

Adsorption of fluids in confined disordered media from inhomogeneous replica Ornstein-Zernike equations

Orest Pizio¹ and Stefan Sokolowski²

¹*Instituto de Química de la Universidad Nacional Autónoma de México, Circuito Exterior, Coyoacán 04510, Distrito Federal, México*

²*Department for the Modelling of Physico-Chemical Processes, Faculty of Chemistry, Marie Skłodowska Curie University, 200-31 Lublin, Poland*

(Received 12 February 1997)

The density distribution and pair distribution function for a fluid adsorbed in a slitlike pore filled with a quenched hard-sphere fluid have been investigated using the *inhomogeneous* replica Ornstein-Zernike equations. The one-particle and two-particle functions are related via Born-Green-Yvon equation and the *inhomogeneous* Percus-Yevick approximation is used. The effect of the matrix is to lower the amount of adsorbed fluid in the entire pore at low chemical potentials. For high values of the fluid chemical potential, layering of adsorbed fluid is observed. The solution of the problem is important for gel-exclusion chromatography and in separation science. [S1063-651X(97)52007-1]

PACS number(s): 68.45.-v, 61.20.Gy

The problem of describing the adsorption of fluids in random porous media has received much interest recently. Important experimental observations [1–4], and relevant theoretical developments [5–15] have been concerned with homogeneous systems. Adsorption of fluids in confined *inhomogeneous* disordered media, however, is of much interest in practice for gel-exclusion chromatography and in separation science. This problem is qualitatively more difficult to deal with than the homogeneous case. To our best knowledge, there was only one attempt to consider inhomogeneous fluids adsorbed in disordered porous media [14]. The inhomogeneous replica Ornstein-Zernike (IROZ) equations, supplemented by either Born-Green-Yvon (BGY), or Lovett-Mou-Buff-Wertheim (LMBW) equation for density profiles (DPs), have been proposed to study adsorption of a fluid near a plane boundary of a disordered matrix. The theory has not been followed by any numerical solution. In this paper our main goal is to propose a simple model for adsorption of fluids in confined disordered porous media and to solve it.

Let us consider the adsorption of a fluid consisting of particles m , in a slitlike pore of the width H . The pore walls are normal to the z axis and the pore is centered at $z=0$. The fluid m , i.e., the matrix, in the pore is in an equilibrium with the bulk fluid with the chemical potential μ_m . The fluid is then characterized by the DP $\rho_m(z)$, and by the inhomogeneous pair correlation function $h_{mm}(1,2)$. Due to external factors, the structure of the fluid becomes quenched at a state determined by μ_m , and a confined porous medium is formed.

Now, we would like to investigate adsorption of another fluid, f , in the pore filled by the matrix. The fluid f , in the bulk has the chemical potential μ_f ; at equilibrium the *adsorbed* fluid f reaches the DP $\rho_f(z)$ and is characterized by the inhomogeneous correlation function $h_{ff}(1,2)$. The matrix and fluid species are denoted by the subscripts 0 and 1 [5]. We assume the interactions between particles and between particles and pore walls in a simple form choosing both species as hard spheres of unit diameter:

$$U_{ij}(r) = \begin{cases} \infty, & r < 1 \\ 0, & r > 1 \end{cases}; \quad U(z) = \begin{cases} \infty, & z < 0.5|H-1| \\ 0, & \text{otherwise} \end{cases}, \quad (1)$$

where $i, j=0, 1$.

The evaluation of the matrix structure is irrelevant to the procedure below. The structure of a quenched inhomogeneous matrix is obtained from the inhomogeneous Ornstein-Zernike (OZ2) equation [14,16]

$$h_{00}(1,2) - c_{00}(1,2) = \int d^3\rho_0(z_3) c_{00}(1,3) h_{00}(3,2), \quad (2)$$

supplemented by the LMBW equation for the DP,

$$\frac{\partial \ln \rho_1(z_1)}{\partial z_1} + \frac{\partial \beta U(z_1)}{\partial z_1} = \int d^2 c_{00}(1,2) \frac{\partial \rho_0(z_2)}{\partial z_2}, \quad (3)$$

and the second order Percus-Yevick (PY2) closure,

$$y_{00}(1,2) = 1 + h_{00}(1,2) - c_{00}(1,2). \quad (4)$$

In Eq. (4), $y_{00}(1,2)$ is the inhomogeneous cavity distribution function (CDF). The solution of Eqs. (2)–(4) yields $\rho_0(z)$ and $h_{00}(1,2)$ such that the one-particle CDF $y_0(z)$, $y_0(z) = \rho_0(z) \exp[\beta U(z)]$, outside the pore tends to its limiting value, determined by the configurational chemical potential, $y_0(z \rightarrow \pm \infty) = \exp(\beta \mu_0)$. In fact, the structure of a matrix may be intentionally prepared experimentally given some functions $\rho_0(z)$ and $h_{00}(1,2)$.

The IROZ equations, representing the essence of the procedure, are [14]

$$h_{10}(1,2) - c_{10}(1,2) = \int d^3\rho_0(z_3) c_{10}(1,3) h_{00}(3,2) + \int d^3\rho_1(z_3) c_{c,11}(1,3) h_{10}(3,2), \quad (5)$$

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

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 and c , as appropriate. We apply the BGY equation to couple the DPs with the pair distribution functions (PDFS)

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

where $g_{11}(1,2) = 1 + h_{11}(1,2)$, and the effective one-body potential satisfies the relation,

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

and where $g_{10}(1,2) = 1 + h_{10}(1,2)$.

Equations (5) must be supplemented by the closure relations. An analysis of Stell and co-workers [5,7,13] has shown that the hypernetted chain (HNC) closure is consistent with the ROZ equations for adsorption of fluids in homogeneous disordered matrices, whereas the PY closure belongs to a class of approximations used by Madden and Glandt [6]. For the moment, we focus on rather difficult solution of Eqs. (5)–(7), but not on a detailed study of the effect of a closure. Therefore the PY2 approximation is used. It implies $c_{b,11}(1,2) = 0$, and reads

$$y_{ij}(1,2) = 1 + h_{ij}(1,2) - c_{ij}(1,2), \quad (8)$$

for $(i,j) = (1,0)$ and $(1,1)$.

The influence of the choice of a closure relation on the solution of Eqs. (5)–(7) will be presented in subsequent publications together with simulations; those consuming much time are in progress in our laboratory.

Before discussing the results, we need to comment on the procedure. First, the matrix structure is evaluated from Eqs. (2)–(4). Next, we must solve three equations of the OZ2 type, Eqs. (5)–(8), evidently $h_{10}(1,2) = h_{01}(2,1)$. We apply the boundary condition for the one-particle CDF $y_1(z)$, $y_1(z) = \rho_1(z) \exp[\beta U(z)]$, tends to its limiting value deter-

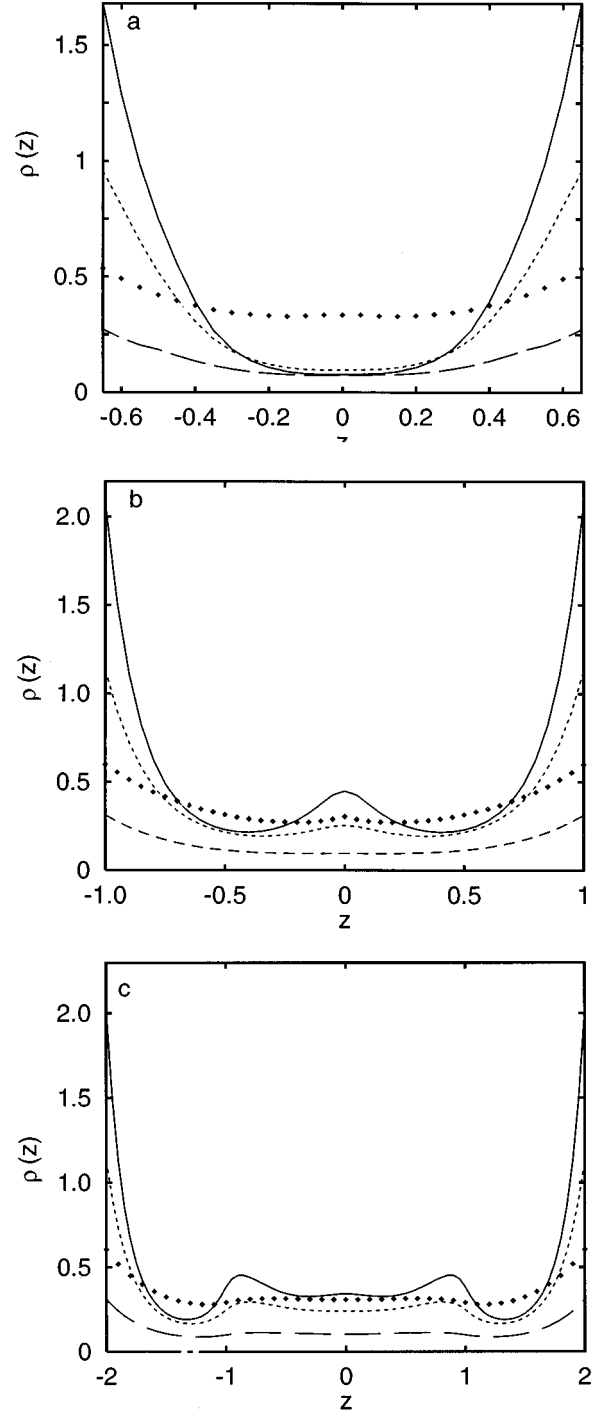


FIG. 1. The density profiles of adsorbed fluid in a slitlike pore of width H . The pore is filled with a hard-sphere matrix in equilibrium with a fluid at the chemical potential $\beta\mu_0=1.721$ (points). The chemical potential of adsorbed fluid, $\beta\mu_1$, is $\beta\mu_1=1.721$ (long-dashed line), $\beta\mu_1=22.503$ (dotted line), and $\beta\mu_1=123.31$ (solid line). The pore width is $H=2.3$ (a), $H=3$ (b), and $H=5$ (c).

mined by the configurational part of the fluid chemical potential. The method of the solution implies an expansion of the two-particle functions into Fourier-Bessel series [16]. The threefold integrations reduce then to the sums of one-dimensional integrations. The grid size in the z -direction $\Delta z=0.05$ has been fixed, and 73 terms in the Fourier-Bessel expansion have been included. The BGY equation contains

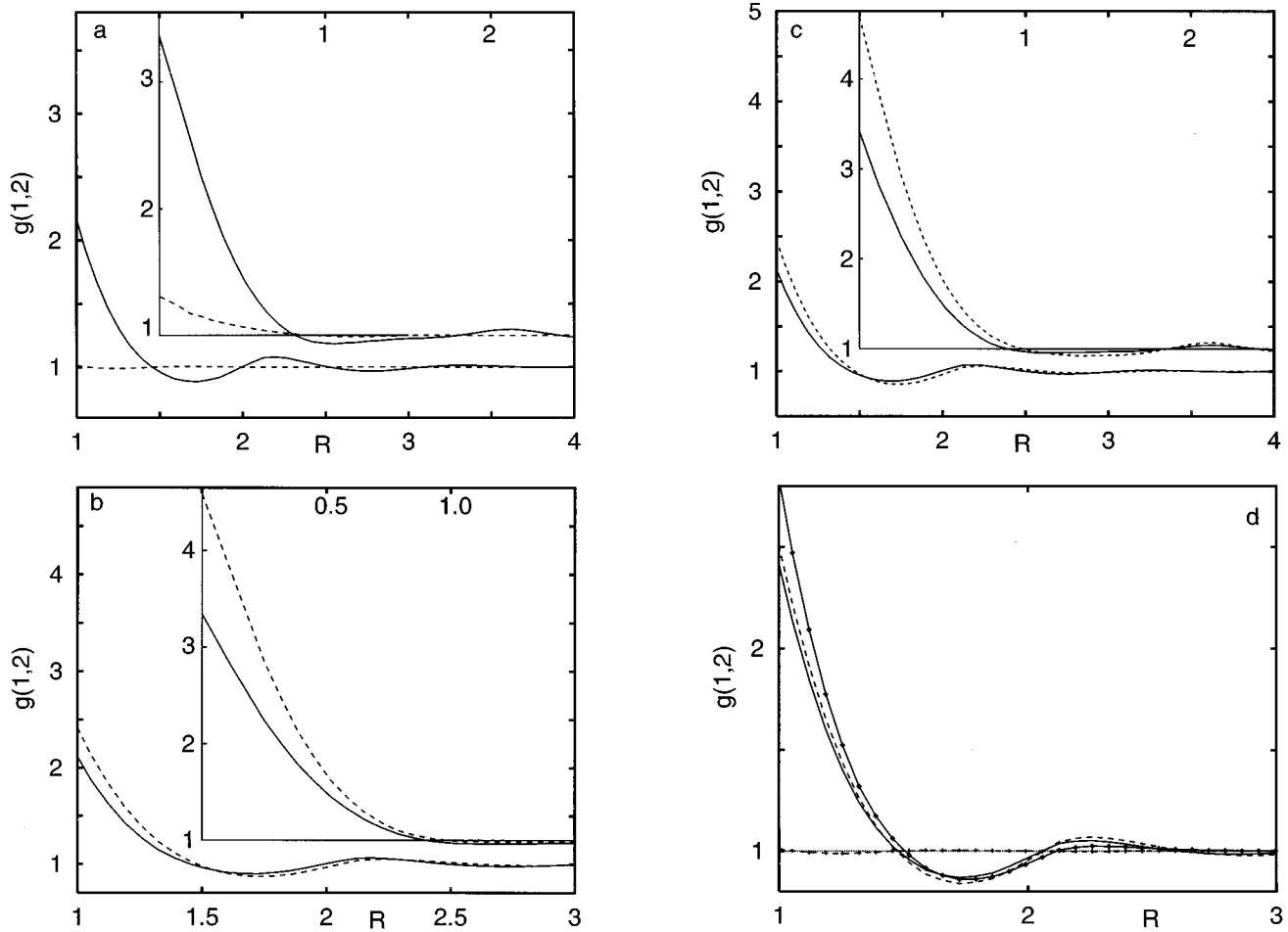


FIG. 2. The fluid-fluid pair distribution functions (a)–(c) and fluid-matrix distribution functions (d). The matrix and adsorbed fluid are considered at $\beta\mu_0=1.721$ and $\beta\mu_1=123.31$, respectively. The pore width is $H=2.3$ (a), $H=3$ (b), and H (c). In (a)–(c) the solid lines correspond to $g_{11}(z_1=0, z_2=0, R)$ and the dashed lines are for $g_{11}[z_1=0.5(H-1), z_2=0.5(H-1), R]$. The solid and dashed lines in the insets to (a)–(c) correspond to the blocking contributions to the functions listed above, i.e., in the plane located at the pore center and on the pore wall. In (d) the fluid-matrix functions are given. The lines with points are for $H=2.3$, the lines without points are for $H=3$. The dashed lines are for $g_{10}(z_1=0, z_2=0, R)$, whereas the solid lines are for $g_{10}[z_1=0.5(H-1), z_2=0.5(H-1), R]$.

the δ -function due to the derivative of the pair interactions. The integrals in Eqs. (6) and 7 are then onefold and contain the “contact” values of the functions $g_{ij}(z_1, z_2, \sqrt{R^2+z_{12}^2}=1)$ for $(i, j)=(1, 0)$ and $(1, 1)$, those have been evaluated by interpolation.

We have calculated the DPs (Fig. 1) and the inhomogeneous PDFS (Fig. 2) for pore widths $H=2.3$, $H=3$, and $H=5$. In the case of adsorption of hard spheres, the width of the pore $H=2.3$, corresponds to the second minimum of the solvation force between walls, as it follows Monte Carlo simulations and from the solution of the inhomogeneous OZ equation [17]. Correspondingly, for the system of hard spheres, the solvation force between walls has a maximum at $H=3$. The largest value of H , $H=5$, corresponds to a wide pore.

The chemical potential of the matrix, for the three pores considered has been fixed: $\beta\mu_0=1.721$. The bulk matrix density ρ_0 corresponding to this value of $\beta\mu_0$, if the Carnahan-Starling (CS) equation is used, equals to 0.3. The bulk fluid chemical potential $\beta\mu_1$ has been chosen as to provide $\rho_1=0.3$ ($\beta\mu_1=1.721$), $\rho_1=0.5$ ($\beta\mu_1=22.50$), and $\rho_1=0.6$ ($\beta\mu_1=123.31$), if the same equation of state is used.

For the sake of convenience we operate with the values of adsorbed fluid density below. We are aware that the application of the CS equation is slightly inconsistent with the applied theory; however, it is used only to estimate the bulk fluid densities.

The DPs that are shown in Fig. 1 manifest the following features. If a fluid at a low bulk density is adsorbed in matrix-filled pores of different width its density is much lower in the pore center than at pore walls. Moreover, for a narrow pore this region of low adsorption is observed for high bulk fluid densities. Due to a small pore width and to the presence of matrix particles, fluid particles cannot be accommodated in the pore center. As in the case of matrix-free pores, the profiles exhibit layering of an adsorbed fluid at high bulk densities in wider pores, similarly to the case of matrix-free pores.

In general, the effect of the matrix is to lower the amount of adsorbed fluid in comparison with the adsorption in matrix-free pores [17]. Adsorbed fluid structure is, however, similar to the case of matrix-free pores only either for wider pores, or low matrix densities. Our conclusions are relevant to one-component hard sphere fluid and only one, arbitrarily

chosen, hard sphere matrix density. Various and possibly unusual behavior of the profile $\rho_1(z)$ can be expected in the case of different matrix and fluid particles diameters due to a stronger influence of the matrix blocking contribution on the pair correlations, in contrast to the case of equal diameters [13]. A more sophisticated shape of $\rho_1(z)$ should result from external fields of complex geometry and/or more sophisticated interactions.

The PDFS of fluid particles, g_{11} and fluid-matrix PDFS g_{10} for $\rho_1=0.6$ are given in Fig. 2. The pair correlations in our model are governed by the matrix and fluid densities and by pore width. For a narrow pore the fluid particles fit close to the pore walls; thus, the lateral fluid-fluid and fluid-matrix correlations are much stronger when they are close to the walls than when they are in the pore center. In contrast to this behavior, for wider pores, the in-plane pair correlations between fluid particles are slightly stronger at the center of the pore than at pore walls, if the separation of particles is not large. The in-plane fluid-matrix PDFS are almost similar at the center of the pore and at the pore walls for wide pores, they are, however, very different for the narrowest pore in question. We conclude that in a wide pore the pair correlations behave similarly in a pore filled by a matrix and in a matrix-free pore. In a narrow pore the effect of confinement and of matrix obstacles determines pair correlations. We have performed also the calculations of the blocking part of the inhomogeneous fluid-fluid distribution functions. However, for the model with equal diameters of matrix and fluid

species the blocking effects are weak, even for small interparticle separations. A comprehensive study of the quenched matrix effect on the fluid distributions in a system with arbitrary diameters of particles would require to involve the *inhomogeneous* HNC approximation or *inhomogeneous* renormalized closures such as RPY and RHNC [7,13].

To summarize, we have solved the inhomogeneous replica OZ equations for the model of inhomogeneously quenched matrix and inhomogeneous fluid. The simplest model and approximation have been used to probe methodological tools. At a given value of the matrix chemical potential, we observed that for narrow pores the DP and pair correlations of adsorbed fluid are determined by the effect of pore confinement augmented by the presence of quenched matrix species. For wider pores the profiles and pair correlations become qualitatively similar to those for adsorbed fluid in a matrix-free pore. The effect of matrix parameters and of the quenching conditions seems more interesting to investigate for the case of arbitrary diameters of particles.

Most importantly, we expect novel results, if more sophisticated approximations for the IROZ equations will be used and for the models that include attractive interactions. Interesting phenomena can arise for specially prepared matrix structures. Undoubtedly, the options listed above may yield unexpected, rich structural and thermodynamic behavior of *partly quenched confined systems*. Prospects for investigations in the field that has just been opened by the solution of IROZ equations seem promising.

-
- [1] B. J. Frisken and D. S. Cannell, Phys. Rev. Lett. **69**, 632 (1992).
- [2] M. C. Goh, W. I. Goldberg, and C. M. Knobler, Phys. Rev. Lett. **58**, 1008 (1987).
- [3] A. P. Y. Wong, S. B. Kim, W. I. Goldberg, and M. H. W. Chan, Phys. Rev. Lett. **70**, 954 (1993).
- [4] S. B. Dierker and P. Wiltzius, Phys. Rev. Lett. **66**, 1185 (1991).
- [5] J. A. Given and G. Stell, Physica A **209**, 495 (1994).
- [6] W. G. Madden and E. D. Glandt, J. Stat. Phys. **51**, 537 (1988).
- [7] J. A. Given and G. Stell, J. Chem. Phys. **97**, 4573 (1992).
- [8] D. M. Ford and E. D. Glandt, Phys. Rev. E **50**, 1280 (1994).
- [9] E. Pitard, M. L. Rosinberg, G. Stell, and G. Tarjus, Phys. Rev. Lett. **74**, 4361 (1995).
- [10] C. Vega, R. D. Kaminsky, and P. A. Monson, J. Chem. Phys. **99**, 3003 (1993).
- [11] K. S. Page and P. A. Monson, Phys. Rev. E **54**, R29 (1996).
- [12] M. L. Rosinberg, G. Tarjus, and G. Stell, J. Chem. Phys. **100**, 5172 (1994).
- [13] E. Lomba, J. A. Given, G. Stell, J. J. Weis, and D. Levesque, Phys. Rev. E **48**, 233 (1993).
- [14] W. Dong, E. Kierlik, and M. L. Rosinberg, Phys. Rev. E **50**, 4750 (1994).
- [15] A. Meroni, D. Levesque, and J. J. Weis, J. Chem. Phys. **105**, 1101 (1996).
- [16] S. Sokolowski, J. Chem. Phys. **73**, 3507 (1980).
- [17] D. Henderson, S. Sokolowski, and D. T. Wasan, J. Stat. Phys. (to be published).