Temperature Dependence of Domain Kinetics in Two Dimensions

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Monte Carlo simulations have been carried out to study the effect of temperature on the growth kinetics of a circular grain. As predicted by $d=3$ theories of domain kinetics, the circular domain shrinks linearly with time as $A(t)=A_0-\alpha t$, where A_0 and $A(t)$ are the initial and instantaneous areas, respectively. However, in contrast to $d=3$, the slope α is strongly temperature dependent for $T \geq 0.6T_c$. An analytical theory which considers the thermal fluctuations agrees with the T dependence of the Monte Carlo data in this regime.

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The kinetics of domain growth is a subject of paramount interest in the field of metallurgy. Phenomenological theories[1-3] have been developed to explain the growth of domains (or grains) in the ordering of a three-dimensional ($d=3$) alloy with two equivalent sublattices quenched from high to low temperatures. The basic assumption of these theories is that the driving force for shrinking or growth of a domain is the surface energy of the interfaces between the grains of the two sublattices. All treatments predict that the average grain size, R, increases algebraically (i.e., $R \sim t^{1/2}$) as a function of time t. However, the earlier phenomenological theories[1-3] and the recent field-theoretic approach of Allen and Cahn[4] differ strongly in their predictions of the temperature dependence of the growth law, especially near the critical temperature T_c. Experiments on Fe-Al at temperatures much below T_c support[4] all of the above theories which predict an exponential temperature dependence that comes from the Arrhenius behavior of the attempt frequency. However, neither approach takes into account the effect of thermal or roughening[5] fluctuations on the growth dynamics.

The present work demonstrates the importance of roughening fluctuations on the growth dynamics. Since the effect of thermal fluctuations is stronger in $d=2$ than in $d=3$, we have carried out Monte Carlo (MC) simulations on circular domains instead of spherical ones. Both the MC simulations and a model calculation show that these fluctuations are responsible for the strong temperature dependence of the growth rate for $d=2$. Our results are particularly relevant to the problem of domain growth in surface science. In recent years, the kinetics of domain (or island) growth of adsorbed atoms on surfaces has been investigated. In a number of MC studies on chemisorption[6-8] and physisorption systems, domains of different degenerate ground states have been reported to grow very slowly. A similar slow evolution of domains has been observed by Lagally, Wong, and Lu[9] in experiments of ordering of oxygen atoms on a tungsten substrate [O/W(110)]. It is, however, difficult to conclude from the experimental studies whether this slow island growth is due to surface inhomogeneities (steps, terraces, vacancies, etc.) or to other reasons. These issues will be resolved when experiments are performed on very clean surfaces.

In our MC studies, the initial configuration is a circular domain of one sublattice surrounded by a sea of one other degenerate sublattice on an $N \times N$ square lattice (Fig. 1). In the standard transcription from a lattice gas to an antiferromagnet,[10] the spins are described by a nearest-neighbor (nn) Ising Hamiltonian

$$H=-\bar{J}\sum_{\substack{ij\\ \langle nn\rangle}} S_i S_j, \tag{1}$$

where $S_i=\pm 1$. The exchange constant $\bar{J}<0$ and for convenience we define $J=-\bar{J}$. The spins

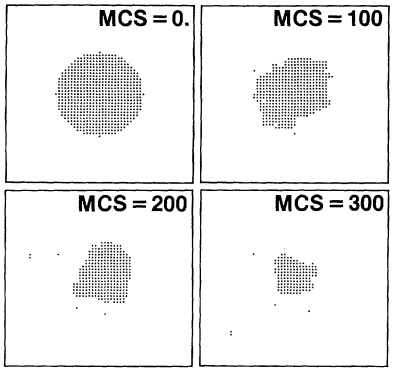

FIG. 1. The evolution of an initially circular domain for various instants of time indicated at the top of each snapshot, for $T=0.6T_c$.

order antiferromagnetically at low temperatures ($T \ll T_c = 2.27J$). Periodic boundary conditions are used with the lattice size N much larger than the initial radius R_0. The spins are exchanged by Kawasaki dynamics. A nearest-neighbor pair of spins is randomly chosen and the change in energy ΔE is computed before and after the spins are exchanged. The transition probability W is then obtained with use of[10]

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

where k_B is the Boltzmann constant and T the temperature. The constant τ sets the time scale. Notice that τ^{-1} is like an attempt frequency and should have an Arrhenius temperature dependence. Thus $\tau \sim \exp(-Q'/k_B T)$, where Q' is an activation energy related to the coupling to the heat bath, so that if $Q' \ll k_B T$, τ is independent of temperature for the growth kinetics. The transition probability W is then compared with a random number r ($0 \leq r \leq 1$), and the spins are exchanged if $W \geq r$. If $W < r$, the old configuration is retained. For Glauber dynamics,[10] a randomly chosen spin is flipped only if the transition probability $W = \tau^{-1} \exp(-\Delta E/k_B T) \geq r$. In both types of dynamics, this procedure is repeated several times and the area of the domain is monitored as a function of time. The average area of the domain is then obtained by averaging the data over at least twenty configurations for $T \leq 0.6T_c$ and forty configurations for $T > 0.6T_c$.

In Fig. 1, we display the snapshots of the evolution of an initially circular domain at different times for $T = 0.6T_c$. For purposes of display every alternate spin in a given configuration has been flipped which results in ferromagnetic domains of up spins (circles) and down spins (white region). It is quite obvious that the circular domain roughens very rapidly because of thermal fluctuations. For $T \leq 0.5T_c$, we found that the circular domain remained essentially circular throughout the evolution, whereas for $T \geq 0.8T_c$, thermal fluctuations are so strong that the domain becomes extremely wavy in less than 10 MC steps.

Both the Kawasaki and Glauber dynamics give qualitatively similar behavior for the kinetics. It is found that the instantaneous average area $A(t)$ decreases linearly with time[11] as shown in the inset of Fig. 2,

$$A(t) = A_0 - \alpha t, \quad (3)$$

where A_0 is the initial area of the domain. This

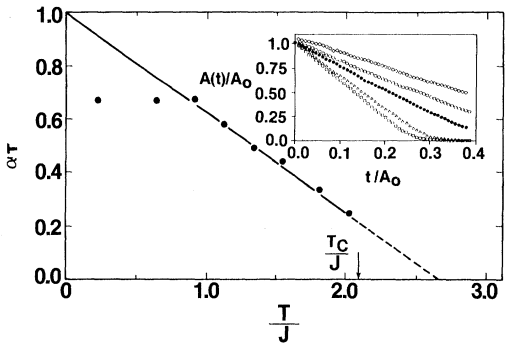

FIG. 2. The slope $\bar{\alpha}$ [Eq. (7)] plotted as a function of temperature, normalized to the exchange J. The points are the results of a Monte Carlo simulation using Glauber dynamics for $R_0 = 20$, and the line is the result of the roughening model. For both the simulations and the model calculation, the hopping time τ has been set to unity. The α obtained from the model calculation is normalized to its $T = 0$ value. Inset: the normalized area $A(t)/A_0$ vs t/A_0 for different temperatures; $T = 0.9T_c$ (diamonds), $T = 0.8T_c$ (open circles), $T = 0.7T_c$ (solid circles), $T = 0.5T_c$ (triangles), and $T = 0.4T_c$ (squares).

is in agreement with the previous theories for $d = 3$.[1-4] Also in Fig. 2, the slope $\alpha\tau$ vs T/T_c is plotted for the case of Glauber dynamics. For $T \leq 0.6T_c$, the slope $\alpha\tau$ is constant as expected from Allen and Cahn[4] and earlier phenomenological[1-3] investigations. However, for $T \geq 0.6T_c$, $\alpha\tau$ decreases linearly with increasing temperature. This deviation is explained below in terms of roughening fluctuations. In the case of Kawasaki dynamics, an additional exponential temperature dependence is found which is due to the exchange dynamics used in the simulation. This is shown in Fig. 3 where $\ln(\alpha\tau)$ vs J/T is plotted. For $T \leq 0.6T_c$, the MC results fall on a straight line with a slope of 0.4. At higher temperatures ($T \geq 0.6T_c$), a strong deviation from the exponential is found. In the inset of Fig. 3, $\alpha' \equiv \alpha\tau \times \exp(0.4J/k_B T)$ vs T/T_c is plotted and a linear decrease (dashed line) of α' is found for $T \geq 0.6T_c$, as in the case of Glauber dynamics (Fig. 2). The deviation of the point at $T = 0.95T_c$ from the linear behavior is presumably due to the presence of critical fluctuations which become increasingly important as $T \to T_c$.

To investigate the role of thermal fluctuations on the rate of shrinking of a circular grain, we use a continuum approximation. Initially ($t = 0$) the order parameter $\Psi(\vec{r}, t)$ is described by a circular region of spin up, $\Psi \simeq 1$ (or one type of sublattice), surrounded by an infinite region of spin

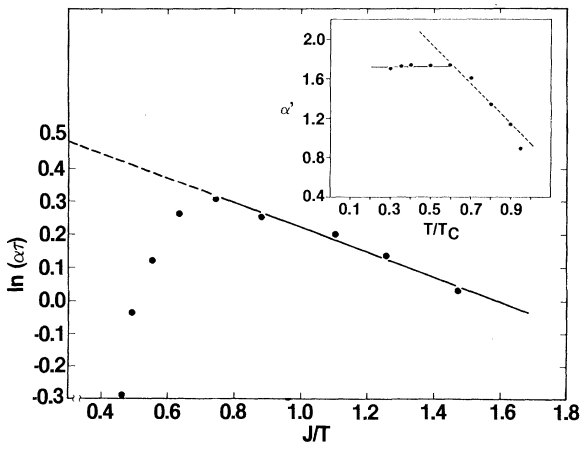

FIG. 3. Logrithm of slope $\alpha\tau$ (obtained with Kawasaki dynamics) is plotted vs J/T for $R_0 = 20$. Inset: $\alpha' \equiv \alpha\tau \exp(0.4J/k_BT)$ vs T/T_c.

down, $\Psi \simeq -1$ (or the other type of sublattice). The time evolution of the order parameter is given by a Langevin equation with nonconserved dynamics.[12-14] With use of polar coordinates and with the assumption of a form for Ψ which represents a nearly circular domain with a boundary given by $r = R(\theta,t)$, it can be shown that such a solution is self-similar. The self-similarity exists only for $r \simeq R$, and for $R \gg 1$, where all lengths are scaled by the lattice constant. An equation can then be derived[13] for the time evolution of the boundary $R(\theta,t)$,

$$\dot{R} = -1/R + R_{\theta\theta}/R^2 + \xi/R^{1/2}. \tag{4}$$

In Eq. (4), the time is scaled by the hopping time τ, which sets the microscopic time scale and which is expected to have an Arrhenius temperature dependence. The dot signifies a time derivative and $R_{\theta\theta}$ is the second derivative of $R(\theta,t)$ with respect to θ. Allen and Cahn[4] studied $d = 3$ systems where thermal fluctuation effects are less important and the stochastic force can be omitted. The noise term ξ is R dependent because of the use of polar coordinates and is responsible for the roughening of the initially circular interface. The correlation function of the noise is

$$\langle \xi(\theta,t)\xi(\theta',t')\rangle = \frac{T}{2J}\frac{\xi_0^2}{M^2}\delta(\theta-\theta')\delta(t-t'). \tag{5}$$

In Eq. (5), M is the equilibrium value of the order parameter and ξ_0 is the full width of the interfacial region. At temperatures not too close to the critical temperature, $T_c \simeq 2.27J$, we take M and ξ_0 approximately equal to 1.

Although an initially straight interface becomes infinitely rough in two dimensions as time goes to infinity, for finite times the roughening is finite. For short times, $R(\theta,t)$ is calculated with a perturbation theory where $R(\theta,t) = R_0 + R_1 + R_2 + \ldots$, with R_0 being independent of T, and R_1 and R_2 being of order $T^{1/2}$ and T, respectively. The results of this perturbation analysis yield the equations of motion

$$\dot{R}_0 = -1/R_0, \tag{6a}$$

$$\dot{R}_1 = \frac{R_1}{R_0^2} + \frac{R_{1\theta\theta}}{R_0^2} + \frac{\xi}{R_0^{1/2}}, \tag{6b}$$

$$\dot{R}_2 = \frac{R_2}{R_0^2} - \frac{R_1^2}{R_0^3} + \frac{R_{2\theta\theta}}{R_0^2} - \frac{2R_1R_{1\theta\theta}}{R_0^3} - \frac{1}{2}\frac{\xi R_1}{R_0^{3/2}}. \tag{6c}$$

The area A of the minority domain is computed as a function of time. Since $A = \int d\theta \langle R^2(\theta,t)\rangle$, only the angle-averaged values of R_0, R_1, and R_2 are needed.

The time rate of change of the area of the minority domain is then derived from Eq. (6), and it is found that

$$\bar{\alpha} \equiv \frac{1}{\pi}\frac{\partial A}{\partial t} = -2\left(1 - \sum_{n=-N}^{N-1}\frac{n^2 G_n}{R_0^2}\right) + \frac{T}{4J} \tag{7}$$

with t still in units of τ, so that $\bar{\alpha} = \alpha\tau$. In Eq. (4), G_n is the nth Fourier component of

$$R_1(\theta,t) = \sum_{n=-N}^{N-1} G_n e^{in\theta}.$$

The cutoff, $N \simeq 2\pi R_0$, is due to the discreteness of the lattice. By Fourier transformation of Eq. (6b), it can be shown that

$$\dot{G}_n = 2G_n(1-n^2)/R_0^2 + T/4\pi J R_0. \tag{8}$$

Equation (7) can be solved for $G_n(t)$, and an approximate evaluation of Eq. (7) (omitting terms of order $1/R_0$) yields $\bar{\alpha} = -2(1 - \frac{3}{8}T/J)$. Numerical solution of Eq. (7) yields similar results for $\bar{\alpha}$, with some radius-dependent corrections.

The approximate expression for $\bar{\alpha}$ is plotted in Fig. 2 along with the results of the MC simulations for Glauber dynamics. The analytical result and the simulations have been fitted at one point, since the overall time scale used in the simulation differs from that of the continuum theory. In both cases τ has been set to unity. The agreement between the theory and the simulation is excellent in the region $T > J$. In this region, $\bar{\alpha}$ is linear in T and is decreased from the rate that would be predicted if fluctuation effects were ignored. The physical origin of this decreasing

rate of shrinking is the roughening of the domain boundary to a noncircular shape by the thermal fluctuations, whose effects are important in two dimensions.[12] These fluctuations effectively increase the area at any given time, thus resulting in a decreasing $\bar{\alpha}$ when compared with $\bar{\alpha}$ calculated from purely deterministic effects. The deviation from the deterministic theory is not small, indicating the effects of these fluctuations, which could be ignored in three dimensions.

At low T, the simulations show a temperature-independent value for $\bar{\alpha}$. This value is about 30% lower than that predicted by the continuum theory when extrapolated to $T=0$. The reason for this discrepancy lies in the effects of the discreteness of both the space lattice and the spins, which does not allow a perfectly circular initial domain. Furthermore, the motion of the domain boundary must proceed in discrete steps, as opposed to the continuous motion allowed in the analysis described above. Thus when compared with a continuum theory for an initially circular domain, lattice and discrete spin effects result in some effective roughness, even at zero temperatures. This effective roughness leads to the T-independent decrease of $\bar{\alpha}$ at low temperatures from the values predicted by the continuum theory.[15]

In conclusion, the roughening of the domain boundary by thermal fluctuations gives rise to a strong temperature dependence of the rate of domain growth. Good agreement is found when the MC results are compared with the roughening model. Scattering experiments on domain kinetics of adsorbed atoms on clean surfaces can test these predictions by investigating the time dependence of widths of Laue spots.

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