Series lectures of phase-field model

02. Therodynamic anaysis of diffusion

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Table of Contents

Table of Contents

Diffusion in substitutional alloys

In binary substitutional alloys, the rate at which solvent (A) and solute (B) atoms can move into a vacant site is not equal, therefore, we have to know **intrinsic** diffusion coefficient D_A or D_B. D_A and D_B are defined such that Fick's first law applies to diffusion relative to the lattice

$$J_\mathsf{A} = -D_\mathsf{A}\frac{\partial c_\mathsf{A}}{\partial x} \tag{1}$$

$$J_\mathsf{B} = -D_\mathsf{B}\frac{\partial c_\mathsf{B}}{\partial x} = D_\mathsf{B}\frac{\partial c_\mathsf{A}}{\partial x} \tag{2}$$

When $D_\mathsf{A} > D_\mathsf{B}$, we have

$$|J_\mathsf{A}| > |J_\mathsf{B}|$$

Another main assumption is the volume of the system is constant. To achieve it, the flux have to be balanced. Since the direction of A atom flux and B atom flux are opposite.

$$-J_\mathsf{A} = J_\mathsf{B} + J_\mathsf{v} \tag{3}$$

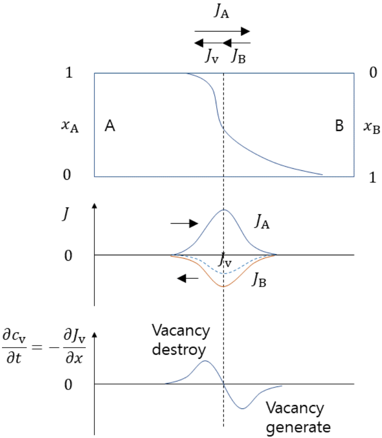

Figure: Interdiffusion and vacancy flow

With Eqs. 1, 2 and 3 we have

$$J_v = (D_A - D_B)\frac{\partial c_A}{\partial x} \tag{4}$$

The velocity at which any given lattice plane moves, v, the plane where the area is A, during a small time interval δt. The plane sweep out a volume

$$Av \cdot \delta t$$

containing

$$Av \cdot \delta t \cdot c_{\mathsf{0}}$$

atoms. This number of atoms is removed by the total number of vacancies crossing the plane in the same time interval,

$$J_{\mathsf{v}} A \cdot \delta t$$

Therefore,

$$J_{\mathsf{v}} = c_{\mathsf{0}} v \qquad c_{\mathsf{0}} = c_{\mathsf{A}} + c_{\mathsf{B}}$$

Then Eq. 4 becomes

$$v = (D_{\mathsf{A}} - D_{\mathsf{B}}) \frac{\partial X_{\mathsf{A}}}{\partial x} \tag{5}$$

where the mole fraction of A,

$$X_{\mathsf{A}} = \frac{c_{\mathsf{A}}}{c_{\mathsf{0}}}$$

We introduce the concept of total flux of A which is combined effect of (i) diffusive flux relative to the lattice and (ii) flux due to the velocity of lattice

$$J'_{\mathsf{A}} = -D_{\mathsf{A}} \frac{\partial c_{\mathsf{A}}}{\partial x} + v c_{\mathsf{A}}$$

With Eq. 5,

$$\begin{aligned}
J'_{\mathsf{A}} &= -D_{\mathsf{A}} \frac{\partial c_{\mathsf{A}}}{\partial x} + (D_{\mathsf{A}} - D_{\mathsf{B}}) \frac{\partial X_{\mathsf{A}}}{\partial x} \cdot c_{\mathsf{A}} \\
&= -D_{\mathsf{A}} \frac{\partial X_{\mathsf{A}}}{\partial x} \cdot \underbrace{c_0}_{c_{\mathsf{A}}+c_{\mathsf{B}}} + (D_{\mathsf{A}} - D_{\mathsf{B}}) \frac{\partial X_{\mathsf{A}}}{\partial x} \cdot c_{\mathsf{A}} \\
&= -(D_{\mathsf{A}} c_{\mathsf{B}} + D_{\mathsf{B}} c_{\mathsf{A}}) \frac{\partial X_{\mathsf{A}}}{\partial x} \\
&= -(D_{\mathsf{A}} X_{\mathsf{B}} + D_{\mathsf{B}} X_{\mathsf{A}}) \cdot c_0 \frac{\partial X_{\mathsf{A}}}{\partial x} \\
&= -\underbrace{(D_{\mathsf{A}} X_{\mathsf{B}} + D_{\mathsf{B}} X_{\mathsf{A}})}_{\tilde{D}} \cdot \frac{\partial c_{\mathsf{A}}}{\partial x}
\end{aligned}$$

The interdiffusion coefficient $\tilde{D}$ is defined by

$$\tilde{D} = D_{\mathsf{A}} X_{\mathsf{B}} + D_{\mathsf{B}} X_{\mathsf{A}} \tag{6}$$

which is known by Darken's equation. Then Fick's first law becomes

$$J'_{\mathsf{A}} = -\tilde{D} \frac{\partial c_{\mathsf{A}}}{\partial x} \tag{7}$$

Atomic mobility

In a multi-component condensed phase, it is more convenient to describe that atoms diffuse as the gradient of chemical potential becomes the driving force, rather than describing that atoms diffuse as the gradient of concentration becomes the driving force.

$$J_\mathsf{B} = v_\mathsf{B} c_\mathsf{B}$$

Drift velocity is now given by

$$v_\mathsf{B} = -M_\mathsf{B} \frac{\partial \mu_\mathsf{B}}{\partial x}$$

Then, the flux is given by

$$\begin{aligned} J_\mathsf{B} &= -M_\mathsf{B} c_\mathsf{B} \frac{\partial \mu_\mathsf{B}}{\partial x} = -M_\mathsf{B} c_\mathsf{B} \frac{d\mu_\mathsf{B}}{d \ln X_\mathsf{B}} \frac{\partial \ln X_\mathsf{B}}{\partial x} \\ &= -M_\mathsf{B} c_0 \frac{d\mu_\mathsf{B}}{d \ln X_\mathsf{B}} \frac{\partial X_\mathsf{B}}{\partial x} = -M_\mathsf{B} \frac{d\mu_\mathsf{B}}{d \ln X_\mathsf{B}} \frac{\partial c_\mathsf{B}}{\partial x} \end{aligned} \tag{8}$$

Thermodynamic factor of diffusion coefficient

The chemical potential of atom B is

$$\mu_{\mathsf{B}} = \mu_{\mathsf{B}}^{\circ} + RT[\ln\gamma_{\mathsf{B}} + \ln X_{\mathsf{B}}]$$

then

$$d\mu_{\mathsf{B}} = RT[d\ln\gamma_{\mathsf{B}} + d\ln X_{\mathsf{B}}]$$

proceed to

$$\frac{d\mu_{\mathsf{B}}}{d\ln X_{\mathsf{B}}} = RT\left[1 + \frac{d\ln\gamma_{\mathsf{B}}}{d\ln X_{\mathsf{B}}}\right] \tag{9}$$

Plug Eq.9 to Eq.8, then

$$J_{\mathsf{B}} = -M_{\mathsf{B}}RT\left[1 + \frac{d\ln\gamma_{\mathsf{B}}}{d\ln X_{\mathsf{B}}}\right]\frac{dc_{\mathsf{B}}}{dx}$$

Compare to Fick's first law,

$$D_{\mathsf{B}} = M_{\mathsf{B}}RT\left[1 + \frac{d\ln\gamma_{\mathsf{B}}}{d\ln X_{\mathsf{B}}}\right]$$

Consistently,

$$D_{\mathsf{A}} = M_{\mathsf{A}} RT \left[1 + \frac{d \ln \gamma_{\mathsf{A}}}{d \ln X_{\mathsf{A}}} \right]$$

For dilute solution, we can approximately state

$$D^*_{\mathsf{B}} = M_{\mathsf{B}} RT$$

$$D^*_{\mathsf{A}} = M_{\mathsf{A}} RT$$

We introduce the thermodynamic factor F,

$$F = 1 + \frac{d \ln \gamma_{\mathsf{B}}}{d \ln X_{\mathsf{B}}}$$

From Gibbs-Duhem relation with trivial modifications,

$$\frac{d \ln \gamma_{\mathsf{A}}}{d \ln X_{\mathsf{A}}} = \frac{d \ln \gamma_{\mathsf{B}}}{d \ln X_{\mathsf{B}}}$$

The thermodynamic factor F is

$$F = 1 + \frac{d\ln\gamma_{\mathsf{B}}}{d\ln X_{\mathsf{B}}} = 1 + \frac{d\ln\gamma_{\mathsf{A}}}{d\ln X_{\mathsf{A}}}$$

also

$$D_{\mathsf{B}} = FD_{\mathsf{B}}^{*} \qquad D_{\mathsf{A}} = FD_{\mathsf{A}}^{*}$$

From dG is

$$dG = \mu_{\mathsf{A}} dX_{\mathsf{A}} + \mu_{\mathsf{B}} dX_{\mathsf{B}}$$

then

$$\begin{aligned}\frac{dG}{dX_{\mathsf{A}}} &= \mu_{\mathsf{A}} + \mu_{\mathsf{B}}\frac{dX_{\mathsf{B}}}{dX_{\mathsf{A}}} = \mu_{\mathsf{A}} - \mu_{\mathsf{B}} \\ &= \mu_{\mathsf{A}}^{\circ} + RT\ln\gamma_{\mathsf{A}} + RT\ln X_{\mathsf{A}} - \mu_{\mathsf{B}}^{\circ} - RT\ln\gamma_{\mathsf{B}} - RT\ln X_{\mathsf{B}}\end{aligned}$$

Take another differentiation,

$$\frac{d^2G}{dX_{\mathsf{A}}^2} = RT\frac{d\ln\gamma_{\mathsf{A}}}{dX_{\mathsf{A}}} + \frac{RT}{X_{\mathsf{A}}} + RT\frac{d\ln\gamma_{\mathsf{B}}}{dX_{\mathsf{B}}} + \frac{RT}{X_{\mathsf{B}}} = \frac{d^2G}{dX_{\mathsf{B}}^2}$$

Proceed to

$$\frac{X_{\mathsf{A}}X_{\mathsf{B}}}{RT}\frac{d^2G}{dX_{\mathsf{A}}^2} = \left[X_{\mathsf{B}}\left(1+\frac{d\ln\gamma_{\mathsf{A}}}{d\ln X_{\mathsf{A}}}\right)+X_{\mathsf{A}}\left(1+\frac{d\ln\gamma_{\mathsf{B}}}{d\ln X_{\mathsf{B}}}\right)\right] = (X_{\mathsf{A}}+X_{\mathsf{B}})F = F$$

Finally, we reach

$$F = \frac{X_{\mathsf{A}}X_{\mathsf{B}}}{RT}\frac{d^2G}{dX_{\mathsf{A}}^2} = \frac{X_{\mathsf{A}}X_{\mathsf{B}}}{RT}\frac{d^2G}{dX_{\mathsf{B}}^2}$$

Eq. 6 can be rewritten by

$$\tilde{D} = F(X_{\mathsf{B}}D_{\mathsf{A}}^* + X_{\mathsf{A}}D_{\mathsf{B}}^*)$$

In similar logic, we have

$$\tilde{M} = c_{\mathsf{A}}c_{\mathsf{B}}\left(M_{\mathsf{A}}c_{\mathsf{B}} + M_{\mathsf{B}}c_{\mathsf{A}}\right) \tag{10}$$