MSE 540 Problem Set 11 Solution

1: When a binary solution $g(X_2, T)$ with $\Omega_1 = \Omega_2 = \Omega$ undergoes spinodal decomposition, the concentration wave $c_2(x) = c_2^\alpha + a(t)\sin kx$ can grow in amplitude, which means solutes can diffuse *up* the concentration gradient. So the interdiffusivity $\tilde{D}(c_2)$ in Fick's 1st law $\mathbf{J}_2 = -\tilde{D}(c_2)\nabla c_2$ can be *negative* for some c_2. Assuming the interdiffusion is caused by vacancy motion, $\tilde{D} = X_1 D_2 + X_2 D_1$, go back to your notes on the form of D_1, D_2 in terms of Onsager coefficients and explain how this could happen. Show that the range of c_2 where uphill diffusion can happen, $\tilde{D}(c_2) < 0$, is exactly the spinodal gap from thermodynamics.

Answer: From Onsager linear response formulation we have

$$D_1 \equiv k_\mathrm{B}T\left(\frac{L_{11}}{c_1} - \frac{L_{12}}{c_2}\right)\left(1 + \frac{d\ln\gamma_1}{d\ln c_1}\right), \quad D_2 \equiv k_\mathrm{B}T\left(\frac{L_{22}}{c_2} - \frac{L_{21}}{c_1}\right)\left(1 + \frac{d\ln\gamma_2}{d\ln c_2}\right), \tag{1}$$

The $\frac{L_{11}}{c_1} - \frac{L_{12}}{c_2}$ and $\frac{L_{22}}{c_2} - \frac{L_{21}}{c_1}$ factors are related to the mobility and should be positive. The $k_\mathrm{B}T(1 + \frac{d\ln\gamma_1}{d\ln c_1}) = k_\mathrm{B}T d\ln\gamma_1 X_1/d\ln X_1 = d\mu_1/d\ln X_1$ and $k_\mathrm{B}T(1 + \frac{d\ln\gamma_2}{d\ln c_2}) = d\mu_2/d\ln X_2$ are thermodynamic factors in diffusivity. They are in fact equal for species 1 and species 2, because of the Gibbs-Duhem relation $0 = X_1 d\mu_1 + X_2 d\mu_2$:

$$X_2 d\mu_2 = -X_1 d\mu_1 \quad\leftrightarrow\quad X_2\frac{d\mu_2}{dX_2} = -X_1\frac{d\mu_1}{dX_2} = X_1\frac{d\mu_1}{dX_1} \quad\leftrightarrow\quad \frac{d\mu_2}{d\ln X_2} = \frac{d\mu_1}{d\ln X_1} \tag{2}$$

We have $\mu_2 = g + (1 - X_2)(dg/dX_2)$, so this common thermodynamic factor is $d\mu_2/d\ln X_2 = X_2(dg/dX_2 - dg/dX_2 + (1 - X_2)d^2g/dX_2^2) = X_2(1 - X_2)d^2g/dX_2^2$. $X_2(1 - X_2)$ is always positive, so the signs of D_1,D_2 and $\tilde{D}$ are the same as d^2g/dX_2^2. The spinodal gap is defined by loss of local stability, $d^2g/dX_2^2 < 0$, so $\tilde{D}$ is negative exactly in the spinodal gap.

2: If an alloy containing β precipitates ($X_{e2}^{\beta} \approx 1$ for all temperatures) at T_1 is given a solution treatment by suddenly heating to a temperature T_2 above the equilibrium β solvus, the precipitate will dissolve. Show with 1D $c_2(x)$ diagrams how the composition should vary in the vicinity of an α/β interface during dissolution if the dissolution is under (i) mixed control, (ii) diffusion control, (iii) interface control. Initially, the system is at T_1, with β composition $X_{e2}^{\beta}(T_1) \approx 1$ and α composition $X_{e2}^{\alpha}(T_1)$ in mutual equilibrium. At T_2, the equilibrium α composition $X_{e2}^{\alpha}(T_2)$. The mean composition of the entire alloy is $X_{02} < X_{e2}^{\alpha}(T_2)$, as shown in Fig. 1.

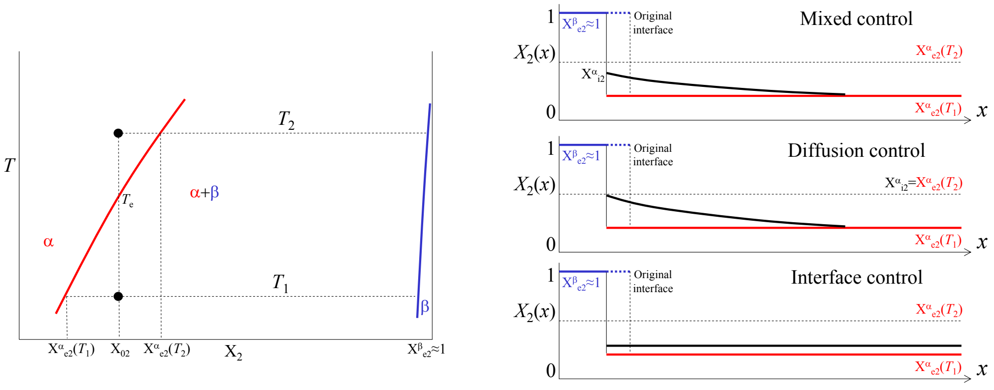

Figure 1:

3: We have derived the Johnson-Mehl-Avrami equation for isothermal transformations (temperature held fixed during transformation), where the nucleation rate $\mathcal{N}$ and growth velocity v are constants of time. Now consider continuous cooling $\Delta T = kt$, where the temperature is changing linearly with time. Suppose the growth velocity v is independent of ΔT and therefore still a constant, but the nucleation rate $\mathcal{N}$ depends on ΔT as $\mathcal{N} = k'(\Delta T)^a$, where k' and a are constants. Show using the time cone method that in 1D nanowire the degree of completion of $\alpha \to \beta$ phase transformation should go as:

$$f_{\beta} \;=\; 1 - \exp\left(-\frac{2vk'k^a t^{a+2}}{(a+1)(a+2)}\right) \tag{3}$$

for this continuous cooling temperature schedule.

Answer: As long as the growth velocity v is constant of time, the necessary and sufficient condition for a point (x, t) to stay α is still that all points in the *reverse time cone* has *refrained* from nucleation. The nucleation rate is now time-dependent, $\mathcal{N} = k'k^a t^a$, however still we can sequentially interrogate different time slices: $t = (0, \Delta t)$, $(\Delta t, 2\Delta t)$, ..., $(t-\Delta t, t)$. In the first time slice $t = (0, \Delta t)$, the probability of nucleation at different spatial points are uncorrelated. The probability that a particular space-time volume element $\Delta t \times \Delta x$ of the first time slice refrains from nucleation is $1 - \mathcal{N}(t = 0)\Delta t \Delta x \approx \exp(-\mathcal{N}(t = 0)\Delta t \Delta x)$, so the total probability that no nucleation occurs within the first time slice of the reverse time cone is

$$\exp(-\mathcal{N}\Delta t\Delta x)\exp(-\mathcal{N}\Delta t\Delta x)...\exp(-\mathcal{N}\Delta t\Delta x) \;=\; \exp(-\mathcal{N}(t=0)w(t=0)\Delta t) \qquad (4)$$

where $w(t = 0)$ is width of the reverse time cone at $t = 0$. If there is no nucleation in the first time slice, we may ask what is the probability that there is also no nucleation in the second time slice. The answer is $\exp(-\mathcal{N}(t = \Delta t)w(t = \Delta t)\Delta t)$, so the probability of no nucleation in the first two time slices is just $\exp(-\mathcal{N}(t = 0)w(t = 0)\Delta t) \exp(-\mathcal{N}(t = \Delta t)w(t = \Delta t)\Delta t)$. We keep asking these "no nucleation" questions sequentially: if any slice says "yes nucleation", (x, t) is β. The probability that the entire reverse time cone has refrained from nucleation is therefore $\exp(-J)$, where

$$J \;=\; \int_0^t d\tau \mathcal{N}(\tau)(2v(t-\tau)) = \int_0^t d\tau 2vk'k^a\tau^a(t-\tau) = \frac{2vk'k^at^{a+2}}{(a+1)(a+2)}. \qquad (5)$$

Thus (3). We see that if $a = 0$, we recover the isothermal Johnson-Mehl-Avrami formula. Also, we see that continuous cooling should yield qualitatively similar TTT curves as isothermal TTT diagram, just with a different numerical exponent.