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Lifshitz-Slyozov scaling for late-stage coarsening with an order-parameter-dependent mobility

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The coarsening dynamics of the Cahn-Hilliard equation with order-parameter-dependent mobility, $\lambda(\phi) \propto (1-\phi^2)^{\alpha}$, is addressed at zero temperature in the Lifshitz-Slyozov limit where the minority phase occupies a vanishingly small volume fraction. Despite the absence of bulk diffusion for $\alpha > 0$, the mean domain size is found to grow as $\langle R \rangle \propto t^{1/(3+\alpha)}$, due to subdiffusive transport of the order parameter through the majority phase. The domain-size distribution is determined explicitly for the physically relevant case $\alpha = 1$.

The phenomenon of spinodal decomposition in, e.g., binary alloys, is usually modeled by the Cahn-Hilliard equation¹

$$\frac{\partial \phi}{\partial t} = \nabla \cdot (\lambda \nabla \mu) = \nabla \cdot \left(\lambda \nabla \frac{\delta F}{\delta \phi}\right) \quad , \tag{1}$$

for the order-parameter field ϕ . Equation (1) takes the form of a continuity equation, $\partial_t \phi = -\nabla \cdot \mathbf{j}$, with current $\mathbf{j} = -\lambda \nabla \mu$, where λ is a transport coefficient ("mobility") and the chemical potential μ is the functional derivative, $\mu = \delta F / \delta \phi$, of a Ginzburg-Landau free-energy functional $F[\phi]$ given by

$$F[\phi] = \int d^d x \left(\frac{1}{2} (\nabla \phi)^2 + V(\phi) \right) \quad . \tag{2}$$

Here $V(\phi)$ is the usual double-well potential whose minima (taken here to be at $\phi = \pm 1$) represent the equilibrium phases.

In conventional treatments of (1), the mobility λ is taken to be a constant, i.e., independent of the order parameter ϕ . Recently, however, there has been considerable interest²⁻⁸ in cases where λ depends explicitly on ϕ , notably through the dependence $\lambda(\phi) = \lambda_0(1 - \phi^2)$. This interest has a physical origin. It has been noticed² that when one models the coupling to an external driving field *E*, such as gravity, through an additional term $F_1[\phi] = -E \int d^d x \ z \phi(\mathbf{x})$ in $F[\phi]$ (where here the field **E** is in the *z* direction), this extra term does not change (1) unless λ depends on ϕ . This is because $\delta F_1 / \delta \phi = -Ez$, and $\nabla^2 z = 0$. Physically, it is clear that an external field of this form accelerates the phase separation, so λ must be ϕ dependent. Indeed, phenomenological derivations^{2,9} of λ yield precisely the form $\lambda \propto (1 - \phi^2)$ alluded to above. Furthermore, the coarsening dynamics of this model has been studied by computer simulations, both with^{5,6,8} and without³ external driving forces. It is therefore interesting to study this problem in its own right, even without external driving forces.

In this paper, we study a general class of systems described by Eq. (1) with

$$\lambda = (1 - \phi^2)^{\alpha} \tag{3}$$

(we absorb the constant λ_0 into the time scale). To make analytical progress, we specialize to the case where the minority phase occupies a vanishingly small volume fraction. For the conventional case ($\alpha = 0$), this is the limit treated by the seminal work of Lifshitz and Slyozov (LS),¹⁰ and by Wagner,¹¹ which leads to the result $\langle R \rangle \propto t^{1/3}$ for the mean domain size, and gives an exact expression for the domainsize distribution. For general $\alpha \ge 0$ we find $\langle R \rangle \propto t^{1/(3+\alpha)}$. We also determine explicitly the domain-size distribution for the physically relevant case $\alpha = 1$. (The other physically relevant case, $\alpha = 0$, has been treated by LS.)

For small volume fractions, coarsening proceeds by nucleation and growth rather than by spinodal decomposition. For present purposes we limit discussion to the late R686

stages of growth, described by the LS evaporationcondensation mechanism, by which large domains [of radius $R > R_c(t)$] grow at the expense of small ones (with $R < R_c$). In this regime the droplet size distribution has the scaling form $n(R) = R_c^{-4} f(R/R_c)$. Before we proceed, two comments are in order. We have

noted that phenomenological considerations indicate that (3) with $\alpha = 1$ is an appropriate form for the mobility in the Cahn-Hilliard equation (1). This being the case, one may wonder about the physical relevance of the conventional (i.e., with $\alpha = 0$) Cahn-Hilliard equation. The point is that thermal noise, omitted from (1), reduces the magnitude of equilibrium order parameter from unity to ϕ_0 . Since thermal fluctuations are irrelevant on large scales,¹ however, one can continue to work with the noise-free equation (1), provided that (inter alia) one uses a renormalized potential whose minima are now at $\pm \phi_0$. The bulk mobility then takes the value $\lambda_{\text{bulk}} = 1 - \phi_0^2 > 0$, and conventional LS behavior is recovered. The relevance of $\alpha = 1$ is then limited to "deep quenches," where the effect of thermal noise is small enough that the predicted $t^{1/4}$ growth extends over a significant time domain (before $t^{1/3}$ LS growth eventually sets in). In simulations, of course, one can simply work at zero temperature, when the $t^{1/4}$ behavior (or $t^{1/(3+\alpha)}$ in general) will describe the asymptotic growth.

The second comment concerns the role of surface diffusion. It has often been stated that (without thermal noise) a factor $(1-\phi^2)$ in the mobility prevents bulk diffusion, and therefore surface diffusion (i.e., diffusion along the interfaces), which leads to $t^{1/4}$ growth, is the dominant coarsening mechanism in this case. It is true that the bulk diffusion constant vanishes for $\alpha > 0$ [see (6) below]. In the far off-critical systems discussed here, however, where the minority phase does not percolate, surface diffusion alone cannot lead to large-scale coarsening. It turns out that for $\alpha > 0$ there is still bulk *transport*, although this of a *subdiffusive*, rather than diffusive, character.

We begin by considering a single spherical domain of "plus" phase, with radius R, immersed in a sea of "minus" phase. We suppose that the minus phase is supersaturated with the plus phase, i.e., $\phi = -1 + \epsilon$ at infinity, and we work in the limit of small supersaturation, $\epsilon \ll 1$. First note that the chemical potential μ is given by

$$\mu = \frac{\delta F}{\delta \phi} = V'(\phi) - \nabla^2 \phi \quad , \tag{4}$$

where the prime indicates a derivative. In the bulk phases, away from the interface, ϕ varies slowly in space and the $\nabla^2 \phi$ term in (4) can be neglected. Setting $\phi = -1 + \tilde{\phi}$ in the minus phase (with $\tilde{\phi} = \epsilon$ at infinity), Eq. (4) gives, to lowest order in $\tilde{\phi}$,

$$\mu(r) = V''(-1)\tilde{\phi}(r) , r > R$$
 . (5)

Inserting this result into (1), using (3) for λ , and retaining the leading terms for $\tilde{\phi} \ll 1$, gives, in the minus phase (away from the interface),

$$\partial_t \tilde{\boldsymbol{\phi}} = 2^{\alpha} V''(-1) \boldsymbol{\nabla} \cdot (\tilde{\boldsymbol{\phi}}^{\alpha} \boldsymbol{\nabla} \tilde{\boldsymbol{\phi}}) \quad . \tag{6}$$

Note that, except for $\alpha = 0$, this equation is not of the usual diffusive form. We shall find, nevertheless, that it still leads to bulk transport, albeit of a subdiffusive character.

We now make the usual assumption (to be verified a posteriori) that the interface moves slowly enough (for large R) that the chemical potential is always in equilibrium with the interface. Then the time-derivative term can be set to zero in (6). Using the linear relation (5) between μ and $\tilde{\phi}$ in the bulk minus phase, (6) can be recast as

$$\nabla^2(\mu^{1+\alpha}) = 0 \quad , \tag{7}$$

a simple generalization of the Laplace equation $\nabla^2 \mu = 0$ obtained when $\alpha = 0$.

What are the boundary conditions on (7)? At infinity, we have

$$\mu(\infty) \equiv \mu_{\infty} = V''(-1)\tilde{\phi}(\infty) = V''(-1)\epsilon \quad . \tag{8}$$

The second boundary condition, at r=R, is just the usual Gibbs-Thomson boundary condition

$$\mu(R) = \sigma/R \quad , \tag{9}$$

where σ is the surface tension. To derive (9), one first writes (exploiting the spherical symmetry) $\nabla^2 \phi = \partial_r^2 \phi + (2/r) \partial_r \phi$ in (4). Then one multiplies (4) by $\partial_r \phi$ and integrates across the interface. Using the fact that $\partial_r \phi$ is sharply peaked at the interface gives $\mu(R)\Delta\phi = -(2/R)\int dr (\partial_r \phi)^2 = -2\sigma/R$, where $\Delta\phi = -2$ is the discontinuity in ϕ across the interface. This reproduces (9).

The solution of (7) with boundary conditions (8) and (9) is

$$\mu^{1+\alpha}(r) = \mu_{\infty}^{1+\alpha} + \left[\left(\frac{\sigma}{R} \right)^{1+\alpha} - \mu_{\infty}^{1+\alpha} \right] \frac{R}{r} , \quad r \ge R .$$
 (10)

The time dependence of R is obtained by considering the flux of material to (or from) infinity. The current j through the minus phase is

$$j(r) = -\lambda \partial_r \mu = -(2\bar{\phi})^{\alpha} \partial_r \mu$$
$$= \frac{2^{\alpha}}{(1+\alpha)[V''(-1)]^{\alpha}} \left[\left(\frac{\sigma}{R}\right)^{1+\alpha} - \mu_{\infty}^{1+\alpha} \right] \frac{R}{r^2} , \quad (11)$$

leading to an outward flux of material f=-2 $\times 4\pi R^2 dR/dt = 4\pi r^2 j(r)$ (where the factor of 2 on the left represents the difference of ϕ between the two phases). This gives

$$\frac{dR}{dt} = \frac{C}{R} \left(\frac{1}{R_c^{1+\alpha}} - \frac{1}{R^{1+\alpha}} \right) \quad , \tag{12}$$

where $C = [2\sigma/V''(-1)]^{\alpha}[\sigma/2(1+\alpha)]$ is a constant, and $R_c = \sigma/\mu_{\infty} = \sigma/\epsilon V''(-1)$ is the critical radius, i.e., the domain will grow if $R > R_c$ and shrink if $R < R_c$.

For the case of zero supersaturation ($\epsilon = 0$), $R_c = \infty$ and $dR/dt = -C/R^{2+\alpha}$. In this case all drops shrink (by evaporation of material to infinity). The collapse time t_c for a drop of initial size R scales as $t_c \propto R^{3+\alpha}$, which already suggests the scaling $R_c(t) \sim t^{1/(3+\alpha)}$ when evaporation and condensation mechanisms compete in the many-domain situation.

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Consider now a dilute assembly of spherical drops of various sizes. The derivation, for general α , of the scaling distribution of sizes follows that of LS for $\alpha = 0$. The basic idea is that one has a time-dependent critical radius $R_c(t)$ which is determined self-consistently. Suppose that, in the late stages of growth, the distribution of domain radii is given by the scaling form

$$n(R,t) = \frac{1}{R_c^4} f\left(\frac{R}{R_c}\right) \quad , \tag{13}$$

where n(R,t)dR is the number of domains per unit volume with radii in the interval (R,R+dR). The prefactor R_c^{-4} ensures that the volume fraction occupied by the domains, $\psi = \int dR \ (4\pi R^3/3)n(R,t)$, is conserved. Inserting (13) into the continuity equation

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial R}(vn) = 0, \qquad (14)$$

where v = dR/dt is the domain-wall velocity given by (12), yields

$$\frac{\dot{R}_{c}}{R_{c}^{5}}(4f+xf') = \frac{C}{R_{c}^{7+\alpha}} \left[\left(\frac{1}{x} - \frac{1}{x^{2+\alpha}} \right) f' + \left(\frac{2+\alpha}{x^{3+\alpha}} - \frac{1}{x^{2}} \right) f \right],$$
(15)

where $\dot{R}_c \equiv dR_c/dt$. Consistency requires that the R_c dependence drop out of this equation. This gives

$$R_c^{2+\alpha} \dot{R}_c = \gamma C \quad , \tag{16}$$

where γ is a constant, implying

$$R_{c}(t) = [(3+\alpha)\gamma Ct]^{1/(3+\alpha)} .$$
 (17)

Thus the characteristic domain size grows as $t^{1/(3+\alpha)}$ as anticipated. This result generalizes the usual $t^{1/3}$ LS growth law.

Using (17) in (16), the latter can be integrated directly, in the form

$$\int \frac{df}{f} = \int \frac{dx}{x} \frac{2 + \alpha - x^{1+\alpha} - 4\gamma x^{3+\alpha}}{\gamma x^{3+\alpha} - x^{1+\alpha} + 1} , \qquad (18)$$

where we remind the reader that x is the scaled radius, $x=R/R_c$.

It would seem that there is a family of solutions, parametrized by γ . In fact this is not so—there is a unique value of gamma, determined following the method used by LS.¹⁰ First we recall that conservation of the order parameter requires that the total volume of the domains in the late-stage scaling regime (where the value of the order parameter in the majority phase approaches -1) be conserved, i.e.,

$$\frac{4\pi}{3} \int_0^\infty dR \ R^3 n(R,t) = \frac{4\pi}{3} \int_0^\infty dx \ x^3 f(x) = \psi, \qquad (19)$$

where ψ is the volume fraction of the minority phase. It follows that there is a maximum value, x_m , of x above which f must vanish. Otherwise, (18) implies $f \sim x^{-4}$ for $x \to \infty$, and the integral (19) will be (logarithmically) divergent. In fact, the denominator of the integral in (18) must have a

double zero at $x = x_m$. To see why this is so, consider the time evolution, for a given domain, of the scaled radius $x = R/R_c$. From (12) one obtains

$$\dot{x} = \frac{R}{R_c} - \frac{RR_c}{R_c^2} \tag{20}$$

$$=\frac{1}{(3+\alpha)\gamma t}\left(\frac{1}{x}-\frac{1}{x^{2+\alpha}}-\gamma x\right)$$
(21)

$$\equiv \frac{1}{(3+\alpha)\gamma t} g(x) \quad , \tag{22}$$

with the last equation defining g(x).

The function g(x) has a single maximum in the interval $(0,\infty)$. If $\gamma < \gamma_0$, where

$$\gamma_0 = \left(\frac{1+\alpha}{3+\alpha}\right) \left(\frac{2}{3+\alpha}\right)^{2/(1+\alpha)} , \qquad (23)$$

then the maximum lies above the x axis and g(x) has two zeros x_1 and x_2 , with $x_1 < x_2$. Under the dynamics (22), if $x < x_1$ initially, then x flows to zero, whereas if $x > x_1$ then x flows to x_2 . However, as $t \to \infty$, $x_2R_c \to \infty$ which violates the conservation of the order parameter. Similarly, if $\gamma > \gamma_0$, g(x) is negative everywhere in $(0,\infty)$, and all domains flow to zero size, which again violates the conservation. We conclude that $\gamma = \gamma_0$.

For $\gamma = \gamma_0$, the maximum of g(x) lies on the x axis, and g(x) has a double zero at

$$x_m = \left(\frac{3+\alpha}{2}\right)^{1/(1+\alpha)} . \tag{24}$$

Equation (18) then gives

$$\ln f(x) = \int \frac{2 + \alpha - x^{\alpha + 1} - 4 \gamma_0 x^{3 + \alpha}}{x(\gamma_0 x^{3 + \alpha} - x^{1 + \alpha} + 1)} \, dx \quad , \qquad x < x_m \quad ,$$
(25)

$$f(x)=0$$
, otherwise. (26)

While this integral cannot be evaluated for general α , the scaling function can be determined for the two cases of greatest physical interest. For $\alpha = 0$,

$$f(x) = a_0 \psi x^2 (3 - 2x)^{-11/3} (x + 3)^{-7/3} \exp\left(-\frac{3}{3 - 2x}\right) , \qquad (27)$$

for $x < x_m = 3/2$, and the usual LS result¹⁰ is recovered. The normalization condition (19) gives $a_0 = 186.13...$

For $\alpha = 1$,

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$$f(x) = a_1 \psi x^3 (2 - x^2)^{-7/2} \exp\left(-\frac{3}{2 - x^2}\right), \qquad (28)$$

for $x < \sqrt{2}$, where $a_1 = 7.785...$ Equation (28) gives the scaling distribution of domain sizes for the modified Cahn-Hilliard equation simulated in Ref. 3, although in that work the domain-size distribution was not measured.

It remains to justify the claim that one need consider only stationary solutions of (6), i.e., that the interfaces move so

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slowly that they can be regarded as stationary while $\tilde{\phi}$ relaxes. In other words, we want to justify the "adiabatic" approximation of treating $\tilde{\phi}$ as given by its equilibrium configuration for the instantaneous positions of the interfaces. We consider late-stage coarsening, when R_c is the only characteristic length scale. Using $\tilde{\phi} = \mu/V''(-1) \sim \sigma/R_c V''(-1)$, Eq. (6) gives the relaxation time of $\tilde{\phi}$, for fixed interfaces, as $t_{\rm rel} \sim R_c^2/V''(-1) \tilde{\phi}^{\alpha} \sim R_c^{2+\alpha} V''(-1)^{\alpha-1}/\sigma^{\alpha}$. From (16), the characteristic interface velocity is $\partial_t R_c \sim C/R_c^{2+\alpha}$, where C is given below Eq. (12). This gives the typical distance moved by an interface in time $t_{\rm rel}$ as $t_{\rm rel}\partial_t R_c \sim \sigma/V''(-1)$. This fixed length (of order the interface thickness) is negligible compared to R_c , justifying the approximation.

We note that the derivation of the $t^{1/(3+\alpha)}$ growth requires that the potential $V(\phi)$ have quadratic minima, since the amplitude of the power-law growth depends (except for $\alpha=0$) on V''(-1) through the constant C in (17). It is interesting that for $\alpha=0$, $R_c(t)$ depends on the potential only through the surface tension σ , and is therefore independent of the detailed form of $V(\phi)$. The question of the appropriate form of the potential for deep quenches deserves further consideration.

We stress that the results presented here are, like the original LS calculation, valid only in the limit where the minority phase occupies an infinitesimal volume fraction. In particular, we anticipate significant corrections to the domain size *scaling function* (28) even for ψ as small as 10^{-2} . This is certainly so for $\alpha = 0$, and improved forms for f(x) have been suggested by a number of authors.¹² It would be interesting to see whether similar techniques can be used for general α .

By contrast, we expect the domain size growth law, $\langle R \rangle \sim t^{1/(3+\alpha)}$, to hold whenever the minority phase consists of isolated domains. Lacasta *et al.*.⁴ measure an effective growth exponent of 0.20 ± 0.01 from *two-dimensional* simu-

lations with $\alpha = 1$ and $\psi = 0.3$. The extrapolation to late times (their Fig. 3) required for comparison with the present predictions does not, however, seem completely straightforward. Also it should be noted that the present theory is restricted to three dimensions. While extension to general d > 2is straightforward, and will not change the growth law, the case d=2 is special (because of the singular form of the Green's function for the Laplacian) and requires a separate study.¹³

If both phases are continuous, one needs to consider the competing surface diffusion process, which leads to $t^{1/4}$ growth for the characteristic length scale (defined now, for example, by the first zero of the pair correlation function). We conclude that, when both phases percolate, bulk transport $(t^{1/(3+\alpha)} \text{ growth})$ dominates for $\alpha < 1$, surface diffusion $(t^{1/4} \text{ growth})$ dominates for $\alpha > 1$, while both processes contribute the same $t^{1/4}$ growth for $\alpha = 1$. For $\psi = 0.5$ (and $\alpha = 1$) Lacasta *et al.*⁴ measure an effective growth exponent of 0.22 ± 0.01 , again below the expected value of 1/4. Longer runs may be helpful in clarifying whether this discrepancy is real.

In summary, the Lifshitz-Slyozov theory of late-stage coarsening has been generalized to a class of models with vanishing bulk mobility. Coarsening occurs by subdiffusive transport of the order parameter through the majority phase. The growth law for the mean domain size, and the scaling form for the domain-size distribution, have been determined in the LS limit where the minority phase occupies a vanishingly small volume fraction. The result for the growth law, however, should hold whenever the minority phase consists of isolated domains.

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