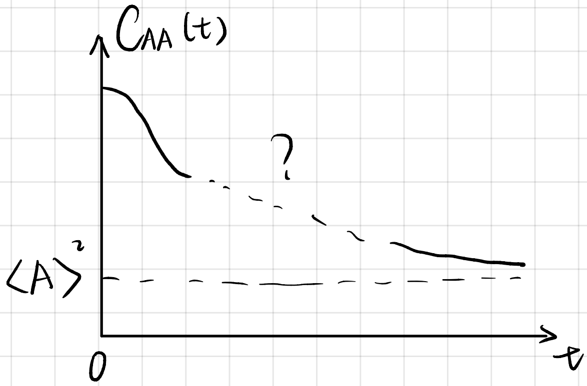


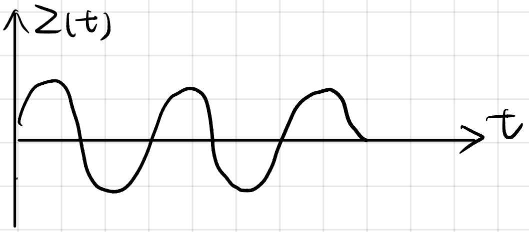
t→∞时 $C_{AA}(t)=\langle A\rangle^2$

$$C^{\delta}_{AA}(t)=\langle (A(0)-\langle A\rangle)(A(t)-A)\rangle$$
$$=\langle \delta A(0)\,\delta A(t)\rangle \qquad C^{\delta}_{AA}(t\to\infty)=\langle A(0)-\langle A\rangle\rangle^2=0$$

例子：

① 速度关联 $Z_x(t)=\langle v_x(0)\cdot v_x(t)\rangle$

若为谐振子模型

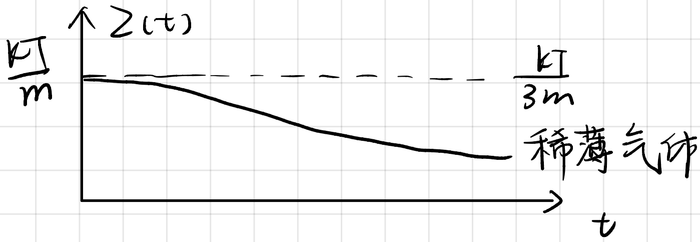


理想气体

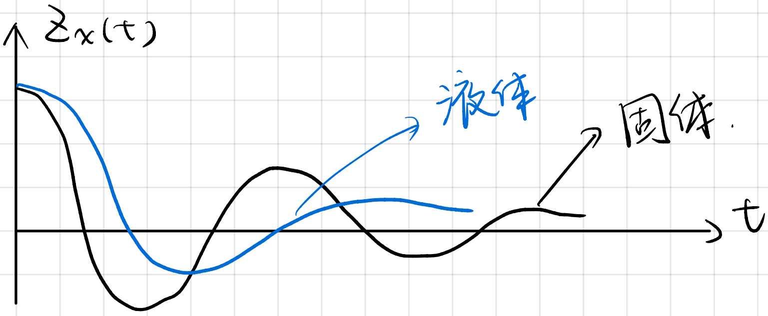
$$\langle v_x(0)\,v_x(t)\rangle=\langle v_x^2(0)\rangle=\frac{kT}{m}$$

稀薄气体

v会有指数衰减



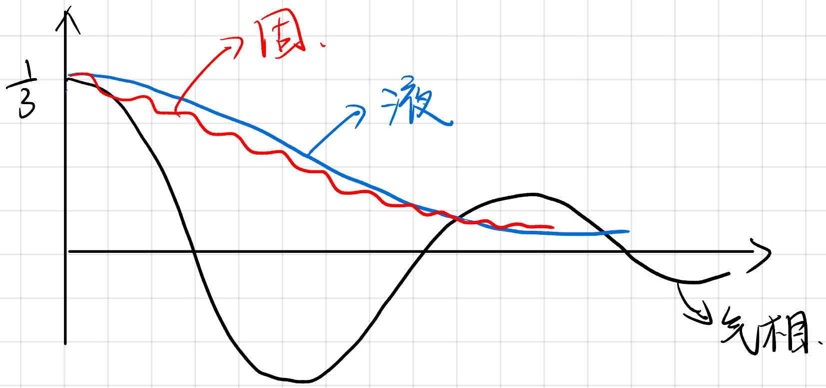
固体：$F_x\sim -kx-\gamma v$，即既有衰减，又有振荡



液体：也会有振荡，但没有固体那么明显

② 取向关联 $\langle \mu_z(0)\mu_z(t)\rangle = \frac{1}{3}\langle \vec{\mu}(0)\cdot\vec{\mu}(t)\rangle$

取 $\vec{\mu}(0)$ 方向为 z 轴，$\vec{\mu}(t)$ 与 $\vec{\mu}(0)$ 夹角为 $\theta \Rightarrow \theta(t)$

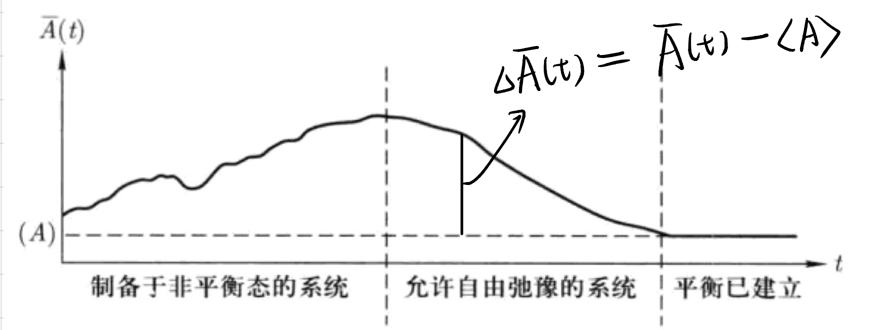


$$I\ddot{\theta} = \vec{L} - \gamma_\theta\dot{\theta}$$

作业 8.1 8.2

Onsager Regression Hypothesis.

Micro → Macro.



O.R.H:
$$\underbrace{\frac{\Delta\bar{A}(t)}{\Delta\bar{A}(0)}}_{\text{宏观}} = \underbrace{\frac{\langle\delta A(0)\,\delta A(t)\rangle}{\langle(\delta A(0))^2\rangle} = \frac{C^{\delta}_{AA}(t)}{C^{\delta}_{AA}(0)}}_{\text{微观}}$$

作业 8.3 (Hint: $\bar{A}(t) = \int d\Gamma\, F(\Gamma) A(t)$，取 $F(\Gamma) = \frac{f_{eq}\cdot A(\Gamma)}{\langle A\rangle}$)

$$\Rightarrow \frac{\Delta\bar{A}(t)}{\Delta\bar{A}(0)} \propto C^{\delta}_{AA}(t) \quad (\Delta\bar{A}(t) = \bar{A}(t) - \langle A\rangle)$$

§8.3. Chemical Kinetics.

1、问题：

$$A \underset{k_{AB}}{\overset{k_{BA}}{\rightleftharpoons}} B$$

反应速率常数如何从微观态得到？

① $dC_A/dt = -dC_B/dt = -k_{BA}C_A(t) + k_{AB}C_B(t)$

$C_A(t) + C_B(t) = C_0$

② $dC_A(t)/dt = 0 \Rightarrow \langle C_A\rangle = \dfrac{k_{AB}C_0}{k_{AB}+k_{BA}}$

$\Delta C_A(t) = C_A(t) - \langle C_A\rangle \Rightarrow \dfrac{d}{dt}\Delta C_A(t) = -(k_{AB}+k_{BA})\Delta C_A(t)$

$\Rightarrow \Delta C_A(t) = \Delta C_A(0)e^{-(k_{AB}+k_{BA})t} \equiv \Delta C_A(0)e^{-t/\tau} \quad \tau \equiv \dfrac{1}{k_{BA}+k_{AB}}$

(宏观动力学)

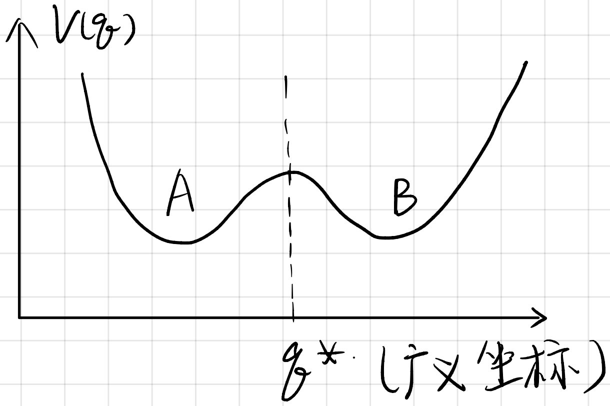
如何将宏观与微观联系？

找到微观量 $\overline{n_A}(t) \propto C_A(t)$，再利用昂萨格假说

$$\frac{\Delta C_A(t)}{\Delta C_A(0)} = \frac{\langle \delta n_A(0)\,\delta n_A(t)\rangle}{\langle \delta n_A(0)^2\rangle}$$

3. 微观力学量

(1) 反应坐标



$$\theta(x) = \begin{cases} 1, & x>0 \\ 0, & x<0 \end{cases}$$

(2) $n_A(t) = H_A[q(t)] = \begin{cases} 1, & q(t) < q^* \\ 0, & q(t) > q^* \end{cases}$

$\quad\;\, ||| $

$\theta[q^* - q(t)]$

$$\langle H_A(q)\rangle = \frac{\int dq\, e^{-\beta V(q)} H_A(q)}{\int dq\, e^{-\beta V(q)}} = \frac{\int_{-\infty}^{q^*} e^{-\beta V(q)}\, dq}{\int_{-\infty}^{+\infty} e^{-\beta V(q)}\, dq} = x_A \left(= \frac{\langle C_A\rangle}{\langle C_A\rangle + \langle C_B\rangle}\right)$$

$\langle H_A^2\rangle = \langle H_A\rangle = x_A$

$\langle (\delta H_A)^2\rangle = \langle H_A^2\rangle - \langle H_A\rangle^2$

$= x_A - x_A^2 = x_A x_B$

(3). O.R.H:

$\to H_A(0)H_A(t)-\langle H_A^2\rangle$

$$\frac{\langle \delta n_A(0)\,\delta n_A(t)\rangle}{\langle(\delta n_A(0))^2\rangle}=\frac{\Delta C_A(t)}{\Delta C_A(0)}=e^{-\frac{t}{\tau}}$$

$\to x_A x_B$.

$$\Rightarrow \langle H_A(0)H_A(t)\rangle - x_A^2 = x_A x_B e^{-t/\tau} \quad ①$$

4. Reaction Rate Constant: k_{BA}.

对①式求导: $\frac{1}{\tau}e^{-\frac{t}{\tau}} = -(x_A x_B)^{-1}\langle H_A(0)\dot{H}_A(t)\rangle$

$$= (x_A x_B)\langle \dot{H}_A(q(0))\,H_A(q(t))\rangle$$

$$\dot{H}_A(q)\big|_0 = \frac{dH}{dq}\cdot\dot{q}\Big|_{t=0}.$$

$$= -\delta(q-q^*)\,\dot{q}\,\Big|_{t=0}. \qquad H_A[q(t)] = 1-H_B[q(t)]$$

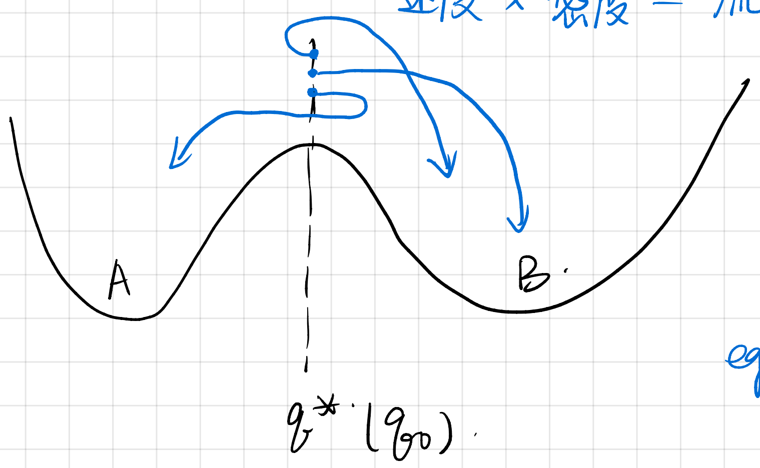
即 $-\langle H_A(0)\dot{H}_A(q)\rangle = -\langle\delta(q_0-q^*)\dot{q}(0)H_A[q(t)]\rangle$

$$= -\underbrace{\langle\delta(q_0-q^*)\dot{q}(0)\rangle}_{q\text{与}\dot{q}\text{无关联}\ \text{“}0\text{”}.} + \langle\delta(q_0-q^*)\dot{q}(0)H_B(q(t))\rangle$$

$$\Rightarrow \tau^{-1}e^{-\frac{t}{\tau}} = \langle\dot{q}(0)\delta(q_0-q^*)H_B(q(t))\rangle(x_A x_B)^{-1}$$

$$\xRightarrow[x_A\cdot x_B]{\text{代入}\tau.} k_{BA}e^{-\frac{t}{\tau}} = \langle \underbrace{\dot{q}(0)\,\delta(q_0-q^*)}_{\to\ \text{flow}.}\,H_B(q(t))\rangle x_A^{-1}$$

速度 × 密度 = 流.



从 $q=q_0$ 开始, 看 t 时刻时到达 $q(t)>q^*$ 的轨线会对 k_{BA} 产生贡献.

eg. $\dot{q}(0)>0$. 向右. $k_{BA}\uparrow$

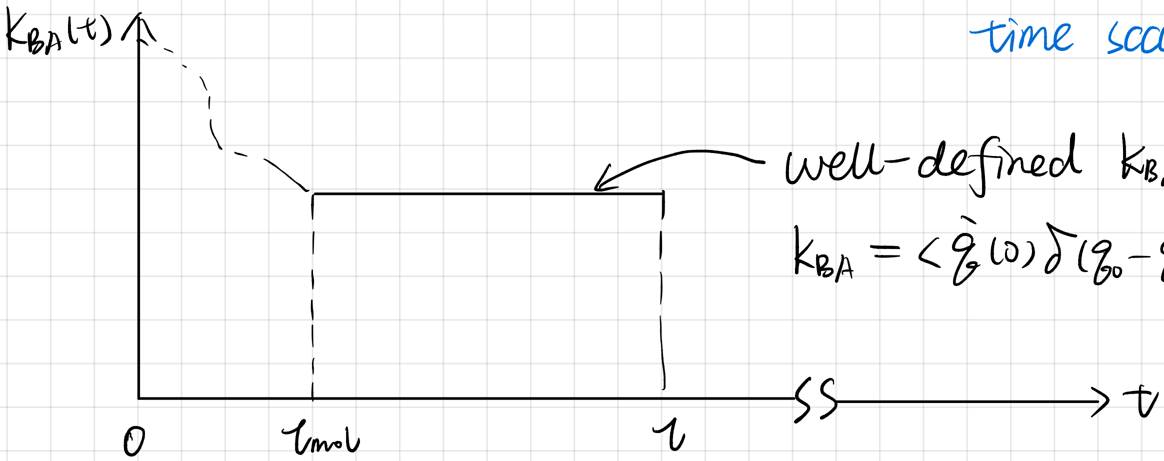
(i) K_{BA}量纲：t^{-1}，则 $\delta(q_0-q^*)$是密度(L^{-1})的量纲. ($\int\delta(q-q^*)dq=1$)

(ii) 为什么 K_{BA} 会有时间依赖性?

我们在推导中用到 $\Delta C_A(t)/\Delta C_A(0) = e^{-\frac{t}{\tau}}$，得到这个结论用到了 K_{BA} 为常数.

因为 K_{BA} 中的时间与 $C_A(t)$ 中的时间尺度不同. K_{BA} 中的 τ 为 τ_{mol}，而 $C_A(t)$ 中的 τ 为宏观上的量级，K_{BA} 成立要求 $\tau_{mol} \ll t \ll \tau_{宏观}$. ($e^{-\frac{t}{\tau_{宏}}} \simeq 1$)

化学反应对于分子的运动是 rare event! 微观与宏观之间要考虑 time scale.



$$k_{BA} = \langle \dot q(0)\,\delta(q_0-q^*)\,H_B[q(t)]\rangle / \chi_A$$

过渡态理论(TST)

假设 $\dot q(0)>0 \Rightarrow$ 到B态 $\dot q(0)<0 \Rightarrow$ 到A态 (忽略反应坐标的 Recrossing)

$$\Rightarrow K_{BA}^{(TST)} = \chi_A^{-1}\langle \dot q(0)\,\delta(q_0-q^*)\,H_B^{TST}[q(t)]\rangle \qquad H_B^{TST}[q(t)] = \begin{cases}1, & v(0)>0\\ 0, & v(0)<0\end{cases} \equiv \theta(v_0)$$

$$\Rightarrow k_{BA}^{TST} = \chi_A^{-1}\langle \dot q(0)\,\delta(q_0-q^*)\,\theta(v_0)\rangle$$

可证明: $K_{BA}^{TST} \equiv k_{BA}(t=0)$. (作业 8.7, 8.8)

Hint: $k_{BA}(t=0) = \chi_A^{-1}\langle \dot q(0)\,\delta(q_0-q^*)\,\overset{=\theta(v_0)}{\underline{H_B(q(t\to 0^+))}}\rangle$

$$\Rightarrow K_{BA}^{TST} = \chi_A^{-1}\langle v(0)\,\theta(v_0)\,\delta(q_0-q^*)\rangle$$

$$= \chi_A^{-1}\langle v(0)\,\theta(v_0)\rangle\langle\delta(q_0-q^*)\rangle$$

$$= \frac{1}{2}\chi_A^{-1}\langle |v|\rangle\langle\delta(q_0-q^*)\rangle$$

§4. 自扩散(Self-Diffusion)

1. 宏观扩散现象

① $n(\vec{r},t) \longrightarrow$ 浓度.

② 守恒方程: $\dfrac{\partial n(\vec{r},t)}{\partial t} = -\nabla\cdot\vec{j}(\vec{r},t)$

③ 流 $\longleftrightarrow$ 浓度关系? $\longrightarrow$ 唯象假说.

Fick 定律: $\vec{j}(\vec{r},t) \propto -\nabla n(\vec{r},t) = -D\nabla n(\vec{r},t)$ D: 扩散系数.

④ 扩散方程: $\dfrac{\partial n(\vec{r},t)}{\partial t} = D\nabla^2 n(\vec{r},t)$ D的量纲: m^2/s

2. 扩散行为

(1) 1D: $\dfrac{\partial n(x,t)}{\partial t} = D\dfrac{\partial^2}{\partial x^2} n(x,t)$.

对 x 作傅立叶变换 $\mathcal{F}[n(x,t)] = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} dx\, n(x,t)\, e^{-ikx} \triangleq \hat{n}(k,t)$.

$$\Rightarrow \frac{\partial}{\partial t}\hat{n}(k,t) = -Dk^2\hat{n}(k,t)$$

$$\Rightarrow \hat{n}(k,t) = \hat{n}(k,0)\,e^{-Dk^2t}$$ (小k,不局域,衰减慢)

其中 $\hat{n}(k,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} n(x,0)\, e^{-ikx}$.

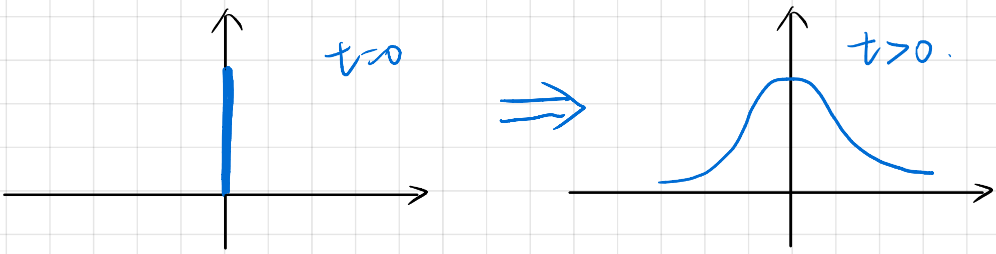
取 $n(x,0) = n_0\,\delta(x)$. 则 $\hat{n}(k,0) = \dfrac{n_0}{\sqrt{2\pi}} \Rightarrow \hat{n}(k,t) = \hat{n}(k,0)\,e^{-Dk^2t}$

$$n(x,t) = \mathcal{F}^{-1}[\hat{n}(k,t)]$$

$$= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} dk \left(\frac{n_0}{\sqrt{2\pi}}e^{-Dk^2t}\right)e^{ikx}.$$

$$= \frac{n_0}{\sqrt{2\pi}}e^{-\frac{x^2}{4Dt}}\int_{-\infty}^{+\infty} dk\, e^{-Dt\left(k-\frac{ix}{2Dt}\right)^2} = \frac{n_0}{2\pi}e^{-\frac{x^2}{4Dt}}\cdot\sqrt{\frac{\pi}{Dt}}$$

$$= \frac{n_0}{\sqrt{4\pi Dt}}e^{-\frac{x^2}{4Dt}} \longrightarrow \text{Gauss分布.} \left(\frac{n_0}{\sqrt{2\pi\sigma}}e^{-\frac{x^2}{2\sigma}} \quad \sigma = 2Dt\right)$$



3D情况：$n(\vec{r},t) = n_0\left(\frac{1}{4\pi Dt}\right)^{\frac{3}{2}} e^{-\frac{r^2}{4Dt}}$

3. Macro $\longleftrightarrow$ Micro

① $\underbrace{\rho(\vec{r},t)}_{\text{微观密度!}} = \sum_i \delta(\vec{r}-\vec{r}_i)$ $\quad \left(\int \rho^{\vec{r}} d\vec{r} = N\right)$

② $n(\vec{r},t)$ 与 ρ 相关，$\delta\rho(\vec{r},t) = \rho(\vec{r},t) - \bar{\rho}$

定义 $C_\rho^\delta = \langle \delta\rho(\vec{r},t)\,\delta\rho(0,0)\rangle$ (时空关联，$t=0$ 时 $\vec{r}=0$，$t=t$ 时，$\vec{r}=\vec{r}$)

$\propto n(\vec{r},t)$

③ O.R.H：$\frac{\partial}{\partial t} C_\rho^\delta(\vec{r},t) = D\nabla^2 C_\rho^\delta(\vec{r},t)$

$\Rightarrow \partial_t C_\rho(\vec{r},t) = D\nabla^2 C_\rho(\vec{r},t) \quad \left(C_\rho(\vec{r},t) = \langle \rho(\vec{r},t)\,\rho(0,0)\rangle\right)$

④ 定义 $P(\vec{r},t)$ 为：0时刻在 $\vec{0}$，t时刻在 $\vec{r}$ 的条件概率

一定有 $P(\vec{r},t) \propto C_\rho(\vec{r},t)$

$\Rightarrow \partial_t P(\vec{r},t) = D\nabla^2 P(\vec{r},t)$

$\Rightarrow \boxed{P(\vec{r},t) = \left(\frac{1}{4\pi Dt}\right)^{\frac{3}{2}} e^{-\frac{r^2}{4Dt}}}$!

4. 均方位移 (Mean Square Displacement MSD)

① $\Delta R^2(t) = \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle$ (对标号粒子)

$= \int d\vec{r}\, |\vec{r}|^2\, P(\vec{r},t)$

$= \int r^2 \left(\frac{1}{4\pi Dt}\right)^{\frac{3}{2}} e^{-\frac{r^2}{4Dt}}\, d\vec{r}$

$= 3\int_{-\infty}^{+\infty} x^2 e^{-\frac{x^2}{4Dt}}\, dx \Big/ \sqrt{4\pi Dt}$

$= 3\times(2Dt) = 6Dt$

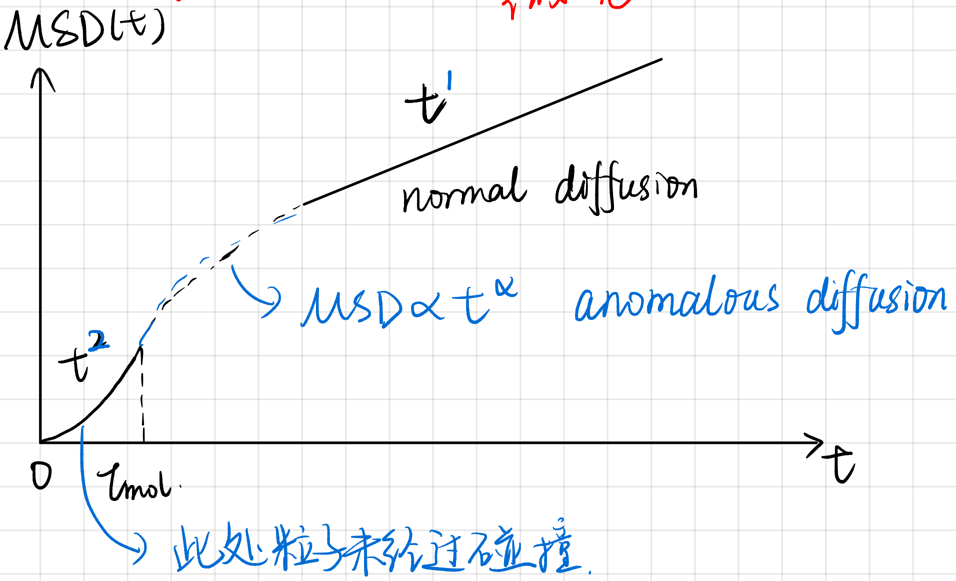
即 $\Delta^2 R(t) = 6Dt \Rightarrow D = \lim_{t\to\infty} \frac{\Delta R^2(t)}{6t}$

宏观

此处 $t\to\infty$ 是指微观上 t 足够长，使宏观扩散方满足

那么 $\underset{宏观}{D}=\lim_{t\to\infty}\frac{\Delta^2 x(t)}{2t}$ 微观

宏观的 D 可以通过微观的 ΔR^2 反映出来.



Green－Kubo 关系

由 $\vec{r}(t)-\vec{r}(0)=\int_0^t \vec{v}(t')dt'$

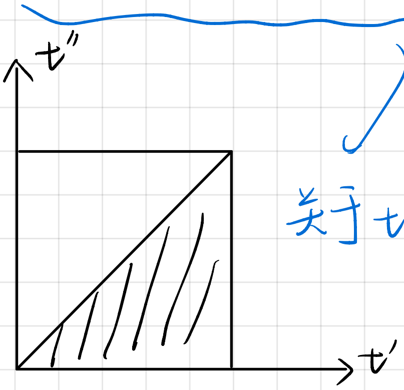
得 $\Delta^2 R(t)=\langle|\vec{r}(t)-\vec{r}(0)|^2\rangle$

$$=\left\langle \int_0^t \vec{v}(t')dt'\cdot\int_0^t \vec{v}(t'')dt''\right\rangle$$

$$=\int_0^t dt'\int_0^t dt''\underbrace{\langle\vec{v}(t')\cdot\vec{v}(t'')\rangle}_{C(t'-t'')}$$

$$=\int_0^t dt'\int_0^t dt''\,C(t'-t'')$$

考察积分限

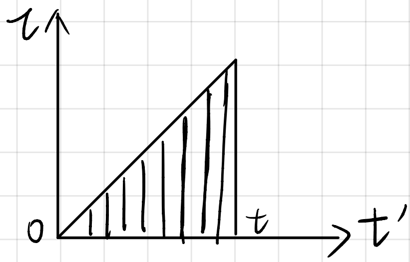


关于 $t'=t''$ 对称，只考虑下半部分.

原式 $=2\int_0^t dt'\int_0^{t'}dt''\,C(t'-t'')$

令 $t'-t''=\tau$

$$=2\int_0^t dt'\int_0^{t'}d\tau\,C(\tau)$$



交换积分顺序

$$\text{原式} = 2\int_0^t d\tau \int_\tau^t dt' \, C(\tau) = 2\int_0^t d\tau \, C(\tau)(t-\tau)$$

$$\Rightarrow MSD = \Delta R^2 = 2\int_0^t d\tau \, C(\tau)(t-\tau)$$

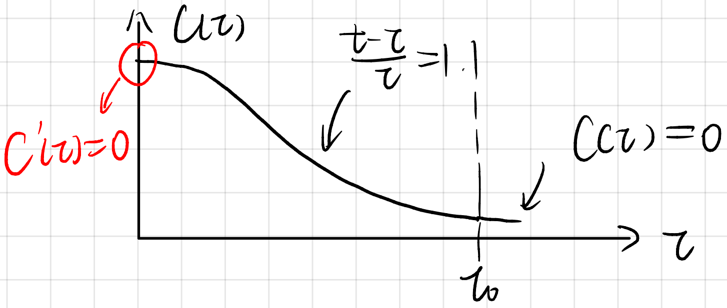
$$D = \lim_{t\to\infty} \frac{\Delta R^2}{6t} = \frac{1}{3}\lim_{t\to\infty}\int_0^t d\tau \, C(\tau)\frac{t-\tau}{t}$$ $t\to\infty$ $\frac{t-\tau}{t}=1$

$$\Rightarrow \boxed{\begin{aligned} D &\simeq \frac{1}{3}\lim_{t\to\infty}\int_0^t C(\tau)d\tau \\ &= \frac{1}{3}\int_0^{+\infty}\langle v(0)\,v(\tau)\rangle d\tau \end{aligned}}$$

将宏观输运与微观涨落关联函数积分相联系.
Green - Kubo 关系

注: $t\to\infty$ $\frac{t-\tau}{t} = 1-\frac{\tau}{t}$

但当 $t\to\infty$ 时, $C(\tau)\to 0$, 使 $\frac{t-\tau}{t}$ 不为1时无贡献



但注意到 $C'(0)\neq 0$. 因为这不是刻维尔体系时间尺度, 这里已经有时间粗粒化.

* Brown 粒子: $C(\tau) \sim \langle v_0^2\rangle e^{-\frac{\tau}{t_0}}$ (3维)

$$\Rightarrow D = \frac{1}{3}\int_0^\infty d\tau \, C(\tau)$$

$$= \frac{1}{3}\langle v_0^2\rangle \int_0^\infty e^{-\frac{\tau}{t_0}} d\tau = \frac{1}{3}\langle v_0^2\rangle t_0 = \frac{k_BT}{m} t_0 \quad (m^2/s)$$

作业. 8. 13.

§5. 线性响应与涨落—耗散定理

1. 静态响应

①

$H \to \rho_e = \frac{e^{-\beta H}}{Z}$ 对平衡态及稳态

$\langle A\rangle = \int d\Gamma \, A\rho_e$ $\quad \hat{L}\rho_{(e)} = 0 \Rightarrow \langle A(t)\rangle = \langle A\rangle$