A MODEL FOR THE TWO-PHASE BEHAVIOR OF FLUIDS IN DILUTE POROUS MEDIA

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ABSTRACT

Experiments show that the coexistence region of a vapor-liquid system or binary liquid mixture is dramatically narrowed when the fluid is confined in a dilute porous medium such as a silica aerogel. We propose a simple model of the gel as a periodic array of cylindrical strands, and study the phase behavior of an Ising system confined in this geometry. Our results suggest that the coexistence region should widen out at lower temperatures, and that the narrowness observed near the critical point may be a fluctuation-induced effect.

INTRODUCTION

Simple liquids and many binary liquid mixtures exhibit phase separation below a critical temperature. When they are confined in dilute porous media such as silica gels, however, their phase behavior is dramatically altered. For example, Wong and Chan showed that the vapor-liquid coexistence curves of ^{4}He and nitrogen are shifted to lower temperatures and higher densities, and are narrowed by factors of order 15 or more[1]. In addition, Zhuang and Cannell recently found that the coexistence curve of the binary isobutyric acid/water mixture is greatly narrowed when a silica gel is present[2]. The fact that two vapor-liquid systems and a binary liquid mixture show the same behavior when confined in dilute gels suggests some degree of universality in the phenomenon. However, it is highly surprising that a small amount of impurity in the form of a dilute gel can have such a pronounced effect on the phase diagram.

In this work, we propose a simple model that permits analytical treatment and appears to capture the observed behavior. Previous theoretical approaches have concentrated on the effects of disorder in the gel structure by modeling the system as a random field Ising model[3], and have failed to reproduce the observed narrow coexistence curve. In contrast to the random field approach, we neglect disorder and instead focus on the effects of strong surface-fluid interactions, which preferentially attract one phase over the other to the surface of the gel strands. To capture aspects of the gel structure without including disorder, we model the porous medium as a periodic array of cylindrical strands. A dilute silica gel, with volume fraction between 1-5%, is a fractal network of thin strands up to some crossover length, ξ_x, typically between 20-100 nm, and is random at larger length scales[4]. By modeling this structure as a periodic system, we neglect disorder as well as the fractal character of the structure[5], but we preserve the characteristic mesh size ξ_x as the lattice spacing of the periodic network, and we retain the fact that the internal surface is correlated into strands of nonzero radius a. The model reproduces a narrow coexistence region near the critical point, in qualitative agreement with the experimental results. At

lower temperatures, however, we find that the coexistence region widens abruptly. This prediction provides a challenge to experiments.

THEORY AND ANALYSIS

The specific model porous medium that we have studied is an hexagonal array of infinitely long thin cylinders of radius a, which represent gel strands, spaced at a distance ξ_x apart. We take advantage of the proximity to a critical point to make use of universality and to couch the problem in terms of the Ising model. Thus, we picture the space in between strands as filled with a lattice of spins that can point either up or down, and that are coupled by nearest-neighbor ferromagnetic interactions. We follow previous work in the wetting literature by assuming that each cylindrical surface exerts a local surface field, H_1, that prefers spins at the surface to point up[6]. In addition, there is a uniform magnetic field, H, applied to all spins. The interesting regime is where H favors spins to point down, in opposition to H_1; if both H and H_1 favor up-spins, then the system will lie in the single-phase region with most spins pointing up[7]. We make the further approximation of coarse-graining the system and using Landau-Ginzburg theory to solve for the magnetization as a function of position, $m(\vec{r})$. The main advantage of our periodic model is that the magnetization profile is also spatially periodic. In addition, the magnetization is independent of z, the coordinate along the axial direction of the strands. It is therefore sufficient to solve for $m(\vec{r})$ in the two-dimensional hexagonal unit cell. Finally, we adopt the Wigner-Seitz approximation, replacing the hexagonal unit cell by a circular one of the same area. Thus, the final geometry that we solve is a circular annulus, where the inner radius is the strand radius a and the outer radius b is related to the distance between strands ξ_x by $b(\xi_x) = \xi_x 3^{1/4}/\sqrt{2\pi}$. In order to ensure continuity of the derivative of $m(\vec{r})$, the radial derivative of the magnetization at the boundary of the unit cell must be zero. The free energy functional to be minimized is

$$\Omega[m] = \Omega_s(m_s) + \int_a^b dr(r/a)\left[f_B(m(r)) - Hm(r) + \frac{1}{2}\kappa^2(\frac{dm}{dr})^2\right], \qquad (1)$$

where H is the uniform magnetic field and κ is a molecular length related to the interaction range. The surface free energy Ω_s is a function of the magnetization at the surface of the strand at $r = a$:

$$\Omega_s(m_s) = -H_1 m_s - \frac{1}{2}gm_s^2, \qquad (2)$$

where H_1 is the surface field and g, the surface enhancement parameter, is typically negative to reflect the fact that spins at the surface have fewer neighbors than those in the bulk[6]. Finally, the bulk free energy is

$$f_B(m) = \frac{1}{2}tm^2 + \frac{1}{4}um^4, \qquad (3)$$

where $u > 0$ sets the width of the coexistence curve of the pure system. The parameter t is proportional to the reduced temperature $(T-T_c)/T_c$. When H is negative, the minimum of

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the bulk free energy lies at a negative value of m. Thus, Eq. 1 represents the competition of three effects: the surface term favors a high positive magnetization near the strand because H_1 is positive, the bulk free energy favors a negative magnetization away from the strand because H is negative, and the square gradient term favors gradual spatial changes in the magnetization. Minimization of Eq. 1 yields a second-order, nonlinear differential equation for $m(r)$ that we solve numerically, using a relaxation method[8]. We then compute the average magnetization $\bar{m} = 2\int_a^b drr m(r)/(b^2 - a^2)$. The resulting $\bar{m}$ vs. H isotherms are used to construct the coexistence curve.

The results of the analysis are shown in Fig. 1, where we have plotted the phase diagram in the magnetization-temperature plane. The solid line represents the coexistence curve of the pure system, while the dashed line is the coexistence curve of the system confined in a 4%-volume-fraction periodic gel. Note that the presence of the gel causes the critical point to shift to higher magnetization, $\bar{m}_c > 0$, and lower temperature, $t_c < 0$. The shift towards higher magnetization results from the preference of the surface for up-spins, while the shift towards lower temperature results from the competition between the surface field, $H_1 > 0$, and the bulk magnetic field, $H < 0$, which discourages long-range order. This qualitative shift of the critical point to higher $\bar{m}$ and lower t is consistent with experimental results, but there are significant differences. For example, the dashed coexistence curve in Fig. 1 is much wider than the experimentally observed coexistence curve. The second and more significant difference lies in the position of the new coexistence curve. The right edge of the dashed curve in Fig. 1 falls outside the bulk coexistence curve, while the right edge of the experimental curve falls well inside the bulk coexistence curve[1].

The fact that a mean field treatment of the periodic model fails to yield a narrow coexistence curve may indicate that fluctuations are important. Experimental evidence also points in this direction. The narrow coexistence curves observed experimentally in the confined vapor-liquid [1] and binary liquid [2] systems lie well inside the critical region of the corresponding pure systems. Thus, mean field theory provides a poor approximation to the equation of state of the pure system in the temperature regime of the experiments.

Widom scaling represents the simplest way to include fluctuation effects; it is a phenomenological generalization of mean field theory that incorporates the effects of fluctuations on the equation of state by using renormalized exponent values[9]. The approach has been useful to several other problems involving inhomogeneous composition profiles, such as the vapor-liquid interface near the critical point[10] and the critical adsorption profile near a planar surface[11]. According to Widom scaling, one simply replaces the bulk free energy in Eq. 3 with the more general form

$$f_B(m) = \frac{1}{x}t|m|^x + \frac{1}{y}u|m|^y, \tag{4}$$

where $y > x$ and $x \geq 2$. The resulting critical exponents can be expressed in terms of x and y: for example, the coexistence curve exponent is $\beta = 1/(y - x)$, and the correlation length exponent is $\nu = \frac{1}{2}(y - 2)/(y - x)$ [12]. The choice $x = 3$, $y = 6$ yields the exponent values $\beta = 1/3$, $\nu = 2/3$, which are are close to the three-dimensional Ising estimates: $\beta \approx 0.33$, $\nu \approx 0.63$.

The results of using Eq. 4 with $x = 3$ and $y = 6$ on our periodic model are strikingly different from the mean-field results. The phase diagrams in the temperature-

magnetization plane and field-temperature plane are shown in Fig. 2. There are now two critical points crowning two narrower coexistence curves (a "double hump"). Below a triple point, marked t_t in Fig. 2, we recover the usual wide two-phase coexistence region. The triple point in the $t - \bar{m}$ diagram corresponds to the point at which two arms branch off in the $H - t$ diagram, the left-hand hump in the $t - \bar{m}$ plane corresponds to the lower arm and the right-hand hump corresponds to the upper arm in the $H - t$ diagram. We note that, although each phase may be represented in terms of a single average magnetization $\bar{m}$ as in Fig. 2, the phases are actually inhomogeneous, with high positive magnetization near the strands and lower magnetization between strands. Last, if the field H_1 is decreased below a critical value H_{1c}, the double hump disappears, leaving a single narrow hump with a shoulder. When H_1 is decreased further the shoulder disappears, and the single coexistence curve widens and moves upwards to approach the bulk coexistence curve. Since the double-hump only exists if H_1 is sufficiently strong, it can be viewed as a result of the strong surface interaction and the high surface-area/volume ratio in the periodic porous medium.

The physical origin of the double-hump behavior lies in the balance of effects that determine the shapes of the profiles. As stated above, an equilibrium profile is produced by a competition between the surface field H_1, bulk field H, and terms contributing to the interfacial energy. Increasing the exponent ν decreases the cost to form interfaces and thus alters the balance between these three effects.

Our prediction in Fig. 2 may be consistent with experimental results, which are limited to a small region near the critical point. The experimental data may represent the top of the left hump, and the right hump may exist only at temperatures below the range of the existing data. This possibility remains to be tested by experiments. Note that the width of the left-hand coexistence region is still only roughly a factor of 3 times smaller than the bulk coexistence curve, as compared to the experimentally observed factor of 15. Part of the remaining discrepancy may be due to the fractal nature of the gel, or the form of the surface interaction, which here we have crudely modeled as a contact interaction.

SUMMARY

In summary, we have shown that an Ising system confined in a dilute array of cylindrical strands shows unexpectedly rich phase behavior that may be consistent with puzzling experimental results. In particular, we find a phase diagram with two narrow coexistence curves, with two critical points, or a narrow coexistence region with a shoulder. Although experiments have observed that the coexistence region is extremely narrow near the critical point, our results imply that the coexistence region should widen at lower temperatures, below the range of existing data. The unusual behavior that we have predicted is markedly different from the phase behavior of the pure, unconfined system, and results from the strong surface interaction and the high surface-area/volume ratio of the porous medium. Both surface and bulk effects contribute to the phase behavior. The importance of both surface and bulk effects is characteristic of true mesoscopic systems such as near-critical fluids confined between two plates or in cylindrical pores. In such systems, however, the correlation length for composition fluctuations in the fluid is limited by the plate spacing
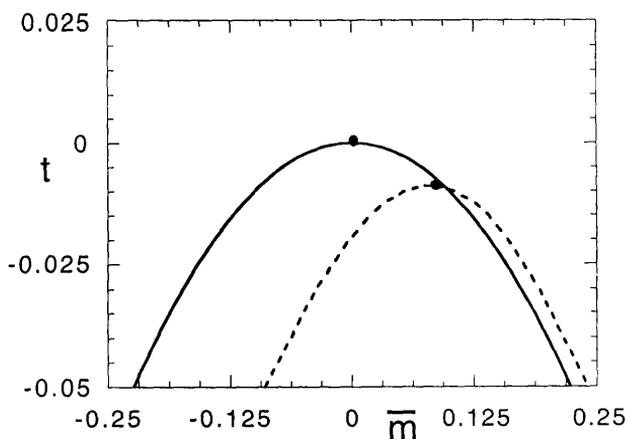
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Fig. 1 The mean-field coexistence curve of the periodic model (dashed) for a 4%-volume-fraction gel with $H_1/k_BT = 2$, $g/k_BT = -1$ and $u = 1$. The coexistence curve of the pure system (solid) is shown for comparison.
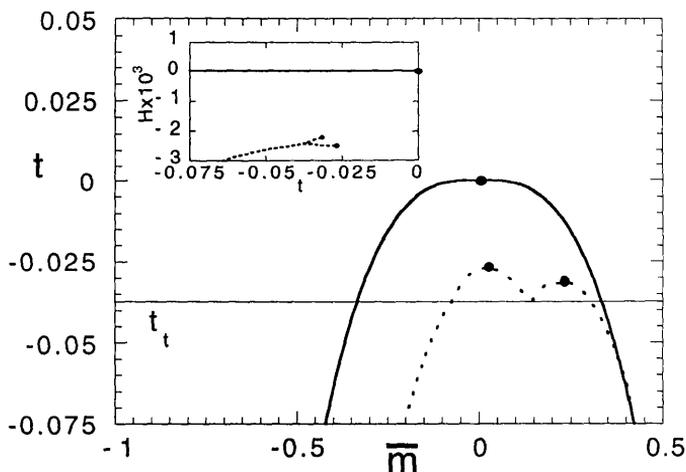

Fig. 2 The coexistence curve (dashed) of the periodic model calculated using Widom scaling under the same conditions as in Fig. 1. There are two critical points and a triple point at a reduced temperature t_t. The coexistence curve of the pure system (solid), also calculated using Widom scaling, is shown for comparison. Inset: The corresponding phase diagram in the $H - t$ plane showing the forked coexistence line (dashed); the coexistence line of the pure system at $H = 0$, $t > 0$ (solid) is shown for comparison.

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or pore size. In the case of a dilute porous medium, the fluid occupies nearly all of the sample volume, so there are no complicating finite-size effects. Thus, a near-critical fluid in a dilute porous gel is an illuminating example of a *macroscopic*, fully three-dimensional system that displays *mesoscopic* behavior. Support of the Petroleum Research Fund and Exxon Education Fund is gratefully acknowledged.

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