Spinodal Decomposition Process [pln34]

Unmixing process from unstable mixed macrostate initiated by local fluctuations unimpeded by energy barriers.

Normal diffusion (in 1D) as benchmark. It is realized in stable solutions: solute particles migrate from regions of high to regions of low concentration.

- ▷ $\phi(x,t)$: volume fraction of solute,
- ▷ $J(x,t)$: flux of solute particles,
- ▷ D: diffusion constant.

(1) Fick's law: $J = -D\dfrac{\partial\phi}{\partial x}$ (constitutive equation)

(2) continuity equation: $\dfrac{\partial\phi}{\partial t} = -\dfrac{\partial J}{\partial x}$ (conservation law)

(3) diffusion equation: (1) & (2) $\Rightarrow$ $\dfrac{\partial\phi}{\partial t} = D\dfrac{\partial^2\phi}{\partial x^2}$.

Reverse diffusion: solute particles spontaneously migrate from regions of low to regions of high concentration.

General direction of particle migration: from regions of high to regions of low chemical potential. Inside spinodal region, where mixing is unstable, gradient of chemical potential is opposite to gradient of concentration.

Phenomenological model of reverse diffusion:

(4) Exchange chemical potential: $\mu \doteq \mu_{\mathrm{p}} - \mu_{\mathrm{s}}$.

(5) Transport equation: $J_{\mathrm{p}} = -M\dfrac{\partial\mu}{\partial x}$.

(6) Free-energy functional: $F = A\displaystyle\int dx \left[f_0(\phi) + \kappa\left(\frac{d\phi}{dx}\right)^2\right]$.

- ▷ J_{p}: flux of solute particles relative to solvent,
- ▷ $M > 0$: Onsager transport coefficient,
- ▷ A: cross sectional area perpendicular to gradient,
- ▷ $f_0(\phi)$: free-energy density of homogeneous macrostate,
- ▷ $f_0''(\phi) < 0$ inside spinodal region,
- ▷ κ: gradient energy coefficient with $\kappa > 0$ favoring homogeneity.

Exchange chemical potential (4) from (6) via variational derivative:

$$(7) \qquad \mu = f_0'(\phi) - 2\kappa\frac{d^2\phi}{dx^2} \quad \text{(first term consistent with [pex46])}.$$

Resulting transport equation (5):

$$(8) \qquad J_{\mathrm{p}} = -Mf_0''(\phi)\frac{\partial\phi}{\partial x} + 2M\kappa\frac{\partial^3\phi}{\partial x^3} \quad \text{(constitutive law)}.$$

Continuity equation:

$$(9) \qquad \frac{\partial\phi}{\partial t} = -\frac{\partial J_{\mathrm{p}}}{\partial x} \quad \text{(conservation law)}.$$

Cahn-Hilliard equation for reverse diffusion:

$$(8) \qquad \frac{\partial\phi}{\partial t} = Mf_0''(\phi)\frac{\partial^2\phi}{\partial x^2} - 2M\kappa\frac{\partial^4\phi}{\partial x^4}, \qquad D_{\mathrm{eff}} = Mf_0'' < 0.$$

Linearizing assumptions: $M,\ f_0'',\ \kappa$ are treated as constants.

Solution of linearized Cahn-Hilliard equation from [pex20]:

$$\phi(x,t) = \phi_0 + a\cos(qx)\exp\big(R(q)t\big), \quad R(q) \doteq M(|f_0''|q^2 - 2\kappa q^4),$$

- ▷ $R(q)$: amplification factor,
- ▷ $|f_0''|$: measure for instability of mixed macrostate,
- ▷ q: wave number of emerging morphological pattern,
- ▷ q_0: wave number with maximum amplification.

Amplification at $q < q_0$ (longer wavelengths) suppressed owing to the need of longer-distance transport.

Amplification at $q > q_0$ (shorter wavelengths) suppressed due to the higher cost of interfacial energy (encoded in κ).

Experimental evidence: [psl5]

- microscopy $\rightarrow$ random patterns emerge with characteristic pixel size (encoded in q_0).
- light scattering $\rightarrow$ observation of pattern coarsening (nonlinear effect).

[extracted in part from Jones 2002]