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Degenerate mobilities in phase field models are insufficient to capture surface diffusion

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Phase field models frequently provide insight into phase transitions and are robust numerical tools to solve free boundary problems corresponding to the motion of interfaces. A body of prior literature suggests that interface motion via surface diffusion is the long-time, sharp interface limit of microscopic phase field models such as the Cahn-Hilliard equation with a degenerate mobility function. Contrary to this conventional wisdom, we show that the long-time behaviour of degenerate Cahn-Hilliard equation with a polynomial free energy undergoes coarsening, reflecting the presence of bulk diffusion, rather than pure surface diffusion. This reveals an important limitation of phase field models that are frequently used to model surface diffusion. © 2015 AIP Publishing LLC.

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A key problem in modelling phase transitions in materials lies in linking macroscopic interfacial motion and mesoscopic dynamics. A common approach is phase field models, which replace a sharp interface with order parameters that are continuous across the interface. Phase field models can be constructed from systematic coarse-graining of the microscopic Hamiltonian and are often written as a gradient minimisation of a certain microscopic free energy functional.^{1–3} As such, they provide the crucial link between microscopic interactions and the kinetics of phase separation and pattern formation.

Mesoscopic phase field descriptions have been widely used in the literature as their numerical approximation is less complicated than the approximation of macroscopic descriptions based on sharp interfaces. By using a continuous order parameter field, phase field approaches are versatile enough to capture topological changes and replace the numerically challenging task of interface tracking with integration of a time-dependent partial differential equation. Therefore, the phase field formalism is increasingly used as a numerical approximation for a wider class of free boundary problems than what the free energy describes microscopically.^{4–6}

A particularly noteworthy class of free boundary problem is when the velocity of the interface v_n is proportional to the surface Laplacian of the mean curvature κ and

$$v_n = \mathcal{M} \Delta_s \kappa, \quad (1)$$

where \mathcal{M} is the mobility. Equation (1) is known as the surface diffusion flow and has been used as a model for many complex processes such as electromigration in metals,⁷ heteroepitaxial growth,⁸ and more recently solid-solid dewetting.⁹

The Cahn-Hilliard equation with degenerate mobility is the commonly used phase field model to approximate surface diffusion (e.g., Refs. 7–14), where the order parameter u is conserved and satisfies (in dimensionless units)

$$u_t = -\nabla \cdot \mathbf{j}, \quad \mathbf{j} = -\epsilon M(u) \nabla \mu, \quad (2a)$$

$$\epsilon \mu = -\epsilon^2 \nabla^2 u + f'(u), \quad (2b)$$

$$f(u) = \frac{1}{4}(1 - u^2)^2, \quad M(u) = 1 - u^2, \quad (2c)$$

where $M(u)$ is the mobility function; \mathbf{j} is the flux; μ is the chemical potential; ϵ is the interfacial tension which determines the width of the interface; and $f(u)$ is the bulk free energy. Throughout the paper, we will assume the no-flux condition $\mathbf{n} \cdot \mathbf{j} = 0$, and the variational Neumann condition $\mathbf{n} \cdot \nabla u = 0$ on the boundaries of the solution domain. The two pure phases are denoted by $u = \pm 1$, and the interface is located at the contour $u = 0$.

The precise form of the mobility is usually chosen on thermodynamic grounds.^{15,16} For the lattice-gas entropy $s(u) = u \log u + (1 - u) \log(1 - u)$, the Einstein relation stipulates that the mobility is related to the entropy function $s(u)$ via $M(u) = (\partial^2 s / \partial u^2)^{-1} = 1 - u^2$. This motivates the choice of mobility in (2).

More elaborate multiphase-field models have been constructed in the literature to describe phase transition when multiple phases coexist^{17,18} as is the case for many technologically important alloys. In addition, the inverse problem of relating physical parameters of the phases to the form of the free energy and the interfacial tension is non-trivial.^{19,20} Here, for simplicity, we restrict ourselves to considering a binary system with only two phases and consider a simple quartic free energy; as is seen in the analysis below, the fact the coarsening occurs in the sharp interface limit is a generic feature of the system (2) independent of its parameterisation.

We are interested in the long-time behaviour when the initial mixture has separated into regions where u is either close to 1 or to -1 , except for regions of width $O(\epsilon)$ close to the interface over which u transitions between these two regions. Heuristically, the width of this interface layer decreases as $\epsilon \rightarrow 0$. One may think that if the mobility function is degenerate and vanishes at the pure phases, the flux normal to the interface is suppressed and therefore only surface diffusion via mass flux tangential to the interface can occur. However, this heuristic argument neglects the fact that the gradient of the interface diverges as $\epsilon \rightarrow 0$. Therefore,

whether the degenerate mobility function is sufficient to suppress the normal mass flux at leading order is unclear.^{21,22}

The key result of this paper is the presence of a nonlinear bulk diffusion term at leading order for the interface velocity, and the correct sharp interface limit that describes the quasistationary evolution of the interface ζ , located at $u = 0$, is given by

$$\nabla \cdot (\mu \nabla \mu) = 0, \quad \text{in } \Omega_-, \quad (3a)$$

$$\mu = \frac{2}{3}\kappa, \quad \text{on } \zeta, \quad (3b)$$

$$v_n = \frac{2}{3}\Delta_s \kappa + \frac{1}{4}\mu \nabla_n \mu \quad \text{on } \zeta, \quad (3c)$$

$$\nabla_n \mu = 0, \quad \text{on } \partial\Omega_{\text{ext}}, \quad (3d)$$

where v_n is the normal velocity, and the definitions of Ω_- and ζ are given in Figure 1. The possibility of bulk diffusion was noted in earlier works^{21,23} and analysed recently by Dai and Du.²⁴ However, in Ref. 24, the analysis was done on the (unphysical) solution branch with $|u| > 1$ in some region. Our analysis below considers the physical branch of solution where $|u| < 1$ everywhere and derives the limiting model as $\epsilon \rightarrow 0$. It can be shown using rigorous mathematical analysis that the physical branch with $|u| < 1$ everywhere exists for all parameter values.²⁵

To begin our analysis, we drop the time derivative from (2). Rewriting the Laplacian in polar coordinates, and resolving the boundary layer near the interface by noting that the interface is $O(\epsilon)$ thick, we obtain the leading order solution

$$u_0(r) = \tanh\left(\frac{r - r_0}{\epsilon}\right), \quad \mu = \mu|_{\zeta}. \quad (4)$$

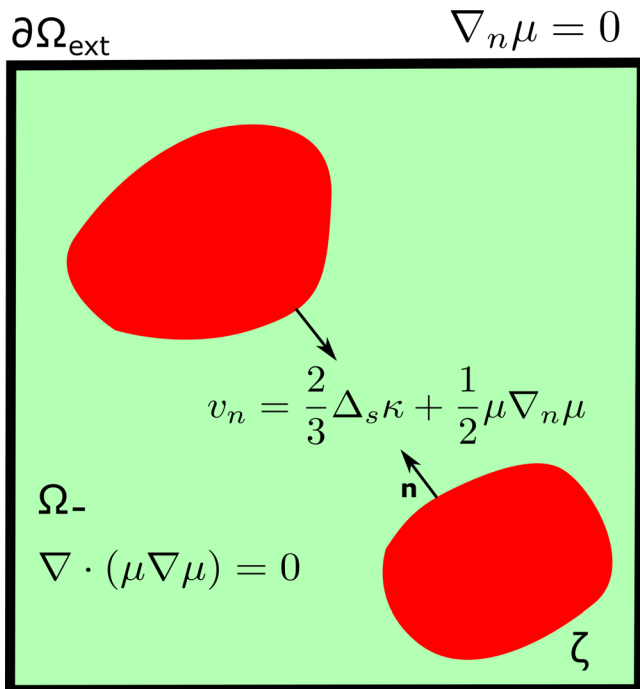


FIG. 1. Illustration of the asymptotic structure of the degenerate mobility case. The domain Ω_{ext} is split into interfaces ζ where $u = 0$ which enclose the solid domains Ω_+ where $u > 0$ (coloured red), and the region Ω_- with vapor (colored green) where $u < 0$. The normal \mathbf{n} to the interfaces points out of Ω_+ .

Here, r is the radial coordinate with respect to the centre of the osculating circle to the interface, r_0 is the position of the interface in these coordinates, and $\mu|_{\zeta}$ is a constant. Equation (4) reveals how the interface is being represented as a continuous, albeit thin, order parameter profile of width ϵ around $r = r_0$. A key physical intuition is that the relaxation of the local order parameter profile to (4) is rapid (as it is driven by local rearrangement of particles), and the late stage dynamics is quasi-static and determined by the movement of the interface, i.e., change in r_0 .

To put this intuition onto firmer footing, we consider the chemical potential μ away from the interface. There, the system is almost a pure phase (say $u = -1 + \epsilon \tilde{u}$, $\mu = \epsilon \tilde{\mu}$, with $\tilde{u}, \tilde{\mu} = O(1)$), and the spatial variation of u is negligible so that the Laplacian can be neglected. Expanding Equation (2b) in powers ϵ , the leading order term is given by

$$\tilde{\mu} = f''(-1)\tilde{u}, \quad (5)$$

and substituting (5) into (2a), we obtain

$$\tilde{u}_t = M'(-1)\nabla \cdot (\tilde{u}\nabla \tilde{\mu}) = \frac{M'(-1)}{f''(-1)}\nabla \cdot (\tilde{\mu}\nabla \tilde{\mu}). \quad (6)$$

Further, we use the aforementioned quasi-static approximation and assume that \tilde{u}_t is small. Thus, to leading order,

$$\nabla \cdot (\tilde{\mu}\nabla \tilde{\mu}) = 0. \quad (7)$$

The chemical potential at the interface can be obtained by multiplying (2a) by $\partial_r u$, and integrating both sides. Assuming that the azimuthal variations in u are asymptotically smaller than the radial variation, we have

$$\int_{r_0-\eta}^{r_0+\eta} \epsilon \mu \partial_r u dr = \int_{r_0-\eta}^{r_0+\eta} \left[-\frac{\epsilon^2}{r} \partial_r (r \partial_r u) + f'(u) \right] \partial_r u dr, \quad (8)$$

where η is an intermediate lengthscale bridging the interface of width ϵ and the macroscopic lengthscale; Kaplun's extension theorem in asymptotic theory provides a rigorous justification of the existence of such a lengthscale under mild assumptions.²⁶ Close to the interface, u and μ can be approximated by (4). Substituting (4) and $\eta \sim \epsilon \log(1/\epsilon)$ into (8) and taking $\epsilon \rightarrow 0^+$, we obtain

$$\mu|_{\zeta} = \frac{2}{3}\kappa, \quad (9)$$

where $\kappa = 1/r_0$ is the curvature of the interface. The above choice of η satisfies both the requirement that (4) is valid near the interface (we have assumed μ to be constant over short radial distances r ; over $O(1)$ length scales, this is not, in general, the case) and the integrals converge to (9) (for $\eta \gg \epsilon$). From u_0 in (4), it can be readily seen that we have $u_0 \sim \pm 1 + O(\epsilon^\alpha)$ with some positive α for the above choice of η , and this gives (9) in the limit $\epsilon \rightarrow 0^+$ as claimed.

In the quasi-static approximation, we neglect time dependence except for the slow motion of the interface. To obtain the interface velocity, we focus on the boundary layer region and move into a Lagrangian frame by making the transformation $u_t \mapsto u_t - (\mathbf{v} \cdot \nabla)u$. Now, noting that the normal velocity is much larger than the lateral velocity, we have

$(\mathbf{v} \cdot \nabla)u \approx \epsilon^2 v_n \partial_r u$, where $\epsilon^2 v_n$ is the normal velocity, scaled in anticipation of the order of the right-hand side which will turn out to be $O(\epsilon^2)$. Equation (2a) becomes

$$-\epsilon^2 v_n \partial_r u = -\partial_r(\mathbf{j} \cdot \mathbf{n}) - \partial_s(\mathbf{j} \cdot \mathbf{t}), \quad (10)$$

where s denotes the coordinate tangent to the interface, and \mathbf{n} and \mathbf{t} are the (outward pointing) unit normal and the unit tangent vector, respectively. Close to the interface, the tangential flux is given by $\mathbf{j} \cdot \mathbf{t} = -\epsilon M(u) \partial_s \mu = -\epsilon M(u) \partial_s \mu|_\zeta$. Thus, again substituting (4) for u , and integrating over the interface, we arrive at

$$2\epsilon^2 v_n = -[\mathbf{j} \cdot \mathbf{n}]_{r_0-\eta}^{r_0+\eta} + \frac{4}{3} \epsilon^2 \partial_{ss} \kappa. \quad (11)$$

Now, for $\epsilon \ll \eta \ll 1$, we obtain

$$\mathbf{j} \cdot \mathbf{n}|_{r_0+\eta} = -\epsilon M(u) \partial_r \mu = -\epsilon^2 \frac{M'(-1)}{f''(-1)} \mu \partial_r \mu + O(\epsilon^3),$$

and $\mathbf{j} \cdot \mathbf{n}|_{r_0-\eta} = 0$ as the system reaches the pure phase $u = 1$ deep in Ω_+ . Therefore, all in all, we obtain (3c), where we have identified ∂_{ss} with the surface Laplacian Δ_s . Equation (3c) shows that the interface velocity in the sharp interface model has two contributions: one from surface diffusion, Equation (1), which is local to the interface, and another contribution from nonlinear bulk diffusion which satisfies a porous-medium Equation (3a). Unlike pure surface diffusion, the mass flux arising from bulk diffusion couples disjoint solid domains with each other. This results in coarsening where larger solid domains grow at the expense of smaller ones, which cannot happen for pure surface diffusion. Moreover, for non-circular interfaces, the contribution from surface and bulk diffusion enters the interface evolution to the same order, i.e., the effect of the latter does not become negligible compared to the former even when letting $\epsilon \rightarrow 0$.

To test this prediction of our analysis, we consider the relaxation of an azimuthal perturbation to a radially symmetric stationary state with radius r_0 and hence curvature $\kappa = 1/r_0$. For azimuthal perturbations proportional to $\cos m\theta$, the pure solid diffusion model (1) predicts an exponential decay rate

$$\sigma = -\frac{2}{3} \kappa^4 m^2 (m^2 - 1). \quad (12)$$

In contrast, the decay rate in the porous medium model (3) is given by

$$\sigma = -\kappa^4 \left[\frac{2}{3} m^2 (m^2 - 1) + \frac{1}{9} m (m^2 - 1) \tanh(m \log \kappa) \right]. \quad (13)$$

TABLE I. Relaxation rates for $m=2$ obtained from the linearised phase field model are shown for different values of ϵ in the first four columns and compared to the eigenvalues obtained for linearised sharp interface models for pure surface diffusion (12) and the porous medium type model (13) in the next-to-last and the last column, respectively.

ϵ	0.01	0.005	0.002	0.001	Eq. (13)	Eq. (12)
Σ	-133.2	-133.8	-136.3	-137.0	-137.4	-128

Table I shows the decay rate numerically obtained by solving the phase field model, Equations (2). It shows how the decay rate of the azimuthal perturbation to the axisymmetric base state tends to the linearised sharp interface model with the contribution from nonlinear bulk diffusion, rather than to the one for pure surface diffusion.

Our analysis only applies to free energy functions f for which $f'(\pm 1) = 0$ and $f''(\pm 1) > 0$ at the minima $u = \pm 1$. Indeed, according to the asymptotic analysis in Ref. 27, the double obstacle free energy

$$f_{\text{do}}(u) = \begin{cases} 1 - u^2 & \text{if } |u| < 1 \\ \infty & \text{if } |u| \geq 1, \end{cases}$$

gives rise to pure surface diffusion flow for $M(u) = 1 - u^2$ in the sharp interface limit ($\epsilon \rightarrow 0$), and also if the logarithmic free energy $f(u) = -u^2 + \epsilon^\alpha (u \log u + (1-u) \log(1-u))$ with $\alpha > 0$ is used instead.

In conclusion, our analysis establishes that phase field models for pure surface diffusion cannot be realised using the Cahn-Hilliard equation with the degenerate mobility and Ginzburg-Landau free energy as in (2), as was repeatedly assumed in the literature.^{9,10,13,14} A nonlinear bulk diffusion term appears to leading order of the sharp interface limit, hence affecting the coarsening behaviour on the same time scale as surface diffusion. In particular, it allows, on this time scale, disjoint interfaces to coarsen and cannot be suppressed by reducing ϵ .

We note that the derivation presented in this work could be made mathematically robust via matched asymptotic analysis. Such an approach was applied to analyse the Cahn-Hilliard equation with constant mobility.^{28,29} Extending the method of matched asymptotics to model (2) with a degenerate mobility will be the subject of a subsequent publication. The heuristic approach presented here, however, reveals clearly the salient physics involved in the sharp interface limit.

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