THE STRUCTURE OF A LENNARD–JONES FLUID IN A SLIT–LIKE PORE FILLED WITH RANDOM MATRIX FROM INTEGRAL EQUATION THEORY AND FROM MONTE CARLO SIMULATIONS

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The confinement of a Lennard–Jones fluid in a slit–like pore filled with a random hard matrix is studied using the inhomogeneous Ornstein–Zernike equation and grand canonical Monte Carlo simulations. Associative matrix–fluid interactions are considered. Density profiles and pair distribution functions are reported. The agreement of the theoretical and simulation results is satisfactory.

Key words: adsorption, porous materials, replica Ornstein–Zernike equation, computer simulation.

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I. INTRODUCTION

Investigations of adsorption of fluids in disordered and in random matrices commence from the adaptation of the methods of liquid–state statistical mechanics for fluid mixtures [1–16]. According to the usual nomenclature random matrices are those whose particles do not interact between themselves, but interact with all the remaining molecules in the system. Disordered matrices, however, are formed by quenching a fluid composed of particles interacting via model repulsive or repulsive–attractive potentials.

One of the first theoretical approaches to quenched–annealed systems has been proposed by Madden and Glandt [1,2], who obtained a set of Ornstein–Zernike (OZ) type integral equations for the pair correlation functions. Next, Given and Stell [3–5] have generalized the theory of Madden and Glandt, developing the replica Ornstein–Zernike (ROZ) equation. In several papers [6–13] different approximations to pair correlation functions have been studied. A review of the theoretical methods can be found in our recent paper [14].

The theory of inhomogeneous quenched–annealed mixtures is in its infancy. This is not surprising, since the properties of nonuniform systems are more complex and require more sophisticated methods for investigation. However, the nonuniform quenched–annealed systems are of much greater interest for basic and applied research. Formally, the problem of theoretical description of such systems was stated first in Ref. [15], where the inhomogeneous replica Ornstein–Zernike equations, supplemented by either the Born–Green–Yvon (BGY), or by the Lovett–Mou–Buff–Wertheim equation for the density profiles, were proposed to study the adsorption of a fluid near a plane boundary of a disordered matrix. In our recent works [16,17], however, we formulated a theory for a fluid adsorbed in a pore filled with a nonuniform matrix. Specific calculations have been carried out for hard sphere fluid and for hard sphere disordered matrix. A comparison with the Monte Carlo simulation data has indicated that the structure of the system is reproduced correctly by the proposed theory. In subsequrnt papers [18, 19] we applied a similar formalism to describe fluids in contact with porous membranes and adsorption of fluids in pores with molecularly rough walls.

Adsorption of fluids in confined inhomogeneous disordered media is important for several practical applications as, for example, for chromatography [20], for the investigations of adsorption by some modified adsorbents, as well as by the so–called pillared clays [21,22], for example, and for separation. In such systems the specific interactions between the immobilized ("frozen") component and the annealed particles may occur. Thus, the aim of this note is to extend the theory reported in Refs. [16–19] to the case of more sophisticated interparticle forces. In particular, we test the predicted density profiles against the grand canonical Monte Carlo data. The success of the theory would allow us to study several interesting phenomena in the future, such as the capillary condensation in matrix–filled pores, for example.

II. THEORY

In this section we report equations describing the structure of a fluid inside a slit–like pore filled with a random matrix, i.e. a matrix built of frozen ideal gas.

The fluid particles, labelled by subscript 1 interact via the Lennard–Jones (12,6) potential

$$u_{11}(r) = \begin{cases} 4\varepsilon[(\sigma/r)^12 - (\sigma/r)^6] & r < r_c, \\ 0 & r > r_c, \end{cases} \qquad (1)$$

whereas the fluid–matrix potential, besides the Lennard–Jones part, may also contain specific, spherically symmetric intracore (associative) part [23, 24]

$$u_{10}(r) = \begin{cases} \infty & r < r_l, \\ -\varepsilon_a & r_l < r < r_u, \\ 4\varepsilon[(\sigma/r)^12 - (\sigma/r)^6] & r_u < r < r_c, \\ 0 & r > r_c, \end{cases} \quad (2)$$

In the above the matrix particles are distinguished by the subscript 0, r_c is the cut–off distance, r_l and r_u are the lower and upper limits of the square–well associative potential, ε_a is the intracore potential depth (the energy of association) and the remaining parameters have their usual meaning. Specific calculations are performed assuming that the Lennard–Jones parameters for fluid–fluid and for fluid–matrix interaction are the same and that $\varepsilon/kT = 1$, $\varepsilon_a/kT = 3$, $r_l = 0.3\sigma$ and $r_u = 0.4\sigma$. The cut–off distance is $r_c = 3\sigma$. The square–well part of the potential is located deep inside the core of the Lennard–Jones (12,6) function. This location makes unprobable a situation in which more than one fluid particle is bonded to the same matrix particle. However, because the matrix particles can freely penetrate themselves, one fluid particle can be bonded with more than one matrix particle.

Both fluid and matrix are between two hard walls of a slit–like pore of the width H

$$v_i(z) = \begin{cases} \infty & \text{for } z < 0 \text{ and } z > H, \\ 0 & \text{otherwise}, \end{cases} \quad (3)$$

where i stands for 0 and for 1.

The filling of the pore occurs stepwise. At the first stage an empy pore is filled with the matrix species. This process takes place at the chemical potential μ_0, corresponding to the bulk (reference) system density ρ_0. Because the matrix is formed from an ideal gas, its distribution inside the pore is given by the Boltzmann function

$$\rho_0(z) = \rho_{0b}\exp[-v_0(z)/kT] = \begin{cases} \rho_{0b} & \text{for } z < 0 \text{ and } z > H, \\ 0 & \text{otherwise}. \end{cases} \quad (4)$$

During the second step, the fluid, at the chemical potential μ_1 enters the matrix–filled pore. The pair fluid–fluid and fluid–matrix correlations are described by the nonuniform ROZ equations [15–17]

$$\begin{aligned} h_{10}(1,2) - c_{10}(1,2) &= \int d3\rho_0(z_3)c_{10}(1,3)h_{00}(3,2) \\ &+ \int d3\rho_1(z_3)c_{c,11}(1,3)h_{10}(3,2), \\ h_{01}(1,2) - c_{01}(1,2) &= \int d3\rho_0(z_3)c_{00}(1,3)h_{01}(3,2) \\ &+ \int d3\rho_1(z_3)c_{01}(1,3)h_{c,11}(3,2), \quad (5) \\ h_{11}(1,2) - c_{11}(1,2) &= \int d3\rho_0(z_3)c_{10}(1,3)h_{01}(3,2) \\ &+ \int d3\rho_1(z_3)c_{c,11}(1,3)h_{11}(3,2) \\ &+ \int d3\rho_1(z_3)c_{b,11}(1,3)h_{c,11}(3,2), \\ h_{c,11}(1,2) - c_{c,11}(1,2) &= \int d3\rho_1(z_3)c_{c,11}(1,3)h_{c,11}(3,2). \end{aligned}$$

The fluid–fluid pair (h) and direct (c) correlation functions consist of the blocking and connected part, $\varphi_{11}(1,2) = \varphi_{b,11}(1,2) + \varphi_{c,11}(1,2)$, where φ stands for h or c, as appropriate. The definition of the blocking part can be found in refs. [1–3]. Obviously, for random matrix the matrix–matrix correlation functions are $h_{00} \equiv c_{00} \equiv 0$.

Following Refs. [15–17] we use the BGY equation to describe the local density of the fluid, $\rho_1(z)$,

$$\frac{\partial \ln \rho_1(z_1)}{\partial z_1} + \beta\frac{\partial w(z_1)}{\partial z_1} = -\beta \int d2\rho_1(z_2)g_{11}(1,2)\frac{\partial U_{11}(12)}{\partial z_2}, \quad (6)$$

where the effective one–body potential, $w(z)$, satisfies the relation,

$$\frac{\partial w(z_1)}{\partial z_1} = \frac{\partial U(z_1)}{\partial z_1} + \int d2\rho_0(z_2)g_{10}(1,2)\frac{\partial U_{10}(12)}{\partial z_2}, \quad (7)$$

and where $g_{ij}(1,2) = 1 + h_{ij}(1,2)$. It is important to emphasize that a boundary condition results from the fact that the one particle cavity function, $y_1(z) = \rho_1(z)\exp[v_1(z)/kT]$, tends to its limiting value, determined by the configurational fluid chemical potential [25],$\mu_{1,c}$

$$\lim_{z\to\pm\infty} y_1(z) = \exp[\mu_{1,c}/kT] = \alpha_1, \quad (8)$$

where α_1 denotes the fluid activity.

To solve the set of equations (5)–(7), the closure relations for the inhomogeneous pair functions must be specified. We use the second order hypernetted chain (HNC2) closure [1–6]

$$c_{b,11}(i,j) = \exp\{h_{b,11}(i,j) - c_{b,11}(i,j)\} - 1 - \{h_{b,11}(i,j) - c_{b,11}(i,j)\}, \quad (9)$$

for the blocking term of the fluid–fluid function, and

$$[h_{ij}(1,2)+1]\exp[\beta U_{ij}] = \exp\{h_{ij}(1,2) - c_{ij}(1,2)\}, \quad (10)$$

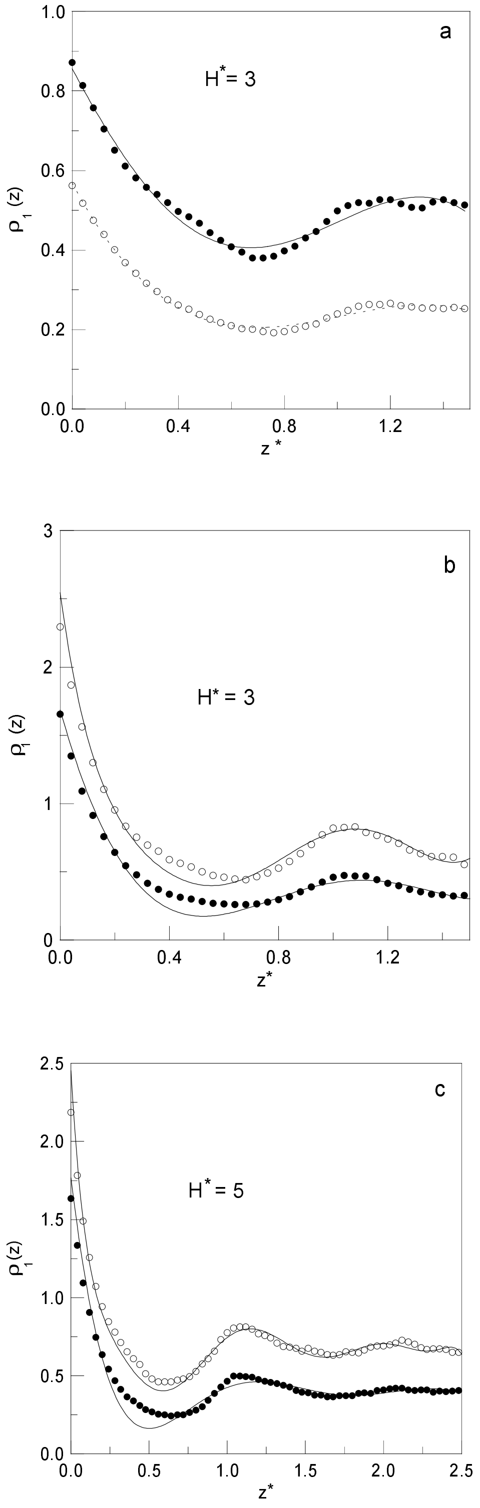

Fig. 1. Fluid density profile as functions of the distance $z^* = z/\sigma$ from the pore wall. Points donote simulational results, whereas curves have been calculated according to the proposed theory. In each Figure the lower curves are for the system with the fluid–matrix associative force switched off and the upper curves — for the systems with the associative interaction being swiched on. The pore width is given in each of the Figure; in part (a) the fluid activity is equal to $\alpha_1^* = 0.5$, whereas in parts (b) and (c) — it is equal to $\alpha_1^* = 5$.

for $(i, j) = (1, 0)$ and $(1, 1)$. We do not use the PY2 closure for this part of the calculation because it has been shown to be inconsistent in this application [5]. In solving the above equations we apply the techniques that were employed earlier [16–17, 26].

III. RESULTS AND DISCUSSION

In addition to theoretical caluclations we have carried out the grand canonical simulations. The technique applied by us was the same as in Refs. [17–19]. In our computer experiments a rectangular cell of dimensions $10\sigma_0 \times 10\sigma_0 \times H$ with periodic boundary conditions in the plane parallel to the pore walls was used. Each run consisted of two steps. In the first step, the pore was filled with randomly distributed noninteracting matrix particles. Next, grand canonical ensemble simulations of the fluid in a pore filled with the matrix species were performed. The calculations were repeated several times starting from different matrix configurations. During the production runs we performed at least 5×10^6 Monte Carlo steps; each step consisted of an attempt to move, an attempt to destroy and an attempt to create a particle that had been selected with equal probability. It was found that usually 10 replicas of the matrix assured good statistics for the determination of the local fluid density. However, the evaluation of the nonuniform pair distribution functions required much longer runs; at least 100 matrix replicas were necessary to calculate the correlation functions for particles parallel to the pore walls.

Our calculations have been carried out for two pore widths, $H^* = H/\sigma = 3$ and $H^* = 5$ and for two activities $\alpha_1 = \exp[\mu_{1,conf}/kT] = 0.5$ and 5. To get reference data, we have also considered the case when the fluid–matrix square–well interaction was switched off, i.e. for $\varepsilon_a/kT = \infty$.

In Fig. 1 we show the density profiles evaluated for the pore $H^* = 3$ at $\alpha_1^* = \alpha_1\sigma^3 = 0.5$ and $\alpha_1^* = 5$ (Figs 1a and 1b) and for the pore $H^* = 5$ at $\alpha^* = 5$. In both cases the matrix density is equal to $\rho_{0b}^* = \rho_{0b}\sigma^3 = 0.5$. In the case of computer simulations the total porosity of both the pores, defined as the ratio of the free space to the total pore volume was nearly identical and equal to ≈ 0.77. Obviously, only a part of the "free pore volume" is available to the fluid particles. In Fig. 1 lines denote the results of theoretical calculations, whereas points abbreviate the simulational data. Note that only every second Monte Carlo point is displayed here. The upper set of the curves has been obtained for switched on square–well (associative) potential, whereas the lower set — for the associative forces switched off.

The discrepancies between simulational and theoretical results increase with the increase of the activity of the fluids, α_1^*. Also, the theoretical results become slightly worse when the associative forces are turned on. The contact values of the density profiles are rather well reproduced. Also, the density at the pore centre resulting from the theory agrees well with the simulational results.

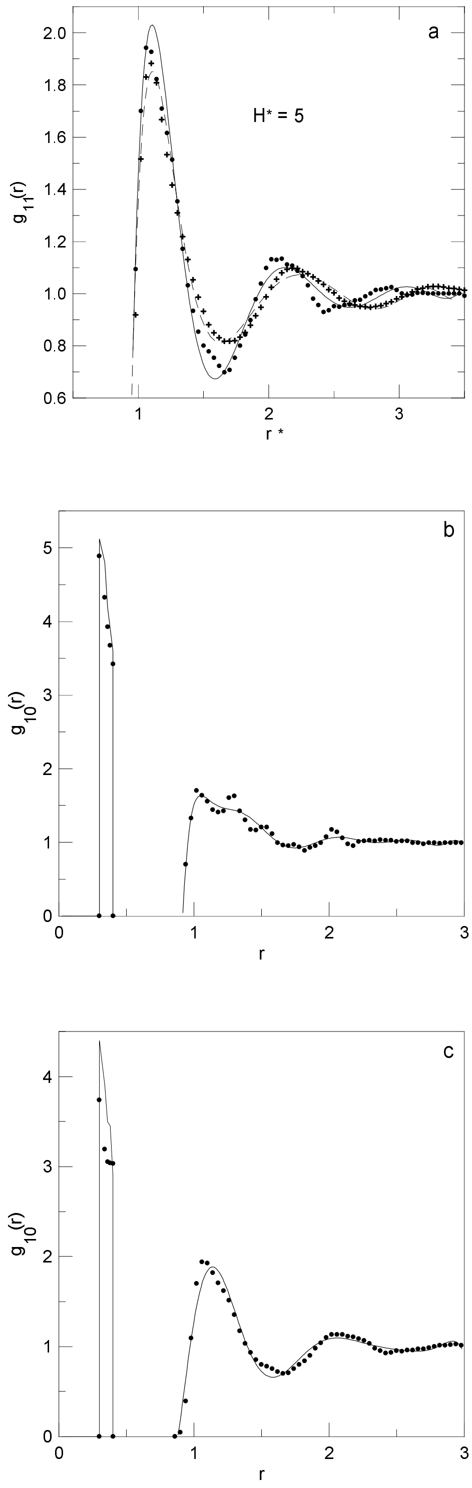

Fig. 2. Pair correlation function for a pair of spheres equidistant from the wall for matrix and fluid spheres in a slit–pore for which $H^* = 5$ and $\alpha_1^* = 5$. The associative interactions are switched on. Part a gives the fluid–fluid sphere correlation function at the pore centre (solid line and cricles) and at the pore wall (dashed line and crosses). Parts b and c give the matrix–fluid correlation function at the pore wall (part b) and at the pore centre (part c). Poins have been evaluated from the Monte Carlo simulations, lines denote the results of the theory. The intramolecular peaks in parts b and c have been reduced by 2.

The largest discrepancies are observed in the vicinity of the first local density minimum.

Figure 2 shows two particle correlation functions g_{ij} for a pair of particles located parallely to the pore walls at the pore wall, $z = 0.02\sigma$ and at the pore centre, $z = H/2$. Similarly to Fig. 1 the points denote the results of computer simulations and lines have been evaluated from theoretical calculations. All these results are for $H^* = 5$ and for $\alpha_1^* = 5$. Part (a) shows the fluid–fluid correlation functions. Solid line and circles denote the function at the pore wall, dashed line and crosses — at the pore centre. Parts (b) and (c) give the fluid–matrix correlation functions, g_{11}. Part b — at the pore centre, and partc — at the pore wall. Note that the "intramolecular" peak, corresponding to the formation of the associative bond has been reduced by 2.

Inspecting the curves given in Fig. 2 we can realize that the pair correlation function at the pore walls seems to be better reproduced by the theory than by the corresponding functions at the pore centre. Similarly to the case of noniniform hard–sphere fluid confined by a slit–like pore filled by nonuniform disordered matrix, the correlations are stronger at the pore centre than at the pore wall. Especially the simulated fluid–matrix pair correlation function given in Fig. 2b exhibits much richer structure than the function resulting from the theory.

In this note we have solved the inhomogeneous replica OZ equations for a model of a random, associatively adsorbing matrix and an inhomogeneous fluid. We have substantially considered the model of a random matrix and Lennard–Jones (12,6) potentials with, in the case of matrix–fluid forces, associative "intracore" well. We have reported the results for the fluid density profiles and some results for the pair correlation functions. We have also used the Monte Carlo simulation technique to yield reference data for the investigated systems. The aim of the work was to test the accuracy of the structure evaluation and the reported results have indicated that the theory in hand predicts the structure of the adsorbed fluid quite successfully. However, the theory is based on Cumming–Stell [27] model for the treatment of the association between matrix and fluid particles. Unfortunately, a generalization of the Wertheim type approach, developed in ref. [28] to the case studied here is not simple. This problem is currently under study. Undoubtfully, the theory applied by us may yield unexpected and rich structural and thermodynamic behavior in partly quenched confined systems. The perspectives for the investigations in the field that has just been opened by the solution of the IROZ equations are very promising. More complex studies of adsorption of fluids in matrix–filled pores will be reported elsewhere.

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ФЛЮЇД ЛЕННАРДА–ДЖОНСА У ЩІЛИНОПОДІБНІЙ ПОРІ, ЗАПОВНЕНІЙ АСОЦІЯТИВНО АДСОРБУЮЧОЮ ВИПАДКОВОЮ МАТРИЦЕЮ

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Вивчено поведінку флюїду зі взаємодією Леннарда–Джонса в порі між двома паралельними поверхнями. Об'єм пори містить твердокулькові частинки, конфіґурація яких є невпорядкованою. Модель відтворює неоднорідну частково заморожену систему. Крім того, модель включає асоціятивну взаємодію між частинками флюїду й невпорядкованою матрицею. Структури флюїду в цій системі досліджували, застосовуючи неоднорідні інтеґральні рівняння типу репліки Орнштайна–Церніке, а також комп'ютерні симуляції в методі Монте–Карло у великому канонічному ансамблі. Одержано профілі густини й неоднорідні парні функції розподілу частинок флюїду. Показано, що теоретичні розрахунки задовільно відтворюють дані комп'ютерного експерименту і теорія може бути застосована до опису адсорбції в порах із невпорядкованим розподілом матричних частинок.