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The ordering processes in a binary liquid mixture confined in a Vycor type of pore and at temperatures near the transition temperature of the pure system $T_c$ are studied using a kinetic Ising model and the method of Monte Carlo simulations. The results for dynamics show quite clear signatures of the pore width but no notable difference between $T > T_c$ and $T < T_c$. In the results for statics, the small angle part of the structure factor increases rapidly as $T$ approaches $T_c$ in the one-phase region. This suggests the onset of ordering but the fluctuation of energy shows no sign of criticality.

Considerable effort has been devoted to understanding the ordering processes in phase-separating binary systems such as alloys and binary liquids [1]. A more difficult problem of current interest concerns the same ordering process of binary liquids in porous media, such as Vycor glasses or silica gels [2]. According to experimental results [3–8], porous media make the liquid mixtures extremely metastable and thus slow in dynamics. In view of the randomness of the confining surfaces, such an effect is not a surprise. What is surprising is the way the media influence the liquid mixtures since it defies, among other things, the usual length-scale arguments. The gelan gum systems [7] and the dilute silica gel systems [8] illustrate this point well.

Consider the silica gels [8]. The gel strands can take up as little as 1.8% of the total volume. This low volume fraction should allow, unless the temperature is very near the critical temperature of the pure system $T_c$, ample space for the liquid mixture to retain much of its bulk cooperative behavior. But it does not: As the temperature is lowered from above $T_c$, the influence of the gel strands may be seen while the system is still in the disordered single-phase region far away from $T_c$. The small angle scattering intensity increases rapidly as $T$ approaches $T_c$ suggesting the onset of ordering, but the onset of ordering is unusual in two ways. First, it occurs above $T_c$ although the phase diagram of the pure mixture (water and isobutyric acid) is normal. Second, it occurs spontaneously without the usual critical (diverging) fluctuations; instead, the ordering process is accompanied by an extremely slow dynamic mode whose amplitude relaxes over many hours.

In order to explain these phenomena, Frisken, Ferri, and Cannell (FFC) argue that, as the critical point is approached (from the single-phase region), clusters of wetting liquid are formed near the gel strands, which then remain immobile [8]. FFC argue further that the spontaneous ordering is driven by the gradient contributions to the free energy which may be reduced by removing the free fluid from gel-rich regions to gel-poor regions. This process begins spontaneously and accounts for the slow

dynamic mode. During this long period, the system may be regarded as being in a steady but nonequilibrium state.

For Vycor glass systems, there is no small angle data for $T$ near $T_c$. But the neutron scattering intensity data of Dierker and Wiltzius [6] appear to suggest an important clue. There is a faint peak in the scattering intensity curve at $q = 0.05$ Å$^{-1}$. The corresponding order-parameter correlation has a length scale of 120 Å, or about twice the pore diameter. This may be interpreted as representing slowly relaxing adsorption layers on the glass walls [9]. The peak is notable at $T$ about 3 °C away from $T_c$ in the one-phase region, and also at about 7 °C away from $T_c$ in the two-phase region. This appears to suggest that the FFC scenario may also apply for Vycor systems.

In a previous paper [10], we studied the phase separation dynamics after a deep quench using a kinetic Ising model. In the present Letter, we study the same type of model at temperatures near $T_c$. Wall "atoms" are arranged on a 158×158 square lattice so as to make approximately 90 interconnected tunnels which provide a confining effect for the spins occupying the rest of the sites. The wall atoms also provide a preferential adsorption effect for nearby spins with an external magnetic field. The Hamiltonian is given by

$$H = -J\sum S_i S_j + h\sum N_i S_i , \tag{1}$$

where $S_i = +1$ (species $A$) or $-1$ (species $B$), and $N_i$ is the number of wall atoms neighboring spin $i$. The external field $h$ is chosen to be $0.8J$.

Because of the wall, the spins lose a great deal of connectivity. The spin correlation is mediated only through the pore space, not through the glass walls. Therefore for a given pair of spins, depending on the orientation of the nearby walls, the Pythagorean distance may be quite irrelevant for the spin correlation function. Under this circumstance, a better measure of the spin correlation is the minimum distance [11], namely, the distance along the minimum path which goes around (not through) the glass walls. Therefore we will measure the spin correlation as
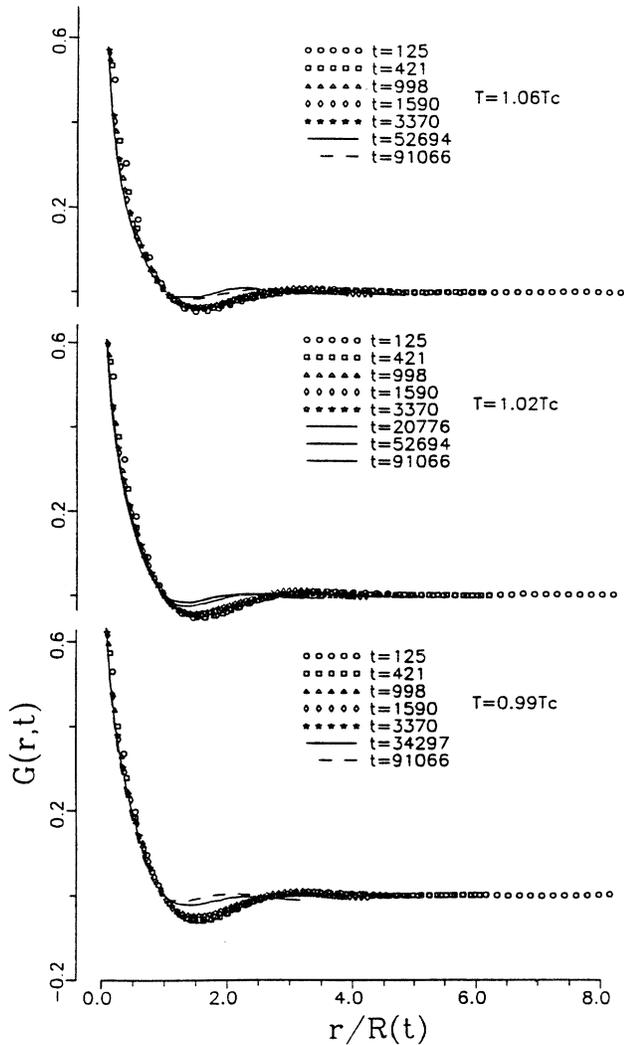
FIG. 1. Scaling plot for the correlation function.



FIG. 2. Typical domain size $R(t)$ at time $t$.

a function of the minimum distance (also called chemical distance or cow distance).

First, we study the dynamics after quenching the system (a critical mixture) from a very high temperature to $T/T_c = 1.06$, 1.02, 0.99, and 0.98, where $kT_c = -2J/\ln(\sqrt{2}-1)$ is now the transition temperature of the two-dimensional pure Ising model; the Boltzmann constant $k$ and the coupling constant $J$ are now set to unity. The time evolution after the quench is based on the Kawasaki spin exchange dynamics which allows spin exchange for nearest neighbors only. Figure 1 shows the early-time scaling behavior of the correlation function, which may be written in the form $G(r,t) = f(r/R(t))$, where $r$ is the minimum distance and $R(t)$ is the average domain size. Thus the scaling behavior of the pure system [12] survives the disorder at early times, but it is hidden in the geometry based on the minimum distance; in the Pyth-
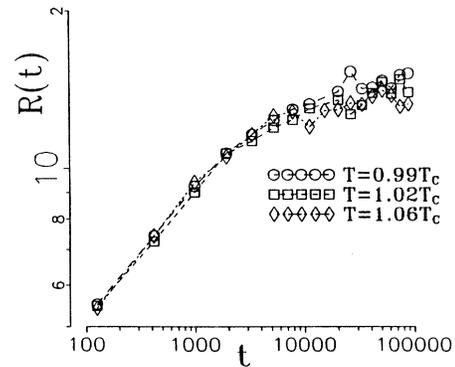
agorean geometry, the scaling behavior is less convincing [13]. The scaling behavior begins to break down at about $t = 1000$ sweeps [14]. As Fig. 2 shows, the domains grow following a power law until the size becomes comparable to the pore width, which occurs at about $t = 1000$. Figure 3 shows the relaxation of $G(r=1,t)$ which has been fitted by the form

$$1 - G(1,t) = c_1 \exp(-t/\tau_1)$$
$$+ c_2 \exp\{-[\ln(t)/\ln(\tau_2)]^2\}. \qquad (2)$$

Here $t = 1000$ marks the dominance of the activation dynamics [15] represented by the second term. When the domain size becomes comparable to $W$, large energy barriers have to be overcome for further growth. The activa-
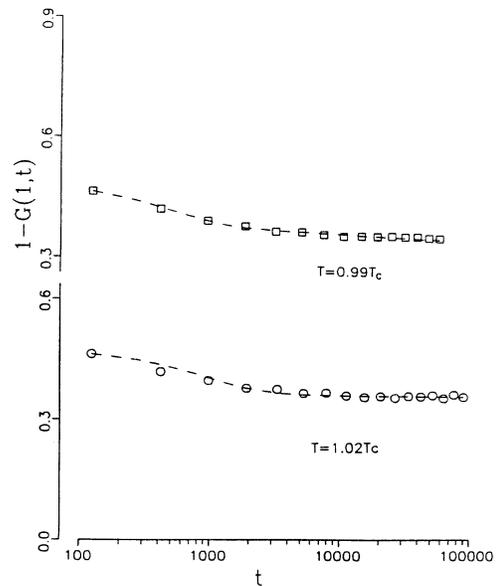


FIG. 3. The relaxation of the short-range correlation function.

tion dynamics signals the onset of this slow process which we will discuss more later. Thus we have found three different signatures of $W$, and the fact that the dynamic behavior shows these signatures suggests that the system never reaches a state where the correlation length is significantly greater than the pore size. This may explain why the usual length scale arguments do not apply. Finally, notice that there is little or no difference between $T > T_c$ and $T < T_c$ in these results. Since the correlation length did not reach the system size during the simulation time, this is not a finite system-size effect. We take it to mean that the ordering process begins at $T > T_c$.

Next, we perform slow-cooling simulations for statics. The temperature is decreased from $T/T_c = 1.22$ by increments of 0.02, and after each reduction of $T$, the first 12000 sweeps are discarded and the next 27000 sweeps are kept for the averaging purpose. The measured quantities are the average energy $\langle E \rangle$ and its fluctuation, $C = (\langle E^2 \rangle - \langle E \rangle^2)/NT$. The structure factor is measured for the last spin configuration for selected values of temperature. The results for $C$ are shown in Fig. 4. It is notable that there is no sign of criticality in the explored range of temperature.

The structure factor $S(q)$ is computed from

$$S(q) = (2/N) \sum_{i<j} \langle S_i S_j \rangle \cos(\mathbf{q} \cdot \mathbf{r}_{ij}) , \qquad (3)$$

where $\mathbf{r}_{ij}$ is now the Pythagorean vector from spin $i$ to spin $j$. The results are shown in Fig. 5. In spite of the noise, there are several features which we consider pertinent. It is notable that $S(q)$ for temperatures around $T/T_c = 1.18$ has the same pattern as found experimentally in the one-phase region far away from $T_c$ [3,6,8]. As the temperature is lowered further, the small angle part of $S(q)$ increases quite drastically in much the same way as FFC found in their gel experiments [8]. Finally, notice a local peak at $q = 7$ (in units of $2\pi/L$, $L = 158$)
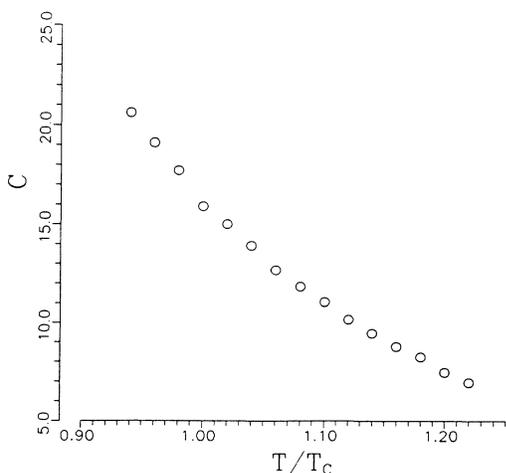
which emerges at about $T/T_c = 1.10$. It suggests a pronounced order parameter correlation in the length scale of about 22 lattice spacings, or about twice the tunnel width. Since the order parameter is conserved, the corresponding domain size may be estimated to be about 11, which is about the pore size. The peak reflects the slowly decaying small domains confined in the pores.

Both the quench simulations and the slow-cooling static simulations suggest that the phase separation begins above $T_c$ although the pure system has a normal phase diagram. In this regard, the present system is quite different from random field magnets [16]. In order to understand this, compare our model Hamiltonian with that of random field Ising magnets. In random field magnets, all spins are subject to an external field which takes on randomly different signs from spin to spin. In contrast, the external fields in the present model carry the same sign. Moreover, the fields act only on those spins neighboring the wall atoms which are arranged in a correlated fashion. Therefore the fields in the present model constitute a highly correlated disorder.

In all random systems, statistical fluctuations leave remarkably large clumpy regions, namely, regions in which fields are all aligned, or bonds take on the same largest
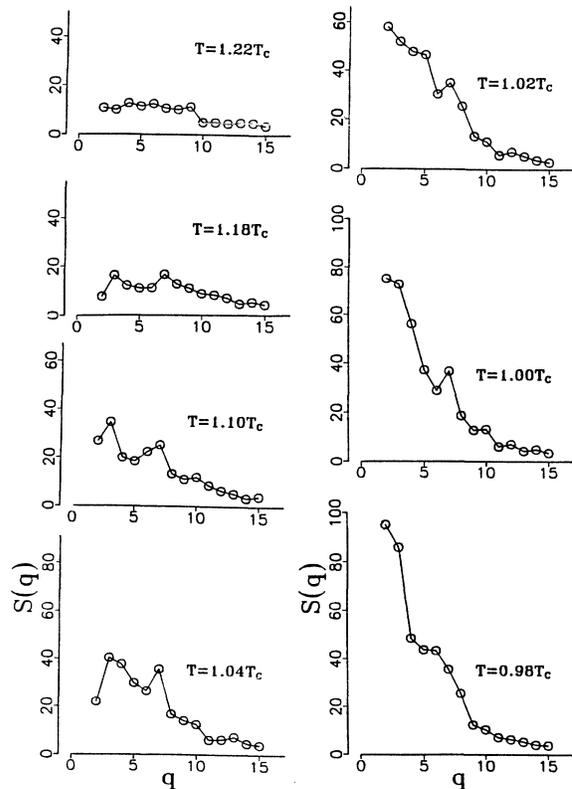


FIG. 4. The fluctuation of energy as a function of $T/T_c$.



FIG. 5. The structure factor $S(q)$ for various $T/T_c$. The wave vector $q$ is given in units of $2\pi/L$, where $L = 158$ is the linear size of the lattice.

value, etc. Such regions (to be called Griffiths clusters) are rare, but still they make their presence known; they cause the Griffiths phase [17] and play the dominant role in the late-time dynamic behavior [18]. If the disorder is correlated as in the present model, there are more Griffiths clusters, and also the size of the clusters becomes larger. In the present model, there are Griffiths clusters along each side of all pore walls.

Examine how the clusters may affect the phase transition from the point of view of Harris [19]. Since all spins on the clusters are subject to the same nonvanishing external field, they favor local transition temperatures higher than $T_c$. But, regarding the wall atoms as a result of site dilution on spins, the regions surrounding each pore wall favor local transition temperatures lower than $T_c$. Our simulation results suggest that the former wins the competition. Moreover, the absence of critical fluctuations indicates that the local competitions from Griffiths clusters are in fact so strong that the system can no longer support a global cooperative behavior characteristic of the second-order phase transitions [20].

Returning back to the results of slow cooling, domains of negative spins are formed in the shape of plugs [21] in each tunnel at $T$ as high as $T/T_c = 1.06$. In order for a global phase separation to take place, however, some of these ill-conceived domains have to break up. This is difficult due to the "grip" of the Griffiths clusters which creates energy barriers. We find that many of the plugs remain in their tunnels for a long time, but some of them do break up—sometimes completely and sometimes partially—which constitutes a very slow and gradual ordering process. The peak in $S(q)$ at $q = 7$ reflects the presence of these long-lasting semifrozen domains. Thus, although our model was designed for Vycor glass systems, the results support the semifrozen wetting cluster scenario of FFC [8] for gel systems.

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