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Phase Separation and Metastability in Binary Liquid Mixtures in Gels and Porous Media

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1. Introduction

Recently, experiments were performed [1] with gels immersed in binary liquid mixtures such as water-lutidine or water-isobutyric acid chosen for their well studied demixing curves and consolute points conveniently located at room temperatures. The gels used are either agarose or polyacrylamide.

One of the most striking phenomena that is observed as the sample approaches the demixing curve from the one-phase region is a gradual appearance of opalescence in a range of a few degrees. This opalescence should be distinguished from critical opalescence seen in the pure A/B mixtures only in the vicinity of the consolute point (in a range of temperatures not wider than mK°). On the contrary, the opalescence here persists even in the two-phase region of the pure A/B mixture, and one does not observe a complete phase separation inside the gel. Nevertheless, since the onset of opalescence resembles qualitatively the demixing curve of the pure A/B mixture, it was suggested [1,2] that a phenomenon of droplets pinning by the random gel structure inhibits a complete phase separation. This effect is quite similar to domain states that are seen [3] in diluted antiferromagnets in presence of a magnetic field. In those systems, as one cools down in presence of the field, neutron scattering experiments show that even at low temperatures the system is composed of domains that are pinned by the random field.

The gel + A/B system has two characteristic lengths : one is the mesh size of the gel (L) and the other is the bare fluid-fluid correlation length (ξ). The behavior is determined by a comparison between these two lengths. In section 2 we show that for $\xi > L$, an analogy can be made between the gel + A/B mixture and random field in magnetic systems. After discussing the equilibrium state in section 3, we generalize a theory proposed by VILLAIN [4] and apply it to the gel case. An explanation of the observed opalescence via droplets pinning by the random structure is given in section 4 and our conclusions in section 5.

Finally we would like to note that although reported experiments exist only for the gel + A/B systems, similar behavior (at least in the regime $\xi > L$) is expected for A/B mixtures in porous solids.

2. Connection with Random Fields

Pure A/B liquid mixtures are usually described by lattice gas models; we would like to extend these models to binary liquid mixtures in a gel. The gel always has an heterogeneous chemical structure. We focus here on rigid gels, which thus act on the liquid mixture as a source of quenched disorder (the same assumption is correct for porous solids). In the opposite limit of flexible gels, thermal fluctuations become important, and one should consider the binary liquid mixture in the gel as a ternary system.

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The main effect of the gel on the A/B mixture is a preferential adsorption [2] of one of the liquid components (in our case the water-component A).

We will describe the system in the regime $L < \xi$ (tight gels or temperatures close to the consolute point). Since ξ is large, the system can be divided into blocks of size L (coarse graining); in each block there is an effective random field $H(r)$ proportional to the average gel concentration in the block. The average of $H(r)$, $\langle H(r) \rangle$, expresses the total preference of the gel plus a contribution from the concentration difference between the liquid inside the gel and in the A/B reservoir into which the gel is immersed. We first discuss the case $\langle H \rangle = 0$ and then include the effect of a non-zero $\langle H \rangle = h$. The order parameter of the system (analogous to the magnetization in magnetic systems) may be defined as $M = (C_A - C_B)/(C_A + C_B)$ where C_A (C_B) is the number density of A (B). The strength of the random field is characterized by the r.m.s. deviation H .

3. Equilibrium Behavior

For convenience, we study a system with an upper critical point for which phase separation occurs at low temperatures. As the system is cooled down from the one-phase region, at thermodynamical equilibrium, a phase separation should be seen as well as a consolute point that depends on the strength of the random field, $T_c(H) < T_c(0)$. This statement is based on the fact that the lower critical dimension (d_l) of the random field Ising model is believed to be two, $d_l = 2$ [5]. Thus demixing occurs in $d = 3$ for small enough random fields, and the shift of the critical temperature is expected to scale as $T_c(H) - T_c(0) \sim H^{-2/\gamma}$ where γ is the compressibility exponent. In the gel, the strength of the random field (i.e. the fluctuations of the gel structure) cannot be varied in a controlled way, thus such a scaling law cannot be verified. Moreover, good estimates for H are difficult to obtain.

In actual experiments, the gel is in contact with an A/B reservoir and the demixing curve is shifted towards higher concentrations of B since the concentration inside the gel and in the reservoir are not the same. Rather in order to balance the chemical potential difference due to the gel preference, the system reaches its equilibrium by creating a difference in concentrations; C_B (in the gel) $< C_B$ (in the reservoir).

To summarize, we expect to see for $\xi > L$ and rigid gels, phase separation in the gel + binary mixture at thermodynamical equilibrium for small enough randomness. Additionally, a shift towards higher C_B values and towards lower temperatures is expected for the demixing curve as a function of the *total* (gel + reservoir) concentration of B. These conclusions coming from equilibrium considerations are not very satisfactory, since they do not provide an explanation to the observed opalescence. In the next section such an explanation based on metastability is proposed.

4. Metastability and Droplet States

In this section we follow some ideas of VILLAIN [4] and propose a theory that explains how the system can be trapped in metastable domain states although phase separation is energetically more preferable. The theory is constructed by assuming a rapid quench from high temperatures to temperatures below T_c . Our starting point is to write the energy barrier between two metastable states. We concentrate on a single domain of "spins down" (a droplet rich in B) with a well-defined radius R embedded in a region of "spins up" (rich in A). At equilibrium, this domain disappears, since phase separation is expected in three dimensions ($d_l = 2$). However, due to effects of random field pinning [4,6] changes in the domain interface are carried out by jumps over energy barriers that exist between "successive" metastable states. Each one of these states is characterized by an average displacement w (which should

be distinguished from the width of the interface (the correlation length ξ). As long as $R > \xi$ the domain is well defined. An expression of the energy barrier would include the following three terms [6] :

$$\Delta F(w,b) = -g \left[b^{d-1} \left(\frac{w}{b}\right)^2 + b^{d-1} \left(\frac{w}{R}\right) \right] + HM (b^{d-1}w)^{1/2}, \quad (1)$$

where g is the interfacial tension between A and B, H is the strength of the random field, M is the magnetization and b is the length scale ($b < R$) for which we consider the interface roughness (w). For each b , maximizing ΔF with respect to w gives the maximal energy barrier :

$$\Delta F_{\max}(b) = g (HMb/g)^{4/3} \quad \text{when } w/R > (w/b)^2 \quad \text{and } d = 3 \quad (2)$$

and

$$\Delta F_{\max}(b) = Rg (HM/g)^2 \quad \text{when } w/R < (w/b)^2. \quad (3)$$

ΔF_{\max} is thus an increasing function of b . The minimal domain size is obtained by comparing ΔF_{\max} in (3) with the available thermal fluctuation kT :

$$R_{\min}(H) = gkT (HM)^{-2} \quad (4)$$

For $R < R_{\min}$, $kT > \Delta F_{\max}$ for all b and the domain will disappear due to thermal fluctuations, whereas for $R > R_{\min}$, $kT > \Delta F_{\max}$ only for the smaller lengths thus pinning of domains is possible for some larger length scales ($b < R$). Equation (4) expresses the temperature-dependence of R_{\min} as the temperature is quenched rapidly from high T . For slow cooling, a freezing of domains is rather expected at T close to T_c since at lower temperatures there is even less thermal fluctuation. This could be the source of opalescence in the gel + A/B experiments.

We consider now a random field with non-zero average h [6] proportional to the distance, in terms of concentration, to the coexistence curve. For the energy barrier (1), a constant field will add a term of the form $hM (wb^{d-1})$ which has the same dependence on w and b as the second term in (1), namely it will just renormalize the radius R_{\min} . In the presence of a constant field h , $R_{\min}(H,h)$ is related to $R_{\min}(H,0)$

$$R_{\min}^{-1}(H,h) = R_{\min}^{-1}(H,0) - hM/g \quad (5)$$

or using (4)

$$R_{\min}^{-1}(H,h) = (HM)^2/gkT - (hM)/g < R_{\min}^{-1}(H,0). \quad (6)$$

For a fixed H , there is a line in the $T - h$ plane for which $R_{\min}(H,h) \rightarrow \infty$. This "freezing line"

$$kT_g = (HM)^2/(hM) \quad (7)$$

is the separation between equilibrium (reversible) behavior at high T and h and between metastable (frozen) behavior at low T and h .

For the gel + A/B this means that freezing of metastable states will occur all around the consolute point ($h \neq 0$). We believe that this is the reason why the onset of opalescence follows the demixing curve. Hysteresis, which usually is associated

with metastability, can be seen if one cools in constant field $h > 0$ or one cools with $h = 0$ and then applies a constant field. For the two procedures different curves for the onset of opalescence is predicted [7].

5. Conclusions

The behavior of binary liquid mixtures immersed in a gel cannot be explained only from equilibrium considerations, and we rather propose an explanation related to random field effects. For $\xi > L$, the opalescence seen in these systems is explained as a phenomenon of domains freezing due to the random structure of the gel. In the other limit $\xi < L$, the problem resembles biphasic flows in porous media [2]. Experimentally, this situation can be achieved by cooling a rich-A gel ($M \approx M_0$) to low temperatures and then increasing the concentration of B in the reservoir ($M \approx -M_0$). In this regime, $\xi < L$, interesting quantities such as the threshold of macroscopic invasion of the other phase into the gel depends on the details of the gel structure [8].

As for additional experiments, it will be interesting to perform experiments where the liquids concentration is also a varying parameter as well as the temperature. Moreover, a method that measures directly the concentration inside the gel (rather than the total gel + reservoir) will facilitate making more quantitative predictions.

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