

Capillary condensation of Lennard-Jones fluid in a slitlike pore filled with quenched disordered matrix

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We have studied a capillary condensation of a Lennard-Jones fluid in a slitlike pore filled with a quenched disordered hard-sphere matrix using the Born–Green–Yvon (BGY) equation with the Fisher–Methfessel (FM) approximation. The solution of the replica Ornstein–Zernike (ROZ) equation in the Percus–Yevick (PY) approximation for a fluid in a homogeneous matrix is used as an input. The adsorption isotherms exhibit hysteresis loops for matrix-free and highly microporous matrix-filled slitlike pores. © 1998 American Institute of Physics. [S0021-9606(98)51927-7]

I. INTRODUCTION

It is well known that simple fluids confined to narrow pores of idealized geometry (e.g., slitlike or cylindrical) exhibit a rich variety of phase transitions.^{1–5} The effect of confinement results in a shift of the bulk coexistence curve—this phenomenon is known as capillary condensation. The coexistence occurs between gaslike and liquidlike (inhomogeneous) phases inside the pore. Moreover, confined fluids may undergo prewetting and layering transitions in competition with capillary condensation. However, real pores are geometrically heterogeneous. Surface roughness of pore walls and their energetic heterogeneity are the factors that can introduce specific features into the phase behavior of confined fluids.^{6–9} Generally modeling of geometrically heterogeneous individual pores involves pore walls built of planar segments larger than the molecular scale, such as steps or wedges.^{10–12} It is of interest to investigate more complicated porous structures that combine the effect of a geometric confinement on the scale of mesoporosity and of finer porosity, or microporosity (of the order of molecular dimensions).

In this work we consider a model of pores built of two parallel infinite walls, the interior of which contains a microporous medium. One experimental realization of the conditions related to our model has been presented recently in Refs. 13 and 14. The ideas on how to model confined quenched-annealed fluids have been borrowed from the theory of quenched-annealed bulk (uniform) systems.^{15–18} The geometrically homogeneous pore is first filled with a fluid of one species (we call it matrix, m) and, after quenching, provide a confined microporous medium for adsorption of another fluid. Dependent on the way of preparation, we can arrive at either an entirely filled microporous slit or a slit with molecularly rough walls.

The experiments on the behavior of fluids in uniform disordered materials^{19–21} indicate that such systems exhibit non-negligible deviations from the phase behavior of bulk

fluids. Kaminsky and Monson²² and Ford and Glandt²³ formulated a mean field theory for phase transitions in homogeneous microporous matrices. Recently Kierlik *et al.*²⁴ have applied the optimized cluster theory of Andersen, Chandler, and Weeks²⁵ to describe phase diagrams of a single-component fluid in uniform disordered porous materials. However, the problem of phase transitions in confined quenched-annealed systems has not been considered so far.

The theory of inhomogeneous QA (IQA) mixtures has been initiated recently,²⁶ and is in its infancy at present. The first results from the numerical solution of inhomogeneous replica Ornstein–Zernike equations (IROZ), complemented by the Born–Green–Yvon (BGY) equation for the density profile have been presented in a series of papers from our laboratory.^{27,28} We have found that the solutions of the IROZ equations agree sufficiently well with computer simulation data for hard sphere adsorbed fluids. Unfortunately, the solutions of the IROZ equations require intensive numerical work. Therefore the study of phase behavior of IQA systems using the IROZ methodology seems problematic. Search for alternatives is of crucial importance for thermodynamics of confined quenched-annealed systems.

The BGY approach and density functional theory have shown to be successful for inhomogeneous simple fluids.^{1,29} There exists a close relationship between the BGY equation with a coarse-grained prescription, developed by Fischer and Methfessel³⁰ (referred below as the FM approximation), and the density functional method.³¹ The BGY-FM approach has been extended for fluid mixtures as well.³² Both, the single- 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 the 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, the application of the BGY-FM theory that relies on the modeling of the 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 in the description of capillary condensation of fluids adsorbed in confined microporous media.

II. THEORY

We consider an IQA fluid in a slitlike pore of the width H .^{27,28} The pore walls are normal to the z axis and the pore is centered at $z=0$. The species m (the matrix component), adsorbed in the pore, is 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 $g_{mm}(1,2)$. Due to external factors the structure of the matrix becomes quenched and a confined microporous medium 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, 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 the following form of the interparticle interactions:

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

$$U_{ff}(r) = 4\epsilon_{ff}\{(\sigma_{ff}/r)^{12} - (\sigma_{ff}/r)^6\}, \quad (1)$$

where $\sigma_{ff} = \sigma = 1$ and $U_{ff}(r)$ has been cut at $r_c = 2.5\sigma$. The interactions between matrix and pore walls is

$$U_{mw}(z) = \begin{cases} 0, & |z| < 0.5H \\ \infty, & \text{otherwise} \end{cases}, \quad (2)$$

whereas the fluid–pore walls interaction is

$$U_{fw}(z) = \epsilon_{fw}\{(z_0/(0.5H-z))^9 - (z_0/(0.5H+z))^3\} + (z_0/(0.5H+z))^9 - (z_0/(0.5H+z))^3, \quad (3)$$

where $\epsilon_{fm} = 4\epsilon_{ff}$ and $z_0 = 0.6\sigma$.

The matrix structure can be obtained by solving the inhomogeneous Ornstein–Zernike equation supplemented by the LMBW equation for the density profile (DP) and the second order Percus–Yevick approximation.²⁷ However, in this work, similar to Ref. 33, the BGY-FM equation for the one-component fluid³⁰ has been used for evaluating $\rho_m(z)$,

$$\frac{\partial \ln \rho_m(z_1)}{\partial z_1} + \frac{\partial \beta U_{mw}(z_1)}{\partial z_1}$$

$$= \int dr_2 z_{12} \rho_m(z_2) g_{mm}^0[\sigma; \tilde{\rho}_m(z_1, z_2)] \frac{1}{r_{12}} \delta(r_{12} - \sigma), \quad (4)$$

which is simply the BGY equation in which the nonuniform pair distribution function at contact, $g_{mm}^0(|\mathbf{r}_1 - \mathbf{r}_2| = \sigma) = h_{mm}^0(|\mathbf{r}_1 - \mathbf{r}_2| = \sigma) + 1$, is approximated by that of a uniform fluid at average density $\tilde{\rho}_m(\mathbf{r}_1, \mathbf{r}_2)$. This density is evaluated as follows:

$$\tilde{\rho}_m(z_c) = \frac{1}{v} \int \rho(\mathbf{r} + \mathbf{r}_c) d\mathbf{r}, \quad (5)$$

In the above, the averaging is done over a sphere of diameter σ and the volume v , centered at the point $\mathbf{r}_c = [\mathbf{r}_1 + \mathbf{r}_2]/2$. The boundary condition for solving Eq. (4) is $y_m(z \rightarrow \pm\infty) = \exp(\beta\Delta\mu_m)$, where $\Delta\mu_m$ is the configurational (without kinetic contribution) 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. This methodology has been shown to be successful for the description of the hard sphere disordered matrix structure up to intermediate values of the chemical potential $\beta\mu_m$.

We now proceed to the problem of evaluation of the fluid structure. In our previous works^{17,18} we have applied the IROZ equations with the BGY equation to couple the density profile with the pair correlation function. However, if one focuses on the evaluation of the local density $\rho_f(z)$ rather than the inhomogeneous pair correlation functions, the application of a multicomponent version of the BGY-FM theory³² may be attempted. The local density of fluid represents the most important property. One then computes the adsorption isotherms by straightforward integration.

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

$$\frac{\partial \ln \rho_f(z_1)}{\partial z_1} + \frac{\partial \beta U_{fw}(z_1)}{\partial z_1}$$

$$= \int d\mathbf{r}_2 z_{12} \rho_m(z_2) g_{mf}^0[\sigma; \tilde{\rho}_m(z_1, z_2), \tilde{\rho}_f(z_1, z_2)]$$

$$\times \frac{1}{r_{12}} \delta(r_{12} - \sigma) + \int d\mathbf{r}_2 z_{12} \rho_f(z_2)$$

$$\times g_{ff}^0[\sigma; \tilde{\rho}_m(z_1, z_2), \tilde{\rho}_f(z_1, z_2)]$$

$$\times \frac{1}{r_{12}} \delta(r_{12} - \sigma) - \beta \frac{\partial}{\partial z_1} \int d\mathbf{r}_2 \rho_f(z_2) U_{ff}^{\text{at}}(r_{12}). \quad (6)$$

The attractive term of the fluid–fluid potential, $U_{ff}^{\text{at}}(r_{12})$, is defined according to the Weeks–Chandler–Andersen prescription,²⁵ however, without optimization of the effective hard sphere diameter, such that $\sigma_{ff} = \sigma$. Similar to Eq. (4), $g_{mf}^0[\sigma; \tilde{\rho}_m(z_1, z_2), \tilde{\rho}_f(z_1, z_2)]$ and $g_{ff}^0[\sigma; \tilde{\rho}_m(z_1, z_2), \tilde{\rho}_f(z_1, z_2)]$ 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. (6) we apply the exact boundary condition $y_f(z \rightarrow \pm\infty) = \exp(\beta\Delta\mu_f)$, 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. (5).³⁰

From the numerical point of view, the solution of Eq. (6) is advantageous in comparison to the solution of the IROZ equations. Moreover, this approach has been proven to perform well in comparison to computer simulations for a hard sphere fluid adsorbed in matrix filled pores in a sufficiently wide range of adsorbed fluid density.³³ Our objective is to apply the BGY-FM extension for inhomogeneous quenched-annealed fluids to study the capillary condensation in matrix-

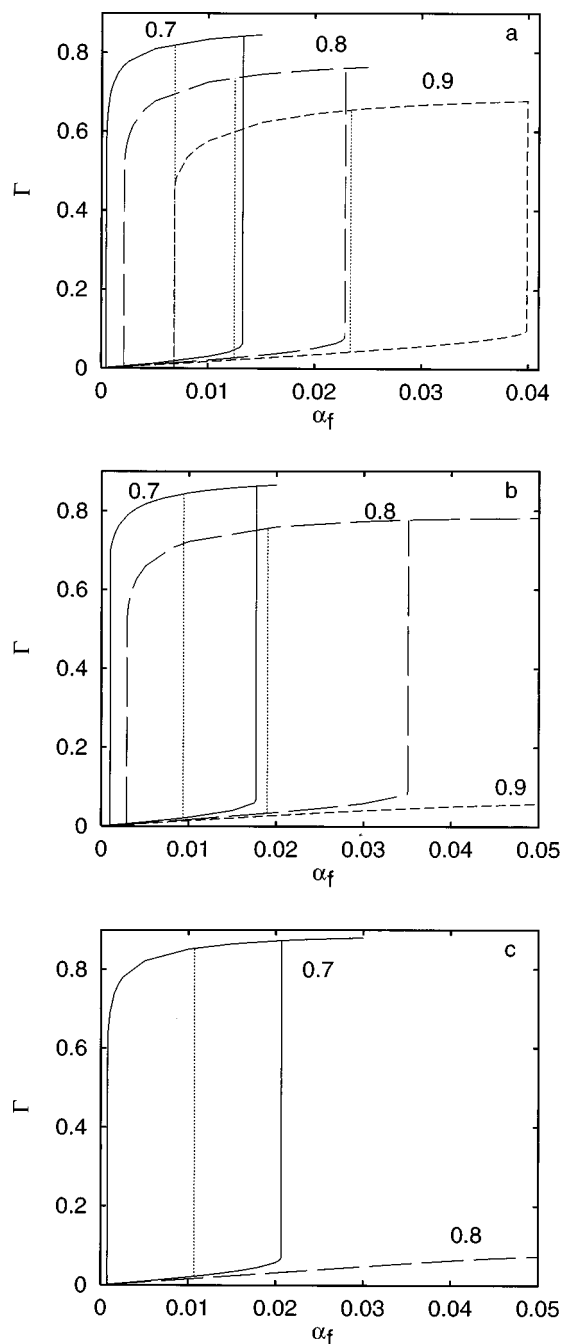


FIG. 1. The dependence of the adsorption isotherms (normalized by matrix porosity) on the activity of adsorbed fluid in a slitlike pore of the width, $H=6$. The results for matrix-free pore and matrix-filled pores at porosity, $p=0.958$, and at $p=0.938$ are shown in (a), (b), and (c), respectively. The solid, long-dashed, and short-dashed lines correspond to $T^*=0.7$; 0.8 and $T^*=0.9$, respectively. Dotted vertical lines correspond to the fluid activity at coexistence.

filled pores. The application of other methods to this phenomenon, at present, seems practically impossible.

In the numerical procedure we were looking for the solution of Eq. (6) at a given temperature and matrix chemical potential. The fluid activity has been incremented by small steps starting from very small values until the jump on the adsorption isotherm occurred. On the other hand, a similar procedure has been performed starting from a high value of the fluid activity decreasing it by a small step until the jump

TABLE I. The values for coexisting adsorptions Γ_g and Γ_l at temperature T^* and at fluid activity α_f , in a slitlike pore, $H_m=6$, filled by a hard sphere matrix at activity α_m .

α_m	α_f	Γ_g	Γ_l	T^*
0.00	0.006 85	0.019 15	0.818 37	0.7
0.00	0.012 48	0.027 00	0.735 00	0.8
0.00	0.023 38	0.043 00	0.654 60	0.9
0.05	0.009 37	0.020 70	0.840 50	0.7
0.05	0.019 00	0.033 50	0.756 70	0.8
0.08	0.010 70	0.022 40	0.853 40	0.7

occurred. These two jumps correspond to the ends of the hysteresis loop appearing for some temperature. The average of two activities has been attributed to the activity at the transition point.

III. RESULTS

The solution of Eqs. (2) and (4) requires the knowledge of the contact values of the homogeneous pair distribution functions, $g_{fm}^0(r)$ and $g_{ff}^0(r)$ in a wide interval of densities. They have been evaluated from the bulk ROZ equations with the PY approximation.³⁴ We are aware, that inaccuracies in calculating these values may influence the final results. Nevertheless, the data are expected to be qualitatively correct.

In this work we have restricted to the pore of intermediate width, $H=6$. Three values for the temperature, $T^*=kT/\epsilon_{ff}$, have been studied, $T^*=0.7$, 0.8, and 0.9. We have considered the matrix empty pore (as a reference) and two matrix-filled pores prepared at the matrix activity, $\alpha_m = \exp[\beta\Delta\mu_m]$, $\alpha_m=0.05$, and $\alpha_m=0.08$. These values correspond to highly porous matrices with porosity, $p=[1 - \int dz \rho_m(z)]/H$; $p=0.958$ for $\alpha_m=0.05$, and $p=0.938$ for $\alpha_m=0.08$. The reason for considering highly porous matrices is that for the homogeneous quenched-annealed systems even dilute matrices yield substantial changes of the phase diagram, see e.g. Refs. 23 and 24.

In Fig. 1 we present the adsorption isotherms for matrix-free pore [part (a)] and matrix-filled pores [parts (b) and (c)] for different temperatures. The adsorption isotherms normalized by the matrix porosity have been defined as follows: $\Gamma = \int dz \rho_f(z)/p$. In the case of the matrix-free pore [Fig. 1(a)] we observe a hysteresis loop at each temperature studied which characterize capillary condensation. That implies that the critical temperature for the matrix-free pore is higher than 0.9. The values for coexisting gaslike and liquidlike adsorptions together with corresponding values for activity at transition are given in Table I.

The results for adsorption in matrix-filled pores are shown in Fig. 1(b) and 1(c). We have observed that for matrices with porosity $p=0.958$ the hysteresis loop disappears for $T^*=0.9$; nevertheless it is observed, at lower temperatures, $T^*=0.7$ and 0.8. In the case of the matrix porosity $p=0.938$ the hysteresis loop disappears for $T^*=0.8$, it is observed, however, for lower temperatures, $T^*=0.7$. We conclude from the presented data that the critical temperature for the vapor-liquid transition is higher in the matrix-free than

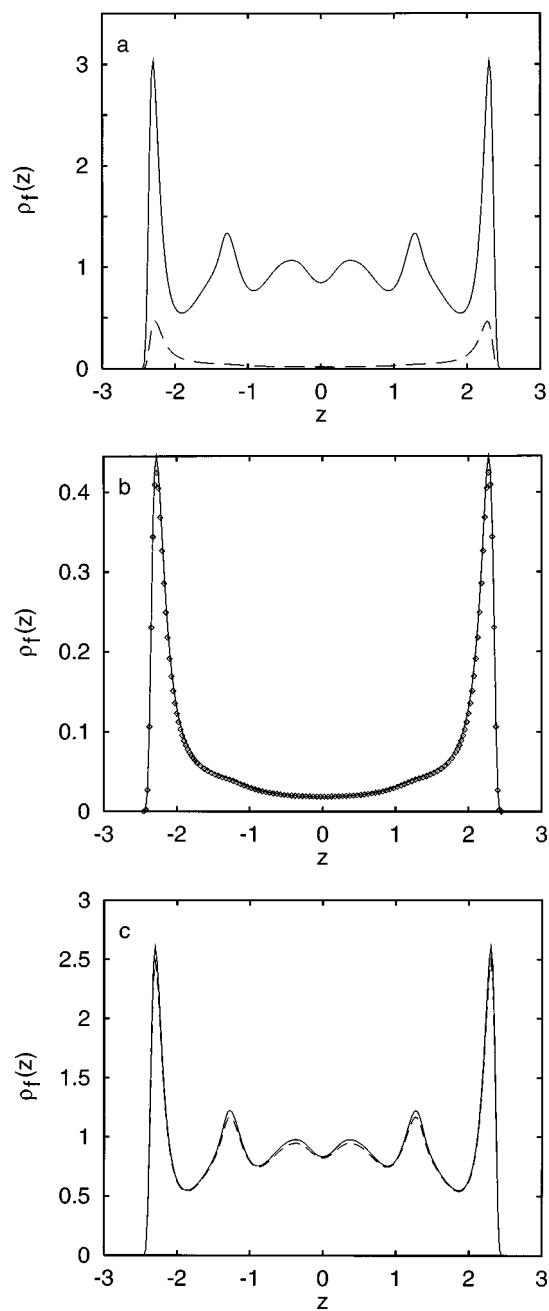


FIG. 2. The gaslike (dashed line) and liquidlike (solid line) density profiles for a fluid at coexistence in a matrix-filled pore at $p=0.938$, $T^*=0.7$ (a); the gaslike density profile (dashed line) for a matrix-filled pore as in (a), and the corresponding density profile at coexistence for matrix-free pore (symbols) (b); the liquidlike density profile at coexistence in a matrix-filled pore at $p=0.958$, $T^*=0.8$ (dashed line) and the corresponding density profile at coexistence in matrix-free pore (solid line). In all cases $H=6$.

in the matrix-filled pore. Moreover, in a given pore the critical temperature decreases with decreasing microporosity.

We have not obtained a complete phase diagram so far. However, from the results given in Table I it follows that the vapor coexisting adsorption shifts towards higher values with decreasing microporosity. The liquid branch also shifts in the same direction. This behavior implies that shrinking of the coexistence envelope does not occur, in contrast to the mean-field type behavior of the coexistence curve for the Lennard-

Jones fluid in a homogeneous matrix with decreasing microporosity.²⁴

Additional insight into the behavior of a fluid in microporous confined systems is provided by the density profiles. We have obtained them and show the corresponding results at coexistence for the case of matrix-filled pores in Fig. 2. The density profiles, $\rho_f(z)$, for the fluid activity at coexistence for a pore with $p=0.938$ at $T^*=0.7$ are shown in Fig. 2(a). The liquidlike profile exhibits much structure in contrast to the vaporlike one. In Fig. 2(b) we compare the vaporlike density profile at coexistence for the matrix-free pore and matrix-filled pore with $p=0.938$, at $T^*=0.7$. The structure of the fluid in the pore under these conditions is almost unchanged. The structure of adsorbed fluid at coexistence in the matrix-free and matrix-filled pore with $p=0.958$, at $T^*=0.8$ also differs negligibly [Fig. 2(c)].

To summarize, we have applied the extension of the BGY-FM approach for simple inhomogeneous fluids to inhomogeneous quenched-annealed simple fluids to study the capillary condensation. We have shown that the temperature of transition is smaller in matrix-filled (microporous) slitlike pores compared with matrix-free pores and exhibits trends for decreasing with decreasing microporosity. Shrinking of the coexistence envelope has not been observed with decreasing microporosity (at low matrix densities), in contrast to the adsorption of fluids in homogeneous disordered matrices. A complete phase diagram following the applied methodology will be presented in a separate work together with computer simulation results.

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- ¹R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Marcel Dekker, New York, 1992), Chap. 2.
- ²R. Evans and U. M. B. Marconi, *J. Chem. Phys.* **86**, 7138 (1987).
- ³P. C. Ball and R. Evans, *J. Chem. Phys.* **89**, 4412 (1988).
- ⁴R. Evans, U. M. B. Marconi, and P. Tarazona, *J. Chem. Soc., Faraday Trans. 2* **82**, 1763 (1986).
- ⁵B. K. Peterson, J. P. R. B. Walton, and K. E. Gubbins, *J. Chem. Soc., Faraday Trans. 2* **82**, 1789 (1986).
- ⁶K. Karykowski, A. Patrykiewicz, W. Rzyzko, and S. Sokolowski, *Thin Solid Films* **249**, 236 (1994).
- ⁷G. Chmiel, K. Karykowski, A. Patrykiewicz, and S. Sokolowski, *Mol. Phys.* **81**, 691 (1994).
- ⁸W. Gac, A. Patrykiewicz, and S. Sokolowski, *Surf. Sci.* **306**, 434 (1994).
- ⁹W. Gac, A. Patrykiewicz, and S. Sokolowski, *Thin Solid Films* **298**, 22 (1997).
- ¹⁰W. Steele and M. J. Boyan, *Langmuir* **5**, 625 (1989).
- ¹¹D. Schoen and S. Dietrich, *Phys. Rev. E* **56**, 499 (1997).
- ¹²D. Henderson, S. Sokolowski, and D. Wasan, *Phys. Rev. E* (in press).
- ¹³G. Viramontes-Gamboa, J. L. Arauz-Lara, and M. Medina-Noyola, *Phys. Rev. Lett.* **75**, 759 (1995); G. Viramontes-Gamboa, M. Medina-Noyola, and J. L. Arauz-Lara, *Phys. Rev. E* **52**, 4035 (1995).
- ¹⁴J. L. Arauz Lara and M. Medina-Noyola (personal communication).
- ¹⁵W. G. Madden and E. D. Glandt, *J. Stat. Phys.* **51**, 537 (1988).
- ¹⁶W. G. Madden, *J. Chem. Phys.* **96**, 5422 (1992).
- ¹⁷J. A. Given and G. Stell, *Physica A* **209**, 495 (1994).
- ¹⁸J. A. Given and G. Stell, in *XVth International Workshop on Condensed Matter Theories*, edited by L. Blum and F. B. Malik (Plenum, New York, 1993).

- ¹⁹S. B. Dierker and P. Wiltzius, *Phys. Rev. Lett.* **66**, 1185 (1991).
- ²⁰M. Y. Lin, S. K. Sinha, G. M. Drake, X. I. Wu, P. Thiyagarajan, and H. B. Stanley, *Phys. Rev. Lett.* **72**, 2207 (1994).
- ²¹B. J. Frisken, F. Ferri, and D. S. Cannell, *Phys. Rev. E* **51**, 5922 (1995).
- ²²R. D. Kaminsky and P. A. Monson, *Chem. Eng. Sci.* **49**, 2967 (1994).
- ²³D. M. Ford and E. D. Glandt, *Phys. Rev. E* **50**, 1280 (1994).
- ²⁴E. Kierlik, M. L. Rosinberg, G. Tarjus, and P. A. Monson, *J. Chem. Phys.* **106**, 264 (1997).
- ²⁵J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971).
- ²⁶W. Dong, E. Kierlik, and M. L. Rosinberg, *Phys. Rev. E* **50**, 4750 (1994).
- ²⁷O. Pizio and S. Sokolowski, *Phys. Rev. E* **56**, R63 (1997).
- ²⁸A. Kovalenko, D. Henderson, S. Sokolowski, and O. Pizio, *Phys. Rev. E* **57**, 1824 (1998).
- ²⁹Y. Zhou and G. Stell, *Mol. Phys.* **66**, 767 (1989); **66**, 791 (1989).
- ³⁰J. Fischer and M. Methfessel, *Phys. Rev. A* **22**, 2836 (1980).
- ³¹J. Fischer and U. Heinbuch, *J. Chem. Phys.* **88**, 1909 (1988).
- ³²S. Sokolowski and J. Fischer, *Mol. Phys.* **70**, 1097 (1990).
- ³³S. Sokolowski and O. Pizio, *Phys. Rev. E* (in press).
- ³⁴E. Lomba, J. A. Given, G. Stell, J. J. Weis, and D. Levesque, *Phys. Rev. E* **48**, 233 (1993).