Beyond Cahn-Hilliard-Cook ordering theory: Early time behavior of spatial-symmetry-breaking phase transition kinetics

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We extend the early time ordering theory of Cahn, Hilliard, and Cook (CHC) so that our generalized theory applies to solid-to-solid transitions. Our theory involves spatial-symmetry breaking (the initial phase contains a symmetry not present in the final phase). The predictions of our generalization differ from those of the CHC theory in two important ways: exponential growth does not begin immediately following the quench and the objects that grow exponentially are not necessarily Fourier modes. Our theory is consistent with simulation results for the long-range antiferromagnetic Ising model.

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The early time dynamics of systems quenched into unstable states is of considerable interest [1–8]. The first effective theory to treat this process was developed by Cahn and Hilliard [1] and by Cook [2]. The Cahn-Hilliard-Cook (CHC) theory applies to processes such as spinodal decomposition and continuous ordering [4] and predicts that the early evolution of the equal time structure factor following the quench is characterized by exponentially growing Fourier modes. A primary assumption of the CHC theory is that the initial evolution of the system is driven by noise (i.e., if the noise was absent, the system configuration would not evolve at all following the quench). Solid-to-solid transitions violate this assumption. Our use of the term "noise" refers both to the dynamical noise and to the randomness in the initial conditions.

In this Brief Report we introduce a generalized theory which describes the early time kinetics of spatial-symmetry breaking transitions. We will show that the kinetics can be separated into two well defined stages for systems with effective long-range interactions. In the first stage symmetry breaking fluctuations grow nonexponentially. In the second stage the evolution crosses over to exponential growth analogous to CHC. When the initial phase is a solid, we predict that the objects which grow exponentially are not Fourier modes.

Binder [5] showed that the CHC theory is valid only when the effective interaction range is large, $R \gg 1$ [9]. Binder's prediction has been confirmed in Ising model simulations [10,11]. There is evidence that many physical systems, such as polymers [5] and metals [12], have effective long-range interactions. It is therefore natural to develop our theory in the context of a long-range model.

When R is large, the noise is effectively small. We will demonstrate this below by rewriting the dynamical equations of motion in terms of dimensionless lengths (in units of R), whereupon all noise terms are damped by the factor $R^{-d/2}$. This suggests expansion of the system configuration in powers of $R^{-d/2}$ [13] which separates the noise independent *background* (of order $R^0=1$) from the noise dependent *fluctuations* (of order $R^{-d/2}$). Roughly speaking, the background represents the overall shape of the system configuration and the fluctuations represent typically small deviations from the background. The CHC theory applies only when the background does not evolve in time. In the case of solid-to-solid transitions, the background does evolve in time. By construction, the evolution of the background is noise independent, and we will show that the background maintains its initial rotational and translational symmetries.

We say that the phase transition involves *spatial-symmetry breaking* if the initial phase contains a rotational or translational symmetry not present in the final phase [14]. When spatial-symmetry breaking occurs, we will show that the background evolves toward a configuration that minimizes the free energy subject to symmetry constraints. This configuration is a stationary point of the free energy and is unstable to symmetry breaking fluctuations. We distinguish between two stages of early time evolution: stage 1, in which the background is evolving, and stage 2, in which the background has sufficiently converged to the constrained free energy minimum. For R sufficiently large, we predict that the growth of symmetry breaking fluctuations changes from nonexponential (stage 1) to exponential (stage 2) [15]. Stage 2 evolution in many ways resembles the CHC theory.

The mathematical development of our theory occurs in the context of a time dependent Ginzburg-Landau model with explicit long-range Kac interactions [17]. The nonconserved field $\phi(\vec{x},t)$ plays the role of an order parameter and evolves according to the Langevin dynamics,

$$\frac{\partial \phi(\vec{x},t)}{\partial t} = -M \frac{\delta F_R[\phi]}{\delta \phi(\vec{x},t)} + \sqrt{M}\,\tilde{\eta}(\vec{x},t). \tag{1}$$

$F_R[\phi]$ is the free energy of the configuration ϕ at time t and R represents the effective interaction range. The Gaussian white noise $\tilde{\eta}(\vec{x},t)$ has zero mean and second moment $\langle \tilde{\eta}(\vec{x},t)\tilde{\eta}(\vec{x}',t')\rangle = k_B T \delta(t-t')\delta(\vec{x}-\vec{x}')$. We set $M=1$ corresponding to the rescaling of time, $t \to t' = t/M$. The drift term is given by

$$-\frac{\delta F_R[\phi]}{\delta \phi(\vec{x})} = \int d^d\vec{x}'\, \Lambda_R(\vec{x}')\phi(\vec{x}-\vec{x}') + f[\phi(\vec{x})] + h \tag{2a}$$

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$$= (\Lambda_R * \phi)(\vec{x}) + f[\phi(\vec{x})] + h, \tag{2b}$$

where Λ_R is a Kac potential of the form $\Lambda_R(\vec{x}) = R^{-d}\Lambda(\vec{x}/R)$. The function f represents entropic forces deriving from the degeneracy in coarse graining ϕ. Without loss of generality, we set $f(\phi)|_{\phi=0} = 0$. The symbol h either represents an external field or chemical potential.

We scale all lengths by R so that Eq. (1) simplifies to

$$\frac{\partial u(\vec{r},t)}{\partial t} = -\frac{\delta F[u]}{\delta u(\vec{r},t)} + R^{-d/2}\eta(\vec{r},t), \tag{3}$$

where $\vec{r} = \vec{x}/R$, and

$$u(\vec{r},t) = \phi(\vec{x},t), \tag{4}$$

$$-\frac{\delta F[u]}{\delta u(\vec{r})} = (\Lambda * u)(\vec{r}) + f[u(\vec{r})] + h. \tag{5}$$

The parameter R in Eq. (1) appears solely as a prefactor to the noise term. The term $\eta(\vec{r},t) = R^{d/2}\tilde{\eta}(\vec{x},t)$ represents Gaussian white noise with zero mean and second moment $\langle \eta(\vec{r},t)\eta(\vec{r}\,',t')\rangle = k_B T \delta(t-t')\delta(\vec{r}-\vec{r}\,')$, which follows from the identity $a^{-d}\delta(\vec{x}/a) = \delta(\vec{x})$.

The form of Eq. (3) suggests expanding u in the small parameter $R^{-d/2}$,

$$u = u^{(0)} + R^{-d/2}u^{(1)} + R^{-d}u^{(2)} + \cdots. \tag{6}$$

We substitute Eq. (6) into Eq. (3) and obtain the dynamical equations,

$$\frac{\partial u^{(0)}}{\partial t} = -\frac{\delta F[u^{(0)}]}{\delta u} = \Lambda * u^{(0)} + f(u^{(0)}) + h, \tag{7}$$

$$\frac{\partial u^{(1)}}{\partial t} = \mathcal{L}u^{(1)} + \eta, \tag{8}$$

where

$$\mathcal{L}\psi = \Lambda * \psi + f'(u^{(0)})\psi \tag{9}$$

and $f'(u) = df/du$. We remark that the nonlinear dynamics of $u^{(0)}$ in Eq. (7) is deterministic and decoupled from higher orders. The dynamics of $u^{(1)}$ is stochastic, linear, and depends on $u^{(0)}$ through $\mathcal{L}$.

As we have mentioned, the CHC theory emerges as the evolution of $u^{(1)}$ when $u^{(0)}$ is a stationary point of the free energy. Let us see how this works for a disorder-order transition occurring after a rapid quench from infinite to finite temperature and $h=0$ [recall that $f(0)=0$]. At $t=0$ the system is initially disordered so Eq. (7) has the trivial solution $u^{(0)} = 0$ for all time. With this solution, Eq. (8) can be solved in Fourier space,

$$u^{(1)}(\vec{k},t) = u^{(1)}(\vec{k},0)e^{D(\vec{k})t} + \int_0^t dt'\, e^{D(\vec{k})(t-t')}\eta(\vec{k},t'), \tag{10}$$

where $D(\vec{k}) = \Lambda(\vec{k}) + f'(u^{(0)}=0)$. The structure factor $S(k,t) = \langle|\phi|^2\rangle/V$ can be calculated using Eq. (4), thus reproducing the CHC theory. For spin systems the volume V equals the total number of spins because the lattice spacing is taken to be unity.

We can determine the time scale for which the CHC theory is applicable. Equation (6) is meaningful when the neglected $O(R^{-d})$ terms are small. One requirement is that $R^{-d/2}u^{(1)} \ll u^{(0)} \simeq 1$. The exponential growth of $u^{(1)}$ from Eq. (10) suggests that the linear theory breaks down at a time $t \sim \ln R$ [5,11].

For many phase transitions (such as solid to solid) we need to consider the evolution of both $u^{(0)}$ and $u^{(1)}$. Equation (8) predicts exponential growth of $u^{(1)}(t)$ whenever $\mathcal{L}$ is time independent, which from Eq. (7) occurs when $\delta F/\delta u^{(0)}(x,t) = 0$. In general, the initial configuration $u^{(0)}(t=0)$ will not be such a stationary point. We will show that, due to symmetry breaking, $u^{(0)}$ converges to an unstable stationary configuration u^*. Correspondingly, $\mathcal{L}$ will converge to a time independent operator. This instability of u^* means that $\mathcal{L}$ will have positive eigenvalues, corresponding to the unstable symmetry breaking growth modes.

Let G be the symmetry group containing rotations under which both $u^{(0)}(\vec{r},0)$ and $\Lambda(\vec{r})$ are invariant and containing translations under which $u^{(0)}(\vec{r},0)$ is invariant. To show that Eq. (7) preserves these symmetries we discretize

$$u^{(0)}_{t+\Delta t} = u^{(0)}_t + \Delta t[\Lambda * u^{(0)}_t + f(u^{(0)}_t) + h]. \tag{11}$$

A short calculation establishes that if $u^{(0)}_t$ is invariant under G then so is $u^{(0)}_{t+\Delta t}$. By induction, this establishes that $u^{(0)}(\vec{r},t)$ is invariant under G for all t [18].

How does $u^{(0)}$ evolve for a phase transition with symmetry breaking? We see from Eq. (7) that $F[u^{(0)}]$ is nonincreasing. Physically, F must be bounded from below, so we expect $u^{(0)}$ to converge to some configuration u^*. This convergence occurs on a time scale independent of R because R does not appear in Eq. (7). We know that u^* is not the stable phase for a symmetry breaking transition because Eq. (7) preserves the spatial symmetries of the initial configuration. Therefore we expect that u^* is an unstable free energy stationary point. Parallel to the evolution of $u^{(0)}$, symmetry breaking fluctuations $R^{-d/2}u^{(1)}$ evolve according to Eq. (8). These fluctuations are unstable and, if $u^{(0)}$ has sufficiently converged to u^*, will grow exponentially for a time proportional to $\ln R$, analogous to the predictions of CHC.

We conclude that spatial-symmetry breaking phase transition kinetics can be decomposed into two stages:

(1) $t \lesssim t_0$: Nonlinear evolution of $u^{(0)}$ toward u^*, a configuration of minimum free energy subject to symmetry constraints. The configuration u^* is not the stable phase. The dynamical equation for $u^{(1)}$ is linear but has an explicit time dependence. Note that t_0 is independent of R.

(2) $t_0 \lesssim t \lesssim \ln R$: To a good approximation $u^{(0)}$ has converged to u^*. The linear theory of $u^{(1)}$ becomes analogous to the CHC theory and describes exponential growth of the unstable symmetry breaking modes.

These two stages are illustrated in Fig. 1(b). In contrast, there is no stage 1 process in the CHC theory, as illustrated in Fig. 1(a).

Phase transition kinetics *without* spatial-symmetry breaking, such as solid to fluid, are qualitatively different. Here $u^{(0)}$ will evolve toward u^* but, unlike the symmetry breaking case, u^* is the stable phase because no spatial symmetries are lost in the transition from initial to final configuration (sym-

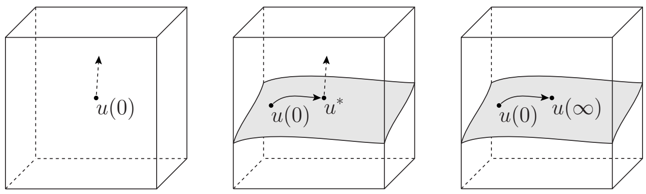

FIG. 1. (a) The CHC theory is applicable if the initial configuration $u(0)$ is a free energy stationary point. CHC describes the immediate exponential growth of Fourier modes, lasting a time $t \sim \ln R$. (b) For symmetry breaking transitions (e.g., solid to solid) the early time kinetics of $u(t)$ has two stages. In the first stage the leading order contribution to u evolves deterministically and nonlinearly toward a symmetry-constrained (shaded plane) free energy minimum u^* over a time scale $t \sim 1$. In the second stage, symmetry breaking modes grow exponentially for a time $t \sim \ln R$. (c) Without symmetry breaking (e.g., solid to fluid) the leading order contribution to u evolves deterministically toward the stable phase $u(\infty)$ over a time scale $t \sim 1$.

metry breaking does not occur). Note that all the interesting dynamics in this transition occurs through $u^{(0)}$, which is independent of the noise. This process is illustrated in Fig. 1(c).

Let us see how exponential growth arises in the second stage of a symmetry breaking transition by considering Eq. (7). Because $\mathcal{L}$ is a real and symmetric linear operator, it has a complete orthonormal eigenbasis and real eigenvalues [19]. The eigenvectors of $\mathcal{L}$ are Fourier modes only if $u^{(0)}$ is uniform. We can express the dynamics of $u^{(1)}$ in the eigenbasis of $\mathcal{L}$,

$$\frac{\partial u_v^{(1)}}{\partial t} = \sum_{v'} \mathcal{L}_{vv'} u_{v'}^{(1)} + \eta_v = \lambda_v u_v^{(1)} + \eta_v, \tag{12}$$

where v and λ_v represent the corresponding eigenvectors and eigenvalues of $\mathcal{L}$. The subscripts indicate eigenbasis components, for example, $u_v = \int d^d\vec{r} v(\vec{r}) u(\vec{r})$ and $\mathcal{L}_{vv'} = \int d^d\vec{r} v(\vec{r}) \mathcal{L} v'(\vec{r}) = \lambda_v \delta_{vv'}$. The eigenvectors are normalized, and we can show that $\langle \eta_v(t) \eta_{v'}(t')\rangle = \delta_{vv'}\delta(t-t')$.

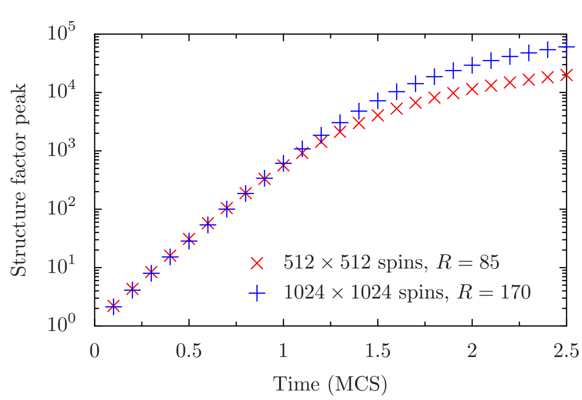

FIG. 2. (Color online) Evolution of the structure factor peak ($\langle |\phi_{\max}|^2\rangle / V$) for the fluid-stripe transition in the antiferromagnetic Ising model following a critical ($h=0$) quench. The CHC theory correctly predicts exponential growth, beginning immediately after the quench for this transition.

For times $t \gtrsim t_0$ the operator $\mathcal{L}$ is time independent and Eq. (12) can be solved directly,

$$u_v^{(1)}(t) = u_v^{(1)}(t_0) e^{\lambda_v (t-t_0)} + \int_{t_0}^{t} dt' e^{\lambda_v (t-t')} \eta_v(t'). \tag{13}$$

The exponential growth of $u^{(1)}$ is apparent. We can express $u^{(1)}$ in the Fourier basis,

$$u^{(1)}(\vec{k},t) = \sum_v v(\vec{k}) u_v^{(1)}(t), \tag{14}$$

where $v(\vec{k})$ is the Fourier representation of the eigenvector v. If R is sufficiently large and there is a single largest eigenvalue λ_v, then a single eigenvector v will grow exponentially faster than all others. In this case, and at sufficiently large times, we can approximate

$$u^{(1)}(\vec{k},t) \approx v(\vec{k}) \left[u_v^{(1)}(t_0) e^{\lambda_v (t-t_0)} + \int_{t_0}^{t} dt' e^{\lambda_v (t-t')} \eta_v(t') \right]. \tag{15}$$

We see that the exponential growth of the eigenvector v implies exponential growth of all the Fourier modes of $u^{(1)}$, $\langle |u^{(1)}(\vec{k},t)|^2\rangle \propto e^{2\lambda_v t}$. These Fourier modes eventually dominate all other contributions to the structure factor $S = \langle |\phi(\vec{k},t)|^2\rangle / V$, provided that the linear theory is valid ($t \lesssim \ln R$).

We now compare our generalized theory to simulations of the two-dimensional (2D) antiferromagnetic Ising model with a long-range square interaction. This model contains a disordered *fluid* phase, as well as *clump* and *stripe* solid phases [20,21]. In the clump phase, localized regions of enhanced magnetization are arranged on a square lattice. In the stripe phase, regions of enhanced magnetization are arranged in periodic stripes. All fluid-to-solid phase transitions involve symmetry breaking, as do the transitions between clump and stripe phases. In contrast, solid-to-fluid transitions do not in-

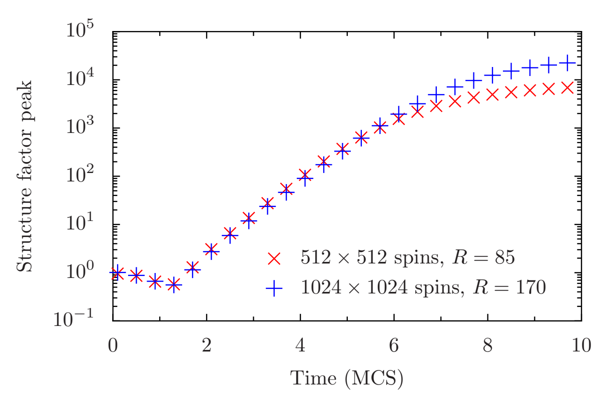

FIG. 3. (Color online) Evolution of the structure factor peak ($\langle |\phi_{\max}|^2\rangle / V$) for the fluid-clump transition following an off-critical ($h \neq 0$) quench. The initial growth has two stages, confirming the prediction of our generalized theory. The first stage is nonexponential and is independent of R. The second stage is exponential growth of the symmetry breaking modes (in this case Fourier modes) in analogy to the CHC theory.

volve symmetry breaking because the uniform fluid phase contains all possible spatial symmetries.

We use single-spin flip Monte Carlo dynamics to simulate the Ising system. At each update a spin is selected at random and flipped with the Glauber transition probability $p=(1+e^{\beta\Delta E})^{-1}$. Time is measured in units of Monte Carlo steps per spin (MCSs).

In Figs. 2 and 3 we display the peak of the structure factor, $S(\vec{k},t)=\langle\phi(\vec{k},t)^2\rangle/V$, for fluid-to-solid phase transitions following critical ($h=0$) and off-critical ($h=0.8$) quenches. The final phases are stripes and clumps, respectively. In both cases the temperature is reduced from $T=\infty$ to 0.05. The critical and off-critical transitions are described, respectively, by the CHC theory and our generalization. As predicted, the off-critical dynamics can be separated into two stages: initial nonexponential growth followed by an extended period of exponential growth. The growth modes are Fourier modes for both types of quenches considered because the initial phase is disordered.

In summary, we have shown that the CHC theory can be generalized to describe solid-to-solid transitions. The key ingredient of this generalization is spatial-symmetry breaking. The predictions of our generalized theory differ from those of the CHC theory in two fundamental ways: (1) the exponential growth of the symmetry breaking modes does not immediately follow the quench and (2) these symmetry breaking modes are not generally Fourier modes. We have performed simulations of the long-range antiferromagnetic Ising model for the off-critical fluid-to-solid transition and have confirmed the existence of a transient stage preceding exponential growth of the structure factor. A separate paper demonstrates the application of our theory to the case of the long-range antiferromagnetic Ising model stripe-to-clump transition [20]. We point out that our theory was developed in the ideal case of defect free initial conditions.

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