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Molecular dynamics on diffusive time scales from the phase-field-crystal equation

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We extend the phase-field-crystal model to accommodate exact atomic configurations and vacancies by requiring the order parameter to be non-negative. The resulting theory dictates the number of atoms and describes the motion of each of them. By solving the dynamical equation of the model, which is a partial differential equation, we are essentially performing molecular dynamics simulations on diffusive time scales. To illustrate this approach, we calculate the two-point correlation function of a fluid.

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Molecular dynamics (MD) has long been a powerful tool to study statistical mechanical systems (for an introduction, see, e.g., Ref. [1]). By postulating the interaction between atoms and solving the resulting equations of motion, precise information about each atom is known. One of the drawbacks of MD, however, is that too much information is captured. For example, atomic motions in MD simulations are resolved on atomic time scales, whereas in many systems the relevant time scales are diffusive. This makes MD computationally demanding, if not completely inapplicable, in many cases of interest where long time scales are required. In this Rapid Communication we pursue an approach to attain long time scales, starting not from individual particles but from a continuum description of matter known as the phase-field-crystal (PFC) model [2–6].

The starting point of the PFC model is that crystalline materials are governed by a free energy functional that penalizes departures from periodicity of the density in the same way that the Landau theory of phase transitions uses a functional that penalizes spatial gradients of the order parameter. The PFC model is formulated in terms of an order parameter representing the local density, and is constructed so that the free energy functional is minimized by a periodic order parameter configuration. Despite its simplicity and minimal physical input, the PFC model can reproduce both qualitative and semiquantitative (i.e., scaling) properties of multicrystalline solidification [4], dislocation dynamics [7], fracture, grain boundary energetics [4], elastic (phonon) interactions [8], grain coarsening [9], linear and nonlinear elasticity [4], and plasticity [10]. The PFC model has also been extended to binary systems [5,10], and can be related to density functional theory [5]. Recent applications of the renormalization group technique [11–13] and adaptive mesh refinement have improved the computational efficiency of the model, with resultant computational times several orders of magnitude times faster than MD [11,14].

Although the PFC model represents microscopic configurations, it is not MD. The model describes the collective properties of the crystal, but it does not attempt to describe the motion of each individual atom. One can regard the peaks in the order parameter as representing local density maxima, and thus be identified as PFC "atoms." However, although the order parameter $\rho(\vec{x},t)$ tends to form PFC atoms in order to minimize the total energy of the system, their number is not conserved. This neglect of the actual atomic configuration, and the resulting absence of vacancies in the description, prevents us from using the model to describe faithfully microscopic phenomena that involve atomic hopping and vacancy diffusion.

The goal of this paper is to modify the PFC model such that it describes not only the collective behavior, but also the motions of individual atoms. We will see that this can be done by constraining the value of the order parameter to be positive. By so doing, instead of being an abstract order parameter, $\rho(\vec{x},t)$ becomes a physical density—the number of atoms in the model can be controlled by adjusting a single parameter, ρ_0. The resulting theory is a MD simulation: we can specify the temperature, number of atoms, and the interaction potential between atoms. As an illustration of this approach we simulate a simple fluid and reproduce the form of the standard two-point pair distribution function.

Inclusion of Vacancies. In real materials, vacancies are present when the local density is low, i.e., when there are not enough atoms to fill the space. In the PFC model, however, even if the value of the order parameter is small, which is analogous to the low density situation, a perfect periodic configuration can still be formed because there is no constraint, or energy penalty, for negative values of the order parameter. Therefore, as long as the system is in a periodic state, such as the two-dimensional (2D) triangular phase, any uniform configuration will evolve to a spatially periodic one in equilibrium. Thus, the notion of vacancies is not respected in this model. If a vacancy is created through a special initial condition, the free volume will simply diffuse throughout the crystal as the configuration readjusts its periodicity.

We can stabilize vacancies by imposing a constraint on the order parameter—we forbid the order parameter to be negative. In this case, if the local order parameter is not high enough, instead of forming a periodic state that extends to negative values, the system can form a periodic structure in some region, while leaving a very low, or zero, density in another. The number of atoms is then conserved and the zero density regions are identified with vacancies.

We now identify the region of the phase diagram in which vacancies are present and stable, and we do this by calculat-

ing the energy of a state with vacancies, working for simplicity in two dimensions. The PFC model is given by the free energy density [3,4]

$$f = \frac{\rho}{2}[r + (1 + \nabla^2)^2]\rho + \frac{\rho^4}{4}, \tag{1}$$

where $r<0$ is the undercooling parameter and ρ_0 is the mean value of the order parameter. The dynamics follows the "modified" PFC formulation [8],

$$\frac{\partial^2 \rho}{\partial t^2} + \beta \frac{\partial \rho}{\partial t} = \alpha^2 \nabla^2 \frac{\delta F}{\delta \rho} + \eta, \tag{2}$$

where $F \equiv \int f d^d x$ is the total free energy of the system, α and β are parameters that control the evolution, and η is a Gaussian white noise satisfying the usual fluctuation-dissipation theorem. It is helpful to introduce the ansatz for the one-mode approximation to the triangular state in two dimensions,

$$\rho(\vec{x}) = A \sum_{j=1}^{3} (e^{i\vec{k}_j \cdot \vec{x}} + e^{-i\vec{k}_j \cdot \vec{x}}) + \rho_0, \tag{3}$$

where $\vec{k}_{1,2,3} = \hat{x}, (\sqrt{3}/2)\hat{y} \pm (1/2)\hat{x}$ are the basis wave vectors of the triangular phase. Substituting this ansatz into Eq. (1), and averaging over the whole system gives the free energy density as a function of the constant amplitude, A,

$$f_0(\rho_0, A) = \frac{45}{2}A^4 - 12A^3\rho_0 + \frac{\rho_0^2}{4}(2 + 2r + \rho_0^2) + 3A^2(r + 3\rho_0^2). \tag{4}$$

Minimizing $f_0(\rho_0, A)$ with respect to A gives two roots,

$$A_{\pm}(\rho_0) = \frac{1}{15}(3\rho_0 \pm \sqrt{-15r - 36\rho_0^2}), \tag{5}$$

where the solutions that minimize the energy are $A = A_+$ for $\rho_0 > 0$ and $A = A_-$ for $\rho_0 < 0$. The roots are real for $\rho_0 < \sqrt{-5r/12}$ (recall that $r<0$).

Now, let us consider the effect of the constraint that the density be positive. Examining Eq. (3), we see that the summation is bounded by ± 6, so requiring $\rho(\vec{x}, t) \geq 0$ is equivalent to requiring $|A| \leq \rho_0/6$. However, Eq. (5) shows that $|A_+(\rho_0)| > \rho_0/6$ for all values of r and ρ_0, so the ground state $A = A_+$ is forbidden by the constraint. The ground state must be given by some other configuration.

There are at least two possible configurations for the ground state. First, the ground state can still be perfectly periodic with an amplitude $A \neq A_+$ satisfying $|A| < \rho_0/6$. Second, the ground state can partition itself into two domains—a perfectly periodic domain with average density ρ_1 and amplitude A_1 satisfying $|A_1| \leq \rho_1/6$, and a domain with $\rho(\vec{x}) = 0$. The second domain corresponds to vacancies. To see which is realized in practice, we have to calculate the energy of these two states, and recognize that the ground state is the one with lower total energy.

Let us first calculate the free energy density of a perfectly triangular state. Since $A = A_+$ is forbidden, we are left with three options for A: $A = A_-$, which is the other local minimum of the free energy, and $A = \pm \rho_0/6$. The latter two are the boundary values satisfying the condition $|A| \leq \rho_0/6$. By examining Eq. (4), one can see that $f_0(\rho_0, \rho_0/6) \leq f_0(\rho_0, -\rho_0/6)$, so we can ignore the $A = -\rho_0/6$ solution. The free energy density of the periodic state is then

$$f_{per}(\rho_0) = f_0\left(\rho_0, \frac{\rho_0}{6}\right) \tag{6}$$

if $|A_-(\rho_0)| > \rho_0/6$, and otherwise,

$$f_{per}(\rho_0) = \min\left[f_0(\rho_0, A_-(\rho_0)), f_0\left(\rho_0, \frac{\rho_0}{6}\right)\right] \tag{7}$$

where $\min(a,b)$ denotes the minimum of a and b. Substituting $A_-(\rho_0)$ and $\rho_0/6$ into Eq. (4) gives the explicit expressions

$$f_0(\rho_0, A_-(\rho_0)) = -\frac{13}{500}\rho_0^4 + \frac{7r + 25}{50}\rho_0^2 - \frac{1}{10}r^2 - \frac{20r\rho_0 + 48\rho_0^3}{375}\sqrt{-15r - 36\rho_0^2}, \tag{8}$$

$$f_0\left(\rho_0, \frac{\rho_0}{6}\right) = \frac{1}{288}[133\rho_0^4 + (144 + 168r)\rho_0^2]. \tag{9}$$

Now, let us compare the energy of these two possible ground states. If the system is perfectly periodic over the whole domain, whose area is designated B_0, then the free energy is given by

$$f_{whole}(\rho_0) = B_0 f_{per}(\rho_0). \tag{10}$$

If the whole system instead partitions itself into one domain made up of a triangular phase having mean density $\rho_1 > \rho_0$, with the remaining domain having $\rho = 0$, the free energy is given by (for simplicity, surface energy between the two phases is neglected in this calculation)

$$f_v(\rho_0) = B_1 f_{per}(\rho_1) = \left(\frac{\rho_0}{\rho_1}\right) B_0 f_{per}(\rho_1), \tag{11}$$

where B_1 is the area of the triangular domain. The second equality is obtained by using the conservation of mass $\rho_0 B_0 = \rho_1 b_1$. The difference between these two free energies, $\Delta f \equiv f_v - f_{whole}$, is

$$\Delta f = B_0 \rho_0 \left(\frac{f_{per}(\rho_1)}{\rho_1} - \frac{f_{per}(\rho_0)}{\rho_0}\right). \tag{12}$$

It is important to note that ρ_1 is a parameter that we can choose to minimize the energy of the second possible state; the only constraint is that $\rho_1 \geq \rho_0$ because $B_1 \leq B_0$.

For vacancies to exist, we require that $\Delta f < 0$ for some values of $\rho_1 > \rho_0$. We note, however, that for the solution $A = A_-$, $f_0(\rho_0, A_-(\rho_0))/\rho_0$ is an increasing function of ρ_0 (see Fig. 1) and so Δf is positive for this branch of the solution. In other words, no vacancy is present in this solution. Therefore, in order to have vacancies in the ground state, we require this branch of the solutions to be forbidden by the constraint; i.e., we require $|A_-(\rho_0)| > \rho_0/6$, which by Eq. (5) is equivalent to requiring

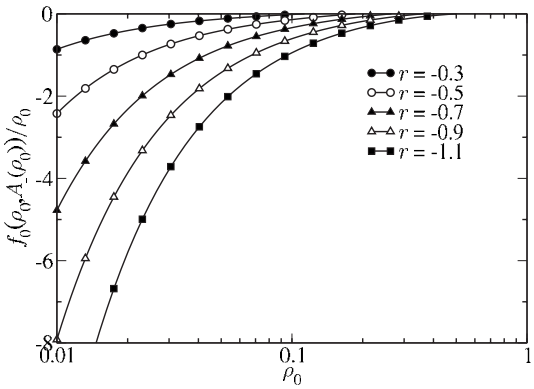

FIG. 1. The function $f_0(\rho_0, A_-(\rho_0))/\rho_0$ is an increasing function of ρ_0, plotted for various values of r. The x axis is plotted on logarithmic scale in order to resolve the curves.

$$\rho_0, \rho_1 < \sqrt{-12r/53}. \tag{13}$$

On the other hand, it is easy to show from Eq. (9) that $f_0(\rho_0, \rho_0/6)/\rho_0$ has a minimum (for $r < -6/7$) at

$$\rho_{min} = \sqrt{(-48 - 56r)/133}. \tag{14}$$

Thus, if $\rho_0 \leqslant \rho_{min}$ and $r < -6/7$, the system can minimize the total free energy by partitioning itself into two domains: a triangular phase made up of atoms, with average density $\rho = \rho_{min}$, and a region of vacancies where $\rho = 0$. Combining Eqs. (13) and (14) indicates that the minimum also satisfies the constraint $|A_-(\rho_0)| > \rho_0/6$ so long as $r > -636/343$. We also note that the area of the triangular phase, $B_1 = B_0(\rho_0/\rho_1)$, is directly proportional to the mean density, ρ_0. So by adjusting ρ_0, we can control the number of atoms in the PFC model. This shows that the addition of the constraint, $\rho(\vec{x}) > 0$ for all $\vec{x}$, does indeed promote the $\rho(\vec{x})$ from an abstract order parameter to a physical density, which dictates the number of atoms in the system.

To summarize, the various constraints define the region

$$\rho_{min} < \sqrt{\frac{-48 - 56r}{133}} \quad \text{and} \quad -\frac{636}{343} < r < -\frac{6}{7}, \tag{15}$$

where the triangular phase and stable vacancies can coexist. The area fraction of the triangular phase is ρ_0/ρ_{min}, and the amplitude is $A = \rho_{min}/6$. The rest of the domain has zero density and thus is composed of vacancies. These results are summarized in Fig. 2.

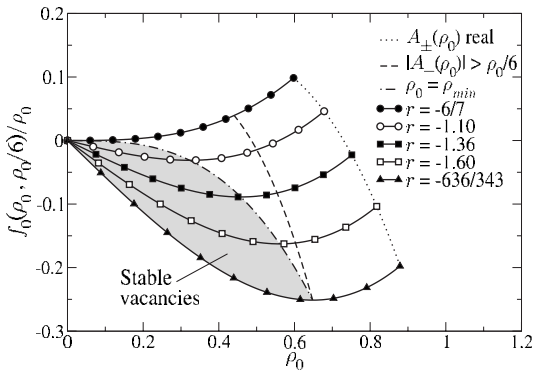

FIG. 2. Window in which stable vacancies can coexist with a triangular phase. A minimum in $f_0(\rho_0, \rho_0/6)/\rho_0$ exists at $\rho_{min} = \sqrt{(-48-56r)/133}$ for $r \leqslant -6/7$, and this minimum is forbidden by the constraint $|A_-(\rho_0)| \leqslant \rho_0/6$ for $r > -636/343$.

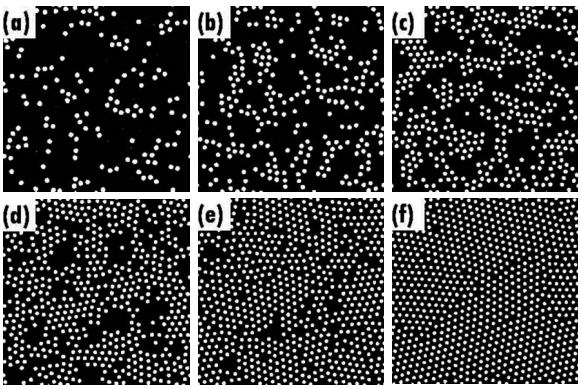

FIG. 3. PFC simulations with different values of ρ_0 for $r = -0.9$. The number of atoms increases with ρ_0. (a)–(f) correspond to $\rho_0 = 0.06$, 0.08, 0.10, 0.12, 0.14, and 0.16.

Implementation. In order to implement the positive density constraint, we add a vacancy term, $f_{vac}(\rho)$, to the free energy density that penalizes negative values of $\rho(\vec{x}, t)$. As long as the repulsion from negative values is strong enough to avoid $\rho < 0$, the result should not depend on any particular choice of $f_{vac}(\rho)$. Of the many possible choices for $f_{vac}(\rho)$, we use

$$f_{vac}(\rho) = H(|\rho|^n - \rho^n), \tag{16}$$

with $n = 3$ and $H = 1500$, because this turns out to be numerically convenient and stable.

With the vacancy term, Eq. (16), we can numerically verify the analytical calculation for the coexistence between the periodic phase and vacancies. Figure 3 provides results from simulations with $r = -0.9$ and different values of ρ_0, showing clearly that the number of atoms increases with ρ_0. In addition, Fig. 4 shows that the PFC atomic density (i.e., the number of atoms per unit area) indeed increases linearly with ρ_0, as expected. The curve starts to saturate at around $\rho_0 = 0.15$, as opposed to the prediction from Eq. (15), $\rho_{min} \approx 0.134$. This discrepancy is not surprising for several reasons: In the analytical calculation, we consider only the one-

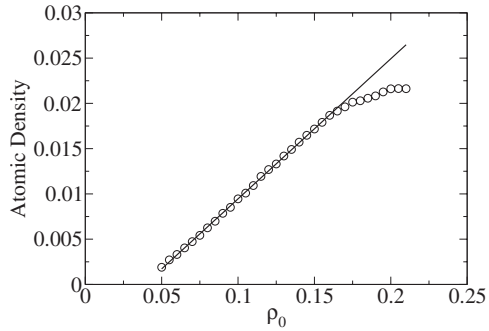

FIG. 4. The PFC atomic density increases linearly with the order parameter, ρ_0, when the vacancy term is added to the model. $r = -0.9$ is used. The curve starts to saturate at around $\rho_0 = 0.15$, as opposed to the analytical prediction $\rho_0 = \sqrt{(-48-56r)/133} = 0.134$.

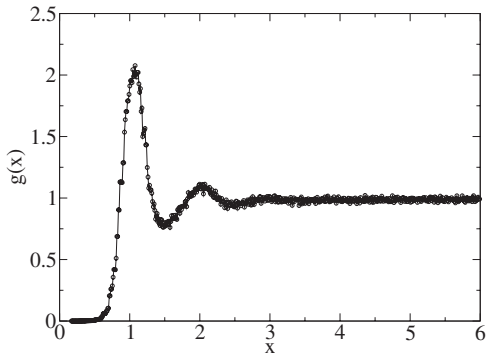

FIG. 5. The two-point correlation function of a liquid using the PFC model. Parameters are $r=-0.9$, $\rho_0=0.09$, $\alpha=15$, and $\beta=0.9$.

mode approximation in the ansatz; we did not account for the surface energy between the triangular phase and the vacancies; and we did not account for thermal fluctuations, introduced in the simulation to help the system equilibrate faster.

With the modifications described above, the PFC simulation operates similar to a molecular dynamics simulation, but on diffusive time scales many orders of magnitude faster than pure molecular dynamics [4]. We can control the number of atoms and the temperature in the system by adjusting ρ_0 and the magnitude of thermal noise, η, respectively. The interaction potential between individual PFC atoms is specified by the PFC free energy (specifically the gradient terms) and is controlled by the undercooling r. In fact, by decreasing the value of ρ_0 such that the system is dilute enough, we can simulate a liquid using the PFC model. We simulated such a liquid with parameters $r=-0.9$, $\rho_0=0.09$, $\alpha=15$, and $\beta=0.9$. A typical result is shown in Fig. 3(b). Figure 5 shows the two point correlation function, $g(x)$, extracted from the simulation. It resembles the two-point correlation function of a liquid—a correlation hole, a strong nearest-neighbor correlation, and a weak correlation with atoms one or two atomic spacings away [1].

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