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Phase behavior of near-critical fluids confined in periodic gels

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Experiments show that the coexistence region of a vapor-liquid system or binary liquid mixture is narrowed dramatically 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. [S1063-651X(97)01301-9]

When near-critical simple liquids or binary liquid mixtures are confined in dilute porous media such as silica gels, their phase behavior is altered dramatically. Wong and co-workers showed that the vapor-liquid coexistence curves of ^{4}He [1] and of nitrogen [2] are shifted to lower temperatures and higher densities and are narrowed by factors of 3–14 in silica gels that occupy only a few percent of the total volume. Zhuang and Cannell recently found similar results for isobutyric acid–water mixtures [3]. The fact that all three of these near-critical fluids show the same behavior 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 paper, we propose a simple model that may capture the observed behavior. Previous theoretical approaches have concentrated on the effects of disorder in the gel structure [4–7]. In contrast, 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. A dilute silica gel, with volume fraction between 1% and 5%, is a fractal network of thin strands up to some crossover length ξ_x, typically between 20 and 100 nm, and is random at larger length scales [8]. We model this structure as a periodic system. Thus we neglect the fractal character of the structure as well as the disorder [9], 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. Only by neglecting disorder and isolating the effects of strong surface preferential attraction can we determine how important disorder really is.

When a near-critical fluid is imbedded in our periodic model porous medium, we find 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. These results provide a challenge to experiments. In addition, they show that disorder in the gel structure may be less important to the observed behavior than the large internal surface area of the gel.

The specific model porous medium that we have studied is a 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 couch the problem in terms of a Landau-Ginzburg theory for the Ising model. Thus we picture the space in between strands as filled with a magnetization $m(\vec{r})$. The main advantage of our model is that $m(\vec{r})$ is spatially periodic and 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. We adopt the Wigner-Seitz approximation, replacing the hexagonal unit cell by a circular one of the same area [11]. 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 normal derivative of the magnetization at the boundary of the unit cell must be zero. The free energy per length functional to be minimized is

$$\Omega[m] = \Omega_s(m_s) + \Omega_b[m], \tag{1}$$

where Ω_s and Ω_b are, respectively, the surface and bulk contributions to the free energy. In the following, all energies are scaled in terms of the thermal energy k_BT.

The free energy per length Ω_s is a function of the magnetization m_s at the surface of the strand at $r=a$:

$$\Omega_s(m_s) = -\frac{2\pi a}{\zeta^2}(H_1 m_s + \tfrac{1}{2}gm_s^2), \tag{2}$$

where $H_1 > 0$, the surface field, favors positive magnetization at the strand surface 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 [12]. The parameter ζ is an interaction length that we will set equal to the two-phase correlation length amplitude ξ_0^-, defined by the relation $\xi^- = \xi_0^-|t|^{-\nu}$, where ξ^- is the correlation length in the two-phase region of the bulk system and $t=(T-T_c)/T_c$ is the reduced temperature. Finally, the bulk free energy per length is

$$\Omega_b[m] = 2\pi \int_a^b dr\, r\left[f_B(m(r)) - Hm(r) + \frac{\kappa^2}{2}\left(\frac{dm}{dr}\right)^2\right], \tag{3}$$

where H is the uniform magnetic field density and κ^{-1} is a molecular length related to the interaction range. In the regime of interest, the uniform field H is negative, in opposition to the surface field H_1 [12]. The function $f_B(m)$ is the free energy density of a uniform system with average magnetization m. The Landau expansion to fourth order for $f_B(m)$ is

$$f_B(m) \propto \tfrac{1}{2}tm^2 + \tfrac{1}{4}um^4. \tag{4}$$

The coefficient $u>0$ sets the width of the coexistence curve of the bulk system and t is the reduced temperature. Minimization of Eq. (1) yields a second-order, nonlinear differential equation for $m(r)$ that we solve numerically, using a relaxation method. We then compute the average magnetization $\langle m\rangle = 2\int_a^b dr\, r\, m(r)/(b^2-a^2)$. The resulting $\langle m\rangle$ vs H isotherms are used to construct the coexistence curve.

The results of the mean-field 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 critical point shifts to higher magnetization $\bar{m}_c>0$ due to the surface field. It also shifts to lower temperature $t_c<0$ due to competition between the surface field $H_1>0$ and the bulk magnetic field $H<0$, which discourages long-range order [13]. This shift of the critical point is consistent with experimental results, but there are important differences: the dashed coexistence curve in Fig. 1 is much wider than the experimentally observed coexistence curve and, more significantly, the mean-field analysis fails to reproduce an important qualitative feature of the experimental coexistence curve. The right edge of the experimental curve falls well inside the bulk coexistence curve, so that the dense phase in the gel system is *less dense* than the dense (liquid) phase in the bulk [1]. The mean-field analysis does not capture this surprising result: the right edge
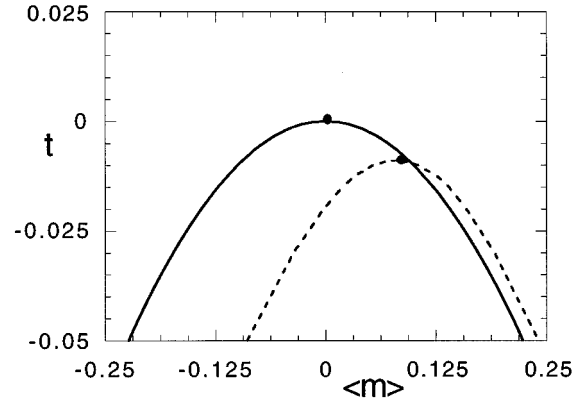

FIG. 1. Mean-field coexistence curve of the periodic model (dashed) for a 4% volume fraction gel with $H_1/k_BT=2$, $g/k_BT=-1$, and $u=1$. The coexistence curve of the pure system (solid) is shown for comparison.

of the dashed curve in Fig. 1 falls outside the bulk coexistence curve, implying that the dense phase of the gel system is *more dense* than the dense phase in the bulk.

The mean-field treatment of the periodic model may be inadequate because it neglects fluctuations. The narrow coexistence curves observed experimentally in the confined vapor-liquid [1] and binary liquid [3] 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. To rectify this, we have used a parametric equation of state, the Schofield-Litster-Ho linear model [14,17]. This general approach, of using Eq. (3) with a more accurate form for the bulk free energy f_B than Eq. (4), has been useful to several other problems involving inhomogeneous composition profiles, such as the vapor-liquid interfacial tension [15], the critical adsorption profile near a planar surface [16], and fluid interfacial tensions near a critical end point [17,18]. Note, however, that we have assumed that the exponent η is zero, while Refs. [16–18] have gone beyond our approximation by allowing η to be nonzero.

The equation of state of the linear model is described by a set of three coupled equations relating the reduced temperature t, magnetization m, and magnetic-field density H through the variables r and θ:

$$m(\theta) = r^\beta \tilde{m}(\theta),$$

$$t(\theta) = r\tilde{k}(\theta),$$

$$H(\theta) = r^{\beta\delta}\tilde{l}(\theta). \tag{5}$$

where $\tilde{m}$, $\tilde{k}$, and $\tilde{l}$ are functions that obey the symmetry properties of m, t and h, respectively. The one-phase region is described by $r>0$ and $0\leq|\theta|<1$. At coexistence, $\theta=\pm1$. The functional forms chosen by Schofield, Lister, and Ho are $\tilde{m}=\tilde{m}_0\theta$, $\tilde{k}=1-b^2\theta^2$, and $\tilde{l}=\tilde{l}_0\theta(1-\theta^2)$, where $\tilde{m}_0$ and $\tilde{l}_0$ are normalization parameters and the parameter b is given by $b^2=(\gamma-2\beta)/\gamma(1-2\beta)$ [14], where γ is the susceptibility exponent and β is the magnetization exponent. This choice is exact within the epsilon expansion to order

ϵ^2, and Fisher and Upton [17] find the linear model works reasonably well in the single-phase region even in three dimensions, using modern critical amplitude estimates [19].

The drawback of this linear model is that it is not well behaved inside the bulk coexistence region, which is where the new coexistence curve of the gel system lies. In order to explore behavior in this region, we follow Fisher and Upton and use polynomially interpolated linear models [17]. In analogy with the one-phase parametric equation of state, we use the variable $r > 1$, and a new variable $\bar{\theta}$, $|\bar{\theta}| < 1$, to describe the two-phase region, with $\bar{\theta} = \pm 1$ at coexistence. Similarly, we define

$$m(\bar{\theta}) = r^{\beta} \bar{m}(\bar{\theta}),$$

$$t(\bar{\theta}) = r\bar{k}(\bar{\theta}),$$

$$H(\bar{\theta}) = r^{\beta\delta} \bar{l}(\bar{\theta}). \tag{6}$$

The functions $\bar{m}, \bar{k}$, and $\bar{l}$ are chosen to be polynomials in $\bar{\theta}$. The coefficients of the polynomials are determined by matching to the functions $\tilde{m}$, $\tilde{k}$, and $\tilde{l}$ at the coexistence curve $\theta = \bar{\theta} = \pm 1$, so that the equation of state and its first two derivatives with respect to m are continuous there [17]. We choose $\bar{m} = \bar{m}_0 \bar{\theta}$, $\bar{k} = -(1 - c^2 \bar{\theta}^2)$, and $\bar{l} = \bar{l}_0 [\bar{\theta} - (1 + a_5) \bar{\theta}^3 + a_5 \bar{\theta}^5]$. We find that $c^2 = 2 - b^2$, $\bar{m}_0 = \tilde{m}_0$, $\bar{l}_0 = -0.3607 \tilde{l}_0$, and $a_5 = -3.0905$. The only other constraint on the form of the equation of state inside the two-phase region is the magnitude of the interfacial tension. We find that the polynomials chosen above yield an estimate of the universal ratio $U_1^+ = \sigma(\xi^+)^2/k_B T_c \approx 0.40$, where σ is the interfacial tension and ξ^+ is the correlation length above T_c at $H = 0$. This is consistent with experimental estimates $U_1^+ = 0.39 \pm 0.01$ [20].

The results of using the interpolated linear model on our periodic gel are strikingly different from the mean-field results of Fig. 1. The phase diagrams in the temperature-magnetization plane and field-temperature plane are shown in Fig. 2 [21]. There are now two critical points crowning two narrower coexistence curves (a ''double hump'') [22]. 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. Finally, 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. The magnetization profiles are shown in Fig. 3, for a fixed temperature $t = -0.068$ above the triple point at $t_t = -0.0725$. Profiles 1 and 2 coexist across the left-hand hump and profiles 3 and 4 coexist across the right-hand hump of Fig. 2. This different behavior appears to be induced by fluctuations since it does not appear in mean-field theory. However, we note that a different parametric model, namely, the trigonometric model [17], which is well-behaved in the two-phase region, produces a single wide coexistence curve for realistic parameter values [23]. Thus our analysis
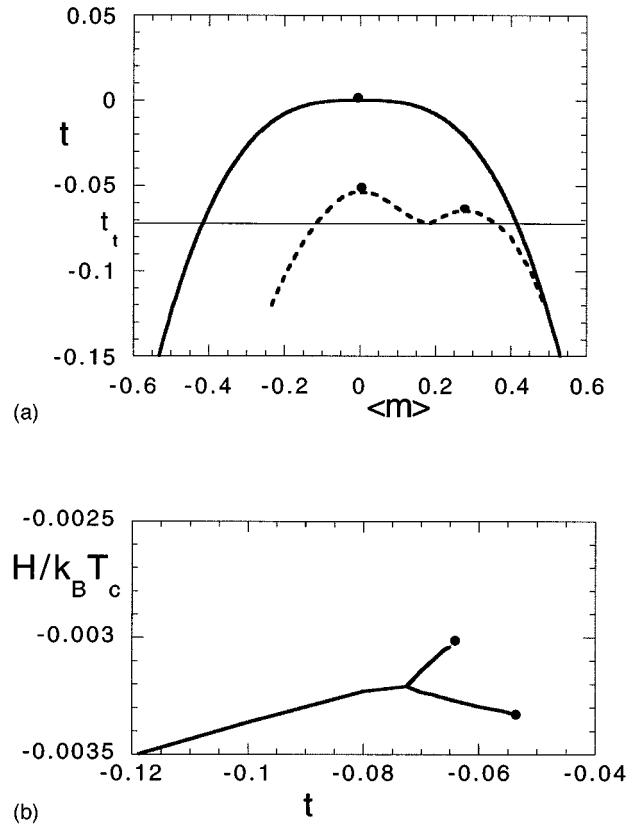

FIG. 2. (a) Coexistence curve (dashed) of the periodic model calculated using the interpolated linear model (see Refs. [16,18]) for a 4% volume fraction gel with $H_1/k_B T = 2$ and $g/k_B T = -1$. There are two critical points and a triple point at t_t. The coexistence curve of the corresponding pure system (solid) is shown for comparison. (b) Phase diagram in the H-t plane showing the forked coexistence line. The corresponding coexistence line of the pure system lies at $H = 0$ and $t \lesssim 0$.

does not *prove* that there are two critical points; it only shows that such behavior may be possible when fluctuation effects are included.

The result in Fig. 2 may be qualitatively consistent with experimental findings. Recent data of Chan and co-workers [24] show that the coexistence region does indeed widen out at lower temperatures, as we predict. The data in Refs. [1,3] may represent the top of the higher hump. Note that the width of each hump is narrower by a factor of roughly 3 compared to the width of the bulk curve. This is comparable to the narrowing observed for nitrogen in aerogel, but far smaller than the narrowing observed for ^{3}He in aerogel [2,1]. We can reproduce narrower coexistence curves by including a longer-ranged surface interaction (arising from van der Waals interactions, for example), instead of a contact surface interaction [see Eq. (2)]. When we include this, the left-hand edge of the coexistence region is shifted towards the right (higher magnetization), while the right-hand edge is nearly unaffected. Both humps remain comparable in width, so each hump becomes narrower by roughly 50%. The fractal nature of the gel may further narrow the coexistence region since positive magnetization should condense in regions dense in strands, shifting the left-hand edge of the coexist-
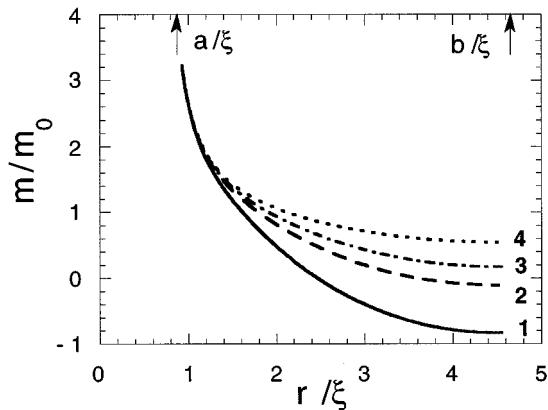
FIG. 3. Magnetization profiles corresponding to coexisting phases at a temperature $t = -0.07$ above the triple point at $t = -0.0735$. The inner radius a and outer radius b of the unit cell are shown by arrows. Profiles 1 and 2 coexist across the left hump and profiles 3 and 4 coexist across the right hump. The magnetization is scaled by the magnetization m_0 of the coexisting bulk phases and distance is scaled by the correlation length ξ of the bulk system. Thus $m(r/\xi)/m_0 = \pm 1$ correspond to the coexisting magnetizations of the pure system at the same temperature.

ence region further to the right. In addition, variations in the local gel density may shift the relative heights of the two critical points since regions less dense in gel will prefer to phase separate at higher temperatures. We note that our model does capture the important qualitative feature mentioned earlier: the dense phase of the left-hand hump is less dense than the dense phase of the pure system.

Trends in the gel volume fraction are also consistent with experimental results [1]. The gel volume fraction ϕ_g is varied in our model by changing the ratio of the outer and inner diameters of the unit cell b/a. As ϕ_g increases, the coexistence region is suppressed to lower temperatures and the humps grow narrower and more pronounced. Trends with H_1 are also sensible. As we decrease H_1, the humps become less pronounced and the coexistence region shifts upward in temperature. Below a threshold value, however, the double hump disappears leaving a narrow coexistence curve that widens out at lower temperatures into a shoulder instead of a second hump. As we decrease H_1 further, this shoulder gradually disappears, and the coexistence curve widens and moves upward to the left to approach the bulk coexistence curve [25].

Finally, we note that the appearance of a second critical point has been observed in two other calculations of near-critical fluids in porous media. Pitard, Rosinberg and Tarjus [6] have used liquid state theory to study a near-critical fluid confined in a disordered porous matrix made of quenched spheres. Within the mean-spherical approximation, they find that the coexistence region is narrowed relative to the bulk and that a second critical point appears at lower temperatures. However, in their case, the heights of the two critical points are reversed from our result shown in Fig. 2. Their results are consistent with recent Monte Carlo simulations by Page and Monson [7] on the same model [26]. Perhaps disorder additionally favors the instability of the system to two critical points and shifts the heights of the critical points relative to the periodic case.

In summary, we have shown that an Ising system confined in a dilute periodic array of cylindrical strands can show unexpectedly rich phase behavior that may be consistent with puzzling experimental results. Although the coexistence region is extremely narrow near the critical point, our results imply that it should widen at lower temperatures. 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 to volume ratio of the porous medium. Both surface and bulk effects contribute to the phase behavior. This is characteristic of true mesoscopic systems such as near-critical fluids confined between two plates. In such systems, however, the correlation length for composition fluctuations in the fluid is limited by the plate spacing. In dilute aerogels, 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.

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