② $H \to H+\Delta H$ 　ΔH 很小

$\Delta H = -M(\Gamma)\cdot f$ 　M, f 为共轭量. 问此时 $\langle A\rangle \to \langle A\rangle + \langle \Delta A\rangle$

③ $$\langle A\rangle_{H+\Delta H} = \frac{\int d\Gamma\, e^{-\beta(H+\Delta H)} A(\Gamma)}{\int d\Gamma\, e^{-\beta(H+\Delta H)}}$$

分母 $$\int e^{-\beta(H+\Delta H)} d\Gamma = \int e^{-\beta H}(e^{-\beta\Delta H})\, d\Gamma = \int e^{-\beta H}(1-\beta\Delta H)\, d\Gamma$$
$$= Z - \beta Z \frac{\int e^{-\beta H}\Delta H\, d\Gamma}{Z} = Z\left(1-\beta\langle\Delta H\rangle_H\right)$$

则 $$\langle A\rangle_{H+\Delta H} \approx \frac{\int d\Gamma\, e^{-\beta H}(1-\beta\Delta H)A(\Gamma)}{Z\left(1-\beta\langle\Delta H\rangle_H\right)}$$
$$\approx \frac{1}{Z}\int d\Gamma\, e^{-\beta H}\underbrace{(1-\beta\Delta H)(1+\beta\langle\Delta H\rangle_H)}_{}A$$

$(1+\beta\langle\Delta H\rangle_H - \beta\Delta H + \underbrace{\beta^2\Delta H\langle\Delta H\rangle_H}_{\text{忽略}})$

$$\approx \langle A\rangle_H + \frac{\beta}{Z}\int d\Gamma\, e^{-\beta H}(\langle\Delta H\rangle A - A\cdot\Delta H)$$

$$\Rightarrow \langle A\rangle_{H+\Delta H} = \langle A\rangle_H + \beta\left(\langle A\rangle\langle\Delta H\rangle - \langle A\cdot\Delta H\rangle\right)$$

这里 B 为 ΔH, $t=0$

由于 $C_{AB}(t) = \langle A(0)B(t)\rangle$

$C^{\delta}_{AB}(t) = \langle A(0)B(t)\rangle - \langle A\rangle\langle B(t)\rangle$

$= \langle \delta A(0)\,\delta B(t)\rangle$

$$= \langle A\rangle_H - \beta C^{\delta}_{A\cdot\Delta H}(0)$$

$$\Rightarrow (\Delta A)_{H\to H+\Delta H} = -\beta C^{\delta}_{A(\Delta H)}(0).$$

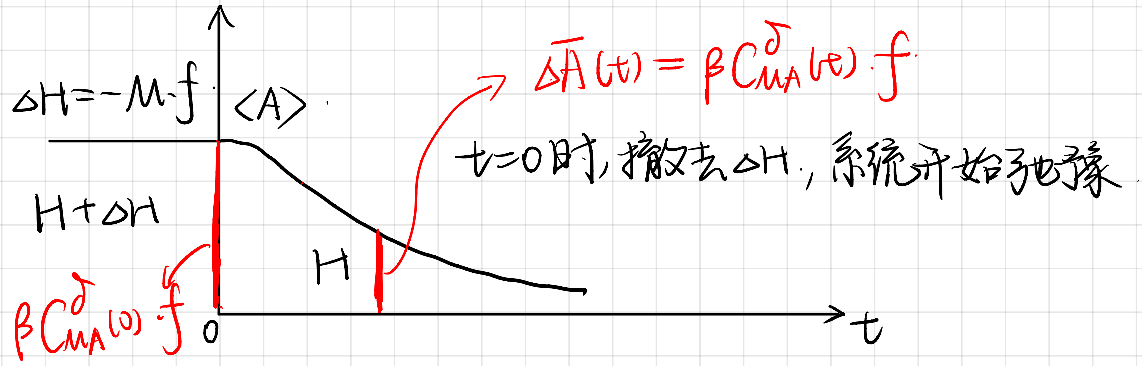
也就是说, 不论 ΔH 是什么, 我都能通过已知的平衡求出响应.

代入 $\Delta H = -M\cdot f \Rightarrow (\Delta A) = \beta C^{\delta}_{AM}(0)\cdot f$

☆☆

这里 f 为外场, 通过改变系统中与 f 耦合的 M 使力学量 A 改变.

2、静态弛豫过程



① $t=0,\quad F(\Gamma) = \dfrac{e^{-\beta(H+\Delta H)}}{\int e^{-\beta(H+\Delta H)}d\Gamma} = \dfrac{e^{-\beta H}(1-\beta\Delta H)}{Z(1-\beta\langle\Delta H\rangle)} \approx \dfrac{e^{-\beta H}}{Z}(1+\beta\langle\Delta H\rangle - \beta\Delta H)$

$$t>0,\quad \begin{cases} \bar{A}(t) = \int \underbrace{d\Gamma\ F(\Gamma)}_{\text{初始的分布}}\ A(\Gamma,t) \\ \dfrac{dA}{dt} = \underbrace{\hat{L}_H A = \{H,A\}}_{\text{力学量演化由H决定}} \end{cases}$$

② $\bar{A}(t) = \int d\Gamma\ \dfrac{e^{-\beta H}}{Z}(1-\beta\Delta H + \beta\langle\Delta H\rangle)\cdot A(t)$ $\qquad \int d\Gamma\ \dfrac{e^{-\beta H}}{Z} A(t) = \langle A\rangle$

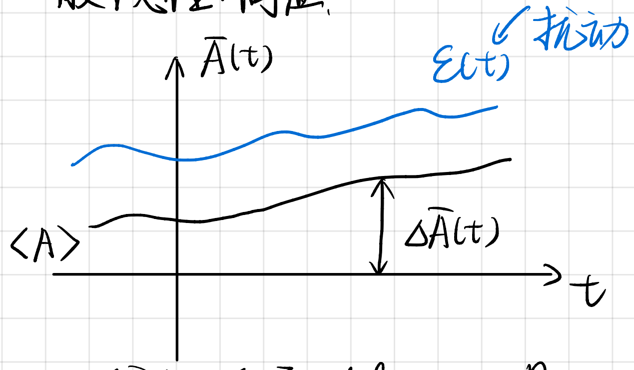
$$= \langle A\rangle + \beta\left[-\langle(\Delta H)A(t)\rangle + \langle A\rangle\langle\Delta H\rangle\right]$$

$$= \langle A\rangle + \beta\left(-C^{\delta}_{\Delta H,A}(t)\right) \quad \text{代入 } \Delta H = -f\cdot M$$

$$= \langle A\rangle + \beta C^{\delta}_{MA}(t)\cdot f$$

$\Rightarrow \Delta\bar{A}(t) = \beta C^{\delta}_{MA}(t)\cdot f$ $\qquad$ 作业 8.14

一般线性响应



(1) 线性响应 (liner − Response).

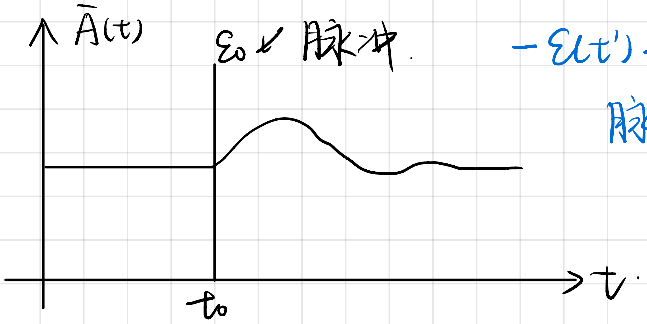
$\varepsilon(t) \rightarrow \lambda\varepsilon(t) \Rightarrow \Delta\bar{A}(t) \rightarrow \lambda\Delta\bar{A}(t)$.

(2) $\Delta\bar{A}(t) = \int_{-\infty}^{+\infty} \underbrace{\chi(t,t')}_{} \varepsilon(t')\,dt'$ → 响应函数.

若 $\chi(t,t')$ 与 $\varepsilon(t')$ 无关 $\Rightarrow \Delta\bar{A}(t,\lambda\varepsilon) = \lambda\,\Delta\bar{A}(t,\varepsilon)$

响应函数：$\chi(t,t')$

(i) 取 $\varepsilon(t') = \varepsilon_0\delta(t'-t_0)$.



$-\varepsilon(t')\cdot M(T) = \Delta H(t')$

脉冲通过M与哈密顿量耦和.

$$\Delta\bar{A}(t) = \int_{-\infty}^{+\infty} \chi(t,t')\,\varepsilon_0\,\delta(t'-t_0)\,dt' = \varepsilon_0\,\underline{\chi(t,t_0)}$$

t_0时刻对t的影响.

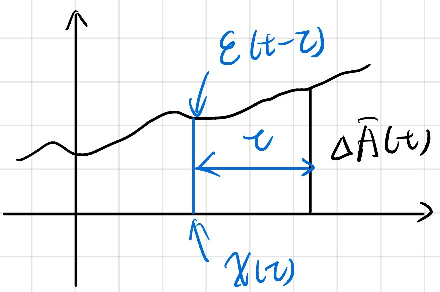
(ii) $\chi(t,t') = \dfrac{\delta\Delta\bar{A}(t)}{\delta\varepsilon(t')}$ → 泛函表示

(iii) 因果性.

$\chi(t,t') = 0$ if $t' > t$. $\longrightarrow \Delta\bar{A}(t) = \int_{-\infty}^{t} \chi(t,t')\,\varepsilon(t')\,dt'$

(iv) 稳态性质: $\chi(t,t') = \chi(t-t')$

$$\Rightarrow \Delta\bar{A}(t) = \int_{-\infty}^{t} \chi(t-t')\,\varepsilon(t')\,dt' \overset{\tau=t-t'}{=\!=} \underbrace{\int_0^{\infty} \chi(\tau)\,\varepsilon(t-\tau)\,d\tau}_{}$$



距离现在时间 τ之前的信号对现在的影响.

FDT: (Fluctuation − Disspation Theorem).

(1) 利用 $\chi(t-t')$ 与 $\varepsilon(t')$ 无关!

考虑静态弛豫过程. $\varepsilon(t') = \begin{cases} f, & t<0 \\ 0, & t\geq 0 \end{cases}$ f与M耦合.

$$\Delta\bar{A}(t) = \int_{-\infty}^{t} \chi(t-t')\,\varepsilon(t')\,dt'$$

$\tau = t - t'$

$$= f\int_{-\infty}^{0} \chi(t-t')\,dt' = f\int_{t}^{\infty}\chi(\tau)\,d\tau.$$

利用静态弛豫过程，已知 $\boxed{\Delta\bar{A}(t) = f\cdot\beta\, C_{MA}^{\delta}(t)}$ ☆

那么 $\boxed{\int_{t}^{\infty}\chi_{MA}(\tau)\,d\tau = \beta\, C_{MA}^{\delta}(t).}$ ☆

两边求导：$\boxed{\underline{\chi_{MA}(t)} = -\beta\frac{d}{dt}C_{MA}^{\delta}(t) = \underline{-\beta\frac{d}{dt}C_{MA}(t)} \quad (t>0)}$

$\chi_{MA}(t) = 0\,,\quad t<0$

响应　　　　涨落.

\+ 频域表示

$$\chi_{AA}(t) = \begin{cases} -\beta\frac{d}{dt}C_{AA}^{\delta}(t) & , t>0 \\ 0 & , t<0 \end{cases}$$

实部　　虚部

$$\tilde{\chi}(t) = \int_{-\infty}^{+\infty}\chi(t)\,e^{-i\omega t}dt = \chi'(\omega) + i\,\chi''(\omega)$$ （′与″不代表求导）

$$\chi'(\omega) = \int_{0}^{+\infty}\chi(t)\cos\omega t\,dt \qquad \chi''(\omega) = \int_{0}^{+\infty}\chi(t)\sin\omega t\,dt$$

$t<0,\ \chi(t)=0$

$$\chi''(\omega) = \int_{0}^{\infty}\left[-\beta\frac{d}{dt}C_{AA}^{\delta}(t)\right]\sin(\omega t)\,dt.$$

$$= -\beta\, C_{AA}^{\delta}(t)\sin(\omega t)\Big|_{0}^{\infty} + \beta\omega\int_{0}^{\infty}C_{AA}^{\delta}(t)\cos(\omega t)\,dt$$

$$= \beta\omega\int_{0}^{\infty}C_{AA}^{\delta}(t)\cos(\omega t)\,dt$$

而 $\tilde{C}(\omega) = \int_{-\infty}^{+\infty}C_{AA}^{\delta}(t)\,e^{i\omega t}dt = 2\int_{0}^{\infty}C_{AA}^{\delta}(t)\cos(\omega t)\,dt.$

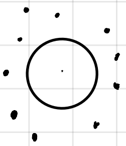
则 $\chi''(\omega) = \frac{1}{2}\beta\omega\,\tilde{C}(\omega).$ 频域上的 FDT

响应的 Fourier 积分中虚部 $\chi''(\omega)$ 与耗散有关，上式建立了耗散与涨落的关系

§6. Brownian 运动

1. 问题

N+1 个粒子



花粉运动 $\vec{x}(t)$

Δt 远大于分子运动时间尺度.

$x(t)$ 相对于分子运动而言是 slow variable.

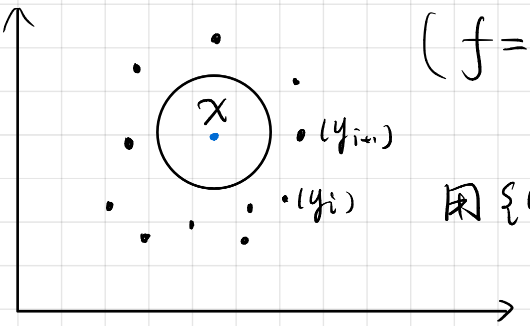
唯象: $m\dot{v} = \underbrace{-\gamma v}_{\text{摩擦}} + \underbrace{\xi(t)}_{\text{random force}} \longrightarrow$ 朗之万方程. 多自由度 → 单自由度. **粗粒化!** 涨落来自于此

2. 运动方程.

$$H = \underbrace{H_0(x)}_{\text{体系}} + \underbrace{H_b(\{y_i\})}_{\text{环境}} \underbrace{- x f}.$$

体系与环境的耦合.

$(f = \sum_i C_i f_i \longrightarrow$ 线性 couple$)$.



用 $\{y_i\}$ 描述 H_b. x 描述 H_0 (花粉)

$$\dot{p} = m\ddot{x} = -\frac{\partial H}{\partial x} = \frac{-\partial H_0}{\partial x} + f.$$

$$\Rightarrow m\ddot{x} = -\frac{\partial H_0(x)}{\partial x} + f(t).$$

③ $f(t) = ?$

而 f 与 x 耦合.

$$\Delta\bar{A}(t) = \int \chi(t-t')\, \mathcal{E}(t')\, dt'$$

无粒子(花粉)时, $f_b(t)$.

$$\boxed{f(t) - f_b(t) = \int_0^t \chi_{ff}(t-t')\, x(t')\, dt'}$$

认为粒子的运动 x 扰动了环境 (bath), 使环境产生了 $f(t)$, 这里在 bath 的角度求 $f(t)$.

$$\chi(t) = \begin{cases} -\beta \frac{d}{dt} C_b(t), & t > 0 \\ 0, & t < 0 \end{cases}$$

$$C_b(t) = \langle \underbrace{f_b(0)}_{\text{未扰动}} f_b(t) \rangle = C_b^{\delta}(t)$$

即将花粉对 bath 的扰动产生的 $f(t)$ 看为 bath 自身的涨落.

④
$$f(t) - f_b(t) = \int_0^t -\beta\left[\frac{d}{d(t-t')} C_b(t-t')\right] x(t')\, dt'$$

$$= \int_0^t \beta \frac{d}{dt'} C_b(t-t')\, x(t')\, dt'$$

将粒子运动 $x(t)$, $\dot{x}(t)$ 与 $f(t)$ 相联系. ☆

$$= \beta C_b(t-t')x(t')\Big|_0^t - \beta\int_0^t C_b(t-t')\dot{x}(t')dt'$$

$$= \beta C_b(0)x(t) - \beta C_b(t)x(0) - \beta\int_0^t C_b(t-t')\dot{x}(t')dt'$$

⑤ $$m\ddot{x}(t) = \left(-\frac{dV_0(x)}{dx} + \beta C_b(0)x(t)\right) - \int_0^t \beta C_b(t-t')\dot{x}(t')dt' + \left(f_b(t) - \beta C_b(t)x(0)\right)$$

t'时刻的速度通过环境影响到当前的运动

$$= -\frac{d}{dx}\underbrace{\left(V_0(x) - \frac{1}{2}\beta C_b(0)x^2\right)}_{\text{有效势场 } \bar{V}(x)} - \int_0^t \beta C_b(t-t')\dot{x}(t')dt' + \underbrace{\delta f_b(t)}_{\text{random force}}$$

$\langle \delta f_b(t)\rangle = 0$ $\quad\langle \delta f_b(t)\delta f_b(0)\rangle = \langle f_b(0)f_b(t)\rangle = C_b(t)$.

$$\Rightarrow \boxed{m\ddot{x} = -\frac{d}{dx}\bar{V}(x) - \int_0^t \beta C_b(t-t')x(t')dt' + \delta f_b(t)}$$

广义朗之万方程.

memory kernel.

非马尔科夫过程 (memory term).
过去的影响累积到现在.

3. Langevin 方程

(1) $m\ddot{x} = -\int_0^t \beta C_b(t-t')\dot{x}(t')dt' + \delta f_b(t) = -\int_0^t \beta C_b(\tau)\dot{x}(t-\tau)d\tau + \delta f_b(t)$

(2) Markovian 近似.(记忆很短，只有$\tau\approx0$时 $C_b(\tau)\neq0$).

则 $m\ddot{x} = -\dot{x}(t)\int_0^{t\to\infty}\beta C_b(\tau)d\tau + \delta f_b(t)$

$= -\gamma\dot{x}(t) + \delta f(t)$. 回到朗之万方程.

$$\Rightarrow \boxed{\gamma = \beta\int_0^\infty C_b(t)dt}$$

(3) $C_b(t) = 2\underbrace{\sigma}_{\text{噪声强度 (白噪声)}}\delta(t) = \langle f_b(0)f_b(t)\rangle$ (一点记忆也没有)

$$\Rightarrow \gamma = \beta\int_0^{+\infty}2\sigma\delta(t)dt = \beta\sigma \quad \left(\int_0^{+\infty}\delta(t)dt = \frac{1}{2}\right)$$

则 $\Rightarrow \Gamma = k_B T \gamma$ ☆☆ F.D.T

噪声：涨落 $\Leftrightarrow$ 摩擦：耗散.

$$m\ddot{x} = -\gamma v + \xi(t). \quad \langle \xi(t)\xi(t')\rangle = 2k_BT\gamma\delta(t-t').$$

$\Gamma = k_BT\gamma$，噪声与摩擦的关联是必然的，因为我们本来研究N+1个粒子，但我们只关心"花粉"，其余粒子的作用被人为化分为摩擦与噪声，这两者本来就是同源的，因此必然有强的关联.

$\langle f\rangle \neq 0$ $\quad$ $\langle \xi\rangle = 0$.

4. 朗之万方程的一些性质.

① $m\dot{v} = -\gamma v + f(t)$.

$\langle f(t)\rangle = 0 \quad \langle f(t) f(t')\rangle = 2\Gamma\delta(t-t')$.

② $v(t) = v(0)e^{-\frac{\gamma t}{m}} + \int_0^t dt' \left(e^{-\frac{\gamma(t-t')}{m}}\right)\frac{f(t')}{m}$.

③ $\langle v(t)\rangle = v(0)e^{-\frac{\gamma t}{m}}$. (对噪声求平均，固定粒子).

$\xrightarrow{t\to\infty} \langle\langle v(t)\rangle\rangle = 0$ (对系综平均，不固定粒子，时间尺度分离).

④ $\langle v(0)v(t)\rangle = \langle v^2(0)\rangle e^{-\frac{\gamma t}{m}} + \int_0^t dt' e^{\frac{-\gamma(t-t')}{m}} \frac{\langle v(0) f(t')\rangle}{m}$ $\quad \langle v(0) f(t')\rangle = 0$.

$$= \langle v^2(0)\rangle e^{-\frac{\gamma t}{m}}$$

⑤ Green-Kubo : $D = \int_0^\infty \langle v(0)v(t)\rangle dt = \langle v^2(0)\rangle \frac{m}{\gamma}$. (一维).

$$\xrightarrow[\langle\langle\cdot\rangle\rangle]{t\to\infty} = \underbrace{\frac{k_BT}{m}}_{\langle v^2(0)\rangle}\cdot\frac{m}{\gamma} = \frac{k_BT}{\gamma}. \Rightarrow \boxed{D = \frac{k_BT}{\gamma}} \quad \text{F.D.T}$$

注：许多教材中 $D = \mu k_BT$ $\quad \mu$：迁移率. $\Rightarrow \mu = \frac{1}{\gamma}$.

而对球形粒子. $\gamma = 6\pi\eta R$. $\Rightarrow D = \frac{k_BT}{6\pi\eta R}$.