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RAPID COMMUNICATIONS

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Droplet distribution for the two-dimensional Cahn-Hilliard model: Comparison of theory with large-scale simulations

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We numerically solve the Cahn-Hilliard equation in two dimensions for very large system sizes and for two different values of the volume fraction ϕ. We present results for the scaling function of the droplet distribution function and compare it with several different theoretical predictions. We find that for $\phi=0.05$ the agreement between simulation results and recent theoretical predictions are reasonably good, while none of the existing theories seem to agree well with the simulation data for $\phi=0.21$.

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The dynamics of nucleation and growth for systems undergoing a first-order phase transition has received much attention in recent years [1]. This process occurs, for instance, when a binary mixture with sufficiently small fraction (ϕ) of one of the constituents is suddenly cooled from a uniform, high-temperature phase to a point within the coexistence region. In this case, the evolution of the system proceeds by nucleation and growth of droplets of the minority phase. It is, thus, of utmost importance to characterize the time evolution of the droplet distribution function, which determines the number of droplets of a given size as a function of time.

Many theoretical studies of the final stages of this nucleation process (known also as Ostwald ripening) have been carried out for both two- and three-dimensional systems [2–8]. The main feature shared by all these analytical calculations is that they involve some systematic or approximate expansion in terms of the volume fraction and are supposed to be valid only for small values of ϕ (typically less than 10%). Previous numerical studies of this process, using both microscopic models (spin-exchange kinetic Ising model [9]) and continuum models (Langevin model with a conserved order parameter or the so-called Cahn-Hilliard model [10]) have established that the late-time behavior of the system can be described in terms of scaling with a time-dependent length $R(t)$ which corresponds to the average size of the droplets. These studies find that both the scattering intensity and the cluster distribution functions show scaling behavior at late enough times. However, these numerical studies are carried out for relatively large volume fractions [11] and, thus, no systematic comparison of droplet distribution functions with analytical theories can be done.

In this Rapid Communication we present a detailed numerical study of the two-dimensional Cahn-Hilliard model in the nucleation regime for very small volume fractions

and make a detailed comparison with existing analytical theories. We find that for $\phi=0.05$ the agreement between simulation results and recent theoretical predictions are reasonably good while none of the existing theories seem to agree well with the simulation data for $\phi=0.21$. We believe that comparison with the scaling functions found in this study will be a good test for future theories in two dimensions valid over a larger range of volume fractions.

In the Cahn-Hilliard theory of the dynamics of first-order phase transitions, one considers a conserved concentration field, $\psi(\mathbf{r},t)$, which represents the difference in the local concentration of the two components of the mixture. It is assumed that the time variation of this conserved field is governed by the functional derivative of a free-energy functional given in terms of a Ginzburg-Landau expression. After suitable rescaling of distance, time, and concentration field [12], the resulting equation of motion is

$$\frac{\partial\psi(\mathbf{r},t)}{\partial t}=\tfrac{1}{2}\nabla^2(-\psi+\psi^3-\nabla^2\psi)\,. \tag{1}$$

A numerical study of the previous equation is very demanding in terms of computer time and memory, even for two-dimensional systems. First, the system has to evolve over a sufficient period of time in order to reach the scaling regime. On the other hand, as time increases, the number of droplets decreases. If one wants to study the behavior of the droplet distribution function at late times, one needs a very large system in order to reach the late stages with a reasonable number of droplets to avoid finite-size effects and to obtain statistically meaningful results.

We have numerically integrated Eq. (1) using a second-order Runge-Kutta scheme and periodic boundary conditions. We have chosen a mesh size $\delta x=1.0$ for the Laplacian discretization on a square lattice of size 540^2 for volume fraction $\phi=0.05$ and 256^2 for $\phi=0.21$. With this choice for δx we have found that droplets grow circular in shape and that the radius of gyration, R_g, of a given droplet is proportional to the geometrical radius and that the mass of the droplet (total number of particles of the minority phase in it) is given by $2\pi R_g^2$ to a great accuracy (better than 1%). On the other hand, larger choices for δx produce droplets that reflect the underlying symmetry of the square lattice used in the numerical discretization.

In our study, we have considered two volume fractions: $\phi=0.05$ and 0.21. Particularly for the smaller volume fraction considered, one has to be very careful with the initial condition. Since the system is in the metastable region of the phase diagram, a strong fluctuation is needed in the initial distribution of the order parameter in order to allow for the growth of the initial random nuclei. We chose the initial configuration to be a Gaussian distribution centered at $\psi_0=0.9$ with a variance of magnitude 5. For this particular choice of the initial configuration the magnitude of the order parameter is very large initially at random points on the lattice and one needs a very small time step for the stability of the numerical integration in the initial stage. However, the order parameter settles down to values smaller than unity very soon and the time step can be increased safely. We have carried out the numerical integration up to $t=20000$ (in the above dimensionless units). From $t=0$ to 100 the time step is chosen to be $\delta t=0.001$, from $t=100$ to 1000 the time step is $\delta t=0.025$, and for $t>1000$ δt is fixed at 0.05. In order to average over the initial random configurations, we have performed 60 runs with different initial conditions. The same parameters have been used for the case of volume fraction $\phi=0.21$ except that the Gaussian distribution for the initial field is centered at $\psi_0=0.58$. We have computed, among other quantities, the probability distribution function $f_R(R,t)$, such that $f_R(R,t)\delta R$ is the probability of finding a droplet of radius between $R-\delta R/2$ and $R+\delta R/2$ [13]. Even for a 540^2 lattice the number of droplets at late times is not very large (around 30–40 for the smallest volume fraction $\phi=0.05$) and the values of δR necessary to get smooth data need to be increased with time.

The theoretical studies predict that the droplet distribution function should have a scaling form valid at late times. The scaling assumption is that there is only one relevant length. This can be defined, for instance, as the mean value of the radius:

$$\langle R(t)\rangle=\int_0^\infty R f_R(R,t)dR\,. \tag{2}$$

It is, then, natural to define the new scaling variable, $x_0=R/\langle R(t)\rangle$. It is obvious that the mean value of x_0 is $\langle x_0\rangle=1$. The probability density function for the variable x_0 is

$$f_{x_0}(x_0,t)=\frac{dR}{dx_0}f_R(R,t)=\langle R(t)\rangle f_R(R,t)\,. \tag{3}$$

Scaling affirms that, at late enough times, the function $f_{x_0}(x_0,t)$ is independent of time t, i.e., $f_{x_0}(x_0,t)=f_{x_0}(x_0)$. We have checked this scaling form for the droplet distribution function using the simulation data. As shown in Fig. 1, scaling holds quite well for $\phi=0.05$ for $t>4000$. Although we do not show it here for lack of space, scaling holds for $\phi=0.21$ as well. The details of these calculations will be published elsewhere [14].

The theories differ in their predictions for the scaling function $f_{x_0}(x_0)$. In order to compare with theoretical predictions, one needs to note that the scaling variable

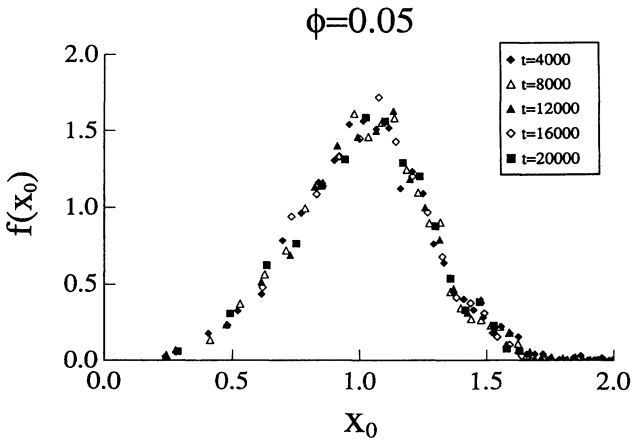

FIG. 1. Simulation data for cluster distribution function for different times and for $\phi=0.05$.

used in different theories varies from one to another. In general, the scaling variable x is defined as $x=R/R^*(t)$, where $R^*(t)$ is some time-dependent length that might or might not coincide with $\langle R(t)\rangle$. However, due to the scaling hypothesis, one can affirm that $R^*(t)$ will be proportional to $\langle R(t)\rangle$, and so the scaling variables x_0 used in our study and the general scaling variable x introduced in the theory will also be proportional to each other, i.e., $x_0=x/a$ with a some time-independent constant. By using the relation $\langle x_0\rangle=1$ we can conclude that $a=\langle x\rangle$ and then $x_0=x/\langle x\rangle$. The probability density function of x, $f_x(x)$, will be related to the probability density function of x_0 by the relation

$$f_{x_0}(x_0)\frac{dx}{dx_0}f_x(x)=\langle x\rangle f_x(x)=\langle x\rangle f_x(x_0\langle x\rangle)\,. \quad (4)$$

This relation allows us to compare the simulation data with the theoretical predictions.

Let us now briefly review the different theoretical predictions. One theoretical study extends the Lifshitz-Slyozov (LS) theory [5] to two dimensions [4,15] and is only valid in the limit $\phi\to 0$. This is the only theory that yields an explicit expression for the scaling function $f_x^{\rm LS}(x)$, namely,

$$f_x^{\rm LS}(x)=\tfrac{8}{27}x^2\left(1-\frac{2x}{3}\right)^{-28/9}\left(1+\frac{x}{3}\right)^{-17/9}\times\exp\left(\frac{-4x}{9-6x}\right). \quad (5)$$

The distribution is cut off for values $x\geq 1.5$. For this distribution one obtains $\langle x\rangle=1.0665$.

The next theoretical prediction we consider is that of Ardell [4]. The author has recently extended his earlier theory for two-dimensional systems. This theory includes the effect of diffusive correlations among nearest-neighbor clusters by introducing an *ad hoc* cutoff limit in the diffusion geometry. The distribution function needs to be evaluated numerically.

In Marqusee's theory [2], the surrounding droplets are considered an "effective medium" and the distribution function is derived in a self-consistent fashion. Again, no closed form for the distribution is found and it needs to be evaluated numerically for each volume fraction. Marqusee's theory has recently been extended and generalized by Zheng and Gunton [3]. They use a new expansion parameter (instead of $\phi^{1/2}$ used by Marqusee) and show that there is no finite cutoff for the scaled distribution function. However, the authors expect that this scheme breaks down for $\phi>0.01$.

Recently, Yao, Elder, Guo, and Grant (YEGG) [8] have used a mean-field approach for both two- and three-dimensional systems. In their theory, many droplet correlation effects are approximated in the same manner as the Thomas-Fermi approach for a Coulombic system. This theory is inapplicable where the screening length is close to the average radius of droplets and the authors found that the calculations break down for $\phi>0.085$ in two dimensions.

In Figs. 2 and 3 we compare the predictions of different theories with the numerical data for volume fractions $\phi=0.05$ and 0.21, respectively. For an easier comparison with different theories, we show the result for the distribution functions only for the latest time ($t=20000$) in the above figures. In the above figures we do not show LS and Zheng and Gunton results, since these distribution functions are much too different from the simulation results. The LS scaling function is sharper and much higher in the peak (the maximum height of the LS distribution function is about 2.5) than the corresponding numerical data. These discrepancies are expected since, as mentioned earlier, the LS results are only valid in the limit of zero volume fraction. On the other hand, the calculations for Zheng and Gunton [3] yield a distribution function which is much too short near the peak (for $\phi=0.05$ the maximum height of the Zheng and Gunton distribution function is about 1.0). It seems that this theory does not work well for these volume fractions. For $\phi=0.05$ we find that the data agrees reasonably well (Fig. 2) with the predictions of Yao *et al.* [8] and Ardell [4] (actually the

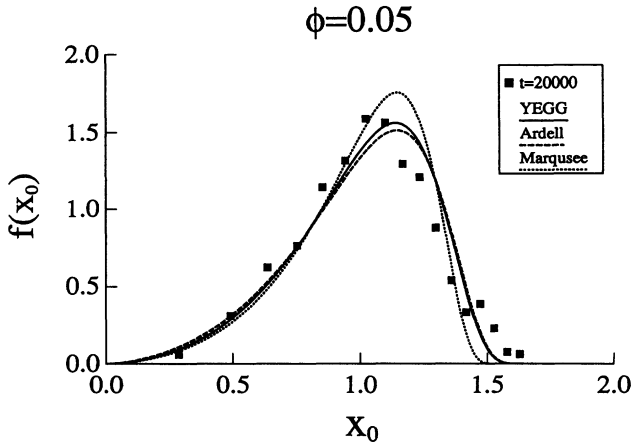

FIG. 2. Simulation data for cluster distribution function at the latest time ($t=20000$) for $\phi=0.05$ compared with various theories.

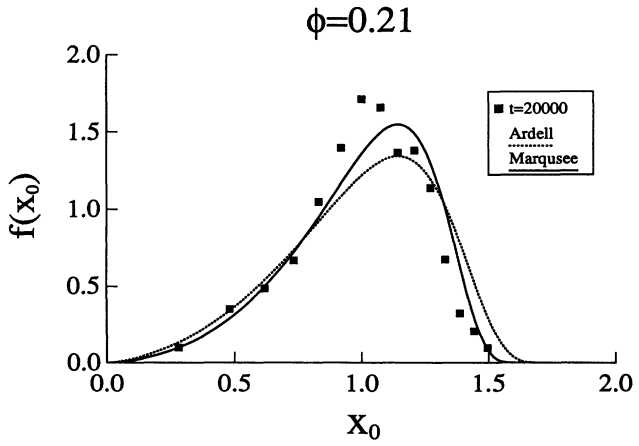

FIG. 3. Simulation data for cluster distribution function at the latest time ($t=20000$) for $\phi=0.21$ compared with various theories.

difference between these two theories are very small except near the peak). We note that there are small differences between the theoretical predictions and the numerical data both near the peak and the tail of the distribution. It seems that the location of the maximum is slightly different in the numerical distribution function. Since the uncertainties in the numerical results are larger near the tail of the distribution, it is difficult to judge whether the discrepancy near the tail is real or not.

For $\phi=0.21$, the theory of Yao *et al.* does not yield any result and Ardell's result does not compare well with the simulation data (Fig. 3). It seem that, for this volume fraction, Marqusee's theoretical result comes close to the simulation results. However, there appears to be some systematic differences between the data and the theory [16]. It seems, then, that a complete theoretical description of the nucleation and growth process in two dimensions is still incomplete and we hope that our numerical work will direct attention to this direction.

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