

Lecture 32

review!

From the Langevin equation:

$$F_{\text{Appl}} + F_{\text{friction}} + F_{\text{random}} = ma \approx 0$$

\uparrow \uparrow
 $-\frac{\partial \mu}{\partial x}$ $- \gamma v$

We can derive P.C.M.

$$\mu(x) \rightarrow \mu(x_0)$$

flux $J \neq 0$

" μ is equalized when particles stop flowing" or "difference in μ is driving force for particles"

(Joules/mole \cdot n = $\frac{N}{\text{mole}}$) force per mole of particles

$$-\frac{\partial \mu}{\partial x} = F_{\text{Appl}}$$

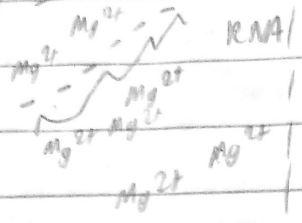
$P_i: \mu_i(T, P, \dots)$
 $\rightarrow \mu_i(T, P, \dots)$
 chemical potential can depend on x

ex #3: Fick's Law of Diffusion

ex #2: HWK II.2

Lecture 33: (read right to left)

How does $\frac{\partial c}{\partial t}$ depend on gradient $\frac{\partial c}{\partial x}$?



Let's calculate some particle laws:

Assume only 1 chemical (drop "i")

chemical potential $\mu^{(0)}$ constant

Temperature, pressure, etc., are constant

$$\mu = \mu^{(0)} + RT \ln c$$

$$\frac{d\mu}{dx} = \frac{d\mu^{(0)}}{dx} + RT \frac{dc}{c} = 0 + RT \frac{dc}{c}$$

use postulate to write down flux:

$$J_x = -RT \mu c \frac{dc}{dx} \quad (J_x = -D_c \frac{\partial \mu_i}{\partial x})$$

$$= -RT \mu \frac{dc}{dx} \quad (\text{Fick's 1st Law})$$

Continuity: $\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = RT \mu \frac{\partial^2 c}{\partial x^2}$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (\text{Fick's 2nd Law})$$

ex: #1: equilibrium

$$J = -D_i \frac{\partial \mu_i}{\partial x}$$

$$\mu_{gi} = \mu_i^{(0)} + RT \ln(c_i)$$

$J=0$ at equilibrium

$$\rightarrow \frac{\partial \mu_{gi}}{\partial x} = 0$$

$$0 = \frac{d\mu_i^{(0)}}{dx} + RT \frac{d \ln(c_i)}{dx}$$

$$d\mu_i^{(0)} = -RT d \ln(c_i)$$

$$\int_0^{\mu_i(x)} d\mu_i^{(0)} = -RT \int_{c_0}^{c(x)} d \ln(c_i)$$

$$\mu_i(x) = -RT (\ln c_i(x) - \ln c_0)$$

Apply $\hat{\sigma}$ to both sides

$$c_i(x) = c_i(0) e^{-\mu_i(x)/RT}$$

Useful formulas:

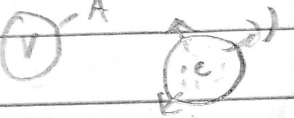
$$\frac{\partial^2 G}{\partial x \partial t} = \frac{\partial^2 G}{\partial t \partial x}$$

$$\frac{\partial}{\partial x} \frac{\partial G}{\partial t} = \frac{\partial}{\partial t} \frac{\partial G}{\partial x}$$

$$\frac{\partial}{\partial x} (S) = \frac{\partial}{\partial t} \mu_i$$

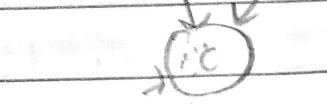
$$-S_i = \frac{\partial \mu_i}{\partial t}$$

Continuity formula:



$$D \cdot J = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} > 0$$

$$\frac{\partial c}{\partial t} < 0$$



$$D \cdot J < 0 \quad \frac{\partial c}{\partial t} > 0$$



$$D \cdot J = 0 \quad \frac{\partial c}{\partial t} = 0$$

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$

"continuity equation"