Anisotropic Coarsening: Grain Shapes and Nonuniversal Persistence

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We solve a coarsening system with small but arbitrary anisotropic surface tension and interface mobility. The resulting size-dependent growth shapes are significantly different from equilibrium microcrystallites, and have a distribution of grain sizes different from isotropic theories. As an application of our results, we show that the persistence decay exponent depends on anisotropy and, hence, is nonuniversal.

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The geometrical Wulff construction [1] gives an explicit relation between the anisotropic surface tension and the resulting equilibrium crystal shape. This marks an early and dramatic success in quantitatively connecting morphology to the interfacial properties of a material. However, distinct Wulff microcrystallites must be in "splendid isolation"—with negligible exchange between them in comparison to the internal dynamics required to equilibrate [2]. In contrast, dilute phase separating alloys and coarsening polycrystallites exhibit growing microcrystalline droplets or grains with non-negligible interactions. While it has been shown that anisotropy influences the morphology for these and other coarsening systems [3,4], such effects have not been quantitatively understood for even the simplest models of curvature-driven growth.

The understanding of the late-stage coarsening of interacting *isotropic* phases (see, e.g., [5]) was significantly advanced by the models of Lifshitz and Slyozov [6] and Wagner [7] for locally conserved diffusive and globally conserved curvature-driven coarsening, respectively. These mean-field theories correctly capture a remarkable amount of coarsening phenomenology, and are exact in the dilute limit. With this inspiration, we generalize Wagner's model—an interacting ensemble of coarsening droplets, evolving to continually lower their surface energy without local conservation laws, but with conserved *total* volume—to include arbitrary anisotropy in the surface tension and the interface mobility. We solve the model perturbatively in anisotropy strength, and relate the interfacial properties to the resulting nontrivial grain shapes. These "growth shapes" are contrasted with those of equilibrium (Wulff-constructed) grains to highlight the connection between dynamics and microcrystallite morphology. We then compare our results on the ensemble of grains to Wagner's isotropic solution to demonstrate anisotropy effects on coarsening correlations, including the effect on persistence exponents.

Our model is applicable to single-phase polycrystallite coarsening, where distinct grains are distinguished only by their crystallographic orientation (see [8–10]). Most theoretical studies of polycrystallites focus on their cellular structure, specifically on the static and dynamical description of the vertices where three or more grain boundaries meet. However, vertex-based models have significant shortcomings when anisotropy is included, since it modifies both the distribution of the number of vertices per grain [4] and the otherwise fixed angles formed where three grains adjoin [8]. Furthermore, von Neumann's law, a direct relationship in two dimensions (2D) between the number of vertices per grain and its area growth rate [9], no longer applies. With anisotropy, the evolution of a grain's area requires the complete specification of grain shape—including the orientations and, in general, the nonuniform curvatures of the interfaces.

We present a complementary vertex-free approach to examine grain shape via an anisotropic dynamical mean-field theory. The neighboring grains outside the grain of interest are treated as providing an isotropic mean field. We retain the crystallinity of the grain through an anisotropic surface tension and interface mobility, which results in the anisotropic Wagner theory. (A similar connection can be made between isotropic Wagner theory and soap froths [11].) Ultimately, a synthesis of the present work with vertex-based models is desirable [12].

We find a dynamical scaling solution typical of late-stage coarsening systems [5], including clean polycrystallites. The characteristic length scale grows as a power law, $L \sim t^{1/2}$, as expected for curvature-driven growth [10]. In the scaling regime the initial conditions are "forgotten," and the morphology, when scaled by the growing length, $L(t)$, is invariant. Grain shapes of particular scaled size are also time independent. These growth shapes are generally quite different from equilibrium Wulff shapes—even when the mobility is isotropic! The isotropic grain size distribution is also modified by anisotropy, as discussed later.

With our results, we can answer the question of universality in persistence decay exponents. The persistence is the fraction of the system that has not been crossed by a domain wall up to time t [13–15]. The decay of persistence to zero, $P \sim t^{-\theta}$, even from a starting time deep within the scaling regime, implies that every point in the system will eventually "realize" that equilibrium has not yet been reached. Persistence decay is a *local* signature of the nonequilibrium dynamics of the system. The degree of universality of this dynamical exponent has remained an open issue since no precise results have been obtained before for models with nontrivial temperature dependence [16]. (Simulations have not yet found any temperature dependence within their accuracy [17].) Since anisotropy varies with temperature, our model provides such a nontrivial temperature dependence in a coarsening system that we can then analytically relate to the resulting structure and to the persistence exponent, θ [14]. We find that θ depends on both the anisotropies of the surface tension and of the interface mobility, so the persistence exponent is nonuniversal in anisotropic systems [18].

We restrict ourselves to 2D, where the distinct temperature-dependent anisotropies of the surface tension $\sigma(\psi)$ and the interface mobility $M(\psi)$ may be defined in terms of the angle ψ between the interface normal and an arbitrary crystallographic axis. The anisotropic Allen-Cahn equation [19,20] is then derived from the linear response of the interface to the local drive given by the Gibbs-Thompson condition, $[\sigma(\psi) + \sigma''(\psi)]\kappa$, where σ is the surface tension, and κ is the local interface curvature. The stiffness, $\sigma + \sigma''$, reflects the local change of extent *and* orientation of the interface due to a deformation. By allowing the interface mobility to depend on orientation [21], and by including an applied field λ coupled to one of the phases, we obtain the normal interface velocity,

$$v_n = -M(\psi)\{[\sigma(\psi) + \sigma''(\psi)]\kappa - \lambda\}. \qquad (1)$$

We now consider an ensemble of polycrystallite grains. Our mean-field approximation entails keeping only the crystalline anisotropy of each grain (ignoring its neighbors), neglecting vertices, and determining a self-consistent mean-field λ to represent the effects of neighboring grains that may be growing or shrinking. The conservation of the total area of all of the grains uniquely determines $\lambda(t)$, resulting in precisely the anisotropic Wagner theory.

To proceed, we Fourier expand the anisotropic surface tension and mobility,

$$\sigma(\psi) = \sigma_0\left\{1 + \delta\sum_{k=1}^{\infty}[\sigma_k\cos(k\psi) + \tilde{\sigma}_k\sin(k\psi)]\right\}, \qquad (2)$$

$$M(\psi) = M_0\left\{1 + \delta\sum_{k=1}^{\infty}[m_k\cos(k\psi) + \tilde{m}_k\sin(k\psi)]\right\}, \qquad (3)$$

where δ is introduced to organize a perturbative calculation. We parametrize each grain by a polar radius $R(\phi)$, as depicted in Fig. 1, from which the interface orientation follows: $\psi(\phi) = \phi - \arctan(R'/R)$ where $R' \equiv dR/d\phi$. Considering only smooth grain profiles, we relate normal and radial growth velocities, $v_r(\phi) = v_n\sqrt{1 + (R'/R)^2}$, and calculate the curvature $\kappa(\phi) = [R^2 + 2R'^2 - RR'']/(R^2 + R'^2)^{3/2}$. We then expand R,

$$R(\phi) = R_0\left\{1 + \sum_{k=0}^{\infty}[\rho_k\cos(k\phi) + \tilde{\rho}_k\sin(k\phi)]\right\}, \qquad (4)$$

with coefficients

$$\rho_k(x) = a_k(x)\delta + b_k(x)\delta^2 + \dots, \qquad (5)$$

and similarly for $\tilde{\rho}_k$ [22]. Grain sizes are labeled with a reduced length $x \equiv R_0/L$, where $L \equiv (M_0\sigma_0 t/2)^{1/2}$. For $\delta = 0$ we recover Wagner's isotropic theory, with the familiar distribution of grain sizes (see [7,11,14]):

$$f(x) = \epsilon F_2 x\exp[-4/(2 - x)]/(2 - x)^4. \qquad (6)$$

(The ϵ prefactor is the area fraction of a randomly selected subset of grains—used later to calculate persistence.) For convenience, we *define* R_0 by the requirement that x maintains this *isotropic* grain-size distribution up to an anisotropy-dependent normalization, $F_2 = F_2^{(0)} + \delta^2 F_2^{(2)} + \dots$. This requirement leads to nonzero ρ_0 terms in the expansion (4) but conveniently preserves the range of scaled sizes, $x \in [0, 2]$. (Note that $\tilde{\rho}_0 = 0$.) Physical length scales, such as the grain perimeter, can be consistently derived from our results, as discussed below.

The resulting interface equations for the ensemble of grains may be solved order by order in δ [23]. The zeroth order results reproduce the isotropic theory; the first order equations are new, and serve to determine a size-dependent grain shape through $a_k(x)$:

$$x(2 - x)^2 a_k'(x) - 4(k^2 + x - 2)a_k = 4(1 - k^2)\sigma_k + 4(1 - x)m_k, \qquad (7)$$

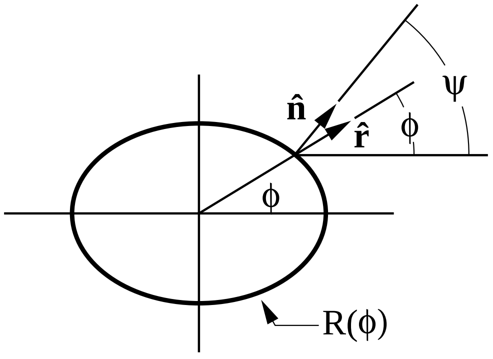

FIG. 1. An anisotropic drop illustrating ϕ, the polar coordinate, and $\psi(\phi)$, the angle of the interface normal at the point $[R(\phi), \phi]$.

for $k > 1$, with an identical equation for $\tilde{a}_k$ in terms of $\tilde{\sigma}_k$ and $\tilde{m}_k$. For $k > 1$, the solution is

$$a_k(x) = m_k + (\sigma_k - m_k)(1 - 1/k^2)[1 + \Omega(k, v)], \tag{8}$$

where $\Omega(k, v) \equiv 2\Gamma(2 - k^2, v)v^{k^2-2}e^v$, and $v \equiv k^2x/(2 - x)$. We also have $a_0(x) = a_1(x) = 0$, the latter by our choice of coordinate origin [22]. Clearly the grain shapes depend on grain size, through Ω. Even when the surface tension is isotropic ($\sigma_k = 0$, for all $k > 0$), we can obtain anisotropic grain shapes through the interface mobility. This is illustrated in Fig. 2 for a particular choice of $M(\psi)$.

At all orders of δ the equations for the grain shape are similar to (7), although the right-hand side will include products of lower-order solutions. While these equations are progressively more difficult to solve, we can iteratively demonstrate that the solutions are finite at every order of δ [23].

In the special case where $m_k = \sigma_k$ for all k, grains of all sizes have the equilibrium Wulff shape. This result holds *to all orders* in δ, and is due to a remarkable symmetry held by the interface Eq. (1). The equilibrium grain shape is given by

$$R_{\mathrm{eq}}(\phi) = \frac{R_0}{\sigma_0} \min_{\phi'} \left| \frac{\sigma(\phi')}{\cos(\phi' - \phi)} \right| . \tag{9}$$

For this Wulff shape, a variational calculation shows that $[\sigma(\psi) + \sigma''(\psi)]\kappa$ is independent of angle [23], from which we obtain $v_r \propto M(\psi)\sqrt{1 + (R'/R)^2}$ for all angles. If and only if the *dynamical* mobility anisotropy equals that of the *static* surface tension—that is, $M(\psi) \propto \sigma(\psi)$—then we recover $v_r \propto R_{\mathrm{eq}}(\phi)$, the condition for Wulff grains to keep their shape while evolving. This symmetry, evident in (8), leads to size-independent drop shapes and also shows up in the drop size distribution and persistence results, as discussed below.

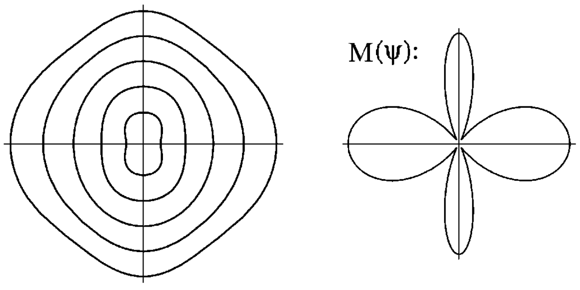

FIG. 2. First order grain shapes for various sizes (not to scale) with an isotropic surface tension σ_0 but with a particular anisotropic mobility $\delta m_2 = 0.4$ and $\delta m_4 = 0.9$ (all other $m_k = \tilde{m}_k = 0$). The scaled grain sizes are, from the innermost, $x = 0.01$, 0.5, 1, 1.5, and 1.99. For no value of x is there a circular grain, the equilibrium Wulff shape. Angles for which $M(\psi)$ is larger correspond roughly to larger radius in growing (larger) grains, and smaller radius in shrinking (smaller) grains.

However, the dynamic mobility and the static surface tension will *not* be proportional except by special construction. Regardless, in physical systems M and σ have different temperature dependences so that equality could not be maintained as temperature varies. In the general case, we will have size-dependent drop shapes given, to first order, by (8). In comparison, the Wulff construction gives $a_k^{\mathrm{eq}} = \sigma_k$ as the leading contribution to the equilibrium grain shape. Even with an isotropic mobility, $m_k = 0$, growth shapes differ from equilibrium and depend on grain size.

The isotropic grain size distribution (6) applies only to our index R_0 [22]. Physically relevant lengths, such as extracted from the grain perimeter or the area, will generally have different distributions. For example, the area $A = \frac{1}{2}\int_0^{2\pi} d\phi\, R(\phi)^2$ can be used to define $R_A = \sqrt{A/\pi}$, where

$$R_A = R_0\left[1 + \delta^2\left(b_0 + \frac{1}{4}\sum_k \{a_k^2 + \tilde{a}_k^2\}\right) + O(\delta^3)\right]. \tag{10}$$

A scaled size $z = R_A/L$ may then be introduced, which will be related to x by $z = x[1 + \delta^2 h(x) + O(\delta^3)]$. The "area radius" distribution $g(z)$ is then determined by $g(z)\,dz = f(x)\,dx$ so that

$$g(z) = f(z) - \delta^2 \frac{d}{dz}[zf(z)h(z)] + O(\delta^3), \tag{11}$$

where $f(x)$ is the isotropic distribution [23]. The grain perimeter distribution follows similarly, though with a different function $h(x)$. [In the special symmetric case, where $m_k = \sigma_k$ for all $k \geq 1$, all physical lengths have the same distribution. Since the grain shapes are size independent, $h(x) = h_0$, and $g(z)$ and $f(x)$ can differ only by an overall normalization.]

We may also calculate the slow decay of persistence due to the evolution of a small area fraction ϵ of randomly chosen grains, following [14,23,24]. The persistence $P_>$ of the region outside the chosen grains decays due to growing grains via $\partial_t P_> = -v_> P_>$. The rate of encroachment of growing grains, $v_>$, can be calculated from the grain shapes and (1). The power-law decay of persistence follows directly from the result $v_> \propto 1/t$, with persistence exponent $\theta = tv_>$. Anisotropy appears at $O(\delta^2)$. The calculation is lengthy and details are reported elsewhere [23]; however, the result simplifies to

$$\theta = \theta_0 + \delta^2 \sum_{k=1}^{\infty} \theta_k^{(2)}[(m_k - \sigma_k)^2 + (\tilde{m}_k - \tilde{\sigma}_k)^2] + O(\delta^3), \tag{12}$$

where $\theta_0 \simeq 0.487\,97\epsilon$ is the 2D persistence exponent for the isotropic case [14]. We find that θ equals the isotropic value θ_0 only when $M(\psi) \propto \sigma(\psi)$ (this holds to all orders due the symmetry mentioned earlier) and differs from θ_0 for any other anisotropic conditions. The order ϵ coefficients $\theta_k^{(2)}$ are easily determined by numerical integration, and are well approximated by a large k expansion: $\theta_k^{(2)}/\epsilon \approx 0.091\,262\,4 - 0.303\,588\,8/k^2 + 0.274\,454\,8/k^4 + 0.189\,615/k^6$ is accurate to within 1% at $k = 2$ and 0.004% for $k \geq 4$.

The persistence exponent depends continuously on both the mobility and surface tension, and, consequently, on the temperature. The 2D Ising model provides an estimate of the magnitude of the effect. The anisotropic surface tension is known analytically for $0 \leq T \leq T_c$ [25], though the anisotropic mobility is known only for Glauber (nonconserved) dynamics at temperatures near zero [26]. Using the leading contribution (12), we find for our dilute, globally conserved dynamics $\theta \simeq 1.0344\theta_0$ as $T \rightarrow 0$, while the isotropic value θ_0 is, hence, recovered as $T \rightarrow T_c^-$. The variation with temperature is small but nonzero.

In conclusion, we have constructed a mean-field model for 2D polycrystallite coarsening with anisotropic surface tension and mobility. We find an exact scaling solution with size-dependent grain shapes that are generally unrelated to the equilibrium Wulff shape. We use our solution to calculate the exponent describing persistence decay, and find that it is *continuously dependent on anisotropy* and, hence, nonuniversal with respect to temperature [18]. We expect that persistence exponents are generically temperature-dependent in anisotropic systems, even at volume fractions where a droplet description is inappropriate.

While our results for the growth shapes are exact in the dilute limit with small anisotropy, numerical and experimental studies are needed to explore beyond these limits. For comparisons with our expressions for drop shapes (8), drop size distributions (11), and persistence exponents (12), both the anisotropic surface tension and interfacial mobility must be characterized—this is straightforward in coarse-grained models (see [23]). Experimentally, twisted nematics provide a direct realization of anisotropic Wagner theory [27]. For polycrystallite films, our mean-field approximation can be tested by *determining* $\{\sigma_k\}$ and $\{m_k\}$ by fitting average (aligned) grain shapes.

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