统计热力学 $\Longrightarrow$ 经典热力学 $\Longrightarrow$ 平衡

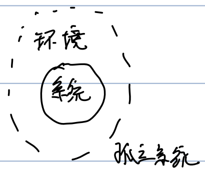
基本假设：1. 微观结构（量子态）出现概率相同

2. 在宏观可分辨时间内，系统遍历所有微观结构

特征时间：每种运动自由度都有特征时间

特征长度：每种运动自由度都有特征长度

环境



$$\Delta S_{孤} = \Delta S_{系统} + \Delta S_{环境} \geq 0$$

$$dS_{环} = \frac{-dQ}{T_{环}}$$ 可逆

严格满足 $dS_{环} = \frac{-dQ}{T_{环}}$ 才能称为理想环境

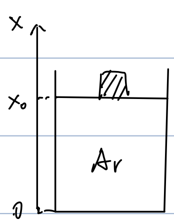
实际环境并不是总能和系统合并为满足热力学孤立系统

热力学环境 = 标准熵源

非平衡态热力学

全域平衡态 —— 局域平衡态

线性非平衡态热力学

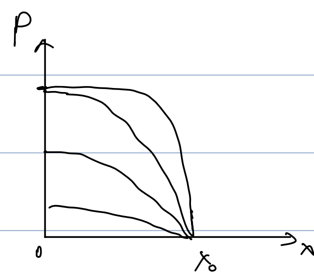


迅速移走重物，

$t=0$，$P=$ 常数 $=P_{外}$

$t=0+dt$ $P=$ 常数 $>P_{外}$

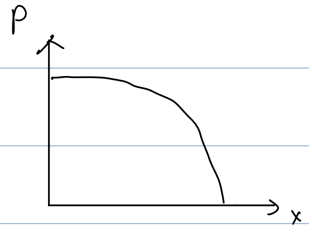
$t>dt$ $P\neq$ 常数



非平衡态

强度性质的梯度和广度性质的通量

强度性质p



梯度　　强度性质

$$\vec{\Lambda}_B = \left(\frac{\partial B}{\partial z}\right)\vec{z}$$　　空间

方向　　单位向量

若 $\vec{\Lambda}_B \neq 0$ 则 B 耦合广度性质 C 的通量

广度性质

$$J_c = \frac{1}{a}\cdot\left(\frac{\partial c}{\partial t}\right)$$　　时间

通量　　面积

$J_c = -k_c\cdot\vec{\Lambda}_B$　　(B、C耦合)　　$\{$ T和Q、$\overbrace{\mu \text{和} n}^{x,p}$、mV和V $\}$

传热　　传质　　动量

强度性质的差异带来驱动力

输运过程

传热　　$J_Q = -k_Q\cdot\frac{\partial T}{\partial z}$

热导率

k_Q

从分子结构/相互作用看

固体　　冰　　低频晶格振动

液体　　水　　类振动(非整体)、对流

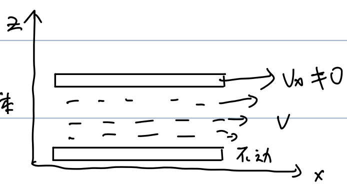
气体　　水蒸气

铜　　电子导体，电子参与导热

金刚石　　晶格振动

石墨　　电子导体＋晶格振动　　} 小能隙

传动量



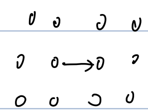
$$\frac{\partial V_x}{\partial z} \neq 0$$

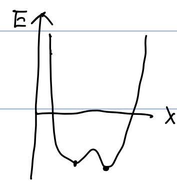
$$J_p = -\eta\cdot\left(\frac{\partial V_x}{\partial z}\right)$$

黏度

分子间相互作用越大，η越大

η





$$\frac{\rho_{\text{激发态}}}{\rho_{\text{基态}}} = e^{-\frac{\Delta E}{RT}}$$

反比于 η

传质

分子扩散　　Fick第一定律　　$J_n = -D\frac{\partial[i]}{\partial z}$　　(来自实验)

$$\Lambda_\mu = \frac{\partial \mu}{\partial z} = \frac{\partial(\mu^\circ + RT\ln a)}{\partial z} = RT\overset{\text{扩散系数}}{\frac{\partial \ln a}{\partial z}} = RT\left(\frac{\partial \ln x}{\partial z} + \underbrace{\boxed{\frac{\partial \ln \gamma}{\partial z}}}_{\approx 0}\right)$$

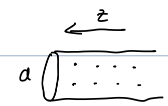
$$\approx RT \cdot \frac{1}{x} \cdot \frac{\partial x}{\partial z}$$

或 $\approx RT \cdot \frac{1}{[i]} \cdot \frac{\partial [i]}{\partial z}$

(扩散的驱动力) $\Lambda_\mu = \frac{RT}{[i]} \cdot \Lambda_{[i]}$

(阻力) η . $V_{漂移}$. 粒子大小 (d) . $F_{摩擦} = 3\pi d \eta V_{漂移}$

粒子漂移的速度



$V_{漂移} \cdot dt \cdot a = dV$

$dn = [i] \cdot dV$

稳态扩散 $F_{扩散} = F_{摩擦}$

单分子：$\frac{kT}{[i]} \cdot \Lambda_{[i]} = -3\pi d \eta V_{漂移}$

$$J_n = \frac{1}{a} \cdot \frac{\partial n}{\partial t}$$

$$= \frac{1}{a} \cdot \frac{[i] \cdot a\, V_{漂移}\, dt}{dt}$$

$$= [i] \cdot V_{漂移}$$

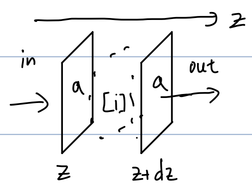
$\Lambda_{[i]} = \frac{\partial [i]}{\partial z}$ $\quad J_n = -D\,\Lambda_{[i]}$

$$\Lambda_{[i]} = \frac{-3\pi d \eta V_{漂移} \cdot [i]}{kT}$$

$$J_n = -D \cdot \frac{-3\pi d \eta V_{漂移} \cdot [i]}{kT} = [i] \cdot V_{漂移}$$

$\therefore D = \frac{kT}{3\pi d \eta}$ (Stokes - Einstein 公式)

Fick 第二定律：$\frac{\partial [i]}{\partial t} = D\frac{\partial^2 [i]}{\partial z^2}$



$$\frac{\partial [i]}{\partial t} = \frac{dn}{dV \cdot dt} = \frac{dn}{a\,dz \cdot dt}$$

$J_c = \frac{1}{a} \cdot \frac{\partial c}{\partial t}$ $\quad dC = a \cdot dt \cdot J_c$

$J_{in} = -D\left.\frac{\partial [i]}{\partial z}\right|_z$ $\quad \therefore dn = a\,dt \cdot (J_{in} - J_{out})$

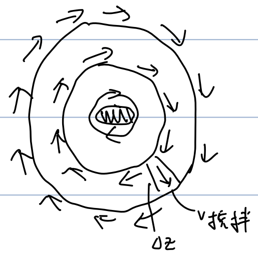
$J_{out} = -D\left.\frac{\partial [i]}{\partial z}\right|_{z+dz}$ $\quad \frac{\partial [i]}{\partial t} = \frac{a \cdot dt \cdot J_{in} - J_{out}}{a \cdot dt \cdot dz} = \frac{J_{in} - J_{out}}{dz}$

$$= \frac{1}{dz} \cdot \left(-D\left.\frac{\partial [i]}{\partial z}\right|_z + D\left.\frac{\partial [i]}{\partial z}\right|_{z+dz}\right)$$

泰勒展开 $\left.\frac{\partial [i]}{\partial z}\right|_{z+dz} = \left.\frac{\partial [i]}{\partial z}\right|_z + \left.\frac{\partial^2 [i]}{\partial z^2}\right|_z \cdot dz + \overset{\text{高阶无穷小}}{\cdots}$

$$\therefore \frac{\partial[i]}{\partial t} = \frac{1}{dz}\cdot D\cdot \frac{\partial^2[i]}{\partial z^2}\Big|_z \cdot dz = D\frac{\partial^2[i]}{\partial z^2}$$

同心圆搅拌



$$\frac{\partial[i]}{\partial t} = \frac{\Delta n}{a\cdot\Delta z\cdot\Delta t} = \frac{1}{\Delta z}\left(J_{in} - J_{out}\right)$$

$$J_n = [i]\cdot v_{搅拌}$$

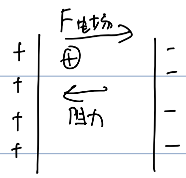
$$\frac{\partial[i]}{\partial t} = \frac{v_{搅拌}}{\Delta z}\left([i]|_z - [i]|_{z+dz}\right)$$

$$= -\frac{v_{搅拌}}{\Delta z}\cdot\frac{\partial[i]}{\partial z}\cdot dz = -v_{搅拌}\frac{\partial[i]}{\partial z}$$

扩散+搅拌 $$\frac{\partial[i]}{\partial t} = D\frac{\partial^2[i]}{\partial z^2} - v_{搅拌}\frac{\partial[i]}{\partial z}$$

布朗运动与自扩散 $$\Delta x = \sqrt{2D\Delta t}$$

带电离子在电场中运动



$$F_{电场} = ze\cdot E_{电场}$$

$$F_{摩擦} = 3\pi d\eta\cdot v_{迁移}$$

$$v_{迁移} = \frac{zeE_{电场}}{3\pi d\eta}$$

比例常数/迁移率 $$u = \frac{ze}{3\pi d\eta}$$

$$v_{迁移} = u\cdot E_{电场}$$

摩尔电导率 $$\kappa_{电导,m} = \frac{\kappa_{电导}}{[i]} = zuF$$

无限稀释 $$\kappa^{\circ}_{电导,m} = (z_{阳}u_{阳}\nu_{阳} + z_{阴}u_{阴}\nu_{阴})F$$

$$= \nu_{阳}\kappa^{\circ}_{阳,电导,m} + \nu_{阴}\kappa^{\circ}_{阴,电导,}$$