Introduction

研究大量粒子运动的学科

$PV = NRT$ 热的传导 状态变化 熵

理想气体：无分子间作用 → 无势能

用相空间表示分子状态 $6N$ $\{p, q\}$

$$E = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m} = H(p, q)$$

$S = k \ln W$ W 表示的是概率而非相空间体积

Stirling 近似

$$N! = \int_0^{\infty} e^{-x} x^N \, dx \quad (\text{数学归纳法})$$

Laplace 近似 $\int g(x)\,dx$

令 $h(x) = \ln g(x)$ $\int g(x)\,dx = \int e^{h(x)}\,dx$

$$\int e^{h(x)}\,dx = \int \exp\left(h(x_0) + h'(x_0)(x-x_0) + \frac{1}{2} h''(x_0)(x-x_0)^2\right) dx$$

$$h'(x_0) = 0 \Rightarrow \int \exp\left(h(x_0) + \frac{1}{2} h''(x_0)(x-x_0)^2\right) dx$$

$$= \exp(h(x_0)) \int \exp\left(-\frac{1}{2} \frac{(x-x_0)^2}{-h''(x_0)^{-1}}\right) dx$$

$$\frac{d}{dx}\left[-x+N\ln x\right]=-1+\frac{N}{x} \quad x_0=N$$

$$\frac{d^2}{dx^2}\left[-x+N\ln x\right]=-\frac{N}{x^2} \Rightarrow \sigma^2=\frac{x_0^2}{N}=N$$

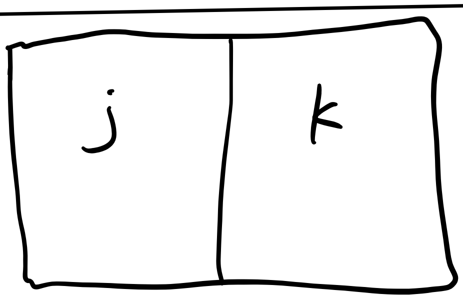
$$N! \approx e^{-N}N^N\sqrt{2\pi N}$$

$$\ln N! \approx N\ln N-N+\cancel{\frac{1}{2}\ln(2\pi N)}$$

$$\ln N! \approx N\ln N-N$$

$$P(q,p)=P_q(q)\,P_p(p)$$

$$S=k\ln P \Rightarrow S(E,V,N)=S_q(V,N)+S_p(E,N)$$



$$P(N_j,N_k)=\frac{N_{T,jk}!}{N_j!N_k!}\left(\frac{V_j}{V_{T,jk}}\right)^{N_j}\left(\frac{V_k}{V_{T,jk}}\right)^{N_k}$$

期望 $\langle N_j\rangle=N_{T,jk}\left(\frac{V_j}{V_{T,jk}}\right)$ $\langle N_k\rangle=N_{T,jk}\left(\frac{V_k}{V_{T,jk}}\right)$

$$\delta N_j=\left[N\left(\frac{V_j}{V_{T,jk}}\right)\left(1-\frac{V_j}{V_{T,jk}}\right)\right]^{\frac{1}{2}}$$

$$=\left[\langle N_j\rangle\left(\frac{V_k}{V_{T,jk}}\right)\right]^{\frac{1}{2}}$$

① $\frac{N_j}{V_j}=\frac{N_{T,jk}}{V_{T,jk}}$

$$\frac{\delta N_j}{\langle N_j\rangle} \simeq \sqrt{\frac{1}{\langle N_j\rangle}}\sqrt{\frac{V_k}{V_{T,jk}}}$$

令 $\Omega_q(N,V) = \frac{V^N}{N!}$

$$\Rightarrow P(N_j, N_k) = \frac{\Omega_q(N_j,V_j)\,\Omega_q(N_k,V_k)}{\Omega_q(N_{T,jk}, V_{T,jk})}$$

$$\ln[P(N_j,N_k)] = \ln \cdots$$

定义 $S_q(N,V) = k\ln\Omega_q(N,V) + kXN$

X 和 k 是任意常数（其他系统时有用）

$$S_{q,jk}(N_j,V_j,N_k,V_k) = S_q(N_j,V_j) + S_q(N_k,V_k)$$

$$= k\ln[P(N_j,N_k)] + S_q(N_{T,jk},V_{T,jk})$$

$$\ln P(N_j,N_k)\big|_{equil} \approx -\frac{1}{2}\ln(2\pi\langle N_j\rangle(V_k/V_{T,jk}))$$

$$N_{T,jk} > \langle N_j\rangle \gg \ln\langle N_j\rangle$$

$$\Rightarrow S_{q,jk}(N_j,V_j,N_k,V_k) = S_q(N_j,V_j) + S_q(N_k,V_k)$$

$$= S_q(N_{T,jk}, V_{T,jk})$$

用 Stirling 公式 $S_t(N,V) \approx kN[\ln(\frac{V}{N})+X]$

$$E = \sum \frac{|p|^2}{2m}$$

$$P(E_j,E_k) = \frac{\int_{-\infty}^{+\infty} \delta(E_j - \sum_{i=1}^{N_j} \frac{|\vec{p_{j,i}}|^2}{2m}) dp_j \int_{-\infty}^{+\infty} \delta(E_k - \sum_{\ell=1}^{N_k} \frac{|\vec{p_{k,\ell}}|^2}{2m}) dp_k}{\int_{-\infty}^{+\infty} \delta(E_{T,j,k} - \sum_{i=1}^{N_{T,j,k}} \frac{|p_i|^2}{2m}) dp}$$

分母满足 $\int_0^{\infty} P(E_j, E-E_j)\, dE_j = 1$

δ : $\int_{-\infty}^{+\infty} f(x)\delta(x-x_0)\, dx = f(x_0)$

定义 $\Omega_p(E_\alpha, N_\alpha) = \int_{-\infty}^{+\infty} \delta(E_\alpha - \sum_{i=1}^{N_\alpha} \frac{|\vec{p_{\alpha,i}}|^2}{2m})\, dp_\alpha$

$$P(E_j,E_k) = \frac{\Omega_p(E_j,N_j)\,\Omega_p(E_k,N_k)}{\Omega_p(E_{T,j,k}, N_{T,j,k})}$$

$$\Omega_p(E,N) = \int_0^{+\infty} S_n p^{3N-1} \delta(E - \frac{p^2}{2m})\, dp \quad (p^2 = 2mx$$

$$pdp = mdx)$$

$$= S_n \int_0^{+\infty} (2mx)^{(3N-1)/2} \delta(E-x)(2mx)^{-\frac{1}{2}}\, m\, dx$$

$$\Omega_p(E,N) = S_n\, m\, (2mE)^{3N/2-1}$$

$$S_n = n\frac{\pi^{n/2}}{n/2}$$

$$\Rightarrow \Omega_p(E,N) = \frac{3N\pi^{3N/2}}{(3N/2)!} m(2mE)^{3N/2-1}$$

$$\ln \Omega_p(E,N) \approx N\left[\frac{3}{2}\ln\left(\frac{E}{N}\right) + X\right]$$

$$P(E_j, E_{T,jk} - E_j) \propto (E_j)^{3N_j/2-1} (E_{T,jk} - E_j)^{3N_k/2-1}$$

$$\frac{\partial}{\partial E_j} \ln P(E_j, E_{T,jk} - E_j) = \left(\frac{3N_j}{2} - 1\right)\frac{1}{E_j} - \left(\frac{3N_k}{2} - 1\right) \cdot \frac{1}{E_{T,jk} - E_j} = 0$$

$$\Rightarrow \langle E_j \rangle = \frac{3N_j - 2}{3N_{T,jk} - 4} E_{T,jk}$$

这里期望和概率最大值接近

$$\approx \frac{N_j}{N_{T,jk}} E_{T,jk} \Rightarrow \frac{\langle E_j \rangle}{N_j} = \frac{E_{T,jk}}{N_{T,jk}}$$

②

平衡状态.

$$\frac{\partial^2}{\partial E_j^2} \ln(E_j, E_{T,jk} - E_j) = -\left(\frac{3N_j}{2} - 1\right)\frac{1}{E_j^2} - \left(\frac{3N_k}{2} - 1\right)\frac{1}{(E_{T,jk} - E_j)^2}$$

$$E_j \approx E_{T,jk} N_j / N_{T,jk} \quad 3N_j/2 - 1 \approx 3N_j/2$$

$$\Rightarrow \frac{\partial^2}{\partial E_j^2} = -\frac{3N_j^2}{2E_j^2}\left(\frac{N_{T,jk}}{N_j N_k}\right)$$

$$= -6 E_j^{-2}$$

$$6E_j^2 = \frac{\langle E_j \rangle^2}{N_{T,jk}}\left(\frac{2N_k}{3N_j}\right)$$

$$\frac{6E_j}{\langle E_j \rangle} = \sqrt{\frac{1}{N_j}}\left(\frac{2N_k}{3N_{T,jk}}\right)^{\frac{1}{2}}$$

$$S_{p\text{-}tot}(E_j, N_j, E_k, N_k) \equiv k \ln P(E_j, N_j, E_k, N_k)$$

$$+ S_p(E_{T,jk}, N_{T,jk}) = S_p(E_j, N_j) + S_p(E_k, N_k)$$

$$k \ln P(E_j, N_j, E_k, N_k) \propto \ln N_j \ll c$$

$$S_p(E_{T,jk}, N_{T,jk}) \propto N_{T,jk}$$

$$S_p(E, N) \approx kN\left[\frac{3}{2}\ln\left(\frac{E}{N}\right) + X\right]$$

既记熵的最大 <=> 平衡 传热.

$$S_j(E_j, V_j, N_j) = kN_j\left[\frac{3}{2}\ln\left(\frac{E_j}{N_j}\right) + \ln\left(\frac{V_j}{N_j}\right) + X\right]$$

$$\frac{\partial}{\partial E_j} = 0 \Rightarrow \frac{\partial}{\partial E_j} S_j(E_j, V_j, N_j) + \frac{\partial E_k}{\partial E_j}\frac{\partial}{\partial E_k} S_k(E_k, V_k, N_k)$$

$$= \frac{\partial}{\partial E_j} S_j(E_j, V_j, N_j) - \frac{\partial}{\partial E_k} S_k(E_k, V_k, N_k)$$

$$= 0$$

$$\Rightarrow \frac{\partial S_j}{\partial E_j} = \frac{\partial S_k}{\partial E_k}$$

$$\frac{\partial S_j}{\partial E_j} = k N_j \frac{\partial}{\partial E_j} \left[\frac{3}{2} \ln\left(\frac{E_j}{N_j}\right) + \ln\left(\frac{V_j}{N_j}\right) + X \right]$$

$$= \frac{3k}{2} \frac{N_j}{E_j}$$

$$\Rightarrow \frac{E_j}{N_j} = \frac{E_k}{N_k}$$

小洞

$$\frac{\partial}{\partial N_j} S = 0 \Rightarrow \frac{\partial S_j}{\partial N_j} = \frac{\partial S_k}{\partial N_k}$$

$$\Rightarrow \frac{E_j}{N_j} = \frac{E_k}{N_k} \Rightarrow \frac{N_j}{V_j} = \frac{N_k}{V_k}$$

活塞

$$\frac{\partial}{\partial V_j} S = 0 \Rightarrow \frac{N_j}{V_j} = \frac{N_k}{V_k}$$

Hamilton情况（有势能）

还是可以拆开 $E_k - M_k$

忽略子系之间的交换 量级 $Na^{\frac{2}{3}}$

$$Na^{\frac{2}{3}} / Na = Na^{-\frac{1}{3}}$$

温度 压强

$$P(p,q) = \frac{1}{\Omega(E,V,N)} \delta(E - H(p,q))$$

$$\left(= \frac{1}{h^{3N} N!} \right) ?$$

$$\Omega = \left(\frac{1}{h^{3N} N!} \right) \int dp \int dq \, \delta(E - H(pq))$$

$$P(\vec{p}_1, \vec{r}_1) = \int dp_2 \cdots dp_N \int dr_2 \cdots dr_N \, P(p,q)$$

$$= \frac{1}{\Omega} \int \cdots\cdots \int \cdots\cdots \delta(E - H_N(pq))$$

边缘分布

$$= \frac{\Omega(E - |\vec{p}_1|^2/2m, V, N-1)}{\Omega(E,V,N) \, h^{3N} N!}$$ 不依赖 $\vec{r}_1$

对 r 积分 $\Rightarrow P = \frac{V}{N h^3} \frac{\Omega \cdots\cdots}{\Omega(E,V,N)}$

$\frac{p_i^2}{2m}$ 相对 E 很小 泰勒展开

$$\ln P(\vec{p_i}) \approx \ln\Omega(E,V,N-1) - \frac{|p_i|^2}{2m}\frac{\partial}{\partial E}$$

$$\ln\Omega(E,V,N-1) - \ln\Omega(E,V,N) + \ln\left(\frac{V}{Nh^3}\right)$$

N 很大 $\ln\Omega(E,V,N-1) \simeq \ln\Omega(E,V,N)$

令 $\frac{\partial}{\partial E}\ln(E,V,N) = \beta$

$$\Rightarrow \ln P(\vec{p_i}) \approx -\beta|\vec{p_i}|^2/2m + K$$

$$\Rightarrow P(\vec{p_i}) = \left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} \exp\left(-\beta\frac{|\vec{p_i}|^2}{2m}\right)$$

$\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}}$ 是归一化常数

$$P(p_x) = \sqrt{\frac{\beta}{2\pi m}} \exp\left(-\beta \frac{p_x^2}{2m}\right)$$

$$Ft = mv = p$$

$$F\Delta t = \int \Delta p_x \, P(p_x, \Delta t) \, dp_x$$

$\Delta t v_x = \Delta t p_x / m$ 里的粒子

墙面积 A. $A \Delta t p_x / m \rightarrow \frac{N A \Delta t p_x}{V m}$

$$\Delta p_x = 2 p_x$$

$$\Rightarrow F\Delta t = \int_0^\infty \sqrt{\frac{\beta}{2\pi m}} \exp\left(-\beta \frac{p_x^2}{2m}\right) 2p_x$$

$$\frac{N A \Delta t p_x}{V m} \, dp_x$$

$$P = F/A \Rightarrow P = \frac{2N}{Vm} \sqrt{\frac{\beta}{2\pi m}} \int_0^\infty \exp\left(-\beta \frac{p_x^2}{2m}\right) p_x^2 \, dp_x$$

$$\Rightarrow PV = N\beta^{-1}$$

$$\Rightarrow PV = N k_B T \quad \text{其中 } \beta = \frac{1}{k_B T}$$

$$\frac{\partial S}{\partial V} = kN\frac{1}{V} = \frac{kP}{k_B T} = \frac{P}{T} \quad (k = k_B)$$

$$\frac{\partial S}{\partial E} = k_B \beta = \frac{1}{T}$$

$$= k_B N \frac{3}{2E} = \frac{1}{T} \Rightarrow E = \frac{3}{2} N k_B T$$

$$\frac{\partial S}{\partial N} = \frac{-\mu}{T}$$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} d\lambda$$

Canonical Ensemble

和热源接触 T 三

$S_R = k_B \ln \Omega_R(E_R)$

$E_T = E + E_R$

$$P(E) = \frac{\Omega(E)\,\Omega_R(E_T - E)}{\Omega_T(E_T)}$$

$E_R \gg E \quad E_T \gg E$

$$\Rightarrow \ln P(E) = \ln \Omega(E) + \ln \Omega_R(E_T - E) - \ln \Omega_T(E_T)$$

$\ln \Omega_R$ 对 E 作展开

$$\ln P(E) = \ln \Omega(E) + \ln \Omega_R(E_T)$$

$$- E\left(\frac{\partial \ln \Omega_R(E_T)}{\partial E_T}\right)$$

$$- \ln \Omega_T(E_T) + O\left((E/E_T)^2\right)$$

$T = T_R \qquad \beta = \frac{1}{k_B T} = \beta_R$

$$\frac{\partial \ln \Omega_R(E_T)}{\partial E_T} = \beta_R = \frac{1}{k_B T}$$

$\ln \Omega_R(E_T)$ 和 $\ln \Omega_T(E_T)$ 常数

$$\Rightarrow \ln P(E) = \ln \Omega(E) - \beta E - \ln Z$$

$$P(E) = \frac{1}{Z}\,\Omega(E)\exp(-\beta E)$$

Z: 配分函数 归一化常数