$$G_{\text{观测}}=\sum_\nu\left[\frac{1}{N}(\text{在 } N \text{ 次观测中观测到态 } \nu \text{ 的次数})\right]G_\nu,$$

1. 基本假设：遍历性假设

在一个宏观测量时间内，宏观系统已经遍历各种允许的微观状态（以一定的概率），测得的物理量是各遍历的微观态的统计平均.

存在非遍历系统，但无法避免的扰动与损耗使实际的系统总是遍历性系统.

2. 系综：当宏观系统处于热力学平衡态时，所有满足约束条件的（极大量的）可能微观态的集合

(1) N(粒子数). V(体积). E(能量) 作为状态参量.

—— 微正则系综.

E固定 + V固定：无热交换的孤立平衡系统

(2) N.V.T 作为参量 —— 正则系综.

N.V.T 固定：无功有热达到热平衡的封闭系统.

(3). μ.V.T 作为参量 —— 巨正则系综

达到热平衡，达到粒子数平衡的开放系统.

(4). N.P.T 作为参量 —— 等温等压系综.

有功有热，达到平衡的封闭系统.

$G = H - TS = E + PV - TS = N\mu$

$\Rightarrow E = TS - PV + N\mu$

则 $dE = TdS + SdT - pdV - Vdp + Nd\mu + \mu dN$

得到 $SdT - Vdp + Nd\mu = 0$

说明 μ.P.T 不独立.

等几率原理：对于固定能量，粒子数，体积的宏观平衡系统，其达到每个微观态的概率是相同的

$$\epsilon=\sum_{j=1}^{3N}\epsilon_i=\frac{\pi^2\hbar^2}{2ma^2}\sum_{j=1}^{3N}n_j^2,\quad V_{3N}=\frac{\pi^{3N/2}}{\Gamma(3N/2+1)}R^{3N}$$

$$\Phi(E)=\frac{1}{2^{3N}N!}\frac{\pi^{3N/2}}{(3N/2)!}\left(\frac{2ma^2E}{\pi^2\hbar^2}\right)^{3N/2}$$

$$\Omega(E)=\frac{1}{2^{3N}N!}\frac{\pi^{3N/2}}{(3N/2)!}\left(\frac{2ma^2}{\pi^2\hbar^2}\right)^{3N/2}E^{3N/2-1}\mathrm{d}E.$$

$$V_N=C_NR^N, S_N=NC_NR^{N-1}.$$

$$=\pi^{N/2}\quad I_N=NC_N\int_0^\infty \mathrm{d}r\, r^{N-1}e^{-r^2}=\frac{N}{2}C_N\Gamma\left(\frac{N}{2}\right),$$

$$\frac{\Omega(E)}{dE/E}=\frac{(2\pi mE)^{3N/2}}{N!\,(\frac{3}{2}N-1)!}V^N\cdot\frac{1}{h^{3N}}$$

$$\ln\Omega=f(N)+\frac{3}{2}N\ln E+N\ln V+\ln\frac{dE}{E}$$

$$\beta=\left.\frac{\partial\ln\Omega}{\partial E}\right|_{V,N},\qquad S=k\ln\Omega(N,V,E),$$

$$\beta p=\left.\frac{\partial\ln\Omega}{\partial V}\right|_{E,N},\qquad E=\frac{3}{2}NkT,\quad p=\frac{NkT}{V}.$$

$$\beta\mu=-\left.\frac{\partial\ln\Omega}{\partial N}\right|_{V,E},$$

考察一个和环境达到共同温度 T 的系统，他们共同组成一个孤立体系

$$\Omega_{\mathrm{T};\nu}=\Omega_{\mathrm{B}}(E_{\mathrm{B}})\Omega_{\mathrm{S}}(E_\nu)=\Omega_{\mathrm{B}}(E_{\mathrm{T}}-E_\nu).$$

$$P_\nu=\frac{e^{-\beta E_\nu}}{\sum_\nu e^{-\beta E_\nu}},\qquad \ln\frac{P(E)}{P(\langle E\rangle)}=\exp\left[-\frac{1}{2}\left(\frac{E-\langle E\rangle}{\langle E\rangle\sigma_E}\right)^2\right].$$

$$P(E)=\frac{\Omega(E)e^{-\beta E}}{Q}\qquad C_V\equiv\left.\frac{\partial\langle E\rangle}{\partial T}\right|_{N,V},$$

$$\langle(\delta E)^2\rangle=kT^2C_V.$$

$$\sigma_E\equiv\frac{\sqrt{\langle(\delta E)^2\rangle}}{\langle E\rangle}=\frac{\sqrt{kT^2C_V}}{\langle E\rangle}\sim\mathcal{O}\left(\frac{1}{\sqrt{N}}\right),$$

根据热力学定律：$dE = TdS - pdV + \mu dN$.

Helmholtz 自由能定义：$A \equiv E - TS$.

$\Rightarrow dA = -SdT - pdV + \mu dN$.

则 $\left(\frac{\partial A}{\partial T}\right)_{N,V} = -S$

Gibbs − Helmholtz 关系：

热力学 宏

$$\left(\frac{\partial}{\partial T}\frac{A}{T}\right)_{N,V}=\frac{1}{T}\frac{\partial A}{\partial T}-\frac{A}{T^2}=-\frac{TS+A}{T^2}=-\frac{E}{T^2}$$

$$\frac{\partial}{\partial\beta}(\beta A)=-\left(\frac{\partial\ln Q}{\partial\beta}\right)$$

$$Q=\sum_E\Omega(E)e^{-\beta E}\simeq\Omega(\langle E\rangle)e^{-\beta\langle E\rangle}.$$

$$A=-\frac{1}{\beta}\ln Q+\frac{1}{\beta}f(N,V),$$

其中 $f(N,V)$ 是和温度无关的一个函数。考虑到事实：当只有一个态存在时，$\langle E\rangle=E_0$ 且 $Q=e^{-\beta E_0}$ 以及 $S=0$，因此 $f(N,V)=0$. 故有

$$A=-kT\ln Q,\qquad q_x=\sum_{n=1}^\infty e^{-\beta\pi^2\hbar^2n_x^2/2mL^2},$$

$$q=\frac{V}{\Lambda^3}\quad \text{求和变成积分}$$

$$S=k\ln Q+\frac{\langle E\rangle}{T}.\qquad \ln Q=N\ln q-N\ln N+N$$

$$\ln Q=N\ln q-N\ln N+N=N\ln V+\frac{3N}{2}\ln\left(\frac{2\pi mk_BT}{h^2}\right)-N\ln N+N,\qquad (2.87)$$

$$dA = -SdT - pdV + \mu dN$$

$$dA = -kT\,d\ln Q - k\,dT\ln Q$$

$$\Rightarrow kT\,d\ln Q = (S - k\ln Q)dT + pdV - \mu dN$$

$$\left.\frac{\partial \ln Q}{\partial T}\right|_{N,V} = \frac{S - k\ln Q}{kT}, \quad Q = \Omega(\langle E\rangle)e^{-\beta\langle E\rangle},$$

$$-A = TS - E,$$

$$\left.\frac{\partial \ln Q}{\partial V}\right|_{T,N} = \frac{p}{kT},$$

$$\left.\frac{\partial \ln Q}{\partial N}\right|_{V,T} = -\frac{\mu}{kT}.$$

$$E_\nu = \sum_i n_i\epsilon \equiv m_\nu\epsilon, \quad \Omega = \frac{N!}{m!(N-m)!},$$

$$\ln\Omega = N\ln N - (N-m)\ln(N-m) - m\ln m,$$

$$S = k\ln\Omega = Nk\ln(1+e^{-\beta\varepsilon}) + \frac{Nk\beta\varepsilon}{e^{\beta\varepsilon}+1}$$

$$= \begin{cases} 0, & T\to 0^+\ \beta\to+\infty \\ 0, & T\to 0^-\ \beta\to-\infty \\ Nk\ln 2, & T\to\pm\infty,\ \beta\to 0 \end{cases}$$

$$Q = \sum_\nu e^{-\beta E_\nu} = \sum_{n_1,\cdots,n_N=0,1}\prod_{i=1}^N e^{-\beta\epsilon n_i} = \prod_{i=1}^N\sum_{n_i=0,1} e^{-\beta\epsilon n_i} = (1+e^{-\beta\epsilon})^N.$$

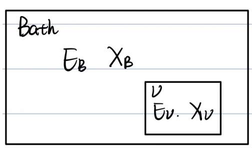
$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Q = \frac{N\epsilon}{1+e^{\beta\epsilon}}. \quad S = \frac{E}{T} + k\ln Q$$

$$= Nk\ln(1+e^{\beta\epsilon}) - \frac{Nk\beta\epsilon}{1+e^{-\beta\epsilon}}.$$

但为何会有负温度这种反直觉的情况出现呢？这是由于我们考虑的体系过于理想，实际上无法完美地制备一个二能级体系，因此对于负温度我们是无法观察到的。负温度的描述完全是一种量子效应，这在经典体系中是不被允许的。

巨正则系综：$V\ T\ \mu$.　N被释放　$\xi = -\beta\mu$

等压系综：$N\ T\ p$.　V被释放　$\xi = \beta p$



$$E = E_\nu + E_B = \text{const}$$

孤立 $X = X_\nu + X_B = \text{const}$

$$P_\nu = e^{-\beta E_\nu - \xi X_\nu}/\Xi$$

$$\langle E\rangle = \sum_\nu P_\nu E_\nu = -\left.\frac{\partial\ln\Xi}{\partial\beta}\right|_{Y,\xi}$$

$$\langle X\rangle = \sum_\nu P_\nu X_\nu = -\left.\frac{\partial\ln\Xi}{\partial\xi}\right|_{Y,\beta}$$

$$\langle(\delta E)^2\rangle = -\left.\frac{\partial\langle E\rangle}{\partial\beta}\right|_{Y,\xi} = \left.\frac{\partial^2\ln\Xi}{\partial\beta^2}\right|_{Y,\xi}$$

$$\langle(\delta X)^2\rangle = -\left.\frac{\partial\langle X\rangle}{\partial\xi}\right|_{Y,\beta} = \left.\frac{\partial^2\ln\Xi}{\partial\xi^2}\right|_{Y,\beta}$$

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$
$$= k[\beta dE + \beta p dV - \beta\mu dN]$$

$$\boxed{S = k\ln\Xi + k\beta E + k\xi X}$$

代入 Gibbs 熵公式作为验证

$$S_G = -k\sum_\nu P_\nu\ln P_\nu$$

巨正则系综

$$\Xi \equiv \sum_\nu e^{-\beta(E_\nu-\mu N_\nu)}, \quad S = k\ln\Xi + \frac{E-\mu N}{T},$$

$$\langle E\rangle = -\left.\frac{\partial\ln\Xi}{\partial\beta}\right|_{V,\beta\mu}.$$

$$\langle N\rangle = \left.\frac{\partial\ln\Xi}{\partial(\beta\mu)}\right|_{V,\beta}.$$ (无负号)

在巨正则系综中有

$kT\ln\Xi = TS + \mu N - E = pV$.　($G = E+pV-TS$.

即 $pV = kT\ln\Xi$.　　单组分 $G = \mu N$).

两边全微分可得

$$pdV + Vdp = k\ln\Xi\,dT + kT\,d\ln\Xi \quad ①$$

对 S：$dE = TdS - pdV + \mu dN$

$$dG = -SdT + Vdp + \mu dN$$

对于单组分系统 $G = \mu N$.　$dG = d\mu N + \mu dN$.

得到 $Vdp = SdT + Nd\mu$. 代入①式

$$d\ln\Xi = \frac{S - k\ln\Xi}{kT}dT + \frac{p}{kT}dV + \frac{N}{kT}d\mu.$$

$$S = k\ln\Xi + \left(\frac{\partial\ln\Xi}{\partial T}\right)_{\mu,V}kT \quad \langle(\delta N)^2\rangle = \frac{\partial\langle N\rangle}{\partial(\beta\mu)},$$

$$p = kT\left(\frac{\partial\ln\Xi}{\partial V}\right)_{T,\mu}.$$

$$N = kT\left(\frac{\partial\ln\Xi}{\partial\mu}\right)_{V,T}. \quad \frac{P(N)}{P(\langle N\rangle)} = \exp\left[-\frac{\left(\frac{N-\langle N\rangle}{\langle N\rangle}\right)^2}{2\sigma_N^2}\right],$$

时，有 $P(N)\propto\delta(N-\langle N\rangle)$. 对于巨配分函数也有

$$\Xi = \sum_\nu e^{-\beta(E-\mu N)} = \sum_N e^{\beta\mu N}\sum_E{}' e^{-\beta E} \simeq e^{\mu\langle N\rangle}\sum_E{}' e^{-\beta E_\nu},$$

等压系综　N, T, p.

配分函数 $Z = \sum_\nu e^{-\beta(E_\nu+\beta V_\nu)} = Z(N,\beta,\beta p)$.

$$\langle E\rangle = -\left.\frac{\partial\ln Z}{\partial\beta}\right|_{V,\beta p}.$$

$$\langle V\rangle = -\left.\frac{\partial\ln Z}{\partial(\beta p)}\right|_{N,\beta}.$$

$$-kT\ln Z = E + pV - TS = G.$$

$$dG = -S\,dT + V\,dp + \mu\,dN.$$

$$d\ln\mathcal{Z} = \frac{S - k\ln\mathcal{Z}}{kT}dT - \frac{V}{kT}dp - \frac{\mu}{kT}dN$$

$$\begin{cases} S = k\ln\mathcal{Z} + \left(\frac{\partial\ln\mathcal{Z}}{\partial T}\right)_{N,p} kT. \\ V = -kT\left(\frac{\partial\ln\mathcal{Z}}{\partial p}\right)_{N,T}. \\ \mu = -kT\left(\frac{\partial\ln\mathcal{Z}}{\partial N}\right)_{p,T} \end{cases}$$

$$\langle(\delta N)^2\rangle = \sum_{i,j}\langle n_i n_j\rangle - \langle n_i\rangle\langle n_j\rangle.$$

$$\langle(\delta N)^2\rangle = \sum_j \langle n_j^2\rangle - \langle n_j\rangle^2 = \sum_j \langle n_j\rangle - \langle n_j\rangle^2 = m\langle n_i\rangle(1-\langle n_i\rangle).$$

根据巨正则系综的关系

$$\rho = \frac{\partial\rho}{\partial(\beta\mu)}\bigg|_\beta, \qquad \beta p = \rho,$$

$\rho \equiv \langle N\rangle/V$. 当温度固定时,

$$d\mu = \frac{1}{\rho}dp,$$

理想气体所满足的化学势

$$\mu = kT\ln\frac{\rho}{\rho^\ominus} + \mu^\ominus(kT),$$

$$\frac{\partial\beta p}{\partial\rho}\bigg|_\beta = \frac{\partial p}{\partial\mu}\frac{\partial\beta\mu}{\partial\rho} = 1,$$

$$\eta = \begin{cases} 1, & \text{Fermion} \\ -1, & \text{Boson} \end{cases} \quad \Xi = \sum_\nu e^{-\beta(E_\nu - \mu N_\nu)} = \prod_k \sum_{n_k} e^{-\beta n_k(\varepsilon_k - \mu)}$$

$$\Xi = \prod(1 + \eta e^{-\beta(\varepsilon_k - \mu)})^\eta,$$

$$\langle n_k\rangle_{\mathrm{FD}} = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1},$$

$$\langle n_k\rangle_{\mathrm{BE}} = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}. \quad \varepsilon_k \geq \varepsilon_0 \geq \mu.$$

$$\langle\delta n_k \delta n_k'\rangle = \langle n_k n_k'\rangle - \langle n_k\rangle\langle n_k'\rangle = \delta_{kk'}[\langle n_k\rangle \mp \langle n_k\rangle^2].$$

在经典极限下，体系趋于无关联粒子体系，此时需要

1. 粒子态的数目远远大于粒子的数目。
2. $\langle n_k\rangle \ll 1$.
3. $e^{-\beta\mu} \gg 1$, 即化学势为一个绝对值很大的负数。
4. $\langle N\rangle \ll q$.
5. $\left(\frac{V}{N}\right)^{\frac{1}{3}} \gg \frac{h}{\sqrt{2\pi mkT}}$

我们从全同粒子的分布来说明上述结果的等价性。当化学势十分负时，两种分布都趋于 Maxwell-Boltzmann 分布，即有

$$\langle n_k\rangle \to e^{-\beta(\varepsilon_k - \mu)}$$

此时 $\langle n_k\rangle \ll 1$. 总粒子数也满足

$$\langle N\rangle = e^{\beta\mu}q,$$

即 $q \gg \langle N\rangle$. 此时有

$$\frac{\langle n_k\rangle}{\langle N\rangle} = \frac{e^{-\beta\varepsilon_k}}{q}.$$

当粒子数足够大时，正则配分函数和巨配分函数之间满足

$$\ln Q = \ln\Xi - \beta\mu N = -\beta\mu N + \eta\sum_k \ln[1 + \eta e^{-\beta(\varepsilon_k - \mu)}].$$

有 $e^{-\beta(\varepsilon_k-\mu)} \ll 1$, 故

$$\ln Q = -\beta\mu N + \sum_k e^{-\beta(\varepsilon_k - \mu)} = -\beta\mu N + N \simeq \ln\frac{q^N}{N!},$$

$$\Phi(\varepsilon) = \frac{1}{8}\frac{4\pi}{3}\left(\frac{\varepsilon L}{\pi\hbar c}\right)^3 \times 2, \quad \rho(\varepsilon) = \Phi'(\varepsilon) = \frac{V\varepsilon^2}{\pi^2\hbar^3c^3},$$

$$\langle E\rangle = \frac{V}{\pi^2\hbar^3c^3}\int_0^\infty d\varepsilon\,\frac{\varepsilon^3}{e^{\beta\varepsilon} - 1} = \frac{V}{\pi^2c^3}\int_0^\infty d\omega\,\frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1}.$$

单位体积的能谱密度为

$$p(\omega, T) = \frac{1}{\pi^2c^3}\frac{\hbar\omega^3}{e^{\hbar\omega/k_BT} - 1}. \qquad \langle E\rangle = \frac{\pi^2k_B^4T^4}{15c^3\hbar^3}V.$$

$$F_p = \int_0^\infty du\, u^p e^{-u}\sum_{n=0}^\infty e^{-nu} = \sum_{n=1}^\infty\int_0^\infty du\, u^p e^{-nu} = \sum_{n=1}^\infty \frac{1}{n^{p+1}}\Gamma(p+1),$$

$$\zeta(x) \equiv \sum_{n=1}^\infty \frac{1}{n^x}, \quad \zeta(4) = \frac{\pi^4}{90},$$

同理，我们可以计算配分函数为

$$\ln\Xi = \frac{\pi^2 V}{45\hbar^3c^3\beta^3},$$

这里我们用到了

$$\int_0^\infty du\, u^2\ln(1 - e^{-u}) = -\frac{1}{3}F_3.$$

$$E = 3k_BT\ln\boxed{Q}, \qquad PV = \frac{1}{3}E.$$

$$P = \frac{k_BT\ln\boxed{Q}}{V},$$

$\tilde{x}_i = \sqrt{m_i}x_i$ 和 $\tilde{p}_i = p_i/\sqrt{m_i}$, 则

$$H = \sum_i \frac{\tilde{p}_i^2}{2} + \frac{1}{2}\sum_{ij}K_{ij}\tilde{x}_i\tilde{x}_j,$$

$$\ln Q = \sum_{k=1}^{3N}\left[-\frac{\beta\hbar\omega_k}{2} - \ln(1 - e^{-\beta\hbar\omega_k})\right]$$

$$E = \sum_k \frac{\hbar\omega_k}{2} + \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1} \qquad \int_0^{\bar\omega} d\omega\, g(\omega) = 3N.$$

$$C_V = \int_0^{\bar\omega} d\omega\, g(\omega)\frac{k_B e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT} - 1)^2}\left(\frac{\hbar\omega}{k_BT}\right)$$

$g(\omega) = 3N\delta(\omega-\omega_{\rm E})$ $C_V = \dfrac{3Nk_B e^{\hbar\omega_{\rm E}/k_BT}}{(e^{\hbar\omega_{\rm E}/k_BT}-1)^2}\left(\dfrac{\hbar\omega_{\rm E}}{k_BT}\right)$

3 维晶格振动中，格波具有一个纵波和两个横

$$\Phi(k) = \frac{1}{8}\frac{4\pi}{3}\left(\frac{kL}{\pi}\right)^3 = \frac{Vk^3}{6\pi^2},\quad \omega_{\rm L} = k_{\rm L}v_{\rm L},\quad \omega_{\rm T} = k_{\rm T}v_{\rm T},$$

$\theta_{\rm D} \equiv \hbar\bar{\omega}/k_B$, 则热容为

$$C_V = 9Nk_B\left(\frac{T}{\theta_{\rm D}}\right)^3\int_0^{\theta_{\rm D}/T}\mathrm{d}u\,\frac{e^u u^4}{(e^u-1)^2}$$

低温下 $\theta_{\rm D}/T \to \infty$ $C_V = \dfrac{12\pi^4 Nk_B}{5}\left(\dfrac{T}{\theta_{\rm D}}\right)^3 \propto T^3$

$$\varepsilon_{\boldsymbol{n}} = \frac{\pi^2\hbar^2}{2mL^2}(n_x^2+n_y^2+n_z^2)\qquad \frac{h}{\sqrt{2\pi mk_BT}},$$

$\boldsymbol{k} = \pi\boldsymbol{n}/L$，能量表示为 $q = \dfrac{V}{\Lambda^3}$, $\langle E\rangle = \dfrac{3}{2}Nk_BT$, $pV = Nk_BT$.

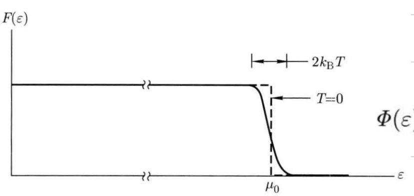
$$\varepsilon_{\boldsymbol{k}} = \frac{\hbar^2\boldsymbol{k}^2}{2m},$$

$$\ln Q = N\ln q - N\ln N + N = N\ln V + \frac{3N}{2}\ln\left(\frac{2\pi mk_BT}{h^2}\right) - N\ln N + N,$$

$$\langle N\rangle = 2\int_0^\infty \mathrm{d}n_x\int_0^\infty \mathrm{d}n_y\int_0^\infty \mathrm{d}n_z F[\varepsilon(k)]$$

$$= 2\iiint_0^\infty \frac{1}{(\pi/L)^3}\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z F[\varepsilon(k)]$$

$$T = 0,\ \mu_0 = \frac{p_{\rm F}^2}{2m} = \frac{\hbar^2k_{\rm F}^2}{2m}.\quad \langle N\rangle = \frac{2V}{(2\pi)^3}\frac{4}{3}\pi k_{\rm F}^3.$$

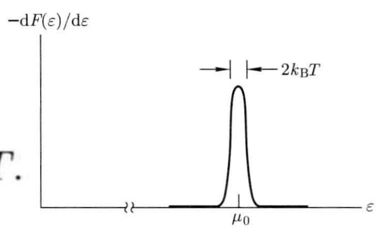


$$\Phi(\varepsilon) = \int_0^\varepsilon \mathrm{d}x 2\rho(x)x.$$

$$\langle E\rangle = \sum_j\langle n_j\rangle\varepsilon_j = 2\int_0^\infty \mathrm{d}\varepsilon\rho(\varepsilon)F(\varepsilon)\varepsilon = -\int_0^\infty \mathrm{d}\varepsilon\,\Phi(\varepsilon)\frac{\mathrm{d}F}{\mathrm{d}\varepsilon},$$

$$\langle E\rangle = -\sum_{m=0}^\infty\frac{1}{m!}\left[\frac{\mathrm{d}^m\Phi}{\mathrm{d}\varepsilon^m}\right]_{\varepsilon=\mu_0}\int_0^\infty\left[\frac{\mathrm{d}F}{\mathrm{d}\varepsilon}\right](\varepsilon-\mu_0)^m\mathrm{d}\varepsilon$$

$=(常数) + (k_{\rm B}T)^2(另一个常数) + O(T)^4.$



$C_v \propto T.$

$$N = \int_0^{\mu_0}\mathrm{d}\varepsilon\,g(\varepsilon) = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu_0^{3/2},$$

$$E = \int_0^{\mu_0}\mathrm{d}\varepsilon\,g(\varepsilon)\varepsilon = \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu_0^{5/2} = \frac{3}{5}N\mu_0.$$

$$g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}.\quad \mu_0 = \frac{\hbar^2}{2m}(3\pi^2n)^{2/3}$$

$$\Phi(\varepsilon) = \frac{4\pi}{3}\times\left(\frac{mL^2\varepsilon}{2\pi^2\hbar^2}\right)^{3/2}\times 2 = \frac{1}{3\pi^2}\frac{V}{\hbar^3}(2m\varepsilon)^{3/2},$$

$$E = \int_0^\infty\mathrm{d}\varepsilon\left[F(\mu) + (\varepsilon-\mu)\frac{\mathrm{d}F}{\mathrm{d}\varepsilon}\bigg|_\mu + \frac{1}{2}(\varepsilon-\mu)^2\frac{\mathrm{d}^2F}{\mathrm{d}\varepsilon^2}\bigg|_\mu + \cdots\right](-n_{\rm F}') \equiv \sum_{m=0}^\infty\frac{1}{m!}\frac{\mathrm{d}^mF}{\mathrm{d}\varepsilon^m}\bigg|_\mu L_m,$$

$$L_m \equiv -\int_0^\infty\mathrm{d}\varepsilon\,(\varepsilon-\mu)^m n_{\rm F}'(\varepsilon) = \int_0^\infty\mathrm{d}\varepsilon\,(\varepsilon-\mu)^m\frac{\beta}{[1+e^{\beta(\varepsilon-\mu)}][1+e^{-\beta(\varepsilon-\mu)}]}$$

$$L_m = \frac{1}{\beta^m}\int_{-\beta\mu}^\infty\mathrm{d}u\,\frac{u^m}{(1+e^u)(1+e^{-u})}\quad F(\varepsilon) \equiv \int_0^\varepsilon\mathrm{d}\varepsilon'\,g(\varepsilon')\varepsilon'$$

$$N = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2 + \mathcal{O}(\beta\mu)^{-4}\right]$$

$$N = \int_0^\infty\mathrm{d}\varepsilon\,g(\varepsilon)n_{\rm F}(\varepsilon) = \sum_{m=0}^\infty\frac{1}{m!}\frac{\mathrm{d}^m\Phi}{\mathrm{d}\varepsilon^m}\bigg|_\mu L_m,\qquad (2.147)$$

$$E = \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu^{5/2}\left[1 + \frac{5\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2 + \mathcal{O}(\beta\mu)^{-4}\right]$$

$$E = \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu^{5/2}\left[1 + \frac{5\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2 + \mathcal{O}(\beta\mu)^{-4}\right]$$

$$\mu_0^{3/2} = \mu^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right) + \mathcal{O}(\beta\mu)^{-4}\right]$$

$$\frac{E}{E|_{T=0}} = 1 + \frac{5\pi^2}{12}\left(\frac{k_BT}{\mu_0}\right)^2 + \mathcal{O}(\beta\mu_0)^{-4},$$

$C_V^{(\rm e)} = \dfrac{\pi^2}{2}Nk_B\dfrac{T}{T_{\rm F}}$ $g(E) = C\sqrt{E}$

$\beta PV = \ln H$ 积分 $\Rightarrow$ $\ln H = \frac{2}{3}\beta\langle E\rangle$

$$\int_0^\infty f(E)Q'(E)\mathrm{d}E \approx Q(E_F) + \frac{\pi^2}{6}(k_BT)^2Q''(E_F)$$

2.8 Bose-Einstein 凝聚

首先让我们来考察一般无相互作用粒子的巨配分函数，考察

$$\ln \Xi = \sum_k \eta \ln(1+\eta e^{-\beta(\varepsilon_k-\mu)}) \longrightarrow \int_0^\infty d\varepsilon\, g(\varepsilon)\eta \ln(1+\eta e^{-\beta(\varepsilon-\mu)}), \quad (2.156)$$

对于自由粒子，在周期边界条件下满足态密度

$$g(\varepsilon) = \frac{dV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}, \quad (2.157)$$

其中 d 是单能级由于其他自由度导致的简并（如自旋导致电子中 $d=2$.），因此巨配分函数为

$$\ln \Xi = \frac{dV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\beta^{-3/2}\int_0^\infty du\, u^{1/2}\eta\ln(1+\eta z e^{-u}), \quad (2.158)$$

这里我们定义了 $z\equiv e^{\beta\mu}$, 结合热波长的定义 $\Lambda \equiv h/\sqrt{2\pi m k_B T}$, 我们有

$$\ln\Xi = \frac{2d}{\sqrt{\pi}}\frac{V}{\Lambda^3}\int_0^\infty du\, u^{1/2}\eta\ln(1+\eta z e^{-u}), \quad (2.159)$$

根据关系 $\beta pV = \ln\Xi$, 有

$$\beta p\Lambda^3 = \frac{2d}{\sqrt{\pi}}\int_0^\infty du\, u^{1/2}\eta\ln(1+\eta z e^{-u}) = \frac{4d}{\sqrt{\pi}}\int_0^\infty dx\, x^2\eta\ln(1+\eta z e^{-x^2}), \quad (2.160)$$

$$\beta p\Lambda^3 = \frac{4d}{\sqrt{\pi}}\sum_{k=1}^\infty\int_0^\infty dx\, x^2\eta(-1)^{k-1}\frac{(\eta z e^{-x^2})^k}{k}, \quad (2.162)$$

为了保证求和的收敛性，需满足条件

$$0 \le e^{\beta\mu}e^{-x^2} < 1, \quad (2.163)$$

对于经典粒子，化学势远远小于-1，此时满足上述条件；对于 Bose 子，化学势小于最低能级，大部分情况下可满足；对于 Fermi 子，在高温时，化学势逐渐减小，满足收敛条件，低温时由于积分中指数的衰减，因此还可以接受，但不是一种好的近似。考虑到

$$\int_0^\infty dx\, x^2 e^{-kx^2} = -\frac{d}{dk}\int_0^\infty dx\, e^{-kx^2} = \frac{\sqrt{\pi}}{4}k^{-3/2}, \quad (2.164)$$

$$\beta p\Lambda^3 = d\sum_{k=1}^\infty(-\eta)^{k+1}z^k k^{-5/2}, \quad (2.165)$$

故能量

$$\langle E\rangle = \frac{3}{2}k_B T\ln\Xi = \frac{3}{2}pV, \quad (2.166)$$

粒子数

$$\langle N\rangle = \frac{dV}{\Lambda^3}\sum_{n=1}^\infty\frac{(-\eta)^{n+1}z^n}{n^{3/2}}. \quad (2.167)$$

在经典极限下，$z\to 0$ 且 $d\to 1$，此时求和只保留到首项，即

$$\ln\Xi = \frac{V}{\Lambda^3}e^{\beta\mu} = \langle N\rangle, \quad (2.168)$$

即回到理想气体

$$pV = Nk_BT \quad (2.169)$$

和

$$E = \frac{3}{2}Nk_BT. \quad (2.170)$$

考虑无相互作用的 Bose 子流体，其 Hamilton 量为

$$H = \sum_i\frac{p_i^2}{2m}, \quad (2.171)$$

根据之前的讨论，其巨配分函数为

$$\ln\Xi = \frac{V}{\Lambda^3}\sum_{n=1}^\infty\frac{z^n}{n^{5/2}} - \ln(1-z), \quad (2.172)$$

最后一项来自于 $\varepsilon_0 = 0$ 时会导致求和发散，因此需要将这一点的贡献去掉。粒子数为

$$\langle N\rangle = \frac{V}{\Lambda^3}\sum_{n=1}^\infty\frac{z^n}{n^{3/2}} + \frac{z}{1-z}, \quad (2.173)$$

此时可以看出固定粒子数，降低 V 或者 T 都会导致 z 增大，此时

$$n_0 = \frac{1}{e^{-\beta\mu}-1} = \frac{z}{1-z} \quad (2.174)$$

逐渐增大而成为一个宏观量，我们称开始转变的点为凝聚温度（或者凝聚密度，此时对应的是体积）。定义凝聚温度满足

$$N(T_c) = \frac{V}{\Lambda^3}\sum_{n=1}^\infty\frac{1}{n^{3/2}} = \frac{V}{h^2}(2\pi m k_B T_c)^{3/2}\zeta(3/2),$$

即

$$T_c = \left[\frac{N(T_c)}{V\zeta(3/2)}\right]^{2/3}\frac{2\pi\hbar^2}{mk_B}, \quad (2.176)$$

对于 He-4 来说，其密度为 $\rho = 0.145\,\mathrm{g/cm^3}$, 故凝聚温度为 3.12K.

当 $T > T_c$ 时，n_0 相比于 N 为小量，因此 $n_0/N \simeq 0$. 当 $T < T_c$ 时，此时

$$N = \frac{V}{\Lambda^3}\zeta(3/2) + n_0 = N\left(\frac{T}{T_c}\right)^{3/2} + n_0, \quad (2.177)$$

即此时有标度关系

$$\frac{n_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}. \quad (2.178)$$

考察此时的热容，根据巨配分函数求得能量

$$E = \frac{3}{2}\zeta(5/2)\frac{V}{\beta\Lambda^3}, \quad (2.179)$$

则热容为

$$C_V = \frac{\partial E}{\partial T} = \zeta(5/2)\frac{15}{4}k_B\frac{V}{\Lambda^3} \propto T^{3/2}, \quad (2.180)$$

因此也同样可以得到

$$\frac{C_V}{C_V(T_c)} = \left(\frac{T}{T_c}\right)^{3/2}. \quad (2.181)$$

根据同样的过程，对于密度来说，有标度关系

$$\frac{n_0}{N} = 1 - \frac{\rho_c}{\rho}. \quad (2.182)$$

对于经典粒子，化学势远远小于-1，此时满足上述条件；对于 Bose 子，化学势小于最低能级，大部分情况下可满足；对于 Fermi 子，在高温时，化学势逐渐减小，满足收敛条件，低温时由于积分中指数的衰减，因此还可以接受，但不是一种好的近似。考虑到

4、求 $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ 的化学平衡常数。

【答】由平衡条件 $\sum_B \nu_B\mu_B = 0$ 可以推得

$$\frac{\rho(H_2O)}{\rho(H_2)\rho^{\frac{1}{2}}(O_2)} = K_\rho = \frac{q_{evr}(H_2O)/\Lambda^3(H_2O)}{q_{evr}(H_2)/\Lambda^3(H_2)[q_{evr}(O_2)/\Lambda^3(O_2)]^{\frac{1}{2}}}$$

其中

$$\lambda(H_2O) = \left(\frac{h^2\beta}{2\pi m(H_2O)}\right)^{\frac{1}{2}};\lambda(H_2) = \left(\frac{h^2\beta}{2\pi m(H_2)}\right)^{\frac{1}{2}};\lambda(O_2) = \left(\frac{h^2\beta}{2\pi m(O_2)}\right)^{\frac{1}{2}}$$

$$q_{evr}(H_2O) = [g_0^{(e)}(H_2O)e^{-\beta\epsilon_0^{(e)}(H_2O)}]\left[\prod_{i=1}^{3}\frac{e^{-\frac{1}{2}\beta\hbar\omega_i(H_2O)}}{1-e^{-\beta\hbar\omega_i(H_2O)}}\right]\left[\frac{1}{\sigma(H_2O)}\left(\frac{8\pi^2}{\beta h^2}\right)^{\frac{3}{2}}(\pi ABC)^{\frac{1}{2}}\right]$$

$$q_{evr}(H_2) = [g_0^{(e)}(H_2)e^{-\beta\epsilon_0^{(e)}(H_2)}]\left[\frac{e^{-\frac{1}{2}\beta\hbar\omega(H_2)}}{1-e^{-\beta\hbar\omega(H_2)}}\right]\left[\frac{1}{\sigma(H_2)}\frac{8\pi^2}{\beta h^2}I(H_2)\right]$$

$$q_{evr}(O_2) = [g_0^{(e)}(O_2)e^{-\beta\epsilon_0^{(e)}(O_2)}]\left[\frac{e^{-\frac{1}{2}\beta\hbar\omega(O_2)}}{1-e^{-\beta\hbar\omega(O_2)}}\right]\left[\frac{1}{\sigma(O_2)}\frac{8\pi^2}{\beta h^2}I(O_2)\right]$$

$$g_0^{(e)}(H_2O) = 1; g_0^{(e)}(H_2) = 1; g_0^{(e)}(O_2) = 3; \sigma(H_2O) = \sigma(H_2) = \sigma(O_2) = 2$$

$$q_{转动}(T) = \sum_{J=0}^\infty(2J+1)\exp\left[-\frac{J(J+1)\beta\hbar^2}{2I_0}\right]$$

$$q_{振动}(T) = \sum_{v=0}^\infty\exp\left[-\left(\frac{1}{2}+v\right)\beta\hbar\omega_0\right].$$

$$q_{转动}(T) \approx \int_0^\infty dJ(2J+1)\exp[-J(J+1)\beta\hbar^2/2I_0] = \frac{T}{\theta_{转动}},$$

$$Q(\beta, V, N_1, \cdots, N_r) = \frac{1}{N_1!}\frac{1}{N_2!}\cdots\frac{1}{N_r!}q_1^{N_1}q_2^{N_2}\cdots q_r^{N_r}$$

$$\beta\mu_i = \left(\frac{\partial(\beta A)}{\partial N_i}\right)_{\beta,V,N_j} = \ln N_i - \ln q_i.$$

$$q_i = \frac{V}{\lambda_i^3}q_i^{(内)} \quad K = \prod_{i=1}^{r}\left[\frac{q_i^{(内)}}{\lambda_i^3}\right]^{\nu_i}$$

$$q = q_t q_n q_e q_v q_r/\sigma,$$

对于线型分子

$$q_r = \frac{T}{\theta_r},$$

$$\theta_r \equiv \frac{\hbar^2}{2Ik_B}.$$

$$q_r = \pi^{1/2}\left(\frac{8\pi^2 k_B T}{h^2}\right)^{3/2}(I_x I_y I_z)^{1/2}.$$

$$q_{v_i} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}},$$

$$q_n = \prod_B (2I_B + 1)e^{-\beta\varepsilon_0^{(n)}}$$

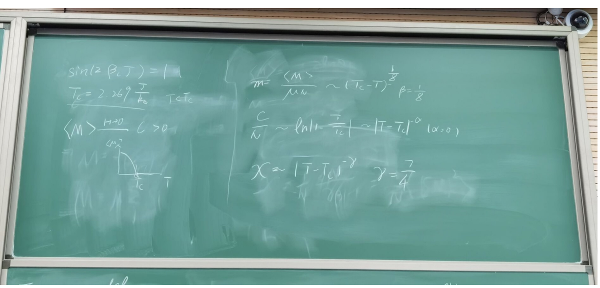
$$q_v = \prod_{i=1}^{3n-5,\ 3n-6} q_{v_i} \qquad q_e = g_e(0)e^{-\beta\varepsilon_e(0)}$$

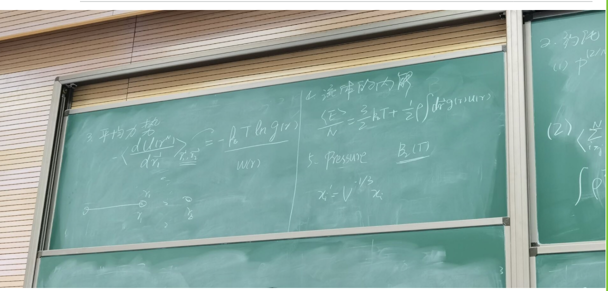
若电子能级也冻结于基态 $q_{evr} = g_0^{(e)} e^{-\beta\varepsilon_0^{(e)}} q_{vr}$

$$3n\begin{cases} t & 3 \\ r < & 2 \text{ 线性} \\ & 3 \text{ 非线性} \\ v & 3n-5/3n-6 \uparrow \end{cases}$$

σ: H_2O 2 NH_3 3 CH_4 12 C_6H_6 12

这里的 σ 为对称数，在经典极限下表述分子点群的第一类（群表示行列式为 1）元素的个数，对于双原子分子，若两原子不同，则其为 1；若相同，则为 2.





$$q_r = \sqrt{\pi}\,\frac{T^3}{\theta_x\theta_y\theta_z}$$

$pV = kT\ln\Xi = \frac{\langle E\rangle}{3}$

$S = k\ln\Xi + \frac{E}{T} = 4k\ln\Xi$

$$\int_0^\infty \frac{x^3}{e^x - 1}dx = \frac{\pi^4}{15}$$

$$N = \frac{V}{\lambda^3}\sum_{n=1}^{+\infty}\frac{z^n}{n^{3/2}} + \frac{z}{1-z}$$

$$N(\rho_c) = \frac{V_c}{\lambda^3}\sum_{n=1}^{+\infty} n^{\frac{3}{2}}$$

$$\frac{n_0}{N} = 1 - \frac{V}{V_c} = 1 - \frac{\rho_c}{\rho}$$

$\langle N\rangle =$

$m \sim (T_c - T)^{\frac{1}{8}}$

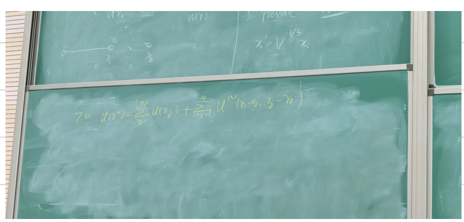
$\frac{C}{N} \sim \ln|1 - \frac{T}{T_c}|$ 0

$\chi = |T - T_c|^{-\gamma}, \gamma = \frac{7}{4}$

MFT $m \sim (-t)^{\frac{1}{2}}$ $h \sim m^3$ $\delta = 3$

$C \sim |t|^{\alpha}$ $\alpha = 0$

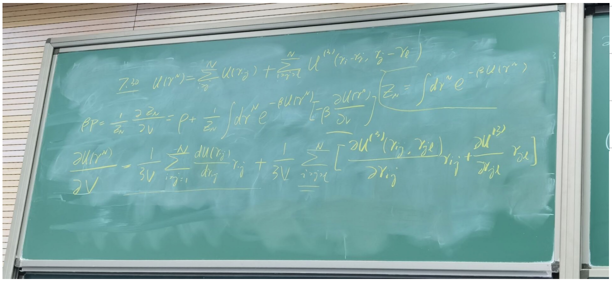
$\chi \sim |t|^{-1}$ $\gamma = 1$

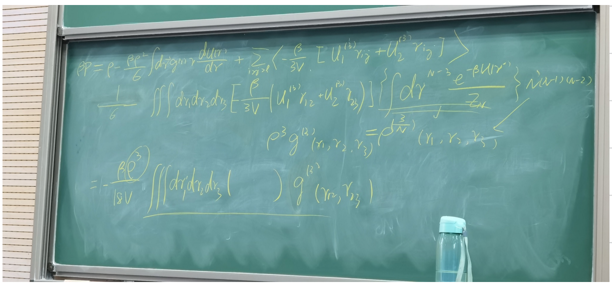


前面两页选择填空，基本都是基本概念，比如各种系综定义，BEC等。解答题前面两个和作业很相似，有一道是写平衡常数的

期末两页填空选择，六道大题，依稀记得有化学平衡，算能态密度，玻色子和费米子的相关计算 $B_2(T)$ 线性响应理论

$$Q=\frac{1}{N!\Lambda^{3N}}\int dr^N e^{-\beta U(r^N)}$$





由于系统中每个原子都会发生散射，则在检测器中有波的叠加：

$$(\text{总散射波})=f(k)\frac{e^{i\boldsymbol{k}_{\text{out}}\cdot\boldsymbol{R}_D}}{|\boldsymbol{R}_c-\boldsymbol{R}_D|}\sum_{j=1}^{N}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_j},$$

为看出其原因，将 $S(k)$ 中对所有粒子的求和分成两部分：对自身的部分，即 $l=j$，和不同粒子的部分，即 $l\neq j$. 前者有 N 项，后者有 $N(N-1)$ 项，于是有

$$\begin{aligned}
S(k)&=1+N^{-1}N(N-1)\left\langle e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)}\right\rangle\\
&=1+N^{-1}\frac{N(N-1)\int dr^N e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)}e^{-\beta U}}{\int dr^N e^{-\beta U}}\\
&=1+N^{-1}\underbrace{\int d\boldsymbol{r}_1\int d\boldsymbol{r}_2}_{\int d\boldsymbol{r}_1\int d\boldsymbol{r}_{12}}\underbrace{\rho^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2)}_{\rho^2 g(r_{12})}e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)}\\
&=1+\rho\int d\boldsymbol{r}g(r)e^{i\boldsymbol{k}\cdot\boldsymbol{r}}.
\end{aligned}$$

② $H\to H+\Delta H$ $\quad \Delta H=-M(\Gamma)f$ $\quad \langle A\rangle\to\langle A\rangle+\langle\Delta A\rangle$ $\quad \beta\Delta H\ll$

③ $\langle A\rangle_{H+\Delta H}=\dfrac{\int d\Gamma e^{-\beta(H+\Delta H)}A(\Gamma)}{\int d\Gamma e^{-\beta(H+\Delta H)}}\approx\dfrac{\int d\Gamma e^{-\beta H}(1-\beta\Delta H)A}{Z(1-\beta\langle\Delta H\rangle)}$

$=\langle A\rangle_H+\beta(\langle A\rangle\langle\Delta H\rangle-\langle A\cdot\Delta H\rangle)$

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

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

2.静态弛豫过程 $\quad t=0\quad F(t)=\dfrac{e^{-\beta(H+\Delta H)}}{\int e^{-\beta(H+\Delta H)}d\Gamma}$

$t>0\quad\begin{cases}\bar{A}(t)=\int d\Gamma F(\Gamma)A(\Gamma,t)\\ \dfrac{d\bar{A}(t)}{dt}=\dot{A}=\{H,A\}\end{cases}$

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

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

利用 $\chi(t-t')$ 与 $\epsilon(t')$ 无关，考虑静态弛豫过程 $\quad \epsilon(t')=\begin{cases}f, & t<0\\ 0, & t>0\end{cases}$

$\Delta\bar{A}(t)=\int_{-\infty}^{t}\chi(t-t')\epsilon(t')dt'=f\int_{-\infty}^{0}\chi(t-t')dt'=f\int_{t}^{+\infty}\chi(\tau)d\tau=f\beta C^{\delta}_{MA}(t)$

$\chi(t)=\begin{cases}-\beta\dfrac{d}{dt}C^{\delta}_{MA}(t) & (t>0)\\ 0 & (t<0)\end{cases}$

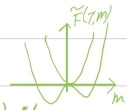
⑧. 自由能：$G(T,H) = -kT\ln Q$

$m = \tanh(\beta\mu H + \beta z J m)$

$= \frac{1}{2}NzJm^2 - NkT\ln\{2\cosh(m\beta\mu H + \beta z J m)\}$

$\frac{1}{\cosh^2 x} = 1 - \tanh^2 x$

$= \frac{NzJm^2}{2} - NkT\ln[2(\frac{1}{1-m^2})^{\frac{1}{2}}]$



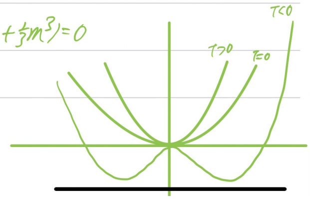
$G(T,H) \to \tilde{F}(T,m) = G(T,H) + Hm \to \tilde{F}(T,m)$

$G(T,H) \simeq (-\frac{1}{2}k_BT_c\tau m^2 - \frac{1}{12}k_BT_c m^4 - k_BT_c\ln 2) \times N$

$f(T,m) = g(T,H) + H\mu m = g(T,H) + k_BT_c(m\tau + \frac{1}{3}m^3)\cdot m$

$= \frac{1}{2}k_BT_c\tau m^2 + \frac{1}{12}k_BT_c m^4 - k_BT\ln 2$

$\frac{\partial f(T,m)}{\partial m} = 0 \Rightarrow (\tau m + \frac{1}{3}m^3) = 0$



$P = -(\frac{\partial F}{\partial V})_{N,T}$ $F = -kT\ln Q$

$Q = \frac{1}{N!\Lambda^{3N}}\underline{\int dr^N e^{-\beta U(r^N)}} \to Z_N$

$\Rightarrow P = \frac{k_BT}{Z_N}(\frac{\partial}{\partial V}Z_N)_{N,T}$ $U = \frac{1}{2}\sum_{i\neq j} u(V^{\frac{1}{3}}r_{ij})$

$Z_n \to V^N\int_0^1 d\vec{r}_1 - d\vec{r}_N\, e^{-\beta U(V^{\frac{1}{3}}\vec{r}_1, \cdots, V^{\frac{1}{3}}\vec{r}_N)}$

$\Rightarrow \frac{\partial Z_N}{\partial V} = \frac{N}{V}Z_n + V^N\int d\vec{r}^{\,N}\frac{\partial}{\partial V}(e^{-\beta U(r^N)})$

$\frac{\partial U(r^N)}{\partial V} = \frac{1}{2}\sum_{i\neq j}\frac{\partial}{\partial V}(u(r_{ij})) = \frac{\partial u(r_{ij})}{\partial r_{ij}}(\frac{\partial r_{ij}}{\partial V})$ (✡)

$r_{ij} \propto V^{\frac{1}{3}} \to \frac{dr_{ij}}{dV} = \frac{r_{ij}}{3V}$

(✡) $\to V^N\int dr^N(-\beta)e^{-\beta U}[\frac{1}{2}\sum_{i\neq j}\frac{r_{ij}}{3V}\frac{\partial u(r_{ij})}{\partial r_{ij}}]$

$= \frac{-\beta}{6V}\int dr^N e^{-\beta U}(\sum_{i\neq j} r_{ij}\frac{\partial u(r_{ij})}{\partial r_{ij}})$

$= \frac{-\beta N(N-1)}{6V}\int dr^N\, r_{12}\frac{\partial u(r_{12})}{\partial r_{12}}e^{-\beta U}$

$= -\frac{\beta}{6V}\int d\vec{r}_1 d\vec{r}_2\, r_{12}\frac{\partial u(r_{12})}{\partial r_{12}}\cdot[N(N-1)\int dr^{N-2}e^{-\beta U}]$

$= -\frac{\beta}{6V}\int d\vec{r}_1 d\vec{r}_2\, r_{12}\frac{\partial u(r_{12})}{\partial r_{12}}\rho^2 g(\vec{r}_1,\vec{r}_2)Z_N$

$= \frac{\beta}{6}\int d\vec{r}\; r\frac{du}{dr}\rho^2 g(r)$

$\Rightarrow \beta P = \rho - \frac{\beta}{6}\rho^2\int d\vec{r}\, g(r)\, r\frac{\partial u(r)}{\partial r}$