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Vapor-liquid phase equilibrium in random microporous matrices

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The theory developed by Madden and Glandt [J. Stat. Phys. **51**, 537 (1988)] for fluids in disordered microporous matrices is extended. A perturbation theory approach is used to obtain the free energy of the confined fluid, with the interparticle potential as the perturbation variable. The theory is combined with a mean-field approximation and applied to a system of square-well particles for which vapor-liquid coexistence envelopes are obtained. The effects of matrix density on the coexistence properties are explored, and a comparison is done with previous experiment and lattice modeling.

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I. INTRODUCTION

The behavior of fluids confined in disordered microporous materials is a subject of great interest. Much experimental work has been done in an attempt to understand the effects of such host media on the phase transitions of binary mixtures [1]. The liquid-vapor phase transition of pure ^{4}He in a silica aerogel was studied by Wong and Chan [2]. They discovered that the coexistence curve of the confined fluid was markedly different from that of the bulk: the curve was an order of magnitude smaller in width and the critical temperature was slightly depressed. Theoretical studies of confined fluids have generally been limited to either "single pore" models [3], which lack the ability to represent a truly disordered structure, or lattice models [4]. Madden and Glandt [5] have introduced a continuum model for a fluid in a porous material which seems well suited for application to these problems.

Madden and Glandt [5] have addressed the problem of calculating the structure of a fluid equilibrated within a disordered microporous solid, viewed as a rigid matrix of interaction sites. In their formalism, the fluid-matrix system is treated essentially as a binary mixture, with the stipulation that the matrix structure is completely unaffected by the presence of the imbibed fluid. Structure in this system is described by correlation functions analogous to those used in equilibrium liquid-state theory. Ford and Glandt [6] and Rosinberg, Tarjus, and Stell [7] have shown that these correlation functions can be used to calculate thermodynamic properties of the fluid in the matrix, in ways similar to those used in equilibrium liquid-state theory. For practical reasons, the usefulness of these routes to the thermodynamics is often limited to very simple interparticle potential models [6]. It is therefore desirable to develop a perturbation theory approach to the calculation of thermodynamic properties, treating more realistic potentials as perturbations of simpler ones. We introduce such a theory in this paper, which is organized as follows. Section II provides background on the Madden-Glandt formalism, Sec. III gives the perturbation theory derivation, Sec. IV describes a model potential to which the theory is applied, Sec. V shows the results of these calculations, and Sec. VI discusses the results and possible future directions.

II. FLUID-MATRIX SYSTEMS

As mentioned previously, the Madden-Glandt view of a fluid-matrix system is that of a binary mixture where one component is completely quenched and thus immobile [5]. The correlation functions used to describe structure are analogous to those used for equilibrium fluids; the pair correlation functions $\rho_{\alpha\gamma}(\mathbf{r}_1,\mathbf{r}_2)$ give the probability density for simultaneously finding a particle of species α within $d\mathbf{r}$ of $\mathbf{r}_1$ and a particle of species γ within $d\mathbf{r}$ of $\mathbf{r}_2$. The matrix is regarded as being produced by an instantaneous thermal quench of a fluid in equilibrium at a higher temperature, and thus having a pair correlation function identical to that of such a fluid. For simplicity we neglect the restructuring of the matrix during quenching. This assumption does not affect the essential physics of the results reported below. For further convenience, in this paper we will present results only for statistically homogeneous systems, (i.e., having no external fields except that produced by the matrix itself) and spherically symmetric interparticle potentials. In such cases, the simplification $\rho_{\alpha\gamma}(\mathbf{r}_1,\mathbf{r}_2)=\rho_{\alpha\gamma}(|\mathbf{r}_1-\mathbf{r}_2|)=\rho_{\alpha\gamma}(r)$ can be made.

The total correlation functions $h_{\alpha\gamma}(r)$ are trivially related to the $\rho_{\alpha\gamma}(r)$ by $h_{\alpha\gamma}(r)=\rho_{\alpha\gamma}(r)/(\rho_\alpha\rho_\gamma)-1$, where ρ_σ is the number density of species σ. Using standard techniques of topological reduction [8], Madden and Glandt found the total correlation functions for a fluid-matrix system to be

$$\begin{aligned} h_{\alpha\gamma} = \{ &\text{the sum of all topologically distinct, simple, connected graphs with one root} \\ &\text{1-point of species } \alpha\text{, one root 1-point of species } \gamma\text{, some or no fluid field} \\ &\rho_f \text{ points, some or no obstacle field } \rho_m \text{ points, and some or no } f \text{ bonds} \\ &\text{between the appropriate pairs of points, with no articulation points and } \textit{no shielding sets}\} \; . \end{aligned} \tag{1}$$

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Here α and γ represent either of the components, f (for a fluid particle), or m (for a matrix obstacle). There are three types of Mayer f bonds present; they are related to the pairwise interaction potentials $\phi_{\alpha\gamma}$ by $f_{ff}=\exp\{-\beta\phi_{ff}\}-1$, $f_{fm}=\exp\{-\beta\phi_{fm}\}-1)$, and $f_{mm}=\exp\{-\beta_m\phi_{mm}\}-1$. Here $\beta=(kT)^{-1}$ and $\beta_m=(kT_m)^{-1}$, where T is the temperature at which the total system now exists while T_m is the temperature at which the matrix component was equilibrated before the thermal quench. A shielding set is defined as a set of obstacle points (root and/or field) whose removal would disconnect a graph into fragments, at least one of which is no longer connected to a root and contains at least one fluid point. The restriction of no shielding sets in Eq. (1) is what differentiates these correlation functions from those of a true equilibrium binary mixture. Physically, this restriction guarantees that the matrix particles do not rearrange when fluid is introduced.

Madden and Glandt [5] also generated a set of Ornstein-Zernike equations for the correlation functions. Given and Stell [9] showed that this set of equations was not completely consistent with the correct topological specifications given in Eq. (1) and presented a corrected set, derived from a different formalism, termed the "replica Ornstein-Zernike (ROZ) equations":

$$h_{mm}=c_{mm}+\rho_m c_{mm}\circ h_{mm} \ , \tag{2}$$

$$h_{fm}=c_{fm}+\rho_m c_{fm}\circ h_{mm}+\rho_f c_c\circ h_{fm} \ , \tag{3}$$

$$h_{ff}=c_{ff}+\rho_m c_{fm}\circ h_{mf}+\rho_f c_c\circ h_{ff}+\rho_f c_b\circ h_c \ , \tag{4}$$

$$h_c=c_c+\rho_f c_c\circ h_c \ , \tag{5}$$

$$h_{ff}=h_c+h_b \ , \tag{6}$$

$$c_{ff}=c_c+c_b \ , \tag{7}$$

where $\circ$ denotes a convolution. Here the direct correlation functions are defined in the usual way:

$$c_{\alpha\gamma}=\{\text{the sum of all graphs in } h_{\alpha\gamma} \text{ with no nodal points}\} \ . \tag{8}$$

The correlation functions with subscript b are defined as

$$h_b=\{\text{the sum of all graphs in } h_{ff} \text{ such that all paths between the two fluid root points pass through at least one } \rho_m \text{ field point}\} \ , \tag{9}$$

$$c_b=\{\text{the sum of all graphs in } c_{ff} \text{ such that all paths between the two fluid root points pass through at least one } \rho_m \text{ field point}\} \ . \tag{10}$$

Solving Eqs. (2)–(7) in an appropriate closure will yield all of the correlation functions. The traditional closures used in liquid-state theory may be applied to the fluid-matrix system. One of the simplest and most successful closure for short-range potentials is the Percus-Yevick (PY) closure. For this system we may write it as

$$c_{\alpha\gamma}=f_{\alpha\gamma}y_{\alpha\gamma} \ , \tag{11}$$

where $y_{\alpha\gamma}=[h_{\alpha\gamma}+1]\exp(\beta\phi_{\alpha\gamma})$. Equation (11) shows that in the PY closure all graphs in $c_{\alpha\gamma}$ contain an f bond directly connecting the two roots. Therefore, all of the graphs which make up c_b are neglected, and Eqs. (2)–(7) can be simplified by setting $c_b=0$. In fact, the set of equations obtained in this approximation is equivalent to the set originally proposed by Madden and Glandt [5]. Other closures may be used, but in this work we will use only PY.

Madden and Glandt [5] also derived an expression for the excess Helmholtz free energy of the fluid in the matrix

$$-\beta A_f^c=\{\text{the sum of all topologically distinct, simple, connected graphs consisting of one or more fluid field } \rho_f \text{ points, some or no obstacle field } \rho_m \text{ points, and some or no } f \text{ bonds between the appropriate pairs of points, such that the diagrams contain at least two points and are free of articulation points and shielding sets}\} \ . \tag{12}$$

Ford and Glandt [6] and Rosinberg, Tarjus, and Stell [7] have independently derived a rigorous equation for the excess chemical potential of the fluid, which may be written as

$$\beta\mu_f^c=\beta\mu_f^c(\rho_f=0)-\int_0^{\rho_f}d\rho_f'\tilde{c}_c(k=0;\rho_f') \ , \tag{13}$$

where $\tilde{c}_c(k=0;\rho_f')$ is the Fourier transform of c_c in the limit of zero wave vector. This is similar to the compressibility equation for equilibrium fluids and was found to give excellent results when applied to hard-sphere fluids in hard-sphere matrices [6,10]. In principle, Eq. (13) could be applied to systems with any reasonable interparticle potentials. However, it is well known from equilibrium liquid-state theory that when using more realistic potentials (e.g., Lennard-Jones), there are regions of state space within which no solutions to the Ornstein-Zernike equations can be found. As a result, large regions of state space are not amenable to analysis by compressibility equations like Eq. (13). This is likely also true for the fluid-matrix system and motivates the development of the perturbation theory in the next section.

III. PERTURBATION THEORY

We propose that the change in A_f^c with respect to a variation in the pair potentials can be expressed as

$$\delta(A_f^c)=\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta A_f^c}{\delta\phi_{ff}(\mathbf{r}_1,\mathbf{r}_2)}\delta\phi_{ff}(\mathbf{r}_1,\mathbf{r}_2) +2\int d\mathbf{r}_1 d\mathbf{q}_1 \frac{\delta A_f^c}{\delta\phi_{fm}(\mathbf{r}_1,\mathbf{q}_1)}\delta\phi_{fm}(\mathbf{r}_1,\mathbf{q}_1) . \tag{14}$$

Note that the vectors $\mathbf{r}_i$ denote the coordinates of fluid particles while the vectors $\mathbf{q}_j$ denote those of quenched obstacles. Equation (14) is analogous to the expression for an equilibrium binary mixture of f and m [8], the only difference is the absence of a term in $\delta\phi_{mm}$ here. Such a term should not be included for the present case because the quenched matrix structure is determined independently of the fluid, and a perturbation of the matrix-matrix potential at this level is not physically meaningful.

The pair correlation functions ρ_{ff} and ρ_{fm} can be expressed as functional derivatives of the configurational free energy

$$\begin{aligned}\rho_{ff}(\mathbf{r}_1,\mathbf{r}_2)&=2\frac{\delta A_f^c}{\delta\phi_{ff}(\mathbf{r}_1,\mathbf{r}_2)} ,\\ \rho_{fm}(\mathbf{r}_1,\mathbf{q}_1)&=2\frac{\delta A_f^c}{\delta\phi_{fm}(\mathbf{r}_1,\mathbf{q}_1)} .\end{aligned} \tag{15}$$

In contrast to the case of an equilibrium binary mixture, the matrix-matrix pair correlation function ρ_{mm} cannot be described in an analogous manner. From a graph theoretical viewpoint, this is due to the fact that all of the graphs in A_f^c contain at least one fluid field point, while the graphs in ρ_{mm} do not contain any fluid points. This reflects the physical reality of a matrix structure which is completely unaffected by the addition of a fluid.

Equations (15) can be combined with Eq. (14) to yield

$$\delta(-\beta A_f^c)=\frac{\beta}{2}\left\{\int d\mathbf{r}_1 d\mathbf{r}_2 \rho_{ff}(\mathbf{r}_1,\mathbf{r}_2)\delta\phi_{ff}(\mathbf{r}_1,\mathbf{r}_2) +2\int d\mathbf{r}_1 d\mathbf{q}_1 \rho_{fm}(\mathbf{r}_1,\mathbf{q}_1)\delta\phi_{fm}(\mathbf{r}_1\mathbf{q}_1)\right\} . \tag{16}$$

It is desirable to perform a functional integration [11] of Eq. (16) from a reference system to the system of interest. To this end, we assume that each of the two full pair potentials can be split into a reference part (subscript o) and a perturbation (subscript p) part:

$$\phi_{ff}=\phi_{ff,o}+\phi_{ff,p}, \quad \phi_{fm}=\phi_{fm,o}+\phi_{fm,p} . \tag{17}$$

If we choose the one-parameter linear scheme

$$\phi_{ff,\alpha}=\phi_{ff,o}+\alpha\phi_{ff,p}, \quad \phi_{fm,\alpha}=\phi_{fm,o}+\alpha\phi_{fm,p} , \tag{18}$$

with α varying from 0 to 1, then the integration of Eq. (16) yields

$$[-\beta A_f^c]=[-\beta A_f^c]_o+\left[-\frac{\beta}{2}\right]\left\{\int_0^1 d\alpha\int d\mathbf{r}_1 d\mathbf{r}_2 \rho_{ff}(\mathbf{r}_1,\mathbf{r}_2;\phi_{ff,\alpha})\phi_{ff,p}(\mathbf{r}_1,\mathbf{r}_2) +2\int_0^1 d\alpha\int d\mathbf{r}_1 d\mathbf{q}_1 \rho_{fm}(\mathbf{r}_1,\mathbf{q}_1;\phi_{fm,\alpha})\phi_{fm,p}(\mathbf{r}_1,\mathbf{q}_1)\right\} . \tag{19}$$

Assuming that the full pair potentials can be parametrized as in Eq. (17) and the free energy is known in the reference system, the free energy of the system of interest can be found via Eq. (19). Note that in order to calculate the free energy with this equation, the pair correlation functions must be obtained for many values of the integration variable α.

The following mean-field approximation greatly reduces the computational expense of evaluating Eq. (19) without sacrificing all of the interesting physics:

$$\begin{aligned}\rho_{ff}(\mathbf{r}_1,\mathbf{r}_2;\phi_{ff,\alpha})&=\rho_f(\mathbf{r}_1)\rho_f(\mathbf{r}_2) ,\\ \rho_{fm}(\mathbf{r}_1,\mathbf{q}_1;\phi_{fm,\alpha})&=\rho_f(\mathbf{r}_1)\rho_m(\mathbf{q}_1) .\end{aligned} \tag{20}$$

The spatial correlations between particles are thus neglected when calculating the contribution of the perturbative part of the potential. This same assumption is the basis for the van der Waals equation of state for equilibrium fluids. Since the pair correlation functions no longer depend on the parameter α, Eq. (19) can be simplified to

$$(-\beta A_f^c)=(-\beta A_f^c)_o-\beta\left\{\frac{\rho_f^2}{2}V\int d\mathbf{r}\,\phi_{ff,p}(\mathbf{r}) +\rho_f\rho_m V\int d\mathbf{r}\,\phi_{fm,p}(\mathbf{r})\right\} \tag{21}$$

for a statistically homogeneous system.

The chemical potential of the fluid in the matrix will be of primary interest for the calculation of phase equilibrium. Using the definition

$$\beta\mu_f^c = \left[\frac{\partial \beta A_f^c}{\partial N_f}\right]_{\beta,V} , \tag{22}$$

we may obtain the mean-field theory expression for the configurational chemical potential of a fluid in a quenched matrix

$$\beta\mu_f^c = \beta\mu_{f,o}^c + \rho_f \int d\mathbf{r}\,\beta\phi_{ff,p}(\mathbf{r}) + \rho_m \int d\mathbf{r}\,\beta\phi_{fm,p}(\mathbf{r}) \; . \tag{23}$$

The total chemical potential is given by $\beta\mu_f = \beta\mu_f^c + \beta\mu_f^{\mathrm{id}}$, where μ_f^{id} is the chemical potential of a bulk ideal gas at the same density and temperature as the imbibed fluid.

IV. FLUID-MATRIX MODEL

The matrix structure considered in this paper is that produced by the instantaneous quench of an equilibrium fluid of hard spheres of diameter d, at a reduced density $\rho_m d^3$; the pair density function ρ_{mm} is thus identical to that of such a fluid. The fluid particles have square-well interactions with both the matrix particles and each other

$$\phi_{ff} = \begin{cases} \infty, & 0 < r < d \\ -\varepsilon_{ff}, & d < r < \lambda_{ff} d \\ 0, & r > \lambda_{ff} d, \end{cases}$$
$$\phi_{fm} = \begin{cases} \infty, & 0 < r < d \\ -\varepsilon_{fm}, & d < r < \lambda_{fm} d \\ 0, & r > \lambda_{fm} d \; . \end{cases} \tag{24}$$

Note that we have chosen the same hard core size d for the fluid and matrix particles. Also, in this paper we will only present results for the case where $\lambda_{ff} = \lambda_{fm} = 1.25$ and $\varepsilon_{fm}/\varepsilon_{ff} = 1$. The square-well model was chosen as perhaps the simplest continuum model which exhibits liquid-vapor equilibrium. It is also convenient because it is a straightforward perturbation of the hard-sphere potential, and good thermodynamic results have been obtained for hard-sphere fluids in matrices of hard spheres [6,10]. Using the hard-sphere system as the reference, Eq. (23) can be "customized" to describe this particular model:

$$\frac{\mu_f}{\varepsilon_{ff}} = (\beta\mu_f^{\mathrm{id}})\frac{kT}{\varepsilon_{ff}} + (\beta\mu_{f,\mathrm{HS}}^c)\frac{kT}{\varepsilon_{ff}} - \frac{4\pi}{3}\rho_f d^3(\lambda_{ff}^3 - 1) - \frac{4\pi}{3}\rho_m d^3(\lambda_{fm}^3 - 1)\frac{\varepsilon_{fm}}{\varepsilon_{ff}} \; . \tag{25}$$

The subscript HS indicates the hard-sphere reference system. The quantity $\beta\mu_f^{\mathrm{id}}$ is rigorously given by $\ln(\rho_f \Lambda_f^3)$. However, the thermal de Broglie wavelength Λ_f is a function only of fluid particle mass and temperature, so we may make the substitution $\beta\mu_f^{\mathrm{id}} = \ln(\rho_f d^3)$ without altering the phase equilibrium calculations in this paper.

V. RESULTS

The first step in obtaining μ_f from Eq. (25) is to calculate the residual chemical potential of the hard-sphere fluid within the matrix $\beta\mu_{f,\mathrm{HS}}^c$. For this purpose, we chose to use Eq. (13). The c_c were calculated from the ROZ equations (2)–(7) in the PY closure (11) using the appropriate hard-sphere potentials. The numerical method of Labik, Malijevsky, and Vonka [12] was used to solve the ROZ equations; the correlation functions were discretized using a grid of 2048 points with a spacing of 0.004d. The trapezoidal rule was used to perform the numerical integration in Eq. (13), and the spacing was $\Delta\rho_f d^3 = 0.01$. The chemical potential of the fluid at infinite dilution in the matrix was calculated from the Carnahan-Starling expression [13]. More details regarding this type of calculation can be found in Ref. [6].

Once the hard-sphere chemical potential is known as a function of fluid density, a temperature kT/ε_{ff} can be chosen and an isotherm of μ_f/ε_{ff} vs $\rho_f d^3$ can be generated from Eq. (25). An example of such an isotherm is shown in Fig. 1 for a matrix density of $\rho_m d^3 = 0.1$. Note that the curve has a loop, similar to those seen in the van der Waals theory of equilibrium fluids, indicating liquid-vapor coexistence. This loop should be replaced by a horizontal line joining the two values of $\rho_f d^3$ at coexistence [14]. The coexistence density pair must satisfy the requirements of equal chemical potential and equal pressure. Using a replica formalism, Rosinberg, Tarjus, and Stell [7] have derived the correct form of the Gibbs-Duhem equation for a fluid-matrix mixture

$$0 = -V\,dp + S_f\,dT + N_f\,d\mu_f - \left[\frac{\partial\Omega_f}{\partial\rho_m}\right]_{V,T,\mu_f} d\rho_m \; , \tag{26}$$

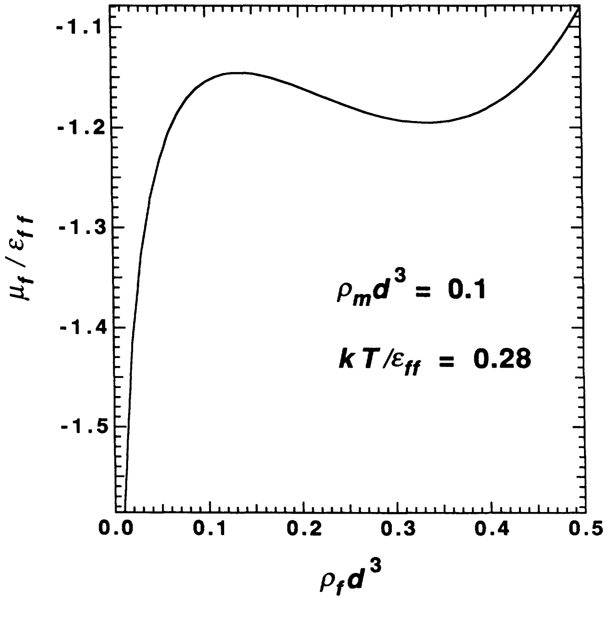

FIG. 1. An adsorption isotherm for the model system at $\rho_m d^3 = 0.1$ and $kT/\varepsilon_{ff} = 0.28$. Note the van der Waals loop, which should be replaced by a straight line joining the two coexistence densities.

where V is the total system volume, p is the pressure of the fluid, S_f is the entropy of the fluid, N_f is the number of fluid particles in the system, and Ω_f is the grand potential of the fluid. Holding the temperature and matrix density ρ_m constant, the equal pressure requirement becomes

$$\int_{\rho_1}^{\rho_2}\mu_f d\rho_f-(\rho_2-\rho_1)\mu_f(\rho_1 \text{ or } \rho_2)=0 \ , \tag{27}$$

where ρ_1 and ρ_2 are two fluid densities which have equal chemical potential. The coexistence pair for a given isotherm is determined by trial and error using Eq. (27). Adsorption isotherms at temperatures above a critical value T_c do not display liquid-vapor coexistence.

A series of adsorption isotherms for the system with $\rho_m d^3=0.1$ is shown in Fig. 2. The $kT/\varepsilon_{ff}=0.309$ curve is the critical isotherm. For any given temperature below this, there is coexistence at one particular value of the chemical potential; the locus of coexistence densities is indicated by a dotted line. This coexistence envelope is perhaps the most interesting feature in the figure, and the effects of matrix density on its shape can be seen in Fig. 3. Note that the ordinate in Fig. 3 is temperature rather than chemical potential. The solid curve is the result for a pure fluid; it was calculated from Eq. (25) by setting $\rho_m d^3=0$ and using the highly accurate Carnahan-Starling relationship [13] for $\beta\mu_{f,\mathrm{HS}}^c$. The other three curves are results for different matrix densities, as indicated in the figure. The calculation of coexistence points was not carried out for total system densities ($\rho_m d^3+\rho_f d^3$) above 0.7, so that reasonable fluidlike packing conditions were not exceeded.

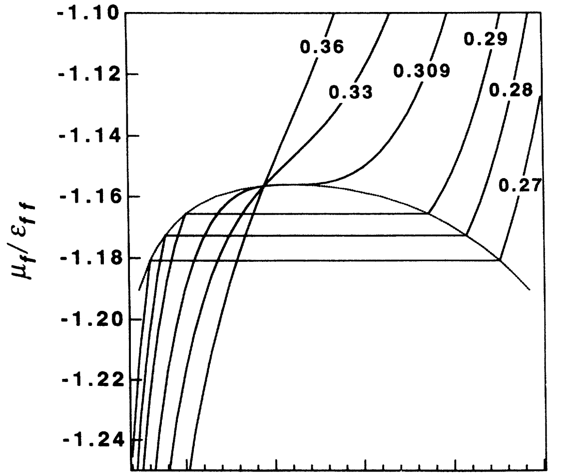

FIG. 2. A series of isotherms for the model system at $\rho_m d^3=0.1$. Each curve is labeled with the corresponding value of kT/ε_{ff}. The locus of coexistence densities is traced by the dotted curve.

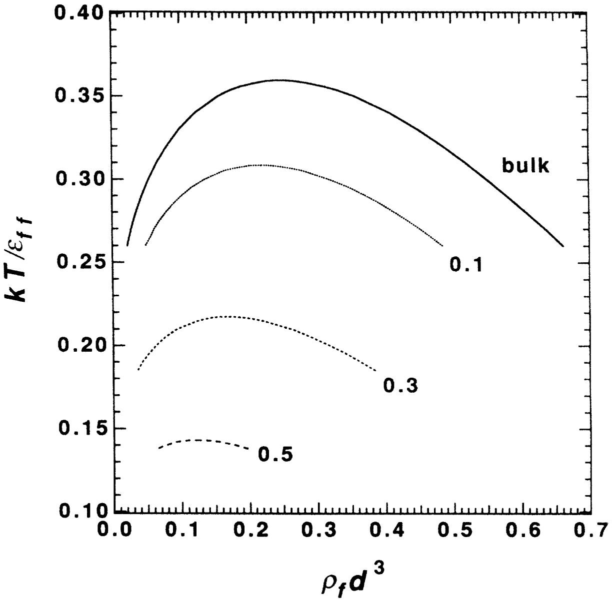

FIG. 3. Portions of coexistence envelopes. Each curve is labeled with the corresponding value of the matrix density $\rho_m d^3$.

VI. DISCUSSION

From a qualitative point of view, the results presented in the last section are somewhat in accord with previous experimental and theoretical studies. It is of interest to attempt a comparison of our results with the experimental findings of Wong and Chan [2], in spite of the fact that the interparticle potentials used here are quite simple and were in no way designed to model ^{4}He in a silica aerogel. For example, the characteristic pore size in our model was approximately equal to (or less than) the size of a fluid particle, while the structure of the aerogel was found to be fractal in nature, exhibiting no dominant pore length over the range of 20–5000 Å [2]. Thus, the model fluid considered here is much more severely confined than the one in the experiments. For our closest-matching model ($\rho_m d^3=0.1$), we found a decrease of about 15% in critical temperature from the bulk value, compared with the less than 1% decrease noted by Wong and Chan. Wong and Chan also observed an increase in critical density and a severe reduction in the coexistence curve width; we found a decrease in critical density and a more moderate shrinking of the envelope.

The phenomenon of decreasing critical temperature with increasing confinement has been observed in studies of single, geometrically ideal pores. For example, Peterson *et al.* [3] noted a decrease in critical temperature with decreasing pore radius for fluids in cylindrical pores. To make a comparison with their data, an average pore radius was estimated at each of our matrix densities using an expression introduced by Torquato and Avellaneda [15]. A plot of critical temperature as a function of the inverse of the pore radius is given in Fig. 4; the circles are our results, while the triangles represent the density functional theory results of Peterson *et al.* for Lennard-Jones fluids in cylindrical pores. The question of agreement be-

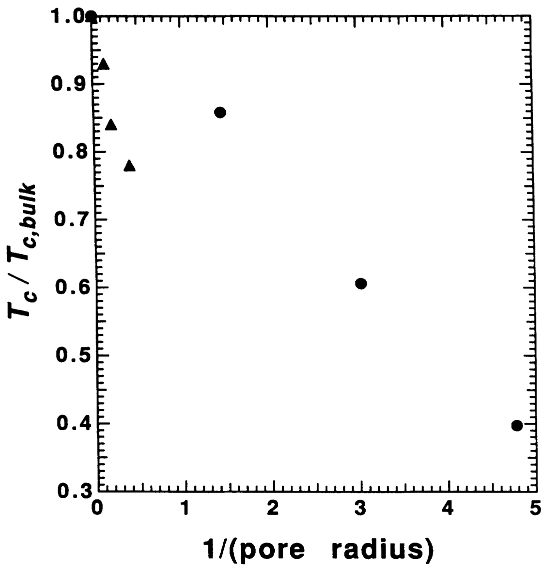

FIG. 4. Fluid critical temperature (reduced by the bulk critical temperature) as a function of the inverse of the dimensionless pore radius r^*. The circles are the results from this paper for fluids in disordered matrices, with the average pore radius estimated by the method of Rikvold and Stell [16]. The triangles are the density functional theory results of Peterson *et al.* for Lennard-Jones fluids in single cylindrical pores [3]. The pore radius is dedimensionalized by d for the results of this work and by the Lennard-Jones σ parameter for the results of Peterson *et al.*

tween the two sets of results is left unanswered as they are clearly in different regimes, with our data in the limit of an extremely confined fluid.

Maritan *et al.* [4] have recently suggested that the asymmetric random-field Ising model (RFIM) is more appropriate for the study of confined fluids than the conventional symmetric one. In that model, an uncorrelated fraction q of the lattice sites has a favorable adsorption field, while the remainder of sites have an unfavorable one. The favorable field is meant to represent the fluid-solid interaction and the unfavorable one effectively tunes the chemical potential of the fluid. They used the model to predict a schematic phase diagram for a confined fluid and suggested that the transition observed by Wong and Chan [2] was from a "vapor plus wetting layer" phase to a liquidlike phase. In a mean-field context at small q and large favorable field, their RFIM predicts that the critical temperature of a lattice fluid with infinitely long ranged interactions is given by

$$T_c = T_{c,\text{bulk}}(1-q) , \tag{28}$$

where $T_{c,\text{bulk}}$ is the critical temperature of the bulk fluid. It is of interest to attempt an extension of Eq. (28) to our continuum model. A reasonable analogue of q for the continuum model is the probability that a randomly inserted point lands inside the square well of a matrix particle. This probability can be calculated for a given matrix density using an approximate expression developed by Rikvold and Stell [16]. At $\rho_m d^3 = 0.1$, Eq. (28) yields $kT_c/\varepsilon_{ff} = 0.342$, which is 11% larger than the actual value calculated above (0.309). Agreement for higher matrix densities is worse. These differences should not be surprising if it is taken into account that the interactions in our model are short ranged and that the adsorption "sites" are highly correlated.

The asymmetric RFIM of Maritan *et al.* admits the possibility that the critical exponent of the vapor plus wetting layer to liquid phase transition has a bulklike value, rather than the much smaller value predicted by the symmetric RFIM; a bulklike exponent was indeed found experimentally by Wong and Chan. Unfortunately, neither the wetting transition nor the value of the critical exponent can be probed in the mean-field approximation. The study of wetting in a continuum fluid-matrix system requires calculation of the h_{fm} correlation function (i.e., a density profile), but such correlations are ignored in the mean-field theory. The mean-field approximation also unavoidably results in the classical value of $\frac{1}{2}$ for the critical exponent.

The mean-field theory has another important characteristic, pertaining to the square-well model in particular. It can be seen from Eq. (25) that the effects of imposed chemical potential and of the fluid-matrix interactions appear combined in the single variable

$$\mu_f + \frac{4\pi}{3}\rho_m d^3(\lambda_{fm}^3 - 1)\varepsilon_{fm} . \tag{29}$$

Thus, varying the $\varepsilon_{fm}/\varepsilon_{ff}$ ratio does not alter the shape of the coexistence envelope, but only its translational position with respect to the absolute chemical potential coordinate. The possibly interesting competition between fluid-fluid and fluid-solid attractive interactions is lost in the mean-field approach; only the total value of the attractive field matters.

There is still interesting behavior that can be explored within the mean-field approximation, however. Changing the fluid to matrix hard-core size ratio, for example, alters the coexistence envelope in a nontrivial way. Vega, Kaminsky, and Monson [10] have noted that in the limit of very large matrix particles, the structure in a Madden-Glandt system becomes very similar to that in the corresponding equilibrium binary mixture; this may imply similar thermodynamic behavior as well. The effect of correlations in the matrix structure, an important issue, could be explored by systematically varying h_{mm}. Phase coexistence of confined binary mixtures or in systems with more realistic potentials may also be studied.

It should be noted that the mean-field approximation is not inherent in our entire derivation; it may be avoided by using Eq. (19) as a starting point. Of course, the motivation for using a mean-field approach was that the correlation functions in Eq. (19) could not always be obtained in regions of interest for more complicated potentials. In this case, the phase "regions of interest" refers to the states inside the coexistence envelope. However, Lomba [17] has shown that a substantial portion of the envelope may be obtained without knowing the correlation functions at all points inside the coexistence region. Of course, an integration of the Gibbs-Duhem relationship through the region where the functions are not known is impossible, so separate routes to the chemical potential and pressure are required. It may be possible to use Eq. (19) and the definitions of chemical potential and pressure as partial derivatives of A_f to obtain a large part of the coexistence envelope, without resorting to the mean-field approximation. Another possible route to the pressure is the correct form of the virial equation for a fluid-matrix system, recently derived by Rosinberg, Tarjus, and Stell [7].

In conclusion, a perturbation theory approach to the calculation of the free energy of a fluid in a Madden-Glandt system has been presented. The theory has been applied to a simple interparticle potential model in a mean-field context and vapor-liquid coexistence diagrams for the confined fluid were obtained. It was found that the critical temperature, critical density, and width of the coexistence envelope all decreased with increasing matrix concentration. These qualitative results are in partial agreement with those from experiment, single pore models, and lattice studies. Extensions of the theory to other potential models, with and without the mean-field approximation, are under way.

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