RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 50, NUMBER 6 DECEMBER 1994

Phase separation of binary fluids confined in a cylindrical pore: A molecular dynamics study

Zhengping Zhang and Amitabha Chakrabarti
Department of Physics, Kansas State University, Manhattan, Kansas 66506

(Received 6 September 1994)

Phase separation of a binary Lennard-Jones fluid confined in a cylindrical pore is studied by molecular dynamics simulations. The wetting interaction of the fluid molecules with the walls of the single pore is derived from the Lennard-Jones potential. Existence of long-lived metastable states is found even in the presence of hydrodynamic modes. Other effects of the hydrodynamic interactions on the formation of wetting layers are discussed. Our results are consistent with recent experimental observations.

PACS number(s): 47.55.Mh, 68.45.Gd, 64.60.−i

Binary fluid mixtures inside porous media have attracted considerable recent attention from both experimentalists and theorists because of their rich phase behavior and potential applications [1–6]. The general features found in such systems, in contrast to those in the bulk mixtures, are metastability and strong history dependence in phase separation. During the phase separation of binary fluids in porous media such as Vycor glasses [1], the two phases do not separate completely even deep inside the coexistence region; instead, they form many long-lived microdomains, rich in either one phase or the other. These indicate that the dynamical evolution of the ordering process in such systems may be crucial for understanding the phase behavior. Although theoretical understanding of phase separation in these systems is far from complete, two different interpretations have been introduced. First, the metastability is interpreted as slow dynamics arising from the random convolutions of the pore surface by mapping the phase separation onto the conserved dynamics of a random field Ising model [7]. It has been criticized, however, that such a mapping is not applicable for low-porosity media such as Vycor glasses [5]. The second interpretation is to relate the metastability to the geometric confinement of the binary mixture inside the pores. Theoretical work introducing this scenario [2,3] emphasizes the wetting phase diagram inside a single pore, since it is argued that the wetting behavior of the fluids at pore surfaces plays a major role in preventing macroscopic phase separation. Such a single-pore model without any randomness has been used as a model system to understand various effects observed in experiments with Vycor glass. This single-pore model allows for various long-lived metastable configurations (called "plugs" and "capsules") whose stability depends on the temperature and the strength of the interaction of the pore surface with one of the components of the mixture. However, in previous studies of this single-pore model with either Monte Carlo (MC) [3,5] or Langevin simulations [6], the dynamics of binary fluids has not been taken into account properly. It is, thus, an open question whether the metastability seen in previous simulations would remain under the influence of hydrodynamic modes of fluids. Therefore it is important to carry out a molecular dynamics simulation study on binary fluids in confined geometry so that the hydrodynamic interactions can be included naturally.

In this paper we present the results of a molecular dynamics simulation study of the binary fluid mixtures confined in a cylindrical pore. The phase separation of symmetric binary mixtures is studied through temperature quench experiments. The growth exponent, characterizing the temporal increment of the domain size before confinement effects become important, is much larger than the purely diffusive growth exponent of $\frac{1}{3}$, thus underscoring the importance of the hydrodynamic modes in our simulations. We find that the dynamics of phase separation is strongly affected by various metastable states, even in the presence of hydrodynamics interactions. We found the existence of the so-called "plug" phase at low temperature in our simulations, but no evidence for a stable "tube" phase at high temperature when the difference between the wetting potentials of the two species is small.

Our model system consists of two symmetric species A and B confined in a cylindrical pore with a periodic boundary condition in the direction of its symmetric axis. The molecules of the same species interact via the Lennard-Jones potentials

$$U_{AA}(r)=U_{BB}(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], \tag{1}$$

where the parameters ϵ and σ are used as units of energy and distance in our simulations. The potentials are truncated at 2.5σ to save CPU time for numerically solving the equations of motion. In order to start the phase separation after a quench, the interactions between the different species are assumed to be

$$U_{AB}(r)=4\epsilon[(\sigma/r)^{12}]. \tag{2}$$

This interaction is turned on after an initial equilibration in which all molecules interact with the same potentials as described in Eq. (1). Assuming that the fluid molecules interact with the molecules of the pore surface through the Lennard-Jones-like potentials, we also derived [8] the wetting potentials of the fluids subject to the presence of pore surface as the following:

$$U_w(r)=\epsilon_w^\beta\left\{E\left(\frac{\pi}{2},\frac{r}{R}\right)[2.\dot{6}R^2\xi^{-3}-5.\dot{3}R^4\xi^{-4}+2.345\,8\dot{3}R^2\xi^{-6}-41.0\dot{6}R^4\xi^{-7}+177.6R^6\xi^{-8}-273.0\dot{6}R^8\xi^{-9}+136.5\dot{3}R^{10}\xi^{-10}]\right.$$
$$\left.+F\left(\frac{\pi}{2},\frac{r}{R}\right)[-\xi^{-2}+2.\dot{6}R^2\xi^{-3}+64.968\,75\xi^{-5}+15.2\dot{3}R^2\xi^{-6}-76R^4\xi^{-7}+128R^6\xi^{-8}-68.2\dot{6}R^8\xi^{-9}]\right\}, \qquad (3)$$

where F and E are the Legendre elliptic integrals [9] of the first and the second kind respectively, r is the distance measured from the symmetry axis of the cylindrical pore, R is the radius of the pore, and $\xi=R^2-r^2$. (The overdot signifies a repeated digit.) R and r are measured in units of σ. The constant ϵ_w^β determines the overall strength of the wetting force and depends on the wettability of the different species to the pore surface (i.e., $\beta=A,B$). The wetting potentials are truncated at r_c where $U_w(r_c)\approx U_{AA}(2.5\sigma)$, i.e., the molecules located at $r<r_c$ are not affected by the wetting potentials. In most cases we considered $r_c\approx 2.8\sigma$.

The simulations are carried out at constant volume with a reduced fluid number density $\rho^*=N\sigma^3/V\approx 0.8$, where N is the total number of molecules in the system of volume V. To check possible effects of finite size, two systems with 4000 and 12 000 molecules are studied intensively. The larger system is confined in cylindrical pore of $R=8.7\sigma$ and $L=69.6\sigma$, where R and L are the radius and the length of the pore, respectively. The geometric parameters of the smaller system are $R=6.0\sigma$ and $L=54\sigma$. Quenches at several reduced temperatures T^*, in units of ϵ, below the bulk consolute temperature (which is about 8.0 in this unit [10]) are performed under the influence of the wetting potentials after initial equilibration in which no wetting potential is considered. The system is then evolved isothermally by rescaling velocities of the molecules every time step. The time is measured in units of $\tau=(m\sigma^2/\epsilon)^{1/2}$, where m is the mass of the fluid molecule. Two different algorithms, namely, the "velocity Verlet" method with an integration time $\delta t=0.001\tau$ and the fifth-order predictor-corrector method with $\delta t=0.002\tau$ [11], are used in our simulations in order to avoid possible errors due to using a particular algorithm. The process of phase separation is then studied by monitoring the decay of the total interaction potential energy between the two species, and by calculating the order parameter profiles, defined as $[\rho_A(\mathbf{r},t)-\rho_B(\mathbf{r},t)]/\rho_{\rm av}$, both in the radial direction and in the symmetric axis direction of the pore as a function of time, where ρ_A and ρ_B are local concentrations of the species A and B and $\rho_{\rm av}$ is global average of the molecule density.

In initial equilibration, we observed the familiar layer structure of monatomic fluids in the vicinity of the pore surface [12] by measuring the radial density distribution of molecules averaged over the z axis, the symmetry axis of the cylindrical pore. After the initial equilibration, the quenches started with the configurations in which the species A and B were well mixed. The decay in the repulsive potential energy between the different species, $U_{AB}(t)$ in Eq. (2), was observed in the quenches. It measures the reduction of interfaces between the species A and B and, therefore, is a good indicator of the phase separation process. The domain growth exponent in the late stage, α, can be estimated from the data for $U_{AB}(t)$ in combination with the relation of $U_{AB}\sim t^{-\alpha}$ [10]. An effective exponent of $\alpha=0.78\pm0.01$ is obtained as the best fit to the data in the late time regime before the confinement effect became important. This result is obtained from data averaged over six independent runs at $T^*=1.4$. We believe that the growth exponent obtained in this way is an effective exponent since its value is somewhat smaller than the theoretically predicted value of $\alpha=1$ [13]. However, this value is consistent with the effective exponents computed in other simulations in the presence of hydrodynamic interactions [14,10]. Since this value of α is much greater than the purely diffusive exponent of $\frac{1}{3}$, it is clear that hydrodynamic modes are playing a major role in our simulations.

In Fig. 1(a) we present a typical pattern of the evolution in the order parameter profile in the z direction after a deep quench at low temperature, $T^*=1.4$, for no difference in wettability of the two species. The system starts with a well-mixed configuration of A and B molecules with a flat profile for the order parameter at zero value (not shown), and finally breaks up into several domains of A and B fluids that are alternately present in the z direction [15]. It can be seen directly in the corresponding configuration snapshot taken at a late time as shown in Fig. 1(b). In contrast to the order parameter profile in the z direction, the same quantity in the radial direction stays around the zero value with small fluctuations. These results convincingly demonstrate that a long-lived plug phase is formed.

In Fig. 2 we show the evolution of the order parameter profile in the radial direction at a low temperature, $T^*=1.4$, for a large difference in wettability of the two different species ($\epsilon_w^A=0.4$ and $\epsilon_w^B=0.2$). There are sharp fluid layers of the species A in the vicinity of the pore surface and the fluid cylinder of the species B at the center of the pore. In combination with the observation of a trivial profile in the z direction, the profile of Fig. 2 shows that a stable tube phase is formed. Due to the small number of molecules in the simulation the nonlayer section of the fluid A is not observed in our simulations although it is expected to be formed next to the layers in real systems. When the quench temperature is increased, such a tube phase can still be observed in this case although the interface is less sharp than previous quenches at lower temperatures because of the large thermal fluctuations. Further increasing the difference in wettability makes the interface between A and B sharper and fluctuations in the order parameter profile in the z direction smaller. These behaviors are observed in all the cases with $\epsilon_w^A/\epsilon_w^B\geqslant 2$.

Figure 3 shows the same measurements as shown in Fig. 2 but for small difference in wettability of the two species ($\epsilon_w^A=0.25$ and $\epsilon_w^B=0.2$) at high temperature $T^*=7.0$. In contrast to the previous cases, no evidence can be found in Fig. 3 for the formation of a stable tube phase although data

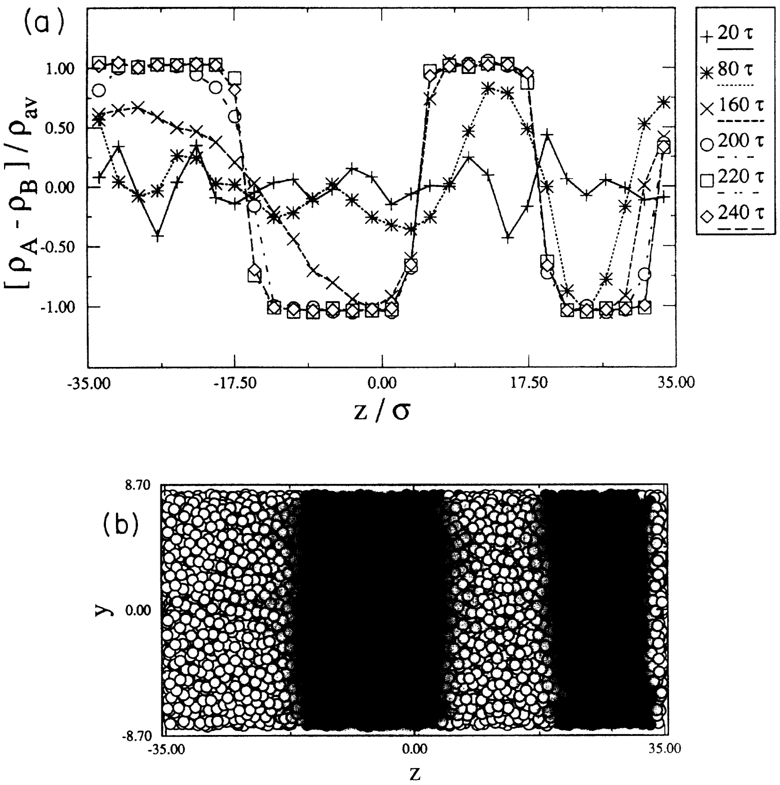

FIG. 1. (a) Time evolution of the order parameter $[\rho_A(\mathbf{r},t)-\rho_B(\mathbf{r},t)]$ profile in the z direction normalized by the average fluid density ρ_{av}, after a quench to $T^*=1.4$. The data refer to the system of 12 000 molecules confined in a cylindrical pore of $R=8.7\sigma$ and $L_z=69.6\sigma$. The wettabilities of the species A and B are $\epsilon_w^A=\epsilon_w^B=0.2\epsilon$, respectively. The lines are to guide the eye. (b) The configuration at $t=260\tau$ of the system corresponding to (a). The data is shown as a view in the x direction. The symbols ○ and ● refer to the species A and B, respectively. The size of the symbols does not correspond to the size of the molecules in the simulations.

for much later times, in comparison with data presented in Fig. 2, are already included. Note that the tendency to form a tube phase actually *decreases* during the evolution. It is inconsistent with the theoretical prediction [2] that the tube phase is generally stabilized at high temperature regime. A similar behavior is always observed in all the quenches at various high temperatures, up to the bulk consolute point, with various ratio of ϵ_w^A to ϵ_w^B in the range of $\epsilon_w^A/\epsilon_w^B \leq 1.5$. However, if the quench temperature is decreased in these cases, the long-lived plug phase as shown in Fig. 1 is formed. We note here that similar results were obtained in previous MC simulation studies [3]. Since the mean-field calculations are carried out in the presence of longer range interactions, the difference between MC simulation results and theoretical predictions was explained previously as an artifact of the short range wetting potentials used in the simulations [3]. We point out that the wetting potentials used in our present simulations are van der Waals type, the same kind of potentials used in the mean-field theory [2]. Our results indicate, then, that the details of the mean-field calculations may not be valid in more realistic situations.

Let us now compare our data with recent experimental results of the mixtures of polyvinyl methyl ether (PVME) and water confined in a one-dimensional capillary [4,16]. In the case of the mixtures of PVME and water with symmetrical composition, which we are interested in, only a long-lived plug phase was found although an unstable tube phase was observed in the very beginning of the experiments. We point out that for shallow quenches with a small difference of the wettability of the two components, we have also observed a strong tendency to form wetting layers in early times after the quench, but these layers subsequently became

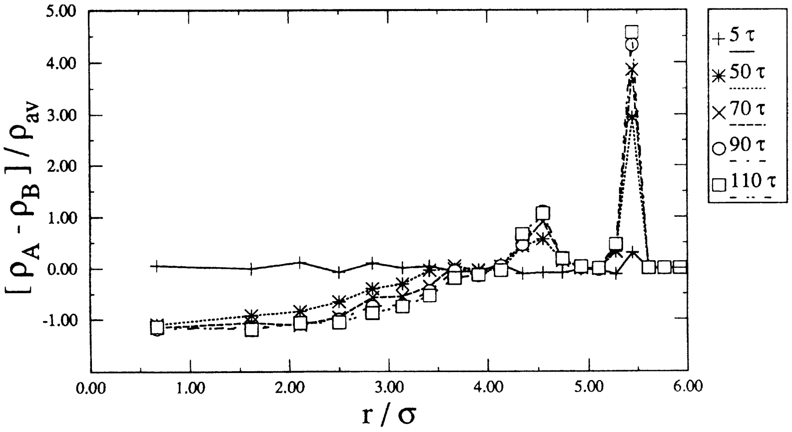

FIG. 2. Time evolution of the order parameter profile in the radial direction normalized by the average density after a quench to $T^*=1.4$. Data points are shown for each ring with an equal area of cross section. Averages over the length of the cylindrical pore are made. The data refer to the system of 4000 molecules confined in a cylindrical pore of $R=6.0\sigma$ and $L_z=54.0\sigma$. The wettabilities of the species A and B are $\epsilon_w^A=0.4\epsilon$ and $\epsilon_w^B=0.2\epsilon$, respectively. The lines are to guide the eye.

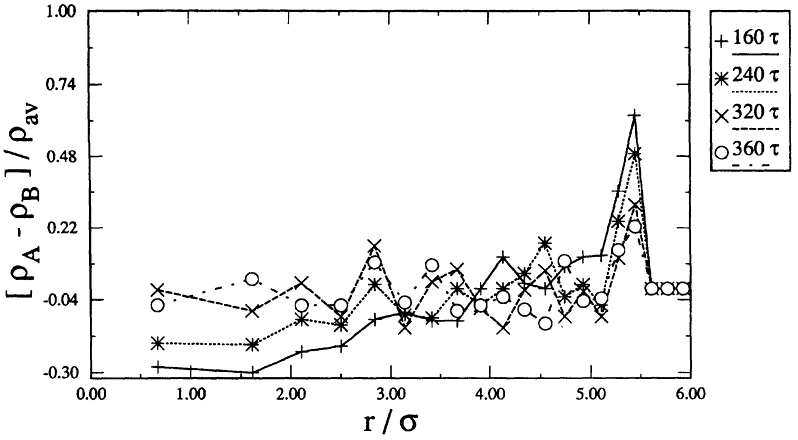

FIG. 3. Time evolution of the order parameter profile in the radial direction normalized by the average density after a quench to $T^* = 7.0$. The parameters of the simulation are the same as in Fig. 2, except that the wettabilities of the species A and B are $\epsilon_w^A = 0.25\epsilon$ and $\epsilon_w^B = 0.2\epsilon$, respectively.

unstable (see Fig. 3). It is worth noting that the experimental results in the case of symmetrical composition are only available for somewhat deep quenches. It will be very useful to do similar experiments for shallow quenches in order to resolve this issue.

In summary, we have performed molecular dynamics simulations to study the phase separation phenomena of a binary Lennard-Jones fluid confined in a cylindrical pore. We find that long-lived metastable phases exist even in the presence of hydrodynamic modes. This indicates that the existence of the metastability is independent of the details of the microscopic dynamics. We also study the stability of the tube phase at various temperatures. In addition, we note that the wetting potential derived for the cylindrical pore in this work should be useful in research related to the wetting phenomena in a cylindrical geometry.

This work has been supported by a grant from the National Science Foundation (DMR-9312596). The computer calculations were carried out under an NSF grant of computer time from the Pittsburgh Supercomputing Center.

---

[1] See, for example, W. I. Goldburg, in *Dynamics of Ordering Processes in Condensed Matter*, edited by S. Komura and H. Furukawa (Plenum, New York, 1988).

[2] A. J. Liu, D. J. Durian, E. Herbolzheimer, and S. A. Safran, Phys. Rev. Lett. **65**, 1897 (1990).

[3] A. J. Liu and G. S. Grest, Phys. Rev. A **44**, R7894 (1991).

[4] H. Tanaka, Phys. Rev. Lett. **70**, 53 (1993).

[5] L. Monette, A. J. Liu, and G. S. Grest, Phys. Rev. A **46**, 7664 (1992).

[6] A. Bhattacharya, M. Rao, and A. Chakrabarti, Phys. Rev. E **49**, 524 (1994).

[7] F. Brochard and P. G. de Gennes, J. Phys. Lett. (Paris) **44**, 785 (1983); P. G. de Gennes, J. Phys. Chem. **88**, 6469 (1984); D. Andelman and J. F. Joanny, in *Scaling Phenomena in Disordered Systems*, edited by R. Pynn and A. Skjeltorp (Plenum, New York, 1985).

[8] To obtain the close form for the wetting potential, a continuous approximation of the pore surface has been made. That is, an integral over the surface of the cylindrical pore, $\int\int_S dS\, U(S,r)$ was performed with the approximation that its length is infinitely long, where $U(S,r)$ refers to the contributions of the cell, dS, on the surface to the potential at r. $U(S,r)$ is, furthermore, assumed to be a Lennard-Jones potential with its strength being scaled properly.

[9] *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1964).

[10] W.-J. Ma, A. Maritan, J. R. Banavar, and J. Koplik, Phys. Rev. A **45**, R5347 (1992).

[11] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1989).

[12] P. Keblinski, W.-J. Ma, A. Maritan, J. Koplik, and J. R. Banavar, Phys. Rev. E **47**, R2265 (1993).

[13] E. Siggia, Phys. Rev. A **20**, 595 (1979).

[14] O. T. Valls and J. E. Ferrell, Phys. Rev. E **47**, R36 (1993).

[15] We note here that no average over individual runs was made in Fig. 1(a). Such an average will not give us useful information because of the translational symmetry in the z direction. However, we have observed the same pattern of evolutions in all of our individual runs with the same parameters.

[16] H. Tanaka, Phys. Rev. Lett. **70**, 2770 (1993).

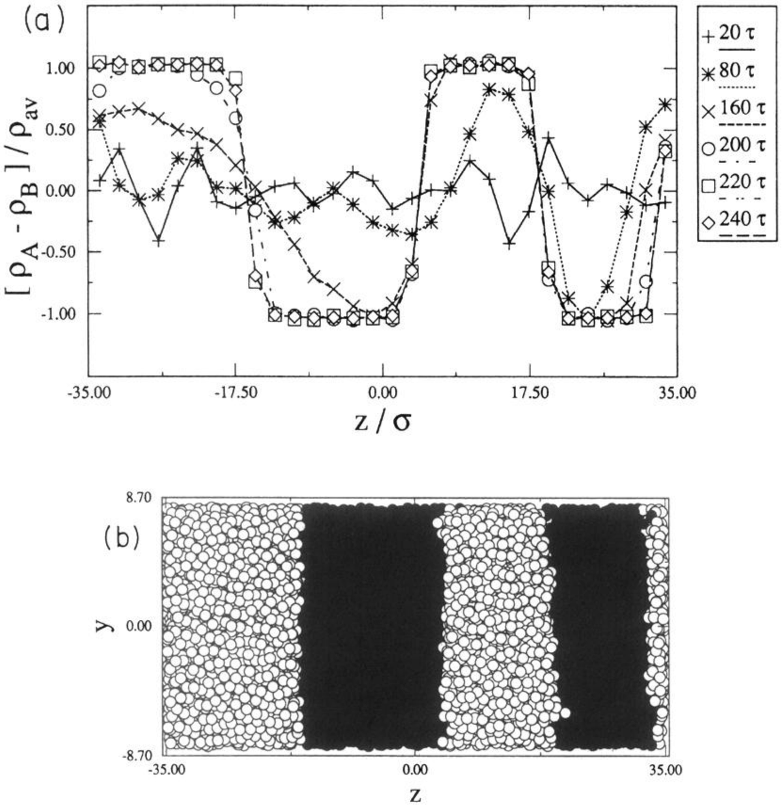

FIG. 1. (a) Time evolution of the order parameter $[\rho_A(\mathbf{r},t) - \rho_B(\mathbf{r},t)]$ profile in the z direction normalized by the average fluid density ρ_{av}, after a quench to $T^* = 1.4$. The data refer to the system of 12 000 molecules confined in a cylindrical pore of $R = 8.7\sigma$ and $L_z = 69.6\sigma$. The wettabilities of the species A and B are $\epsilon_w^A = \epsilon_w^B = 0.2\epsilon$, respectively. The lines are to guide the eye. (b) The configuration at $t = 260\tau$ of the system corresponding to (a). The data is shown as a view in the x direction. The symbols ○ and ● refer to the species A and B, respectively. The size of the symbols does not correspond to the size of the molecules in the simulations.