Simple views on critical binary liquid mixtures in porous glass

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A simple scenario, different from previous attempts, is proposed to resolve the problem of the slow phase separation dynamics of binary liquid mixtures confined in porous Vycor glass. We demonstrate that simply mutual diffusion, renormalized by critical composition fluctuations and geometrical hindrance of the porous glass, accounts for the slow phase separation kinetics. Capillary invasion studies of porous Vycor glass by the critical isobutyric acid–water mixture, close to the consolute solution temperature, corroborate our analysis.

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Despite diligent efforts through a variety of experimental, theoretical, and numerical work, no general concensus has emerged concerning the phase separation behavior of binary liquid mixtures confined in porous Vycor glass, except that such processes appear extremely slow compared to the bulk [1–18]. Two different approaches, the random field Ising model [1,2] and the single pore picture [7], attempted to account for these observations. In the random field Ising model, pinning of composition fluctuations is assumed to occur when the coherence length of the fluctuations becomes larger than the typical pore size; the variations of the chemical potential, due to the randomness of the glass over this length scale, would be at the origin of such effect. In the single pore picture, wetting due to confinement would limit domain growth to roughly the typical pore size. In this work, we propose a simpler scenario in order to elucidate this problem. Close to the consolute solution point, simply mutual diffusion, with renormalized transport coefficients arising from composition fluctuations and the geometrical hindrance imposed by the random porous network, accounts for the slow phase separation dynamics in porous glass.

In bulk, the dynamical evolution of a binary liquid mixture, following a temperature quench below the critical solution temperature T_c is governed by a range of successive and distinct mechanisms which bring the system to thermodynamic equilibrium [19]. For a temperature quench at the critical composition, the initial stage of phase separation involves an unstable state undergoing spinodal decomposition triggered by thermal fluctuations of the composition. ''Up hill'' mutual diffusion produces segregation and amplification of spatial modulations of composition. As nonlinear effects set in, well-defined domains with almost the final equilibrium concentrations and sharp interfaces are progressively formed. Interface-induced flow leads to further coarsening of the domains. A subsequent hydrodynamic instability, arising from a competition between interfacial and gravitational stresses, ruptures the interconnected domain structures. The resulting sedimentation of domains due to buoyancy forces brings the liquid to its stratified two-phase thermodynamic equilibrium structure.

Porous Vycor glass [20] is characterized by an interconnected porous network with a typical pore diameter [9] of 7 nm. Clearly, phase separation of a liquid mixture in such a confined environment cannot proceed through mechanisms involving macroscopic features such as distinct interfaces, hydrodynamic flows, and domain sedimentation. Nevertheless, both the random field Ising and single pore scenarios, which evolved from the interpretation of light-scattering studies [3–6,8,12], assumed the presence of domains with well-defined compositions and interfaces in the porous medium [1–16]. In contrast, nuclear magnetic resonance (NMR) studies [17] showed no evidence for such domain structures in Vycor glass. However, some composition variations on macroscopic scales were observed with NMR microimaging 14 days following the quenching of the temperature [17].

Thus, of all the liquid-liquid demixing mechanisms observed in bulk [19], mutual diffusion appears to be the only physically plausible process that could survive in the confined environment of porous Vycor glass. Such a sole diffusive process would bring about material equilibrium, albeit resulting in slower phase separation kinetics in absence of other mechanisms. Moreover, geometrical hindrance imposed by the random porous network would lead to further reduction of diffusion.

To estimate time scales associated with this simple proposal, first consider the mutual diffusion coefficient of composition fluctuations represented by the Stokes-Einstein relationship $D = kT/5\pi\eta\xi$, where k is Boltzmann's constant, T the temperature, η the dynamical viscosity of the liquid, and ξ the correlation length of the critical composition fluctuations. Below T_c, $\xi = \xi_0(1 - T/T_c)^{-v}$, with ξ_0 a system dependent amplitude, and v the critical exponent. For the isobutyric acid–water (IBA-H$_2$O) mixture [21]. $T_c = 26.9\ °C$, and $\xi_0 = 3.62$ Å. At 1 °C below T_c, with $\eta = 2.35 \times 10^{-2}$ Poise for this mixture [21,22], and with $v = 0.625$ from renormalization group calculations, one finds $D = 8.83 \times 10^{-8}$ cm^2/s. Hence, mutual diffusion of composition fluctuations would require 150 days to spread along a distance of 1.5 cm. This critical slowing down arises from the renormalization of the transport coefficient by critical composition fluctuations.

When a liquid mixture is imbed in Vycor glass, further reduction of mutual diffusion would occur due to the tortu-

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osity of the porous network. To evaluate this effect, consider self-diffusion of a pure liquid confined in such a medium. For instance, the self-diffusion coefficient of cyclohexane in porous Vycor glass is decreased by a factor of 3.3 with respect to its bulk value [17]. If such a factor is applicable for mutual diffusion, then 1.4 year would be required for composition fluctuations of IBA/H_2O described above to diffuse along a 1.5 cm sample of Vycor glass.

While self-diffusion does not exhibit critical behavior, additional lowering of self-diffusion coefficients in a critical binary mixture in a porous medium is nevertheless observed [17]. The self-diffusion coefficient of cyclohexane in the aniline–cyclohexane critical mixture below the bulk T_c in Vycor glass, is reduced by a factor of 11.8 compared to the bulk value of cyclohexane. Curtailing mutual diffusion by this factor, implies that almost five years would be needed for IBA/H_2O fluctuations to disperse along a Vycor glass rod as sketched above.

Thus, mutual diffusion of composition fluctuations can account for the slow phase separation dynamics observed in porous Vycor glass. To substantiate this simple view, we have investigated the capillary flow invasion of the critical IBA/H_2O mixture in porous Vycor glass above and close to T_c. The invasion bears resemblance to phase separation since both processes involve transport properties to achieve material equilibrium in a porous medium.

Our capillary flow invasion experiments involve the displacement of nitrogen gas in Vycor glass by the critical IBA/H_2O binary mixture. The invasion length R of a liquid in a porous glass at time t is given by a modification of the Washburn-Rideal equation [23,24], i.e.,

$$R^2 = \frac{r \gamma \cos(\theta)}{2q \eta} t, \qquad (1)$$

where r is the typical pore radius, γ the surface tension, θ the contact angle, and q a dimensionless factor to take into account the tortuosity of the porous network; $q = 2.43$ for porous Vycor glass [24]. The invasion diffusion coefficient, D_I, was measured for IBA and H_2O individually, and for the mixture at the critical composition of 0.396 weight fraction of IBA, as a function of temperature. The experimental values of D_I were compared to those calculated from Eq. (1) by measuring γ with the bubble pressure method [25], with the temperature dependence of η [21,22,26], known values for q [24] and r [9,20], and using θ as an adjustable parameter.

The experimental protocol involved dropping a clean porous Vycor glass sample, perfused with N_2 gas, partly into the liquid which consisted of either H_2O, IBA, or the critical mixture. Nitrogen plays a passive role in the experiments; Vycor samples dried under vacuum produced identical results. The invasion process was filmed with a video camera. Due to the difference in refractive index of Vycor imbibed with N_2 or liquid, R could be easily measured from a video monitor (see Fig. 1). Spectroscopic grade IBA was obtained from Aldrich Chemical, verified with gas chromatography mass spectrometry, and used without further purification. Water was deionized to 18.0 $M\Omega$ cm with a Barnstead Nanopure system. T_c was determined visually, before and after each run of invasion, by slowly reducing the temperature and observing for phase separation of the bulk critical mixture.
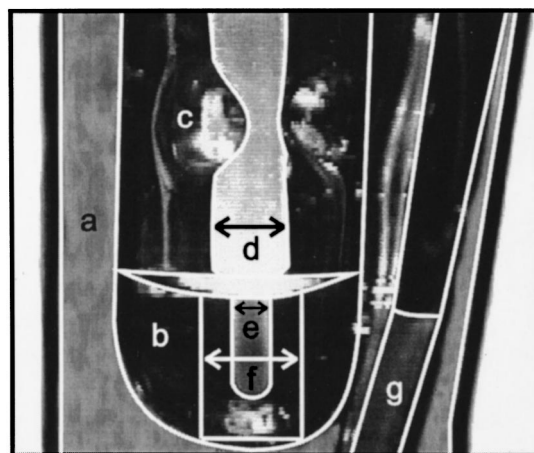

FIG. 1. Digitized image of the capillary invasion cell: porous Vycor glass cylinder imbibed with N_2 gas above (d) and in (e) the critical mixture (b). The Vycor glass cylinder is held vertically by positioning protuberances (c). The whole cell is immersed in a water bath (a) monitored with a platinum temperature probe (g). The distinction between the Vycor cylinder diameter in air (d) and in the critical mixture (f) arises solely from differences in refractive indices. The invasion length R is given by the difference in distances $(f - e)/2$.

Five independent runs of invasion were performed at each temperature. The temperature was monitored with a platinum probe, and controlled with a Haake F3 bath and Lakeshore DRC-93CA temperature controller to within ±5 mK over a 20 min. period. Porous Vycor glass rods (3.6 mm diameter) were obtained from Corning, thoroughly cleaned according to their procedure [20], and washed with copious amounts of water to remove all acid.

Figure 2 shows the kinetics of some typical invasion profiles for IBA, H_2O, and the critical mixture (CM) at 31 °C. The solid lines represent the initial behavior of R^2 as calculated from Eq. (1) with $\theta_{H_2O} = 0°$, $\theta_{IBA} = 53.1°$, and $\theta_{CM} = 31.8°$. These contact angles were kept fixed for all calculations of D_I at all temperatures. The deviations from linearity observed with increasing time in Fig. 2 can be ascribed to dimensionality and surface tension effects. Figure 3 displays the temperature dependence of the experimental D_I (data
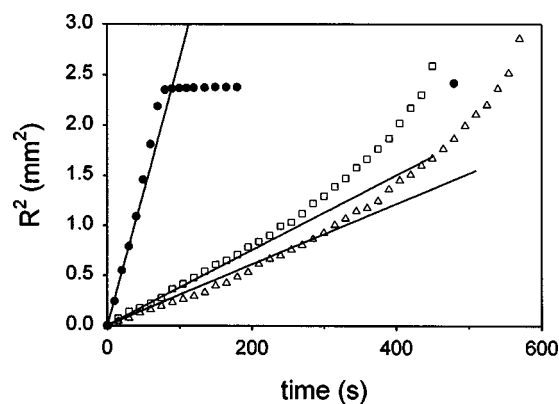
FIG. 2. Kinetics of invasion profiles of H_2O (circles), IBA (squares), and the critical mixture (triangles) with the corresponding calculated initial profiles (solid lines) from Eq. (1) as described in the text.
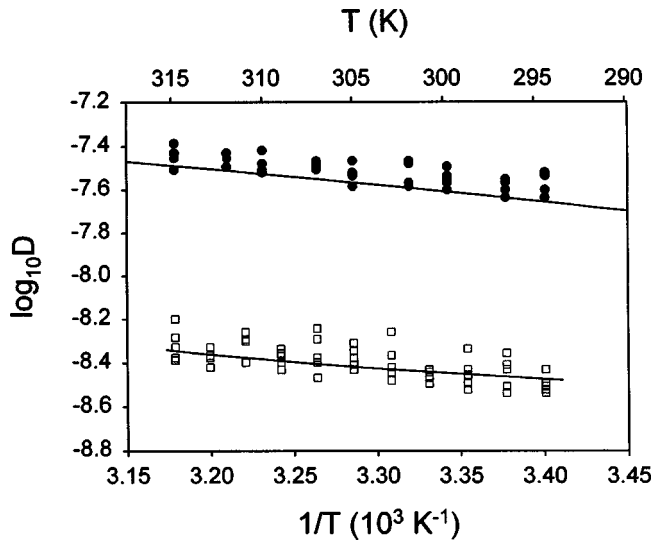
FIG. 3. Temperature dependence of the experimental invasion diffusion coefficients for H_2O (circles) and IBA (squares) and corresponding calculated values (solid lines) based on Eq. (1) as described in the text.

FIG. 4. Temperature dependence (reduced temperature T_r) of the experimental invasion diffusion coefficients (D) for the IBA/H_2O critical mixture (data points where the typical error bars represent one standard deviation) and the calculated values (solid line) based on Eq. (1) as described in the text. Also superimposed is the temperature dependence of the bulk correlation length, ξ, with the diamond corresponding to $\xi = r$ the typical pore size.

points) and the calculated values (solid lines) from Eq. (1) for H_2O and IBA. The activation energies are 2.82 ± 0.37 kcal/mole for H_2O, and 3.44 ± 0.55 kcal/mole for IBA.

The experimental (data points) and calculated (solid line) D_I are shown for the critical mixture of IBA/H_2O as a function of the reduced temperature $(T - T_c)/T_c$ in Fig. 4. Superimposed is the bulk correlation length of the critical composition fluctuations (dashed line, the diamond corresponds to $\xi = r$). As ξ grows beyond the typical pore size, the occurrence of metastability, as expected from the random field Ising model and the single pore picture, would presumably lead to a decrease or even the vanishing of D_I in contrast to the behavior observed in Fig. 4. Selective invasion by a preferential wetting phase only, for instance water or a water-rich phase, should yield different calculated values for D_I in Fig. 4 and would be inconsistent with NMR results of binary mixtures in porous Vycor glass [17,27]. The surface tension of a binary liquid mixture does not exhibit critical behavior [28]. However, the dynamical viscosity is renormalized by critical composition fluctuations [21,22]. Thus, the agreement between the experimental and the calculated D_I, which
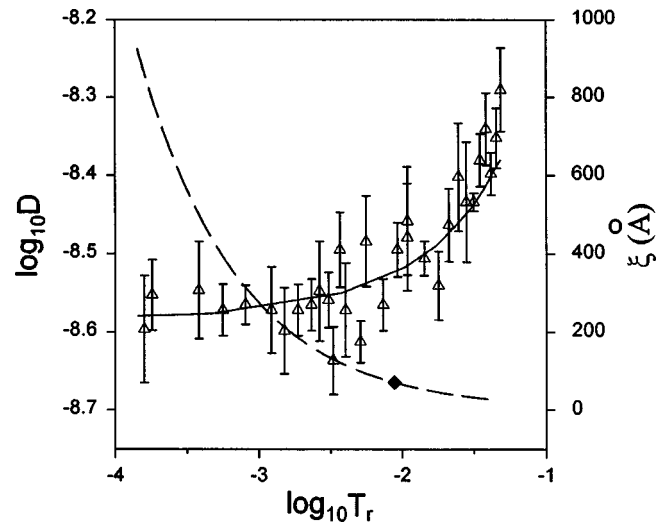
both reflect the presence of critical fluctuations, confirms that only the renormalization of transport coefficients are required to rationalize the data.

Both phase separation and capillary invasion of the critical binary mixture IBA/H_2O in porous Vycor glass can be explained simply on the basis of the renormalization of mutual diffusion by critical composition fluctuations and geometrical hindrance imposed by the porous network. Other critical binary mixtures in porous Vycor glass should behave similarly by appealing to universality. While some aspects of critical binary mixtures in porous media might be related to features advocated by the random field Ising model [1,2] and the single pore picture [7], our analysis demonstrates that these scenarios are not necessary to explain the slow phase separation kinetics.

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