Sharp interface limits of phase-field models

K. R. Elder\textsuperscript{1}, Martin Grant\textsuperscript{2}, Nikolas Provatas\textsuperscript{2,3} and J. M. Kosterlitz\textsuperscript{4}

\textsuperscript{1}Department of Physics, Oakland University, Rochester, MI, 48309-4487
\textsuperscript{2}Physics Department, Rutherford Building, 3600 rue University, McGill University, Montréal, Québec, Canada H3A 2T8.
\textsuperscript{3}Pulp and Paper Research Institute of Canada, 570 St. Jean Blvd, Montréal, Québec, Canada H9R-3L9.
\textsuperscript{4}Department of Physics, Brown University, Providence, RI 02912.

(December 29, 2021)

The use of continuum phase-field models to describe the motion of well-defined interfaces is discussed for a class of phenomena, that includes order/disorder transitions, spinodal decomposition and Ostwald ripening, dendritic growth, and the solidification of eutectic alloys. The projection operator method is used to extract the “sharp interface limit” from phase field models which have interfaces that are diffuse on a length scale \(\xi\). In particular, phase-field equations are mapped onto sharp interface equations in the limits \(\kappa \ll 1\) and \(\xi v / D \ll 1\), where \(\kappa\) and \(v\) are respectively the interface curvature and velocity and \(D\) is the diffusion constant in the bulk. The calculations provide one general set of sharp interface equations that incorporate the Gibbs-Thomson condition, the Allen-Cahn equation and the Kardar-Parisi-Zhang equation.

05.70.Ln, 64.60.My, 64.60.Cn, 81.30.Hd

I. INTRODUCTION

Many inhomogeneous systems involve domains of well-defined phases separated by thin interfaces. These include non-equilibrium systems where phases are separating by spinodal decomposition or nucleation and growth \([1]\), or where solidification occurs by dendritic growth \([2]\) or by the growth of eutectic crystals \([3]\). The phenomenological description of these phenomena involves the motion of well-defined sharp interfaces. The origin of such descriptions is often transparent, being obtained by symmetry arguments and common sense. Nevertheless the properties of sharp interface models can be quite subtle as is the case for dendritic growth.

Unfortunately sharp interface models are difficult to simulate since this usually involves solving a diffusion equation subject to moving boundary conditions at the interfaces. A more convenient approach is to simulate models which describe the bulk phases as well as the interface structure. While these models are wasteful in terms of simulating bulk regions \([4]\), no explicit boundary tracking is needed. This is the key element to a popular method for studying systems out of equilibrium, called “phase-field” modeling. In such an approach one or more continuous fields which are functions of space \(\vec{r}\) and time \(t\), are introduced to describe the phases present. Typically these fields vary slowly in bulk regions and rapidly, on length scales of the order of the correlation length, \(\xi\), near interfaces. The free energy functional \(F\) determines the phase behavior and, with the equations of motion, gives a complete description. In other contexts, such as critical dynamics \([4,5]\), the fields are the order parameters distinguishing the phases. In a binary alloy, for example, the local concentration or sublattice concentration can be described by such fields. The ideas involved in this approach have a long history, going back to van der Waals \([6]\). Within the materials community, the use of continuum field models is associated particularly with the work of Cahn and collaborators \([7,8]\).

Phase field models provide a complete microscopic description, but are not necessarily appropriate for a particular system. These models apply to a large number of microscopic systems only when \(\xi\) is much larger than any particular microscopic length, such as the lattice spacing, involved in the surface structure. Interpreted in the sense of describing the universal features of many microscopic models, \(\xi\) is a mesoscopic length representative of microscopic structure. In a similar manner sharp-interface models apply to a large number of continuum field models of pattern formation or phase separation in the limit that the length scales defined by the patterns are much larger than \(\xi\). An important difference exists however in the construction of the two approaches. Standard sharp-interface models are constructed from phenomenological descriptions of interfaces, while phase field models can be constructed to explicitly obey the fundamental principles of statistical mechanics.

While continuum phase field models provide a fundamental approach which is clear and workable, it is important to establish the connection between this description and the sharp interface description. The main difficulty which arises is how to take account of the finite thickness \(\xi\) of the diffuse interface of the continuum model. There has been a great deal of discussion in the literature on how this process is to be undertaken. Some workers have extracted the interface equations by taking the limit where the interface width of the phase field model goes to zero \([9]\) for the Stefan problem of a pure material. This approach is not very useful since the interface width is always finite. More recently these calculations have been extended for special choices of the free energy functional \(F\) to include an interface of non-zero width \([10,11]\).
The purpose of this paper is to provide a clear and detailed derivation of the sharp interface equations. The approach follows the projection operator method of Kawasaki and Ohta [2], is generally applicable and eliminates the counter intuitive necessity of limiting the derivation of the sharp interface limit to some artificial form of the free energy functional $F$. This general calculation provides one set of equations that relate the parameters of the phase field equations to those of the sharp interface equations for a broad class of phenomena including order-disorder transitions, dendritic growth, phase separation in binary alloys, eutectic growth, and surface roughening. In particular, thermodynamic consistency is automatic in the present approach for nonzero interface widths. This is in contrast to the unphysical approach of taking the limit of a zero interface width, which requires fine tuning of the free energy to obtain a thermodynamically consistent theory.

The structure of the paper is as follows. In the next section a general introduction to phase field and sharp interface equations is given. This is followed by a detailed calculation of the sharp interface equations from a set of phase field equations. The usefulness of the sharp interface equations is then illustrated by considering the linear stability of planar interface separating various phases.

II. DESCRIBING INTERFACE PHENOMENA USING PHASE-FIELD MODELS

To see the relationship between the two approaches, it is useful to construct the simplest equilibrium and non-equilibrium descriptions of surfaces by both methods. The main ideas developed below appear in the more general case discussed in the following sections. These ideas are present in work by Allen and Cahn [3] on the motion of anti-phase boundaries in the kinetics of an order-disorder transition in a binary alloy. This work recovers the sharp interface description from the phase-field model in the appropriate limit and predicts an experimentally testable consequence of a finite $\xi$.

First, consider a surface in equilibrium. The reason why droplets are spheres and interfaces are locally flat is that these shapes minimize surface area. The excess free energy of a surface is proportional to its area $A$,

$$\Delta F = \sigma A$$  

where the proportionality constant $\sigma$ is the surface tension. This simple common sense approach is the sharp interface model.

Contrast this with the phase field approach. The free energy functional $F(\psi)$ for the scalar order parameter $\psi(\vec{r})$ has the following familiar form, consistent with reflection symmetry $F(\psi) = F(-\psi)$

$$F\{\psi\} = \int d\vec{r} \left[ \frac{1}{2} K_\psi \nabla^2 \psi^2 + f(\psi) \right],$$  

where $K_\psi > 0$ so that the square gradient interaction gives the free energy cost for inhomogeneities and the local bulk free energy has a double well form satisfying $f(\psi) = f(-\psi)$. An example is the $\psi^4$ form

$$f = -\frac{a}{2} \psi^2 + \frac{b}{4} \psi^4,$$  

where $a \propto (T_o - T) > 0$ with $T_o$ the mean field critical temperature and $b > 0$ is a constant.

The motivation for employing such free energy functionals is as follows. First, the free energy functional is constructed of local or bulk terms, $f(\psi)$, which interact through the gradient term. Secondly $F$ must be an analytic function since it describes a microscopic system and should not be confused with the true thermodynamic free energy, $F \equiv -k_B T \ln \sum_\psi \exp(-F/k_B T)$ where $k_B$ is Boltzmann’s constant, which is non analytic at a phase transition [4]. The square gradient term is the simplest way for the model to be well defined on small length scales. Higher-order gradient terms, such as $K_4(\nabla^2 \psi)^2$ could, in principle, describe correlations on still smaller scales, such as the internal structure of the interface. This is analogous to what is described by the Percus-Yevick or hypernetted-chain theories of dense fluids [4]. In the absence of any specific experimental motivation, however, terms proportional to $K_4$ may be ignored.

From the point of view of identifying and studying a well defined microscopic model, the square gradient free energy provides a complete description. Alternatively, the square gradient theory describes a large class of microscopic models provided we consider mesoscopic scales $\xi(K)/a_o \gg 1$, where $a_o$ is a lattice constant.

It is particularly convenient that the microscopic phase field description is so “close” to mean field theory. In that approximation, $f$ is simply the bulk free energy density. In practice, the form of the free energy functional $F$ can be constructed straightforwardly with reference to the phase diagram of interest. While one can also construct microscopic lattice gas models of phenomena such as phase separation and dendritic solidification [5], using similar arguments of universality and simplicity, such models do not have this convenient feature.

If fluctuations are small, the equilibrium behavior of the model is determined by the mean field approximation

$$\frac{\delta F}{\delta \psi} = -K_\psi \nabla^2 \psi + \frac{\partial f}{\partial \psi} = 0.$$  

The homogeneous bulk solutions, valid well below $T_c$, are given by $\partial f/\partial \psi_{eq} = 0$ and are equal to,

$$\psi = \pm \psi_{eq} = \pm \sqrt{a/b}.$$  

for the bulk free energy given in Eq. (3). Fluctuations around the bulk solutions satisfy

$$\langle (\psi(\vec{r}) - \psi_{eq})(\psi(0) - \psi_{eq}) \rangle \sim e^{-r/\xi}.$$  

(6)
for $r \gg \xi$, where $\xi = \sqrt{K_\psi/2a}$ and $(\cdots)$ represents an ensemble average.

Now consider a system with a flat interface located at $y = 0$ when $\psi(\vec{r})$ depends only on $y$ and the interface profile $\psi^\text{in}(y)$ is the solution of

$$-K_\psi \frac{\partial^2 \psi^\text{in}}{\partial y^2} + \frac{\partial f}{\partial \psi^\text{in}} = 0. \tag{7}$$

with $\psi^\text{in}(\pm \infty) = \pm \psi_{eq}$. Solving by quadratures gives

$$\frac{1}{2}K_\psi \left(\frac{\partial \psi^\text{in}}{\partial y}\right)^2 = f(\psi^\text{in}) \tag{8}$$

from which Eq. (1) follows immediately. In contrast to the sharp interface approach, this yields an explicit form for the surface tension

$$\sigma_\psi = K_\psi \int dy \left(\frac{\partial \psi^\text{in}}{\partial y}\right)^2. \tag{9}$$

For the particular form of $\mathcal{F}(\psi)$ of Eq. (2) and Eq. (3), one finds

$$\psi^\text{in}(y) = \psi_{eq} \tanh \left(\frac{y}{2\xi}\right) \tag{10}$$

and

$$\sigma_\psi = \frac{2K_\psi \psi_{eq}^2}{3\xi}. \tag{11}$$

The contrast between the sharp-interface model and the phase-field model is revealing. Both give the same macroscopic description but the phase field approach gives a complete description down to the smallest length scale.

Now consider a sharp interface that is in local but not global equilibrium due to a gentle curvature. For simplicity consider phenomena where the order parameter is not conserved, such as occurs when a binary alloy undergoes an order-disorder transition and $\psi$ is the sublattice concentration. The interface moves to locally reduce the surface area and surface free energy with an interface velocity $v$. Expanding $v$ in a Taylor series in powers of $\kappa$ gives

$$v = -\nu \kappa \tag{12}$$

to lowest order in the curvature. This is the sharp interface theory for the motion of anti-phase boundaries. Note that, since $\nu$ is the only coefficient which enters the theory and has dimensions of a diffusion constant, any time-dependent length $R(t)$ must satisfy

$$R(t) = (\nu t)^n, \tag{13}$$

by dimensional analysis, where the growth exponent

$$n = 1/2. \tag{14}$$

Such an approach was first done by Lifshitz [10] and by Turnbull [17]. The sharp interface treatment alone cannot predict the value of $\nu$. An additional argument, which turns out to be incorrect for the motion of antiphase boundaries, was used to predict $\nu \propto \sigma_\psi \Gamma_\psi$, where $\Gamma_\psi$ is a mobility.

A first principles approach to this phenomenon is due to Allen and Cahn [8]. Neglecting noise, the equation of motion for the non-conserved sublattice concentration is

$$\frac{\partial \psi}{\partial t} = -\Gamma_\psi \frac{\delta \mathcal{F}}{\delta \psi} = -\Gamma_\psi \left[-K_\psi \nabla^2 \psi + \frac{\partial f}{\partial \psi}\right]. \tag{15}$$

Allen and Cahn denoted the position of the antiphase boundary by a curved, time-dependent interface $u(\vec{r}, t) = 0$. They then looked for solutions of the form $\psi(\vec{r}, t) = \psi^\text{in}(u(\vec{r}, t))$. This gives

$$\frac{\partial \psi}{\partial t} = -\nu \frac{\partial \psi^\text{in}}{\partial u} = -\Gamma_\psi \left[-K_\psi \frac{\partial^2 \psi^\text{in}}{\partial u^2} - K_\psi \kappa \frac{\partial \psi^\text{in}}{\partial u} + \frac{\partial f}{\partial \psi}\right], \tag{16}$$

where $\kappa = -\nabla \cdot \hat{n}$ with $\hat{n} = \nabla u/|\nabla u|$ the unit vector normal to the interface and $u(\vec{r}, t)$ a coordinate in the direction $\hat{n}$. Eliminating $\partial f/\partial \psi^\text{in}$ using Eq. (7) gives Eq. (12) where, in contrast to the sharp interface theory, one obtains an explicit expression for the transport coefficient,

$$\nu = K_\psi \Gamma_\psi. \tag{17}$$

Results in the presence of stochastic noise have been obtained by many authors, particularly Bausch, Domb, Janssen and Zia [13], and by Kawasaki and Ohta [12].

Although both approaches correctly find that the normal velocity is proportional to the curvature, the Allen-Cahn result for $\nu \propto \kappa$ is noteworthy. The earlier theory, which argued $\nu \propto \sigma_\psi \Gamma_\psi$ implies a strong dependence of the velocity $v$ on interfacial thickness since $\sigma \propto 1/\xi$, from Eq. (11). In contrast, Allen and Cahn predict that $v$ is independent of interfacial thickness. This was clearly demonstrated in an experiment by Pindak et al. [19] where they studied orientational patterns in freely suspended dipolar smectic C liquid crystal films. Since their smectic C films have a permanent electric dipole moment of magnitude $P$, the director angle $\phi$ can be oriented with an electric field of magnitude $E$. The free energy is

$$\mathcal{F} = \int d\vec{r} \left[\frac{1}{2}K(\nabla \phi)^2 - EP \cos \phi\right], \tag{18}$$

so the width of the interface,

$$\xi \propto 1/\sqrt{E}, \tag{19}$$

can be varied easily. The experiments directly verify that the size of a domain of stable orientation grows as $R(t) = (\nu t)^{1/2}$, where $\nu$ is independent of interface width.
in accord with the prediction of Allen and Cahn \[8\]. In addition, the experiments show that the sharp interface result, \(v \propto \kappa\), is independent of interface width provided \(\xi/R \ll 1\).

It is straightforward to include an external field \(c\) coupling linearly to \(\psi\). Then \(\mathcal{F} \rightarrow \mathcal{F} + \mathcal{F}_{\text{ext}}\) with

\[
\mathcal{F}_{\text{ext}} = -\int d\mathbf{r} c \psi
\]

and one of the phases becomes metastable depending on the sign of \(c\), so that the interface translates even if it is flat. Hence

\[
v = v_0(c) - \nu \kappa
\]

with \(v_0(c) \propto c\). This allows one to simulate Kolmogorov-Avrami-Johnson-Mehl growth of droplets \[20\] and, in the presence of noise, Kardar-Parisi-Zhang dynamic roughening \[22\].

Other processes can be simulated when one of the phases is metastable and the growth of the stable from the metastable phase is controlled by a conservation law. This describes solidification of a metastable supercooled liquid phase and the growth of the stable solid is limited by the diffusion of latent heat from the surface of the moving solid front. The external field \(c\) is then proportional to the latent heat. In the sharp interface formulation, \(c\) obeys a diffusion equation in the bulk phases

\[
\frac{\partial c}{\partial t} = D_c \nabla^2 c,
\]

where \(D_c\) is a diffusion constant.

The steady state velocity \(v\) of the interface is given by integrating Eq. (22) across the interface to obtain

\[
v \propto \hat{n} \cdot \left( D_c^+ \nabla c^+ - D_c^- \nabla c^- \right)
\]

where the superscripts \(\pm\) refer to the values of the normal gradient of \(c\) on either side of the interface. The condition of local equilibrium at the interface is

\[
\delta c \propto \kappa
\]

which is a Gibbs-Thompson condition relating the local excess concentration \(\delta c\) to the curvature. This says that excess external driving force is balanced by the curvature \(\kappa\). In regimes of high undercooling, this is sometimes supplemented by an additive term proportional to \(v\), describing kinetic undercooling.

To study this by a phase-field approach, let \(c\) be a continuous function of space and time which is conserved:

\[
\frac{\partial c(\mathbf{r}, t)}{\partial t} = \Gamma_c \nabla^2 \delta \mathcal{F} / \delta c
\]

where \(\Gamma_c\) is the mobility of the field \(c\). For the model to be well defined, a self energy for \(c\) or a positive additive contribution to \(\mathcal{F}\) of the form

\[
\mathcal{F}_c \propto \int d\mathbf{r} \left[ \frac{1}{2} K_c |\nabla c|^2 + \frac{1}{2} K_\psi |\nabla \psi|^2 + f(\psi, c) \right]
\]

must be included. Within a mean-field approximation, this gives a homogeneous equilibrium solution \(c \propto \psi\). Note that the interface invades the metastable phase because of \(\mathcal{F}_{\text{ext}}\) but it must also satisfy the conservation of \(c\) as defined by Eqs. (23) and (24). This implies that the interface deforms into a parabolic shape, dumping excess \(c\) to the sides while propagating forward at a constant velocity. The parabolic shape has a constant growth velocity in the forward direction, satisfying the fact the system is driven with a constant thermodynamic force, while lateral growth has a velocity \(\sim t^{-1/2}\), thereby satisfying the conserved diffusion equation for \(c\).

It turns out that, although this is the right approach, the implementation needs some fine tuning. First, when considering dendritic growth, the theory of microscopic solvability \[22\] has shown that dendrites require an anisotropic surface tension to be well defined. Hence, one must let \(K \rightarrow K(|\nabla \psi|/|\nabla \psi|)\) in some convenient prescribed way. Next, in a very useful paper, Kobayashi \[23\] has noted that, to keep the equilibrium solutions \(\psi_{eq}\) from shifting appreciably when \(c\) is applied, \(\mathcal{F}_{\text{ext}}\) of Eq. (26) should be modified to

\[
\mathcal{F}_{\text{ext}} = -\int d\mathbf{r} \psi c \nabla \Psi(\psi)
\]

where \(\Psi(\psi)\) is an odd function of \(\psi\) satisfying

\[
\partial \Psi / \partial \psi_{eq} = 0.
\]

For example, if \(\psi_{eq} = \pm 1\), one can choose \(\partial \Psi / \partial \psi = (1 - \psi^2)^2\). Other forms are possible.

Finally, one can choose to make the \(c\) field phase separate by replacing the self-energy term in the free energy of Eq. (28) with a double well form, analogous to Eq. (3). This permits the study of eutectic crystallization \[3\]. In the remainder of this paper a detailed implementation of these ideas is given, making connections to the sharp interface limit.

### III. EQUILIBRIUM

Consider two fields, a non-conserved phase field \(\psi\) and a conserved field \(c\). The phase field distinguishes between, for example, liquid and solid phases and the \(c\) field can be taken as a concentration. The free energy functional describing the system can be written as

\[
\mathcal{F}(\psi, c) = \int d\mathbf{r} \left[ \frac{1}{2} K_\psi |\nabla \psi|^2 + \frac{1}{2} K_c |\nabla c|^2 + f(\psi, c) \right]
\]

where \(f(\psi, c)\) is the local bulk free energy density and the gradient terms account for interfaces and inhomogeneities as discussed above. The dynamics of these fields
are described by the equations of motion for the non-conserved $\psi$, Eq. (13) and the conserved concentration $c$,

$$\frac{\partial c}{\partial t} = \Gamma_c \nabla^2 \delta F = \Gamma_c \nabla^2 \left[ -K_c \nabla^2 c + \frac{\partial f}{\partial c} \right]. \quad (30)$$

where $\delta F(\psi, c)/\delta c = \mu$ is a chemical potential and $\Gamma_c$ is a mobility. The usual additive noise terms, related to the transport coefficients $\Gamma_{c,\psi}$ by fluctuation-dissipation relations [1,5], have been neglected for simplicity. In mean field theory, the equilibrium states of the system with an interface normal to $\hat{y}$ are defined by

$$K_\psi \frac{\partial^2 \psi}{\partial y^2} = \frac{\partial f}{\partial \psi} \quad (31)$$

and

$$K_c \frac{\partial^2 c}{\partial y^2} = \frac{\partial f}{\partial c} - \mu_{eq} \quad (32)$$

where $\mu_{eq}$ is the chemical potential of the uniform equilibrium states. Integrating Eq. (32) over $c$ gives the Maxwell’s equal area construction rule,

$$\int_{c_1}^{c_2} dc \left( \frac{\partial f}{\partial c} - \mu_{eq} \right) = 0, \quad (33)$$

where $c_1$ and $c_2$ are defined by $\partial f/\partial c|_{c_1, c_2} = \mu_{eq}$.

For a generic $f(c, \psi)$ there may be many possible equilibrium and metastable states contained in this free energy. For illustration, consider the following bulk free energy

$$f(\psi, c) = u \frac{T}{T_M} \left[ c \ln c + (1 - c) \ln (1 - c) \right]$$

$$+ \left( \alpha \Delta T - \beta (c - \frac{1}{2})^2 \right) \Psi(\psi) - \frac{1}{2} \psi^2 + \frac{1}{4} \psi^4. \quad (33)$$

where $\Psi(\psi) = 2\psi - 4\psi^3/3 + 2\psi^5/5$, $\Delta T \equiv (T - T_M)/T_M$ with $T_M$ the melting temperature and the other phenomenological parameters are determined by matching to experimental phase diagrams. If these parameters are chosen as $\alpha = \beta = 1.0$ and $u = 0.6$, the mean-field phase diagram shown in Fig. (1) emerges. As can be seen, this phase diagram contains liquid/solid and solid/solid coexistence regimes. For this symmetric free energy the melting temperature at $c = 1/2$ is denoted $T_M$ and the critical point of the solid/solid coexistence regime is at $(c, T) = (1/2, T_c)$ with $T_c < T_M$. As the parameter $u$ is decreased, $T_c$ increases until the solid/solid coexistence region collides with the liquid/solid coexistence regime when $T_c > T_M$ and a eutectic point is formed at $(c, T) = (1/2, T_E)$ as shown in Fig. (2).

As can be seen from the phase diagrams of Figs. (1) and (2), this simple free energy contains many phases and, in conjunction with appropriate equations of motion, can be used to study a wide variety of phenomena. A number of ‘quenches’ have been highlighted on these diagrams to illustrate several different kinetic processes that may arise.
ner to include all the possible quenches shown in Figs. 1 and 2. To construct the relevant sharp interface equations no reference will be made to the explicit form of the bulk free energy term \( f \). It is assumed that \( f \) has been chosen merely so that all the phases of interest are well defined.

IV. NON-EQUILIBRIUM

The goal of this section is to derive the sharp interface equations for a systems described by a free energy functional \( F \) (such as is given by Eqs. (29) and (33) and the Langevin equations given in Eqs. (15) and (30)). These latter equations should be supplemented by additive stochastic noises, \( \eta_0(\vec{r},t) \) and \( \eta_c(\vec{r},t) \) of zero mean and correlations \( \langle \eta_0(\vec{r},t)\eta_0(\vec{r}',t') \rangle = 2\Gamma_0T\delta(\vec{r}-\vec{r}')\delta(t-t') \) and \( \langle \eta_c(\vec{r},t)\eta_c(\vec{r}',t') \rangle = 2\Gamma_cT\nabla^2\delta(\vec{r}-\vec{r}')\delta(t-t') \) with \( \langle \eta_0\eta_c \rangle = 0 \) as required by the fluctuation dissipation theorem. With these stochastic noises, the dynamical equations Eq. (14) and Eq. (30) are the simplest equations which respect the macroscopic conservation laws and also ensure that the system evolves towards its ultimate state of thermal and mechanical equilibrium with its external environment.

The asymptotic analysis proceeds by expanding around a planar equilibrium interface described by Eqs. (11) and (12). The interface can be taken out of equilibrium by either gently curving it or by making one of the two bulk phases metastable. In the former case, a gentle curvature is one in which the radius of curvature \( 1/\kappa \) is large compared to the interface width or correlation length. Thus one small dimensionless expansion parameter is \( \kappa \xi \). In the latter case, the difference between the free energy of the stable and metastable phases causes the interface to propagate into the metastable phase. If the free energy difference is small the propagation velocity \( v \) is small. In this context, a small velocity means that the interface moves so slowly that a steady state diffusion field is allowed to form in front of the interface. In other words, the time for the diffusion field to relax when the interface moves a distance \( \xi \) should be much smaller than the time \( \xi/v \) taken for the interface to move that distance. Since the diffusion time \( \tau = \xi^2/D \), this leads to another small dimensionless parameter \( \xi v/D \) which is known as the interface Péclet number. In the following analysis the interface equations will be obtained to lowest order in both small parameters. Technically the expansion to lowest order in both small parameters can be achieved if they are regarded as the same order in the expansion. In the calculations to follow both parameters will be taken to be \( O(\epsilon) \) with \( \epsilon << 1 \).

The calculations make use of the fact that the fields behave qualitatively different close and far from the interface. In the region close to the interface, the fields vary rapidly over distances \( O(\xi) \) while, far from the interface, they vary over distances \( O(\xi/\epsilon) \). If there exists a length scale \( \zeta \) such that \( 1 << \zeta/\xi << 1/\epsilon \), then distinct ‘inner’ and ‘outer’ regions can be defined, as shown in Fig. 1 and it is appropriate to solve in both inner and outer regions and match the solutions at the length scale \( \zeta \). Formally, the technique requires an inner expansion near the interface and an outer expansion far from the interface.

A. Inner Expansion

Consider an inner region defined by \( -\zeta < u < +\zeta \), where \( u \) is a coordinate normal to the interface and \( 1 << \zeta/\xi << 1/\epsilon \). The aim is to obtain asymptotic expansions for the solutions to the evolution equations (12) and (30) valid in this inner region. The latter can be written in a compact form as

\[
\frac{1}{\Gamma_c} \frac{\partial c}{\partial t} = \nabla^2 \delta \mu \tag{34}
\]

where

\[
\delta \mu = \mu(\vec{r}) - \mu_{eq} = -K_c \nabla^2 c + \frac{\partial f}{\partial c} - \mu_{eq} \tag{35}
\]

The first step is to partition the system into two regions \( V_+ \) and \( V_- \) bounded by surfaces \( S_+ \) and \( S_- \) respectively. The region \( V_+ \) is defined by \( 0 < u < \zeta \) and similarly for \( V_- \). The position of the interface between both bulk regions is defined as \( u(\vec{r},t) = 0 \). These definitions are purely formal, but to fix ideas, the surface \( u(\vec{r},t) = 0 \) may be regarded as the surface near which the fields \( c, \psi \) vary rapidly over distances \( O(\xi) \). It is then useful to define Green’s functions \( G^\pm(\vec{r},\vec{r}') \) in the regions \( -\zeta < u < 0 \) (\( G^- \)) and in \( 0 < u < \zeta \) (\( G^+ \)) obeying

![FIG. 3. Illustration of inner and outer regions used in computations.](image-url)
\[ \nabla^2 G^\pm(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') \]  

(36)

and satisfying the boundary conditions, \( G(\vec{r}, \vec{r}') = 0 \)
at \( u = 0 \) and \( u' = 0 \), \( \partial G(\vec{r}, \vec{r}')/\partial u = 0 \) at \( u = \pm \zeta \),
\( \partial G(\vec{r}, \vec{r}')/\partial u' = 0 \) at \( u' = \pm \zeta \), and periodic in the other directions. Note that both \( \vec{r} \) and \( \vec{r}' \) lie in the same region, \( V_+ \) or \( V_- \).

Multiplying Eq. (34) by \( G^\pm \) and integrating over \( \vec{r}' \in V_\pm \) gives
\[
\delta \mu(\vec{r}) = \int_{V_\pm} d\vec{r}' G^\pm(\vec{r}, \vec{r}') \frac{\partial c'}{\partial t} + \oint_{S_\pm} dS' \cdot \left( \delta \mu' \nabla^\mp G^\pm - G^\pm \nabla^\mp \delta \mu' \right)
\]

(37)

where \( \delta \mu' = \delta \mu(\vec{r}') \) defined as in Eq. (35), \( \int_{V_\pm} d\vec{r}' \) denotes integration over \( V_\pm \) defined by \( 0 < u(\vec{r}') < \zeta \) and \( \oint_{S_\pm} dS' \) denotes integration over the boundaries \( S_\pm \) enclosing \( V_\pm \), and similarly for \( V_- \) enclosed by \( S_- \). Multiplying Eq. (35) by \( \partial \psi^{in}/\partial u \) where \( \psi^{in}(u) \) is determined by the solution of Eqs. (31) and (32) for a planar interface in thermal equilibrium and integrating over \( -\zeta < u < +\zeta \) gives
\[
B + S = \int_{-\zeta}^{+\zeta} du \frac{\partial \psi^{in}}{\partial u} \int_{V_\pm} d\vec{r}' G^\pm(\vec{r}, \vec{r}') \frac{\partial c'}{\partial t} + \int_{S_\pm} dS' \cdot \left( \delta \mu' \nabla^\mp G^\pm - G^\pm \nabla^\mp \delta \mu' \right)
\]

(38)

where \( B = B^+ + B^- \) and \( S = S^+ + S^- \) with
\[
B^\pm = \pm \frac{1}{\Gamma_c} \int_{0}^{+\zeta} \frac{\partial \psi^{in}}{\partial u} \int_{V_\pm} d\vec{r}' G^\pm(\vec{r}, \vec{r}') \frac{\partial c'}{\partial t},
\]

(39)

\[
S^\pm = \pm \int_{0}^{+\zeta} \frac{\partial \psi^{in}}{\partial u} \oint_{S_\pm} dS' \cdot \left( \delta \mu' \nabla^\mp G^\pm - G^\pm \nabla^\mp \delta \mu' \right).
\]

(40)

An analogous formula for \( \psi \) is obtained by multiplying Eq. (13) by \( \partial \psi^{in}/\partial u \), with \( \psi^{in}(u) \) the solution of Eqs. (31) and (32), and integrating over \( -\zeta < u < +\zeta \) to obtain
\[
\frac{1}{\Gamma_\psi} \int_{-\zeta}^{+\zeta} du \frac{\partial \psi^{in}}{\partial u} \frac{\partial \psi^{in}}{\partial t} = + \frac{1}{\Gamma_\psi} \int_{-\zeta}^{+\zeta} du \frac{\partial \psi^{in}}{\partial u} \left( K_\psi \nabla^2 \psi - \frac{\partial f}{\partial \psi} \right).
\]

(41)

Each term in the above equations can be systematically expanded in powers of \( \epsilon \). In this paper, attention is restricted to the terms \( O(\epsilon) \) as much of the relevant physics is apparent at this order. Going to higher order in \( \epsilon \) does not yield any new physical insight but does require considerable book-keeping skill.

To facilitate the expansion, \( c(\vec{r}, t) \), \( \psi(\vec{r}, t) \) and the chemical potential \( \mu(\vec{r}, t) \) are expanded in a power series in \( \epsilon \),

\[ \begin{align*}
c(\vec{r}, t) &= c^{in}_0(u(\vec{r})) + \epsilon \delta c^{in}_1 + \epsilon^2 \delta c^{in}_2 + \cdots \\
\psi(\vec{r}, t) &= \psi^{in}_0(u(\vec{r})) + \epsilon \delta \psi^{in}_1 + \epsilon^2 \delta \psi^{in}_2 + \cdots \\
\mu(\vec{r}, t) &= \mu^{in}_0(u(\vec{r})) + \epsilon \delta \mu^{in}_1 + \epsilon^2 \delta \mu^{in}_2 + \cdots
\end{align*} \]

(42)

where the superscript ‘in’ refers to the inner solution. To expand the Laplacian in powers of \( \epsilon \), it is useful to introduce a curvilinear coordinate system with one coordinate \( u \) along the local normal to the interface and \( (d - 1) \) coordinates \( \vec{s} \) perpendicular to \( u \) and tangent to the interface. For simplicity a two-dimensional system is considered where \( s \) is the scalar arc length. Note that the \( O(\epsilon^0) \) terms, \( c^{in}_0 \) and \( \psi^{in}_0 \) in Eq. (42), are the equilibrium planar interface solutions of Eqs. (31) and (32).

At this early stage of the calculations it is worth pointing out that the exact position of the interface has not been specified. The choice of the exact interface position is somewhat flexible to within a distance \( \xi \) and there is no particular reason for choosing the interface position to be defined by \( \psi(u(\vec{r}, t) = 0) = 0 \) as is often done in the literature. Indeed, this particular choice can lead to unreasonable constraints on the free energy for a mapping between the phase field model and the sharp interface limit to be possible. In this work the interface will be chosen to be the Gibbs surface defined so that the excess surface concentration is equal on both sides of the interface. This is in essence a solvability condition which ensures that the chemical potential is continuous across the interface.

The transformation from Cartesian to curvilinear coordinates (see Appendix A) leads to the formal expansion
\[
\xi^2 \nabla^2 = L_0 + \epsilon L_1 + \epsilon^2 L_2 + \cdots
\]

(43)

where the specific form of \( L_n \) depends on the expansion. In the inner region, derivatives of the fields with respect to \( u \) are much larger than derivatives with respect to \( s \) which are identically zero when the curvature \( \kappa \) and the Péclet number vanish. This is taken into account by introducing the dimensionless variables \( \bar{u} \) and \( \bar{s} \) which are \( O(\epsilon^0) \) by \( u = \xi \bar{u} \) and \( s = \xi \bar{s} \). As shown in Appendix A, this scaling leads to
\[
\begin{align*}
L_0 &= \partial_{\bar{u}} \bar{u} \\
L_1 &= \bar{\kappa} \partial_{\bar{u}} \\
L_2 &= \partial_{\bar{s}} \bar{s} - \bar{\kappa}^2 \bar{u} \partial_{\bar{u}}
\end{align*}
\]

where the dimensionless curvature, \( \bar{\kappa} \equiv \kappa / \epsilon \), is of order unity.

Lastly, the time derivatives in Eqs. (31) and (32) must be expanded in \( \epsilon \). For these calculations, it is convenient to work in the frame in which the interface is stationary so that
\[
\frac{\partial}{\partial t} \bigg|_{\vec{r}} = \frac{\partial}{\partial t} \bigg|_{(u,s)} - \vec{v} \cdot \nabla
\]

(44)

where \( \vec{v} \) is the interface velocity which has components normal and tangential to the interface. The time derivative on the right hand side corresponds to relaxation.
dynamics not accounted for by motion of the interface. When this operator acts on the fields, \(c\) and \(\psi\), the tangential component and time derivative are of order \(\epsilon^3\) and can be dropped \([28]\). Thus to \(\sim O(\epsilon^2)\), \(\partial/\partial t\) becomes;

\[
\begin{align*}
\frac{\partial}{\partial t} & = -\frac{v_1}{\tau} \frac{\partial}{\partial u} + O(\epsilon^2) + \cdots \quad (45)
\end{align*}
\]

where the normal velocity has been expanded in a power series in \(\epsilon\),

\[
v_{\text{normal}} \equiv -\frac{\partial u}{\partial t} = \frac{\xi}{\tau} \sum_{m=1}^{\infty} \epsilon^m v_m. \quad (46)
\]

Using these expansions and expanding \(f\) around \(\epsilon_0^{in}\) and \(\bar{\psi}_0^{in}\) the right hand sides of Eqs. \([33]\) and \([41]\) become

\[
\begin{align*}
\int_{-\zeta}^{+\zeta} d\bar{u} \frac{\partial \bar{c}^{in}}{\partial \bar{u}} \left[ \mu_0 + \bar{K}_c \xi^2 \nabla^2 c - \frac{\partial f}{\partial c} \right] &= \int_{-\zeta}^{+\zeta} d\bar{u} \frac{\partial \bar{c}^{in}}{\partial \bar{u}} \left[ \left( \mu_0 + \bar{K}_c \mathcal{L}_1 c^{in} \right) - \epsilon \left( \bar{K}_c \mathcal{L}_1 c^{in} + \mathcal{L}_0 \delta c^{in} - \epsilon_1^{in} f_1^{(2,0)} - \epsilon_1^{in} f_1^{(1,1)} \right) + O(\epsilon^2) \right] \quad (47)
\end{align*}
\]

and

\[
\begin{align*}
\int_{-\zeta}^{+\zeta} d\bar{u} \frac{\partial \bar{\psi}_{\psi}^{in}}{\partial \bar{u}} \left[ \bar{K}_c \bar{G}^2 \nabla^2 \bar{\psi} - \frac{\partial f}{\partial \bar{\psi}} \right] &= \int_{-\zeta}^{+\zeta} d\bar{u} \frac{\partial \bar{\psi}_{\psi}^{in}}{\partial \bar{u}} \left[ \left( \bar{K}_c \mathcal{L}_1 \bar{\psi}_0^{in} \right) - f_1^{(1,1)} \right] + O(\epsilon^2) \quad (48)
\end{align*}
\]

where \(f_i^{(n,m)} = \partial^{n+m} f/\partial \bar{c}^n \partial \psi^{m} \big|_{\bar{c}_0^{in} = \bar{\psi}_0^{in}}\), \(\bar{K}_c \equiv K_c / \xi^2\), \(\bar{K}_c \equiv K_c / \xi^2\), and \(\zeta = \zeta / \xi\). Terms of \(O(\epsilon^0)\) vanish by construction. For later use, it is convenient to perform partial integrations on combinations of terms \([27]\)

\[
\begin{align*}
\int_{-\zeta}^{+\zeta} d\bar{u} \frac{\partial \delta c^{in}}{\partial \bar{u}} \left( \bar{K}_c \bar{G}^2 \nabla^2 \bar{\psi} - f_1^{(2,0)} \right) \delta \psi^{in} &= \int_{-\zeta}^{+\zeta} d\bar{u} \delta c^{in} \left( \bar{K}_c \bar{G}^2 \nabla^2 \bar{\psi} - f_1^{(2,0)} \right) \frac{\partial \delta c^{in}}{\partial \bar{u}} \\
&= \int_{-\zeta}^{+\zeta} d\bar{u} \delta c^{in} f_1^{(1,1)} \frac{\partial \delta \psi^{in}}{\partial \bar{u}} \quad (49)
\end{align*}
\]

and

\[
\begin{align*}
\int_{-\zeta}^{+\zeta} d\bar{u} \frac{\partial \bar{\psi}_{\psi}^{in}}{\partial \bar{u}} \left( \bar{K}_c \bar{G}^2 \nabla^2 \bar{\psi} - f_1^{(2,0)} \right) \delta \psi^{in} &= \int_{-\zeta}^{+\zeta} d\bar{u} \delta \bar{\psi}_{\psi}^{in} \left( \bar{K}_c \bar{G}^2 \nabla^2 \bar{\psi} - f_1^{(2,0)} \right) \frac{\partial \delta \psi^{in}}{\partial \bar{u}} \\
&= \int_{-\zeta}^{+\zeta} d\bar{u} \delta \bar{\psi}_{\psi}^{in} f_1^{(1,1)} \frac{\partial \delta \psi^{in}}{\partial \bar{u}} \quad (50)
\end{align*}
\]

since derivatives of \(\psi^{in}_0\) and \(\bar{\psi}_0^{in}\) vanish at \(\bar{u} = \pm \zeta\) in the limit \(\zeta = \zeta / \xi >> 1\).

To complete the calculation, the left-hand sides of Eqs. \([33]\) and \([41]\) are expanded to lowest order in \(\epsilon\). The expansion for \(\psi\) in Eq. \([41]\) is straightforward

\[
\begin{align*}
\frac{1}{\Gamma \psi} \int_{-\zeta}^{+\zeta} d\bar{u} \frac{\partial \bar{c}^{in}}{\partial \bar{u}} \frac{\partial \bar{\psi}}{\partial \bar{u}} &= \frac{1}{\Gamma \psi} \int_{-\zeta}^{+\zeta} d\bar{u} \frac{\partial \bar{c}^{in}}{\partial \bar{u}} \frac{\partial \bar{\psi}_{\psi}^{in}}{\partial \bar{u}} \\
&= -\frac{v_1}{\tau} \frac{\sigma_\psi}{K_c \Gamma \psi} + O(\epsilon^2) \quad (51)
\end{align*}
\]

where

\[
\sigma_\psi = K_c \int_{-\zeta}^{+\zeta} d\bar{u} \left( \frac{\partial \bar{\psi}_{\psi}^{in}}{\partial \bar{u}} \right)^2. \quad (52)
\]

The equivalent expansion for \(c\) is more complicated. The algebra is given in Appendix B. Formally, the results of these calculations can be written as

\[
B + S = \epsilon (S_1 / \tau + S_1) + \epsilon^2 (S_2 / \tau + S_2) + \cdots \quad (53)
\]

where \(S_n\) and \(S_n\) are given in Appendix B.

Putting all these results together gives the following two equations to \(O(\epsilon)\)

\[
\frac{v_1}{\tau} \frac{\sigma_\psi}{K_c \Gamma \psi} = -\frac{\bar{\kappa} \sigma_\psi}{\xi} - A_1 \quad (54)
\]

and

\[
\begin{align*}
\Delta c \delta c^{in}_0(0, s) = -\frac{\sigma_\psi \bar{c}}{\xi} + A_1 \\
&- \frac{v_1(s)\xi^2}{\tau \Gamma_c} \int_{-\zeta}^{+\zeta} d\bar{u} \left[ \bar{c}^{out}(\bar{u}) - c^{in}_0(\bar{u}) \right]^2 \\
&- \frac{\partial \delta \mu^{in}_1}{\partial \bar{u}} \bigg|_{-\zeta}^{+\zeta} \int_{-\zeta}^{+\zeta} d\bar{u} \left[ \bar{c}^{out}(\bar{u}) - c^{in}_0(\bar{u}) \right] \\
&- \frac{\partial \delta \mu^{in}_1}{\partial \bar{u}} \bigg|_{-\zeta}^{+\zeta} \int_{-\zeta}^{+\zeta} d\bar{u} \left[ \bar{c}^{out}(\bar{u}) - c^{in}_0(\bar{u}) \right] \quad (55)
\end{align*}
\]

where \(\Delta c \equiv c^{in}_0(\bar{u}) - c^{in}_0(\bar{u})\) is the miscibility gap,

\[
\begin{align*}
c^{out}_0(\bar{u}) = \begin{cases} 
\frac{c^{in}_0(\bar{u})}{\zeta} & \bar{u} < 0 \\
\frac{c^{in}_0(\bar{u})}{\zeta} & \bar{u} > 0 
\end{cases}
\end{align*} \quad (56)
\]

\[
\begin{align*}
\sigma_\epsilon &= K_c \int_{-\zeta}^{+\zeta} d\bar{u} \left( \frac{\partial \delta \psi^{in}_0}{\partial \bar{u}} \right)^2 
\end{align*} \quad (57)
\]

and

\[
A_1 = \int_{-\zeta}^{+\zeta} d\bar{u} \left( \frac{\partial \delta \psi^{in}_0}{\partial \bar{u}} \right)^2 f_1^{(1,1)} \quad (58)
\]

Equation \([55]\) gives the chemical potential \(\mu\) of the inner solution at the interface (i.e., at \(\bar{u} = 0\)) which must be matched to the outer solution at \(\bar{u} = \pm \zeta\). An expression for \(\delta \mu^{in}(\pm \zeta)\) can be obtained by expanding Eq. \([34]\) to \(O(\epsilon)\).
Integrating Eq. (59) twice, first from $\bar{u}$ to $\zeta$ and then from 0 to $\bar{u}$ yields

$$\delta\mu_1^{in}(\zeta, s) = \delta\mu_1^{in}(0, s) + \zeta \frac{\partial \delta\mu_1^{in}}{\partial \bar{u}}|_{+\zeta} + \frac{\delta\mu_1^{in}}{\tau \Gamma_c} \int_{0}^{\zeta} d\bar{u}[c_{0}^{out}(\bar{u}) - c_{0}^{in}(\bar{u})]$$ (60)

and similarly for $\delta\mu_1^{in}(-\zeta)$. From Eqs. (55) and (56) we obtain

$$\Delta c\delta\mu_1^{in}(\pm\zeta, s) = \sigma_{c,K}/\epsilon + A_1 \pm \Delta c\zeta \frac{\partial \delta\mu_1^{in}}{\partial \bar{u}}|_{\pm\zeta} - \frac{\delta\mu_1^{in}}{\tau \Gamma_c} \int_{-\zeta}^{+\zeta} d\bar{u}[c_{0}^{out}(\bar{u}) - c_{0}^{in}(\bar{u})]^2$$ (61)

The integrals in Eq. (61) can be written in a more useful form by noting that $\zeta > 1$ in the inner region so that $c_{0}^{in}(\pm\bar{u}) = c_{0}^{in}(\pm\infty)$ for $|\bar{u}| \geq \zeta$. Eq. (61) becomes

$$\Delta c\delta\mu_1^{in}(\pm\zeta, s) = \sigma_{c,K}/\xi + A_1 \pm \Delta c\zeta \frac{\partial \delta\mu_1^{in}}{\partial \bar{u}}|_{\pm\zeta} - \frac{\delta\mu_1^{in}}{\tau \Gamma_c} \int_{-\zeta}^{+\zeta} d\bar{u}[c_{0}^{out}(\bar{u}) - c_{0}^{in}(\bar{u})]^2$$ (62)

One last result will be needed and is obtained by integrating Eq. (55) over $-\zeta < \bar{u} < +\zeta$

$$v_1 = -\tau \Gamma_c \frac{\Delta c\zeta}{\Gamma_c} \left( \frac{\partial \delta\mu_1^{in}}{\partial \bar{u}}|_{+\zeta} - \frac{\partial \delta\mu_1^{in}}{\partial \bar{u}}|_{-\zeta} \right)$$ (63)

The solution for $\delta\mu_1^{in}(\pm\zeta)$ must be matched to the solution in the outer region.

### B. Outer Expansion

Far from the interface, the fields $\psi$ and $c$ vary slowly in space and are close to the bulk equilibrium values $\psi_{eq}$ and $c_{eq}$. Variations of the fields in the bulk regions far from the interface take place on length scales $O(\zeta/\epsilon)$ in all directions which implies that suitable dimensionless space and time coordinates are $(\bar{u}, \bar{s}, \bar{t}) \equiv (\epsilon u/\xi, \epsilon s/\xi, \epsilon^2 t/\tau)$.

Expanding $\psi(r)$ about the bulk equilibrium solution $\psi(r) = \delta\psi^{out}(r) + \psi_{eq}$ gives

$$\frac{\partial \delta\psi^{out}}{\partial t} = \Gamma_c \left( K \psi \frac{\nabla^2 \delta\psi^{out}}{\psi_{eq}} - \frac{\partial f^{eq}}{\partial \psi^{out}} - \frac{\partial^2 f^{eq}}{\partial \psi^{out}^2} \delta\psi^{out} - \frac{1}{2!} \frac{\partial^3 f^{eq}}{\partial \psi^{out}^3} \delta\psi^{out}^3 - \cdots \right)$$ (64)

By definition, $(\partial f^{eq}/\psi_{eq}) = 0$ and, since $\delta\psi^{out} = 0$ in the limit $\epsilon \to 0$, Eq. (54) is linear at $O(\epsilon)$. Furthermore, $(\partial^2 f^{eq}/\psi^{2})_{eq} > 0$ so that $\delta\psi^{out}$ vanishes exponentially with time for all wavelengths. Thus, $\delta\psi^{out}$ is trivial in the outer region and can be ignored. It is convenient to expand $c^{out}$ and $\mu^{out}$ in the outer region as

$$c^{out}(r) = c_0^{out} + \epsilon c_1^{out} + \cdots$$

$$\mu^{out}(r) = \mu_0^{out} + \epsilon \mu_1^{out} + \cdots$$ (65)

where $c_0^{out}$ is given by Eq. (56). At $O(\epsilon^3)$ in dimensionless variables, in the lab frame

$$\frac{\partial \delta\mu_1^{out}}{\partial t} = \frac{\tau \Gamma_c}{\xi^2} \nabla^2 \delta\mu_1^{out}$$ (66)

where $\nabla \equiv (\xi/\epsilon)\nabla$ is the scaled dimensionless derivative suitable for the outer region. This simplifies to a linear diffusion equation for the chemical potential inside the bulk phases which reads, in dimensional units,

$$\frac{\partial \mu^{out}}{\partial t} = D_c \nabla^2 \mu^{out}$$ (67)

where $D_c = \Gamma_c (\partial c^{out}/\partial c^{out})_{eq}$ is a diffusion constant. The value of $D_c$ depends on the bulk equilibrium phase considered.

### C. Matching and the Gibbs Surface

To solve the diffusion problem of Eq. (67), initial values $\delta\mu_1^{out}(\bar{u} = 0, \bar{s})$ are required. These are to be obtained by matching to the inner solution $\delta\mu_1^{in}(\bar{u}, \bar{s})$ at $\bar{u} = \bar{\zeta}$.

To obtain $\delta\mu_1^{out}(\bar{u} = 0, \bar{s})$ from $\delta\mu_1^{out}(\bar{u} = \pm\bar{\zeta}, \bar{s})$ with $\bar{\zeta} = \epsilon\bar{c}$, it is useful to Taylor expand about $\bar{u} = \bar{\zeta}$.

$$\delta\mu_1^{out}(\bar{u}, \bar{s}) = \delta\mu_1^{out}(\pm\bar{\zeta}, \bar{s}) + (\bar{u} \mp \bar{\zeta}) \frac{\partial \delta\mu_1^{out}}{\partial \bar{u}}|_{\pm\bar{\zeta}} + \cdots$$ (68)

In the outer region, $\bar{\zeta} \ll 1$ and this expansion is valid at $\bar{u} = 0$

$$\delta\mu_1^{out}(\pm\bar{\zeta}, \bar{s}) = \delta\mu_1^{out}(0, \bar{s}) \pm \bar{\zeta} \frac{\partial \delta\mu_1^{out}}{\partial \bar{u}}|_{\pm\bar{\zeta}} + \cdots$$ (69)

Since $\delta\mu_1^{out}(\pm\bar{\zeta}) = \delta\mu_1^{in}(\pm\zeta)$, we can use Eq. (62) and Eq. (63) to obtain
$\Delta c \delta \mu^\text{out}_1(0, \tilde{s}) = \frac{\sigma_c \tilde{c}_0}{\xi} + A_1$

$- \frac{v_1(\tilde{s}) \xi^2}{\tau \Gamma_c} \int_{-\infty}^{+\infty} d\tilde{u} [c^\text{in}_0(\tilde{u}) - c^\text{out}_0(\tilde{u})]^2$

$- \frac{\partial \delta \mu^\text{in}_1}{\partial u} |_{-\zeta} \int_{-\infty}^{0} d\bar{u} [c^\text{out}_0(\bar{u}) - c^\text{in}_0(\bar{u})]$

$- \frac{\partial \delta \mu^\text{in}_1}{\partial u} |_{+\zeta} \int_{0}^{+\infty} d\bar{u} [c^\text{out}_0(\bar{u}) - c^\text{in}_0(\bar{u})]$

$+ \Delta c \frac{v_1(\tilde{s}) \xi^2}{\tau \Gamma_c} \int_{0}^{+\infty} d\bar{u} [c^\text{out}_0(\bar{u}) - c^\text{in}_0(\bar{u})] \quad (70)$

which gives the appropriate boundary value of $\delta \mu^\text{out}_1(0, \tilde{s})$. The inner solution $\delta \mu^\text{in}_1(0)$ differs from the outer solution $\delta \mu^\text{out}_1(0)$ since the matching is done at $\tilde{u} = \bar{\zeta}$ and extrapolated linearly to $\tilde{u} = 0$ by Eq. (69). The extrapolation and matching of $\delta \mu^\text{in}_1$ to $\delta \mu^\text{out}_1$ is illustrated pictorially in Fig. (4).

FIG. 4. Matching of $\delta \mu^\text{in}_1(u)$ (dashed line) with $\delta \mu^\text{out}_1(u)$ (solid line) at $u = \pm \zeta$.

The right hand side of Eq. (71) appears to depend on whether the inner and outer solutions are matched at $u = +\zeta$ or $u = -\zeta$ because of the last term. This ambiguity is eliminated by defining the interface to be a Gibbs surface at $u = 0$ defined by the condition

$$\int_{-\infty}^{+\infty} d\tilde{u} [c^\text{out}_0(u) - c^\text{in}_0(u)] = 0 \quad (71)$$

This can always be satisfied by choosing the position of the interface at $u = 0$ to be such that Eq. (72) is satisfied. In essence, the interface position is determined by the condition that the excess concentration on one side of the interface is exactly compensated by the deficit on the other, as shown in Fig. (4). This can be regarded as a solvability condition.

Another result that will be needed is obtained by matching the first derivative of the chemical potential is obtained from Eq. (68) which reads, in dimensional units

$$v \Delta c = - \Gamma_c \left[ \frac{\partial \delta \mu^\text{in}_1}{\partial u} \bigg|_{+\zeta} - \frac{\partial \delta \mu^\text{in}_1}{\partial u} \bigg|_{-\zeta} \right]. \quad (72)$$

Matching derivatives of the inner and outer solutions for $\mu$ and extrapolating back to $u = 0 \pm$ by Eq. (68), gives the standard result

$$v \Delta c = - \Gamma_c \left[ \frac{\partial \mu^\text{out}_1}{\partial u} \bigg|_{0+} - \frac{\partial \mu^\text{out}_1}{\partial u} \bigg|_{0-} \right] \quad (73)$$

since $\mu^\text{out}(u)$ is linear for $0 < |u| < \zeta$ from Eq. (68). Finally, combining Eqs. (44), (71) and (73), gives the chemical potential at a moving, curved interface

$$\Delta c (\mu^\text{out}(0, s) - \mu_{eq}) = - \sigma_c \tilde{c} + \mathcal{E}^2 v + A_1 + O(\epsilon^2) \quad (74)$$

where $A_1$ is given by Eq. (58) and

$$\mathcal{E}^2 \equiv \frac{1}{\Gamma_c} \int_{-\infty}^{+\infty} d\tilde{u} \left[ |c^\text{out}_0(\tilde{u})|^2 - |c^\text{in}_0(\tilde{u})|^2 \right]. \quad (75)$$

V. SUMMARY OF RESULTS

All the results can be combined into a single set of boundary layer equations that can describe many different physical phenomena. Typically the boundary layer equations are written in terms of the concentration, which is the outer region is simply related (to order $\epsilon$) to the chemical potential by the relationship

$\Delta c \delta \mu^\text{out}_1(0, \tilde{s}) = \frac{\sigma_c \tilde{c}_0}{\xi} + A_1$.
\[ \delta \mu = \frac{\partial \mu}{\partial c} \bigg|_{eq} \delta c. \]  

(76)

Combining this result with Eqs. (74) and (54) gives the Gibbs Thomson relation in dimensionless units

\[ \frac{\delta c(0, s)}{\Delta c} = -d_o \kappa(s) - \beta v. \]  

(77)

where \( d_o \) is the capillary length given by,

\[ d_o = \frac{\sigma}{(\Delta c)^2 (\partial \mu/\partial c)_{eq}}. \]  

(78)

\[ \sigma \equiv \sigma_c + \sigma_\psi \]  

is the total surface tension given by,

\[ \sigma = \int_{-\infty}^{\infty} du \left[ K_\psi \left( \frac{\partial \psi_{in}}{\partial u} \right)^2 + K_c \left( \frac{\partial c_{in}}{\partial u} \right)^2 \right], \]  

(79)

and \( \beta \) is the coefficient of kinetic undercooling given by

\[ \beta = -\frac{1}{(\Delta c)^2 (\partial \mu/\partial c)_{eq}} \left[ \frac{\sigma_\psi}{K_\psi \Gamma_\psi} - \mathcal{E}^2 \right]. \]  

(80)

Equation (77) provides a boundary condition at the interface for the diffusion equation of Eq. (67) which can be written as

\[ \frac{\partial \delta c}{\partial t} = D_c \nabla^2 \delta c, \]  

(81)

where

\[ D_c \equiv \Gamma_c \frac{\partial \mu}{\partial c} \bigg|_{eq}. \]  

(82)

This must be solved in conjunction with Eq. (73) which may be written,

\[ \Delta c v(s) = \left[ D_c \frac{\partial \delta c}{\partial u} \right]_{0^-} - \left[ D_c \frac{\partial \delta c}{\partial u} \right]_{0^+}. \]  

(83)

To understand of the significance of each term that enters the above equations it is useful to consider some limiting cases. First consider the case in which the concentration field is a constant slightly different from \( c_{eq} \), the equilibrium value, \( c = c_{eq} + \delta c \). If \( \delta \mu \) is the chemical potential difference between the phases defined by the non-conserved field at \( u = +\infty \) and \( -\infty \), then Eq. (77) reduces to the Allen-Cahn equation in a field,

\[ v = -K_\psi \Gamma_\psi \left( \kappa + \frac{\delta \mu \Delta c}{\sigma_\psi} \right). \]  

(84)

From this point of view the kinetic undercooling can be thought of as the simply the relaxation of surface tension in a non-conserved field. Thus the Gibbs Thomson equation is equivalent to the Allen Cahn equation in the appropriate limit.

The other simplifying case is when the non-conserved field is a constant as in a pure liquid or solid phase. In this case, the sharp interface equations remain the same except the coefficients \( \sigma \) and \( \beta \) become

\[ \sigma = \sigma_c \]  

(85)

and

\[ \beta = -\frac{E}{(\Delta c)^2 (\partial \mu/\partial c)_{eq}}. \]  

(86)

For the conserved case of Model B, \( \beta \) is always negative. This term takes into account the lag of the concentration field behind a moving front. When the interface is moving, the interfacial profile cannot instantaneously relax to the correct equilibrium shape \( c_{eq} \). For the conserved field, this correction is roughly as important as dynamic relaxation in the bulk phase, as will be seen in the next section.

VI. LINEAR ANALYSIS

To illustrate the influence of the various terms that enter the sharp interface model it interesting to study the dynamics of fluctuations around an almost planar interface. To fix ideas it is useful to consider an interface separating two phases that is defined by the equation \( y = h(x, t) \) as shown in Fig. (6). In the calculations to follow it will be assumed that \( \nabla h(x, t) \) is a small parameter. This is an additional constraint not implicit in the sharp interface models.

\[ \sigma \]  

\[ \beta \]  

\[ v = \frac{\gamma}{\sqrt{1 + (\partial h/\partial x)^2}} \]  

(87)
and

$$\kappa = -\frac{1}{\gamma^3} \frac{\partial^2 h}{\partial x^2},$$  (88)

where $\gamma \equiv \sqrt{1 + (\partial h/\partial x)^2}$.

### A. Non-conserved dynamics

As discussed in the preceding section, the sharp interface equations reduce to the Allen-Cahn equation in a field when the conserved field is a constant. When a single valued interface as described above is considered, Eq. (21) reduces to the Kardar, Parisi, Zhang (KPZ) equation in the absence of noise. Substituting Eqs. (87) and (88) into Eq. (84) and linearizing in $h$ gives

$$\frac{\partial h}{\partial t} = \nu \frac{\partial^2 h}{\partial x^2} + \lambda \left( \frac{\partial h}{\partial x} \right)^2$$  (89)

where $h \to h - \lambda t$, $\nu \equiv \Gamma \psi K_F$, and $\lambda \equiv -\nu \delta \mu \Delta c/\sigma$. The additive noise term $\lambda(x,t)$ in the standard KPZ equation appears when stochastic noise is included in the fundamental Langevin equations.

As a specific example, consider the following free energy:

$$F = \int d\vec{r} \left( -\frac{a}{2} \psi^2 + \frac{K_F}{2} |\nabla \psi|^2 + \frac{b}{4} \psi^4 + d \delta c \psi + \frac{w}{2} (\delta c)^2 \right)$$  (90)

where $\delta c \equiv c - c_{eq}$ and $c$ is a constant. For this free energy, a planar interface is stationary when $d \to 0$. This interface is defined by the equations:

$$\psi_0 = \psi_{eq} \tanh \left( \frac{u}{2\xi} \right),$$

$$c_{eq} = c_{eq} - \frac{d}{w} \psi_0^2,$$

$$\mu_{eq} = 0,$$  (91)

where $\xi = \sqrt{K_F/2a}$ and $\psi_{eq} = \sqrt{a/b}$. Thus the miscibility gap, surface tension, and deviations of the chemical potential are given by

$$\Delta c = -\frac{d}{w} \Delta \psi = -2 \frac{d}{w} \psi_{eq},$$  (92)

$$\sigma_{\psi} = \frac{2 K_F \psi_{eq}^2}{\xi},$$  (93)

and

$$\delta \mu = \frac{\partial \mu}{\partial c} \delta c = w \delta c.$$  (94)

Thus the coefficient $\lambda$ is given as

$$\lambda = \Gamma \psi K_F (d \delta c) \frac{\Delta \psi}{\sigma_{\psi}} = \Gamma \psi (d \delta c) \frac{3}{a} \sqrt{\frac{K_F b}{2}}.$$  (95)

### B. Conserved dynamics

Now consider an almost planar interface separating two phases of different concentration with the same free energy as occurs for example in spinodal decomposition. Since concentration is a conserved field Eqs. (77), (81), and (83) must be solved simultaneously. For simplicity, a two sided model in which $\partial \mu/\partial c$ is the same on both sides of the interface will be considered. This implies that the parameters $d_o, \beta$ and $D$ are the same in both phases. It is straightforward to perform the calculations in the more general case but this does not introduce any new physics and is not very illuminating. In the limit $(\partial h/\partial x)^2 \ll 1$ it is convenient to seek solutions of Eq. (81) of the form

$$\delta c(u, x) = \delta c(0) e^{(ikx - q|u| + \omega t)},$$  (96)

where $u \equiv y - h(x, t)$. For this perturbation it is easy to show that the dimensionless quantities $\bar{\omega} \equiv \omega d_o^2/D_c$, $\bar{k} \equiv kd_o$, $\bar{q} \equiv qd_o$ and the dimensionless kinetic coefficient $\bar{\beta} \equiv \beta D_c/d_o$ satisfy

$$\bar{\omega} = \frac{-2\bar{q}^3}{1 - 2\bar{q}(1 + |\bar{\beta}|)}$$

$$\bar{k}^2 = \bar{q}^2 - \bar{\omega}.$$  (97)

![FIG. 7. Dispersion relation for a planar interface separating two conserved phases of equal free energy. The four lines plotted in this figure correspond from right to left $-\bar{\beta} = 0, 10, 100$ and 1000.](image_url)

In the long wavelength limit ($\bar{k} \to 0$), $\bar{k} \approx \bar{q}$ and $\bar{\omega} \approx -2\bar{q}^2$, as expected. It is also interesting to note that in the short wavelength limit ($\bar{k} \to \infty$), $\bar{q} \to 1/(2 + 2|\bar{\beta}|)$ and $\bar{\omega} \approx -\bar{k}^2$. The crossover from the diffusion limited $\omega \sim -k^2$ at short wavelength to the asymptotic long wavelength behavior $\omega \sim -k^5$ occurs at smaller values.
of $\kappa$ as the kinetic coefficient $\beta$ becomes more negative. This behavior is sketched in Fig. (7).

This analysis shows that the term $1 + 1/\beta$ gives rise to diffusive (i.e., $\omega \sim -k^2$) behavior and is associated with relaxation in the bulk and in the interface shape. For example if solutions of the form $e^{ik\cdot\vec{x} - \eta|\vec{x}|}$ are sought instead of Eq. (96) this term becomes simply $1/\beta$. Thus the ‘1’ represents diffusive relaxation in the bulk and the $\beta$ represents relaxation of the interface shape.

A model commonly used to study spinodal decomposition is known as the Cahn-Hilliard model or Model B in the Halperin and Hohenberg classification scheme. The free energy for this model can be written:

$$\mathcal{F} = \int d\vec{r} \left( -\frac{a}{2} c^2 + \frac{b}{4} c^4 + \frac{K_c}{2} |\nabla c|^2 \right)$$

(98)

and

$$\frac{\partial c}{\partial t} = \Gamma_c \nabla^2 \delta \mathcal{F}/\delta c.$$  

(99)

For this model a stationary planar interface is given by

$$\phi^c_0 = c_{eq} \tanh \left( \frac{y}{2\xi} \right),$$  

(100)

where $\xi = \sqrt{K_c/2a}$ and $c_{eq} = \sqrt{a/b}$. The coefficients entering the sharp interface equations are then:

$$d_s = \frac{1}{6} \xi,$$

(101)

$$\beta = -\frac{\xi}{D_c} \rightarrow \bar{\beta} = -6,$$  

(102)

and

$$D_c = 2\Gamma_c a.$$  

(103)

C. Non-conserved and conserved Dynamics

Now consider the stability of a stable phase invading a super-saturated liquid phase at constant velocity. This is precisely the situation considered by Langer et al. [4] in the absence of kinetic undercooling and without relaxation kinetics in the bulk phases. It is easy to show that the only solution for a planar front moving at constant velocity which is consistent with the sharp interface model (i.e., Eqs. (97), (93), and (33)) is

$$\frac{\delta c_0}{\delta c} = \begin{cases} \exp(-\nu y'/D_c) - 1 - \beta v & y' > 0 \\ -\beta v & y' < 0 \end{cases}$$

(104)

where $\nu$ is the velocity of the front and $y' = y - vt$ is a coordinate in the co-moving reference frame.

The stability of this moving front can be determined by studying perturbations about the planar front solution of Eq. (104). We seek solutions of the form

$$\frac{\delta c}{\delta c} = \delta c_0 + \begin{cases} \delta \exp(ik\cdot\vec{x} + \omega t - qy') & y' > 0 \\ \delta \exp(ik\cdot\vec{x} + \omega t + q'y') & y' < 0 \end{cases}$$

(105)

where $q, q' > 0$ and the position of the perturbed front is at

$$y' = h(\vec{x},t) \equiv h_k \exp(ik\cdot\vec{x} + \omega t).$$

(106)

To linear order in $h_k$ and $\delta t$, it is straightforward to show that the dimensionless $\bar{\omega}$ and $k$ are determined by

$$\bar{q}' = \bar{q} - 2/\bar{l},$$

$$\bar{\omega} = \frac{2(q - 2/\bar{l})(1/\bar{l} - \bar{q} - 1/\bar{l})}{1 - 2(q - 1/\bar{l})(1 - \bar{\beta})},$$

$$k^2 = \bar{q}(\bar{q} - 2/\bar{l}) - \bar{\omega}$$

(107)

where $\bar{l} = 2D_c/d_{sv}$ and $\bar{\beta} = \beta D_c/d_{sv}$. The dispersion relation for $\bar{\omega}(k)$ is plotted in Fig. (8) for $\bar{l} = 100$ and several values of $\bar{\beta}$. Note that, in contrast to Model B where the kinetic coefficient has a definite sign $\beta < 0$, in Model C it can have either sign. Note also that, when $l \rightarrow \infty$, Eq. (107) reduces to the result of Eq. (17) for conserved Model B dynamics, as it should.

![FIG. 8. The linear dispersion relation for the Mullins Sekerka instability including the kinetic coefficient $\bar{\beta}$, for $\bar{l} = 100$.](image)

A simplified version of the general system discussed in this paper has been extensively used to study single phase solidification phenomena [10]. The free energy $\mathcal{F}$ can be written as

$$\mathcal{F} = \int d\vec{r} \left( f(\psi) + \frac{b\lambda}{2} \Phi^2 + \frac{W^2}{2} |\nabla \psi|^2 \right)$$

(108)

where $\Phi \equiv c + h(\psi)$ with
\[ f(\psi) = -\frac{\psi^2}{2} + \frac{\psi^4}{4} \]
\[ h(\psi) = \frac{15}{16} \left( \psi - \frac{2}{3} \psi^3 + \frac{1}{5} \psi^5 \right). \]  

With this form of \( f(\psi) \), the interface width is \( W \). The dynamical evolution is governed by Langevin equations for the conserved field \( c \) and the non-conserved \( \psi \) which, in the noiseless limit, are
\[ \frac{\partial \psi}{\partial t} = -\frac{1}{\tau} \frac{\delta F}{\delta \psi}, \]
\[ \frac{\partial c}{\partial t} = D_c \nabla^2 \frac{\delta F}{\delta c}. \]  

A stationary planar interface is given by
\[ \psi_0^i(u) = \tanh \left( \frac{u}{W \sqrt{2}} \right), \]
\[ c_0^i(u) = -h(\psi_0^i). \]  

For an interface with curvature \( \kappa \) propagating with velocity \( v \), it is tedious but straightforward to use the Gibbs-Thomson relation of Eq. (77) to find
\[ \Phi(0) = -\left( \frac{W}{\lambda} \right) \left( \frac{5}{4 \sqrt{2}} \right) \kappa \]
\[ -\left[ \left( \frac{5}{4 \sqrt{2}} \right) \left( \frac{\tau}{W \lambda} \right) - \left( \frac{209 \sqrt{2}}{840} \right) \left( \frac{W}{D} \right) \right] v. \]  

The term inside the square brackets of Eq. (112) is proportional to the kinetic coefficient \( \beta \) and contains the sum of the positive Model A contribution and the negative Model B part. In principle the kinetic coefficient \( \beta \) can be of either sign in solidification processes while it must be negative for any process described by Model B, such as phase separation in binary alloys.

It is also trivial to show that
\[ v = -D_c \left( \frac{\partial c}{\partial u} + \frac{\partial c}{\partial u} |_{-} \right), \]
\[ \frac{\partial c}{\partial t} = D_c \nabla^2 c. \]  

These results are identical to those found numerically by others [10].

**VII. SUMMARY**

The use of continuum phase-field models to describe phenomena involving the motion of well-defined sharp interfaces is discussed. The phase-field models involve interfaces which are diffuse on a length scale of \( \xi \). Considering a general class of phase-field models, it is shown how equations describing the sharp-interface limit are obtained when \( \xi \ll 1 \) and \( \xi v/D \ll 1 \). It is also shown that the Allen-Cahn equation is a special case of the Gibbs-Thomson relation.

In particular, it should be emphasized that these calculations are independent of the specific form of the free energy functional, provided \( F \) describes well-defined phases. Furthermore the calculations are universal: a large class of free energies give rise to sharp interface equations which differ only in the values of parameters but are of the same functional form. To realize this goal, it is essential that the “sharp-interface limit” involves an interface of finite thickness, \( \xi \). Expansions involving a zero width interface require a delicate and unphysical tuning of parameters in the free energy for thermodynamic consistency. In this work, the small parameters \( \kappa \xi \) and \( v \xi / D \) vanish when the curvature \( \kappa \) and the inverse diffusion length \( v / D \) go to zero for a finite interface thickness \( \xi \). Thus, delicate tuning is not required for thermodynamic consistency in our approach which is based on the fundamental principles of statistical mechanics.

This work opens the way to construct physically consistent sharp interface descriptions of more complicated multiple phase systems such as a solid in contact with a fluid which can support flows. This will involve mode coupling terms in the dynamical equations. Once such Langevin equations are constructed, there should be no conceptual difficulty in deriving the corresponding interface equations.

**ACKNOWLEDGMENTS**

This work was supported by the Natural Sciences and Engineering Research Council of Canada (MG), le Fonds pour la Formation de Chercheurs et l’Aide à la Recherche du Québec (MG), Research Corporation grant CC4787 (KRE), NSF-DMR Grant 0076054 (KRE), and NASA Grant NAG3-1929 (JMK).

**APPENDIX A: CURVILINEAR COORDINATES**

The curvilinear coordinates \((u, s)\) used in the text are related to the Cartesian coordinates in the following manner
\[ \vec{r} = \vec{R}(s) + u \hat{n}(s), \]  

where \( \vec{R} \) is the position of the interface and \( \hat{n}(s) \) is the normal vector (see Fig. 3). The metric tensor \( g_{\alpha \beta} \) of the transformation from Cartesian to curvilinear coordinates is
\[ g = \begin{pmatrix} 1 & 0 \\ 0 & (1 + u \kappa)^2 \end{pmatrix} \]

where \( \kappa = \partial \theta / \partial s \) is the curvature with \( \theta \) the angle between the \( x \)-axis and the tangent to the curve. The Laplacian in \((u, s)\) is then obtained in the usual manner
\[ \nabla^2 = \sum_{\alpha, \beta} \frac{1}{\sqrt{|g|}} \frac{\partial}{\partial x^\alpha} \sqrt{|g|} g^{\alpha \beta} \frac{\partial}{\partial x^\beta} \]
where $x^1 = u$, $x^2 = s$, $g^{\alpha \beta}$ are the components of the inverse of the matrix $g$ and $\kappa_s \equiv \partial \kappa / \partial s$.

\[
\kappa \frac{\partial}{\partial u} + \frac{1}{1 + \kappa \frac{\partial}{\partial u}} \frac{\partial^2}{\partial s^2} \left[ \frac{1}{1 + \kappa \frac{\partial}{\partial u}} \right] - \frac{\kappa_s}{(1 + \kappa \frac{\partial}{\partial u})^3} \frac{\partial}{\partial s} \tag{A2}
\]

where $\kappa = \kappa / \epsilon$ and $\kappa_s = \xi^2 \kappa_s / \epsilon^2$. In terms of these dimensionless variables, the Laplacian becomes

\[
\xi^2 \nabla^2 = \frac{\partial^2}{\partial u^2} + \frac{\kappa}{1 + \kappa \frac{\partial}{\partial u}} \frac{\partial^2}{\partial s^2} + \frac{\epsilon^2}{(1 + \kappa \frac{\partial}{\partial u})^3} \frac{\partial^2}{\partial s^2} - \frac{\epsilon^3 \kappa \frac{\partial}{\partial s}}{(1 + \kappa \frac{\partial}{\partial u})^3} \frac{\partial}{\partial s} \nonumber\]

\[
= \frac{\partial^2}{\partial u^2} + \kappa \left( \epsilon \sum_{n=0}^\infty (-\epsilon \kappa)^n \right) \frac{\partial}{\partial u} + \left( \epsilon^2 \sum_{n=0}^\infty (n+1)(\epsilon \kappa)^n \right) \frac{\partial^2}{\partial s^2} \nonumber\]

\[
- \frac{\kappa_s}{2} \left( \epsilon^3 \sum_{n=0}^\infty (n+1)(n+2)(-\epsilon \kappa)^n \right) \frac{\partial}{\partial s} = L_0 + \epsilon L_1 + \epsilon^2 L_2 + \epsilon^3 L_3 + \cdots \tag{A3}
\]

where

\[
L_0 = \frac{\partial^2}{\partial u^2} \tag{A4}
\]

\[
L_1 = \kappa \frac{\partial}{\partial u} \tag{A5}
\]

\[
L_2 = \frac{\partial^2}{\partial s^2} - \kappa^2 \frac{\partial}{\partial u} \tag{A6}
\]

\[
L_3 = -2\hat{u}\kappa \frac{\partial^2}{\partial s^2} + \kappa^3 \hat{u}^2 \frac{\partial}{\partial u} - \kappa \frac{\partial}{\partial s} \tag{A7}
\]

**APPENDIX B: GREEN’S FUNCTIONS**

It will also be useful to develop an expansion for the inverse of the Laplacian or Green’s function. The Green’s function of interest is defined by

\[
\nabla^2 \bar{G}(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') \tag{B1}
\]

An expansion of the Green’s function can be obtained in a straightforward manner. Let $G(\vec{r}, \vec{r}') = G_0(\bar{u}, \bar{s}; \bar{u}', \bar{s}') + \epsilon G_1(\bar{u}, \bar{s}; \bar{u}', \bar{s}') + \cdots$ where

\[
L_0 G_0 = 0 \tag{B2}
\]

\[
L_0 G_1 + L_1 G_0 = \delta(\bar{u} - \bar{u}') \delta(\bar{s} - \bar{s}') \tag{B3}
\]

\[
L_0 G_2 + L_1 G_1 + L_2 G_0 = 0 \tag{B4}
\]

and so on. The solution for $G_0$ is $G_0 = 0$, so that the lowest order solution for $G$ is $G_1$, which satisfies the equation

\[
\frac{\partial^2}{\partial u^2} G_1(\bar{u}, \bar{s}; \bar{u}', \bar{s}') = \delta(\bar{u} - \bar{u}') \delta(\bar{s} - \bar{s}') \tag{B5}
\]

which has the solution

\[
G_1(\bar{u}, \bar{s}; \bar{u}', \bar{s}') = \begin{cases} 
+\hat{u}\delta(\bar{s} - \bar{s}') & -\zeta < \bar{u} < \bar{u}' < 0 \\
+\hat{u}'\delta(\bar{s} - \bar{s}') & -\zeta < \bar{u} < \bar{u}' < 0,
\end{cases}
\]

\[
G_1^+(\bar{u}, \bar{s}; \bar{u}', \bar{s}') = \begin{cases} 
-\hat{u}'\delta(\bar{s} - \bar{s}') & 0 < \bar{u}' < \bar{u} < +\zeta \\
-\hat{u}\delta(\bar{s} - \bar{s}') & 0 < \bar{u} < \bar{u}' < +\zeta.
\end{cases}
\]

The surface terms $S^\pm$ of Eq. (44) can be expanded as

\[
S^\pm = \pm \int_0^{+\xi} d\hat{u} \frac{\partial^2}{\partial \hat{u}^2} \oint_B ds' \left[ \partial G_1^{\pm}(\hat{u}, \bar{s}; \bar{u}', s') \frac{\partial}{\partial \hat{u}'} \right] \bigg|_B \nonumber\]

\[
= \pm \int_0^{+\xi} d\hat{u} \frac{\partial^2}{\partial \hat{u}^2} \oint_B ds' \sum_{n=1}^\infty \sum_{m=0}^\infty \epsilon^n \frac{\partial}{\partial s'} \left[ \delta \mu_n(\bar{u}, \bar{s}; \bar{u}', s') \frac{\partial G_1^{\pm}}{\partial \hat{u}'} \right] \bigg|_B \nonumber\]

\[
= \epsilon S_1^\pm + \epsilon^2 S_2^\pm + \cdots \tag{B6}
\]

where

\[
S_1^\pm = \pm \int_0^{+\xi} d\hat{u} \frac{\partial^2}{\partial \hat{u}^2} \oint_B ds' \left[ \delta \mu_1 \frac{\partial G_1^\pm}{\partial \hat{u}'} - G_1^\pm \frac{\partial \delta \mu_1}{\partial \hat{u}'} \right] \bigg|_B \nonumber\]

\[
S_2^\pm = \pm \int_0^{+\xi} d\hat{u} \frac{\partial^2}{\partial \hat{u}^2} \oint_B ds' \left[ \delta \mu_2 \frac{\partial G_1^\pm}{\partial \hat{u}'} + \delta \mu_1 \frac{\partial G_2^\pm}{\partial \hat{u}'} - G_2^\pm \frac{\partial \delta \mu_2}{\partial \hat{u}'} - G_1^\pm \frac{\partial \delta \mu_1}{\partial \hat{u}'} \right] \bigg|_B \tag{B7}
\]

where the subscript $B$ indicates that the integrands are evaluated on the boundary at $\hat{u}' = 0^\pm$ and at $\hat{u}' = \pm \zeta$. 

---

**FIG. 9. Curvilinear Coordinates**

In the inner region, the fields vary much more rapidly in the $u$ direction than the $s$ direction. The coordinates $(u, s)$ are rescaled in dimensionless units as $(\bar{u}, \bar{s}) \equiv (u/\xi, s/\xi)$. The dimensionless curvature $\bar{\kappa} = \kappa / \epsilon$ and $\bar{\kappa}_s = \xi^2 \kappa_s / \epsilon^2$. In terms of these dimensionless variables, the Laplacian becomes:

\[
\xi^2 \nabla^2 = \frac{\partial^2}{\partial u^2} + \frac{\kappa}{1 + \kappa \frac{\partial}{\partial u}} \frac{\partial^2}{\partial s^2} + \frac{\epsilon^2}{(1 + \kappa \frac{\partial}{\partial u})^3} \frac{\partial^2}{\partial s^2} - \frac{\epsilon^3 \kappa \frac{\partial}{\partial s}}{(1 + \kappa \frac{\partial}{\partial u})^3} \frac{\partial}{\partial s} \nonumber\]

\[
= \frac{\partial^2}{\partial u^2} + \kappa \left( \epsilon \sum_{n=0}^\infty (-\epsilon \kappa)^n \right) \frac{\partial}{\partial u} + \left( \epsilon^2 \sum_{n=0}^\infty (n+1)(\epsilon \kappa)^n \right) \frac{\partial^2}{\partial s^2} \nonumber\]

\[
- \frac{\kappa_s}{2} \left( \epsilon^3 \sum_{n=0}^\infty (n+1)(n+2)(-\epsilon \kappa)^n \right) \frac{\partial}{\partial s} = L_0 + \epsilon L_1 + \epsilon^2 L_2 + \epsilon^3 L_3 + \cdots \tag{A3}
\]
The $O(\epsilon)$ surface contribution becomes

$$S_1 = S_1^+ + S_1^- = \int_{-\xi}^{+\xi} du \frac{\partial \delta \mu_{in}}{\partial u} \left( \left. \frac{\partial \delta \mu_{in}(\bar{u}, \bar{s})}{\partial \bar{u}} \right|_{-\xi} - \left. \frac{\partial \delta \mu_{in}(\bar{u}', \bar{s})}{\partial \bar{u}'} \right|_{+\xi} + \delta \mu_{in}(a, \bar{s}) \right)$$

$$+ \int_{-\xi}^{+\xi} du \frac{\partial \delta \mu_{in}}{\partial u} \left( \left. \frac{\partial \delta \mu_{in}(\bar{u}, \bar{s})}{\partial \bar{u}} \right|_{-\xi} - \left. \frac{\partial \delta \mu_{in}(\bar{u}', \bar{s})}{\partial \bar{u}'} \right|_{+\xi} + \delta \mu_{in}(a, \bar{s}) \right)$$

$$= \delta \mu_{in}(0, \bar{s}) + \frac{\partial \delta \mu_{in}}{\partial u} \left( \int_{-\xi}^{+\xi} du \left[ \left. \frac{\partial \delta \mu_{in}(\bar{u}, \bar{s})}{\partial \bar{u}} \right|_{-\xi} - \left. \frac{\partial \delta \mu_{in}(\bar{u}', \bar{s})}{\partial \bar{u}'} \right|_{+\xi} + \delta \mu_{in}(a, \bar{s}) \right] \right)$$

$$+ \frac{\partial \delta \mu_{in}}{\partial u} \left( \int_{-\xi}^{+\xi} du \left[ \left. \frac{\partial \delta \mu_{in}(\bar{u}, \bar{s})}{\partial \bar{u}} \right|_{-\xi} - \left. \frac{\partial \delta \mu_{in}(\bar{u}', \bar{s})}{\partial \bar{u}'} \right|_{+\xi} + \delta \mu_{in}(a, \bar{s}) \right] \right).$$

(B8)

To evaluate the bulk contribution $B$, Eq. (39) is expanded in powers of $\epsilon$. Eq. (39) reads

$$B = \pm \frac{1}{\Gamma_c} \int_{0}^{\pm \xi} du \frac{\partial \delta \mu_{in}}{\partial u} \int_{V_{\pm}} d\bar{r} G^0(\bar{r}, \bar{r}') \frac{\partial \delta \mu_{in}(\bar{r}, t)}{\partial t}.$$

(B9)

We note that $\partial \delta \mu_{in}(\bar{r}, t)/\partial t \equiv \nu \partial \delta \mu_{in}/\partial u = O(\epsilon)$ since the normal interface velocity $v = \epsilon v_1 + \cdots$, $\delta \mu_{in} = \epsilon \delta \mu_{in} + \epsilon^2 \delta \mu_{in} + \cdots$, and $G^\pm = G_1^\pm + \cdots$. Naive power counting seems to imply that $B^\pm = O(\epsilon^2)$, but changing variables $\bar{r}' \rightarrow \bar{r}', \bar{s}'$ yields

$$B = \pm \frac{\epsilon^2 \tau_1}{\gamma \Gamma_c} \int_{V_{\pm}} d\bar{r}' d\bar{s}' \sum_{n=1}^{\infty} \sum_{m=1}^{n+m} \epsilon^n m^{m-1} \left( v_1 G_{m}^\pm(\bar{u}, \bar{s}, \bar{u}', \bar{s}') \right) \frac{\partial \delta \mu_{in}}{\partial u} \left. \frac{\partial \delta \mu_{in}}{\partial u} \right|_{\bar{u}, \bar{s}}$$

$$= \epsilon B_1 + \epsilon^2 B_2 + \cdots$$

(B10)

where

$$B_1 = \pm \frac{\epsilon^2 \tau_1}{\gamma \Gamma_c} \int_{V_{\pm}} d\bar{r}' d\bar{s}' \left( v_1 \left. G_{m}^\pm(\bar{u}, \bar{s}, \bar{u}', \bar{s}') \right|_{\bar{u}, \bar{s}} \right) \frac{\partial \delta \mu_{in}}{\partial u}$$

$$B_2 = \pm \frac{\epsilon^2 \tau_1}{\gamma \Gamma_c} \int_{V_{\pm}} d\bar{r}' d\bar{s}' \left( v_1 \left. G_{m}^\pm(\bar{u}, \bar{s}, \bar{u}', \bar{s}') \right|_{\bar{u}, \bar{s}} \right)$$

$$\left( v_2 G_{m}^\pm(\bar{u}, \bar{s}, \bar{u}', \bar{s}') \right) \frac{\partial \delta \mu_{in}}{\partial u} + v_1 \left. \frac{\partial \delta \mu_{in}}{\partial u} \right|_{\bar{u}, \bar{s}} + v_1 \left. \frac{\partial \delta \mu_{in}}{\partial u} \right|_{\bar{u}, \bar{s}}.$$

(B11)

For the Green’s function introduced above, $B_1$ becomes

$$B_1 = B_1^- + B_1^+ =$$

$$= - \frac{\epsilon^2 v_1(s)}{\gamma \Gamma_c} \int_{-\xi}^{+\xi} du \left[ \left. \frac{\partial \delta \mu_{in}(\bar{u})}{\partial u} \right|_{\bar{u}} - c_0^{out}(\bar{u}) \right]^2.$$

(B12)

**APPENDIX C: TWO-SIDED MOBILITY**

In this appendix the sharp interface equations are outlined for a mobility that takes on a constant value in each phase. There is the question of consistency of such a theory in the presence of stochastic noises in the underlying Langevin equations which we do not attempt to answer. We consider the system in the unphysical limit of zero noise. For convenience, the mobility in the phase in the region $u < 0$ ($u > 0$) is denoted $\Gamma_{-c}$ ($\Gamma_{+c}$).

When the mobility $\Gamma_c$ is different in the two phases, the equation of motion for the concentration $c$ becomes

$$\frac{\partial c}{\partial t} = \nabla \left( \Gamma_c \cdot \nabla \delta \mu \frac{\partial c}{\partial \bar{r}} \right) = \nabla \left( \Gamma_c \cdot \nabla \delta \mu \right)$$

$$\Gamma_c \nabla^{2} \delta \mu \mp \left( \nabla \Gamma_c \right) \cdot \nabla \delta \mu.$$ (C1)

The procedure outlined in the main text gives

$$\int_{V_{\pm}} d\bar{r} \frac{G^0(\bar{r}, \bar{r}')}{\Gamma_c} \frac{\partial c}{\partial t} = \delta \mu \left( \nabla \Gamma_c \right) \cdot \nabla \delta \mu.$$

(C2)

The last term in Eq. (C2) is $O(\epsilon^3)$ and can be neglected. It is straightforward to repeat the calculations of Section [16A] for the velocity of the interface and for the chemical potential at the interface. All results remain the same except, the diffusion constant $D_c$ has an obvious dependence on $\Gamma_c$ and

$$\epsilon^2 = \Delta c \int_{0}^{\infty} \frac{du}{\Gamma_c} \left[ \delta c^{in}(u) - c_0^{out}(u) \right]$$

$$+ \int_{-\infty}^{0} \frac{du}{\Gamma_c} \left[ \delta c^{in}(u) - c_0^{out}(u) \right]^2$$

and the interface position $u = 0$ is determined by the solvability condition

$$\int_{0}^{\infty} \frac{du}{\Gamma_c} \left[ \delta c^{out}(u) - c_0^{in}(u) \right] = \int_{-\infty}^{0} \frac{du}{\Gamma_c} \left[ \delta c^{in}(u) - c_0^{out}(u) \right]$$

(C3)

[1] J. D. Gunton, M. San Miguel, and P. Sahni, in Phase Transitions and Critical Phenomena, Vol. 8, ed. C. Domb and J. L. Lebowitz (Academic Press, London, 1983), p. 267. A. J. Bray, Adv. Phys. 32, 357 (1994).

[2] J. S. Langer, Rev. Mod. Phys. 52, 1 (1980). E. Ben-Jacob, N. Goldenfeld, J. S. Langer and G. Schön, Phys. Rev. A 29, 330 (1984). B. Caroli, C. Caroli and B. Roulet,
in *Solids Far From Equilibrium*, ed. by G. Godrèche (Cambridge University Press, Cambridge, 1992). J. B. Collins and H. Levine, Phys. Rev. B **31**, 6119 (1985).

[3] K. R. Elder, F. Drole, J. M. Kosterlitz and M. Grant, Phys. Rev. Lett. **72**, 677 (1994). B. Grossmann, K. R. Elder, M. Grant and J. M. Kosterlitz, Phys. Rev. Lett. **71**, 3323 (1993). K. R. Elder, J. D. Gunton and M. Grant, Phys. Rev. E **54**, 6476 (1996). F. Drole, K. R. Elder, Martin Grant and J. M. Kosterlitz, Phys. Rev. E **61**, 6705 (2000).

[4] The wastefulness of simulating bulk regions can to a large extent be eliminated using adaptive grid methods, see for example N. Provatas, N. Goldenfeld, and J. Dantzig, Phys. Rev. Lett. **80**, 3308 (1998).

[5] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[6] An English translation of van der Waals Ph.D. thesis is given by: J. S. Rowlinson, J. Stat. Phys. **20**, 197 (1979).

[7] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958). J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **31**, 688 (1959).

[8] S. M. Allen and J. W. Cahn, Acta Metall. **27**, 1085 (1978).

[9] G. Caginalp and W. Xie, Phys. Rev. E **48**, 1897 (1993).

[10] A. Karma and W-J. Rappel, Phys. Rev. E **53**, 3017 (1996); *ibid* **57**, 4323 (1998).

[11] R. Ahmgren, SIAM J. Appl. Math **59**, 2086, (1999).

[12] K. Kawasaki and T. Ohta, Prog. Theor. Phys. **67**, 147 (1982). K. Kawasaki and T. Ohta, Prog. Theor. Phys. **68**, 129 (1982). K. Kawasaki and T. Ohta, Physica **118A**, 175 (1983). T. Ohta, D. Jasnow and K. Kawasaki, Phys. Rev. Lett. **49**, 1223 (1982). K. Kawasaki, M. C. Yalabik and J. D. Gunton, Phys. Rev. A **17**, 455 (1978). See also T. Rogers, PhD thesis (University of Toronto, 1989).

[13] N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group*, (Addison-Wesley, 1992).

[14] M. Plischke and B. Bergeersen, *Equilibrium Statistical Physics*, (Prentice Hall, Englewood Cliffs, NJ, 1989) Chapter 4.

[15] See for example: L. Jørgenson, R. Harris, H. Guo, and M. Grant, Phys. Rev. E **48**, 4592 (1993); L. Jørgenson, R. Harris, M. Grant, and H. Guo, Phys. Rev. E **47**, 1235 (1993); and, R. Harris, L. Jørgenson, and M. Grant, Phys. Rev. B **45**, 1024 (1992); and references therein.

[16] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **42**, 1354 (1962) [Sov. Phys. JETP **15**, 939 (1962)].

[17] D. Turnbull, Trans. AIME **191**, 661 (1952).

[18] R. Bausch, V. Domb, H. K. Janssen and R. K. P. Zia, Phys. Rev. Lett. **47**, 1837 (1981). M. Grant and J. D. Gunton, Phys. Rev. B **28**, 5496 (1983). T. Ohta, Ann. Phys. **158**, 31 (1984).

[19] R. Pindak, C. Y. Young, R. B. Meyer and N. A. Clark, Phys. Rev. Lett. **45**, 1193 (1980).

[20] A.N. Kolmogorov, Bull. Acad. Sci. USSR, Mat. Ser. 1, 335 (1937). M. Avrami, J. Chem. Phys. **7**, 1103 (1939). W.A. Johnson and A. Mehl, Trans. Am. Inst. Min. Eng. **135**, 416, (1939).

[21] M. Kardar, G. Parisi and Y. C. Zhang, Phys. Rev. Lett. **56**, 889 (1986). See the derivation of the Kardar-Parisi-Zhang equation in, B. Grossmann, H. Guo and M. Grant, Phys. Rev. A **43**, 1727 (1991).

[22] E. Ben-Jacob, N.D. Goldenfeld, B. G. Kotliar, and J. S. Langer, Phys. Rev. Lett. **53**, 2110 (1984). See the review of Y. Pomeau and M. Ben Amar, in *Solids Far From Equilibrium*, ed. C. Godrèche (Cambridge University Press, Cambridge, England, 1991).

[23] R. Kobayashi, Physica D **63**, 410 (1993).

[24] This Green’s function is useful only if all the appropriate terms do not have a constant piece.

[25] In two dimensions there is a logarithmic correction to this result.

[26] We integrate over the equations using, for example, $\partial \psi / \partial u$ because this is the variable conjugate to the linear displacement of the surface, that is, the Goldstone mode.

[27] The last equality in Eqs. (49) and (50) was obtained using the relationships

$$\frac{\partial}{\partial u} \left( \frac{\partial f(c, \psi)}{\partial c} \right) = \frac{\partial^2 f(c, \psi)}{\partial c \partial \psi} \frac{\partial c}{\partial u} + \frac{\partial^2 f(c, \psi)}{\partial c \partial \psi} \frac{\partial \psi}{\partial u}$$

and

$$\frac{\partial}{\partial u} \left( \frac{\partial f(c, \psi)}{\partial \psi} \right) = \frac{\partial^2 f(c, \psi)}{\partial \psi^2} \frac{\partial \psi}{\partial u} + \frac{\partial^2 f(c, \psi)}{\partial \psi^2} \frac{\partial c}{\partial u}$$

and

$$\frac{\partial}{\partial u} \left( \frac{\partial f(c, \psi)}{\partial \psi} \right) = \frac{\partial^2 f(c, \psi)}{\partial \psi^2} \frac{\partial \psi}{\partial u} + \frac{\partial^2 f(c, \psi)}{\partial \psi^2} \frac{\partial c}{\partial u}$$

[28] In two dimensions the tangential component of the time derivative can be written $v_T \partial / \partial s$, where $v_T$ accounts for flow of concentration (or $\psi$) along the interface. $v_T$ must be $O(e)$ since it is zero when $e = 0$. Furthermore in the inner region $s$ is scaled with $e$ so $v_T \partial / \partial s \sim O(e^2)$. When this term operates on $c$ or $\psi$ it becomes $O(e^3)$, since both $c$ and $\psi$ are independent of $s$. The time derivative in the moving frame $\partial / \partial t_{(u,s)}$ is also at least $O(e^3)$. This term accounts for the relaxation of fluctuations around the steady state profile not due to motion of the interface. For the concentration field fluctuations relax as $t \sim (\text{length})^2$ which implies $\partial / \partial t_{(u,s)} \sim O(e^2)$. As with the tangential component this term becomes $O(e^3)$ when operating on $c$. For $\psi$, fluctuations relax exponentially fast and thus this term can be neglected.