Liquid-Liquid Equilibria in Porous Glasses:
Molecular Simulations and Experimental Results

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Abstract

We present results from experiments and simulations for the effects of confinement on liquid-liquid phase equilibria. Experimental phase diagrams for the nitrobenzene/n-hexane mixture in controlled pore glasses are obtained by nonlinear dielectric effect and light transmission measurements. We also use computer simulations of a Lennard-Jones mixture in several cylindrical pores to study the short-time dynamics of phase separation upon temperature quenching.

(translated abstract goes here)

1. Introduction

The best-known phase transitions in porous systems are those of capillary condensation (the analogue of the liquid-vapor transition in the bulk phase) and wetting (in which a liquid in contact with a surface abruptly covers it as a thick layer.) Other bulk phase transitions also have confined analogues; in this study we consider the liquid-liquid transition.

Liquid-liquid equilibria are of interest in connection with oil recovery, lubrication, coating technology, water purification, and chromatography. The effects of confinement on the shape and position of the liquid-liquid coexistence curve are largely unknown, but are of great importance in these areas.

In this paper we present results from experiments and computer simulations concerning the thermodynamic and kinetic properties of liquid-liquid phase separation in very small pores. The experimental systems are a mixture of nitrobenzene and n-hexane adsorbed in two different samples of controlled pore glass; we have determined complete constant-pressure phase diagrams for these systems. These experiments suggest that phase separation in pores is kinetically limited; the presence of the pore structure prevents the liquids from separating into two macroscopic domains, as they would in a bulk system. For the simulation study we have chosen an idealized single-pore model and studied the dynamics of phase separation, in order to better understand this kinetic effect.

Porous glasses are often used as a stationary phase in chromatography [1, 2]. Controlled pore glasses (CPGs) and the related Vycor glasses have excellent mechanical properties and

can be prepared with a wide range of porosities and pore sizes [3]. The pore size distribution of these materials is approximately gaussian, and quite narrow. They can be modified to include a variety of functional groups, and the adsorption strength of the glasses can be adjusted over a wide range of values [2]. CPGs have highly networked structures with locally cylindrical pore sections, as shown by electron microscopy [2]. Because these materials are considered "well-characterized" and can be prepared with a wide range of properties, they have been used frequently as a substrate in the study of the fundamental properties of confined systems [4–6].

2. Experimental method

We have studied a mixture of nitrobenzene and n-hexane in the bulk phase and in two different porous glasses, with mean pore diameters of 100 nm and 7.5 nm, and void volumes around 35%. The glass samples were from Bio-Rad (100 nm sample) and CPG, Inc. (7.5 nm sample) and were chemically inert and contained no ions.

We used non-linear dielectric effect (NDE) and light transmission measurements to determine the (T,X) phase diagrams in both bulk and pore systems. These methods have been described in greater detail elsewhere [4, 7]; we give only a brief description here. Each set of measurements was made along a path of decreasing temperature at constant composition. The initial temperature was above the liquid-liquid critical point, and was reduced until the phase transition was observed. This was repeated at different compositions to find the entire liquid-liquid coexistence curve.

The nonlinear dielectric effect is defined as the change in the medium permittivity in a strong electric field. NDE is sensitive to fluid inhomogeneities and diverges as the temperature is brought near to the critical temperature; it can thus be used to locate the phase boundary near the critical point.

We also used light transmission data to determine the temperature at which phase separation occurs in the mixture for both bulk mixtures and mixtures in controlled pore glasses. At separation the mixtures become turbid, which is signaled experimentally by a strong drop-off in the photodiode voltage. In the results that follow, these data are combined with phase boundary locations by NDE. The details of the experimental apparatus and procedures are the same as in previous work [7].

3. Simulation model and methods

Rather than directly simulate the mixture of nitrobenzene and hexane, we have chosen to study a much simpler system in order to better understand the qualitative aspects of dynamic phase separation in porous systems.

We have simulated a *symmetric* Lennard-Jones binary mixture, in which the properties of both pure fluids are identical; the attractive well-depth of the potential between the two species is reduced to 0.65ε in order to induce liquid-liquid phase separation. (ε is the well-depth in the pure liquid.) At the density used in these studies, this mixture has a critical mole fraction of 0.5, and a bulk-phase critical temperature $k_B T_c \simeq 1.64\varepsilon$, determined from Monte Carlo simulations in the semi-grand ensemble [8].

Our pore model consists of a smooth-walled cylindrical void in a material composed of a continuum Lennard-Jones solid; the potential parameters for the pore-fluid interactions are chosen to model the adsorption of argon in pores of carbon dioxide, in accord with earlier simulations of confined fluids [9].

We have studied the dynamical phase separation of the liquid mixture in several pore systems using *Quench Molecular Dynamics*. In this technique we equilibrate a mixture at constant mole fraction and density at a supercritical temperature using molecular dynamics simulation, which amounts to the numerical solution of the equations of motion by finite-difference algorithm. The temperature is controlled by thermostatting the equations of motion [10]. After equilibration, the system is quenched (by resetting the thermostat) in a single time-step to a temperature inside the phase coexistence curve, which induces phase separation. The trajectory is continued for as long as possible, and the phase separation is observed.
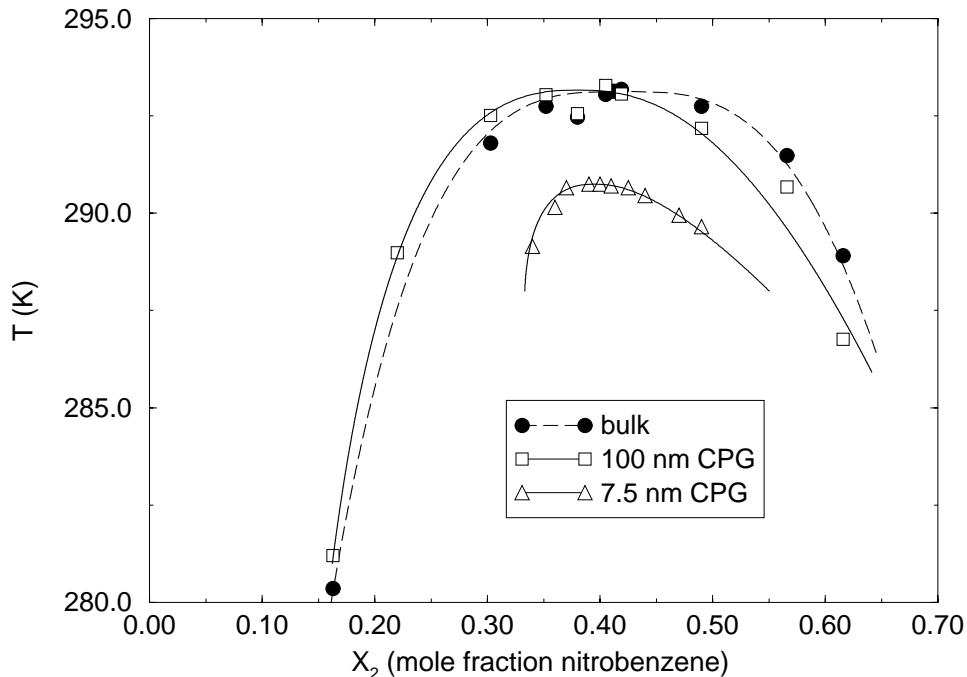
Figure 1. (T,X) phase diagrams for the nitrobenzene/n-hexane mixture in the bulk phase, 100 nm controlled-pore glass and 7.5 nm controlled pore glass. The points are experimental data, while the smooth curves are Ising-like fits to the data. The mole fractions reported for the pore systems are those of the bulk liquid in equilibrium with the pore systems.

The *average domain size* in such a computer experiment can be directly measured by calculating the autocorrelation function of the local selectivity (or mole-fraction) of the mixture as a function of position along the pore axis [11]. This function oscillates with wavelength equal to the average domain size. In what follows, we report the position of the first minimum of this function as characteristic of the domain size.

We present results from five different quench experiments, in cylindrical pores of radius 3σ, 5σ and 7σ, where σ is the diameter of a fluid particle. All three experiments were run at a mole fraction of 0.5. The initial high temperature was $k_BT = 5.0\varepsilon$ in all systems. Each data set is either averaged data from at least eight independent runs in systems with approximately 10,000 particles, or data from a single run of a 100,000 particle system. In all studies the pores were periodic in the axial direction, with lengths chosen to give a reduced density of $0.838\sigma^{-3}$.

Large system sizes are necessary for these studies because the quality of the domain size data varies with the number of domains, which can be small if the domains grow large. These calculations were all run using a parallel molecular dynamics code based on a one-dimensional decomposition scheme. The calculations for the 10,000 particle systems were done on 15 to 20 processors of the IBM SP2 computer at the Cornell Theory Center, and for the 100,000 particle systems on 64 processors of the Cray T3D computer at the Pittsburgh Supercomputing Center.

4. Results

The (T,X) phase diagrams for three different experimental systems are shown in Figure 1. These are the liquid-liquid coexistence curves for the bulk mixture, the mixture adsorbed in a glass sample with average pore size of 100 nm, and the mixture adsorbed in a glass sample with average pore size of 7.5 nm. The critical temperatures in the three systems decrease from 293.21 ± 0.01K in the bulk system to 293.16 ± 0.01K in the 100 nm glass to 290.75 ± 0.01K in the 7.5 nm glass. The critical mole fraction shifts towards the hexane-rich side, from 0.42 in the bulk phase to near 0.38 for both of the pore systems. This is due to hexane being more strongly adsorbed to the silica surface than nitrobenzene. There also appears to be a consider-
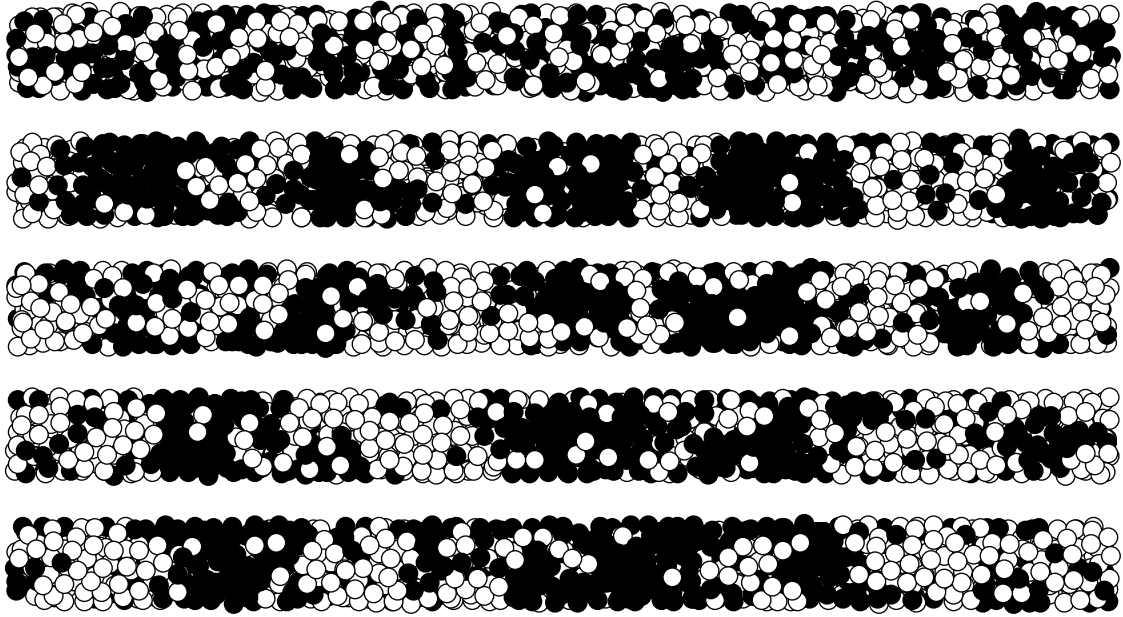
Figure 2. Molecular dynamics "snapshots" of phase separation in the 3σ radius pore system. These snapshots were taken at reduced times of $t = 0\tau$, 750τ, 1500τ, 2250τ and 3000τ (6.5 ns) reading from top to bottom. The pore walls are not shown. Note that these snapshots are of "sections" of the pore; the actual simulation cells are much longer than these.

able "narrowing" of the top of the phase envelope as the pore size is reduced. By plotting the coexistence width against reduced temperature, we estimate the effective critical exponent β in these systems to be 0.33 in the bulk phase, 0.41 in 100 nm glass, and 0.47 in 7.5 nm glass. (This last value is quite close to the mean-field exponent of 0.5.)

The light transmission data for the pore systems indicate that the phase separation is incomplete on a macroscopic scale; the samples remain turbid at temperatures far below the critical point. We hypothesize that the phase separation is limited by the pore structure, and that the final state of the fluid is one of many microscopic domains which stretch across each cylindrical section of pore and do not condense further.

Dynamic phase separation in the bulk phase is relatively well understood. For mole fractions far from critical, upon quenching the separation proceeds by a fast precipitation of small droplets, with later growth through a diffusion-limited process of droplet aggregation. This leads to a power-law growth in which the average domain radius in the system scales as $t^{1/3}$. For systems with near-critical mole fractions, this process is replaced by one in which the two phases form multiply-connected tubular network structures; this network then coarsens over time. This coarsening is driven in part by hydrodynamic forces and appears to have different growth exponents at short and long times, which have been estimated as 0.6 and 1.0, respectively [12, 13].

In confined systems we expect that bulk-like behavior might be observed at short times, when the length-scale of the phase separation is much smaller than the pore size. At later times (larger domains), the pore structure should interfere with the phase separation process. Our computer simulations allow us to directly observe this change.

A series of molecular dynamics snapshots from the quench simulation in the smallest pore are shown in Figure 2. At short times the two phases form small, poorly-defined domains, which show large fluctuations. At later times these domains grow, apparently through a condensation mechanism. Even at late times the domain boundaries are poorly defined. In the larger systems (snapshots not shown) the domain boundaries at late times are sharper, and directly bisect the
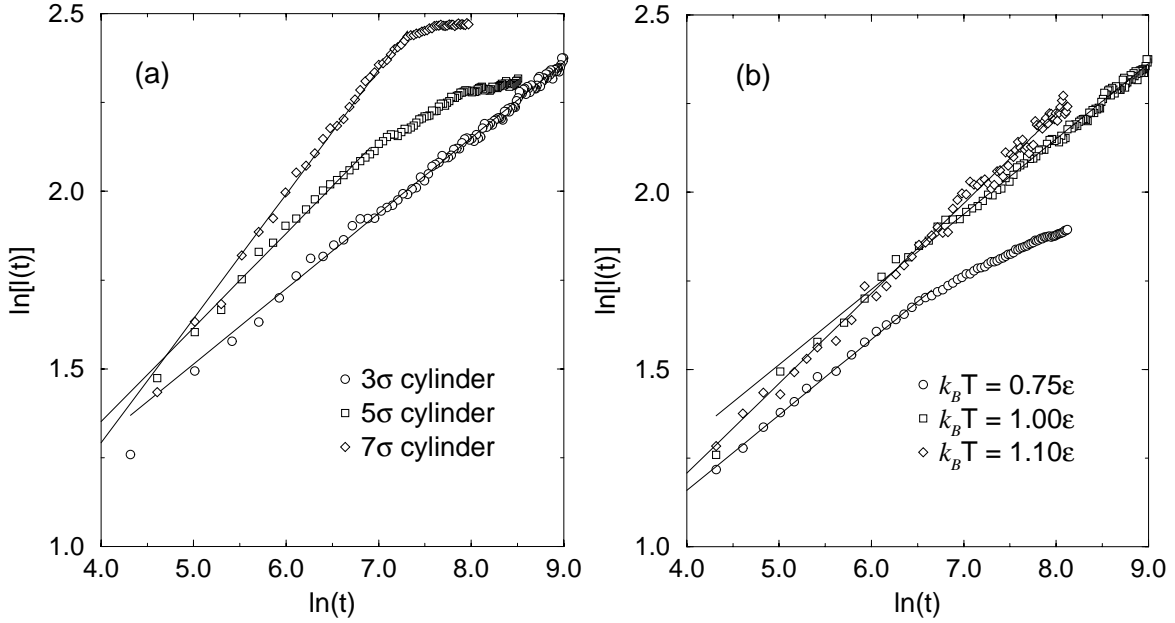
Figure 3. (a) Growth in average domain size $l(t)$ with time after quench, for three different sizes of cylindrical pore. (b) $l(t)$ data for three quenches in the 3σ pore system with different quench temperatures. All data are shown on log-log plots to reveal the power-law growth form. Lines are nonlinear χ^2 fits to the data, with errors estimated by a power-variance approximation [14].

pore.

Domain growth data for quench experiments in all three pores is shown in Figure 3a. The quench temperatures in these experiments were all the same, $k_B T = 1.0\varepsilon$. In all three pores the domains grow according to power laws at short times. The exponent for this growth in the 7σ radius cylinder is 0.35 ± 0.01, the exponent in the 5σ cylinder is 0.27 ± 0.01, and the exponent in the 3σ cylinder is 0.212 ± 0.003. All three exponents are significantly lower than those observed in bulk mixtures. That the exponent is dependent on pore diameter is an unexpected observation, not predicted by simple one-dimensional diffusion arguments.

In the two larger pores there is a noticeable slowing down at later times; the power-law behavior does not continue above a certain length scale, and the curves become very nearly flat at the latest times observed. In the larger system of 7σ radius this crossover is quite sharp and occurs at $l(t) \simeq 11\sigma$, while in the smaller 5σ radius pore the change is more gradual, beginning when $l(t) \simeq 9\sigma$. In the smallest pore, the power-law growth persists to the longest times we are able to simulate.

We believe that this qualitative difference in behavior occurs because the different systems have different phase diagrams and different (pore) critical temperatures. We have estimated the critical temperatures for the 7σ, 5σ and 3σ cylinders to be $k_B T_c \simeq 1.33\varepsilon$, $k_B T_c \simeq 1.28\varepsilon$, and $k_B T_c \simeq 1.15\varepsilon$, respectively. Because the fluid in the smallest pore is quite close to its critical temperature, the surface tension will be very small and the domain wall structure will fluctuate strongly. This gives the domains a larger "mobility" than those in the larger pores, which allows diffusion-driven growth to proceed at much later times. In order to test this hypothesis, we re-ran the quench in the 3σ pore at higher and lower temperatures; these data are shown in Figure 3b. At the lowest quench temperature there is definitely a crossover from power-law growth to a slower growth mode at an average domain size near 6σ, while in the quenches at higher temperatures the power-law growth continues to much later times.

5. Conclusions

Both simulations and experiments indicate that confinement can strongly affect the thermo-dynamic and kinetic properties of liquid-liquid phase separation. The critical temperature is

always lowered from its bulk value, and the critical mole fraction is shifted to favor the component more strongly adsorbed. In addition, it appears that the critical exponents are shifted from their bulk values; the size of this shift is determined by the properties of the porous material. The kinetics of phase separation are also strongly affected by confinement; the presence of a pore network restricts the growth of large domains of each phase, so that liquid mixtures in pores are kinetically prevented from complete separation; this has been termed "micro-phase separation" [6], as it is complete on a microscopic length scale but incomplete on a macroscopic one. We found the kinetic restrictions on phase separation to be temperature dependent, and most severe at low temperatures.

We are currently extending this study in both experimental and simulation scope. By determining experimental phase diagrams in more porous substrates we plan to quantitatively correlate the shift in critical parameters with the structural properties of the material. In the simulation study we are implementing a more realistic model of the porous material. We have recently developed a molecular-scale model for controlled pore glass that is considerably more realistic than the single cylinder used here [15], and we are currently repeating the simulations of this study in this new substrate model.

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