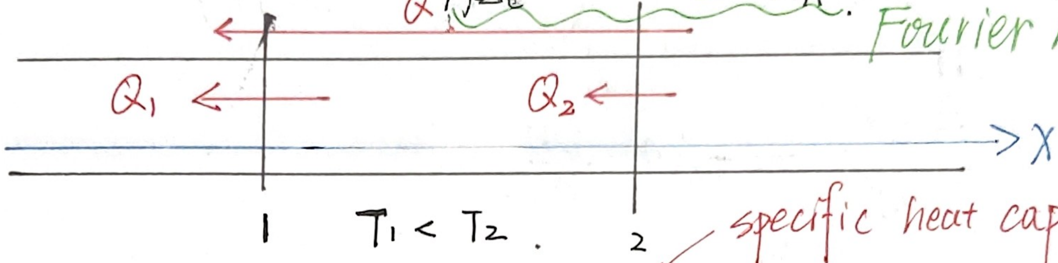
Rates of Processes
- transport of Energy : Heat Conduction
- transport of Momentum : Viscosity
- transport of Particles : Diffusion

1. Heat Conduction. $\frac{Q}{A\Delta t} = -k_t \frac{dT}{dx}$ thermal conductivity

Fourier heat conduction Law.



specific heat capacity.

$$Q = Q_2 - Q_1 \quad ; \quad Q = -c\,m\,dT = -c\rho A\Delta x\, dT.$$

$$\frac{\partial Q}{\partial t} = \frac{\partial Q_2}{\partial t} - \frac{\partial Q_1}{\partial t} = -\left(A k_t \frac{\partial T}{\partial x}\Big|_2 - A k_t \frac{\partial T}{\partial x}\Big|_1\right)$$

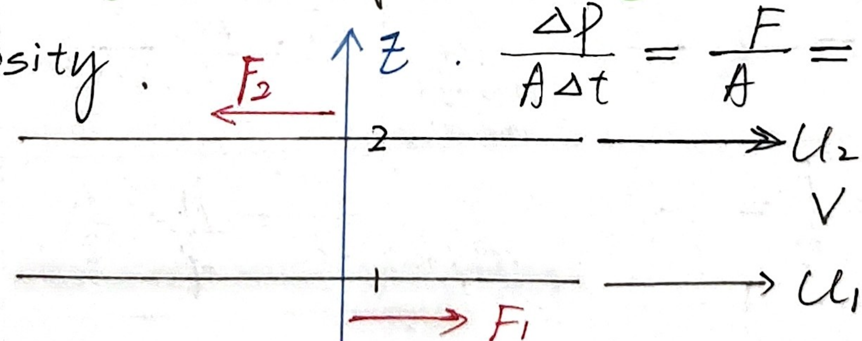
$$-c\rho A\Delta x \frac{\partial T}{\partial t} = -A k_t\left(\frac{\partial T}{\partial x}\Big|_2 - \frac{\partial T}{\partial x}\Big|_1\right)$$

$$\Downarrow$$

Heat equation. $\frac{\partial T}{\partial t} = \frac{k_t}{c\rho}\frac{\partial^2 T}{\partial x^2} = K \frac{\partial^2 T}{\partial x^2}$.

coefficient of viscosity

2. Viscosity. $\frac{\Delta p}{A\Delta t} = \frac{F}{A} = \eta \frac{du}{dz}$.



$$\frac{\Delta p}{A\Delta t}\Big|_1^2 = \frac{F_2}{A} - \frac{F_1}{A} = \eta\left(\frac{\partial u}{\partial z}\Big|_2 - \frac{\partial u}{\partial z}\Big|_1\right)$$

$$\frac{m}{A}\frac{\partial u}{\partial t} = \frac{\rho A\Delta z}{A}\frac{\partial u}{\partial t} = \rho\Delta z \frac{\partial u}{\partial t}.$$

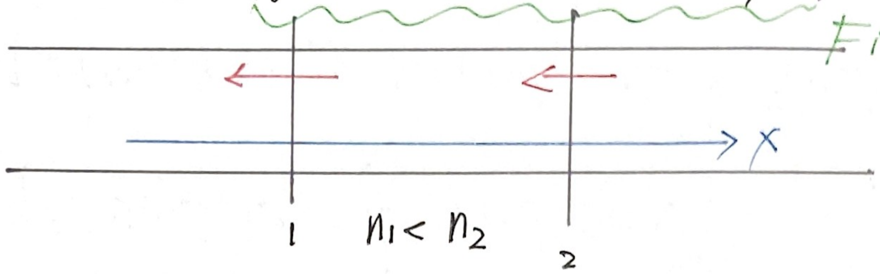
$$\Downarrow$$

$$\frac{\partial u}{\partial t} = \frac{\eta}{\rho}\frac{\partial^2 u}{\partial z^2}.$$

3. Diffusion.

$$\frac{N}{A\Delta t} = J_x = -D\frac{dn}{dx}$$ diffusion coefficient

Fick's Law



$$\frac{N_2}{A\Delta t} - \frac{N_1}{A\Delta t} = -D\left(\frac{\partial n}{\partial x}\Big|_2 - \frac{\partial n}{\partial x}\Big|_1\right)$$

$$\parallel \qquad\qquad \parallel$$

$$-\frac{\partial}{\partial t}\frac{nA\Delta x}{A\cancel{\Delta t}} = -\Delta x\cdot\frac{\partial n}{\partial t}$$

$$\Downarrow$$

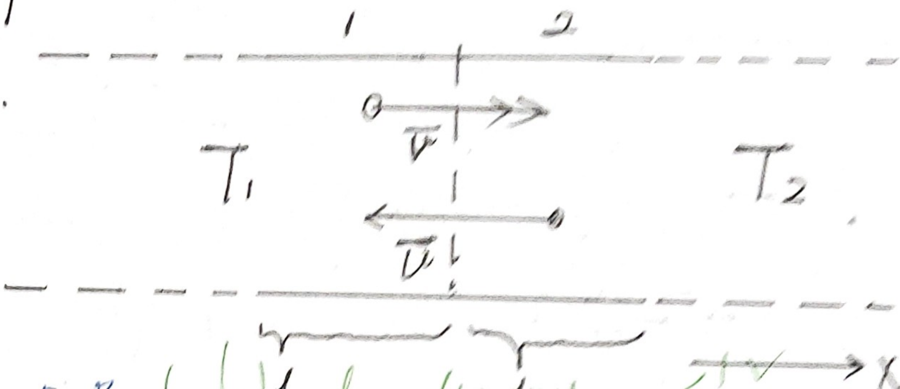
$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}.$$ Fick's second law.

4. Conclusion.

Transport of	Equation (I). for surfaces	Constant	Equation (II). for functions	Function.
Energy Q Heat conduction	$\frac{Q}{A\Delta t} = -k_t\frac{dT}{dx}$	k_t Thermal Conductivity	$\frac{\partial T}{\partial t} = \frac{k_t}{c\rho}\cdot\frac{\partial^2 T}{\partial x^2}$	$T(x,t)$.
Momentum Δp Viscosity	$\frac{\Delta p}{A\Delta t} = \frac{\lvert F_x\rvert}{A} = \eta\frac{du_x}{dz}.$	η coefficient of Viscosity	$\frac{\partial u_x}{\partial t} = \frac{\eta}{\rho}\frac{\partial^2 u_x}{\partial z^2}.$	$u_x(z,t)$
Particles N Diffusion.	$\frac{N}{A\Delta t} = J_x = -D\frac{dn}{dx}$	D. Diffusion coefficient	$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}$	$n(x,t)$

Who Determines k_t, η, D. ~ Analysis By Kinetic Theory

For Ideal Gas.



1. k_t

$$\frac{Q}{A\Delta t} = -k_t \frac{dT}{dx}$$

probability 50%. $\left(\frac{1}{2d}\right)$ l d = dimension $< \begin{matrix} 1 \\ 2 \\ 3 \end{matrix}$

mean free path.

$$Q = \frac{1}{2}\left(U_{1\to 2} - U_{2\to 1}\right)$$

$$Q = -\frac{1}{2}(U_2 - U_1) = -\frac{1}{2}\left(\frac{fNk}{2}T_2 - \frac{fNk}{2}T_1\right)$$

$$\frac{Q}{A\Delta t} = -\frac{fNkl}{4A\Delta t}\frac{T_2 - T_1}{l} = -k_t\frac{dT}{dx}.$$

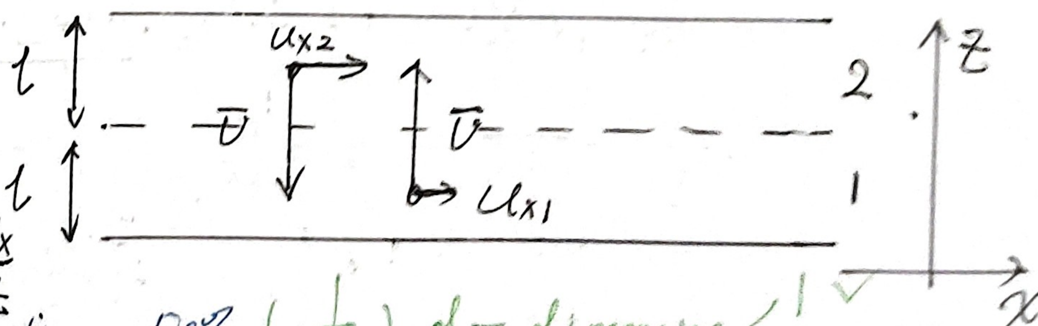
$$\therefore k_t = \frac{fNkl}{4A\Delta t} = \frac{fk}{4}\frac{Nl}{Al}\frac{l}{\Delta t} = \frac{fk}{4}\frac{N}{V}\, l\, \bar{v}$$

$$l = \frac{V}{4\pi r^2 N} \qquad \bar{v} = \sqrt{\frac{fkT}{m}}$$

$$\Downarrow$$

$$\therefore k_t = \frac{fk}{4}\cdot\frac{1}{4\pi r^2}\cdot\sqrt{\frac{fk}{m}}\cdot\sqrt{T} \Longrightarrow k_t \propto \sqrt{T}.$$

2. η.



$$\left|\frac{\Delta p}{A\Delta t}\right| = \frac{|F_x|}{A} = \eta\frac{du_x}{dz}$$

probability 50% $\left(\frac{1}{2d}\right)$ d = dimension $< \begin{matrix} 1 \\ 2 \\ 3 \end{matrix}$

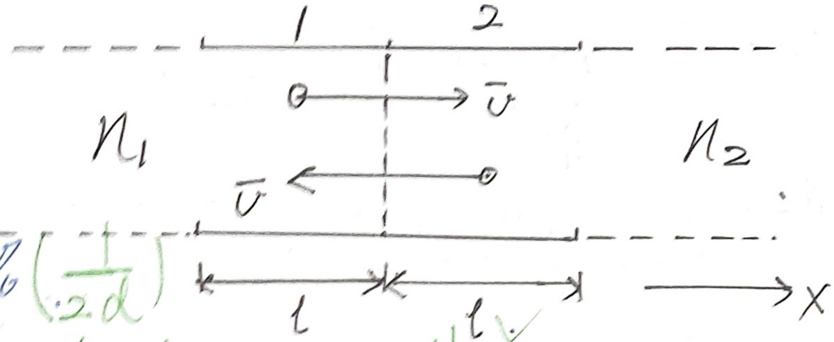
$$|\Delta p| = \frac{1}{2}\left(mu_{x1} - mu_{x2}\right)N = \frac{1}{2}mN(u_{x2} - u_{x1})$$

$$\left|\frac{\Delta p}{A\Delta t}\right| = \frac{mNl}{2A\Delta t}\frac{u_{x2} - u_{x1}}{l} = \eta\frac{du_x}{dz}.$$

$$\therefore \eta = \frac{mN}{2A}\frac{l}{\Delta t} = \frac{mNl}{2Al}\frac{l}{\Delta t} = \frac{m}{2}\frac{N}{V}\, l\, \bar{v}$$

$$\eta = \frac{m}{2}\frac{1}{4\pi r^2}\sqrt{\frac{fk}{m}}\sqrt{T} \Longrightarrow \eta \propto \sqrt{T}$$

3. D.



$$\frac{N}{A\Delta t} = J_x = -D\frac{dn}{dx}$$

probability 50% $\left(\frac{1}{2d}\right)$

$$N = \frac{1}{2}(n_1 A l - n_2 A l)$$

d = dimension = $\langle{}^{1}_{2}{}_{3}$. l ✓

$$\frac{N}{A\Delta t} = -\frac{1}{2}\frac{Al l}{A\Delta t}\frac{n_2 - n_1}{l} = -D\frac{dn}{dx}$$

$$\therefore D = \frac{1}{2} l \frac{l}{\Delta t} = \frac{1}{2} l \bar{v}, \quad l = \frac{V}{4\pi r^2 N} \quad \bar{v} = \sqrt{\frac{fkT}{m}}$$

$$D = \frac{1}{2}\frac{V}{4\pi r^2 N}\sqrt{\frac{fk}{m}}\cdot\sqrt{T}$$ However. $pV = NkT$

$$\therefore \frac{V}{N} = k\frac{T}{p} \quad \therefore D = \frac{1}{2}\cdot\frac{1}{4\pi r^2}\sqrt{\frac{fk}{m}}\cdot k\cdot\frac{(T)^{\frac{3}{2}}}{p} \propto \frac{(T)^{\frac{3}{2}}}{p}$$

4. Conclusions.

(1) Expressions of $k_t \cdot \eta \cdot D$.

Which kinds of molecule

density

mean free path

$$\bar{v} = \frac{l}{\Delta t}$$

collision interval

$\boxed{\text{Macroscope:}}$

$$\frac{Q}{A\Delta t} = -k_t\frac{dT}{dx}, \quad k_t = \frac{fk}{4}\left(\frac{N}{V}\right)\boxed{(l)\cdot(\bar{v})}$$

$$\frac{F_x}{A} = \frac{\Delta p}{A\Delta t} = \eta\frac{du_x}{dz}, \quad \eta = \frac{m}{2}\left(\frac{N}{V}\right)\boxed{(l)(\bar{v})}$$

$$J_x = \frac{N}{A\Delta t} = -D\frac{dn}{dx}, \quad D = \boxed{\frac{1}{2}\frac{l^2}{\Delta t}} = \frac{1}{2}\boxed{(l)(\bar{v})}$$

$\boxed{\text{Microscope}}$

(2). Gas: $k_t \propto \sqrt{T}$, $\eta \propto \sqrt{T}$, $D \propto (T)^{\frac{3}{2}}$

$T\uparrow \Rightarrow k_t\uparrow$ $\quad T\uparrow \Rightarrow \eta\uparrow$ $\quad T\uparrow \Rightarrow D\uparrow$.

Lquid & Solid:

$$T\uparrow \Rightarrow \eta\downarrow$$

more likely to transfer...

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$T\downarrow \Rightarrow$ interactions $\uparrow$.

Caused by interactions between molecules.

关于扩散系数

定义一：$\vec{J} = -D\nabla \cdot n(x,y,z)$；

$\vec{J} = -D\cdot\left(\frac{\partial n}{\partial x}, \frac{\partial n}{\partial y}, \frac{\partial n}{\partial z}\right)$

$$\begin{cases} J_x = -D\frac{dn}{dx} \\ J_y = -D\frac{dn}{dy} \\ J_z = -D\frac{dn}{dz} \end{cases}$$

定义二：$\langle \vec{r}^2 \rangle = 2Dt\times d = 6Dt \ (d=3)$

证明定义一与定义二等价的思路：

定义一 $\Longleftrightarrow D = \frac{1}{2d}\frac{l^2}{\Delta t} \Leftrightarrow l^2 = 2D\Delta t\times d$

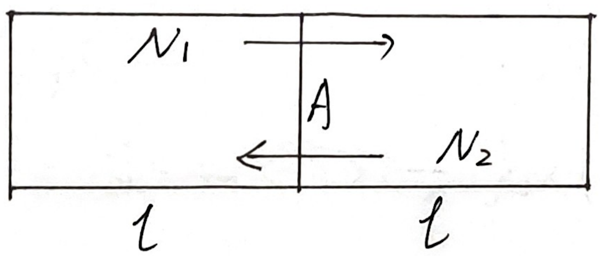
$l^2 = 2D\Delta t\times d \Updownarrow$

定义一 ⇘ 定义二

定义二 $\Longleftrightarrow \langle \vec{r}^2\rangle = 2Dt\times d$

(一) 推导D的微观表达式 $l^2 = 2D\Delta t\times d$

借鉴方法：
- 研究对象选分界面两侧厚度为l的物体（参考k_t）
- 从一维推广到d维（参考理想气体P）



$N_1 = n_1\cdot Al$

$N_2 = n_2\cdot Al$

$J_x = \frac{1}{2}\left(\frac{N_1-N_2}{A\Delta t}\right)$

(1) 一维

$$J_x = \frac{1}{2}\left(\frac{N_1-N_2}{A\Delta t}\right) = -\frac{1}{2}\frac{Al(n_2-n_1)}{A\Delta t} = -\frac{1}{2}\frac{l^2}{\Delta t}\frac{dn}{dx}$$

(2) 一维推广到d维

① 将l代换为l_x（l在x轴方向上分量）

$$l^2 = l_x^2 + l_y^2 + l_z^2;\quad l_x^2 = \frac{1}{d}l^2$$

② 将概率/占比 $\frac{1}{2}$ 代换为 $\frac{1}{2d}$（d个维度，$2d$个方向）

$$J_x = -\frac{1}{2d}\frac{l^2}{\Delta t}\frac{dn}{dx} = -\frac{1}{2}\frac{l^2}{d\Delta t}\frac{dn}{dx}$$

$$D = \frac{1}{2}\frac{l^2}{d\Delta t} \Leftrightarrow l^2 = 2D\Delta t\times d$$

(二) 由 $l^2 = 2D\Delta t \times d$. 推 $\langle \vec{r}^2 \rangle = 2Dt \times d$.

取 $t = \lambda \cdot \Delta t$ 若 $\langle \vec{r}^2 \rangle = \lambda l^2$ 则可以推出.

所以. 只需证. $\langle \vec{r}^2 \rangle = \lambda l^2$.

参考 QMB 笔记. One Dimensional Random Walk.

如 对于一维 有 $\langle \vec{r_x}^2 \rangle = \lambda_x l^2 = \lambda l_x^2$. 从一维到 d 维/三维.

$\vec{r}^2 = \vec{r_x}^2 + \vec{r_y}^2 + \vec{r_z}^2$

$\langle \vec{r}^2 \rangle = \langle \vec{r_x}^2 \rangle + \langle \vec{r_y}^2 \rangle + \langle \vec{r_z}^2 \rangle = \lambda l^2$

(1) $\langle \vec{r_x}^2 \rangle = \lambda_x l^2 = \left(\frac{\lambda}{3}\right) l^2 = \frac{1}{3}\lambda l^2$

(2) $\langle \vec{r_x}^2 \rangle = \lambda l_x^2 = \lambda\left(\frac{l^2}{3}\right) = \frac{1}{3}\lambda l^2$

另法.

$\vec{r_x} = \sum_i \vec{r_{xi}}$

$\langle \vec{r_x}^2 \rangle = \langle \sum_i \sum_j \vec{r_{xi}} \cdot \vec{r_{xj}} \rangle$

$= \sum_i \sum_j \langle \vec{r_{xi}} \cdot \vec{r_{xj}} \rangle$

其中 $\langle \vec{r_{xi}} \cdot \vec{r_{xj}} \rangle = \begin{cases} \langle \vec{r_{xi}}^2 \rangle = l^2 & (i=j) \\ \langle \vec{r_{xi}} \rangle \cdot \langle \vec{r_{xj}} \rangle = 0 & (i \neq j \text{ 独立}) \end{cases}$

$\therefore \sum_i \sum_j \langle \vec{r_{xi}} \cdot \vec{r_{xj}} \rangle = \lambda_x l^2$

从而 $\langle \vec{r}^2 \rangle = \lambda l^2$.

进而. $l^2 = 2D\Delta t \times d$.

$\Updownarrow$

$\lambda l^2 = 2D(\lambda \Delta t) \times d. \Leftrightarrow \langle \vec{r}^2 \rangle = 2Dt \times d$.

(三) D 的两重含义.

1. 由定义一; $\vec{J} = -D \nabla \cdot n(x,y,z) = -D\left(\frac{\partial n}{\partial x}, \frac{\partial n}{\partial y}, \frac{\partial n}{\partial z}\right)$.

Flux $\vec{J}$ 沿 $n(x,y,z)$ 负梯度方向. (n 减少最快方向)

$|\vec{J}| = \frac{\Delta N}{A\Delta t}$, D 为其中比例系数. n 浓度 n 宏观 一群粒子

2. 由定义二; $\langle \vec{r}^2 \rangle = 2D\cancel{t} \cdot d$. $\vec{r}$ 位移 ~ 微观 单个分子

位移方平方的期望 正比于时间. D 为比例系数的一部分.

Random Walks 中的维数

$\langle x^2\rangle - \langle x\rangle^2 = D(x) = \sigma^2$ 方差

由于 $\langle \vec{x}\rangle = \vec{0}$ 所以 $\sigma^2 = \langle x^2\rangle$

当 $\vec{x}$ 为一维随机变量：$\langle \vec{x}^2\rangle = 2Dt = \sigma^2$

为二维 ………：$\langle \vec{x}^2\rangle = 4Dt = \sigma^2$

为三维 ………：$\langle \vec{x}^2\rangle = 6Dt = \sigma^2$

$\vec{r} = (x, y, z) = (r, \theta, \varphi)$. 三维

$\vec{r} = (x, y) = (r, \theta)$ 投影到二维

$\langle \vec{r}^2\rangle$ 是二维随机变量的均方 所以 $\langle \vec{r}^2\rangle = 4Dt$

对 $\vec{r}$ 取模 $|\vec{r}| = r$ 是一维随机变量 方差为 $\sigma^2(|\vec{r}|) = 2Dt$

正态分布 $(\mu=0)$ $P(r) = \dfrac{1}{\sigma\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}$ 当 $\sigma^2 = 2Dt$

$$P(r) = \frac{1}{\sqrt{4\pi Dt}} \cdot e^{-\frac{x^2}{4Dt}}$$

t 可以取 Δt. 对应 r 取 $\underbrace{\Delta|\vec{r}|}_{\text{一维随机变量}} \neq |\Delta\vec{r}|$

辨析. $\langle|\vec{r}|^2\rangle$ $\begin{cases} = \text{一维随机变量 } |\vec{r}|^2 \text{ 的期望} \\ = \sigma^2(\vec{r}) = d\text{维随机变量 } \vec{r} \text{ 的方差} \end{cases}$

$\Delta|\vec{r}|$ 是 $\vec{r}$ 向径向的投影 (d维 $\to$ 1维) 的变化量 ~ 1维 Random Walk

从而其方差 $\sigma^2(\Delta|\vec{r}|) = 2D\Delta t$

* $\sigma^2(\Delta|\vec{r}|^2) = 2D\Delta t$；$\sigma^2(\vec{r}) = 2Dt \times d$.

* 一维变量直方图：曲线拟合（平面）

二维变量直方图：曲面拟合（空间）

* $\vec{r}$ 为 d 维向量 ~ d 维 Random Walk

$$\sigma^2(\vec{r}) = \langle \vec{r}^{\,2} \rangle = (2Dt) \times d$$

$\vec{r}$ 投影到径向（r 轴）$\sim$ d 维 → 1维 Random Walk

$|\vec{r}|$. 再取其在 Δt 内的变化量 $\boxed{\Delta|\vec{r}|}$

$$\sigma^2(\Delta|\vec{r}|) = 2D\Delta t$$

求均方 $\langle \vec{r}^{\,2} \rangle$；求 $\langle \vec{r}^{\,2} \rangle - t$ 斜率

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$D = \dfrac{k_B T}{6\pi\eta r}$. 热学角度 ~ D ~ 统计角度 $\begin{cases} \text{均方}: \langle \vec{r}^{\,2} \rangle = (2Dt) \times d \\ \text{方差}\ \sigma^2(\Delta|\vec{r}|) = 2D\Delta t \end{cases}$

$D = \mu k_B T$.

扩散系数.

求 $|\Delta\vec{r}|$ 的方差.
