PHYSICAL REVIEW E VOLUME 58, NUMBER 2 AUGUST 1998

Born-Green-Yvon approach to the local densities of a simple fluid in a slitlike pore filled with a quenched disordered matrix

Stefan Sokołowski
Department for the Modelling of Physico-Chemical Processes, Faculty of Chemistry, MSC University, 200-31 Lublin, Poland

Orest Pizio
Instituto de Química de la UNAM, Circuito Exterior, Coyoacán 04510, México Distrito Federal, Mexico

(Received 12 February 1998)

The local density of a hard-sphere fluid adsorbed in a slitlike pore filled with a quenched disordered hard-sphere matrix is studied from the Born-Green-Yvon equation with the Fisher-Methfessel approximation. The solution of the replica Ornstein-Zernike equation in the Percus-Yevick approximation for a fluid in a homogeneous matrix is used as an input. The density profiles are compared with simulation data. It is shown that the theory works well for low and intermediate matrix densities. The approach seems promising for a description of capillary condensation and other phenomena in matrix-filled pores. [S1063-651X(98)01408-1]

PACS number(s): 61.25.−f, 61.20.−p, 61.43.Dq, 68.45.Da

Recently, much attention has been paid to describing the structure and thermodynamics of quenched-annealed (QA) fluid mixtures. In particular, cluster expansions for the distribution functions and thermodynamic properties and replica Ornstein-Zernike integral equations have been developed [1–4]. Several simple model QA systems have been investigated; see, e.g., Refs. [5–12]. The theory of inhomogeneous QA (IAQ) mixtures is in its initial state, since the properties of nonuniform systems are more complex and require more sophisticated tools. The problem of IQA fluids was first stated formally in Ref. [13]. The inhomogeneous replica Ornstein-Zernike equations (IROZ), complemented by either the Born-Green-Yvon (BGY), or the Lovett-Mou-Buff-Wertheim (LMBW) equation for the density profiles, were proposed to study the adsorption of a fluid near a plane boundary of a semi-infinite disordered but uniform matrix. However, the first results from numerical solution of IROZ equations and computer simulation data for an IQA fluid were presented in our very recent works [14,15]. We found that the solutions of the IROZ equations agree sufficiently well with computer simulation data for hard-sphere adsorbed fluids; unfortunately, they require intensive numerical work. Therefore, the study of the phase behavior of IQA systems using the IROZ methodology seems problematic. A search for alternatives is of crucial importance for the thermodynamics of confined QA systems.

The BGY approach and density functional theory have been shown to be successful for inhomogeneous simple fluids [16]. There exists a close relationship between the BGY equation with a coarse-grained prescription, developed by Fischer and Methfessel (referred to below as the FM approximation) [17], and the density functional method [18]. The BGY-FM approach was extended for fluid mixtures as well [19]. Both, the single-component and multicomponent versions of the BGY-FM theory agree reasonably well with simulations. Moreover, in the case of single-component nonuniform fluids, the FM approach leads to a description of wetting transitions, and is simpler to use than sophisticated density functional methods. At present, an extension of density functional methods to the case of QA nonuniform systems is conceptually difficult. On the other hand, an application of the BGY-FM theory that relies on the modeling of contact values of the nonuniform pair distribution function seems possible. Our main objective in this work is to generalize the BGY-FM approach for IQA systems as a possible alternative for the application of the IROZ equations.

Similar to Refs. [14,15], we consider an IQA fluid in a slitlike pore of width H. The pore walls are chosen normal to the z axis, and the pore is centered at $z=0$. The species m (the matrix component), adsorbed in the pore, is assumed to be in equilibrium with its bulk counterpart at the chemical potential μ_m. The structure of the matrix is characterized by the density profile $\rho_m(z)$ and by inhomogeneous pair correlation function $h_{mm}(1,2)$. Due to external factors the structure of the matrix becomes quenched, and a confined porous medium (a matrix-filled slitlike pore) is formed. Now we consider adsorption of another fluid f in that pore. The thermodynamic state of the fluid f in the bulk is determined by the chemical potential μ_f. After equilibration in the pore, in the presence of matrix species, the fluid f exhibits the density distribution $\rho_f(z)$. Its pair correlation function is denoted by $h_{ff}(1,2)$.

For explorative purposes, we assume a simple form for the interactions between particles and pore walls, choosing both species as hard spheres of the same diameter σ, $\sigma=1$,

$$U_{ij}(r)=\begin{cases}\infty, & r<\sigma\\ 0, & r>\sigma,\end{cases}$$

$$U_i(z)=\begin{cases}\infty, & z>0.5|H-\sigma|\\ 0, & \text{otherwise},\end{cases} \tag{1}$$

where $i,j=m,f$ are the species indices.

The matrix structure can be obtained by solving the inhomogeneous Ornstein-Zernike equation supplemented by the LMBW equation for the density profile and the second order Percus-Yevick approximation [14] with the exact boundary condition $y_m(z\to\pm\infty)=\exp(\beta\Delta\mu_m)$, where $\Delta\mu_m$ is the con-

1063-651X/98/58(2)/2652(4)/$15.00 PRE 58 2652

figurational part of the chemical potential for the matrix species, and $y_m(z)=\exp[\beta U_m(z)]\rho_m(z)$ is the one-particle cavity distribution function.

The BGY-FM approach for a one-component fluid may serve as an alternative for evaluating matrix local density. It leads to the following equation for $\rho_m(z)$ [17],

$$\frac{\partial \ln \rho_m(z_1)}{\partial z_1}+\frac{\partial \beta U(z_1)}{\partial z_1} = \int d\mathbf{r}_2 z_{12}\rho_m(z_2) g^0_{mm}[\sigma;\tilde{\rho}_m(z_1,z_2)]\,\frac{1}{r_{12}}\,\delta(r_{12}-\sigma), \tag{2}$$

which is nothing else but the BGY equation in which the contact value of the nonuniform pair distribution function, $g^0_{mm}(|\mathbf{r}_1-\mathbf{r}_2|=\sigma)=h^0_{mm}(|\mathbf{r}_1-\mathbf{r}_2|=\sigma)+1$ is approximated by the contact value for a uniform fluid at average density $\tilde{\rho}_m(\mathbf{r}_1,\mathbf{r}_2)$. This density is evaluated as follows:

$$\tilde{\rho}_m(z_c)=\frac{1}{v}\int \rho(\mathbf{r}+\mathbf{r}_c)d\mathbf{r}. \tag{3}$$

In the above, the averaging is done over a sphere of diameter σ and volume v, centered at a point $\mathbf{r}_c=[\mathbf{r}_1+\mathbf{r}_2]/2$. The boundary condition for solving the BGY equation is the same as for the LMBW equation.

The fluid structure in Refs. [14,15] has been obtained from the IROZ+BGY equations. The solution of the IROZ equations is the most time-consuming part of the numerical procedure. However, if one focuses on the evaluation of the local density of the adsorbed fluid rather than the inhomogeneous pair correlation functions, the application of a multicomponent version of the BGY-FM theory [19] may be attempted. Actually, the local density distribution of fluid particles in confined quenched-annealed systems represents the most important property. One then obtains the adsorption isotherms by straightforward integration.

To obtain the local fluid density in the IQA of this work, we propose an approximation similar to the BGY-FM equation for a two-component fluid of matrix and fluid particles,

$$\begin{aligned}\frac{\partial \ln \rho_f(z_1)}{\partial z_1}+\frac{\partial \beta U(z_1)}{\partial z_1} &= \int d\mathbf{r}_2 z_{12}\rho_m(z_2) g^0_{mf}[\sigma;\tilde{\rho}_m(z_1,z_2),\tilde{\rho}_f(z_1,z_2)] \\ &\quad\times\frac{1}{r_{12}}\,\delta(r_{12}-\sigma)+\int d\mathbf{r}_2 z_{12}\rho_m(z_2) \\ &\quad\times g^0_{mm}[\sigma;\tilde{\rho}_m(z_1,z_2),\tilde{\rho}_f(z_1,z_2)]\,\frac{1}{r_{12}}\,\delta(r_{12}-\sigma).\end{aligned} \tag{4}$$

Similar to Eq. (2), $g^0_{mf}[\sigma;\tilde{\rho}_m(z_1,z_2),\tilde{\rho}_f(z_1,z_2)]$ and $g^0_{ff}[\sigma;\tilde{\rho}_m(z_1,z_2),\tilde{\rho}_f(z_1,z_2)]$ are the contact values, evaluated for the *uniform* QA system at the densities $\tilde{\rho}_m(z_1,z_2)$ and $\tilde{\rho}_f(z_1,z_2)$. In the solution of Eq. (4) we have applied the exact boundary condition $y_f(z\to\pm\infty)=\exp(\beta\Delta\mu_f)$, where $y_f(z)$ is the cavity distribution function. In the case of equal size matrix and fluid particles, the averaged densities $\tilde{\rho}_m$ and $\tilde{\rho}_f$ are calculated according to Eq. (3) [17]. However, when both species are of different sizes, the definitions of averaged densities developed in Ref. [19] might be useful.

From the numerical point of view, the solution of Eq. (6) is advantageous, if compared with the solution of the IROZ equations. The idea behind this is simply to avoid the solution of the IROZ equations, that is, to obtain necessary input into the BGY equation in the exact formulation of the problem (i.e., in the IROZ+BGY equation) not from the IROZ equation but from the solution of the usual ROZ equations, at some averaged density. The aim of our calculations was to

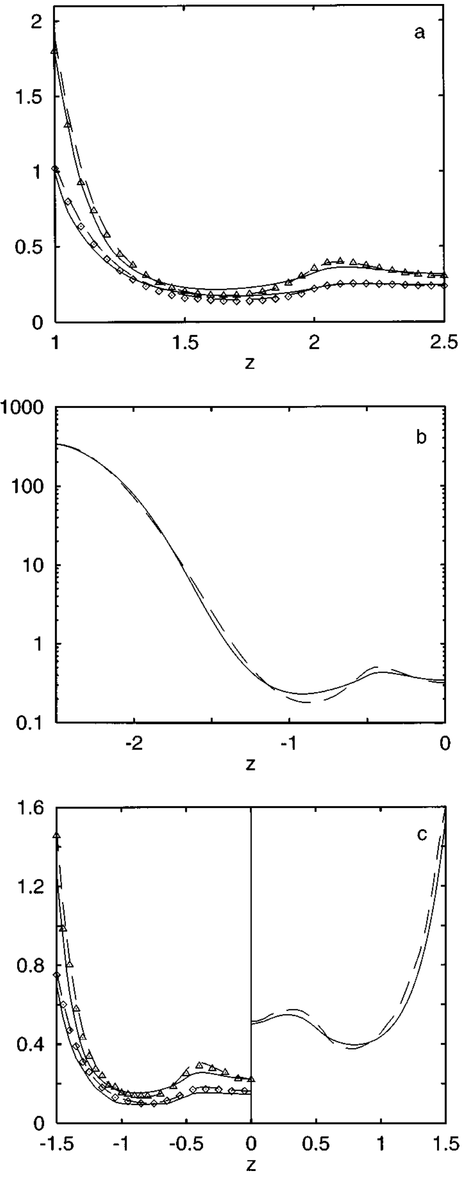

FIG. 1. The density profiles [parts (a) and (c)] and the cavity distribution function [part (b)] of the fluid in matrix-filled slitlike pore, $H=4$. The symbols denote the results of computer simulations [15], the solid lines are the results of the FM-type theory, and the dashed lines have been evaluated from the IROZ theory. The chemical potential of matrix is $\beta\Delta\mu_m=0.935$ [parts (a) and (b)] and $\beta\Delta\mu_m=3.1136$ [part (c)]. The chemical potential of the fluid is $\beta\Delta\mu_f=3.1136$ [the lower curves in part (a) and in the left panel of part (c)], 4.8147 [the upper curves in part (a) and in the left panel of part (c)], and 5.8346 [part (b)]. The right panel in part (c) shows the matrix density profile (at $\beta\Delta\mu_m=0.935=3.1136$).

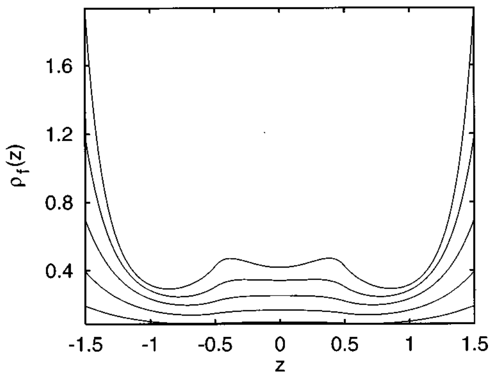

FIG. 2. The density profiles for a fluid adsorbed in a matrix-filled pore $H=4$ with $\beta\Delta\mu_m=0.5429$. The chemical potential of fluid species is $\beta\Delta\mu_f=0.5747$, 0.5429, 1.7316, 3.1136, and 4.8147 (the solid lines from bottom to top).

test the FM-type theory in the simplest case of equal size matrix and fluid particles confined in a slitlike, hard-wall pore. We have compared the resulting density profiles with the results of the IROZ theory [14] and with grand canonical ensemble Monte Carlo simulations [15].

The solution of Eqs. (2) and (4) requires a knowledge of the contact values of the homogeneous pair distribution functions $g^0_{fm}(r)$ and $g^0_{ff}(r)$ in a wide interval of densities. These have been evaluated from bulk ROZ equations with the PY approximation. The inaccuracies in calculating contact values [7] may influence the final results, but we would like to test the simplest (and fastest) possible method.

In Fig. 1, we show the results for a narrow pore, $H=4$. In parts (a) and (b) we choose $\beta\Delta\mu_m=0.935$, that corresponds to the bulk matrix density $\rho^0_m=0.334\,25$, if the Carnahan-Starling equation of state is used. In part (c) of this figure, the chemical potential of the matrix is higher, $\beta\Delta\mu_m=3.1136$ $(\rho^0_m=0.5)$. The values for $\beta\Delta\mu_f$ range from 3.1136 to 5.8346 (i.e., the bulk fluid density ρ^0_f ranges from 0.5 to 0.65). From Figs. 1(a) and 1(b), we conclude that for a low density matrix both FM and IROZ theories give similar profiles. Obviously, when the chemical potential of the fluid increases, the deviations of the FM profiles from IROZ profiles and from the simulational data become more pronounced. The FM theory seems to be more accurate in the region close to the pore walls. However, in the inner part of the pore the FM-type theory smooths the oscillatory character of the profile and leads to a somewhat lower average fluid density at the pore center. When $\beta\Delta\mu_m$ increases, the deviations of the FM theory from the second-order theory (which agrees well with the simulational data [15]) increase, [Fig. 1(c)]. We expect the FM theory to give reasonable results up to bulk fluid densities of order 0.7, provided that the matrix density is not too high. This is not surprising, because for simple nonuniform fluids Sokolowski and Fischer [19] observed that the theory fails at very high fluid densities.

In Fig. 2, we show the evolution of the fluid density profiles from the BGY-FM approach in a slitlike pore of width $H=4$, with the fluid chemical potential at $\beta\Delta\mu_m=-0.5747$, $(\rho^0_m=0.2)$. We observe the development of common adsorbed fluid layering in the narrow pore. These profiles permit us to obtain the amount of adsorbed fluid, $\Gamma=A\int\rho_f(z)dz/P$, where the porosity P is defined as $P=A\int dz[1-\rho_m(z)]$, and A denotes the surface area of a single pore wall. The dependencies of Γ on the bulk fluid pressure p (computed from the Carnahan-Starling equation of state) are given in Fig. 3. The amount of adsorbed fluid is higher in a matrix with lower porosity, as well as in narrower pores. The adsorbed amount increases in both cases with increasing bulk pressure.

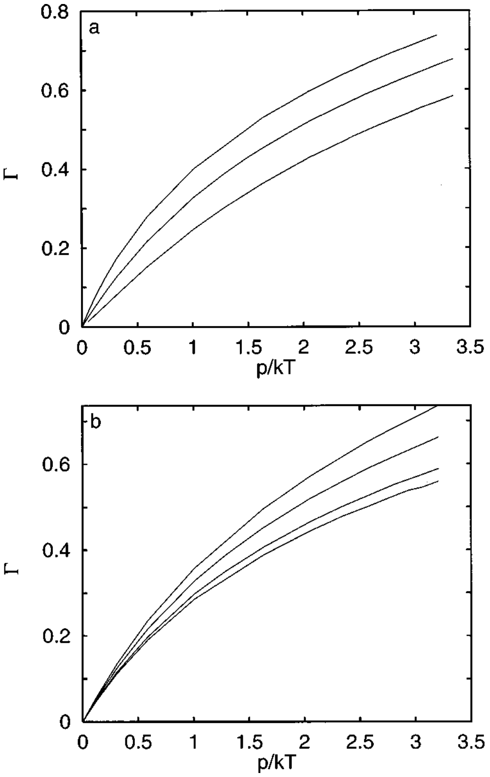

FIG. 3. The amount of adsorbed fluid on the bulk pressure for matrices with different microporosity [part (a)] and for different pore width [part (b)]. In part (a) the matrix chemical potential is $\beta\Delta\mu_m=0.5747$, 0.5429 and 1.7316 (the curves from top to bottom), $H=4$. In part (b) the matrix chemical potential is fixed $\beta\Delta\mu_m=0.5429$, and $H=3$, 4, 7, and 11 (the curves from top to bottom).

To summarize, we have proposed an extension of the BGY-FM approach for simple inhomogeneous fluids to inhomogeneous quenched-annealed simple fluids. We have shown that this very simple theory works sufficiently well for low and intermediate matrix densities for slitlike pores. Our results for the density profiles agree with computer simulation data and with much more sophisticated IROZ equations complemented by the BGY or LMBW equation. The adsorption isotherms calculated in this study have been shown to behave qualitatively correctly on the confined matrices' porosity, and on the bulk pressure. Most importantly, we expect that the approach developed would permit one to study the phase behavior of confined quenched-annealed fluids.

This project was supported in parts by DGAPA of the UNAM, Grant No. IN111597, and by the National Council for Science and Technology (CONACyT), Grant No. 25301E.

[1] W. G. Madden and E. D. Glandt, J. Stat. Phys. **51**, 537 (1988).
[2] W. G. Madden, J. Chem. Phys. **96**, 5422 (1992).
[3] J. A. Given and G. Stell, Physica A **209**, 495 (1994).
[4] J. A. Given and G. Stell, in *XVIth International Workshop on Condensed Matter Theories*, edited by L. Blum and F. B. Malik, (Plenum, New York, 1993).
[5] K. S. Page and P. A. Monson, Phys. Rev. E **54**, R29 (1996).
[6] C. Vega, R. D. Kaminsky, and P. A. Monson, J. Chem. Phys. **99**, 3003 (1993).
[7] E. Lomba, J. A. Given, G. Stell, J. J. Weis, and D. Levesque, Phys. Rev. E **48**, 233 (1993).
[8] A. Meroni, D. Levesque, and J. J. Weis, J. Chem. Phys. **105**, 1101 (1996).
[9] E. Kierlik, M. L. Rosinberg, G. Tarjus, and P. A. Monson, J. Chem. Phys. **106**, 264 (1997).
[10] A. Trokhymchuk, O. Pizio, M. Holovko, and S. Sokołowski, J. Chem. Phys. **106**, 200 (1997).
[11] E. Pitard, M. L. Rosinberg, G. Stell, and G. Tarjus, Phys. Rev. Lett. **74**, 4361 (1995).
[12] D. M. Ford and E. D. Glandt, Phys. Rev. E **50**, 1280 (1994).
[13] W. Dong, E. Kierlik, and M. L. Rosinberg, Phys. Rev. E **50**, 4750 (1994).
[14] O. Pizio and S. Sokołowski, Phys. Rev. E **56**, R63 (1997).
[15] A. Kovalenko, D. Henderson, S. Sokołowski, and O. Pizio, Phys. Rev. E **57**, 1824 (1998).
[16] R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992).
[17] J. Fischer and M. Methfessel, Phys. Rev. A **22**, 2836 (1980).
[18] J. Fischer and U. Heinbuch, J. Chem. Phys. **88**, 1909 (1988).
[19] S. Sokołowski and J. Fischer, Mol. Phys. **70**, 1097 (1990).