Diffusion in Multicomponent Solids
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Lecture - 41
Non-Ideality as Driving Force

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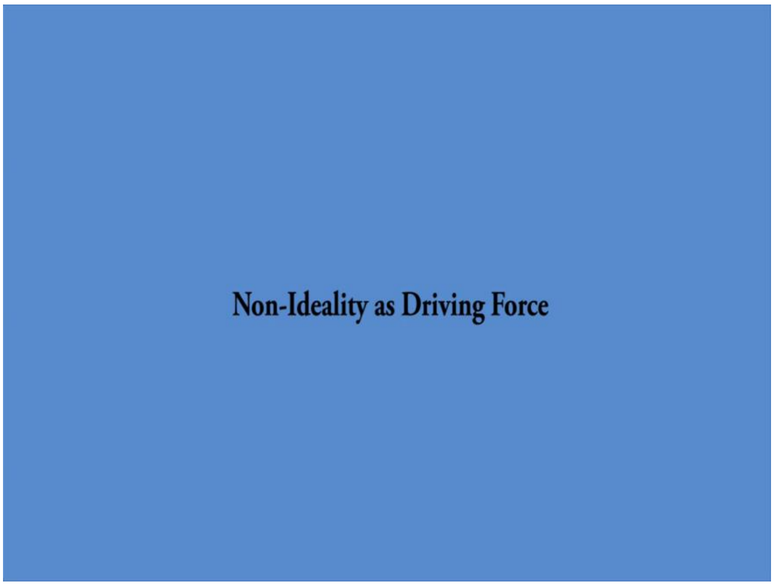

Non-Ideality as Driving Force

Welcome to the 41st lecture of the open course on diffusion in multicomponent solids. In this lecture I shall explain how non-ideality of mixing gives rise to a drift velocity and hence non-ideality of solution can be considered as a driving force.

Welcome back. In the last class, we have seen how the external driving force gives rise to a drift contribution to the diffusion flux terms. Today we will see that non-ideality of mixing or non-ideality of solution also can be treated as a driving force that gives rise to a drift velocity. We will talk about it today.

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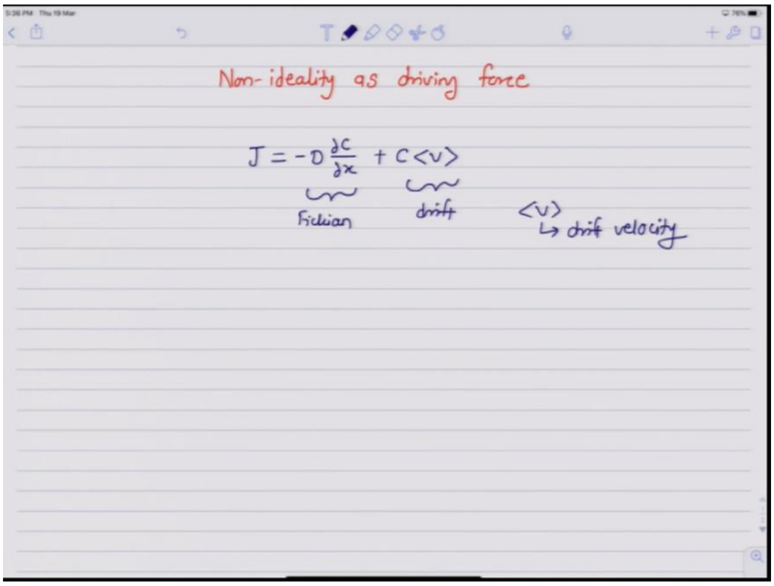

Non-ideality as driving force

$$J = \underbrace{-D\frac{\partial c}{\partial x}}_{\text{Fickian}} + \underbrace{C\langle v\rangle}_{\text{drift}}$$

$\langle v\rangle$
↳ drif velocity

For a binary system, we know the flux term has two contributions. We can write:

$$J = -D\frac{\partial C_A}{\partial x} + C\langle v\rangle$$

Here, D refers to the diffusion coefficient, the first term is the Fickian term which depicts the contribution because of the concentration gradient and the second term here is the drift term. v refers to the drift velocity and C is the concentration.

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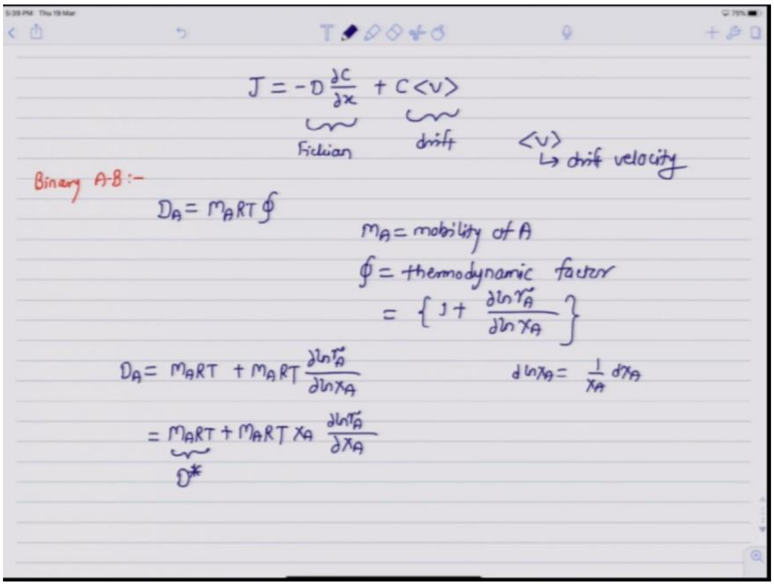

$$J = \underbrace{-D\frac{\partial c}{\partial x}}_{\text{Fickian}} + \underbrace{C\langle v\rangle}_{\text{drift}}$$

$\langle v\rangle$
↳ drif velocity

Binary A-B :-

$D_A = M_A RT\phi$

$M_A =$ mobility of A

$\phi =$ thermodynamic factor

$= \left\{1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A}\right\}$

$D_A = M_A RT + M_A RT\frac{\partial \ln \gamma_A}{\partial \ln x_A}$

$d\ln x_A = \frac{1}{x_A}dx_A$

$= \underbrace{M_A RT}_{D^*} + M_A RT\, x_A \frac{\partial \ln \gamma_A}{\partial x_A}$

Now we have seen the intrinsic diffusion coefficient D_A can be expressed as:

$$D_A = M_A RT\Phi$$

where M_A is the atomic mobility of A and Φ is the thermodynamic factor, which is given as:

$$\Phi = \text{thermodynamic factor} = 1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}$$

Here γ_A is the thermodynamic activity coefficient of A and X_A is the mole fraction of A in the solution. Now, it should be remembered again that this expression we derived for a binary system let us say for binary AB system. And we also assumed that molar volume is constant and also the chemical potential of vacancies is zero throughout. That is the vacancies are at equilibrium everywhere, so that is the assumption. Otherwise we will need multiple mobility terms. If we substitute for Φ in the expression for D_A, we can write:

$$D_A = M_A RT + M_A RT \frac{\partial \ln \gamma_A}{\partial \ln X_A}$$

Simplifying $\partial \ln X_A$ this comes out to be:

$$D_A = M_A RT + M_A RT \frac{\partial \ln \gamma_A}{\partial \ln X_A} = M_A RT + M_A RT X_A \frac{\partial \ln \gamma_A}{\partial X_A}$$

But:

$$D^* = M_A RT$$

where D^* is the tracer diffusivity, that is the diffusivity under negligible concentration gradient.

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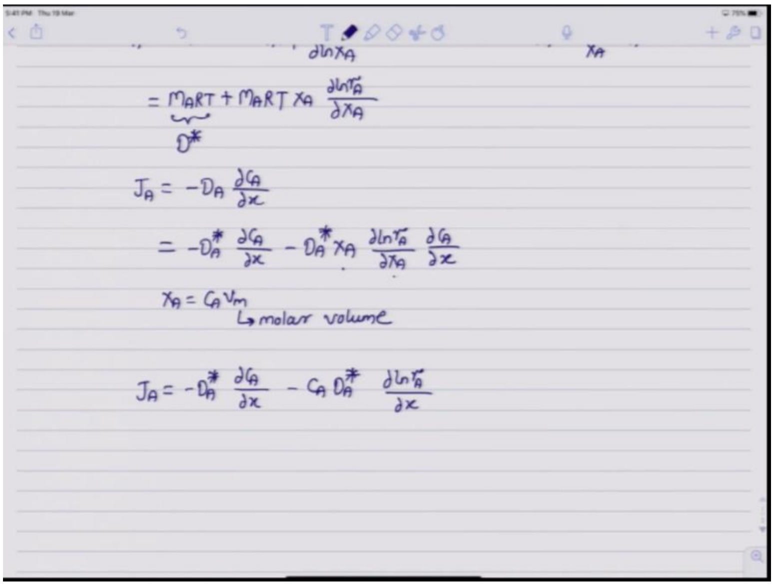

$\partial \ln x_A$ $\quad x_A$

$$= \underbrace{M_A RT}_{D^*} + M_A RT\, x_A \frac{\partial \ln \gamma_A}{\partial x_A}$$

$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

$$= -D_A^* \frac{\partial C_A}{\partial x} - D_A^* x_A \frac{\partial \ln \gamma_A}{\partial x_A} \frac{\partial C_A}{\partial x}$$

$x_A = C_A V_m$

↳ molar volume

$$J_A = -D_A^* \frac{\partial C_A}{\partial x} - C_A D_A^* \frac{\partial \ln \gamma_A}{\partial x}$$

If we write the equation for intrinsic diffusion flux in absence of any external driving force, we can write:

$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

And if we substitute for D_A we get:

$$J_A = -D_A \frac{\partial C_A}{\partial x} = -D_A^* \frac{\partial C_A}{\partial x} - D_A^* X_A \frac{\partial \ln \gamma_A}{\partial X_A} \frac{\partial C_A}{\partial x}$$

Now:

$$X_A = C_A V_m$$

where V_m refers to the molar volume of the alloy. And if we assume molar volume to be constant, then we can replace X_A at both places with $C_A V_m$. So we get:

$$J_A = -D_A^* \frac{\partial C_A}{\partial x} - D_A^* C_A \frac{\partial \ln \gamma_A}{\partial x}$$

Now if we compare this expression with the first equation that we wrote, we know that the first term is the Fickian term with the diffusion coefficient as D_A^*. And D_A^* also refers to the intrinsic diffusion coefficient for ideal solution. This is because for an ideal solution the thermodynamic factor would be unity and for ideal solution:

$$D_A = D_A^*$$

So in the equation of flux first part we can also think as an ideal part and the second part is because of the non-ideality.

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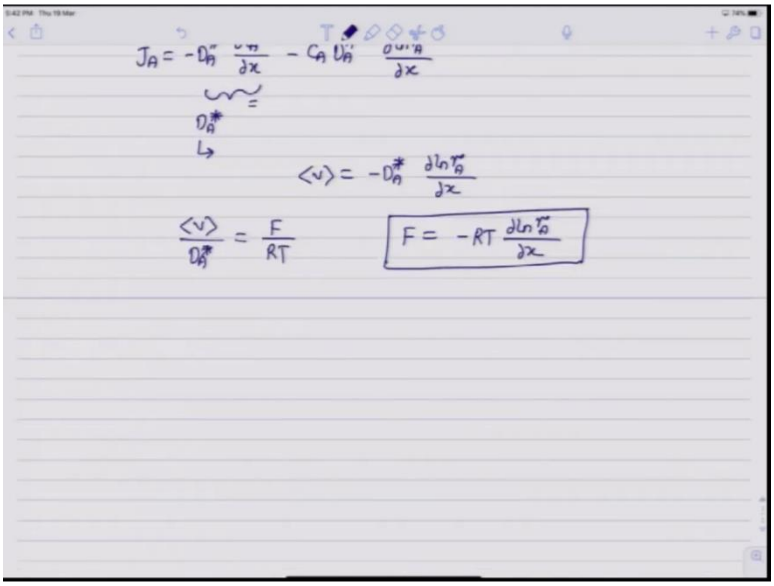

$$\langle v \rangle = -D_A^* \frac{\partial \ln \gamma_A}{\partial x}$$

$$\frac{\langle v \rangle}{D_A^*} = \frac{F}{RT}$$

$$\boxed{F = -RT \frac{\partial \ln \gamma_A}{\partial x}}$$

If we compare with the drift term there, we get the expression for drift velocity as:

$$\langle v \rangle = -D_A^* \frac{\partial \ln \gamma_A}{\partial x}$$

Now in an ideal solution, we can write from the Nernst- Einstein equation:

$$\frac{\langle v \rangle}{D_A^*} = \frac{F}{RT}$$

And we substitute for $\langle v \rangle$, we get the expression for driving force F as:

$$F = -RT \frac{\partial \ln \gamma_A}{\partial x}$$

Essentially this tells me that the gradient in thermodynamic activity coefficient acts as a driving force.

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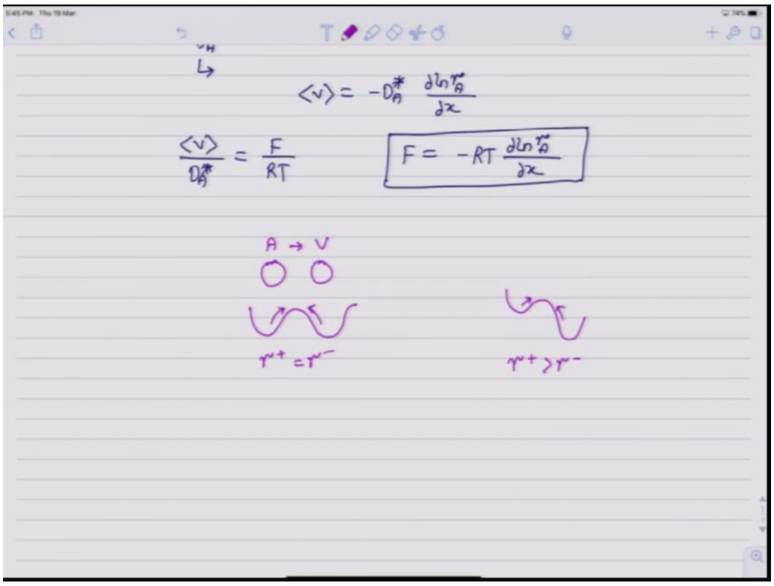

Now, how we can explain this physically? Again imagine the jumps of the atoms. As the atom jumps from the position A to this position V here and if the solution is ideal then there are no thermodynamic interactions between the atoms. The energy after the jump should be same as the energy before the jump, if there exists a concentration gradient. And we have seen the energy wells can be drawn like this. So, the jump frequency in the forward direction should be same as the jump frequency in the reverse direction because the activation barrier will be same.

But if the solution is non-ideal, then obviously the activation barrier in the forward and reverse direction are not same because if the chemical potential is decreasing from left to right, then the lattice site on the right side will be at a lower potential energy well than the one on the left side. And the activation barrier in the forward direction is not same as the activation barrier in the reverse direction. So, we know here:

$$\gamma^{+} > \gamma^{-}$$

And because of these differences in the jump frequencies in forward and reverse direction, there will be a drift associated with it. Essentially, the gradient in activity coefficient can be considered as a driving force. If the solution is non-ideal, γ will change with composition and hence in the presence of concentration gradient γ will change with the distance coordinate x and it will give rise to a drift term. Okay. That is all for today. Thank you.