$$F_N = -kT\ln Q_{cl} = -k_BT(\ln Z_n - 3N\ln\lambda - \ln N!)$$

$$\mu = F_N - F_{N-1} = -k_BT\left(\ln\frac{Z_n}{Z_{n-1}} - \ln\lambda^3 - \ln N\right)$$

$$= -k_BT\ln\frac{Z_n}{Z_{n-1}} + k_BT\ln(N\lambda^3)$$

$$Z_n = \int e^{-\beta U(r^N)}dr^N \qquad Z_{n-1} = \int e^{-\beta U(r^{N-1})}dr^{N-1}$$

为了处理 Z_n/Z_{n-1}. 定义 $U_N(\varepsilon) = \sum_{j=2}^{N} u(r_{1j})\cdot\varepsilon + \sum_{2<i<j<N} u(r_{ij})$

$\varepsilon=1$：N个粒子系统

$\varepsilon=0$：$n-1$个粒子与一个孤立粒子系统.

用ε构建某种从无相互作用到有相互作用的系统.

$$Z_n^\varepsilon(\varepsilon) = \int e^{-\beta U_\varepsilon(r^N)}dr^N = \begin{cases} Z_{n-1}\cdot V, & \varepsilon=0 \\ Z_n, & \varepsilon=1. \end{cases}$$

$$\ln\frac{Z_n}{Z_{n-1}} = \ln\frac{Z_n^\varepsilon(\varepsilon=1)}{Z_n^\varepsilon(\varepsilon=0)}\cdot V = \ln V + \ln\frac{Z_n^\varepsilon(1)}{Z_n^\varepsilon(0)}$$

$$\ln\frac{Z_n^\varepsilon(1)}{Z_n^\varepsilon(0)} = \ln Z^\varepsilon(1) - \ln Z^\varepsilon(0) = \int_0^1 d\varepsilon\,\frac{\partial}{\partial\varepsilon}\ln Z_n^\varepsilon(\varepsilon)$$

$$\frac{\partial}{\partial\varepsilon}\ln Z_n^\varepsilon = \frac{1}{Z_n^\varepsilon}\frac{\partial}{\partial\varepsilon}Z_n^\varepsilon = \frac{1}{Z_n^\varepsilon}\frac{\partial}{\partial\varepsilon}\int dr^N e^{-\beta U_N(\varepsilon)}$$

$$= \frac{1}{Z_n^\varepsilon}\int dr^N e^{-\beta U_N(\varepsilon)}(-\beta)\left[\frac{\partial}{\partial\varepsilon}U_N(\varepsilon)\right]$$

$$= \frac{-\beta}{Z_n^\varepsilon}\int dr^N e^{-\beta U_N(\varepsilon)}\sum_{j=2}^{N} u(r_{1j})$$

$$= -\frac{(N-1)\beta}{Z_n^\varepsilon}\int dr^N e^{-\beta U_N(\varepsilon)}u(r_{12})$$

$$\int dr^N e^{-\beta U_N(\varepsilon)}u(r_{12}) = \int d\vec r_1 d\vec r_2\, u(r_{12}) \underbrace{\int dr^{N-2}e^{-\beta U_N(\varepsilon)}}_{\frac{\rho^2 g^\varepsilon(\vec r_1, r_2)}{N(N-1)}Z_n}$$

$$= -\frac{\beta V}{N}\int d\vec r\, u(r)\,\rho^2 g^\varepsilon(r)$$

$$= -\beta\rho\int d\vec r\, u(r)\, g^\varepsilon(r)$$

则 $$\frac{\mu}{k_BT} = \ln(\rho\lambda^3) + \underbrace{\beta\rho\int_0^1 d\varepsilon\left[\int d\vec r\, u(r)g_\varepsilon(r)\right]}_{\text{相当于修正项}}$$

注意到理想气体 $\mu = k_BT\ln(\frac{N}{q})$

如何得到 $g(r)$

① $-k_B T \ln g(r) = w(r)$

稀薄的体系 $w(r) = u(r) \Rightarrow g(r) \sim e^{-\beta u(r)}$

② 近似方程.

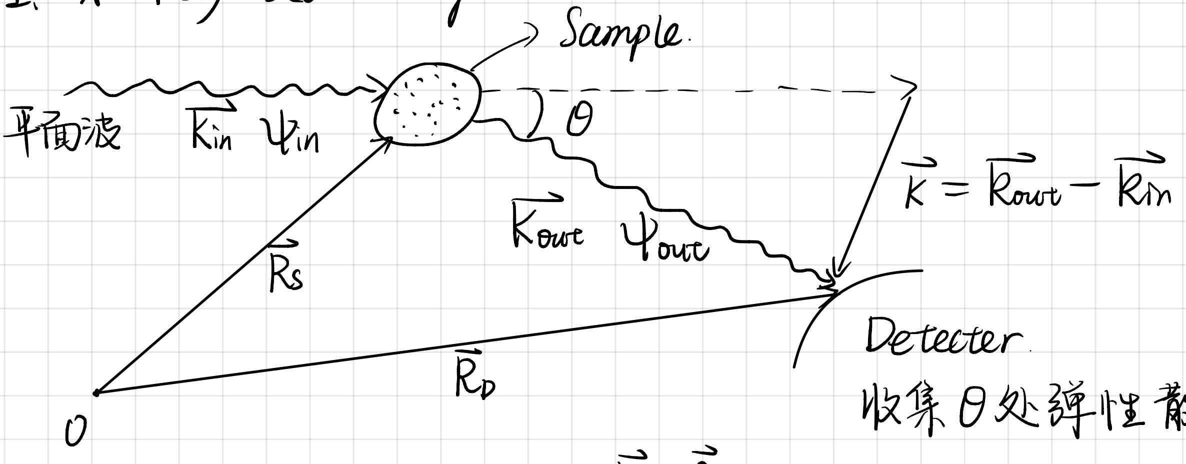
③ 模拟（平衡后直接统计）

④ X射线衍射 —————— 几何结构，结构因子 $S(\vec{q})$

结构因子与 $g(r)$ 有关系

结构因子（Structure factor）

1. X-Ray Scattering



收集θ处弹性散射的波.

入射波为平面波：$\psi_{in} \propto e^{i\vec{k}_{in}\cdot\vec{R}_S}$

出射波为球面波：$\psi_{out} \propto \dfrac{e^{i\vec{k}_{out}\cdot(\vec{R}_D-\vec{R}_S)}}{|\vec{R}_D-\vec{R}_S|}$

注意：θ小时，反应大尺度的信息，同时信号弱. θ不同反应不同尺度的信息.

探测器处 $\psi_D \propto \psi_{in}\cdot\psi_{out}$

$|\psi_D|^2 \longrightarrow$ 强度.

$$\psi_D \sim e^{i\vec{k}_{in}\cdot\vec{R}_S}\cdot\frac{1}{|\vec{R}_D-\vec{R}_S|}e^{i\vec{k}_{out}\cdot(\vec{R}_D-\vec{R}_S)}$$

则 $$\psi_D = \underbrace{f(\vec{K})}_{\text{“原子散射因子”}}e^{i\vec{k}_{in}\cdot\vec{R}_S}\cdot\frac{1}{|\vec{R}_D-\vec{R}_S|}e^{i\vec{k}_{out}\cdot(\vec{R}_D-\vec{R}_S)}$$

$$= \frac{f(\vec{K})}{|\vec{R}_D-\vec{R}_S|}e^{i\vec{k}_{out}\cdot\vec{R}_D}\cdot e^{-i\vec{K}\cdot\vec{R}_S}$$

总的散射波幅（认为样品尺寸很小）

$$\psi_t(\theta) = \frac{f(\vec{k})}{|\vec{R}_D - \vec{R}_S|} e^{i\vec{k}_{out}\cdot\vec{R}_D} \cdot \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}$$ （N个粒子散射）

$$I(\theta) = |\psi_t(\theta)|^2$$

$$= \frac{|f(\vec{k})|^2}{R^2} \left|\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\right|^2$$

$$\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i} \cdot \sum_{j=1}^{N} e^{i\vec{k}\cdot\vec{r}_j}$$

$$= \sum_{i=1}^{N}\sum_{j=1}^{N} e^{-i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}$$

由统计力学的遍历性假设

实验观测强度 $\propto \langle I(\theta)\rangle = A\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} e^{-i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\right\rangle$

定义 $S(\vec{k}) = \frac{1}{N}\left\langle \sum_{i,j=1}^{N} e^{-i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\right\rangle$ 由各向同性，$S(\vec{k}) = S(k)$

$$S(\vec{k}) = 1 + \frac{1}{N}\left\langle \sum_{i\neq j} e^{-i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\right\rangle$$

$$= 1 + \rho\int d\vec{r}\, g(r)\, e^{-i\vec{k}\cdot\vec{r}}$$

由于 $r\to\infty$ 时，$g(r)\longrightarrow 1$. 因此引入 $h(r) = g(r) - 1$

$$S(\vec{k}) = 1 + \rho\int d\vec{r}\, h(r) e^{-i\vec{k}\cdot\vec{r}} + \underbrace{\rho\int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}}_{(2\pi)^3\delta(\vec{k})}$$

$$S(\vec{k}) = 1 + \rho\, h(\vec{k}) + \rho(2\pi)^3\delta(\vec{k})$$ 而我们不考虑 $\vec{k}=0$，此项可以忽略.

作业. 7.16

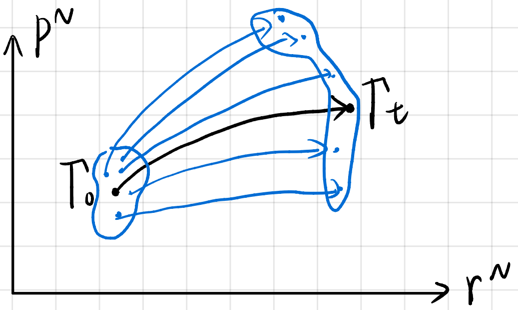
第六章 非平衡统计（初步）

1. 引言

	平衡	非平衡
①	平衡态不随t变化	t、☆
②	状态函数 $(p, T, \mu \cdots)$	状态函数无严格定义（但有时会定义局域平衡的状态函数）
③	分布函数 $e^{-\beta H}$ 不随时间变化，$\rho(\Gamma)$	分布函数随时间演化 $\rho(\Gamma, t)$
④	力学量 $\langle A \rangle$	$A(\Gamma, t)$

§1. 刘维尔方程（经典）

1、



演化方程：

$$\begin{cases} \dot{r}_i = \dfrac{\partial H}{\partial p_i} \\ \dot{p}_i = -\dfrac{\partial H}{\partial r_i} \end{cases}$$

$$p_j(t+\Delta t) = p_j(t) - \left(\frac{\partial H}{\partial r_j}\right)\Delta t$$

$$r_j(t+\Delta t) = r_j(t) + \left(\frac{\partial H}{\partial p_j}\right)\Delta t$$

分布函数 $f(\Gamma, t)\,d\Gamma \qquad d\Gamma = dr^N dp^N$

t时刻，系统位于 $d\Gamma$ 内的概率.

2、刘维尔定理.

$$d\Gamma_t = \delta r^N(t)\, \delta p^N(t)$$

$$\delta r_j(t+\Delta t)\, \delta p_j(t+\Delta t) = \underbrace{\begin{vmatrix} \dfrac{\partial p_j(t+\Delta t)}{\partial p_j(t)} & \dfrac{\partial p_j(t+\Delta t)}{\partial r_j(t)} \\ \dfrac{\partial r_j(t+\Delta t)}{\partial p_j(t)} & \dfrac{\partial r_j(t+\Delta t)}{\partial r_j(t)} \end{vmatrix}}_{J} \delta r_j(t)\, \delta p_j(t)$$

$$J=\begin{vmatrix} 1-\frac{\partial^2 H}{\partial p_j\partial r_j}\Delta t & -\frac{\partial^2 H}{\partial r_j^2}\Delta t \\ \frac{\partial^2 H}{\partial p_j^2}\Delta t & 1+\frac{\partial^2 H}{\partial r_j\partial p_j}\Delta t\end{vmatrix} = 1-\left(\frac{\partial^2 H}{\partial r_j\partial p_j}\right)^2(\Delta t)^2+\left(\frac{\partial^2 H}{\partial r_j^2}\right)\left(\frac{\partial^2 H}{\partial p_j^2}\right)(\Delta t)^2$$
$$= 1+O(\Delta t^2)$$

则 $\delta\Gamma_j(t+\Delta t)=[1+O(\Delta t^2)]\,\delta\Gamma_j(t)$

$$\Rightarrow \lim_{\Delta t\to 0}\frac{\delta\Gamma_j(t+\Delta t)-\delta\Gamma_j(t)}{\Delta t}=\lim_{\Delta t\to 0}\frac{O(\Delta t^2\,\delta\Gamma_i(t))}{\Delta t}=0$$

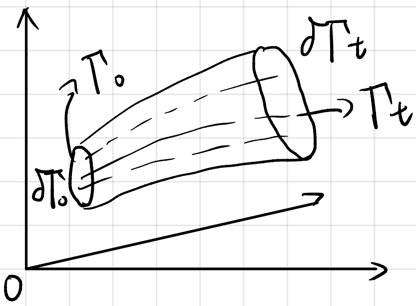
$$\frac{d}{dt}\delta\Gamma(t)=0$$ 相空间体积不变！ $d\Gamma \rightarrow d\Gamma'$

$V = V'$

注：我们是在哈密顿方程满足的情况下推导的以上结论，因此不满足哈密顿方程的体系不满足以上结论，例如有摩擦力。

能量守恒

物理上：系统数目不变。 → 物理学要求

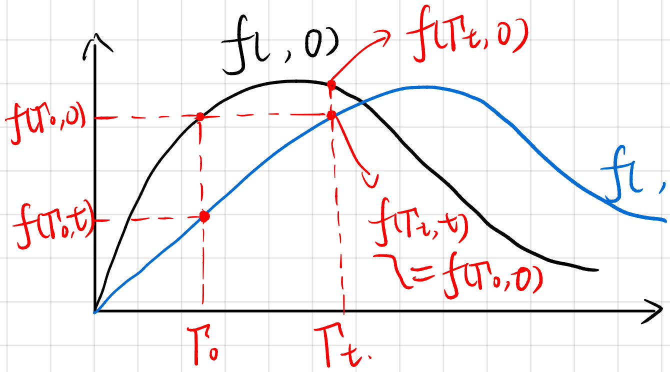


$$f(\Gamma_0,0)\,\delta\Gamma_0=f(\Gamma_t,t)\,\delta\Gamma_t$$

$$\boxed{f(\Gamma_0,0)=f(\Gamma_t,t)}$$ 由刘维尔定理

$$\Downarrow$$

$$\underbrace{\frac{Df}{Dt}}_{\text{沿轨线的变化}}=\underbrace{\frac{\partial f}{\partial t}}_{\text{给定相点}}+\frac{\partial f}{\partial \Gamma}\frac{\partial \Gamma}{\partial t}=0 \quad ☆$$



$$\frac{Df}{Dt}=\frac{\partial f}{\partial t}+\sum_{i=1}^{3N}\left(\frac{\partial f}{\partial p_i}\dot p_i+\frac{\partial f}{\partial r_i}\dot r_i\right)=0$$

$$\Rightarrow \frac{\partial f}{\partial t}=-\sum_{i=1}^{3N}\left(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial r_i}-\frac{\partial H}{\partial r_i}\frac{\partial}{\partial p_i}\right)\triangleq-\underbrace{\hat L}_{\text{刘维尔算符}} f$$ → 刘维尔方程

$$\hat L f=\{H,f\}=\left(\sum_{i=1}^{3N}\frac{\partial H}{\partial p_i}\frac{\partial}{\partial r_i}-\frac{\partial H}{\partial r_i}\frac{\partial}{\partial p_i}\right)f$$

形式解: $f(\Gamma;t)=e^{-t\hat{L}}f(\Gamma;0)$ 对应同一个Γ点,

$\hat{L}$的性质:

(i) 反自伴随: $\int d\Gamma\, f\hat{L}g = -\int d\Gamma\, g\hat{L}f$ ($f(\Gamma),g(\Gamma)\to 0$, 当$\Gamma\to\partial D$)

证明: $\int dr_1 dr_2\cdots dP_{3N}\, f(\Gamma)[\sum_{i=1}^{3N}(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial r_i}-\frac{\partial H}{\partial r_i}\frac{\partial}{\partial p_i})g(\Gamma)]$

$\xrightarrow{\text{分部积分}} -\int dr_1\cdots dP_{3N}[\sum_{i=1}^{3N}(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial r_i}-\frac{\partial H}{\partial r_i}\frac{\partial}{\partial p_i})f(\Gamma)]\cdot g(\Gamma)$

(ii) $\int d\Gamma\, f(e^{t\hat{L}}g)=\int d\Gamma\,(e^{-t\hat{L}}f)g$

证明: $\int d\Gamma\, f(e^{t\hat{L}}g)=\int d\Gamma\, f[1+t\hat{L}+\frac{1}{2}t\hat{L}^2\cdots]g$

$=\int d\Gamma\,(1-t\hat{L}+\frac{1}{2}t^2\hat{L}^2\cdots)f\,g=\int d\Gamma\,(e^{-t\hat{L}}f)g$

(iii) 定态分布: $\frac{\partial f}{\partial t}=0 \Rightarrow \hat{L}f=0$

(a) 若 $f\equiv f(H)\longrightarrow \hat{L}f=0$ eg: $f\propto e^{-\beta H}$

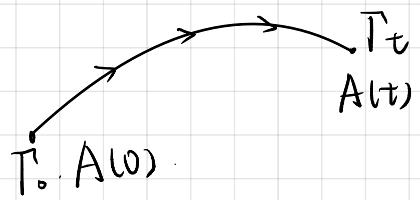
平衡分布是定态分布!但定态分布不一定是平衡分布!

对定态分布 $e^{-t\hat{L}}f=f$

下面考虑力学量 $A(\Gamma)$

(1) A是Γ的函数, A不显含t!

(2) $A(t)=A(\Gamma_0\to\Gamma_t)$, 即A随时间的演化是依赖于Γ的演化.



$A(t)=A(0)+\frac{dA}{dt}\Big|_{t=0}t+\cdots+\frac{1}{n!}\frac{d^nA}{dt^n}\Big|_{t=0}t^n+\cdots$

(Taylor Expansion)

$\frac{dA}{dt}=\frac{dA}{d\Gamma}\dot{\Gamma}=\sum_{i=1}^{3N}(\frac{\partial A}{\partial r_i}\dot{r}_i+\frac{\partial A}{\partial p_i}\dot{p}_i)=\sum_{i=1}^{3N}(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial r_i}-\frac{\partial H}{\partial r_i}\frac{\partial}{\partial p_i})A(\Gamma)$

$=\hat{L}A$

即 $\frac{dA(\Gamma)}{dt}=\hat{L}A(\Gamma)$

对比之前讲分布时 $\frac{Df}{Dt}=0\Rightarrow\frac{\partial f}{\partial t}=-\hat{L}f$ ☆

则 $\frac{d^2A(\Gamma)}{dt^2} = \hat{L}^2 A(\Gamma) \cdots \quad \frac{d^nA(\Gamma)}{dt^n} = \hat{L}^n A(\Gamma)$

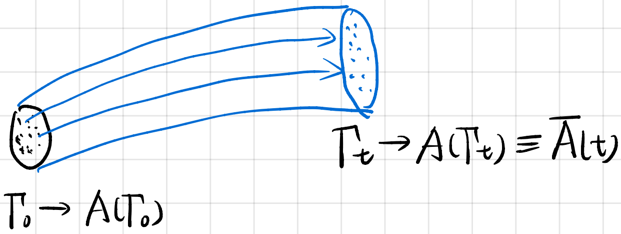
$$\Longrightarrow A(t) = A(0) + t\hat{L}A + \frac{t^2}{2}\hat{L}^2 A + \cdots + \frac{t^n}{n!}\hat{L}^n A + \cdots$$

$$= e^{t\hat{L}} A(0).$$

注意对分布时间一相点 $\begin{cases} f(\Gamma, t) = e^{-t\hat{L}} f(\Gamma, 0) & \text{被动观点} \\ A(\Gamma_0 \to \Gamma_t) = e^{t\hat{L}} A(\Gamma_0) & \text{主动观点} \end{cases}$

$A(t)$ 的平均值 ⟶ 非平衡平均值.

$$\overline{A(t)} = \int d\Gamma_0 \, f(\Gamma_0; 0)\, A(\Gamma_0 \to \Gamma_t)$$



即此处我们认为 $\overline{A(t)}$ 由初始 $f(\Gamma_0;0)$ 一一演化而来!! 因此由 $f(\Gamma_0;0)$ 求 $\overline{A(t)}$ 　$f(\Gamma_0;0)$ 可以为平衡体系.

$$\overline{A(t)} = \int d\Gamma \, f(\Gamma;0)\, A_t(\Gamma \to \Gamma_t)$$

$$= \int d\Gamma \, f(\Gamma;0)\, e^{t\hat{L}} A(\Gamma) = \int d\Gamma \left[e^{-t\hat{L}} f(\Gamma;0)\right] A(\Gamma)$$

$$= \int d\Gamma \, f(\Gamma;t)\, A(\Gamma)$$ 类比于 海森堡表像与薛定谔表像.

§.2. 时间关联函数 (Time - Correlation function)

1. 涨落.

(1) 初态分布 → f_{eq}.

$$\overline{A}(t) = \int d\Gamma \, f_{eq}(\Gamma) A(t) = \int d\Gamma \left(e^{-t\hat{L}} f_{eq}(\Gamma)\right) A(\Gamma) = \int d\Gamma \, f_{eq}(\Gamma) A(\Gamma)$$

$$\Longrightarrow \overline{A}(t) = \langle A \rangle$$

本课程中 "$\langle\ \rangle$" 只能对应平衡系综平均!

(2) $\delta A(t) = \underbrace{A(t)}_{\text{瞬态的}A} - \langle A \rangle \qquad \overline{\delta A(t)} = \overline{A(t)} - \langle A \rangle = 0$

2. T.C.F

(1) 定义: $C_{AB}(t) \stackrel{\text{def}}{=} \langle A(0) B(-t) \rangle = \int d\Gamma f_{eq}(\Gamma) A(\Gamma) B_t(\Gamma \to \Gamma_t)$

(2) 稳态性质

$$C_{AB}(t) = \int d\Gamma f_{eq}(\Gamma) A(\Gamma) [e^{t\hat{L}} B(\Gamma)]$$

$$= \int d\Gamma [e^{-t\hat{L}} f_{eq}(\Gamma) A(\Gamma)] B(\Gamma)$$ 而 $e^{-t\hat{L}} f_{eq}(\Gamma) = f_{eq}(\Gamma)$

$$= \int d\Gamma\, B(\Gamma) [e^{-t\hat{L}} A(\Gamma)] f_{eq}(\Gamma)$$

$$\stackrel{\text{def}}{=} \langle A(-t) B(0) \rangle = C_{BA}(-t)$$

$\Rightarrow$ $C_{AB}(t) = \langle A(0) B(t) \rangle = \langle A(-t) B(0) \rangle = C_{BA}(-t)$ 时间平移的稳态性质

若 $A = B$. $C_{AA}(t) = C_{AA}(-t)$ 自关联函数为偶函数.

(3) $\langle A(0) \dot{B}(t) \rangle = \int d\Gamma f_{eq}(\Gamma) A(\Gamma) [\hat{L} B(t)]$

$$= -\int d\Gamma\, \hat{L} [f_{eq}(\Gamma) A(\Gamma)] B(t)$$

$$= -\int d\Gamma\, [\hat{L} A(\Gamma)] B(t) f_{eq}(\Gamma)$$

$$= -\int d\Gamma\, \dot{A}(0) B(t) f_{eq}(\Gamma) = -\langle \dot{A}(0) B(t) \rangle$$

$\Rightarrow \langle A(0) \dot{B}(t) \rangle = -\langle \dot{A}(0) B(t) \rangle$

若 $A=B$, 则 $\langle A(0) \dot{A}(t) \rangle = -\langle \dot{A}(0) A(t) \rangle$

再取 $t=0 \Rightarrow \langle A(0) \dot{A}(0) \rangle = 0$. eg: $\langle \vec{r}_i, \vec{p}_i/m \rangle = 0$

(4) $\left.\frac{d}{dt}\right|_{t=0} C_{AA}(t) = \frac{d}{dt} \langle A(0) A(t) \rangle$

$$= \langle A(0) \dot{A}(t) \rangle \big|_{t=0}$$

$$= 0.$$

一阶导为0

$\left.\frac{d^2}{dt^2}\right|_{t=0} C_{AA}(t) = \langle A(0) \ddot{A}(0) \rangle$

$$= -\langle \dot{A}(0) \dot{A}(0) \rangle$$

$$= -\langle \dot{A}^2(0) \rangle < 0$$

二阶导小于0