Role of Metastable States in Phase Ordering Dynamics

R. M. L. Evans, W. C. K. Poon and M. E. Cates

Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, U.K.

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We show that the rate of separation of two phases of different densities (e.g. gas and solid) can be radically altered by the presence of a metastable intermediate phase (e.g. liquid). Within a Cahn-Hilliard theory we study the growth in one dimension of a solid droplet from a supersaturated gas. A moving interface between solid and gas phases (say) can, for sufficient (transient) supersaturation, unbind into two interfaces separated by a slab of metastable liquid phase. We investigate the criteria for unbinding, and show that it may strongly impede the growth of the solid phase.

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The influence of metastable states on the dynamics of phase transformations is an important issue in materials physics. Their role has long been acknowledged in metallurgy, where the rate of phase transformation is often limited by conduction of (latent) heat. Indeed, Ostwald’s empirical ‘rule of stages’ asserts that the transformation from one stable phase to another proceeds via all metastable intermediates in turn. In complex fluid systems such as colloidal suspensions, particle diffusion, not heat diffusion, is often rate-limiting. Here too, a strong influence of metastable phases on ordering dynamics has been suggested, e.g. in the phase ordering kinetics of polymer liquid crystals, random-coil polymers, proteins and colloid-polymer mixtures. In this Letter, we propose a simple model to account for the role of metastable states in phase ordering limited by particle diffusion (described by a conserved order parameter; for the nonconserved case, e.g. nematic order, see Refs. [2]).

To establish ideas, consider first a homogeneous fluid of a simple substance which is quenched to a temperature below its triple point. It will separate into two coexisting phases, the gas and the solid, whose densities are given by the construction in Fig. 1. However, in this temperature range, the low density (fluid) branch of the free energy has an additional minimum, representing the metastable liquid phase, whose presence can interfere with the phase separation process. Free energy curves of precisely this form can be realized in several complex fluid systems, notably mixtures of spherical colloids and much smaller polymers. Experiments show that, when such a mixture is prepared with a composition at which a metastable minimum is present, it does not separate quickly into dilute colloidal fluid and dense colloidal crystal (the predicted equilibrium phases). Instead, after an initial latency period (consistent with nucleation) dense but non-crystalline droplets separate out, forming an amorphous sediment which begins to crystallize only on a much longer time-scale.

We can explain these qualitatively robust results within a simple, one-dimensional continuum model if we take due account of the metastable ‘liquid’ minimum in the free energy curve. (We now use ‘gas, liquid, solid’ as generic labels for three phases of increasing densities.) Details of our results will be given elsewhere.

Consider a system with a conserved order parameter (a concentration or density \( \phi \)) at equilibrium. At coexistence, there is an interface between two phases (‘gas’ and ‘solid’) whose densities \( \phi_g \) and \( \phi_s \) are found from the bulk free energy density \( f(\phi) \), as in Fig. 1, by the double-tangent construction, which ensures equality of the chemical potential \( \mu \) and the (osmotic) pressure \( P \) in the two phases. (\( \mu \) is the slope of the tangent and \( P \) its negative intercept.) In minimizing the free energy, we seek the lowest possible double tangent, and may safely ignore local minima such as that labeled ‘liquid’ in Fig. 1. Across the interface, \( \phi \) changes smoothly (as in Fig. 2).

![FIG. 1. Bulk free energy density \( f \) versus concentration \( \phi \), with double tangents for equilibrium binodals (solid line), and metastable binodals (dashed lines). The supersaturation \( \sigma \) for an initial homogeneous state (●) is defined as shown.](image-url)
metastable minima are typically ignored but, as we now show, they can play a crucial role.

For simplicity we consider only one spatial dimension (perpendicular to an interface) and study the evolution of the interfacial density profile. The Cahn-Hilliard equation \( \frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x} \left\{ \Gamma \frac{\partial}{\partial x} \left( \frac{d f(\phi)}{d \phi} - K \frac{\partial^2 \phi}{\partial x^2} \right) \right\} \) for this time evolution is

\[
\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x} \left\{ \Gamma \frac{\partial}{\partial x} \left( \frac{d f(\phi)}{d \phi} - K \frac{\partial^2 \phi}{\partial x^2} \right) \right\}
\]

(1)

where the mobility \( \Gamma \) and curvature constant \( K \) are phenomenological parameters; we are interested in \( f(\phi) \) of the form shown in Fig. 1. Eq. (1) is derived by equating \( \partial \phi / \partial t \) to the divergence of a current \( J = -\Gamma \nabla \mu \) induced by a chemical potential gradient. The chemical potential is defined in terms of a functional derivative, \( \mu = \delta F[\phi]/\delta \phi \), where \( F[\phi] \) is the integral of the local free energy density, \( f(\phi) + K (\nabla \phi)^2 / 2 \).

Consider first an ordinary, smooth solid-gas interface as shown in Fig. 2a. If the solid region is to grow, the interface must move to the right, and this requires a chemical potential gradient in the supersaturated gas phase. Steady-state solutions of Eq. (1) (a uniformly moving interface) are thus unphysical in far field, since a non-zero gradient would have to extend to infinity. However, such solutions do shed light on the local dynamics of the interface since, during the growth stage \([13]\), local rearrangements are much quicker than changes in the far diffusion field driving the interfacial motion. Hence the interface experiences a quasi-constant flux from the supersaturated region; its local dynamics are quasi-steady-state \([13]\). Steady-state solutions of Eq. (1) are calculable to arbitrary accuracy for any form of \( f(\phi) \) and \( \Gamma(\phi) \), and exactly for piecewise-quadratic \( f(\phi) \) and piecewise constant \( \Gamma \) \([13]\). (Constant \( K \) is assumed.) In the latter case, linear stability of an ordinary moving interface (Fig. 3a) can be established rigorously \([13]\). Despite this, we now explore an alternative, ‘split’ mode of interfacial motion.

Since the double-tangent construction identifies states of equal chemical potential and pressure, an interface may form between points on the metastable binodal, such as \( (\phi_A, \phi_B) \) in Fig. 1. So, a split profile such as that shown in Fig. 3b, with well-separated gas-liquid \( (g/l) \) and liquid-solid \( (l/s) \) parts, has only gentle gradients of \( \mu \), and is therefore long-lived. Physically, a moving gas-sol 1d \( (g/s) \) interface (Fig. 3a) is locally stable against this splitting \([13]\), because, if the flux of material from the right onto the \( g/s \) interface is increased (so as to advance the base more than the top, splitting the interface) the curvature, \( \nabla^2 \phi \), is perturbed, setting up currents tending to restore the profile. The \( g/l \) and \( l/s \) interfaces can be described as curvature-bound. This negative feedback mechanism does not operate for the well-split interface of Fig. 2a. In the metastable liquid region, curvature is small, and the Cahn-Hilliard equation reduces to the diffusion equation \([13]\). Material flows to the \( l/s \) interface from the \( g/l \) interface down the intervening concentration gradient, whose sign follows directly from the metastability of the liquid, as can be seen from the double tangent constructions in Fig. 1. If the flux of material onto the \( g/l \) interface is sufficient to increase its separation from the solid droplet, the concentration gradient in the middle region, and hence the restoring flux, will be reduced. So a positive feedback mechanism operates; the split interface is then curvature-unbound.

We have observed curvature-unbinding in numerical solutions of Eq. (1), using \( f(\phi) \) of the form sketched in Fig. 1. A time-sequence is shown in Fig. 3; the initial condition is a sharp step between a solid at density \( \phi_s \) and a supersaturated state \( \phi = \phi_g + \sigma \) within the gas (rather than liquid) well of the free energy curve. Below some critical supersaturation (discussed below), such curvature-unbinding does not occur, and the interface propagates in the conventional (unsplit) mode.

We now analyse the dynamics of a pair of curvature-unbound interfaces. On scales much larger than the characteristic interfacial width \( \sqrt{K / f''} \), the \( g/l \) and \( l/s \) interfaces can be represented by sharp steps at positions \( x_1(t) \) and \( x_2(t) \) respectively (Fig. 3b). Concentrations at the interfaces will be fixed at the metastable binodal values (Fig. 1), so long as interfacial velocities are small \( \langle \dot{x}_1, \dot{x}_2 \rangle \ll \langle \int f''(\phi)^{3/2} K^{-1/2} \Gamma \rangle \). In the gas and liquid regions, evolution is purely diffusive, with diffusion constants \( D_g \) and \( D_l \) respectively; \( D \) is set to zero in the solid phase. Conservation of material requires \((\phi_B - \phi_A) \dot{x}_1 = j_A - j_B\).
These yield tractable equations of motion for the size of the solid droplet:

$$x_2 = \frac{\phi_B - \phi_C}{\phi_D - \phi_C} D_l \int_0^t \frac{dt'}{x_1(t') - x_2(t')}.$$  \hspace{1cm} (3)

and for the size of the solid droplet:

$$\frac{d(x_1 - x_2)}{d(t/\tau)} = \frac{(t/\tau)^{-4/3}}{2(\sigma/c^2/\pi)}.$$  \hspace{1cm} (2)

The control parameter is now the supersaturation **relative to the metastable binodal** $\sigma' = \sigma - (\phi_A - \phi_B)$ (see Fig. 4). Two further approximations are made, whose adequacy has been checked by numerical solution of the full equations \[14\]. The first is that the diffusive field in the gas phase is unperturbed by the motion of the steps, leading to $j_B \approx j_c = D_l (\phi_B - \phi_C)/(x_1 - x_2)$. These yield tractable equations of motion for the size of the metastable liquid region:

and $(\phi_D - \phi_C) x_2 = j_c$, where the fluxes $j_A$, $j_B$, and $j_c$ are defined in Fig. 2b.

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$$\frac{d(x_1 - x_2)}{d(t/\tau)} = \frac{(t/\tau)^{-4/3}}{2(\sigma/c^2/\pi)}.$$  \hspace{1cm} (2)

and for the size of the solid droplet:

$$x_2(t) = \left( \frac{\phi_B - \phi_C}{\phi_D - \phi_C} \right) D_l \int_0^t \frac{dt'}{x_1(t') - x_2(t')}.$$  \hspace{1cm} (3)

Here $\tau \equiv \pi (\phi_B - \phi_A)^2/(D_g \sigma^2)$ and $\sigma_c \equiv (\phi_B - \phi_A) \times \{2\pi (\phi_B - \phi_C) [(\phi_B - \phi_A)^{-1} + (\phi_D - \phi_C)^{-1}] D_l / D_g \}^{1/2}$.

For $0 \leq \sigma' \leq \sigma_c$, solutions of Eq. \[3\] collapse to zero size in a finite time, as might be expected of a metastable phase. We describe these interfaces as **diffusively bound**. (This is a much “looser” binding than the curvature binding discussed above.) After collapse of the metastable slab, the interfaces will curvature-recombine, and the solid will resume the ordinary (unsplit) mode of growth. In contrast, for $\sigma' > \sigma_c$ solutions of Eq. \[3\] have open trajectories. The interfaces are **diffusively unbound**, and the metastable liquid region grows, in principle, for ever. Typical trajectories are shown in Fig. 4.

In the unbound case, to reach the solid, material must diffuse through the liquid phase (down a gradient which becomes flat at the triple point $\sigma_c \to 0$); the growth rate of the solid region is thereby suppressed, by a factor which we find to be of order $(\sigma_c/\sigma')^2$, compared to the case of a curvature-bound interface \[3\].

In this way, solid growth from a supersaturated gas can be strongly arrested by a weakly metastable liquid phase. Fig. 4 shows the size of the solid region $x_2$ at a given late time $t_0$, as a function of supersaturation $\sigma$. For $\sigma' > \sigma_c$, the solution of Eq. \[3\] is shown. For $\sigma' < \sigma_c$, the metastable region collapses at some early time, after which $j_A \approx \sigma \sqrt{D_g/(\pi \tau)}$.

This scenario of diffusive unbinding of interfaces and suppression of crystal growth relies on the initial formation of curvature-unbound interfaces during the nucleation stage. Whereas the critical supersaturation $\sigma_c$ for diffusive unbinding is independent of initial conditions, that for curvature-unbinding defines a region, in the space of initial configurations, with a nontrivial boundary. In our (non-exhaustive) numerical study of evolution of a step function, curvature-unbinding appeared to occur whenever $\sigma' > \sigma_c$; if so, for these initial states at least, the unbinding is diffusively controlled.

Real systems are not infinite and hence the ambient supersaturation must eventually be exhausted. If $L_{\text{nuc}}$ is the typical inter-nuclear spacing, then the time to deplete the ambient supersaturation, $t_{\text{dep}}$ (by growth of
growth in conserved systems caused by metastable states, and that this will remain an important part of any complete theory.

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