IV Transport Phenomena

Lecture 21: Solids and Concentrated Solutions

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1   Transport in Solids

1.1   Diffusion

The general model of chemical reactions can also be used for thermally activated diffusion.
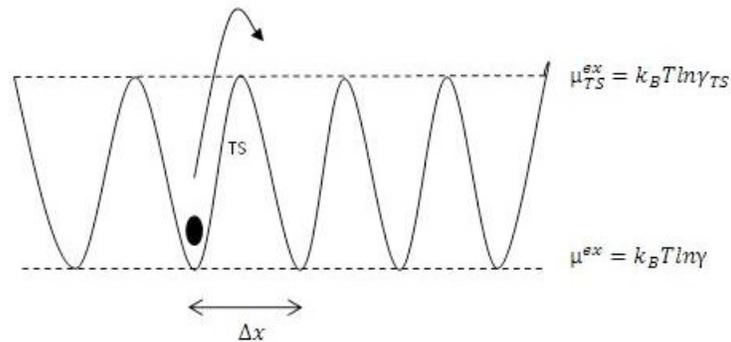
Figure 1: Particle diffusion by thermally activated transitions

Here the excess chemical potential acts like the potential energy of particle state. Thermally activated transition without drift or bias implies a random walk phenomena where the diffusivity is a function of mean-average time between steps and is given by:

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Diffusivity

$$D = \frac{\Delta x^2}{2\tau} \tag{1}$$

$\tau =$ mean time between transitions

The mean average transition time is a function of the potential energy gap between the transition state and stable original state.

$$\tau = \tau_0 e^{(\frac{\mu_{TS}^{ex} - \mu^{ex}}{k_B T})} = \tau_0 \frac{\gamma_{TS}}{\gamma} \tag{2}$$

$\frac{1}{\tau_0} \propto T =$ attempt frequency for transitions, and recall, $\mu^{ex} = k_B T \ln \gamma$.

Finally, we can now write diffusivity of solids in terms of activity coefficients.

$$\boxed{D = \frac{\Delta x^2}{2\tau_0} \frac{\gamma}{\gamma_{TS}}} \tag{3}$$

We go ahead and consider a few specific cases to further simplify the diffusivity expression.

1.1.1 Dilute limit

Commonly accepted hypothesis here is that γ and γ_{TS} do not depend on concentration, c.

$$\therefore \gamma_{TS} = e^{\frac{-E_{TS}}{k_B T}} \text{ and } \gamma = e^{-\frac{E_{min}}{k_B T}}$$

$$\implies D = \frac{\Delta x^2}{2\tau_0} e^{-\frac{\Delta E_A}{k_B T}} \tag{4}$$

where $\Delta E_A = E_{TS} - E_{min}$ is the activation energy barrier.

1.1.2 Ideal solid solution (Lattice gas)

Model:
Consider a lattice gas model where the transition state requires two vacancies. Then we have,

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$$\gamma = \frac{e^{\frac{-E_{min}}{k_B T}}}{(1-c/c_{max})}$$

$$\gamma_{TS} = \frac{e^{\frac{-E_{TS}}{k_B T}}}{(1-c/c_{max})^2}$$

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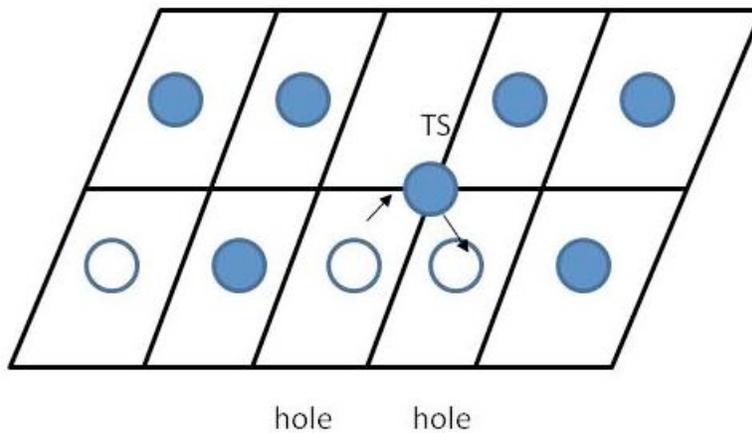
Figure 2: Lattice gas transition state with two required vacancies

$$\therefore D = D_0(1 - \frac{c}{c_{max}}) \tag{5}$$

The factor $(1 - \frac{c}{c_{max}})$ can be understood as the condition probability that the target site ("state 2") after the step is vacant, given that particle starts at a certain position ("state 1").

1.1.3 General case

$$D = f(c, T, \underline{\underline{\sigma}}, ..) = D_0 \frac{\gamma}{\gamma_{TS}} \tag{6}$$

Example: $\underline{\underline{\sigma}}$ =stress tensor. Then $\Delta E_A = \Delta E_A^0 + \underline{\underline{\sigma}} : \underline{\underline{\epsilon_A}}$, where $\underline{\underline{\epsilon_A}}$ is the activation strain tensor, which describes the shape of the transition state. $\implies$ stress-assisted diffusion in solids

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1.2   Drift

We now look at diffusion when there is a gradient in chemical potential as a function of x.

$$\mu_{TS}^{ex} = k_B T ln \gamma_{TS}$$

$$\mu^{ex} = k_B T ln \gamma$$

$$x - \frac{\Delta x}{2} \quad x \quad x + \frac{\Delta x}{2}$$
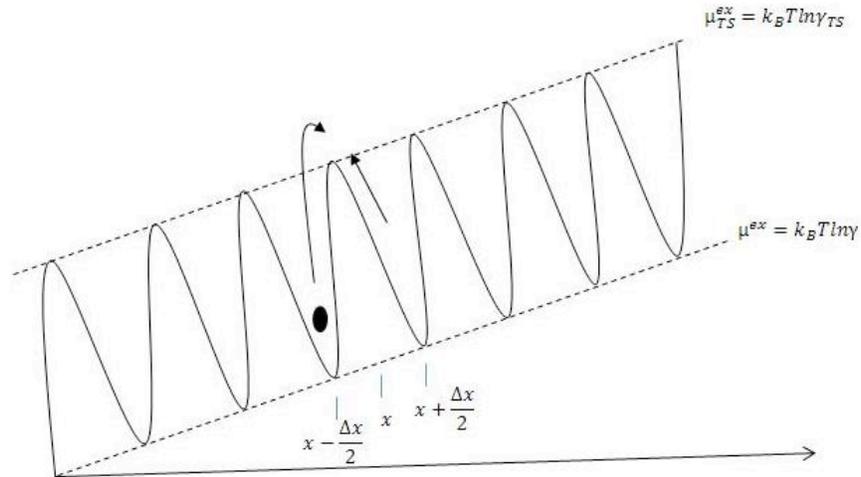
Figure 3: Particle drift due to gradient in chemical potential

A_x

TS
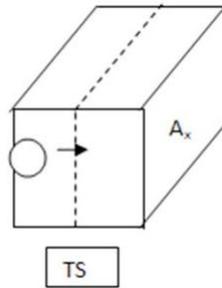
Figure 4: Particle crossing the transition state

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$$V = \frac{1}{c_{max}} : \text{cell volume} \tag{7}$$

$$A_x : \text{cell area} \tag{8}$$

$$\Delta x = \frac{V}{A_x} \tag{9}$$

Flux, $F = \frac{R}{A_x}$, where $R =$reaction rate for net drift in the x direction

$$R = R_0(e^{-(\mu_{TS}^{ex}(x)-\mu(x-\frac{\Delta x}{2}))/k_BT} - e^{-(\mu_{TS}^{ex}(x)-\mu(x+\frac{\Delta x}{2}))/k_BT}) \tag{10}$$

$R_0 = \frac{1}{2\tau_0}$ (since the probability of making the transtion from barrier is $\frac{1}{2}$)

Assume $\mu(x)$ is slowly varying at the molecular scale.

$$\implies \mu(x \pm \frac{\Delta x}{2}) \simeq \mu(x) \pm \frac{\Delta x}{2}\frac{\partial \mu(x)}{\partial x} \tag{11}$$

$\mu(x) = k_BT \ln a(x) = k_BT \ln(\gamma c/c_{max})$ and $|\frac{\Delta x}{k_BT}\frac{\partial \mu}{\partial x}| \ll 1$

$$\begin{aligned}
\therefore F(x) &= \frac{1}{2\tau_0 A_x \gamma_{TS}(x)}\left[e^{\frac{\mu(x-\frac{\Delta x}{2})}{k_BT}} - e^{\frac{\mu(x+\frac{\Delta x}{2})}{k_BT}}\right] \\
&= \frac{-\sinh(\frac{\Delta x}{2k_BT}\frac{\partial \mu}{\partial x})}{\tau_0 A_x \gamma_{TS}}e^{\frac{\mu(x)}{k_BT}} \\
&= \frac{-c(x)V}{\tau_0 A_x}\frac{\gamma(x)}{\gamma_{TS}(x)}\sinh(\frac{\Delta x}{2k_BT}\frac{\partial \mu}{\partial x}) \\
&= -(\frac{\Delta x^2}{2\tau_0})(\frac{\gamma(x)}{\gamma_{TS}(x)})\frac{c(x)}{k_BT}\frac{\partial \mu(x)}{\partial x} \\
&= -(\frac{D}{k_BT})c\frac{\partial \mu}{\partial x}
\end{aligned} \tag{12}$$

Here, $\frac{\partial \mu}{\partial x} =$generalized/thermodynamic force. From a fundamental postulate of nonequilibrium thermodynamics, we know:

$$F = -Mc\frac{\partial \mu}{\partial x} \tag{13}$$

where M is the mobility (velocity/force=1/drag)

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This implies the **Einstein relation**[1]

$$Mk_BT = D \qquad (14)$$

The mobility of a tracer is thus generally related to its diffusivity, even in a concentrated solution (or solid).

Example: Solid solution/Lattice gas

$$\mu = k_BT \ln\left(\frac{c}{c_{max}-c}\right)$$

$$\implies c\frac{\partial \mu}{\partial x} = k_BT c\left[\frac{1}{c} + \frac{1}{c_{max}-c}\right]\frac{\partial c}{\partial x}$$

$$= \left(\frac{k_BT}{1-\frac{c}{c_{max}}}\right)\frac{\partial c}{\partial x}$$

$$\therefore F(x) = -\frac{D}{\left(1-\frac{c}{c_{max}}\right)}\frac{\partial c}{\partial x} \qquad (15)$$

We see that the thermodynamic driving force blows up as $c \to c_{max}$ due to strong effect of excluded volume. However, the tracer diffusivity goes to zero in the same limit due to the lack of available vacancies for particle steps, $D = D_0(1 - \frac{c}{c_{max}})$. This leads to a remarkable cancellation of nonlinear effects, such that the chemical diffusivity is precisely constant for all concentrations and equal to the tracer diffusivity of particles or holes in isolation:

$$F = -D_0\frac{\partial c}{\partial x} \qquad (16)$$

Fick's law

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[1]Einstein originally derived this relation for the special case of Brownian motion of a dust particle in air by equating the mobility (drift velocity per gravitational force) with the inverse of the Stokes drag coefficient for rigid sphere in viscous flow, $M^{-1} = 6\pi\eta R$. This allowed him to predict the diffusivity $D = k_BT/6\pi\eta R$ in terms of the fluid viscosity η and the particle size R in good agreement with experiments later done by Perrin (who earned the Nobel Prize as a result, due to the importance of this theoretical verification in establishing the molecular nature of matter).

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More generally in a crystal, if we assume $D = D_0(1 - \frac{c}{c_{max}})$ for a lattice gas, then for any model of $\mu(c, x, ...)$,

$$\begin{aligned} F &= -Mc\frac{\partial \mu}{\partial x} \\ &= -(\frac{D_0 c_{max}}{k_B T})(\frac{c}{c_{max}})(1 - \frac{c}{c_{max}})\frac{\partial \mu}{\partial x} \end{aligned} \tag{17}$$

A conservation law based on this flux

$$\frac{\partial c}{\partial t} + \frac{\partial F}{\partial x} = 0$$

yields the suitable form of the Cahn-Hilliard equation for a solid solution or lattice gas. (See lecture 38)

2 Concentrated Solution Theory

Recall, chemical potential in a concentrated solution is given by:

$$\begin{aligned} \mu &= kT \ln(\gamma c) \\ &= \underbrace{kT \ln \gamma}_{excess} + kT \ln c \end{aligned} \tag{18}$$

Therefore, the flux F in a concentrated solution is:

$$\begin{aligned} F &= -Mc\frac{\partial \mu}{\partial x} \\ &= -\frac{D}{k_B T}c\frac{\partial \mu}{\partial c}\frac{\partial c}{\partial x} \\ &= -\frac{D}{k_B T}c\Big[\frac{k_B T}{c} + k_B T\frac{\partial \ln \gamma}{\partial c}\Big]\frac{\partial c}{\partial x} \end{aligned} \tag{19}$$

This is rewritten as,

$$F = -D_{chem}(c)\frac{\partial c}{\partial x} \tag{20}$$

Here, D_{chem} has contributions from two effects.

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$$D_{chem} = D \Big[\underbrace{1}_{\text{Fick's law}} + \underbrace{\frac{\partial \ln \gamma}{\partial \ln c}}_{\text{concentrated solution effects}} \Big] \qquad (21)$$

where $D = D_0 \frac{\gamma}{\gamma_{TS}}$

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