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Phase equilibrium in a molecular model of a fluid confined in a disordered porous material

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We present a Monte Carlo simulation study of the phase diagram of an off-lattice molecular model of a fluid in a disordered porous material. The model consists of a Lennard-Jones 12-6 fluid confined in a rigid matrix of spheres and the size parameters are representative of methane in a silica xerogel. The fluid phase diagram shows effects of confinement, wetting, and matrix disorder. Our results provide evidence of two fluid phase transitions. The primary transition is analogous to the bulk vapor-liquid transition while the second transition has its origins in the wetting properties of the fluid in the more confined regions of the matrix. [S1063-651X(96)50907-4]

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The phase behavior of a fluid in a disordered porous material can be expected to be determined by a variety of effects including confinement, wetting phenomena, and how these are affected by the disordered microstructure. This problem has been the subject of considerable recent interest from both an experimental and a theoretical point of view [1]. Experimental studies of vapor-liquid and liquid-liquid phase separation have been made in a variety of porous glasses and gels [2]. These studies have shown that the phase diagram as well as the dynamics of phase separation are dramatically altered by the presence of the gel. Even extremely dilute porous materials such as aerogels can have profound effects on fluid behavior. A striking example of this is provided by the case of ^{4}He in an aerogel [3] that exhibits an extremely narrow vapor-liquid coexistence curve. There does not yet seem to be a single unifying framework within which all the experimental phenomena may be understood.

An important theoretical approach used in understanding these systems has been the study of the random field Ising model [4]. The random field describes the spatially varying preference of the medium for the different fluid phases. There is no effect of confinement in the model and correlations between the random fields that would model correlation effects of potential importance in real systems are usually neglected. Neither does the model provide a description of the role of wetting. However, the central idea of inhomogeneous and disordered equilibrium phases is a key concept in understanding these kinds of systems. Liu and co-workers [5] have suggested that the phase separation dynamics for these systems may be determined by the geometry of the wetting phases that can be modeled within a single-pore approach. Another approach is to apply the methods of liquid state statistical mechanics to off-lattice models of fluids in porous materials [6]. Only very recently have these approaches been applied to the study of phase equilibrium [7,8].

The purpose of this paper is to describe Monte Carlo simulation studies of the phase diagram of an off-lattice molecular model that provides a reasonably realistic picture of the microstructure of a disordered porous material, in this case a silica xerogel, while remaining computationally tractable. The model under consideration includes effects of confinement, wetting, and disorder on the fluid thermodynamics in a realistic way. The phase diagrams we have determined show several interesting effects. First of all, the critical temperature for the vapor-liquid transition is lower than in the bulk as expected for a confined system [9]. The coexistence curve is much narrower than that in the bulk, which appears to be a consequence of both the wetting behavior and the disorder in the matrix. The critical density is likewise determined by the strength of the interaction between the fluid molecules and the porous matrix. In addition to a vapor-liquid transition analogous to capillary condensation, our results provide evidence of an additional transition which is associated with the wetting behavior of the fluid in the denser regions of the matrix. A second transition was recently predicted using a lattice model of a fluid in a porous material using the replica Ornstein-Zernike equation in the mean spherical approximation [10]. A more detailed discussion of our work will be presented elsewhere [11].

The molecular model used in this work is based on one used by Kaminsky and Monson [12] in studies of adsorption in silica xerogel. The adsorbent matrix is modeled via a configuration of hard spheres taken from an equilibrium hard-sphere Monte Carlo simulation. In this model the size ratio between the matrix spheres and fluid molecules is 7.055:1 and the volume fraction of the hard-sphere system used to generate the matrix configuration is 0.386. The interaction between the fluid molecules and the matrix particles has been modeled in two ways. In one case the interaction was a purely repulsive hard-sphere interaction. In other cases attractive forces between the matrix particles and fluid molecules were described by the composite sphere potential in which each matrix sphere is treated as a continuum of interaction centers [12]. In order to vary the strength of the attractive forces while maintaining an approximately constant porosity for the matrix, the following strategy was adopted. The composite sphere potential for methane in silica gel was divided into attractive and repulsive parts in the manner used in the Weeks-Chandler-Andersen perturbation theory [13]. Systems with similar porosity but different attractive interaction strengths were then obtained by progressive addition of the attractive part of the potential to the repulsive reference potential. This has allowed us to investigate the effects of wettability on the phase diagram. The interactions between the fluid molecules were modeled with the Lennard-Jones 12-6 potential truncated at 2.5 molecular diameters.

The Monte Carlo simulations used in this work were carried in the grand canonical ensemble by the usual method [14]. Thirty-two matrix particles were used in a cubic cell with periodic boundaries so that the cell dimensions were about 25×25×25 fluid particle diameters. The number of fluid molecules in the system ranged from just a few at the lowest activities up to about 10^4 at the highest activities considered. The simulation runs typically involved 50×10^6–100×10^6 configurations for equilibration of the system from a given initial condition and an equal number for obtaining the ensemble averages. A configuration consisted of an attempted translation of a randomly chosen fluid molecule followed by either an attempted addition or removal of a fluid molecule. Most of our results are for a single configuration of the matrix, since this was dictated by computational limitations. This might at first seem questionable, since a 32-particle configuration may not be sufficiently representative of the statistical geometry of a hard-sphere system. However, in some cases we carried out calculations for other matrix configurations and the results are quite similar.

In these systems the conditions for equilibrium between two phases at fixed temperature are the equalities of the chemical potential and grand potential densities in the two phases. We have therefore used the Monte Carlo simulations to determine adsorption isotherms of the density versus the chemical potential and we have determined from these the isothermal relationship between the chemical potential and grand potential density [6]. The grand potential density can be determined from an isotherm of fluid density versus chemical potential by integration of the Gibbs adsorption isotherm. For low density states up to any phase transition, this integration can be performed by starting in the low activity limit where the fluid behaves as an ideal gas in an external field. For the dense phase it is necessary to determine the grand potential density at some reference state and then integrate the Gibbs adsorption isotherm starting from that state. To determine this reference state value, we first determined an isotherm of the grand potential density at a temperature above the bulk critical temperature. The grand potential at lower temperatures for dense states could then be determined by integration over temperature of a grand canonical Gibbs-Helmholtz equation. In the cases at lower temperatures where there are apparently two phase transitions on an isotherm, we have not used this procedure for the secondary transition but have simply used the steps in the adsorption isotherms to estimate the location of the transitions.

Figure 1 shows the temperature versus density phase diagram for the system with the (completely repulsive) hard-sphere interaction between the fluid and the matrix. The bulk fluid coexistence curve is also shown as calculated from the accurate equation of state of Johnson, Zollweg, and Gubbins [15], corrected for the effect of truncating the potential. The density and temperature are given in reduced units based on the Lennard-Jones collision diameter and well depth, respectively. The results indicate the presence of two transitions between fluid phases in the system. We associate the larger coexistence region with the vapor-liquid transition. Evidently, the vapor-liquid coexistence region appears at lower temperatures than for the bulk, as would be expected for such a confined system. Also, the condensed phase densities are lower than those in the bulk and the coexistence curve is substantially narrower. Some care should be taken in making such comparisons of density for systems such as the present one, since the volume fraction of the matrix needs to be accounted for and the finite size of the fluid molecules prevents the void space from being uniformly accessible. Nevertheless, in view of the magnitude of the effects seen here, it is reasonable to divide the fluid density by the void fraction to make an approximate comparison with the bulk coexistence curve. The shift in the coexistence curve and its narrowness are, to a significant extent, associated with the repulsive interaction between the fluid and the matrix, which promotes a low fluid density in the neighborhood of the matrix particles and acts to lower the density of condensed phases in the system. Computer graphics visualizations of the system provide some insight into the nature of the coexisting phases. Figures 2 and 3 show snapshots from our Monte Carlo simulations for liquid and vapor states, respectively, close to coexistence at one temperature. Notice that in both cases the spatial distribution of the molecules is highly inhomogeneous and disordered. This is the kind of picture that would be anticipated on the basis of the random field Ising model. What is particularly striking is that for the liquid phase there are extensive regions of the matrix that have very low fluid density. These are the regions where the matrix density is highest and where the repulsive fluid-matrix interaction favors low fluid density. To provide further insight into the role of the disorder, we have, for one of the temperatures, studied a system in which the matrix spheres are arranged in a fcc structure. At the same temperature, this system exhibits a much larger density change during the

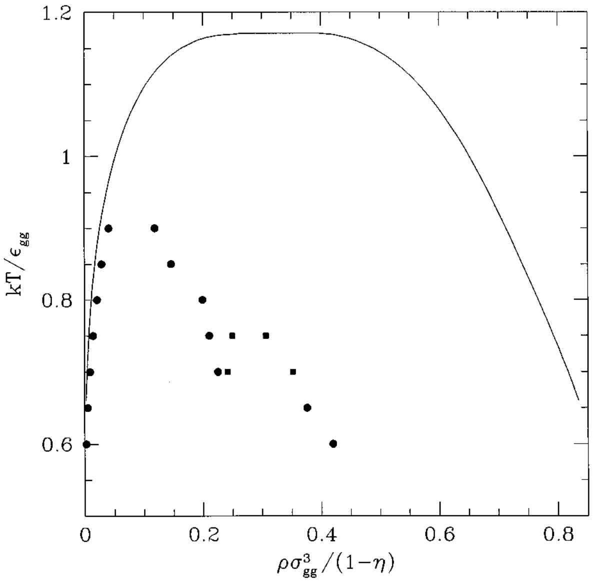

FIG. 1. Phase diagram for a Lennard-Jones 12-6 fluid in a hard-sphere matrix. The solid circles are the saturated vapor and liquid densities and the solid squares represent the coexistence densities at the second transition. The solid line is the coexistence curve for the bulk fluid. η is the volume fraction of the matrix particles and is to be taken as zero for the bulk fluid.

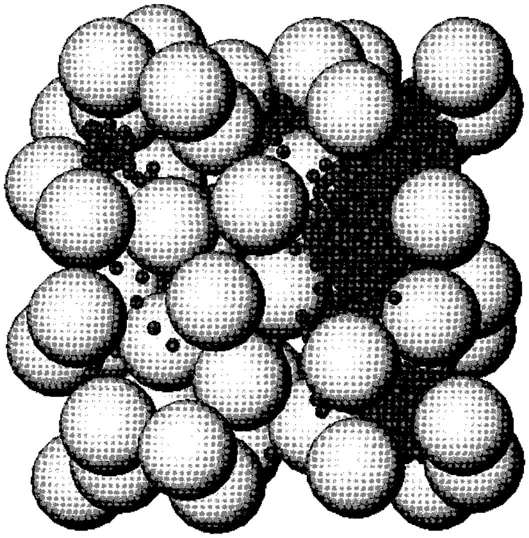

FIG. 2. Computer graphics visualization of a configuration of the fluid in the hard-sphere matrix near the saturated liquid state at a temperature $kT/\epsilon_{gg}=0.75$.

vapor-liquid transition than for the disordered system. Moreover, density distributions of the fluid for both liquid and vapor phases in this system are periodic.

We turn now to the second coexistence region that occurs at low temperature on the high-density side of the vapor-liquid coexistence region. This transition is associated with the change in the fluid density in the high-density regions of the matrix. The physics involves a competition between the repulsive fluid-matrix interactions that favor a lower fluid density in the confined regions of the matrix and the attractive forces between the fluid molecules, which tend to stabilize a high-density phase (where high density permeates a much wider region of the matrix than shown in Fig. 2). The analogy with a predrying transition for a liquid in contact with a plane surface is a tempting one, although the drying transition itself is thought to be either second order or weakly first order [16], making the possibility of observing a predrying transition for a plane surface unlikely.

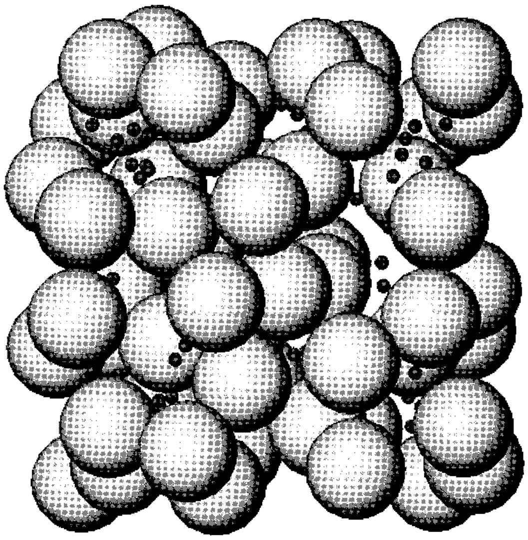

FIG. 3. Computer graphics visualization of a configuration of the fluid in the hard-sphere matrix near the saturated vapor state at a temperature $kT/\epsilon_{gg}=0.75$.

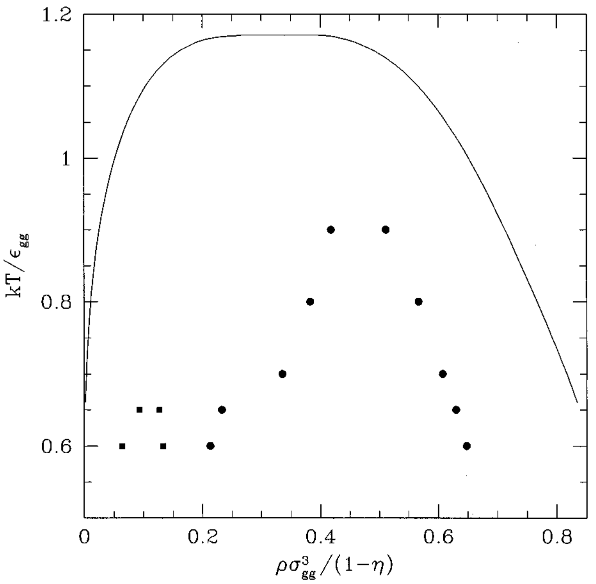

FIG. 4. Phase diagram for the Lennard-Jones 12-6 fluid in a composite sphere matrix with the ratio $\epsilon_{gs}/\epsilon_{gg}=1.144$. The solid circles are the saturated vapor and liquid densities and the solid squares represent the coexistence densities at the second transition. The solid line is the coexistence curve for the bulk fluid. η is the volume fraction of the matrix particles and is to be taken as zero for the bulk fluid.

Next we consider the case of attractive fluid-matrix interactions. We have studied various values of the fluid-matrix attractive interaction strength although here we confine our discussion to the system for which we have most completely determined the phase diagram. Figure 4 shows the phase diagram we have determined for this system. We again see evidence of two phase transitions. We associate the larger coexistence region with the vapor-liquid transition. This is now shifted to higher density than for the bulk and is quite narrow. The shift of the coexistence curve and its narrowness are again strongly associated with the attractive interaction between the fluid and the matrix, which promotes a high fluid density in the neighborhood of the matrix particles and increases the density of the vapor phase in the system. However, comparison with results for a fcc matrix again reveals a substantial role for the disorder. The coexisting phases are again inhomogeneous and disordered. The second coexistence region is again associated with the wetting behavior of the fluid in the denser regions of the matrix and again involves high density permeating the more confined regions of the matrix. This time the second transition occurs on the low-density side of the vapor-liquid coexistence curve. As in the case of the repulsive fluid-matrix interaction, we might be tempted to make an analogy with the prewetting transition for a plane surface and indeed the adsorption isotherms at the relevant temperatures are quite similar to those seen for a planar fluid-solid system exhibiting prewetting [17].

In conclusion, our results indicate that confinement, wetting, and matrix disorder are all important in the system. A key feature of our results is the inhomogeneous and disordered structure of the equilibrium fluid phases, a consequence of the disorder in the matrix. Other important features include the narrowness of the vapor-liquid coexistence region and the occurrence of the second transition at lower temperatures. These features are coupled effects of the matrix disorder and the wetting characteristics of the fluid in the matrix as determined by the relative strengths of the fluid-fluid and fluid-matrix attractive interactions.

Our system is not directly comparable to any of the systems where phase transitions have been studied experimentally. The closest experimental system to that studied here would be adsorption in a silica xerogel [12]. However, the attractive matrix-fluid interactions we have used in our calculations are considerably weaker than those for methane in silica xerogel. In fact, calculations we have done for a system more closely representative of methane in silica gel indicate that the attractive matrix-fluid interactions create a field sufficiently strong to suppress all fluid phase transitions. However, there is certainly a case to be made for further studies of fluids in xerogels at temperatures where phase transitions might occur. In any event, we believe that our results provide some insight into the molecular level behavior of fluids confined in disordered porous materials.

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