Cahn-Hilliard Kinetics and Spinodal Decomposition in a Diffuse System

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1 Background

My interest in this subject has been long standing, but only recently has my research been pushing me towards a more quantitative understanding of this material. A great many systems, both physical and abstract, have constituents with specific energetic interactions. When a system of such interacting particles is subject to fluctuations of a well-defined spectrum (*e.g.* an exponential distribution of energy, like Boltzmann statistics) the system attempts to maximize its degree of *disorder* in a way that is proportional to the magnitude of these fluctuations (*i.e.* temperature). This is, of course, the notion of entropy, and the origin of the energetic term $-TS$ in thermodynamic potentials. Simultaneously, each particle in the system is trying to minimize its energy of interaction with neighboring particles, setting up a competition between the entropy of mixing and the enthalpic benefit of having certain preferred neighbors. This competition leads to a temperature-dependent phase transition.

In the case explored below, this is a so-called 'order-disorder' or 'second-order' transition. Effectively, this means that below a certain critical temperature (or critical value of some other parameter in the system) particles in the system will organize themselves such that enthalpy is minimized. Most often, the specific interactions are such that like-likes-like, hence particles organize spatially by similar type to form unique phases.

The purpose of this tutorial is both to understand some aspects of this entropy-enthalpy competition and subsequently the kinetics of phase separation.

2 Derivation of the Cahn-Hilliard Equation

For the purposes of this tutorial let us assume we are dealing with a 2D binary fluid composed of A and B particles in the limit where diffusion is the major transport mechanism (as opposed to hydrodynamics). Let us define the order-parameter field ϕ such that $\phi = 1$ is a phase completely made of A particles, and $\phi = -1$ is a phase completely made of B particles, with a linear interpolation between those two phases. We assume the interactions of AA and BB are favorable, while $AB = BA$ are unfavorable. If a particle A and a particle B are interacting, this means there is an unfavorable energy associated with a gradient in the field $\nabla\phi$. Obviously, the direction of that gradient does not matter (*i.e.* we have rotational symmetry) and we want energy and its derivatives to be well-defined, thus gradients in the field must be energetically penalized by $|\nabla\phi|^2$ to obey that symmetry.

Many entire text books have been written on the theory of phase transitions, hence we will not dwell on that topic here. We assume that due to the inter-molecular interactions, and interactions with any external fields there is a potential energy landscape, $V(\phi, T)$, that has a temperature dependent transition from a random, high temperature phase, to an ordered, low temperature phase. In the Landau formalism, this can be approximated by a potential of the form

$$V(\phi, T) = c_1(T)\phi^2 + c_2(T)\phi^4, \tag{1}$$

where the coefficients c_i are connected to the precise Hamiltonian of the system, but are unimportant for our analysis. Clearly, when $(\partial^2 V/\partial\phi^2)|_{\phi=0} = 0$, or in other words when c_1 switches sign, something funny happens - the one minimum at $\phi = 0$ vanishes, and yields a state with two distinct minima at non-zero field values - this is the phase transition. With no loss of generality, we will rewrite this potential as

$$V = \frac{1}{4}(a - (b\phi)^2)^2. \tag{2}$$

The stable phases, given by $\partial V/\partial\phi = 0$, are

$$\phi^* = \pm\frac{\sqrt{a}}{b}, \tag{3}$$

with the clear interpretation that real values of ϕ^* are always stable (*i.e.* $a > 0$); the energy barrier between those fixed points is at $\phi = 0$.

We combine this potential with the boundary penalty to form an energy functional for the entire field ϕ in space and time

$$F[\phi(\bar{x}, t)] = \int \left[\frac{1}{4}(a - (b\phi)^2)^2 + \frac{\gamma}{2}|\nabla\phi|^2\right] \mathrm{d}\bar{a} \tag{4}$$

where γ is a constant that penalizes phase boundaries, and has its microscopic origins in the interactions between the A and B particles. Now it's time to apply physical intuition - if ϕ is understood as a measure of particle number, and F is the energy of a particular configuration of ϕ, then the variation in F with respect to ϕ is quantifying how the energy changes when particles change position, or in other words, it defines the chemical potential of the system

$$\frac{\delta F}{\delta\phi} = \mu. \tag{5}$$

From that one simple idea, a quick series of steps brings us to the Cahn-Hilliard equation. All we need to do is remember that Fick's First Law states that the flux of particles in a system is proportional to the gradient of the chemical potential

$$\bar{J} = -D\nabla\mu, \tag{6}$$

and that we cannot create, destroy or switch particles (as we have currently set things up), which means this flux must obey a continuity equation

$$\frac{\partial\phi}{\partial t} + \nabla\cdot\bar{J} = 0, \tag{7}$$

or

$$\frac{\partial\phi}{\partial t} = D\nabla^2\mu. \tag{8}$$

To finish off the derivation we need only calculate the chemical potential

$$\mu = \frac{\delta F}{\delta \phi} = (b^4\phi^3 - ab^2\phi) - \gamma\nabla^2\phi. \tag{9}$$

Finally

$$\frac{\partial \phi}{\partial t} = D\nabla^2\left[(b^4\phi^3 - ab^2\phi) - \gamma\nabla^2\phi\right], \tag{10}$$

where D is playing the role of an effective diffusion coefficient, and in the next section we will extract out a natural length and time scale, such that there is only one free parameter in the Cahn-Hilliard equation.

2.1 Deriving a Natural Length and Time Scale

Let's make the assumption that this system has a natural length scale λ and natural time scale τ, such that $t = \tau\hat{t}$ and $\bar{x} = \lambda\hat{x}$. Then the differentials can be rewritten

$$\frac{\partial}{\partial t} = \frac{1}{\tau}\frac{\partial}{\partial \hat{t}} \tag{11}$$

and

$$\nabla^n = \frac{1}{\lambda^n}\nabla^n_{\hat{x}}. \tag{12}$$

Then the Cahn-Hilliard equation can be written (leaving the subscript off ∇)

$$\frac{\partial \phi}{\partial \hat{t}} = \nabla^2\left[\frac{D\tau ab^2}{\lambda^2}(\alpha^2\phi^3 - \phi) - \frac{D\tau\gamma}{\lambda^4}\nabla^2\phi\right] \tag{13}$$

with $\alpha = b/\sqrt{a}$. This leaves us with two equations and two unknowns, hence we find

$$\tau = \frac{\gamma}{a^2b^4D} \tag{14}$$

and

$$\lambda = \frac{1}{b}\sqrt{\frac{\gamma}{a}}. \tag{15}$$

The Cahn-Hilliard equation is now

$$\frac{\partial \phi}{\partial \hat{t}} = \nabla^2\left[\alpha^2\phi^3 - \phi - \nabla^2\phi\right]. \tag{16}$$

Already we notice two things - first we retrieve the well-known result that the length scale diverges at the phase transition (*i.e.* $\lim \lambda_{a\to 0} = \infty$). Second, we see that the nonlinearity in the PDE is strongest near the phase transition (*i.e.* $\lim \alpha_{a\to 0} = \infty$).

For a given initial condition, $\phi(\hat{x}, 0)$, this equation can be numerically solved, however to make analytic headway, we will employ the so-called 'strong-segregation' limit. This simply means that we are far from the phase transition where particles A and B strongly seek their own kind, such that $\alpha \ll 1$. Hence the Cahn-Hilliard equation is written in a linearized form

$$\frac{\partial \phi}{\partial \hat{t}} = -\nabla^2\left[\phi + \nabla^2\phi\right]. \tag{17}$$

The next section will use this linearized equation to derive wavelength-dependent dynamics and the general linearized solution.

3 Kinetics in Fourier Space

Given the orthonormality and completeness relations, we know that we can represent ϕ by its Fourier Transform

$$\phi(\hat{x},\hat{t}) = \int A_k(\hat{t}) e^{-i\bar{k}\cdot\hat{x}} \mathrm{d}\bar{k}. \tag{18}$$

We can also represent derivatives in space and time using the Fourier Transform, such that

$$\frac{\partial \phi}{\partial \hat{t}} = \int \dot{A}_k(\hat{t}) e^{-i\bar{k}\cdot\hat{x}} \mathrm{d}\bar{k} \tag{19}$$

and for $n = 2, 4$

$$\nabla^n \phi = \int A_k(\hat{t})(-i)^n (\bar{k}\cdot\bar{k})^{n/2} e^{-i\bar{k}\cdot\hat{x}} \mathrm{d}\bar{k} = \int A_k(\hat{t}) i^n |k|^n e^{-i\bar{k}\cdot\hat{x}} \mathrm{d}\bar{k}. \tag{20}$$

Using these two relations, we can write an *independent* dynamic equation for the evolution of each Fourier component

$$\dot{A}_k = (|k|^2 - |k|^4) A_k. \tag{21}$$

This is the classic 'spinodal decomposition' result, stating that instabilities with wavelengths near $|k| = 1/\sqrt{2}$ grow fastest, and that all wavelengths with $|k| > 1$ are exponentially damped, while all wavelengths with $|k| < 1$ grow exponentially. Physically this results in a rapid evolution of features on a certain length scale, followed by a long-time evolution of long-wavelength features (see Figure 1a). Additionally, the dynamics shows a kind of 'scale-invariance', whereby evolution in time is equivalent to increasing the spatial scaling (see Figure 1b).

Lastly, the general solution for the linearized equation is found by solving the dynamics for each wave vector

$$A_k(\hat{t}) = A_k(0) e^{(|k|^2 - |k|^4)\hat{t}}. \tag{22}$$

The initial condition, $\phi(\hat{x}, 0)$, specifies the initial conditions for each wavelength

$$A_k(0) = \frac{1}{2\pi} \int \phi(\hat{x}, 0) e^{i\bar{k}\cdot\hat{x}} \mathrm{d}\hat{x}, \tag{23}$$

such that the general solution is written

$$\phi(\hat{x},\hat{t}) = \int A_k(0) e^{(|k|^2 - |k|^4)\hat{t}} e^{-i\bar{k}\cdot\hat{x}} \mathrm{d}\bar{k}. \tag{24}$$

Phrased differently, if we use a δ-function, then

$$A_k(0) = \frac{1}{2\pi} \int \delta(\hat{x} - \hat{x}') e^{i\bar{k}\cdot\hat{x}} \mathrm{d}\hat{x}, \tag{25}$$

and

$$A_k(0) = \frac{1}{2\pi} e^{i\bar{k}\cdot\hat{x}'}. \tag{26}$$

Substituting this into the general linearized solution gives the Green's Function

$$G(\hat{x},\hat{x}',\hat{t}) = \frac{1}{2\pi} \int e^{(|k|^2 - |k|^4)\hat{t}} e^{-i\bar{k}\cdot(\hat{x}-\hat{x}')} \mathrm{d}\bar{k}, \tag{27}$$

and the general solution

$$\phi(\hat{x},\hat{t}) = \int G(\hat{x},\hat{x}',\hat{t}) \phi(\hat{x}', 0) \mathrm{d}\hat{x}'. \tag{28}$$

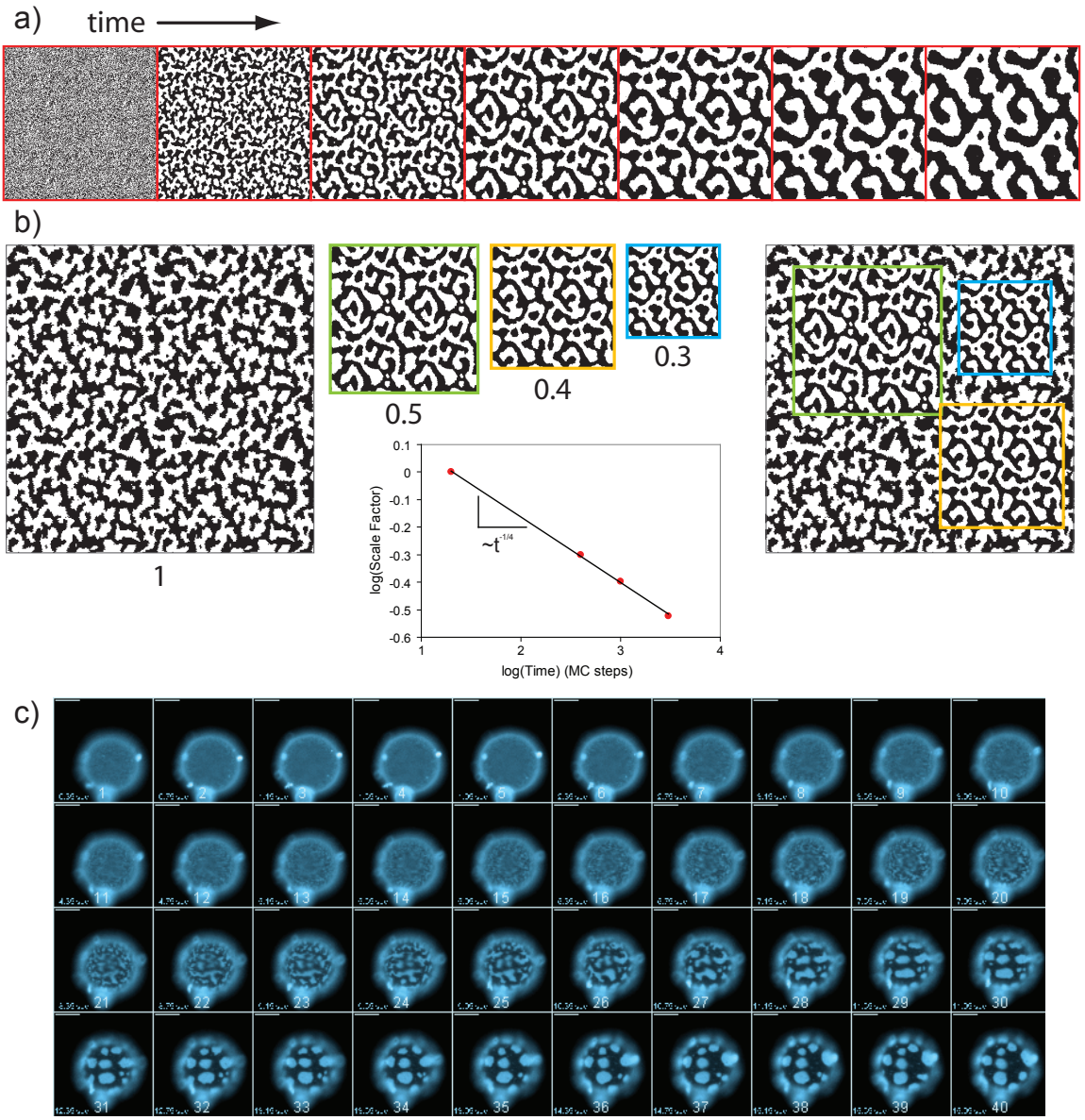

Figure 1: Phase Kinetics in Simulation and Experiment. a) Progression of spinodal decomposition and phase kinetics in a diffuse Monte Carlo simulation in two dimensions with A (white) and B (black) particles at $\langle\phi\rangle = 0$. The frames correspond to pre-quench, 20, 100, 400, 1000, 3000, and 5000 Monte Carlo steps, respectively. Notice short wavelengths disappear quickly, and long wavelengths evolve slowly. Ostwald ripening is also visible during the simulation, as small domains 'evaporate' and join larger domains. b) A qualitative demonstration of scale invariance showing the similarity between frames 20, 400, 1000, and 3000. The scale factors are listed below each frame, and a plot of scale factor vs. time shows a power law relationship with an exponent $\simeq -1/4$. The three scaled images are embedded in the original image, showing the boundary similarity. c) Spinodal decomposition of two phases on a spherical lipid vesicle (experiment). See the videos on YouTube (refs 3 and 4).

4 References

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