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Kinetics of conserved multicomponent systems

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Kinetics of multicomponent quenched systems is studied with the use of a Monte Carlo simulation technique. By employing Kawasaki spin-exchange dynamics, we investigate the time evolution of systems quenched from a high-temperature equilibrium state to low temperatures ($T < T_c$). For "early" times, we find that the mean-cluster radius R for three- and six-component systems grows as $R \cong t^n$, where n is approximately 0.2 as observed in binary alloys.

I. INTRODUCTION

There has been considerable recent interest in the field of kinetics of quenched systems undergoing phase separation and/or ordering.[1] Both theoretical[2–12] as well as experimental[13–29] investigations have revealed interesting and novel physics. Until recently, these studies have been carried out on simple Ising systems quenched from a high-temperature equilibrium state to low temperatures ($T < T_c$). The system is thus in a state far from equilibrium, evolving toward its equilibrium state corresponding to the final quenched temperature. This evolution is generally characterized by the time dependence of some relevant length, for example, the mean radius R of the clusters or the position of the peak in the static structure factor. This mean radius R seems to follow a simple power law, $R \cong t^n$. For two-component conserved systems, the exponent n has been shown to be equal to 0.2 for "early"[21] and $\frac{1}{3}$ for late times.[2,6,24] For two-component nonconserved systems, a number of authors have shown that n is equal to $\frac{1}{2}$ both analytically[9,10,12] and numerically,[25,26] in agreement with experiments.[8] Recently, we[30,31] have studied ordering in nonconserved multicomponent systems and found that the exponent n depends upon the number, Q, of the components present in the system. For large Q it approaches a constant value of 0.41 which has been shown to be relevant for grain growth in metals.[32,33] This interesting study has motivated us to investigate the kinetic behavior of the conserved multicomponent systems which we report in this paper. Apart from fundamental interest, our simulations of the conserved multicomponent systems should be relevant for the phase-separation process in a number of metallurgical[34] and surface[35] systems (or thin films).

II. MODEL AND MONTE CARLO METHOD

The kinetic behavior of multicomponent systems is studied by considering the Q-state ferromagnetic Potts model which is described by the following Hamiltonian:

$$H = -J \sum_{\mathrm{NN}} \delta_{S_i S_j} , \tag{1}$$

where S_i is the Q state of the spin on site i ($1 \le S_i \le Q$) and δ_{ij} is the Kronecker δ function. The sum is taken over all of the nearest-neighbor (NN) spins and the exchange constant $J > 0$. In all of the simulations, we start with a high-temperature equilibrium state of spin configuration with a known fraction of each component Q and rapidly quench to $T < T_c$, where T_c depends on Q. To reduce the boundary effects, we perform the simulations on a large square lattice, $N = 90 \times 90$ sites, and use periodic boundary conditions. To conserve the number of spins of a given component or species, we employ Kawasaki spin-exchange dynamics. We randomly choose a pair of unlike spins and carry out an exchange provided that the transition probability W,

$$W = \tau^{-1} \frac{\exp(-\Delta E / k_B T)}{[1 + \exp(-\Delta E / k_B T)]} , \tag{2}$$

is greater than or equal to a random number r ($0 \le r \le 1$). For $W < r$, the old spin configuration is retained. The spin configuration is stored for analysis at regular intervals. We define the unit of time as one Monte Carlo step (MCS) per spin, which corresponds to N microtrials or spin-exchange attempts, where N is the total number of spins in the system. The results quoted below are averaged between three and six runs.

We have studied the growth kinetics of Potts model for $Q = 3$ and 6 for $T = 0.6T_c$, and $Q = 3$ for $T = 0.8T_c$. To compare our results with simple and well-understood systems, we have reinvestigated the growth kinetics of the binary alloy,[19–24] which is a two-component system and which corresponds to the $Q = 2$ Potts model. The binary-alloy simulations are carried out with $\frac{1}{3}$ concentration of one species and $\frac{2}{3}$ concentration of the other species in order to have a proper comparison with the $Q = 3$ case in which each species has a concentration of $\frac{1}{3}$. In Fig. 1 we display spin configurations for $Q = 3$ for different times during the evolution. Notice that at early times, the clusters are compact and grow with time by coalescing with the clusters of like species. In this manner, the system minimizes the surface boundary or surface energy as can be seen from Fig. 1.

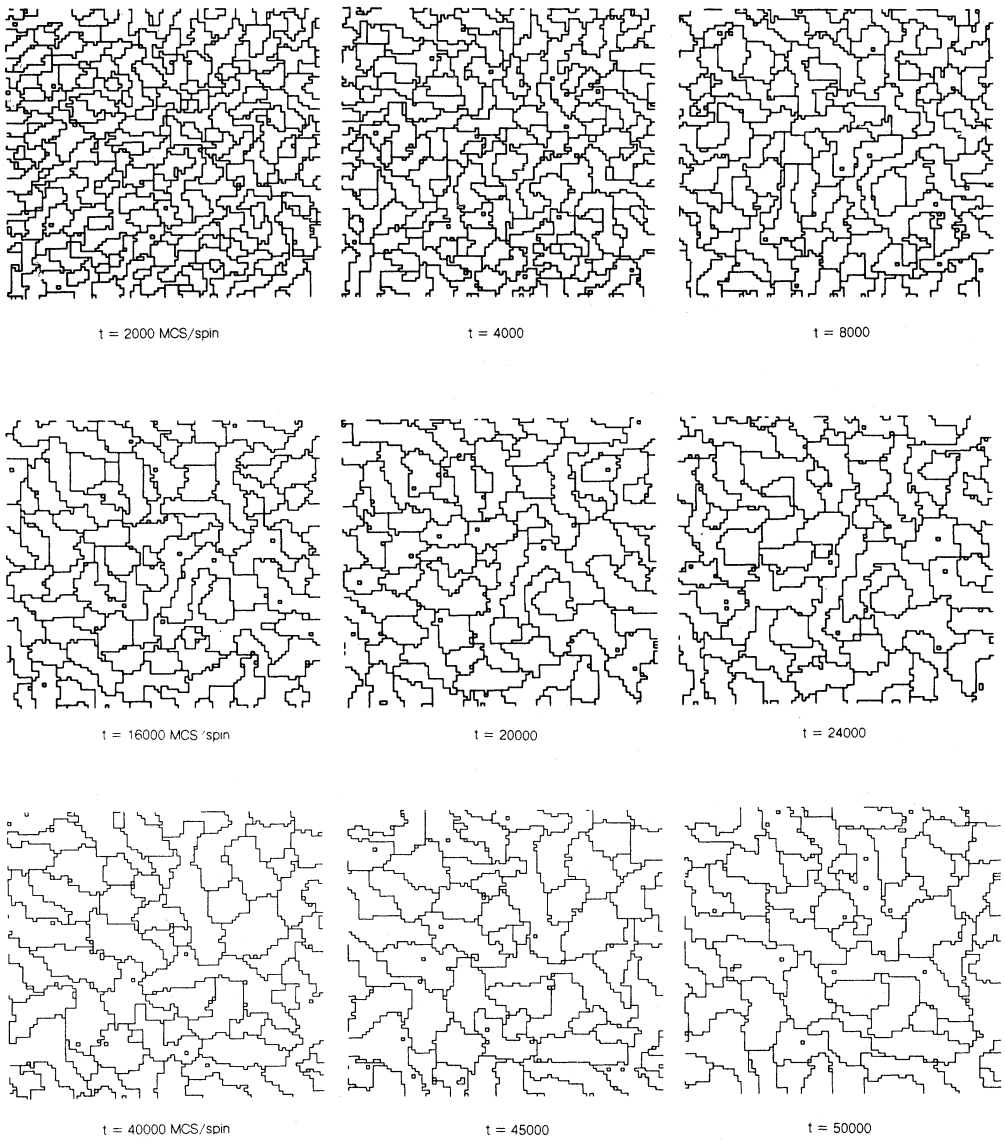

FIG. 1. Spin configurations for the $Q=3$ Potts model on a square lattice that was quenched from high temperature to $T=0.6T_c$. Kawasaki spin-exchange dynamics were used.

The growth kinetics of the system can be studied by monitoring the surface energy or number of surface bonds as a function of time. In $d=2$, the average surface energy is proportional to the mean perimeter of the clusters from which one can obtain the mean radius of the clusters. In other words, the mean energy is proportional to the mean radius of the clusters. To obtain the mean energy, we have averaged our data over six runs for $Q=3$ and three runs for the binary alloy, and fit the average energy with a simple power law[20]

$$E=bt^n\,, \tag{3}$$

where b is a constant. We obtain the exponent n by plotting $\log_{10}(E)$ vs $\log_{10}(t)$. In Figs. 2(a) and 2(b) we display these plots for $Q=3$ and the binary alloy, respectively. After the transients are over (<8000 MCS's), the analysis of the slope gives an exponent $n\cong 0.21$ for $Q=3$ and $n\cong 0.17$ for binary alloys. To check the temperature dependence of the exponent n, we also carried out three runs for $Q=3$ at $T=0.8T_c$ and obtain $n\cong 0.19$. We believe that for early times the exponent n is very close to 0.2 for $Q=3$, as observed in the case of binary alloys[24] for other number fractions of the minority species. For binary alloys, Binder and Stauffer[21] interpreted this early-time growth exponent as resulting from a growth of clusters due to coalescence and dissociation of smaller clusters which move with an effective diffusion constant. To verify this point, we plot the cluster configurations in Figs. 3 and 4 for $Q=3$ and the binary alloy, respectively. For display purposes, we embed the clusters of one component into the sea of the other two components. This clearly demonstrates the occurrence of such events. We

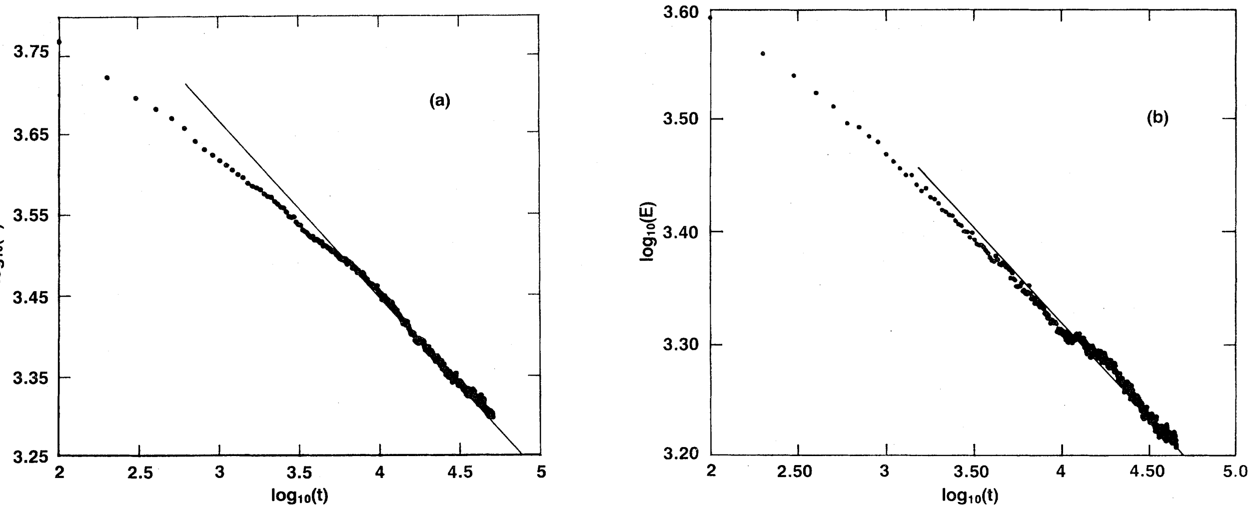

FIG. 2. Plot of $\log_{10}(E)$ vs $\log_{10}(t)$ for (a) the $Q=3$ Potts model and (b) the binary alloy that was quenched from high temperature to $T=0.6T_c$. Dots represent data that has been averaged over six runs for the $Q=3$ Potts model and three runs for the binary alloy. The exponent n is extracted from the slope of the long-time-fitted line. The concentration of the minority species for the binary alloy is $\frac{1}{3}$, while the fraction of each of the three components for the $Q=3$ model is also $\frac{1}{3}$.

find that this growth mechanism persists as late as 50 000 MCS's, which is the maximum time of our simulations. Until this time, the clusters are not sufficiently large or sufficiently far apart that the second growth mechanism, namely, growth due to evaporation and condensation[2] of monomers, becomes the dominant mechanism. Many years ago, Lifshitz and Slyozov[2] discussed the growth of clusters due to evaporation and condensation for very late stages and showed that the exponent $n=\frac{1}{3}$. Owing to computer-time limitations and finite-size effects it is difficult to simulate very late times to observe[24] this $\frac{1}{3}$ exponent. We should point out that we do see growth

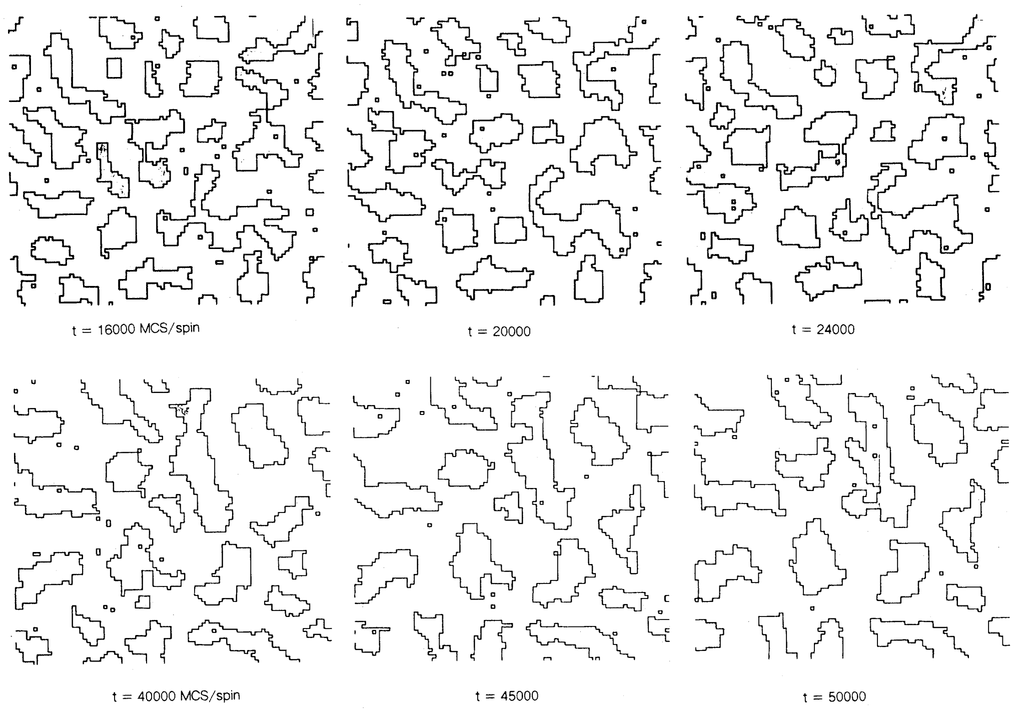
t = 16000 MCS/spin
t = 20000
t = 24000
t = 40000 MCS/spin
t = 45000
t = 50000

FIG. 3. Spin configurations for the $Q=3$ Potts model on a square lattice that was quenched to $T=0.6T_c$. Here, we embed the clusters of one of the components into the "sea" of the other two components. Clusters which grow due to coagulation and dissociation are clearly seen.

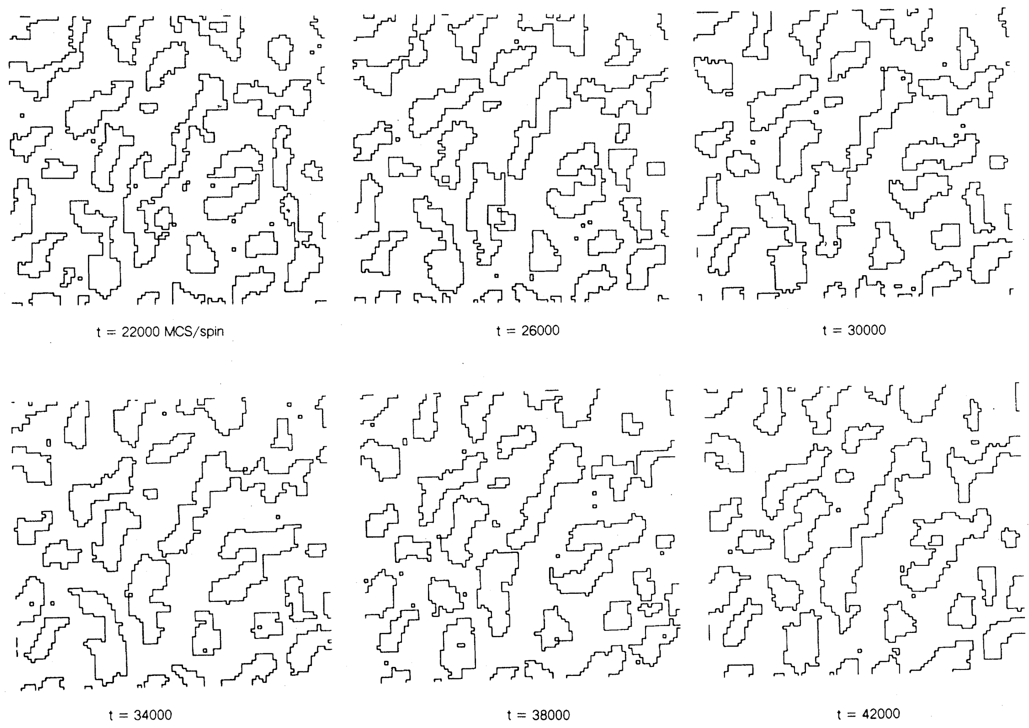

FIG. 4. Spin configuration for the binary alloy quenched to $T = 0.6T_c$. The concentration of one species is chosen to be $\frac{1}{3}$ in order to compare them with the results for $Q = 3$ in Fig. 3.

occurring due to association and dissociation of monomers, however, the dominant mechanism of growth at early times is coagulation-dissociation of small clusters.

In Figs. 5(a) and 5(b) we also display, for $Q = 3$ and the binary alloy, histograms of the cluster-size distribution function $F(x)$, where x is equal to $A/\bar{A}$, $\bar{A}$ being the mean domain area. We have checked the time invariance of the size distribution function and the data exhibited in Fig. 5 is averaged over several different times between 15 000 and 45 000 MCS's. Both of the distribution functions are very similar and exhibit two peaks, one corresponding to large clusters and the other to small clusters (monomers, dimers, trimers, etc). We notice that the area under the peak of small clusters is larger in the case of the binary alloy than that for the $Q = 3$ case, which indicates the existence of more small clusters for the case of the binary-alloy system than for the $Q = 3$ case.

We have also simulated the $Q = 6$ Potts model, mainly to check if there is any dependence of the exponent n on Q as observed in the case of a nonconserved Potts model.[30] In Fig. 6 we display a double logarithmic plot of the mean energy versus time, and from the slope we find that the exponent $n \cong 0.18$. By keeping the statistical errors of the Monte Carlo simulations in mind, we believe that this exponent is also very close to 0.2, as seen for $Q = 3$ and the binary alloy. In the $Q = 6$ case the clusters of a given specie (with total concentration of $\frac{1}{6}$), are found to be very small and distributed far from each other. The growth of these clusters also occurs mainly via a coalescence-dissociation mechanism[21] since clusters are sufficiently small to diffuse.

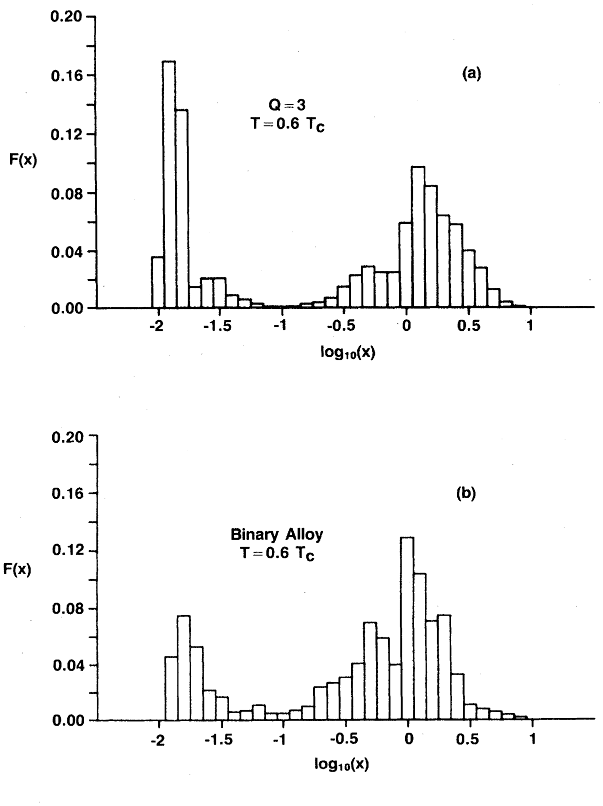

FIG. 5. Averaged size distribution function $F(x)$ for (a) the $Q = 3$ Potts model and (b) the binary alloy with concentration $\frac{1}{3}$ for one component.

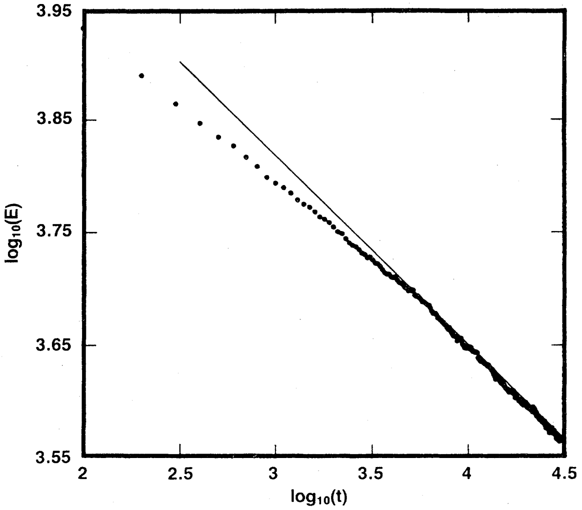

FIG. 6. Plot of $\log_{10}(E)$ vs $\log_{10}(t)$ for the $Q=6$ Potts model that was quenched from high temperature to $T=0.6T_c$. Dots represent data that has been averaged over three runs.

We would like to address the question of whether or not one will ever see the Lifshitz-Slyozov[2] regime (or $\frac{1}{3}$ exponent) in Q-state Potts models. We believe that for very late stages, when the clusters are sufficiently large that they cannot readily diffuse, the only plausible mechanism of growth is evaporation-condensation, which will give $n=\frac{1}{3}$. However, at the present time it is not possible to simulate this late-stage kinetic behavior. The "crossover time" associated with the transition from the first growth mechanism (coalescence-dissociation) to the second growth mechanism (evaporation-condensation) is also important. This crossover time should depend upon the value of Q and will most probably increase with increasing Q. It is also possible that for $Q \geq 3$, the long-time exponent is less than $\frac{1}{3}$, similar to our earlier results on nonconserved Potts models. However, for the small values of Q which are physically interesting in the conserved-spin case, we do not expect the deviation in the long-time exponent from the value of $\frac{1}{3}$ to be significant.

III. CONCLUSIONS

In summary, we have studied the kinetic behavior of the conserved multicomponent ($Q=3$ and 6) systems and find that the early-time-growth exponent is very close to 0.2, as observed in the case of binary alloys. From cluster configurations, we conclude that the main growth mechanism is the coagulation and dissociation of smaller clusters. At present, we are not aware of any experimental study on the kinetics of the conserved multicomponent systems and we hope that this work will motivate experimental investigations.

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