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Crossover from Nonequilibrium Fractal Growth to Equilibrium Compact Growth

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Solidification controlled by vacancy diffusion is studied by Monte Carlo simulations of a two-dimensional Ising model defined by a Hamiltonian which models a thermally driven fluid-solid phase transition. The nonequilibrium morphology of the growing solid is studied as a function of time as the system relaxes into equilibrium described by a temperature. At low temperatures the model exhibits fractal growth at early times and crossover to compact solidification as equilibrium is approached.

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The fractal morphology observed for the growth of clusters and aggregates[1,2] is usually a consequence of a nonequilibrium condition which is introduced either as an intrinsic irreversibility, an effective zero-temperature condition, or simply as a constraint in observation time. By lifting the nonequilibrium condition, one will observe restructuring and compact growth[3-6] of the system which eventually, in thermodynamic equilibrium, will have a compact morphology. A proper study of the crossover from nonequilibrium fractal growth to equilibrium compact growth requires the concept of a temperature as well as a mechanism by which the system can relax into equilibrium. The natural way of meeting both of these requirements is to introduce a model Hamiltonian which governs a spontaneous thermally driven ordering process and which controls the full scenario from nucleation, fractal growth and coarsening of ordered domains, to equilibrium compact growth of the domains.

In this Letter we describe the first theoretical approach to study the crossover from nonequilibrium fractal growth to equilibrium compact growth by using a microscopic interaction model capable of accounting for the cooperative phenomenon of solidification on a lattice. The model is described by a two-dimensional site-diluted Ising Hamiltonian with a solid-fluid phase transition. In this model it is the diffusional characteristics of vacancies in the fluid phase, rather than the diffusion of latent heat away from the solidification front,[7] which leads to fractal growth at early times and at low temperatures. The dynamics of the model is a combination of Glauber-type reversible solid-fluid conversion and Kawasaki-type pair exchange of fluid and vacancies and it provides the essential mechanisms of thermal equilibration. Our main results, which have been obtained by Metropolis Monte Carlo sampling[8] supplemented by a continuum-time method,[9] are as follows: (i) At low temperatures and high dilution the growing solid domains have a fractal geometry at early times characterized by a fractal exponent of $D \simeq 1.75$, similar to that of two-dimensional diffusion-limited aggregation (DLA).[10] As time elapses, the domains become compact. (ii) For a fixed time in the early-time regime, D increases from the DLA value at low temperatures to $D \simeq 2$ as the temperature is increased. (iii) The results of our model calculations have bearing upon recent experimental studies of fractal and compact growth of solid phospholipid domains in monolayers.[11,12]

The model upon which our results are based is a generalization of an aggregation model previously developed to describe far-from-equilibrium fractal growth in impurity-controlled solidification in lipid monolayers.[12] This aggregation model, which bears some resemblance to multiparticle diffusive aggregation models,[13] was arrayed on a square lattice of sites initially occupied by a random dilution of "fluid" particles. By introduction of a seed consisting of "solid" particles and by imposition of the mechanisms of irreversible fluid-solid conversion at the interface and diffusion of vacancies (impurities) in the fluid, each on their own time scale, fractal growth was observed.[12] The fractal morphology of the growing solid was shown to be caused by a high local vacancy concentration at the solidification front. As a generalization of this model, we use here a diluted square-lattice version of the two-state interaction model of Doniach[14] associated with a particular dynamical process.

The two-state interaction model is formulated in terms of Ising spin variables, $\sigma_i = \pm 1$, where $\sigma_i = +1$ refers to the fluid state and $\sigma_i = -1$ refers to the solid state. The two states carry different internal entropies, $S_{+1} \gg S_{-1} = 0$, and different internal energies, $E_{+1} > E_{-1} = 0$. The Hamiltonian is given by

$$\mathcal{H} = \sum_i (E_{\sigma_i} - TS_{\sigma_i})\sigma_i \eta_i - J \sum_{\langle i,j \rangle} (1-\sigma_i)(1-\sigma_j)\eta_i \eta_j , \tag{1}$$

where we have introduced the occupation variables, $\eta_i = 0, 1$, and where the second summation is only over nearest neighbors of the square lattice. Equation (1) is the Hamiltonian of a site-diluted spin-$\frac{1}{2}$ Ising model. For a suitable set of model parameters and below the

percolation threshold, this model has a stiff equilibrium first-order phase transition from a low-temperature phase characterized by particles predominantly in the $\sigma_i = -1$ state (the solid phase) to a high-temperature phase characterized by particles predominantly in the $\sigma_i = +1$ state (the fluid phase). Since the transition is driven by the difference in internal entropy of the two single-particle states, one can at low temperatures immediately relate the particle state to the thermodynamic phase.

The dynamical process associated with the interaction model is devised as a combination of two types of moves: (a) Kawasaki-type nearest-neighbor pair exchange of fluid particles and vacancies, and (b) Glauber-type single-site fluid-solid conversion. The particular realization of the dynamics anticipates that the solidification process may have two distinctly different time regimes: (i) early-time nucleation, growth, and total solidification, and (ii) late-time restructuring and compact growth. In the early-time regime, we have employed conventional Metropolis Monte Carlo sampling where moves (a) and (b) are performed either separately or in combination with a probability proportional to $\exp(-\Delta\mathcal{H}/k_BT)$, where $\Delta\mathcal{H}$ is the change in energy and T is the temperature of the heat bath. The time parameter in this regime is discrete and is given in units of MCS/S (Monte Carlo steps per site). Time is initiated at the occurrence of the first nucleation event. The late-time regime involves the breaking and reformation of bonds which in the present model is much slower than the events dominating the early-time regime. Hence in this regime we have used a version of the continuum-time method of Bortz, Kalos, and Lebowitz[9] in order to speed up the simulation. This method, in which each trial move is successful, requires a grouping of particles and vacancies into classes according to the local field they experience. For each move the time is now incremented by an amount (in units of MCS/S) which depends on the Boltzmann weight of the class in question.[9] The continuum method in its present version has been tested and found to give the same results as conventional Metropolis Monte Carlo sampling.

The calculations are carried out on lattices with 256×256 sites subject to periodic boundary conditions. The Hamiltonian parameters are $E_{+1}/J=2.42$ and $S_{+1}/k_B=20.72$ and the concentration of particles is $\langle\eta_i\rangle=0.1$. Other choices of these parameters lead to results similar to those reported below. The particle concentration has to be low, however, to capture an early-time fractal solidification.[12,13]

Early-time regime.—In Fig. 1(a) are shown typical early-time configurations of the system at $t=5000$ MCS/S for an increasing series of temperatures. From the visual appearance of the solid regions, it is clear that the temperature has a significant influence on the mor-

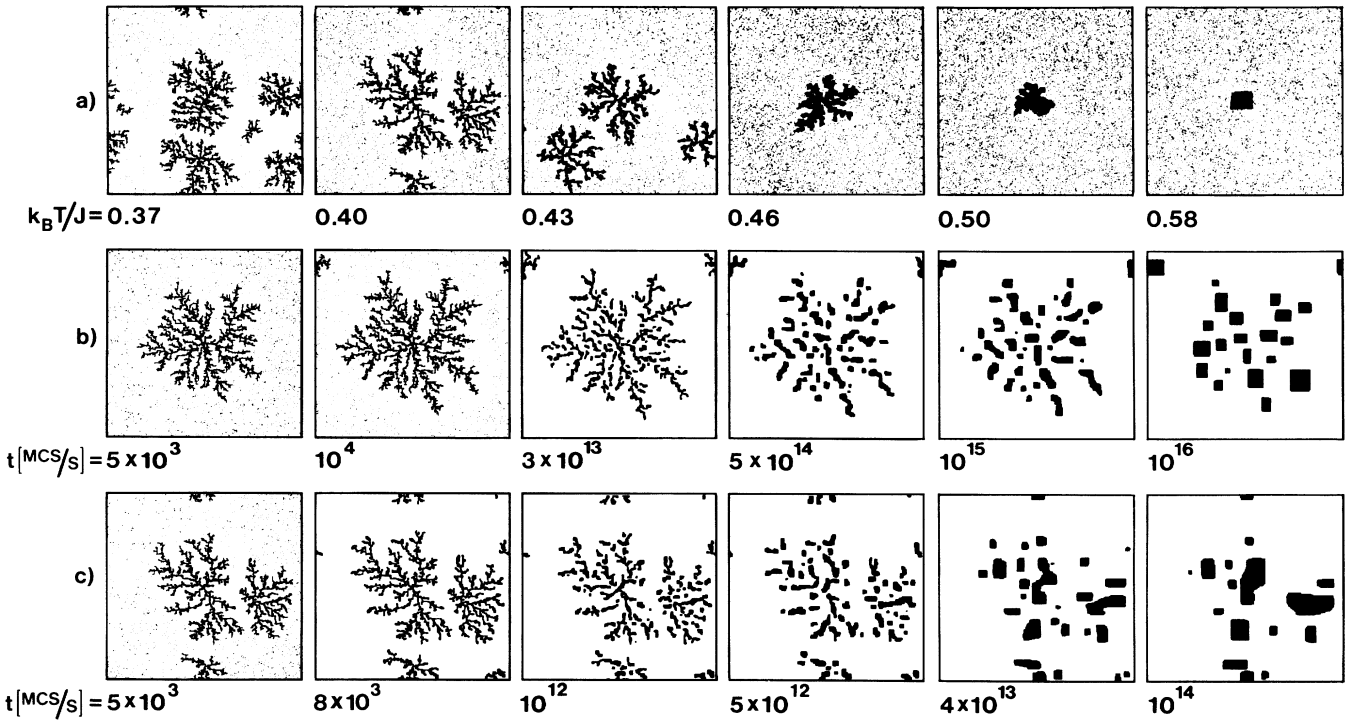

FIG. 1. (a) Typical configurations in the early-time regime, $t=5000$ MCS/S, for different temperatures T. Both fluid and solid particles are denoted by black dots. The connected structures are solid. (b) Typical configurations at different times t, in the late-time regime at temperature $k_BT/J=0.37$. (c) Same as (b) for $k_BT/J=0.40$.

phology. As the growth temperature is increased, there is distinct crossover from tenuous, fractal structures to bulk domains. As clearly seen in Fig. 1(a), this crossover takes place concurrently with a decrease in the high local vacancy concentration in the active growth zone. Hence the crossover may also be considered a transition from vacancy-controlled unstable growth to stable growth. It is noted that at low temperatures there is a high probability that several nucleation centers are formed within the observation time. It is also observed that the equilibrium shape of the solid domains are strongly influenced by the underlying square-lattice structure which is expected since the phase transition is strongly first order. In this early-time regime, restructuring is not important for the morphology. This is observed in two different ways. First, a double-logarithmic plot, Fig. 2, of the number of solidified particles $N(R_g)$ in a cluster versus its radius of gyration R_g shows the same linear relationship

$$\log N(R_g) \sim D \log R_g \tag{2}$$

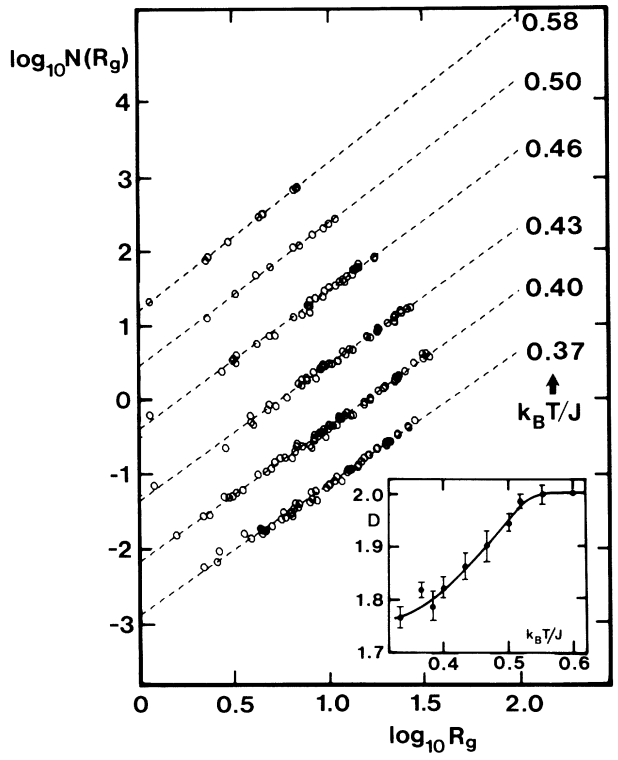

FIG. 2. Double-logarithmic plot of particle content $N(R_g)$ of solidified clusters vs radius of gyration R_g, at time $t=5000$ MCS/S. Results are shown for different temperatures, k_BT/J, cf. Fig. 1. For the sake of clarity, the ordinate has been displaced by arbitrary amounts for curves with $k_BT/J < 0.58$. The resulting fractal dimension D, as a function of temperature, is shown in the inset. The dashed lines indicate linear fits to the data according to Eq. (2).

for all clusters. Since larger radii of gyration for a given cluster correspond to a longer time lapse since its nucleation, one would not expect this to be the case if a significant restructuring took place during the growth process. Second, the time evolution of the growth process up to $t=5000$ MCS/S directly shows that only single-bonded solid particles detach due to thermal fluctuations. This corresponds effectively to a lowering of the sticking probability. The fractal dimension D of the solid clusters as a function of temperature is obtained for each temperature by averaging over 10–70 runs, depending on the temperature. The results given in Fig. 2 show that there is a smooth crossover from $D \simeq 1.76 \pm 0.02$ at $k_BT/J=0.37$ to $D \simeq 2.00 \pm 0.01$ at $k_BT/J=0.58$. As expected, the fractal dimension at low temperatures in the early-time regime is close to that of standard DLA.[10,12]

Late-time regime.— In Figs. 1(b) and 1(c) are shown typical late-time configurations as functions of time for two different temperatures, $k_BT/J=0.37$ and 0.40. As time lapses, all of the material solidifies, the tenuous structures start breaking up, restructuring occurs via melting, and the resulting fragments eventually compactify. The final stage is a kind of sintering process of solid domains in vacuum. This stage, which is extremely slow, will eventually lead to formation of a single solid domain. The overall crossover from fractal morphology to compact solid domains occurs earlier in time the higher the temperature, cf. Figs. 1(b) and 1(c). Similar to Fig. 1(a), Figs. 1(b) and 1(c) show that, as equilibrium is approached, the compact solid domains assume rectangular shapes which reflect the symmetry of the underlying lattice. Since the patterns in Figs. 1(b) and 1(c) at late times display a structure which makes it difficult to define a measure of the morphology and its possible scaling properties, we have not found it feasible to analyze the cluster morphology as a function of time.

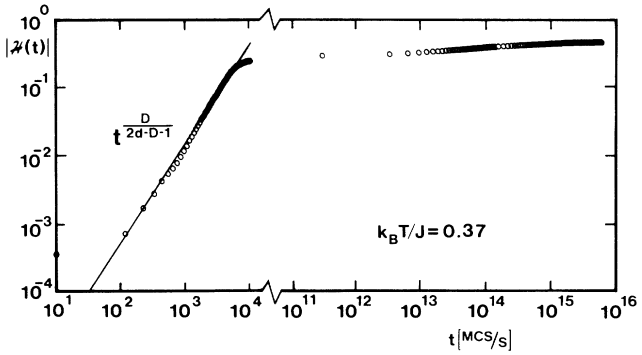

FIG. 3. Double-logarithmic plot of total energy $|\mathcal{H}(t)|$ of particles in solid clusters vs time t at temperature $k_BT/J=0.37$, cf. Fig. 1(b). The early-time regime, $t \lesssim 5000$ MCS/S, which is dominated by diffusion-limited fractal growth, is described by a power law, Eq. (3), given as a solid line.

A quantitative description of the temporal crossover from nonequilibrium fractal growth to equilibrium compact growth may be given in terms of the time evolution of the total energy $\mathcal{H}(t)$ of the particles in one solid cluster. Figure 3 shows a double-logarithmic plot of $|\mathcal{H}(t)|$ vs t for $k_BT/J=0.37$, cf. Fig. 1(b). It is seen that the early-time regime at this temperature is well described by a power law, $|\mathcal{H}(t)| \sim t^{1.45}$. This finding is consistent with the expected scaling behavior in the diffusion-limited fractal growth regime[15]

$$|\mathcal{H}(t)| \sim t^{D/(2d-D-1)}, \tag{3}$$

where d is the Euclidean dimension and the value of D is taken from Fig. 2. Equation (3) is found to hold for all temperatures in the fractal growth regime. For higher temperatures where the growth is stable and compact in both time regimes, $\mathcal{H}(t)$ is described by a simple hyperbolic function.[16] The late-stage process at low temperature is also described effectively by a power law, cf. Fig. 3, $|\mathcal{H}(t)| \sim t^{0.03}$, which implies a very slow (possible logarithmic) sintering process. We have no theory for the dynamics of this process.

The results presented in this Letter are obtained at high dilution. For less diluted systems, the value of the effective early-time fractal exponent increases.[12] In that case, the clusters will be fractal only over length scales up to a certain correlation length (which depends on the degree of dilution) beyond which there is a crossover to tenuous clusters with a uniform density ($D=2$).[13]

The pressure-induced transition from a fluid to a solid phase in phospholipid monolayers spread on an air/water interface is associated with aggregation processes leading to smooth solid domain shapes as well as fractal or dendritic morphologies,[11] depending on the experimental circumstances. In these monolayers, it is the diffusion of a dye impurity only miscible in the fluid phase which is responsible for the tenuous solid domains.[11,12] The two-dimensional model presented in the present work not only identifies and clarifies the nonequilibrium fractal-forming mechanism underlying the experimental observations, but also describes qualitatively the experimentally observed crossover[11] from nonequilibrium fractal growth to equilibrium compact solid domains at late times.

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[15]In the diffusion-limited regime, the following relations hold for the growth of a single cluster, $\rho(R_g) \sim R_g^{D-d}$ and $R_g(t) \sim N^{1/D}(t)$, where ρ is the density, $N(t)$ is the number of particles in the cluster, and R_g is the radius of gyration. Since $\mathcal{H}(t) \sim N(t)$ and

$$dN(t)/dt \sim \{\rho(R_g(t))\}^2 R_g(t) \sim [N(t)]^{[2(D-d)+1]/D},$$

Eq. (3) follows. It should be noted that the temporal scaling is not affected by a possible temperature-dependent variation of the ratio of time scales for the Glauber and Kawasaki dynamics. The time dependence of fractal growth processes has recently been discussed by P. Meakin, in *Time-Dependent Effects in Disordered Materials,* edited by R. Pynn and T. Riste (Plenum, New York, 1987), p. 58.

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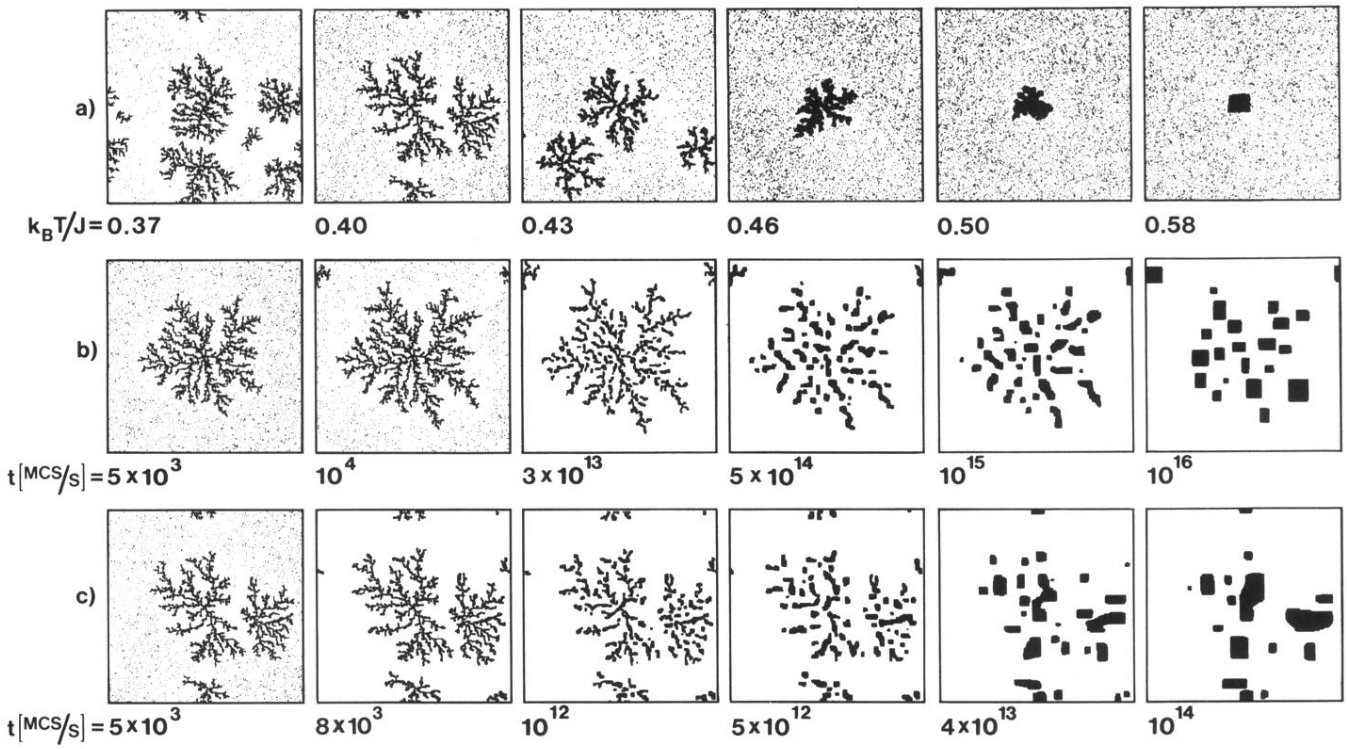

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