

VIII. Phase Transformations

Lecture 39: Reaction-limited Phase Separation

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Last time we presented the classical Cahn-Hilliard theory for phase transformations in closed systems characterized by a conserved order parameter (concentration). In this lecture we adapt the model to electrochemical systems by including Faradaic surface reactions. The resulting model describes evolution of a conserved parameter in an open system that is in contact with an infinite reservoir at fixed chemical potential. This model is a generalization of the Allen-Cahn equation which describes the evolution of non-conserved order parameters during phase transformation.

1 Phase transformation during intercalation and adsorption

The Cahn-Hilliard model, which was derived in the previous lecture, is:

$$\boxed{\begin{aligned} \frac{\partial c}{\partial t} &= \nabla \cdot (Mc \nabla \mu) \\ \mu &= \bar{\mu}(c) - \nabla \cdot \mathbf{K} \nabla c \end{aligned}} \quad (1)$$

where μ is a diffusional chemical potential for an inhomogeneous system. Two boundary conditions are imposed. The first is a variational boundary condition (see 2009 notes for derivation):

$$\hat{n} \cdot (\mathbf{K} \nabla c + \vec{\gamma}'_s(c)) = 0 \quad (2)$$

γ_s is surface tension and may vary with concentration and orientation. Physically, this boundary condition avoids discontinuity in bulk chemical potential at the boundary by prohibiting gradients (bulk phase interface). True surface chemical potential should come from a separate surface contribution to free energy, which we have neglected so far.

The second boundary condition equates the flux across the boundary to a reaction rate:

$$R = \hat{n} \cdot \vec{F} = -\hat{n} \cdot Mc \nabla \mu \quad (3)$$

Butler-Volmer is a logical choice for reaction rate kinetics:

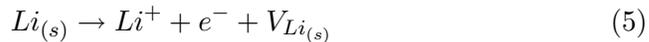
$$R = R_0 \left[e^{(1-\alpha)e\eta/kT} - e^{-\alpha e\eta/kT} \right] \quad (4a)$$

Recall that the variables in the Butler-Volmer equation are:

$$\begin{aligned} R_0 &= \frac{k_0 a^\alpha a_+^{1-\alpha}}{\gamma_A} \text{ (exchange current)} \\ \eta &= \Delta\phi - \Delta\phi_{eq} \text{ (overpotential)} \\ \gamma_A &= \text{activity coefficient of the transition state} \\ &= \frac{1}{1-c} \text{ for excluded volume} \end{aligned} \quad (4b)$$

$\Delta\phi = \phi_e - \phi$ is the interfacial voltage, ϕ is the electrode potential, and ϕ_e is the electrolyte potential. According to our general theory of reactions in concentrated solutions, R should depend on both c and μ . But since μ depends on gradients in c , the reaction rate must also, which is different from classical chemical reaction kinetics. We now have a Butler-Volmer equation for an inhomogeneous system.

Consider the Faradiac reaction in $LiFePO_4$:



$Li_{(s)}$ is lithium in the solid, and $V_{Li_{(s)}}$ is a lithium vacancy in the solid. The diffusional chemical potential (see lecture 13) of lithium is defined using the Cahn-Hilliard formalism:

$$\mu = \mu(Li_{(s)}) - \mu(V_{Li_{(s)}}) = kT \ln a = \bar{\mu}(c) - \nabla \cdot K \nabla c \quad (6)$$

The chemical potentials of Li^+ and e^- are:

$$\begin{aligned} \mu_+ &= \mu(Li^+) = kT \ln a_+ + e\phi \\ \mu_- &= \mu(e^-) = -e\phi_e \end{aligned} \quad (7)$$

If we ignore variations in the Li^+ activity in the electrolyte ($a_+ = 1$), then $\Delta\phi$ is the battery voltage (up to a constant) and $\mu_+ + \mu_- = -e\Delta\phi \equiv \mu_{ext}$. μ_{ext} is an ‘‘external chemical potential’’ that drives the reaction of $Li^+ + e^-$.

At equilibrium, the reaction does not proceed in either direction (zero net reaction rate). Thus $\mu = \mu_+ + \mu_-$ and $\Delta\phi = \Delta\phi_{eq}$. We can use this equilibrium condition to solve for the equilibrium interfacial voltage:

$$\begin{aligned}\mu &= \mu_+ + \mu_- = kT \ln a_+ - e\Delta\phi_{eq} \\ \Delta\phi_{eq} &= \frac{kT \ln a_+ - \mu}{e}\end{aligned}\quad (8)$$

When an external potential μ_{ext} is applied, the system is displaced from equilibrium and the interfacial voltage becomes:

$$\Delta\phi = \frac{kT \ln a_+ - (\mu_+ + \mu_-)}{e} = \frac{kT \ln a_+ - \mu_{ext}}{e}\quad (9)$$

The resulting overpotential is:

$$\boxed{\eta = \Delta\phi - \Delta\phi_{eq} = \frac{\mu - \mu_{ext}}{e}}\quad (10)$$

Thus by varying μ_{ext} with an applied field, we can control the battery voltage and current.

2 Reaction-limited adsorption and phase transformation

Now we will use the inhomogeneous Butler-Volmer equation to develop a model for 2D surface adsorption and intercalation into quasi-2D crystals, as illustrated in figure 1. The following two assumptions are made:

- Fast transport and no phase separation in depth (z) direction in a bulk crystal.
- No transverse diffusion along surface directions (x, y).

Under these assumptions, the CH+reaction model reduces to:

$$\boxed{\frac{\partial c}{\partial t} = -R(c, \mu, \mu_{ext})}\quad (11)$$

which is a nonlinear PDE for c , since $\mu = \bar{\mu}(c) - \nabla \cdot \mathbf{K} \nabla c$. Applying the symmetric Butler-Volmer hypothesis ($\alpha = 1/2$) produces:

$$\begin{aligned}R(c, \mu, \mu_{ext}) &= 2R_0(c, \mu) \sinh\left(\frac{e\eta}{2kT}\right) = 2R_0(c, \mu) \sinh\left(\frac{\mu - \mu_{ext}}{kT}\right) \\ R_0(c, \mu) &= \frac{k_0 \sqrt{aa_+}}{\gamma_A} = k_0(1-c) \sqrt{e^{\mu/kT}}\end{aligned}\quad (12)$$

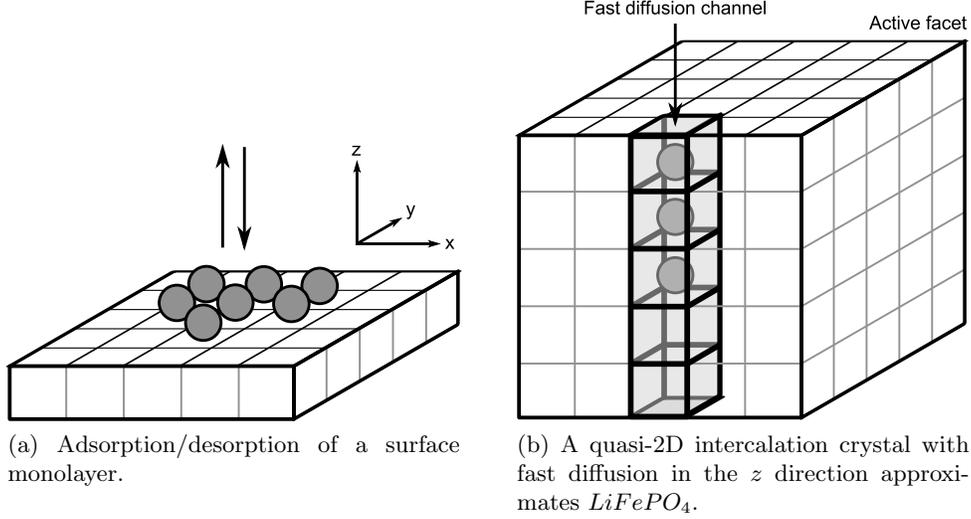


Figure 1: The reaction-limited model is derived for a 2D or quasi-2D system and assumes no transverse surface diffusion in the (x, y) plane.

This is a highly nonlinear second-order PDE, but takes a simpler form for small overpotentials ($\eta = \frac{\mu - \mu_{ext}}{e} \ll kT$). By performing a Taylor expansion on $\sinh(x)$ and keeping only the leading terms, the approximation $\sinh(x) \approx x$ may be made for small x . Equation 11 becomes:

$$\frac{\partial c}{\partial t} \approx \frac{R_0(c, \mu)}{kT} (\mu_{ext} - \mu) \quad (13)$$

This equation describes reaction kinetics for small overpotentials in an inhomogeneous system.

3 Reaction-limited spinodal decomposition

Now let's analyze spinodal decomposition in a system governed by Eq. 13. For simplicity, assume $R_0(c, \mu)/kT = r_0 = \text{constant}$. The governing equation is:

$$\frac{\partial c}{\partial t} = r_0 (\mu_{ext} - \bar{g}'(c) + \kappa \nabla^2 c) \quad (14)$$

This is the Allen-Cahn equation with a forcing potential, and $\tau = \frac{1}{r_0}$ is the characteristic reaction time to fill a site on the active surface (or channel).

Let $c(x, t) = c_0 + \nu$, where c_0 is a constant and $\nu = \epsilon e^{ikx} e^{st}$ is a small perturbation. We want to find the amplification factor s in terms of the

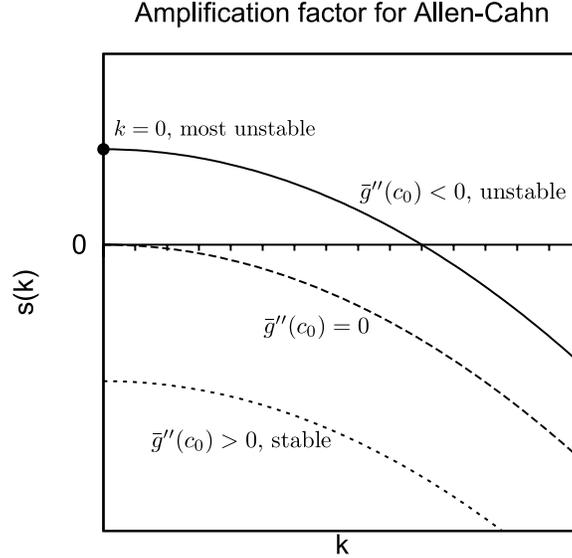


Figure 2: Linear stability of the forced Allen-Cahn equation as a function of wavenumber k . Instability occurs inside the spinodal points, where $\bar{g}''(c_0) < 0$.

wave number k to determine which frequencies will be amplified. Substitute $c = c_0 + \nu$ into Eq. 14:

$$\frac{\partial(c_0 + \nu)}{\partial t} = r_0 (\mu_{ext} - \bar{g}'(c_0) - \nu \bar{g}''(c_0) + \kappa \nabla^2(c_0 + \nu)) \quad (15)$$

For a homogeneous system at equilibrium $\bar{g}'(c_0) = \mu_{ext}$, and the equation simplifies to:

$$\frac{\partial \nu}{\partial t} = r_0 (-\nu \bar{g}''(c_0) + \kappa \nabla^2 \nu) \quad (16)$$

Substituting $\nu = \epsilon e^{ikx} e^{st}$, we obtain:

$$\boxed{s = -r_0 (\bar{g}''(c_0) + \kappa k^2)} \quad (17)$$

which is plotted in figure 2. s is only positive for values of c_0 between the spinodal points, and the most unstable wavelength is $k = 0$. For a finite system of size L , only a discrete spectrum of $k = \frac{2\pi n}{L}, n = 0, 1, 2, \dots$ are permitted. $k_{max} = \frac{2\pi}{L}$ in a discrete system, and therefore $\lambda_{max} \sim L$. We expect to see phase separation into a few large domains on the order of the system size. However, keep in mind that the probability of finding

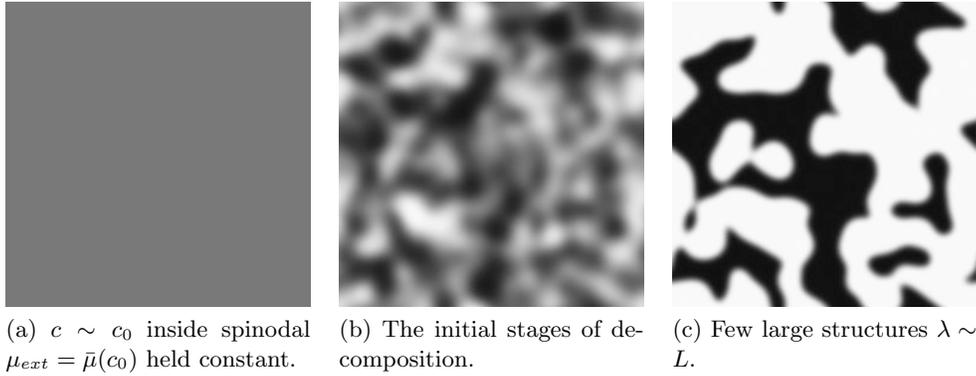


Figure 3: Evolution of Eq. 14, the forced Allen-Cahn equation.

a long-wavelength perturbation decreases with increasing wavelength. A numerical simulation of Eq. 14 is presented in figure 3. In contrast to Cahn-Hilliard evolution, there is no characteristic wavelength apparent in the microstructure.

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