EMA5001 Lecture 6
Determining Diffusion Coefficient & Matano Analysis

FLORIDA INTERNATIONAL UNIVERSITY

Measurement of Diffusion Coefficient

❑With analytical solutions

Diffusion into semi-infinite bar

- Tracer (Self) diffusion coefficient
- Really dilute solid solution (interstitial or substitutional type)

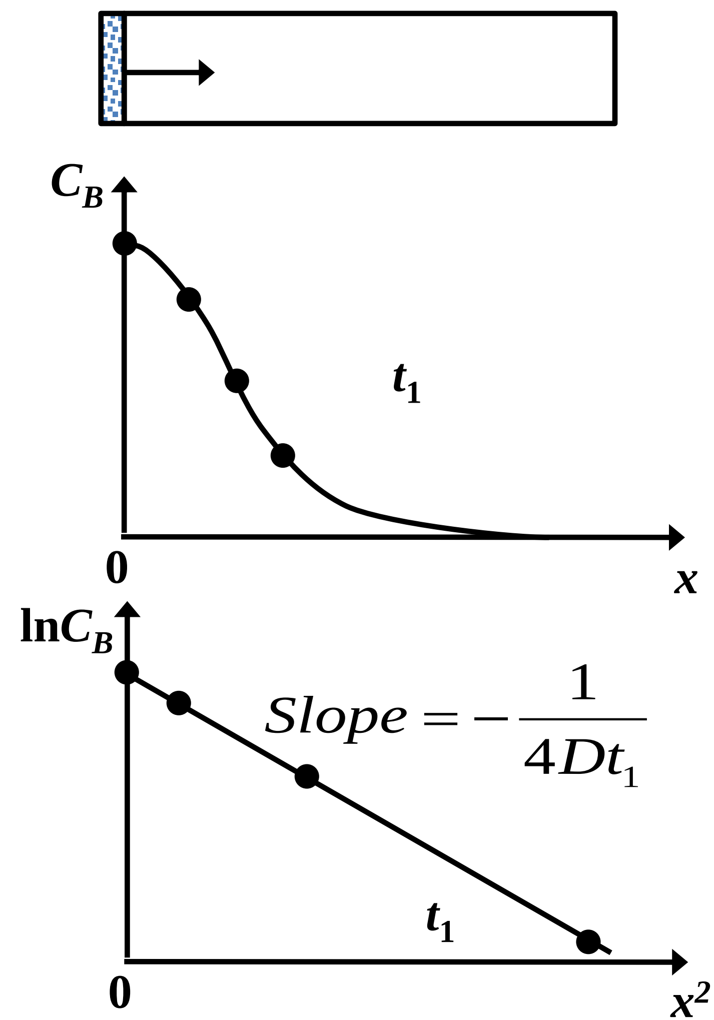
$$\tilde{D} = D_B = D_B^*$$

$$C_B(x,t) = \frac{N}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

For given time t_1, if concentration profile is measured, as $C_B(x)$, then

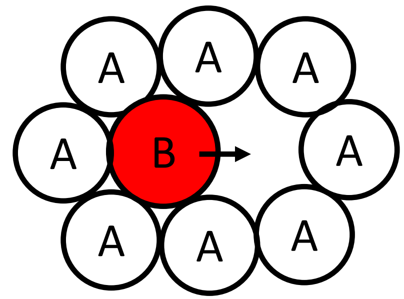
$$\ln C_B(x) = \ln \frac{N}{\sqrt{\pi D t_1}} - \frac{1}{4Dt_1} x^2$$

Plotting $\ln C_B(x)$ vs. x^2, the slope can give D_B



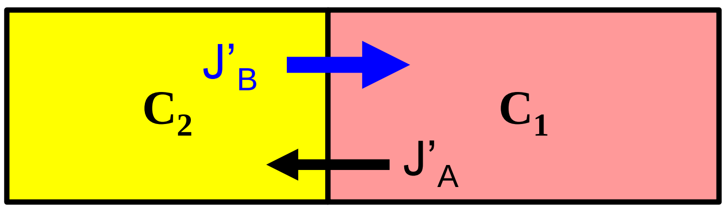
Diffusion Coefficient for Regular Solid Solution

- Diffusion coefficients D_B^* , D_B , and $\tilde{D}$ all change with concentration



- No analytical solutions for Fick's 2nd Law

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right)$$



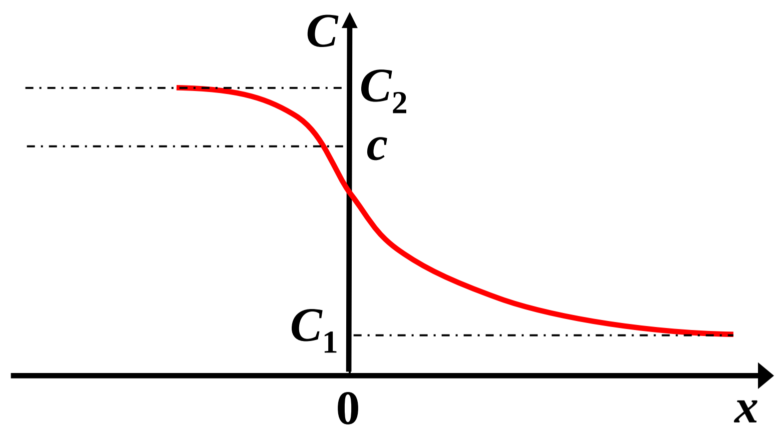
- Matano gave a graphical solution

Initial condition

– $C\ (x > 0) = C_1;\ \ C\ (x < 0) = C_2$

Boundary condition

– $C\ (x \rightarrow \infty) = C_1;\ C\ (x \rightarrow -\infty) = C_2;\ \left.\frac{dC}{dx}\right|_{x\rightarrow\pm\infty} = 0$



Matano Analysis (1)

- **Continue from previous page**

Introduce $\lambda = \dfrac{x}{\sqrt{t}}$

We have

$$\frac{\partial C}{\partial t} = \frac{dC}{d\lambda}\cdot\frac{\partial \lambda}{\partial t} = \frac{dC}{d\lambda}\cdot\frac{\partial\left(\dfrac{x}{\sqrt{t}}\right)}{\partial t} = -\frac{x}{2t^{3/2}}\cdot\frac{dC}{d\lambda} = -\frac{1}{2t}\cdot\left(\frac{x}{\sqrt{t}}\right)\cdot\frac{dC}{d\lambda} = -\frac{\lambda}{2t}\cdot\frac{dC}{d\lambda}$$

$$\frac{\partial C}{\partial x} = \frac{dC}{d\lambda}\cdot\frac{\partial \lambda}{\partial x} = \frac{dC}{d\lambda}\cdot\frac{\partial\left(\dfrac{x}{\sqrt{t}}\right)}{\partial x} = \frac{1}{\sqrt{t}}\cdot\frac{dC}{d\lambda}$$

$$\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) = \frac{d}{d\lambda}\left(D\frac{\partial C}{\partial x}\right)\cdot\frac{\partial \lambda}{\partial x} = \frac{d}{d\lambda}\left(D\frac{1}{\sqrt{t}}\cdot\frac{dC}{d\lambda}\right)\cdot\frac{\partial \lambda}{\partial x} = \frac{1}{\sqrt{t}}\frac{d}{d\lambda}\left(D\frac{dC}{d\lambda}\right)\frac{1}{\sqrt{t}}$$

Therefore,

$$\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) = \frac{1}{t}\cdot\frac{d}{d\lambda}\left(D\frac{dC}{d\lambda}\right)$$

Matano Analysis (2)

- **Continue from p.4**

We have

$$\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)=\frac{1}{t}\cdot\frac{d}{d\lambda}\left(D\frac{dC}{d\lambda}\right)$$

and

$$\frac{\partial C}{\partial t}=-\frac{\lambda}{2t}\cdot\frac{dC}{d\lambda}$$

Fick's 2nd Law

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

is written as

$$-\frac{\lambda}{2t}\cdot\frac{dC}{d\lambda}=\frac{1}{t}\cdot\frac{d}{d\lambda}\left(D\frac{dC}{d\lambda}\right)$$

We have

$$-\frac{1}{2}\lambda\frac{dC}{d\lambda}=\frac{d}{d\lambda}\left(D\frac{dC}{d\lambda}\right)$$

Matano Analysis (3)

- **Continue from p. 5**

We have
$$-\frac{1}{2}\lambda\frac{dC}{d\lambda}=\frac{d}{d\lambda}\left(D\frac{dC}{d\lambda}\right)$$

Multiply both sides with $d\lambda$, we have $-\frac{1}{2}\lambda dC=d\left(D\frac{dC}{d\lambda}\right)$

Integrate with respect to C from C_1 to c, we have $-\frac{1}{2}\int_{C1}^{c}\lambda dC=\int_{C1}^{c}d\left(D\frac{dC}{d\lambda}\right)$

Now put $\lambda=x/\sqrt{t}$ into the equation

We have
$$-\frac{1}{2}\int_{C1}^{c}\frac{x}{\sqrt{t}}dC=\int_{C1}^{c}d\left(D\frac{dC}{dx}\cdot\frac{dx}{d(x/\sqrt{t})}\right)$$

For given time, t is a constant, $-\frac{1}{2\sqrt{t}}\int_{C1}^{c}xdC=\sqrt{t}\int_{C1}^{c}d\left(D\frac{dC}{dx}\right)$

Re-arrange, $-\frac{1}{2t}\int_{C1}^{C}xdC=\int_{C1}^{C}d\left(D\frac{dC}{dx}\right)$

Matano Analysis (4)

- **Continue from p.6**

  We have

$$-\frac{1}{2t}\int_{C1}^{c} x\,dC = \int_{C1}^{c} d\left(D\frac{dC}{dx}\right)$$

  Integration on right side gives

$$-\frac{1}{2t}\int_{C1}^{c} x\,dC = \left(D\frac{dC}{dx}\right)_{C=c} - \left(D\frac{dC}{dx}\right)_{C=C1}$$

  Consider boundary condition of $\left.\frac{dC}{dx}\right|_{C=C1} = 0$

  We have

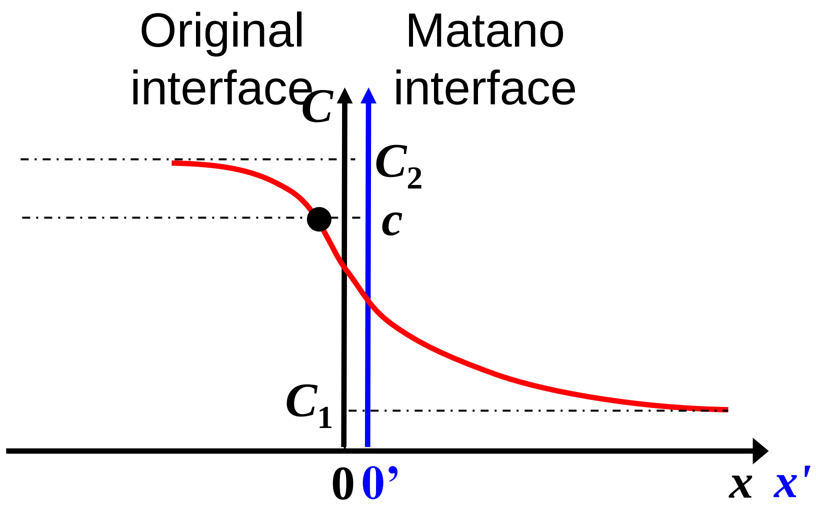
$$-\frac{1}{2t}\int_{C1}^{c} x\,dC = D(c)\left.\frac{dC}{dx}\right|_{C=c}$$

  Inter-diffusion coefficient at concentration c is $D(c) = -\frac{1}{2t}\int_{C1}^{c} x\,dC \cdot \left.\frac{dx}{dC}\right|_{C=c}$

Matano Analysis (5)

- Continue from p. 7

$$D(c) = -\frac{1}{2t}\int_{C1}^{c} x\,dC \cdot \left.\frac{dx}{dC}\right|_{C=c}$$



- Note the integration term $\int_{C1}^{c} x\,dC$ depends on selection of coordinates → Which one?
- Note the deferential term $\left.\frac{dx}{dC}\right|_{C=c}$ approaches infinity as c→ C_2

Boundary condition

$$\left.\frac{dC}{dx}\right|_{x\to\infty} = 0 \quad \Longrightarrow \quad \left.\frac{dx}{dC}\right|_{C\to C2} \to \infty$$

- To make diffusion coefficient finite for c=C_2, the selection of coordinates must make the integration term satisfy $\int_{C1}^{C2} x'\,dC \to 0$

Physical Meaning of Manato Interface

❑Continue from p. 8

$$D(c) = -\frac{1}{2t}\int_{C1}^{c} x' dC \cdot \left.\frac{dx'}{dC}\right|_{C=c}$$

❑Physical Meaning of Matano Interface

- Averaged position weighed with respect to concentration if concentration profile $C(x)$ is invertible to the form of $x(C)$
- The interface where the total net number of atoms lost on one side of the interface due to diffusion equals the total net number of atoms gained on the the other side of the interface
- The interface "across which an equal number of atoms have crossed in both directions"
  http://www.matter.org.uk/matscicdrom/manual/df.html