into a quenched disordered matrix of permeable spheres. The ROZ equations represent out theoretical tools. We have observed that the adsorption in this type of matrices is less dependent on the matrix density, than for the model of impermeable matrix spheres. Higher value of the repulsive barrier lowers slightly the adsorbed density. The effect of confinement of permeable matrix species results in a fluid layering inside matrix species and in different values for $g_{fm}(r)$ on both external surfaces of the barrier.

The considered model is simple. However, it permits several interesting extensions. One of them may be thought in the sophistication of fluid-fluid interaction. If the attractive forces, like in the Lennard-Jones potential, would be included, a study of liquid-vapor transition in fluids adsorbed in disordered microporous media of permeable objects can be attempted. Intuitively one would expect lowering of the critical temperature and shrinking of the coexistence envelope due to the excluded volume effects of matrix species. However, the critical temperature may increase and become closer to the bulk value, if the height of the repulsive fluid-matrix barrier decreases. On the other hand, sophistication of the fluid-matrix interaction may put the system in question closer to the modelling of less idealized, see *e.g.* Ref. 15, 16, and probably more realistic, multimembrane media. Computer simulation of the model considered in this work and some closely related models are now in progress in our laboratory. The Monte Carlo methodology in the grand canonical and in the Gibbs ensemble are employed for the systems in question.

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