Introduction to phase ordering kinetics

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1 Motivation

Main question: What happens if we suddenly bring a system from a one-phase region in the phase diagram to one where several phases coexist? Examples:

- Magnetic materials (e.g. Ising model). Order parameter ϕ: local (coarse-grained) magnetization, *non-conserved*. Interesting case: More than one phase in final state $\Leftrightarrow$ free energy density of homogeneous state, $V(\phi)$, has two equal minima $\Leftrightarrow$ zero field.

  Lower ('quench') T from above to below T_c. What happens? Initially $\phi = \phi_0 = 0$. $V(\phi)$ has negative curvature at $\phi_0 \Rightarrow$ system unstable against local fluctuations. Domains of up- and down-spins appear throughout system, grow in size (coarsen): *Spinodal decomposition*. Never stops, for infinite system always out-of-equilibrium. For large domain size $L(t)$ may expect scaling: $L(t)$ is only relevant length scale. See Figure 1.

- Liquid-gas phase separation (similarly binary alloys etc): Order parameter ϕ is local particle number density, *conserved*, i.e. $\int d\mathbf{r}\, \phi(\mathbf{r}) / \int d\mathbf{r} = \phi_0$ at all times. Conservation implies that ϕ's in the final gas and liquid are determined by double-tangent construction: Chemical potential $\mu(\phi) = V'(\phi)$ and pressure $P(\phi) = \phi\mu(\phi) - V(\phi)$ must be equal in both phases; two conditions that determine ϕ_{liquid} and ϕ_{gas}.

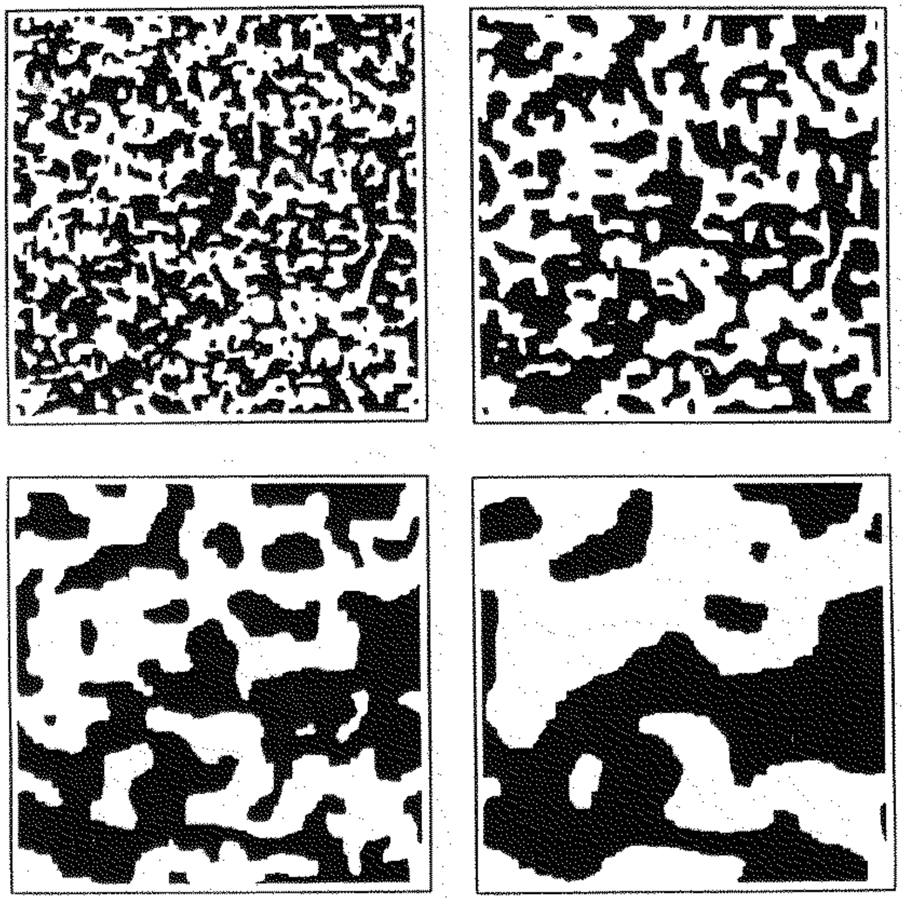
  Quench from above to below T_c. What happens?

  - If final T is low, $V(\phi)$ again has negative curvature at ϕ_0; get spinodal decomposition as before. But details not identical because of conservation law for ϕ.
  - If final T is just inside two-phase coexistence region, $V(\phi)$ has positive curvature at ϕ_0; because of conserved order parameter, ϕ will stay at this metastable value. Later: *Nucleation and growth* — domains of the new phase (e.g. the gas) nucleate by thermal fluctuations; these then grow and eventually coalesce (see Fig. 2). ϕ in the liquid regions adjusts (conservation!); moves from ϕ_0 to ϕ_{liquid} at long times. Again scaling, typical domain size $L(t)$ dominant length scale.

  (Can also get nucleation and growth with non-conserved order parameters. E.g. Ising model in nonzero field for $T < T_c$; reverse field direction. ϕ 'slides down' to nearest metastable local minimum of $V(\phi)$. Later domains of stable phase nucleate and grow. But for long times, system equilibrates (becomes uniform) because now have a preferred state; scaling – if any – possible only before that.)

Many generalizations: E.g. order parameter ϕ could be vector (XY, Heisenberg models...) or tensor (liquid crystals), or "list" of order parameters (species densities in a liquid mixture). Also could have competing phases, e.g. when quenching into or near a three-phase region. We'll ignore most of these. Treatment follows mainly that of Alan Bray, *Adv. Phys.*, 43:357-459, 1994.

60 A. J. Bray



gure 2. Monte Carlo simulation of domain growth in the $d = 2$ Ising model at $T = 0$ (taken from Kissner [8]). The system size is 256×256, and the snapshots correspond to 5, 15, 60 and 200 Monte Carlo steps per spin after a quench from $T = \infty$.

Figure 1: Illustration of spinodal decomposition (in a 2d Ising model at low temperature and in zero field); domains of up- and down-spins grow with time; note the statistical similarity between the snapshots apart from the overall growth in the domain sizes, which is evidence for scaling. Figure courtesy of Alan Bray.

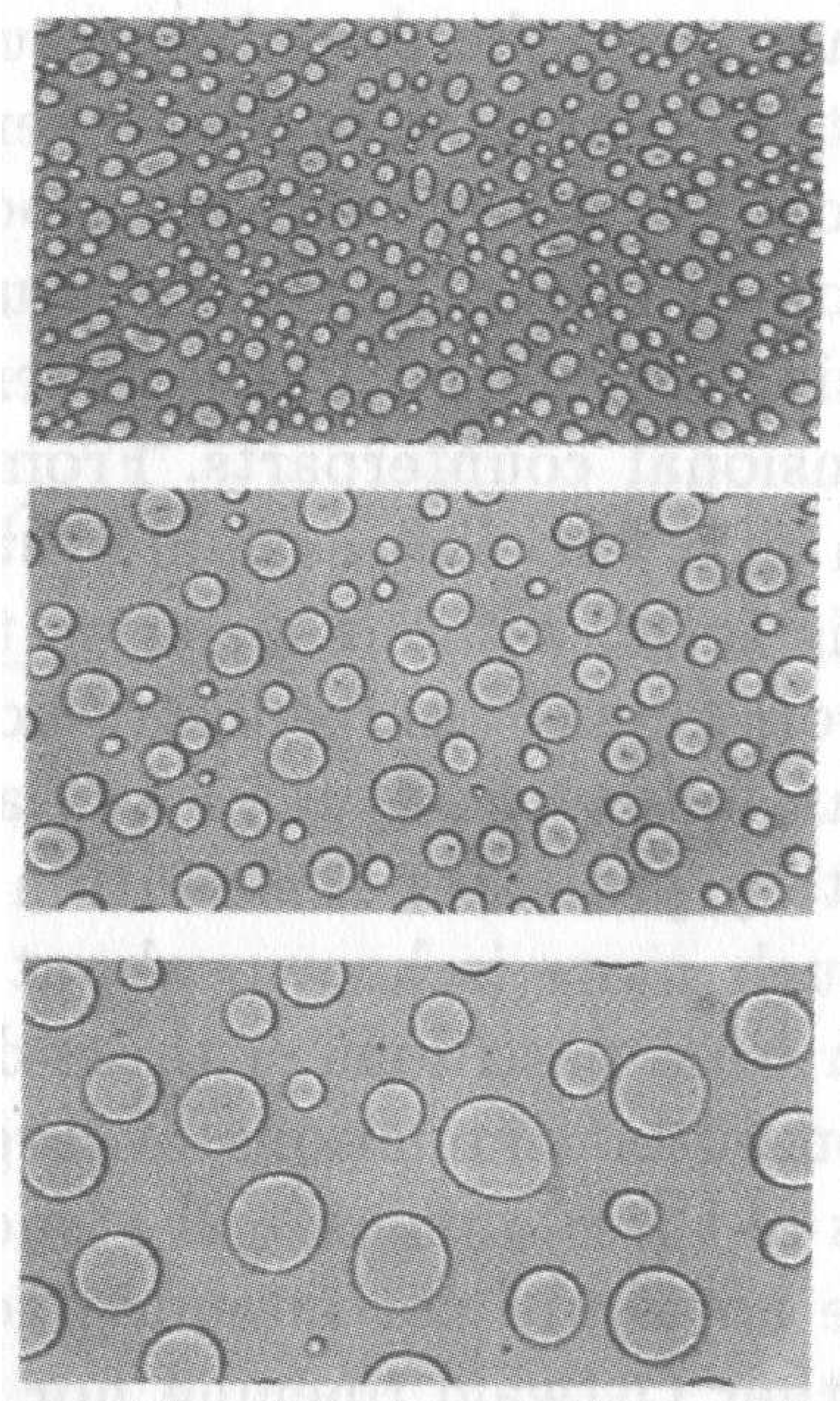


Figure 2: Illustration of growth and coalescence of domains, in a system with conserved order parameter. Figure courtesy of Joel Stavans.

2 Formulating the problem

Need to define a sensible model for the evolution of the coarse-grained, spatially varying order parameter $\phi(\mathbf{r}, t)$. Standard approach: Relate to a free energy (functional); should have $V(\phi)$ as local term plus penalty for interfaces. Simplest (coefficient for interface term can be absorbed by rescaling $V(\phi)$ and F):

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

$V(\phi)$ has double-well structure. By choosing the zero and the scale of ϕ appropriately, can always assume that homogeneous equilibrium states are $\phi = \pm 1$. Non-conserved case: Assume V has two equal minima (s.a.); convention $V(\pm 1) = 0$. Conserved case: Equilibrium values of ϕ determined by double-tangent construction $\Rightarrow$ don't change if add a linear function $a\phi + b$ to $V(\phi)$ $\Rightarrow$ can again assume that $V(\phi)$ has two minima, at $\phi = \pm 1$, with $V(\pm 1) = 0$.

How do we define the dynamics from this? For *non-conserved* order parameter, gradient descent on F is reasonable since systems wants to lower its free energy:

$$\frac{\partial\phi(\mathbf{r})}{\partial t} = -\frac{\delta F}{\delta\phi(\mathbf{r})} = \nabla^2\phi(\mathbf{r}) - V'(\phi(\mathbf{r})) \tag{2}$$

Have absorbed possible rate coefficient Γ in front of right hand side into t. Competition: $\nabla^2\phi$ term drives ϕ to uniform states; $V'(\phi)$ drives ϕ to equilibrium values $\phi = \pm 1$. Eq (2) is called the *time-dependent Ginzburg-Landau* equation (TDGL) or *Model A*. From now on, often just write ϕ instead of $\phi(\mathbf{r})$.

For *conserved* order parameter: Conservation can be guaranteed by starting from continuity equation

$$\frac{\partial\phi(\mathbf{r})}{\partial t} = -\nabla\cdot\mathbf{j}(\mathbf{r})$$

where $\mathbf{j}$ is come current. If transport is diffusive, and driven by gradients of the local chemical potential, have

$$\mathbf{j}(\mathbf{r}) = -\nabla\mu(\mathbf{r}), \qquad \mu(\mathbf{r}) = \frac{\delta F}{\delta\phi(\mathbf{r})} = -\nabla^2\phi(\mathbf{r}) + V'(\phi(\mathbf{r})) \tag{3}$$

So get

$$\frac{\partial\phi(\mathbf{r})}{\partial t} = \nabla^2\mu(\mathbf{r}) = \nabla^2\frac{\delta F}{\delta\phi(\mathbf{r})} = -\nabla^2\left[\nabla^2\phi(\mathbf{r}) - V'(\phi(\mathbf{r}))\right] \tag{4}$$

which is called the *Cahn-Hilliard* equation, or *Model B*.

[Digression: In (3), there is in principle a mobility coefficient Γ, so that $\mathbf{j} = \Gamma\nabla\mu$. We have assumed that Γ is constant and absorbed it into the scaling of time. This is definitely a simplification – we know that in general Γ must be ϕ-dependent, so that $\mathbf{j}(\mathbf{r}) = \Gamma(\mathbf{r})\nabla\mu(\mathbf{r})$. A simple case where this becomes clear is an ideal gas. If ϕ is particle density, then for an ideal gas $V(\phi) = \phi[\ln\phi - 1]$ and the $|\nabla\phi|^2$ terms are absent from the free energy, so that $\mu(\mathbf{r}) = \ln\phi(\mathbf{r})$ and $\nabla\mu(\mathbf{r}) = (1/\phi(\mathbf{r}))\nabla\phi(\mathbf{r})$. On the other hand, for an ideal gas we know that the diffusive current $\mathbf{j}(\mathbf{r})$ is proportional to $-\nabla\phi(\mathbf{r})$, so that the mobility coefficient $\Gamma(\phi)$ must be proportional to ϕ.]

What about thermal noise? Not included explicitly, so effectively working at $T = 0$. Expect that in scaling regime (large domain sizes) this is ok. (Of course details change: E.g. at $T > 0$ have $\phi = \pm M$ with $M < 1$ inside spin-up/down domains in the Ising case. But can be absorbed by rescaling $\phi \to \phi/M$.) When considering nucleation, take $T > 0$ into account implicitly: Yields initial domains of new phase; activated processes, T important for time scale. Later (for large domains, in scaling regime) setting $T = 0$ should again work.

Similar argument for initial state (determined e.g. by initial temperature): Expect short-range correlations in fluctuations of $\phi(\mathbf{r})$; details should be irrelevant once the system has got into the scaling regime.

3 The early time regime

3.1 Spinodal decomposition

3.1.1 Non-conserved order parameter

Look at example of Ising model in zero field, quenched to below T_c. Then initial value of order parameter, $\phi_0(\mathbf{r})$, is $\phi_0 = 0$ on average, with small short-range fluctuations. For early times, can therefore linearize the TDGL (2) around $\phi = 0$, using $V'(\phi) = -|V''(0)|\phi$ since $V''(0) < 0$ and $V'(0) = 0$ from symmetry of V (in the Ising case):

$$\frac{\partial \phi}{\partial t} = \nabla^2 \phi + |V''(0)|\phi \tag{5}$$

Use Fourier components to solve this:

$$\phi_{\mathbf{k}} = \frac{1}{L_{\mathrm{Box}}^{3/2}} \int d\mathbf{r}\, \phi(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}, \qquad \phi(\mathbf{r}) = \frac{1}{L_{\mathrm{Box}}^{3/2}} \sum_{\mathbf{k}} \phi_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

where in a system in a cubic box of side length L_{Box}, with periodic boundary conditions, the wavevector $\mathbf{k}$ can take on the values $\mathbf{k} = (2\pi/L_{\mathrm{Box}})(n_x, n_y, n_z)$ with n_x, n_y, n_z arbitrary integers. Then from (5) ($k \equiv |\mathbf{k}|$)

$$\frac{\partial \phi_{\mathbf{k}}}{\partial t} = \omega_k \phi_{\mathbf{k}} \quad \Rightarrow \quad \phi_{\mathbf{k}}(t) = \phi_{\mathbf{k}}(0) e^{\omega_k t} \qquad \text{with} \quad \omega_k = -k^2 + |V''(0)|$$

So all initial fluctuations with $k < \sqrt{|V''(0)|}$ are unstable and grow exponentially in time; in real space these have length scales above $\sim 1/\sqrt{|V''(0)|}$. The analysis breaks down for times of order $1/|V''(0)|$ where the unstable modes $\phi_{\mathbf{k}}(t)$ and therefore the local $\phi(\mathbf{r}, t)$ become of $\mathcal{O}(1)$. Then domains of equilibrium phases $\phi = \pm 1$ form with domain walls between them and the dynamics becomes controlled by the motion of these domain walls – see later.

3.1.2 Conserved order parameter

In the conserved order parameter case, assume initial state is approximately uniform, with $\phi(\mathbf{r}) = \phi_0$ and $-1 < \phi_0 < 1$ (otherwise are still in a stable one-phase region). Expect that $\phi_0 \approx 1$ corresponds to quench to just inside the coexistence region, whereas ϕ_0 near 0 should be a quench into the spinodal region.

Check this: Set $\phi(\mathbf{r}) = \phi_0 + \tilde{\phi}(\mathbf{r})$ and linearize Cahn-Hilliard equation (4) in $\tilde{\phi}$:

$$\frac{\partial \tilde{\phi}}{\partial t} = -\nabla^4 \tilde{\phi} + V''(\phi_0) \nabla^2 \tilde{\phi} \tag{6}$$

In Fourier space

$$\frac{\partial \tilde{\phi}_{\mathbf{k}}}{\partial t} = \omega_k \tilde{\phi}_{\mathbf{k}} \Rightarrow \tilde{\phi}_{\mathbf{k}}(t) = \tilde{\phi}_{\mathbf{k}}(0) e^{\omega_k t} \qquad \text{with} \quad \omega_k = -k^4 - V''(\phi_0) k^2$$

If $V''(\phi_0) > 0$, all fluctuations decay: $\phi(\mathbf{r}) = \phi_0$ is a stable solution. Corresponds to shallow quench, as expected: need large thermal fluctuation to create domains of new phase.

If $V''(\phi_0) < 0$, $\omega_k = -k^4 + |V''(0)|k^2$, so all modes with $k < k_m = \sqrt{|V''(0)|}$ are unstable. But now ω_k as a function of k has a maximum, at $k = k_m/\sqrt{2}$; these modes grow fastest. In scattering experiments, measure *structure factor*:

$$S(\mathbf{k}, t) = \left\langle \tilde{\phi}^*_{\mathbf{k}}(t) \tilde{\phi}_{\mathbf{k}}(t) \right\rangle = \left\langle \tilde{\phi}^*_{\mathbf{k}}(0) \tilde{\phi}_{\mathbf{k}}(0) \right\rangle e^{2\omega_k t}$$

If initial fluctuations are short-ranged, then $\left\langle \tilde{\phi}^*_{\mathbf{k}}(0) \tilde{\phi}_{\mathbf{k}}(0) \right\rangle$ is independent of $\mathbf{k}$ up to quite large k, so $S(\mathbf{k}, t)$ dominated by $e^{2\omega_k t}$ factor: Maximum at $k = k_m/\sqrt{2}$, shows up as a ring in plots of $S(\mathbf{k}, t)$ which gets brighter.

Breakdown of linear analysis for times of order $1/\omega_{k_m} \sim |V''(0)|^2$. After that, domains form and coarsen. Growing length scale corresponds to decrease in dominant $k \Rightarrow$ radius of ring of $S(\mathbf{k},t)$-maximum shrinks.

3.2 Nucleation and growth

Focus on *conserved* order parameters here. If the quench occurs into a metastable (rather than spinodally unstable region), phase ordering starts via nucleation of domains of the 'new' phase. How big do these need to be in order to be stable and start growing?

Idealize: Say domains are spherical, radius R. Outside a domain, still have $\phi = \phi_0$; inside have new phase with some ϕ_- (expected to be close to -1). Free energy cost for nucleating the domain? Pressure on the outside is $P_0 = \phi_0 V'(\phi_0) - V(\phi_0)$; similarly for P_- on the inside. Let $\Delta P = P_- - P_0$; free energy cost to grow domain to radius R is $-\Delta P(4\pi/3)R^3$. Also create domain wall, with surface tension σ, say. So total free energy cost is

$$\Delta F = 4\pi\sigma R^2 - \frac{4\pi}{3}\Delta P R^3$$

Has maximum

$$\Delta F(R_c) = \frac{16\pi}{3}\frac{\sigma^3}{(\Delta P)^2} \qquad \text{at} \qquad R_c = \frac{2\sigma}{\Delta P} \tag{7}$$

R_c is called *critical droplet radius*: Bigger droplets lower the free energy by *growing*, smaller ones by *shrinking*. Time scale for thermal fluctuations to create critical droplet scales as $\exp[-\Delta F(R_c)/T]$; can be large at low T.

Gap in the argument above: What determines value of ϕ_-? Critical droplet with exactly $R = R_c$ neither grows nor shrinks - should be at equilibrium regarding local particle exchange, hence chemical potentials $\mu(\phi) = V'(\phi)$ equal inside and outside $\Rightarrow \phi_-$ determined from $V'(\phi_-) = V'(\phi_0)$. Can then show that ΔP is indeed positive (need this, otherwise R_c undefined – domains of any size would shrink).

More formal derivation of R_c: Critical droplet is unstable stationary solution of Cahn-Hilliard eq'n (4). Stationarity $\Rightarrow \nabla^2\mu(\mathbf{r}) = 0$. In fact, expect no currents to flow, so stronger criterion $\mathbf{j}(\mathbf{r}) = -\nabla\mu(\mathbf{r}) = 0$, hence $\mu(\mathbf{r}) = \mu =$ constant. Know $\mu(\mathbf{r}) = -\nabla^2\phi + V'(\phi)$ generally; in region far from droplet where $\phi(\mathbf{r}) = \phi_0$ the first term becomes negligible and so $\mu = V'(\phi_0)$. Same argument well inside droplet, where $\phi(\mathbf{r})$ also constant, gives $V'(\phi_-) = V'(\phi_0)$ as before. Eq'n now left to solve:

$$V'(\phi_0) = -\nabla^2\phi + V'(\phi), \qquad \text{hence} \qquad \nabla^2\phi - U'(\phi) = 0$$

where $U(\phi) = V(\phi) - \phi V'(\phi_0)$ is an *effective potential*. Look for radially symmetric solution $\phi(r)$; gives

$$\frac{d^2\phi}{dr^2} + \frac{2}{r}\frac{d\phi}{dr} - U'(\phi) = 0$$

Trick: Multiply by $d\phi/dr$ and integrate from $r=0$ to $r=\infty$. Then

$$\frac{1}{2}\left(\frac{d\phi}{dr}\right)^2\Bigg|_{r=0}^{r=\infty} + \int_0^\infty dr\,\frac{2}{r}\left(\frac{d\phi}{dr}\right)^2 - U(\phi(r))\Bigg|_{r=0}^{r=\infty} = 0 \tag{8}$$

Well inside and outside droplet $d\phi/dr \to 0 \Rightarrow$ first term vanishes. Second term: $d\phi/dr$ is strongly peaked around $r \approx$ droplet radius $R \Rightarrow$ can approximate $2/r \approx 2/R$. Last term: $\phi(r=0) = \phi_-$, and $\phi(r\to\infty) = \phi_0$. So get, using that $R = R_c$ (we're calculating the critical droplet)

$$\frac{2}{R_c}\int_0^\infty dr\,\left(\frac{d\phi}{dr}\right)^2 = \Delta U, \qquad \Delta U = U(\phi_0) - U(\phi_-) \tag{9}$$

Now, using $V'(\phi_0) = V'(\phi_-)$,

$$\Delta U = V(\phi_0) - \phi_0 V'(\phi_0) - [V(\phi_-) - \phi_- V'(\phi_-)] = -P_0 + P_- = \Delta P$$

so (9) agrees with previous result (7) if surface tension of domain wall is given by

$$\sigma = \int_0^\infty dr \left(\frac{d\phi}{dr}\right)^2 \tag{10}$$

This is indeed true; we'll show it below.

4 The scaling regime

This is the regime where any initial fluctuations have grown to the point where there are domains with well-defined walls between them. Let's look at the shape of these.

Simplest case: Flat domain wall. (Relevant in the limit where domains are big, so that wall curvature is very small.) Call g coordinate orthogonal to wall. For non-conserved order parameters, eq (2) gives for a stationary domain wall:

$$\frac{\partial^2\phi}{\partial g^2} = V'(\phi) \tag{11}$$

This is also a stationary solution of (4) for conserved order parameters, so can treat both together. Boundary condition: stable equilibrium state either side far from wall, so $\phi(\pm\infty) = \pm 1$. Multiplying (11) by $\partial\phi/\partial g$ and integrating w.r.t. g gives $\frac{1}{2}(\partial\phi/\partial g)^2 - V(\phi) = \text{constant}$. From boundary conditions, $\partial\phi/\partial g \to 0$ for $g \to -\infty$, and $V(\phi) \to V(-1) = 0$ in same limit, so the constant on the r.h.s. is zero. So

$$\left(\frac{\partial\phi}{\partial g}\right)^2 = 2V(\phi) \tag{12}$$

If we integrate the free energy density (integrand in (1)) from $g = -\infty$ to $g = \infty$ we get the surface tension (free energy cost per unit area) of the domain wall:

$$\sigma = \int dg \left[\frac{1}{2}\left(\frac{\partial\phi}{\partial g}\right)^2 + V(\phi(g))\right] = \int dg \left(\frac{\partial\phi}{\partial g}\right)^2 \tag{13}$$

This shows that (10) is indeed true (using the assumption already exploited earlier, when we replaced $2/r \approx 2/R$, that the critical droplet is much larger than the domain wall thickness ξ, so that the domain wall is almost flat and we can identify r and g). Eq. (13) can also be expressed in terms of $V(\phi)$ alone:

$$\sigma = \int dg \, \frac{\partial\phi}{\partial g}[2V(\phi(g))]^{1/2} = \int_{-1}^{1} d\phi \, [2V(\phi)]^{1/2} \tag{14}$$

Can also see that domain wall energy is localized near domain walls: Setting $\phi = 1 - \epsilon$ for $g \to \infty$, for example, eq (12) yields

$$-\frac{\partial\epsilon}{\partial g} = \sqrt{V''(\pm 1)\epsilon^2} = \epsilon\sqrt{V''(1)}$$

so $1 - \phi \sim \exp[-\sqrt{V''(1)}g]$ and ϕ converges exponentially quickly to its equilibrium (bulk) value away from the wall; the same argument also applies for $g \to -\infty$, of course.

So: domain walls are same for non-conserved and conserved order parameter. Mechanisms by which domains grow are different though; look at these separately.

4.1 Non-conserved order parameter

Intuition: Domain walls have surface tension σ. Similar to soap film: Get force if walls are curved. (In soap bubble, curvature force is balanced by higher air pressure inside bubble.)

Calculate the force per area, F, for a spherical bubble of radius R: If decrease R by δR, F does work $4\pi R^2 \delta R\, F$. This work comes from decrease in surface energy $\delta(4\pi\sigma R^2) = 8\pi\sigma R\,\delta R$, so $F = 2\sigma/R$.

For non-conserved order parameter, curvature force will move domain walls; if friction constant for domain wall motion is η, so that friction force per area for wall moving at speed dR/dt is $\eta\, dR/dt$, get

$$\eta \frac{dR}{dt} = -\frac{2\sigma}{R} = -\frac{(d-1)\sigma}{R} \tag{15}$$

where in the last equality I've indicated the generalization to other dimensions d.

This result should also follow directly from (2) – how? Look at spherical domain of radius R again, inside $\phi = -1$, outside $\phi = +1$. Using spherical symmetry, get

$$\frac{\partial \phi}{\partial t} = \frac{\partial^2 \phi}{\partial r^2} + \frac{d-1}{r}\frac{\partial \phi}{\partial r} - V'(\phi)$$

If $R \gg$ domain wall thickness ξ, expect solution of form $\phi(r,t) = f(r - R(t))$ – wall profile just shifts outwards over time. Insert to get

$$-\frac{dR}{dt} f' = f'' + \frac{d-1}{r} f' - V'(f) \tag{16}$$

Function $f(x)$ changes from -1 to $+1$ in region of width ξ around $x = 0$. So use same trick that lead to (8): Multiply (16) by f' and integrate from $x = -\infty$ to $x = \infty$. f'' and $V'(f)$ terms each give zero contribution, so

$$\int dx\, [f'(x)]^2 \left(\frac{dR}{dt} + \frac{d-1}{x+R} \right) = 0$$

Because $[f'(x)]^2$ is peaked near $x = 0$, can replace $(d-1)/(x+R) \approx (d-1)/R$ and get

$$\frac{dR}{dt} = -\frac{d-1}{R} \tag{17}$$

Comparing with (15), see that indeed get same result if friction constant η and domain wall tension σ are equal, $\eta = \sigma$; can show this independently (but won't here). Integrating (17) gives $R^2(t) = R^2(0) - 2(d-1)t$; so spherical domain of initial radius $R(0)$ vanishes in time $t \sim R^2(0)$. Conversely, after time t expect all surviving domains to be of size $\sim t^{1/2}$ or bigger; suggests growth law of domain size $L(t) \sim t^{1/2}$.

But domains aren't all spherical, more like connected network, so need to generalize approach. Assumption: If domains are large, profile of ϕ across all domain walls is same as for a flat domain wall. So if g is a spatial coordinate locally orthogonal to the domain wall (i.e., measuring distance from the wall; for a spherical domain could take $g = r$) can write $\phi(\mathbf{r}, t) = \phi(g(\mathbf{r}), t)$. Then $\hat{\mathbf{g}} \equiv \nabla g$ has unit length, because g measures distance. So

$$\nabla \phi = \frac{\partial \phi}{\partial g} \nabla g = \frac{\partial \phi}{\partial g} \hat{\mathbf{g}}$$

and

$$\nabla^2 \phi = \frac{\partial^2 \phi}{\partial g^2} \hat{\mathbf{g}} \cdot \hat{\mathbf{g}} + \frac{\partial \phi}{\partial g} \nabla \cdot \hat{\mathbf{g}} = \frac{\partial^2 \phi}{\partial g^2} + \frac{\partial \phi}{\partial g} \nabla \cdot \hat{\mathbf{g}}$$

So the TDGL (2) becomes

$$\frac{\partial \phi}{\partial t} = \frac{\partial^2 \phi}{\partial g^2} + \frac{\partial \phi}{\partial g} \nabla \cdot \hat{\mathbf{g}} - V'(\phi) \tag{18}$$

For l.h.s., use reciprocity relation between ϕ, g and t (which are connected by the function $\phi(g,t)$):

$$d\phi = \frac{\partial \phi}{\partial g} dg + \frac{\partial \phi}{\partial t} dt = \frac{\partial \phi}{\partial g} \left(\frac{\partial g}{\partial \phi} d\phi + \frac{\partial g}{\partial t} dt \right) + \frac{\partial \phi}{\partial t} dt$$

Since the coefficients of $d\phi$ and dt on the r.h.s. must be 1 and 0, respectively, it follows that $(\partial\phi/\partial g)(\partial g/\partial t) + \partial\phi/\partial t = 0$. So (18) becomes

$$-\frac{\partial\phi}{\partial g}\frac{\partial g}{\partial t} = \frac{\partial^2\phi}{\partial g^2} + \frac{\partial\phi}{\partial g}\nabla\cdot\hat{\mathbf{g}} - V'(\phi)$$

If the profile of ϕ across the domain wall is the same as for a flat wall, as assumed, then the first and third terms on the r.h.s. cancel because of (11), so that $\partial g/\partial t = -\nabla\cdot\hat{\mathbf{g}}$. Now $\partial g/\partial t$ is just the domain wall velocity v: the derivative is taken at constant ϕ; the centre of the wall is at $\phi = 0$ and $\partial g/\partial t$ gives the speed of movement of this surface. Also, $K = \nabla\cdot\hat{\mathbf{g}}$ is $d-1$ times the mean local curvature of the domain wall. So we have the *Allen-Cahn equation*:

$$v = -\nabla\cdot\hat{\mathbf{g}} = -K \tag{19}$$

which is the generalization of (17) that we wanted (for a spherical domain, $K = (d-1)/R$). Important: Tells us that motion of domain walls is determined only by their curvature. Details of potential $V(\phi)$ are not important: V just serves to establish well-defined walls between domains.

From the Allen-Cahn equation can now estimate the growth of the typical domain size L more generally. If $L(t)$ is the only relevant length scale in the system (*i.e.* if the scaling assumption holds) then the wall velocity is $v \sim dL/dt$, and the curvature $K \sim 1/L$; thus $L(dL/dt) \sim$ constant, which gives $L(t) \sim t^{1/2}$ as before.

4.2 Conserved order parameter

Why are things different here? Domain walls can't move independently because of conservation law; material must be transported via diffusion through the bulk. So expect (and get!) slower growth of typical domain size $L(t)$.

Look first at bulk (away from domain walls) where ϕ should be approximately constant (and close to ± 1). Set $\phi = \phi_+ + \tilde{\phi}$, with ϕ_+ near 1, and linearize (4):

$$\frac{\partial\tilde{\phi}}{\partial t} = -\nabla^4\tilde{\phi} + V''(\phi_+)\nabla^2\tilde{\phi}$$

In scaling regime, length scale $L(t)$ is large, so ∇^4 term should be negligible compared to $\nabla^2 \Rightarrow$ diffusion equation for $\tilde{\phi}$. Can simplify further: Inside a domain of size L, $\tilde{\phi}$ relaxes (diffusion!) in time $t_{\mathrm{diff}} \sim L^2$. But will see below that wall velocity is only $v \sim 1/L^2$; so walls only move by $\sim L^0 \ll L$ in time t_{diff}. So can assume that $\tilde{\phi}$ (and hence ϕ) is always at equilibrium with the domain walls, which give the boundary conditions as we'll see shortly. Hence, in the bulk, have simply Laplace's equation $\nabla^2\phi = 0$.

To find boundary conditions at domain walls, switch first from ϕ to μ. From (3),

$$\mu = -\nabla^2\phi + V'(\phi) \tag{20}$$

In bulk, can again set $\phi = \phi_+ + \tilde{\phi}$ (similarly in $\phi \approx -1$ domains) and linearize; gives $\mu = -\nabla^2\tilde{\phi} + V''(\phi_+)\tilde{\phi} + V'(\phi_+)$. For large L, first term (spatial variation) is negligible again; so $\mu = V''(\phi_+)\tilde{\phi} + V'(\phi_+)$. Hence, since $\tilde{\phi}$ and ϕ do, μ also obeys Laplace equation $\nabla^2\mu = 0$.

Near a domain wall, both terms in $\mu = -\nabla^2\phi + V'(\phi)$ are important. As in the derivation of the Allen-Cahn equation, can introduce coordinate g orthogonal to wall, to get (compare (18))

$$\mu = -\frac{\partial^2\phi}{\partial g^2} - \frac{\partial\phi}{\partial g}\nabla\cdot\hat{\mathbf{g}} + V'(\phi)$$

Multiply by $\partial\phi/\partial g$ and integrate over $g = -\infty\ldots\infty$; then the first term on r.h.s. drops out (since $\partial/\partial g = 0$ far from the domain wall):

$$\int dg\,\mu(g)\frac{\partial\phi}{\partial g} = -\int dg\,\left(\frac{\partial\phi}{\partial g}\right)^2\nabla\cdot\hat{\mathbf{g}} + \Delta V$$

where $\Delta V = V(\phi_+) - V(\phi_-)$ if ϕ_+ and ϕ_- are the bulk order parameter values away from the wall. Because $\partial\phi/\partial g$ is different from zero only near the wall, can replace the smoothly varying $\mu(g)$ and $K = \nabla\cdot\hat{\mathbf{g}}$ by their values at the wall and pull out of integrals; using also (13) get

$$\mu\Delta\phi = -\sigma K + \Delta V \tag{21}$$

where $\Delta\phi = \phi_+ - \phi_-$. This is a general relation between the vales of μ at the domain wall and the local wall curvature K. If $\phi_\pm \approx \pm 1$ (which is true once domains are large), then $\Delta V \approx 0$ and $\Delta\phi \approx 2$ and we get the *Gibbs-Thomson boundary condition*

$$\mu = -\frac{\sigma K}{2} \tag{22}$$

which determines μ on the domain walls; in the bulk (inside the domains) μ satisfies the Laplace equation $\nabla^2\mu = 0$.

Once we have μ, we can get the interface velocity. Consider a cross-section of the domain wall, in the direction of the coordinate g. The evolution of $\phi(g,t)$ obeys the continuity equation $\partial\phi/\partial t = -\nabla\cdot\mathbf{j}$, with $\mathbf{j} = -\nabla\mu$; along our one-dimensional cross-section, $\partial\phi/\partial t = -\partial j/\partial g$. Integrating over a range of g which includes the interface, get

$$\frac{\partial}{\partial t}\int dg\,\phi = -\Delta j = \Delta\left(\frac{\partial\mu}{\partial g}\right) = \Delta(\hat{\mathbf{g}}\cdot\nabla\mu) \tag{23}$$

where Δ's indicate differences in values between the two sides of the domain wall as before. On the other hand, if the domain wall is moving with speed, then $(\partial/\partial t)\int dg\,\phi = -v\Delta\phi$ and comparing with (23) get

$$v = -\frac{\Delta(\hat{\mathbf{g}}\cdot\nabla\mu)}{\Delta\phi} \tag{24}$$

Simple application: Spherical domain, radius R, of $\phi_- = -1$ inside 'sea' of $\phi_+ = +1$. Using (20) gives $\mu = V'(1) = 0$ at infinity. On the domain wall, at $r = R$, on the other hand, have $\mu = -\sigma K/2 = -\sigma/R$ from (22). Solution of Laplace equation $\nabla^2\mu = 0$ outside domain that obeys these boundary conditions is $\mu = -\sigma/r$; inside simply $\mu = -\sigma/R$. Just outside the domain wall have $\hat{\mathbf{g}}\cdot\nabla\mu = \partial\mu/\partial g = \partial\mu/\partial r = \sigma/R^2$; just inside the value is zero. So from (24), get the wall velocity $v = dR/dt$ as

$$\frac{dR}{dt} = -\frac{\sigma}{2R^2} \tag{25}$$

Integrate: $R^3(t) = R^3(0) - (3\sigma/2)t$. So the 'evaporation time' of a bubble of initial radius R is $t \sim R^3$, much longer than $t \sim R^2$ for the non-conserved case. This makes sense: For conserved order parameter, droplet can only shrink if material (think of ϕ as particle density) is transported to it by diffusion from infinity. $t \sim R^3$ suggests that typical domain size should generally scale as $L(t) \sim t^{1/3}$. Can also be seen from the general equations: From (22), μ on domain walls is $\sim 1/L$ and varies (since the curvature K does) over length scales $\sim L$. The interface velocity v scales as $\nabla\mu$, which gives $v \sim 1/L^2$ (as claimed above, to argue that ϕ and μ always equilibrate by diffusion with the boundary conditions on the domain walls, before the domain walls can move noticeably). This gives $dL/dt \sim 1/L^2$, and therefore $L(t) \sim t^{1/3}$ as suggested already by the result for the spherical domain.

Growth 'just inside' a two-phase region: Lifshitz-Slyozov-Wagner theory

So far have got results for the growth of typical domain size in scaling regime; $L \sim t^{1/2}$ for non-conserved and $L \sim t^{1/3}$ for conserved order parameters. Can we say more, e.g. about the structure of domains, their size distribution? Generally tricky, but possible in a limiting case: For conserved order parameter, if ϕ_0 is just below 1. Corresponds to a 'shallow' quench: Values of $\phi_0 > 1$ are stable as homogeneous phases, so ϕ_0 just below 1 means that we have brought system just inside a two-phase region.

Intuition – what should happen? At long times, have domains of $\phi = \pm 1$, the equilibrium phases. The -1 domains then occupy a fraction $(1-\phi_0)/2$ of volume, and the $+1$ domains a fraction $(1+\phi_0)/2$; this is needed to get on average $\phi_0 = -(1-\phi_0)/2 + (1+\phi_0)/2$ (since ϕ is conserved). If $\epsilon_0 = 1-\phi_0$ is small, volume fraction of -1 phase is $\epsilon_0/2$, also small. So -1 phase is always 'minority phase'; minority domains are far away from each other and have negligible chance of coalescing. So always have spherical minority domains, in a sea of majority phase. Will show that, over time, small domains 'evaporate' and 'condense' onto larger domains; so get decreasing number of domains of increasing size. Must be such that total volume fraction occupied by minority phase is constant ($\epsilon_0/2$ as shown above). LSW theory calculates the size distribution of the domain radii, and the growth law for the typical domain size. For non-infinitesimal ϵ_0, LSW theory should be good description while domains are far apart; breaks down when domains start coalescing and form a connected structure.

In the LSW limit $\epsilon_0 = 1-\phi_0 \ll 1$, can consider domains separately, so look at a single domain of ϕ_- inside sea of ϕ_+. At long times, will have $\phi_\pm \to \pm 1$ but not initially (where $\phi_+ = \phi_0$), so keep $\phi_\pm$ general for now. At infinity, from (20), have

$$\mu = V'(\phi_+)$$

For the boundary condition on the spherical domain wall (at $r = R$) we now need to use the general form (21) of the Gibbs-Thomson boundary condition (because $\phi_\pm \neq \pm 1$); since $K = 2/R$, get

$$\mu = \frac{\Delta V}{\Delta\phi} - \frac{2\sigma}{R\Delta\phi}$$

where $\Delta\phi = \phi_+ - \phi_-$ and $\Delta V = V(\phi_+) - V(\phi_-)$. The solution of the Laplace equation $\nabla^2\mu = 0$ subject to these boundary conditions will be $\mu = a + b/r$ for $r > R$, and $\mu = a + b/R =$ constant for $r \leq R$ as before, for appropriate constants a and b. Get:

$$\mu = V'(\phi_+) + \left(\frac{\Delta V}{\Delta\phi} - V'(\phi_+)\right)\frac{R}{r} - \frac{2\sigma}{\Delta\phi}\frac{1}{r} \qquad (r > R) \tag{26}$$

$$\mu = \frac{\Delta V}{\Delta\phi} - \frac{2\sigma}{R\Delta\phi} \qquad (r \leq R) \tag{27}$$

The result (27) determines ϕ_- as a function of ϕ_+, the order parameter value in the infinite 'sea', and the droplet radius R: From (20) we know that, well inside the droplet, $\mu = V'(\phi_-)$ and comparing with (27) gives the required condition on ϕ_-

$$V'(\phi_-) = \frac{\Delta V}{\Delta\phi} - \frac{2\sigma}{R\Delta\phi} = \frac{V(\phi_+) - V(\phi_-)}{\phi_+ - \phi_-} - \frac{2\sigma}{R(\phi_+ - \phi_-)} \tag{28}$$

(It is easy to show that, for the critical droplet with radius (7) that is initially nucleated inside a sea of $\phi = \phi_0$, this reduces to $V'(\phi_-) = V'(\phi_0)$ as found above.)

From (26,27), we can find $\partial\mu/\partial r$ just inside and outside the domain wall, and get the domain wall velocity from (24) as

$$\frac{dR}{dt} = \left(\frac{\Delta V}{(\Delta\phi)^2} - \frac{V'(\phi_+)}{\Delta\phi}\right)\frac{1}{R} - \frac{2\sigma}{(\Delta\phi)^2}\frac{1}{R^2} \tag{29}$$

In general, for fixed ϕ_+, the r.h.s. is a complicated function of R because ϕ_- itself depends on R through the condition (28). Fortunately, when $\epsilon = 1 - \phi_+$ is small as we assumed, then one can also show that $\phi_- \approx -1$. Then we can set $\Delta\phi = 2$ to leading order; also, ΔV is of second order in the small quantities $\epsilon = 1 - \phi_+$ and $-1 - \phi_-$ and can be neglected. Finally, $V'(\phi_+) \approx -V''(1)\epsilon$ and so (29) simplifies to

$$\frac{dR}{dt} = \frac{V''(1)\epsilon}{2R} - \frac{\sigma}{2R^2} = \frac{\sigma}{2R}\left(\frac{1}{R_c} - \frac{1}{R}\right) \tag{30}$$

where $R_c = \sigma/[V''(1)\epsilon]$ is the critical droplet radius. Initially, when droplets of minority phase are first nucleated, $\epsilon = \epsilon_0$ and the present definition for R_c then agrees with (7) found earlier (if (7) is expanded appropriately for small ϵ_0).

Equation (30) tells us how the growth of droplets will proceed: Droplets smaller than the critical radius will shrink to zero, while larger ones will grow. As the large droplets grow, the volume fraction of minority phase grows towards its long-time value of $\epsilon_0/2$. At the same time, the deviation $\epsilon = 1 - \phi_+$ of the order parameter in the majority phase from its equilibrium value will go to zero; the critical radius thus *increases* (and diverges for $t \to \infty$). So there are two competing effects: Large droplets of minority phase grow, but as they do so, the critical radius R_c also increases and 'overtakes' the radius R of some droplets. These will then shrink to zero, while the largest droplets continue to grow, increasing R_c further etc.

Consider the distribution of droplet radii $n(R,t)$; $n(R,t)dR$ is the number of droplets per unit volume with radii between R and $R + dR$. The total number density of droplets is therefore $n_{\text{total}} = \int dR\ n(R,t)$. The fraction of system volume occupied by the droplets is, for long times, equal to $\epsilon_0/2$ so that

$$V_d \int dR\, R^d n(R,t) = \epsilon_0/2 \tag{31}$$

where V_d is the volume of a unit sphere in d dimensions. $n(R,t)$ evolves in time according to a continuity equation,

$$\frac{\partial n(R,t)}{\partial t} + \frac{\partial}{\partial R}[v(R)n(R,t)] = 0$$

where $v(R)$ is the rate of change of the radius of a droplet of size R; generalize (30) to arbitrary dimension (> 2) to write this as

$$v(R) = \frac{dR}{dt} = \frac{\alpha_d}{R}\left(\frac{1}{R_c} - \frac{1}{R}\right) \tag{32}$$

where, for $d = 3$, $\alpha_d = \sigma/2$.

From discussion above, reasonable to assume that distribution of droplet radii will scale with R_c, so write

$$n(R,t) = R_c^{-1}\tilde{n}(x,t), \qquad \text{where} \quad x = R/R_c$$

Here $\tilde{n}(x,t)$ is normalized exactly as $n(R,t)$, *i.e.* $\int dx\, \tilde{n}(x,t) = \int dR\, n(R,t)$ and so obeys a continuity equation of the same form,

$$\frac{\partial \tilde{n}(x,t)}{\partial t} + \frac{\partial}{\partial x}[\tilde{v}(x,t)\tilde{n}(x,t)] = 0 \tag{33}$$

where

$$\tilde{v}(x,t) = \frac{dx}{dt} = \frac{\dot{R}}{R_c} - \frac{R\dot{R}_c}{R_c^2} = \frac{\alpha_d}{R_c^3}\left(\frac{1}{x} - \frac{1}{x^2}\right) - \frac{\dot{R}_c}{R_c}x \tag{34}$$

is rate of change of x (dependent not just on x but also on time, through $R_c(t)$).

Volume fraction (31) of minority phase is, in terms of $\tilde{n}(x,t)$,

$$V_d R_c^d \int dx\, x^d \tilde{n}(x,t) = \epsilon_0/2 \tag{35}$$

at long times. Since $R_c \to \infty$ for $t \to \infty$, this means that $\tilde{n}(x,t)$ itself cannot become time-independent; but its shape

$$f(x,t) = R_c^d \tilde{n}(x,t)$$

should, if we have a scaling limit. If indeed f becomes independent of t, then $\partial\tilde{n}/\partial t = -d\,\dot{R}_c\,R_c^{-d-1}f$ for long times and inserting into (33) gives

$$-d\frac{\dot{R}_c}{R_c}f(x) + \frac{\partial}{\partial x}[\tilde{v}(x,t)f(x)] = 0 \tag{36}$$

or, after inserting $\tilde{v}(x,t)$ from (34) and rearranging,

$$\left[-(d+1)\frac{\dot{R}_c}{R_c} + \frac{\alpha_d}{R_c^3}\left(-\frac{1}{x^2} + \frac{2}{x^3}\right)\right]f(x) + \left[\frac{\alpha_d}{R_c^3}\left(\frac{1}{x} - \frac{1}{x^2}\right) - \frac{\dot{R}_c}{R_c}x\right]f'(x) = 0 \tag{37}$$

To get a time-independent solution for $f(x)$, all time-dependences must reduce to an overall factor, hence

$$\frac{\dot{R}_c}{R_c} = \gamma \frac{\alpha_d}{R_c^3} \tag{38}$$

from which we get $R_c(t) = (3\gamma\alpha_d t)^{1/3}$ for large t; the exponent has the expected value 1/3 for a system with conserved order parameter. Using (38) in (37) gives

$$\left[-(d+1)\gamma - \frac{1}{x^2} + \frac{2}{x^3}\right] f(x) + \left[\frac{1}{x} - \frac{1}{x^2} - \gamma x\right] f'(x) = 0$$

so that

$$\frac{d \ln f}{dx} = \frac{1}{x} \frac{2 - x - (d+1)\gamma x^3}{\gamma x^3 - x + 1} \tag{39}$$

We almost have our result now – but what is the value of γ? If in (39) the denominator $g(x) = \gamma x^3 - x + 1$ has no zeros for positive x, then $f(x)$ remains nonzero asymptotically, with $d \ln f/dx \sim -(d+1)/x$, so that $f \sim x^{-d-1}$. But then the normalization integral (35), which is

$$V_d \int dx\, x^d f(x) = \epsilon_0/2 \tag{40}$$

in terms of $f(x)$, would be divergent, so we have a contradiction. So the denominator $g(x)$ must have zeros, and $f(x)$ will drop to zero at the first zero along the positive x-axis and be zero for all x greater than that. The boundary of the regime where $g(x)$ has zeros is located at the value of γ where $g(x)$ just touches the x-axis from above, in a double zero. There, have the two conditions $g(x) = \gamma x^3 - x + 1 = 0$ and $g'(x) = 3\gamma x^2 - 1 = 0$, from which it follows that $-x + 1 = -x/3$, hence $x = 3/2$ and $\gamma \equiv \gamma_0 = 1/(3x^2) = 4/27$. The summary of the discussion so far is then that we need to have $\gamma \leq \gamma_0$ to get a properly normalizable $f(x)$.

LSW argued that in fact the correct solution for $f(x)$ is obtained for γ exactly equal to γ_0. To see why, return to (34), which gives the rate of change of the normalized radius $x = R/R_c$ of a droplet. Using the result (38) for the time evolution of R_c, $\tilde{v} = dx/dt$ becomes

$$\frac{dx}{dt} = \frac{1}{3\gamma t}\left(\frac{1}{x} - \frac{1}{x^2} - \gamma x\right) = \frac{1}{3\gamma t} h(x) \qquad \text{where} \quad h(x) = -\frac{g(x)}{x^2}$$

For $\gamma < \gamma_0$, $h(x)$ – which has the same zeros as $g(x)$ – has two zeros x_1 and x_2 on the positive x-axis, and is positive in the range between x_1 and x_2. (Sketch this.) All droplets with values of x initially in this range will then evolve towards x_2 for $t \to \infty$; but then would have a finite density of droplets with diverging radius $R = R_c x_2$, contradicting the fact that the volume fraction of minority phase must stay finite. Since we have already excluded $\gamma > \gamma_0$, $\gamma = \gamma_0$ is the only solution which doesn't give a contradiction. (In fact, what must happen is that γ converges slowly to γ_0 from below; it cannot become equal to γ_0 at finite time since all droplets with $x > 3/2$ at that time would become stuck at $x = 3/2$ for $t \to \infty$, giving the same contradiction as for $\gamma < \gamma_0$.)

Having shown that $\gamma = \gamma_0 = 4/27$, just have to integrate (39) now. Use

$$\frac{1}{x} \frac{2 - x - (4/27)(d+1)x^3}{(4/27)x^3 - x + 1} = \frac{2 - x - (4/27)(d+1)x^3}{(4/27)x(x-3/2)^2(x+3)} \tag{41}$$

$$= \frac{2}{x} - \frac{4d/9 + 1}{x+3} - \frac{5d/9 + 2}{x - 3/2} - \frac{d/2}{(x-3/2)^2} \tag{42}$$

which gives

$$f = \text{constant} \times x^2 (x+3)^{-4d/9-1} (3/2 - x)^{-5d/9-2} \exp[-(d/2)/(3/2 - x)] \tag{43}$$

The constant follows from the normalization condition (40), and is proportional to ϵ_0; the number of droplets is therefore proportional to the final volume fraction of minority phase, as expected. The function $f(x)$ is plotted in Fig. 3.

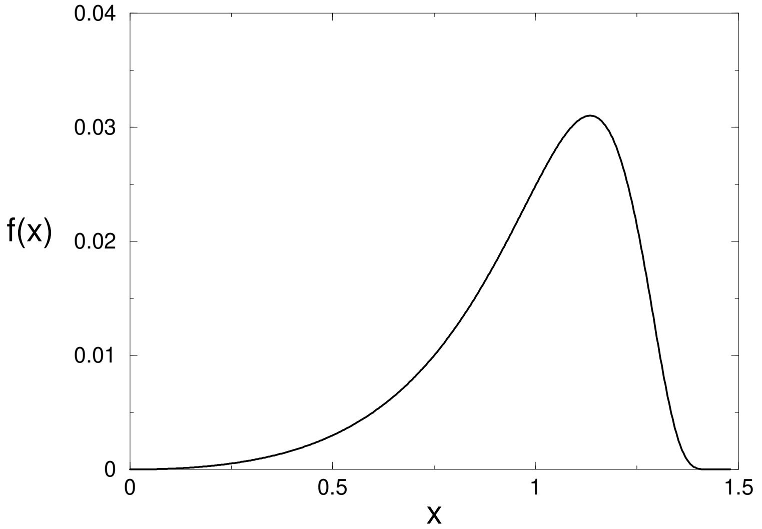


Figure 3: The distribution $f(x)$ of scaled droplet radii $x = R/R_c$, in $d = 3$ dimensions as predicted by LSW theory.

A final check on the solution is to verify the rate at which droplets disappear; from the normalization condition (35), the number density of droplets should scale as $R_c^{-d} \sim t^{-d/3}$, so the rate of droplet disappearance is $\sim t^{-d/3-1}$. To check this, look at the continuity equation (33), which gives for the total number density n_{total} of droplets

$$\frac{dn_{\text{total}}}{dt} = \frac{\partial}{\partial t} \int dx\, \tilde{n}(x,t) = -\tilde{v}(x,t)\tilde{n}(x,t)\Big|_{x=0}^{x=\infty}$$

If $\tilde{n} = R_c^{-d} f$ with f as calculated above, the $x = \infty$ boundary doesn't contribute since $f(x) = 0$ for $x > 3/2$, so that

$$\frac{dn_{\text{total}}}{dt} = \lim_{x\to 0} \tilde{v}(x,t) R_c^{-d} f(x) = \lim_{x\to 0} \left(-\frac{\alpha_d}{R_c^3 x^2}\right) R_c^{-d} \times \text{constant} \times x^2 \sim R_c^{-d-3} \sim t^{-d/3-1}$$

just as expected.

As hinted at above, for $d = 2$ the calculation breaks down; this is because the proportionality constant α_d in (32) becomes zero (which is related to the fact that the solution of Laplace's equation crosses over from $\sim r^{2-d}$ to $\ln r$ when $d \to 2$). Then get logarithmic corrections, but depending on how the limit is taken; for $\epsilon_0 \to 0$ before $t \to \infty$, find $R_c(t) \sim (t/\ln t)^{1/3}$, while for $t \to \infty$ first get $R_c(t) \sim (t/\ln(1/\epsilon_0))^{1/3}$.

5 Outlook

We've looked only at the simplest scenarios. Behaviour gets much richer, for example, when order parameter ϕ is vector. Then structure of 'defects' changes (the only defects we had to consider were domain walls), to e.g. vortices, strings, monopoles etc. These dominate much of the phase ordering behaviour; they also fix the short-range behaviour of correlation functions.

Much more complicated: Binary liquids etc., where transport isn't just by diffusion but also by convection; then Navier-Stokes comes into play and need to solve coupled equations for order parameter and velocity fields. Even when velocity field is imposed and order parameter only 'advected', get quite non-trivial problems; e.g. stretching and break-up of domains.

6 A little exercise: Cahn-Hilliard theory for mixtures

Consider liquid-gas phase separation in a system which contains a mixture of n different particles, with densities $\phi_1(\mathbf{r}) \ldots \phi_n(\mathbf{r}) \equiv \boldsymbol{\phi}(\mathbf{r})$. An appropriate generalization to this case of the free energy functional used in the lectures is

$$F[\boldsymbol{\phi}(\mathbf{r})] = \int d\mathbf{r} \left[\frac{1}{2} \sum_{i,j} G_{ij} \nabla\phi_i(\mathbf{r}) \cdot \nabla\phi_j(\mathbf{r}) + V(\boldsymbol{\phi}(\mathbf{r})) \right]$$

where $\mathbf{G}$, the $n \times n$ matrix with elements G_{ij}, is positive definite.

(a) Derive the Cahn-Hilliard equations for the time evolution of the $\phi_i(\mathbf{r})$.

(b) Assuming that the system is initially homogeneous apart from small fluctuations, $\boldsymbol{\phi}(\mathbf{r}, 0) \approx \boldsymbol{\phi}_0$, linearize the Cahn-Hilliard equation in the small deviations $\tilde{\boldsymbol{\phi}}(\mathbf{r}) = \boldsymbol{\phi}(\mathbf{r}) - \boldsymbol{\phi}_0$. Solve it in Fourier space to show that the solution for wavevector $\mathbf{k}$ is

$$\tilde{\boldsymbol{\phi}}_{\mathbf{k}}(t) = \sum_{\alpha} \boldsymbol{\psi}_k^{\alpha} e^{\omega_k^{\alpha} t}$$

where, for given $k = |\mathbf{k}|$, the $\boldsymbol{\psi}_k^{\alpha}$ and ω_k^{α} are the eigenvectors and eigenvalues of the matrix

$$-k^4 \mathbf{G} - k^2 \mathbf{H}$$

and $\mathbf{H}$ is the matrix of second derivatives of V, $\partial^2 V / \partial\phi_i \partial\phi_j$, at $\boldsymbol{\phi}_0$.

(c) Deduce that, if $\mathbf{H}$ is positive definite, the system is stable in the sense that initial fluctuations will die away.

(d) Conversely, show that if $\mathbf{H}$ has negative eigenvalues, then there will be unstable fluctuation modes that grow in time. Explain why, on the boundary between the cases (c) and (d), one has $\det(H) = 0$. [Note: This is the standard thermodynamic criterion for spinodals in n-component systems.]

(e) Finally, consider a quench just into the spinodal region, i.e. a value of $\boldsymbol{\phi}_0$ for which $\mathbf{H}$ has only a single negative eigenvalue $-\lambda$ with eigenvector $\boldsymbol{\psi}$. If $\mathbf{G}$ is the identity matrix, show that the fastest growing fluctuation in the system has composition $\tilde{\boldsymbol{\phi}}_{\mathbf{k}} \propto \boldsymbol{\psi}$ and wavevector $k = \sqrt{\lambda/2}$.