Model of Interfacial Melting

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A two-dimensional model is proposed to describe systems with phase transitions which take place in terms of crystalline, as well as internal, degrees of freedom. Computer simulation of the model shows that the interplay between the two sets of degrees of freedom permits observation of grain-boundary formation and interfacial melting, a nonequilibrium process by which the system melts at the boundaries of a polycrystalline domain structure. Lipid membranes are candidates for systems with pronounced interfacial melting behavior.

PACS numbers: 64.70.Dv, 61.50.Cj, 61.70.Ng, 87.20.Cn

A very common process in nature is the spontaneous formation and growth of ordered structures and domains in systems which are quenched through an equilibrium phase transition by external changes in thermodynamic potentials. In cases where the ordered structure is highly degenerate, the domains are formed in a large number of thermodynamically equivalent orientations in space. An example is polycrystalline aggregates resulting from thermal quenches below a melting transition temperature, T_m. Such aggregates consist of a distribution of domains (or grains) separated by a random network of grain boundaries. For a pure system, this produces a nonequilibrium state, and normal grain growth and annealing will take place as a function of time.[1] The rate of growth depends on temperature. The driving force for the growth is the reduction of interface area and hence the total interfacial energy.[2] The grain-boundary tension associates the boundary regions with local-equilibrium melting temperatures which are lower than T_m. If the polycrystalline aggregate is heated through T_m, two processes will therefore occur and compete during the nonequilibrium melting process; (i) grain growth, and (ii) melting at the grain boundaries (interfacial melting). It is usually found that the time scales of these two processes are such that either the annealing process is completed before melting takes place, or the grain-boundary region is too small to be monitored experimentally.[3]

In this Letter we propose a microscopic interaction model which allows a detailed study of the interplay between grain growth and grain-boundary melting in a way which enhances interfacial melting phenomena. The nonequilibrium properties of the model are investigated by computer simulation techniques which allow a quantitative study of the interfacial region in terms of interfacial density and energy. Previous theoretical studies of grain-boundary melting and formation[3-10] have focused

on the constrained thermal equilibrium of the interface between a few misoriented regular grains of, for example, Lennard-Jones matter. These studies do not allow for simultaneous grain growth (at best reorientation[7] of the grains close to T_m) since they do not consider a statistical ensemble of grains with a specific topology of the boundary network.

The model on which the present study is based is a two-dimensional lattice model formulated in terms of a set of variables $\{n_i^a, p_i\}_{i=1}^N$ assigned to the N sites of a triangular lattice. n_i^a are lattice-gas variables ($n_i^a = 0,1$) associated with an internal degree of freedom, a, of a two-state ("spin-$\frac{1}{2}$") system, $a = 1,2$; i.e., $n_i^1 = 1 - n_i^2$, all i. The two states carry different internal degeneracies, $D_1 < D_2$. The variables n_i^a are coupled by the lattice-gas Hamiltonian

$$H_L = \sum_{\langle i,j \rangle} \sum_{a,\beta} J_{ij} n_i^a n_j^\beta = J_0 \sum_{\langle i,j \rangle} \sum_{a,\beta} A_a A_\beta n_i^a n_j^\beta, \qquad (1)$$

where $J_0 < 0$ and A_a ($A_1 > A_2$) may be thought of as shape-dependent interaction strengths. H_L is isomorphic[11] to the triangular spin-$\frac{1}{2}$ Ising model in a temperature-dependent magnetic field $[\sim kT \ln(D_2/D_1)]$. Thus H_L leads to a first-order phase transition, provided that the transition temperature is below the critical temperature of the Ising model. The transition, which is driven by the difference in internal entropy of the two states, takes the system from a low-temperature phase with $n_i^1 \simeq 1$ to a high-temperature phase with $n_i^2 \simeq 1$. The transition is signaled by a discontinuity in the order parameter $2\langle n_i^1 \rangle - 1$. Crystallization in terms of translational degrees of freedom is modeled in an approximate manner via the variables p_i which are Potts-type variables, $p_i = 1,2,\ldots,q$. p_i labels the orientation of the crystalline domain with which the site i is associated. Only sites with $a = 1$ can carry Potts variables. The

Potts variables are coupled by the Hamiltonian

$$H_P = J_P \sum_{\langle i,j \rangle} (1 - \delta_{p_i p_j}) n_i^1 n_j^1, \tag{2}$$

where $J_P > 0$ is a measure of grain-boundary energy between domains in different Potts states. Thus the grain-boundary energy is assumed to be nearly isotropic and to be a step function in the orientational angle.[12] H_P is formally equivalent to a dilute q-state Potts model with a temperature-dependent concentration of vacancies. The standard q-state Potts model has been used to describe grain growth in polycrystalline aggregates[12,13] and it was found that the limit of $q \to \infty$, corresponding to infinitely many crystal orientations, is effectively reached for $q \gtrsim 30$. Consequently, we use $q = 30$ in our calculations. H_P leads to a strongly first-order transition from a Potts-ordered to a Potts-disordered phase.

It should be noted that by modeling crystallization processes on a lattice and not taking detailed account of translational degrees of freedom, we are unable to describe more subtle two-dimensional effects, such as "two-dimensional melting" and hexatic phases.[14] However, by treating crystallization in an approximate manner using a lattice model and a discrete Potts representation of grain orientations, we have gained the advantage of being able to deal with large systems which can reveal effects due to the competition between interfacial melting and grain growth. Furthermore, the simple model proposed here makes it easy to define and identify the extent of the interfacial region. This is usually troublesome for systems with true translational degrees of freedom, in particular near the melting transition, where the mobility of particles increases dramatically.[4]

The parameters of Eq. (1) are chosen so as to ensure a first-order transition of the total Hamiltonian $H = H_L + H_P$; specifically we choose $A_1 = 1$, $A_2 = 0.1$, $D_1 = 1$, and $D_2 = 5$. Other choices preserving the first-order nature lead to results qualitatively similar to those presented below. The phase diagram governed by H may, in terms of temperature and J_P/J_0, be described as follows: At large values of J_P/J_0, the two phase transitions are coupled and ordering takes place in terms of the variables n_i and p_i simultaneously. At low values of J_P/J_0, the two transitions decouple, giving rise to an intermediate phase characterized by ordering in the lattice-gas variables and disorder in the Potts variables. This intermediate phase may be thought of as a structurally disordered (glassy) solid. We shall limit ourselves here to the case $J_P/J_0 = 1$ where the two transitions are coupled and interfacial melting may be observed.[15]

The thermal behavior of the model is calculated by importance-sampling Monte Carlo techniques with use of Glauber dynamics.[16] As far as the present problem is concerned, computer simulation has an obvious advantage in that it gives direct access to the instantaneous microstructure of the system and thus permits the study of

inhomogeneous nonequilibrium patterns in real space. The simulations are carried out for different (periodic) lattice sizes, $n = 30^2$, 50^2, and 100^2, employing the following systematics. The system is initiated in its uniformly ordered ground state and subsequently equilibrated at a temperature below the melting temperature T_m. The temperature is then increased in small increments, with the same number of Monte Carlo excitations per site (MCS/S) performed at each temperature, until the system undergoes the transition to the disordered state. This gives the upper limit of the hysteresis loop and corresponds to the point of completion of the melting process, $T_m^+(N)$, which depends on the system size and the number of MCS/S. The temperature is then decreased so that the system reenters the low-temperature phase, this time characterized by a nonequilibrium domain pattern which anneals in time. The temperature is then increased a second time so as to take the system back to the high-temperature phase. Provided that annealing is slow enough, it is during this last thermal scan that interfacial melting may be observed.

Figure 1 gives the results obtained for the lower-state occupancy $\langle n_i^1 \rangle$ as a function of temperature. The equilibration time at each temperature is 2000 MCS/S. The phase transition is signaled by a sharp decrease of $\langle n_i^1 \rangle$ in a narrow temperature region. The hysteresis loop diminishes and thus T_m^+ decreases as the lattice size and the equilibration time are increased. Microstructures typical for various positions along the hysteresis loop are shown for the 100×100 lattice in Fig. 2. Figures 2(a)–2(d)
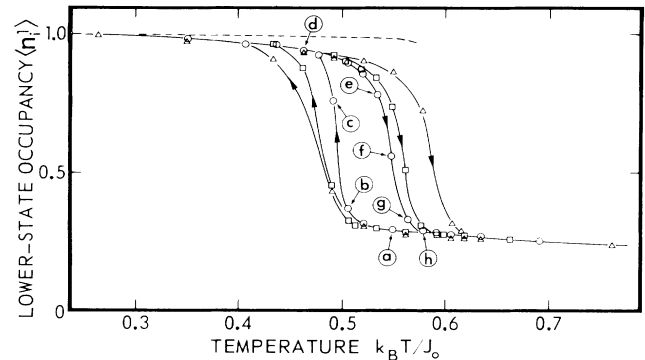

FIG. 1. Lower-state occupancy $\langle n_i^1 \rangle$ as a function of temperature in the region where interfacial melting and grain-boundary formation take place. The data points are obtained from nonequilibrium Monte Carlo calculations on lattices with N sites; $N = 30^2$ (triangles), $N = 50^2$ (squares), and $N = 100^2$ (circles). Each datum point refers to an equilibration time of 2000 MCS/S. The dashed line indicates the low-temperature thermodynamic equilibrium and metastable value of $\langle n_i^1 \rangle$ for states without grain boundaries. The equilibrium melting temperature is around $T_m \simeq 0.55 J_0/k_B$. Microstructures typical for the sequences a–d (grain-boundary formation) and e–h (interfacial melting) are displayed in Fig. 2.
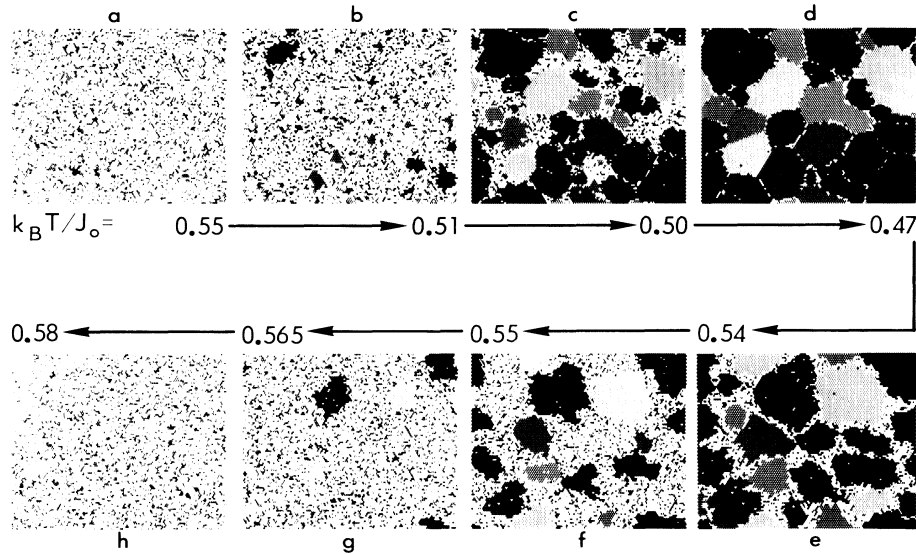
FIG. 2. Microstructures illustrating the nonequilibrium processes of (a)–(d) grain-boundary formation and subsequently (e)–(h) interfacial melting (cf. Fig. 1) for a lattice with 100^2 sites. White areas indicate melted regions and symbols indicate particles in their low-temperature solid conformation, with each symbol labeling a crystal-orientational state (Potts state).

show the nucleation and growth of crystal grains which in (d) are locked into a polycrystalline aggregate. Upon heating such an aggregate, as Figs. 2(e)–2(h) demonstrate, the polycrystal melts at the grain boundaries before any substantial annealing has taken place. During this last process, the crystal domains may be pictured as solid islands floating in a fluid sea of melted material. Upon quenching directly to temperatures below T_m^+, the system evolves in a manner qualitatively similar to that pictured in Figs. 2(a)–2(d), but with a smaller average grain size for the same equilibration time.

A quantitative description of the interfacial melting process may be obtained by calculation of the interfacial energy, $\Delta E(t)$, and the interfacial density, $\eta(t)$, as functions of the reduced temperature, $t = T_m^+(N) - T$:

$$\Delta E(t) = E(t) - E_{eq}(T), \qquad (3)$$

$$\eta(t) = \langle n_i^2(T) \rangle / [\langle n_i^1(T) \rangle - \langle n_i^1(T_m^+) \rangle]. \qquad (4)$$

$E_{eq}(T)$ is the equilibrium energy at T, and $\Delta E(t)$ is therefore a measure of the excess energy associated with the entire domain-wall network or interfacial region. The interfacial density measures the melted fraction relative to the solid fraction in such a way that the interface is defined to cover the entire system at the point where the melting process is completed. Thus, $\eta(t)$ is divergent at $t = 0$. Figure 3 gives the computer simulation results for $\Delta E(t)$ and $\eta(t)$ in the case of a sweep of increasing temperatures starting from a polycrystalline configuration. The equilibration time is again 2000 MCS/S. $\Delta E(t)$ increases smoothly towards T_m^+ and no significant finite-size effects are encountered. In contrast, $\eta(t)$ is

more size dependent, and for 2000 MCS/S the results for $N = 30^2$ deviate significantly from those of the two larger systems, simply because the grains in the small system become comparable in size to the entire lattice. The interfacial density increases dramatically as $T \to T_m^+$. In fact, the entire set of data in Fig. 3 for the two larger systems is accurately represented by a power law $\eta(t) \sim t^{-\gamma}$, with $\gamma \simeq 2$.

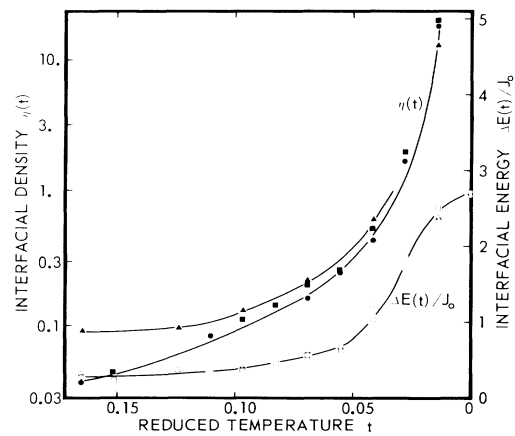Although difficult to observe experimentally, interfa-

FIG. 3. Interfacial density $\eta(t)$ (filled symbols) and interfacial energy $\Delta E(t)$ (open symbols) as functions of reduced temperature t. Results are given for different system sizes, $N = 30^2$ (triangles), 50^2 (squares), and 100^2 (circles). Note that $\eta(t)$ is plotted on a semilog scale.

cial melting is a process which in general should take place in a large number of materials (e.g., as indirectly observed[17] in Bi), provided that the appropriate thermodynamic criteria are fulfilled.[4] We propose that pseudo two-dimensional monolayers and bilayers of lipid molecules are exceptional candidates for pronounced interfacial melting behavior. These lipid membranes form condensed solid phases in terms of translational as well as internal (conformational) degrees of freedom.[18,19] The flexibility of the lipid hydrocarbon chains facilitates the formation of fluid interfaces between crystalline grains of solid (gel) lipid domains. Recent synchrotron x-ray studies[20] of lipid bilayers are consistent with interfacial melting behavior.[19]

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