Beyond Cahn-Hilliard-Cook: Early Time Behavior of 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.

The early time dynamics of systems quenched into unstable states is of considerable interest. The first effective theory to treat this process was developed by Cahn and Hilliard [1] and by Cook [2]. The CHC theory applies to processes such as spinodal decomposition and continuous ordering [3] 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 configuration following the quench is an unstable stationary point of the free energy [4]. This assumption fails for solid-to-solid transitions.

In this paper 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 non-exponentially. 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 [3] has shown that the CHC theory is valid only when the effective interaction range is large, \( R \gg 1 \) [10], as has been confirmed in Ising model simulations [11, 12]. There is evidence that many physical systems, such as polymers [3] and metals [13] have effective long-range interactions. It is therefore natural to develop our theory in the context of a long-range model. If the order parameter is expanded in powers of \( R^{-d/2} \) [14], we can separate the background (of order \( R^0 = 1 \)) from the noise induced fluctuations (of order \( R^{-d/2} \)). We will see that the CHC theory describes evolving fluctuations with a fixed background.

Our early-time theory applies when the background is non-stationary. Such a background occurs for example in the early-time kinetics of a solid-to-solid transition where the lattice quickly contracts or expands before a significant symmetry change occurs. We will show that the evolution of the background is described by noiseless dynamics which explicitly preserves the rotational and translational symmetries of the initial phase. We say that the transition involves spatial symmetry breaking if the initial phase contains symmetries not present in the final phase. When spatial symmetry breaking occurs, we will show that the background evolves to a stationary phase that is unstable with respect to symmetry breaking fluctuations. Our theory predicts that the growth of these fluctuations changes from non-exponential (stage 1) to exponential (stage 2) when the background converges.

The growth of the symmetry breaking fluctuations is described by a linear theory which is valid for a time of order \( \ln R \) [5]. For \( R \) sufficiently large, both stages of our theory are observed.

We develop our theory in the context of a time-dependent Ginzburg-Landau model with explicit long-range Kac interactions [15]. The non-conserved field \( \phi(\vec{x}, t) \) plays the role of an order parameter and evolves according to the Langevin dynamics

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

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

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

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

where \( \Lambda_R \) is a Kac potential of the form \( \Lambda_R(\vec{x}) = R^{-d} \Lambda(\vec{x}/R) \). The function \( f \) represents entropic forces, and \( h \) is an external field or chemical potential. By convention, \( f(\phi)|_{\phi = 0} = 0 \).

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 \( \tilde{r} = \tilde{x}/R \), and
\[
\begin{align*}
\phi(\tilde{x}, t) & = \phi(\tilde{x}) \\
\frac{\delta F[u]}{\delta u(\tilde{r})} & = (\Lambda \ast u)(\tilde{r}) + f(u(\tilde{r})) + h.
\end{align*}
\] (4, 5)

The parameter \( R \) in Eq. (4) appears solely as a prefactor to the noise term. The term \( \eta(\tilde{r}, t) = R^{d/2} \tilde{\eta}(\tilde{x}, t) \) represents Gaussian white noise with zero mean and second moment \( \langle \eta(\tilde{r}, t)\eta(\tilde{r}', t') \rangle = k_B T \delta(t - t') \delta(\tilde{r} - \tilde{r}') \), which follows from the identity \( a^{-d}\delta(\tilde{x}/a) = \delta(\tilde{x}) \).

The form of Eq. (3) suggests expanding \( u \) in the small parameter \( R^{-d/2} \):
\[
u = u^{(0)} + R^{-d/2} u^{(1)} + R^{-d} u^{(2)} + \ldots
\] (6)

We substitute Eq. (6) into Eq. (3) and obtain the dynamical equations
\[
\begin{align*}
\frac{\partial u^{(0)}}{\partial t} & = -\frac{\delta F[u^{(0)}]}{\delta u} = \Lambda \ast u^{(0)} + f(u^{(0)}) + h \quad \text{(7)} \\
\frac{\partial u^{(1)}}{\partial t} & = \mathcal{L}u^{(1)} + \eta,
\end{align*}
\] (8)

where
\[
\mathcal{L}\psi = \Lambda \ast \psi + f'(u^{(0)})\psi,
\] (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,
\[
u^{(1)}(\tilde{k}, t) = \nu^{(1)}(\tilde{k}, 0)e^{D(\tilde{k})t} + \int_0^t dt'dt''e^{D(\tilde{k})(t-t'')}\eta(\tilde{k}, t'),
\] (10)

where \( D(\tilde{k}) = \Lambda(\tilde{k}) + f'(u^{(0)}) = 0 \). The structure factor \( S(k, t) = \langle |\phi|^2 \rangle/V \) can be calculated using Eq. (3), 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 easily determine the time scale for which the CHC theory is applicable. Equation (9) is meaningful when the neglected \( O(R^{-d}) \) terms are small. One requirement is that \( R^{-d/2}u^{(1)} < u^{(0)} \approx 1 \). The exponential growth of \( u^{(1)} \) from Eq. (10) suggests that the linear theory breaks down at a time \( t \approx 1/2 \ln R \).

For many phase transitions (such as solid-to-solid) we need to consider the evolution of both \( u^{(0)} \) and \( u^{(1)} \). Equation (3) 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 condition \( u^{(0)}(t) = 0 \) 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 \( G_i \) and \( G_f \) represent the symmetry groups of rotations and translations of the initial and final phases respectively. We will now show that \( u^{(0)}(\tilde{r}, t) \) is invariant under \( G_i \) provided that the potential \( \Lambda(\tilde{r}) \) shares the rotational symmetries of \( G_i \). Discretization of Eq. (7) with the time step \( \Delta t \) yields
\[
u_{t+\Delta t} = \nu_t + \Delta t(\Lambda \ast \nu_t + f(u^{(0)}) + h).
\] (11)

If \( u^{(0)} \) is invariant under \( G_i \) at time \( t \), it is invariant at time \( t + \Delta t \), which follows from the properties of the convolution operation (●) and the rotational symmetries of \( \Lambda \). Induction establishes the \( G_i \) symmetry of \( u^{(0)} \) for all \( t \).

How does \( u^{(0)} \) evolve for a phase transition with symmetry breaking? We see from Eq. (7) that \( F[u^{(0)}] \) is non-increasing. 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 \( R \). Symmetry considerations ensure that \( u^* \) is not the stable phase: there exists a spatial transformation \( g \) which is in \( G_i \), but not in \( G_f \) (the symmetry breaking condition) under which the configuration \( u^* \) and not the stable phase is invariant. Because \( u^* \) is not the stable phase, we expect that \( u^* \) is an unstable free energy stationary point. Simultaneous to the evolution of \( u^{(0)} \), the dynamical noise induces symmetry breaking fluctuations in \( u^{(1)} \) which are of magnitude \( R^{-d/2} \). These fluctuations are unstable, and if \( u^{(0)} \) has converged, 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. \( t_0 < t \lesssim \ln R \): 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
The exponential growth of Fourier modes, lasting a time \( t \sim \ln R \). 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 non-linearly to a symmetry-constrained (shaded plane) free energy minimum \( u^* \) in a time \( t \sim 1 \). In the second stage, symmetry breaking modes grow exponentially for a time \( t \sim \ln R \). Without symmetry breaking (e.g., solid-to-fluid) the leading order contribution to \( u \) evolves deterministically to the stable phase \( u(\infty) \) in a time \( t \sim 1 \).

Phase transition kinetics without spatial symmetry breaking, such as solid-to-fluid, are qualitatively different. Here \( u^{(0)} \) will evolve to \( u^* \) but, unlike the symmetry breaking case, \( u^* \) is the stable phase because the symmetries of \( G_1 \) are included in \( G_f \) (no symmetries are broken in the transition). 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. (11). Because \( \mathcal{L} \) is a real and symmetric linear operator, it has a complete orthonormal eigenbasis and real eigenvalues. 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 \( \mathcal{L} \):

\[
\frac{\partial u^{(1)}_v}{\partial t} = \sum_{v'} \mathcal{L}_{vv'} u^{(1)}_{v'} + \eta_v = \lambda_v u^{(1)}_v + \eta_v, \tag{12}
\]

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

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

\[
u^{(1)}_v(t) = u^{(1)}_v(t_0) e^{\lambda_v (t-t_0)} + \int_{t_0}^t dt' e^{\lambda_v (t-t')} \eta_v(t'). \tag{13}\]

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

\[
u^{(1)}(\vec{k}, t) = \sum_v v(\vec{k}) u^{(1)}_v(t), \tag{14}\]

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

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

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 \( S = \langle \phi(\vec{k}, t) \rangle / V \), provided that the linear theory is valid \( (t \lesssim \ln R) \).

We now compare our generalized theory to simulations of the 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. 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 involve symmetry breaking because the uniform fluid phase contains all possible spatial symmetries.

For the Ising model with \( R \gg 1 \) a free energy functional \( F[\phi] \) can be derived. Rather than the dynamics of Eq. (11) we use single-spin flip Monte Carlo dynamics to simulate the 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 (MCS).
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. 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 non-exponential 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 future paper will show simulations confirming this theory in symmetry breaking transitions [18]. Finally, we point out that our theory does not apply in the presence of symmetry breaking defects in the initial conditions.

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