

Some notes about SM

BY SUN QUANCHAO

Sustech

电子邮件: 12110811@mail.sustech.edu.cn

目录

1 系综理论	1
1.1 Liouville's theorem	2
1.2 微正则系综	2
1.3 Two level System	3
1.4 正则系综	4
1.4.1 正则系综与热力学函数	4
1.5 巨正则系综	7
1.6 系综理论的一些应用	8
1.6.1 范德瓦尔斯气体	8
2 Quantum statistics 量子统计	12
2.1 Occupation numbers 占据数表象	13
2.2 Incoherent Superposition of States	13
2.3 Density matrix 密度矩阵	13
2.4 纯态与混态	14
2.5 Ensembles in Quantum statistical Mechanics.	15
2.5.1 Vibrational modes 震动	16
2.6 量子系综的应用	17
Fermions:	17
Bosons:	17
2.7 Ideal fermi gas	22
2.7.1 朗道铁磁相变理论	23
2.8 理想玻色系统	25
2.8.1 光子	25
2.8.2 Phonon.声子	26
2.8.3 玻色-爱因斯坦凝聚	28

1 系综理论

microstate

$$\rho(q, p, t) dq dp \equiv \dot{\rho}(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}) \prod_{i=1}^{3N} dq_i dp_i$$

1.1 Liouville's theorem

Liouville's theorem

$$\frac{\partial}{\partial t} \int_{\omega} \rho dp dq$$

$$\rho = |\psi|^2 \quad j = \frac{\langle \vec{p} \rangle}{m} \quad \frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0$$

$$\frac{\partial}{\partial t} \int_{\omega} \rho dp dq = - \oint \rho \vec{v} \cdot \hat{n} d\sigma = - \int_{\omega} v(\rho \vec{v}) dp dq \Rightarrow \int_{\omega} \left[\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) \right] dp dq = 0$$

$$\nabla \cdot (\rho \vec{v}) = \sum_{i=1}^{3N} \left(\frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \dot{p}_i) \right) = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) + \rho \sum_{i=1}^{3N} \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right)$$

$$\Rightarrow \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0$$

$$\frac{\partial \rho}{\partial t} = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} \right) = -\{\rho, H\}$$

如何计算系统内某个物理量的平均?

$$\frac{d\langle O \rangle}{dt} = \int dp dq \frac{\partial \rho(p, q, t)}{\partial t} O(p, q) = \sum_{i=1}^{3N} dp dq O \left(\frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} \right)$$

$$= - \sum_{i=1}^{3N} \int dp dq \rho \left[\left(\frac{\partial O}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial O}{\partial q_i} \frac{\partial H}{\partial p_i} \right) + O \left(\frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial q_i \partial p_i} \right) \right]$$

$$= - \int dp dq \rho \{H, O\} = \langle \{O, H\} \rangle$$

Probability : $\frac{\partial \rho}{\partial t} = 0$ possible solution: $\rho(p, q) = \rho(H(p, q))$

notation : $\frac{d\rho}{dt} = 0$ 恒成立, 但是对于平衡状态下, 有 $\frac{\partial \rho}{\partial t} = 0 = -\{\rho, H\} = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} \right)$.

$$\{\rho, H\} = \rho'(H) \{H, H\} = 0$$

1.2 微正则系综

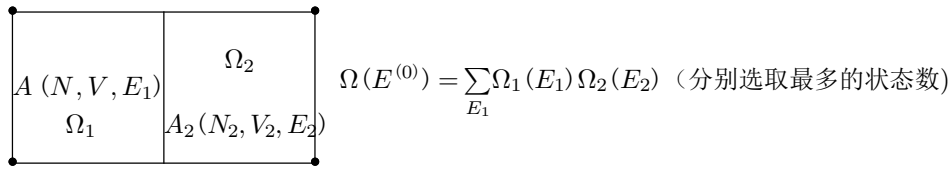
对于一个孤立系统

$$\rho(p, q) = \text{constant. if } E \leq H(p, q) \leq E + \Delta$$

$$\rho(p, q) = 0, \text{ otherwise}$$

↑ Microcanonical ensemble.

$$\text{相空间的体积: } \Gamma = \int dp dq \rho(H(p, q)) \quad S = k_B \ln \Gamma$$



$$\frac{\partial \Omega_1(E_1)}{\partial E_1} \Big|_{E_1=\bar{E}_1} \Omega_2(\bar{E}_2) + \Omega_1(\bar{E}_1) \left(\frac{\partial \Omega_2(E_2)}{\partial E_2} \right) \Big|_{E_2=\bar{E}_2} = 0$$

$$\Rightarrow \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \Big|_{E_1=\bar{E}_1} = \frac{\partial \ln \Omega_2}{\partial E_2} \Big|_{E_2=\bar{E}_2}$$

$$\beta \equiv \frac{\partial \ln \Omega(N, V, E)}{\partial E} \Big|_{N, V, E=\bar{E}} \quad \text{Equilibrium: } \beta_1 = \beta_2$$

$$\left(\frac{\partial S}{\partial E} \right) \Big|_{N, V} = \frac{1}{T} \Rightarrow S = k_B \ln \Omega$$

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

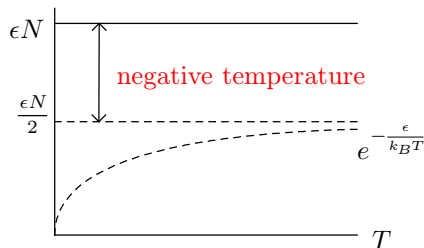
1.3 Two level System

impurity ϵ ————— $|1\rangle$
 \bullet ————— $|0\rangle$

$E = \epsilon N_1$. 概率 $P(\{n_i\}) = \frac{\delta_\epsilon \sum_i n_i, E}{\Omega(E, N)}$, $n_i = 0, 1$. $\Omega(E, N) = \frac{N!}{(N - N_1)! N_1!}$

$$S(E, N) = k_B \ln(\Omega) = k_B (N(1 - \ln N) - \dots) \approx N k_B \left[\left(\frac{E}{N\epsilon} \right) \ln \left(\frac{E}{N\epsilon} \right) + \left(1 - \frac{E}{N\epsilon} \right) \ln \left(1 - \frac{E}{N\epsilon} \right) \right]$$

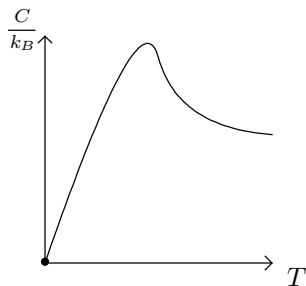
$$\frac{1}{T} = \frac{\partial S}{\partial E} \Big|_N = -\frac{k_B}{\epsilon} \ln \left(\frac{E}{N\epsilon - E} \right) \Rightarrow E(T) = \frac{N\epsilon}{\exp \left(\frac{\epsilon}{k_B T} \right) + 1}$$



负温度指随着温度的升高，熵反而下降。

计算指标 Heat capacity

$$C = \frac{dE}{dT}$$



$$p(n_1) = \sum_{\{n_2, \dots, n_i\}} p(\{n_i\}) = \frac{\Omega(E - n_1\epsilon, N - 1)}{\Omega(E, N)} \quad p(0) = \frac{1}{1 + e^{-\frac{\epsilon}{k_B T}}}, p(1) = \frac{e^{-\frac{\epsilon}{k_B T}}}{1 + e^{-\frac{\epsilon}{k_B T}}}$$

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \quad E \leq H \leq E + \Delta$$

$$\Omega(E) = \frac{1}{h^{3N}} \int_{E \leq H \leq E + \Delta} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}$$

$$\text{球体的计算} \Sigma(E) = \frac{1}{h^{3N}} \int_{H \leq E} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}$$

由于 p, q 与 H, E 无关, 可以直接去 d , 积分得到 $6N$ 维单位球的体积

$$\Sigma = \frac{1}{h^{3N}} V^N \frac{(2\pi m E)^{3/2}}{(3N/2)!}$$

$$\Omega = \frac{\partial \Sigma}{\partial E} \Delta E = \frac{3N}{2} \frac{\Delta E}{E} \Sigma(E)$$

$$\Omega(E) = \frac{\partial \Sigma}{\partial E} \Delta E$$

1.4 正则系综

能量相同的态出现的概率相同。

$$\rho(\mu_s) = \frac{1}{Z} e^{-\beta E_s}$$

$$Z = \sum_{\{\mu_s\}} e^{-\beta E_s}$$

$Z = \sum_{E_s} e^{-F(E_s)/k_B T}$, 作泰勒展开。

1.4.1 正则系综与热力学函数

自由能 $F(E) = E - TS(E)$,

$$\left. \frac{\partial S}{\partial E} \right|_{E=\bar{E}} = \frac{1}{T}$$

$$\left. \frac{\partial F}{\partial E} \right|_{E=\bar{E}} = 1 - T \left. \frac{\partial S}{\partial E} \right|_{E=\bar{E}} = 0$$

$$\left. \frac{\partial^2 F}{\partial E^2} \right|_{E=\bar{E}} = -T \left(\left. \frac{\partial^2 S}{\partial E^2} \right|_{E=\bar{E}} \right) = \frac{1}{T} \left. \frac{\partial T}{\partial E} \right|_{E=\bar{E}} = \frac{1}{TC_V}$$

$$Z = \sum_{E_s} e^{-F(E_s)/k_B T} = e^{-\beta F(\bar{E})} \sqrt{2\pi k_B T^2 C_V}$$

$\sqrt{2\pi k_B T^2 C_V}$ 在热力学极限下不重要

$$E = F + TS = F - T \frac{\partial F}{\partial T} = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) = \frac{1}{k_B} \frac{\partial}{\partial \beta} \left(\frac{F}{T} \right)$$

$$E = -\frac{\partial}{\partial \beta} \ln Z \quad F = -k_B T \ln Z$$

连续情形。

$$Z = \frac{1}{h^{3N} N!} \int dp dq e^{-\beta H(p, q)}$$

$$S = -k_B \sum_{\{\mu_s\}} \rho(\mu_s) \ln \rho(\mu_s)$$

two-level system

$$E = \epsilon \sum_{i=1}^N n_i \quad \rho(\{n_i\}) = \frac{1}{Z} e^{-\beta \epsilon \sum_{i=1}^N n_i}$$

$$\text{-----} \quad \epsilon$$

$$\text{-----} \quad 0$$

$$Z = \sum_{\{n_i\}} e^{-\beta \epsilon \sum_{i=1}^N n_i} = \sum_{\{n_i\}} \prod_i e^{-\beta \epsilon n_i} = \left(\sum_{n_1=0}^1 e^{-\beta \epsilon n_1} \right) \left(\sum_{n_2=0}^1 e^{-\beta \epsilon n_2} \right) \dots \left(\sum_{n_N=0}^1 e^{-\beta \epsilon n_N} \right) = (1 + e^{-\beta \epsilon})^N$$

$$F = -N k_B T \ln(1 + e^{-\beta \epsilon})$$

$$S = -\frac{\partial F}{\partial T} \Big|_N$$

$$= N k_B \ln(1 + e^{-\beta \epsilon}) + N k_B T \left(\frac{\epsilon}{k_B T} \right) \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}}$$

$$E = \frac{N \epsilon e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}}$$

$$\rho_1(n_1) = \frac{e^{-\beta \epsilon n_1}}{1 + e^{-\beta \epsilon}}$$

理想气体 Ideal gas

$$Z = \int \frac{1}{N!} \prod_{i=1}^N \frac{d^3 q_i d^3 p_i}{h^3} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}$$

$$\text{单个粒子 } Z_1 = \int \frac{d^3 q d^3 p}{h^3} e^{-\beta \frac{p^2}{2m}} = \frac{V}{h^3} \int e^{-\beta \frac{p^2}{2m}} d^3 p = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2}$$

$$n \text{ 个粒子 } Z_N = \int \frac{1}{N!} \prod_{i=1}^N \frac{d^3 q_i d^3 p_i}{h^3} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} = \frac{1}{N!} Z_1^N = \frac{1}{N!} V^N \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

$$\text{thermal wavelength } \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$F \cong k_B T \left[\frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + N \ln \frac{V}{N} + N \right]$$

$$\left(\frac{\partial F}{\partial V} \right)_{T, N} = -p \Rightarrow -k_B T \frac{N}{V} \Rightarrow pV = N k_B T$$

$$\left(\frac{\partial F}{\partial T} \right)_{V, \mu} = -S \Rightarrow S = k_B \left[\frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + N \ln \frac{V}{N} + N \right] + k_B \frac{3N}{2}$$

Kardar

$$F = E - TS \rightarrow G = E - TS + pV$$

$$Z(N, T, p) = \int_0^\infty dV \int \frac{1}{N!} \prod_{i=1}^N \frac{d^3 q_i d^3 p_i}{h^3} e^{-\beta \left[\sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + pV \right]}$$

$$G = E - TS + pV = -k_B T \ln Z \approx N k_B T \left[\ln P - \frac{5}{2} \ln(k_B T) + \frac{3}{2} \ln \left(\frac{h^2}{2\pi m} \right) \right]$$

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

$$V = \frac{\partial G}{\partial p} |_{T,N} = \frac{N k_B T}{p}$$

$$Z = \text{Tr}(e^{-\beta \hat{H}}) = \sum_n \langle n | e^{-\beta \hat{H}} | n \rangle$$

$$Z = \sum_{\{\dots\}} e^{-\beta \left(\sum_o \frac{\vec{p}^2}{2m} - \vec{B} \cdot \vec{M} \right)}$$
 先不管第一部分

$$Z = \sum_{\{\sigma_i\}} e^{\beta B \mu_i \sum_{i=1}^N \sigma_i} \quad \sigma_i = \pm 1$$

$$Z = [e^{\beta B \mu_0} + e^{-\beta B \mu_0}]^N = [2 \cosh(\beta B \mu_0)]^N$$

$$G=-k_B\,T\ln Z$$

$$M=-\frac{\partial G}{\partial B}$$

$$\chi(T)=\frac{\partial N}{\partial B}|_{B=0}=\frac{N\mu_0^2}{k_BT}$$

2023.11.07

$$Z(N,T,P)=\int_0^\infty dV\int\frac{1}{N!}\prod_{i=1}^N\frac{d^3q_id^3p_i}{h^3}e^{-\beta(\sum_{i=1}^N\frac{\vec{p}_i^2}{2m}+pV)}$$

$\int_0^\infty dV$ 是为了把引入的变量 V 通过积分积掉 V 的影响。

$$Z=\int\frac{1}{N!}\prod_{i=1}^N\frac{d^3q_id^3p_i}{h^3}e^{-\beta E_s}$$

$$Z=\sum_{\{\mu_s\}}e^{-\beta E_s}$$

1.5 巨正则系综

Grand canonical ensemble (系综的粒子数可以改变的巨正则系综) (T, V, μ 确定)

$$dE = TdS - pdV + \mu dN$$

$$\rho(\mu_s)$$

把剩下的空间和系综当作是一个整体，所有的粒子数为N，

$$\begin{aligned}\rho(\mu_s) &= \frac{\Omega_R(E - E_s, N - N_s)}{\Omega_{R+S}(E, N)} \\ &\approx \frac{1}{\Omega_{R+S}(E, N)} \exp \left[\frac{1}{k_B} \left(S_B(E, N) - \left(\frac{\partial S_B}{\partial E} \right)_{V, N} E_s - \left(\frac{\partial S_R}{\partial E} \right)_{E, V} N_s \right) \right] \\ &= \text{const} \times \exp \left[\frac{1}{k_B} \left(- \left(\frac{\partial S_R}{\partial E} \right)_{V, N} E_s - \left(\frac{\partial S_R}{\partial N} \right)_{E, V} N_s \right) \right] \\ \Rightarrow \rho(\mu_s) &\propto e^{-\beta(E_s - \mu N_s)} \\ \rho(\mu_s) &= \frac{1}{Z} e^{-\beta(E_s - \mu N_s)}\end{aligned}$$

$$Z = \sum_{\{\mu_s\}} e^{-\beta(E_s - \mu N_s)} = \sum_{E_s, N_s} \frac{\Omega(E_s, N_s) e^{-\beta(E_s - \mu N_s)}}{e^{\frac{S}{k_B}}}$$

$$\rho(E_s, N_s) = \frac{1}{Z} \Omega(E_s, N_s) e^{-\beta(E_s - \mu N_s)} = \frac{1}{Z} \exp \left[\frac{1}{k_B} S(E_s, N_s) - \beta(E_s - \mu N_s) \right] = \frac{1}{Z} e^{-\beta \Phi(T, \mu, V)}$$

$$\Phi(T, \mu, N) = \bar{E} - TS - \mu \bar{N}$$

$$\bar{E} - \mu \bar{N} = \Phi + TS = \Phi - T \frac{\partial \Phi}{\partial T} = -T^2 \frac{\partial}{\partial T} \left(\frac{\Phi}{T} \right) = \frac{1}{k_B} \frac{\partial}{\partial \beta} \left(\frac{\Phi}{T} \right) = - \frac{\partial}{\partial \beta} \ln Z$$

$$\text{根据定义有 } \bar{E} - \mu \bar{N} = \frac{1}{Z} \sum_{\{\mu_s\}} (E_s - \mu N_s) e^{-\beta(E_s - \mu N_s)}$$

$$\text{由 } \Phi(T, \mu, N) = \bar{E} - TS - \mu \bar{N} \quad d\Phi = -SdT - pdV - Nd\mu$$

$$\Rightarrow \Phi = -k_B T \ln Z$$

$$S = -\frac{1}{T} \frac{\partial}{\partial \beta} \ln Z + k_B \ln Z$$

$$S = -k_B \sum_{\{\mu_s\}} \rho(\mu_s) \ln \rho(\mu_s)$$

巨正则系综的配分函数为

$$Z = \sum_{N_s=0}^{\infty} (e^{\beta \mu})^{N_s} Z_c(T, N_s, V) = \sum_{N_s=0}^{\infty} Z^{N_s} Z_c$$

1.6 系综理论的一些应用

1.6.1 范德瓦尔斯气体

考虑各个粒子之间存在相互作用

Cumulant expansion

$$G(k) = \langle e^{iky} \rangle = \int dy e^{iky} P(y) = \sum_{r=0}^{\infty} \frac{(ik)^r}{r!} \langle Y^r \rangle$$

$$\ln G(k) = \sum_{r=1}^{\infty} \frac{(ik)^r}{r!} \Xi_r$$

$$\begin{aligned}\Xi_1 &= \langle Y \rangle \\ \Xi_2 &= \langle Y^2 \rangle - \langle Y \rangle^2 \\ \Xi_3 &= \langle Y^3 \rangle - 3\langle Y^2 \rangle \langle Y \rangle + 2\langle Y \rangle^3\end{aligned}$$

范德瓦尔斯气体 状态方程

$$H = \sum \frac{p_i^2}{2m} + \sum_{i < j} v_{ij} \quad v_{ij} \text{ 为相互作用项}$$

$$v_{ij} = v(|\vec{r}_i - \vec{r}_j|)$$

由于粒子之间存在吸引力，气体的压强会略有减小，差别与体积的平方成反比

$$V_{\text{eff}} = V - b \quad b \approx \frac{4\pi}{3} N \left(\frac{r_0}{2} \right)^3$$

$$p = p_{\text{kinetic}} - \frac{a}{V^2}$$

$$p_{\text{kinetic}} V_{\text{eff}} = RT$$

$$\text{范德瓦尔斯气体方程: } (V - b) \left(p + \frac{a}{V^2} \right) = RT$$

Viral expansion

$$p + \frac{a}{V^2} = \frac{RT}{V} \left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{V^2}$$

$$\begin{aligned}\Rightarrow \frac{pV}{RT} &= \left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{RTV} \\ &= 1 + \frac{1}{V} \left(b - \frac{a}{RT} \right) + \left(\frac{b}{V} \right)^2 + \left(\frac{b}{V} \right)^3 \dots \\ &= 1 + \frac{C_2}{V} + \frac{C_3}{V^2} + \dots\end{aligned}$$

Cluster expansion

$$Z_N(V, T) = \frac{1}{N! h^{3N}} \int \prod_i d^3 q_i d^3 p_i \exp \left(-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} - \beta \sum_{i < j} v_{ij} \right) = \frac{1}{N! \lambda^{3N}} Q_N(V, T)$$

$$Q_N(V, T) = \int \prod_i d^3 r_i e^{-\beta \sum_{i < j} u_{ij}}$$

$$\text{近似: } f_{ij} = e^{-\beta u_{ij}} - 1$$

2023.11.10

$$G(k) = \langle e^{-kY} \rangle$$

$$H = \sum \frac{\vec{p}_i^2}{2m} + U(q_1, \dots, q_N)$$

$$\begin{aligned} Z(T, V, N) &= \frac{1}{N!} \int \prod_{i=1}^N \left(\frac{d^3 p_i d^3 q_i}{h^3} \right) \exp \left(-\beta \sum_i \frac{\vec{p}_i^2}{2m} \right) \exp(-\beta U(q_1, \dots, q_N)) \\ &= Z_0 \langle \exp(-\beta U(q_1, \dots, q_N)) \rangle^0 \\ \ln Z &= \ln Z_0 + \sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!} \langle U^l \rangle_c^0 \end{aligned}$$

集团展开

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i < j} v_{ij}(|\vec{r}_i - \vec{r}_j|)$$

体积温度恒定的情况下

$$Z_N(V, T) = \frac{1}{N! h^{3N}} \int d^3 N p d^3 N r \exp \left(-\beta \sum \frac{\vec{p}_i^2}{2m} - \beta \sum_{i < j} v_{ij} \right) = \frac{1}{N! \lambda^{3N}} Q_N(V, T)$$

$$\begin{aligned} Q_N(V, T) &= \int d^3 N r \exp \left(-\beta \sum_{i < j} v_{ij} \right) \\ &= \int d^3 N r \prod_{i < j} (1 + f_{ij}) \end{aligned}$$

其中, $f_{ij} = e^{-\beta v_{ij}} - 1$

$$\begin{aligned} Q_N(V, T) &= \int d^3 r_1 \dots d^3 r_N \left[1 + \sum f_{ij} + \sum f_{ij} f_{ii} + \dots + \right] \\ &= \sum_{\{m_l\}} S(\{m_l\}) \end{aligned}$$

Cluster expansion for a classical gas

Cluster integral

定义: $b_l(V, T) = \frac{1}{l! \lambda^{3l-3} V}$ (sum of all possible l -cluster) (就是所有可能的相互作用)

$$b_1 = \frac{1}{V} [\textcircled{1}] = \frac{1}{V} \int d^3 r = 1$$

$$\begin{aligned} b_2 &= \frac{1}{2! \lambda^3 V} [\textcircled{1} - \textcircled{2}] \\ &= \frac{1}{2 \lambda^3 V} \int f_{12} d^3 r_1 d^3 r_2 \\ &= \frac{1}{2 \lambda^3} \int f_{12} d^3 r_{12} \end{aligned}$$

$$\begin{aligned}
&= \frac{2\pi}{\lambda^3} \int_0^\infty f(r_{12}) r_{12}^2 dr_{12} \\
&= \frac{2\pi}{\lambda^3} \int_0^\infty (e^{-\beta_1 v_{12}} - 1) r_{12}^2 dr_{12} \\
b_3 &= \frac{1}{3! \lambda^6 V} \left[\begin{array}{c} \text{Diagram 1: 1 connected to 2 and 3} \\ \text{Diagram 2: 1 connected to 2, 2 connected to 3} \\ \text{Diagram 3: 1 connected to 3, 2 connected to 3} \\ \text{Diagram 4: 1 connected to 2 and 3, 2 connected to 3} \end{array} \right] \\
&= \frac{1}{6 \lambda^6 V} \int (f_{12} f_{13} + f_{13} f_{23} + f_{12} f_{23} + f_{12} f_{23} f_{13}) d^3 r_1 d^3 r_2 d^3 r_3 \\
&= \frac{1}{6 \lambda^6 V} \left(\int 3V (f_{12} f_{23} d^3 r_{12} d^3 r_{23}) + V \int f_{12} f_{23} f_{13} d^3 r_{12} d^3 r_{13} \right)
\end{aligned}$$

$\sum_{l=1}^N l \cdot m_l = N$, A given set of integers $\{m_l\}$ satisfying the equation, however, dose not uniquely sperify a graph. (l :参与相互作用的粒子个数, m_l 相互作用的个数)

$$\{[\bigcirc] \dots [\bigcirc] (m_1 \uparrow)\} \{[\bigcirc \longleftrightarrow \bigcirc] \dots [\bigcirc \longleftrightarrow \bigcirc] (m_2 \uparrow)\} \left\{ \begin{array}{c} \text{Diagram 1: 1 connected to 2 and 3} \\ \text{Diagram 2: 1 connected to 2, 2 connected to 3} \\ \text{Diagram 3: 1 connected to 3, 2 connected to 3} \\ \text{Diagram 4: 1 connected to 2 and 3, 2 connected to 3} \end{array} (m_3 \uparrow) \right\}$$

每个位置可以填充粒子

$$\begin{aligned}
S\{m_l\} &= \sum_p [\bigcirc]^{m_1} [\bigcirc \longleftrightarrow \bigcirc]^{m_2} \left[\begin{array}{c} \text{Diagram 1: 1 connected to 2 and 3} \\ \text{Diagram 2: 1 connected to 2, 2 connected to 3} \\ \text{Diagram 3: 1 connected to 3, 2 connected to 3} \\ \text{Diagram 4: 1 connected to 2 and 3, 2 connected to 3} \end{array} \right]^{m_3} \\
&= \frac{N!}{(1!)^{m_1} (2!)^{m_2} (3!)^{m_3}} \times \frac{1}{m_1! m_2! m_3! \dots} \times (1! V b_1)^{m_1} (2! \lambda^3 V b_2)^{m_2} (3! \lambda^6 V b_3)^{m_3} \dots \\
&= N! \prod_{l=1}^N \frac{(V \lambda^{3l-3} b_l)^{m_l}}{m_l!} \\
&= N! \lambda^{3N} \prod_{l=1}^N \frac{1}{m_l!} \left(\frac{V b_l}{\lambda^3} \right)^{m_l} \\
&= \sum_{\{m_l\}} N! \lambda^{3N} \prod_{l=1}^N \frac{1}{m_l!} \left(\frac{V b_l}{\lambda^3} \right)^{m_l}
\end{aligned}$$

$$Z_N(V, T) = \frac{1}{N!} \frac{1}{\lambda^{3N}} Q = \sum_{\{m_l\}} \prod_{l=1}^N \frac{1}{m_l!} \left(\frac{V}{\lambda^3} b_l \right)^{m_l}$$

若为巨正则

$$\begin{aligned}
Z_G(Z, V, T) &= \sum_{N=0}^{\infty} Z^N Z_N(V, T) \\
&= \sum_{N=0}^{\infty} Z^N \sum_{\{m_l\}} \prod_{l=1}^{\infty} \frac{1}{m_l!} \left(\frac{V}{\lambda^3} b_l \right)^{m_l} \\
&= \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \dots \left[\frac{1}{m_1!} \left(\frac{V}{\lambda^3} z^1 b_1 \right)^{m_1} \times \frac{1}{m_2!} \left(\frac{V}{\lambda^3} z^2 b_2 \right)^{m_2} \dots \right] \\
&= \prod_{l=1}^{\infty} \left(\sum_{m_l=0}^{\infty} \frac{1}{m_l!} \left(\frac{V}{\lambda^3} z^l b_l \right)^{m_l} \right) \\
&= \prod_{l=1}^{\infty} e^{b_l z^l \frac{V}{\lambda^3}}
\end{aligned}$$

$$= \exp\left(\sum_{l=1}^{\infty} b_l z^l \frac{V}{\lambda^3}\right)$$

$$\therefore \frac{1}{V} \ln Z_G = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l \quad d\Phi = -SdT - pdV - Nd\mu$$

$$\Phi = -k_B T \ln Z \quad p = -\frac{\partial \Phi}{\partial V} = -\frac{\partial}{\partial V} \ln Z$$

$$\therefore \frac{P}{kT} = -\frac{\partial}{\partial V} \ln Z_G = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} Z^l b_l$$

$$\therefore N = -\frac{\partial \Phi}{\partial \mu} \quad Z = e^{\beta \mu} \quad \frac{\partial Z}{\partial \mu} = Z \cdot \beta$$

$$\therefore \frac{N}{V} = -\frac{1}{V} \frac{\partial \Phi}{\partial \mu} = -\frac{1}{V} \frac{\partial \Phi}{\partial Z} \frac{\partial Z}{\partial \mu} = \frac{\beta Z}{V} \frac{\partial}{\partial Z} k_B T \ln Z_G = \frac{Z}{V} \frac{\partial}{\partial Z} \ln Z_G = \frac{Z}{V} \frac{\partial}{\partial Z} \frac{V}{\lambda^3} \sum_{l=1}^{\infty} Z^l b_l = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} l Z^l b_l$$

$$\Rightarrow \left\{ \begin{array}{l} \frac{p}{k_B T} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l Z^l \\ \frac{N}{V} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} l b_l Z^l \end{array} \right\} \quad \text{记 } \mathbf{v} = \frac{V}{N}$$

$$\Rightarrow \frac{p\mathbf{v}}{k_B T} = \sum_{l=1}^{\infty} a_l(T) \left(\frac{\lambda^3}{\mathbf{v}} \right)^{l-1} \Rightarrow \frac{p\mathbf{v}}{k_B T} = \sum a_l(T) \left(\sum_{n=0}^{\infty} n \bar{b}_n Z^n \right)^{l-1}$$

$$\text{联立} \left\{ \begin{array}{l} \frac{p\mathbf{v}}{k_B T} = \sum a_l(T) \left(\sum_{n=0}^{\infty} n \bar{b}_n Z^n \right)^{l-1} \\ \frac{p\mathbf{v}}{k_B T} = \frac{\sum_{l=1}^{\infty} \bar{b}_l Z^l}{\sum_{i=1}^{\infty} l \bar{b}_i Z^i} \end{array} \right\}$$

根据Z的次数相同匹配 a 与 \bar{b} 之间的关系

$$\begin{aligned} a_1 &= \bar{b}_1 = 1 \\ a_2 &= -\bar{b}_2 \\ a_3 &= 4\bar{b}_2^2 - 2\bar{b}_3 \\ \dots &\dots \dots \end{aligned}$$

$$\begin{aligned} \frac{p\mathbf{v}}{k_B T} &= 1 + a_2 \left(\frac{\lambda^3}{2} \right) = 1 - \bar{b}_2 \left(\frac{\lambda^3}{v} \right) = 1 - \frac{1}{2v} \int f_{12} d^3 r_{12} = 1 - \frac{2\pi}{v} \int_0^\infty f_{12} r^2 dr \\ &= 1 + \frac{b}{v} - \frac{a}{v k_B T} \end{aligned}$$

$$\Rightarrow \left[p + \left(\frac{N}{V} \right)^2 a \right] = N k_B T \left[\frac{1}{V} + \frac{N}{V^2} b \right] \Rightarrow \left[p + \left(\frac{N}{V} \right)^2 a \right] (V - Nb) \approx N k_B T$$

2023.11.21

2 Quantum statistics 量子统计

当粒子的尺度与波长相近时，考虑量子效应 ($\lambda = \frac{h}{p}$)

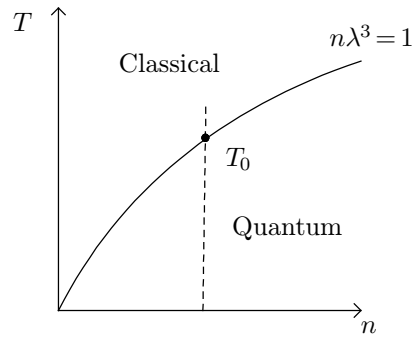
$$\frac{p^2}{2m} = \frac{3}{2} k_B T \text{ (能量均分原理)} \implies \lambda_0 = \frac{h}{\sqrt{3mk_B T}}$$

温度低 \rightarrow 动量小 \rightarrow 波长大 \rightarrow 波长与粒子的间距接近，量子效应不可忽略。

$$\text{热波长 } \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$n = \frac{N}{V} \quad n\lambda^3 \ll 1: \text{classical region} \quad \lambda^3 \text{ 是为了量纲统一}$$

$$n\lambda^3 \approx 1: \text{quantum region}$$



密度一定时，温度超过 T_0 则转变为经典情形

量子力学中考虑全同粒子 (Identical particles)

$$P\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_2, \vec{r}_1) = e^{i\theta}\Psi(\vec{r}_1, \vec{r}_2) \quad P^2 = I \quad [P, H] = 0$$

$$\begin{aligned} H(P\Psi) &= PH\Psi \\ &= PE\Psi \\ &= E(P\Psi) \end{aligned}$$

$$P = e^{i\theta} \quad \theta = 0 \text{ 时对应玻色子} \quad \theta = \pi \text{ 对应费米子} \quad \Psi(\vec{r}_1, \vec{r}_2) = \pm \Psi(\vec{r}_2, \vec{r}_1) \text{ (交换对称 / 反对称)}$$

$$\Psi(\vec{r}_1, \vec{r}_2) = f(\vec{r}_1)g(\vec{r}_2) \pm f(\vec{r}_2)g(\vec{r}_1)$$



当两个相离比较远的时候，玻色子和费米子近似为玻尔兹曼统计。

2.1 Occupation numbers 占据数表象

$$\int d^3r u_{\alpha}^*(\vec{r}) u_{\beta}(\vec{r}) = \delta_{\alpha\beta}$$

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \sum_P \delta_P P[u_{\alpha_1}(\vec{r}_1) \cdots u_{\alpha_N}(\vec{r}_N)]$$

$$\sum_{\alpha_1, \alpha_2, \dots} C(\alpha_1, \alpha_2, \dots) u_{\alpha_1}(\vec{r}_1) \cdots u_{\alpha_N}(\vec{r}_N)$$

$$\text{Fermions} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(\vec{r}_1) & u_1(\vec{r}_2) & \cdots & u_1(\vec{r}_N) \\ u_2(\vec{r}_1) & u_2(\vec{r}_2) & & u_2(\vec{r}_N) \\ \vdots & \vdots & & \vdots \\ u_N(\vec{r}_1) & u_N(\vec{r}_2) & \cdots & u_N(\vec{r}_N) \end{vmatrix}$$

slater行列式?

$$\text{每个态可以占据的粒子数 } n_{\alpha} = \begin{cases} 0, 1, 2, 3, \dots, \infty & \text{for bosons} \\ 0, 1 & \text{for fermions} \end{cases}$$

$|n_1, n_2, \dots, n_N\rangle$ 表示第一个态所有粒子数 n_1 , 第二个态所占据的粒子数 \dots , 第 n 个态 \dots , 这就是占据数表象。

$$\sum_{\alpha} n_{\alpha} = N$$

$$u_R(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$$

$$\sum_{\vec{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3k = \int \frac{d^3r d^3P}{h^3}$$

2.2 Incoherent Superposition of States

$$\Psi = \sum_n C_n(X, t) \psi_n$$

$$\|\Psi\|^2 \rightarrow \sum_{m,n} C_m^*(X, t) C_n(X, t) \psi_m^*(x) \psi_n(x) \quad C_n = r_n e^{i\phi_n}$$

$$C_m^*(X, t) C_n(X, t) \rightarrow e^{i(\phi_m - \phi_n)} r_m r_n$$

2.3 Density matrix 密度矩阵

pure state $\rightarrow |\psi\rangle$ 可以表示出来的态 $\hat{A}, \langle A \rangle_{\psi} = \langle \psi | \hat{A} | \psi \rangle = \text{Tr}(\rho \hat{A})$, $\rho = |\psi\rangle \langle \psi|$

$$A_{mn} = \langle \phi_m | \hat{A} | \phi_n \rangle, P_{mn} = \langle \phi_m | \psi \rangle \langle \psi | \phi_n \rangle$$

$$\begin{aligned} \text{Tr}(\rho \hat{A}) &= \sum_n \langle n | \psi \rangle \langle \psi | \hat{A} | n \rangle \\ &= \sum_n \langle \psi | \hat{A} | n \rangle \langle n | \psi \rangle \\ &= \langle \psi | \hat{A} | \psi \rangle \end{aligned}$$

$$\text{Tr} \rho = 1$$

$$\text{Tr} \rho^2 < 1$$

$$\rho^2 = |\psi\rangle \langle \psi| |\psi\rangle \langle \psi| = \rho$$

2023.12.1

量子统计 离散费米气体 与外界磁场的相互作用

2.4 纯态与混态

纯态:

$\rho = |\psi\rangle\langle\psi|$ $\langle\hat{A}\rangle_\psi = \langle\psi|\hat{A}|\psi\rangle = \text{Tr } \rho\hat{A}$ 纯态的特征: $\text{Tr } \rho^2 = 1$

$$\Leftrightarrow \sum_n \langle n|\psi\rangle\langle\psi|n\rangle = \sum_n |\psi\rangle\langle\psi|$$

系综的系统不处于纯态, 则为混态

混态 (Mixed state):

无法写出波函数, 但有混态的密度矩阵。

已知: $|\psi_1\rangle$ with propability $P_1, \dots, |\psi_i\rangle \dots P_i$ 其中, $\langle\psi_i|\psi_j\rangle = \delta_{ij}$; $P_1 + \dots + P_N = 1$ ψ_i 为纯态

混态的密度矩阵为: $\rho = \sum_i P_i |\psi_i\rangle\langle\psi_i|$

例如自旋 (上或下): $|\psi\rangle = \frac{|\uparrow\rangle + e^{i\theta}|\downarrow\rangle}{\sqrt{2}}$, 两个态的概率为50%, 但不知道态函数。

$$\text{密度矩阵} = \begin{pmatrix} \langle\uparrow|\rho|\uparrow\rangle & \langle\uparrow|\rho|\downarrow\rangle \\ \langle\downarrow|\rho|\uparrow\rangle & \langle\downarrow|\rho|\downarrow\rangle \end{pmatrix}, \text{其中 } \rho = \sum_i P_i |\psi_i\rangle\langle\psi_i| = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$$

混态中物理量的平均值计算 $\langle\hat{A}\rangle = \sum_i P_i \langle\psi_i|\hat{A}|\psi_i\rangle = \text{Tr } \rho\hat{A}$

$$\text{Tr } \rho\hat{A} = \sum_n \left\langle n \left| \sum_i P_i |\psi_i\rangle\langle\psi_i| \hat{A} \right| n \right\rangle = \sum_n \sum_i P_i \langle\psi_i|\hat{A}|n\rangle \langle n|\psi_i\rangle = \sum_i P_i \langle\psi_i|\hat{A}|\psi_i\rangle$$

注意到 $\text{Tr } \rho^2 < 1$, 以下进行证明: (ρ 为实数, $|\psi\rangle$ 为厄密共轭)

$$\rho^2 = \sum_i \sum_j P_i P_j |\psi_i\rangle\langle\psi_i|\psi_j\rangle\langle\psi_j|$$

$$\text{Tr } \rho^2 = \sum_n \sum_{i,j} P_i P_j \langle n|\psi_i\rangle\langle\psi_i|\psi_j\rangle\langle\psi_j|n\rangle = \sum_n \sum_{i,j} P_i P_j \langle\psi_i|\psi_j\rangle\langle\psi_j|n\rangle\langle n|\psi_i\rangle$$

$$\text{Tr } \rho^2 = \sum_{i,j} P_i P_j |\langle\psi_j|\psi_i\rangle|^2 = \sum_{i,j} P_i P_j |\langle\psi_j|\psi_i\rangle|^2 \leq \left(\sum_i P_i \right) \left(\sum_j P_j \right) = 1$$

定理. Liouville equation --Quantum Version

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle \quad -i\hbar \frac{\partial}{\partial t} \langle\psi(t)| = \langle\psi(t)| H$$

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \rho &= i\hbar \sum_i P_i \left(\frac{\partial |\psi_i\rangle}{\partial t} \langle\psi_i| + |\psi_i\rangle \frac{\partial \langle\psi_i|}{\partial t} \right) \\ &= \sum_i P_i (H |\psi_i\rangle \langle\psi_i| - |\psi_i\rangle \langle\psi_i| H) \\ &= [H, \rho] \end{aligned}$$

equilibrium state:

$$\frac{\partial}{\partial t} \rho = 0 \quad \Rightarrow [H, \rho] = 0 \quad \Rightarrow \rho = f(H)$$

2.5 Ensembles in Quantum statistical Mechanics.

Microcanonical (E, N, V 确定), all wavefunctions $|\psi_s\rangle, s = 1, 2, 3, \dots, \Omega$

$$\text{密度矩阵 } \rho = \sum_{s=1}^N \frac{1}{\Omega} |\psi_s\rangle \langle \psi_s|$$

Canonical (T, N, V 确定),

$$H |\psi_s\rangle = E_s |\psi_s\rangle$$

$$\text{经典 } \rho_s = \frac{e^{-\beta E_s}}{Z} \quad Z = \sum_s e^{-\beta E_s}$$

$$\hat{\rho} = \sum_s \frac{e^{-\beta E_s}}{Z} |\psi_s\rangle \langle \psi_s| = \sum_s \frac{1}{Z} e^{-\beta \hat{H}} |\psi_s\rangle \langle \psi_s| = \frac{1}{Z} e^{-\beta \hat{H}}$$

$$Z = \text{Tr } e^{-\beta \hat{H}}$$

Grand canonical (T, μ, V 确定)

$$\hat{\rho} = \sum_s \frac{1}{Z} e^{-\beta(E_s - \mu N_s)} |\psi_s\rangle \langle \psi_s| = \frac{1}{Z} e^{-\beta(\hat{H} - \mu \hat{N})}$$

$$Z = \text{Tr } e^{-\beta(\hat{H} - \mu \hat{N})}$$

定义. 冯诺依曼熵 Von Neumann entropy

$$S = -\text{Tr } (\rho \ln \rho)$$

$$\rho = \begin{pmatrix} P_1 & & 0 \\ & P_2 & \\ 0 & & \dots & \\ & & & P_N \end{pmatrix}$$

$$S = -\sum_s P_s \ln P_s$$

例. A free particle in a box

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

$$\phi_E(r) = \frac{1}{L^3} e^{i\vec{k} \cdot \vec{r}} \quad \vec{k} \equiv (k_x, k_y, k_z) = \frac{2\pi}{L} (n_x, n_y, n_z)$$

$\phi_E(\vec{r})$ 为根据边界条件的波函数, 而 $\phi_E(\vec{r}) = \langle E | r \rangle$, 中 E 为抽象的波函数,

内积表示抽象的波函数在坐标表象下的波函数。

$$\begin{aligned}
\langle \vec{r} | e^{-\beta \hat{H}} | \vec{r}' \rangle &= \left\langle \vec{r} \left| \sum_{E'} |E'\rangle \langle E'| e^{-\beta \hat{H}} \sum_E |E\rangle \langle E| \right| \vec{r}' \right\rangle = \sum_E \langle \vec{r} | \vec{E} \rangle e^{-\beta E} \langle \vec{E} | \vec{r}' \rangle \\
&= \sum_E e^{-\beta E} \phi_E(\vec{r}) \phi'_E(\vec{r}') \\
&= \frac{1}{L^3} \sum_k \exp \left[-\frac{\beta \hbar^2}{2m} k^2 + i \vec{k} \cdot (\vec{r} - \vec{r}') \right] \\
&= \frac{1}{(2\pi)^3} \int \exp \left[-\frac{\beta \hbar^2}{2m} k^2 + i \vec{k} \cdot (\vec{r} - \vec{r}') \right] d\vec{k} \\
&= \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \exp \left[-\frac{m}{2\beta\hbar^2} |\vec{r} - \vec{r}'|^2 \right] \\
&= \frac{1}{V} e^{-\frac{m}{2\beta\hbar^2} |\vec{r} - \vec{r}'|^2} \Leftrightarrow \text{高斯波包} \\
&\quad \text{波包的展宽类似于热波长 } \lambda
\end{aligned}$$

$$\text{Tr} (e^{-\beta \hat{H}}) = V \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} = \int \langle \vec{r} | e^{-\beta \hat{H}} | \vec{r} \rangle d^3r$$

2023.12.5

$$Z = V \left(\frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3}{2}}$$

$$\langle \hat{H} \rangle = \text{Tr} (\hat{H} \rho) = \text{Tr} (\rho \hat{H}) = \frac{\text{Tr} (\hat{H} e^{-\beta \hat{H}})}{\text{Tr} e^{-\beta \hat{H}}} = -\frac{\partial}{\partial \beta} \ln (\text{Tr} e^{-\beta \hat{H}}) = -\frac{\partial}{\partial \beta} \ln Z = -\frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T$$

例. 2.5.1 Vibrational modes 震动

$$Z = \int \frac{dp dq}{h} e^{-\beta \left(\frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2 \right)} = \frac{k_B T}{\hbar \omega} \quad \text{经典情况下}$$

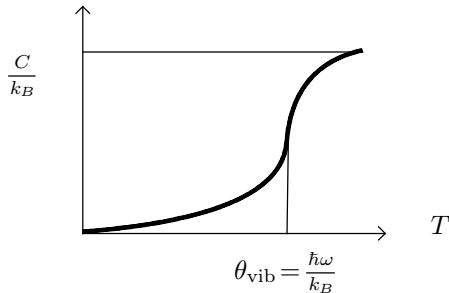
$$\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{\beta} = k_B T$$

$$\text{量子的情形下: } H = \hbar \omega \left(n + \frac{1}{2} \right) = \hbar \omega \left(a^+ a + \frac{1}{2} \right)$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega \left(n + \frac{1}{2} \right)} = \frac{e^{-\frac{1}{2} \beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \xrightarrow{T \rightarrow \infty} \frac{1}{\beta \hbar \omega} = \frac{k_B T}{\hbar \omega}$$

$$E = \langle H \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{\hbar \omega}{2} + \hbar \omega \frac{1}{1 - e^{-\beta \hbar \omega}}$$

$$C = \frac{\partial E}{\partial T} = k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{(1 - e^{\beta \hbar \omega})^2}$$



例. Rotational modes

$$\mathcal{L} = \frac{I}{2}(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) \quad P_\theta = \frac{\partial\mathcal{L}}{\partial\dot{\theta}} \quad P_\phi = \frac{\partial\mathcal{L}}{\partial\dot{\phi}} = I\sin^2\theta\dot{\phi}$$

$$H = \frac{1}{2I} \left(P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta} \right) = \frac{\vec{L}^2}{2I} \quad 1$$

$$Z = \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_{-\infty}^\infty dP_\theta \int_{-\infty}^\infty dP_\phi e^{-\beta H} = \frac{2Ik_B T}{h^2}$$

$$\langle H \rangle = k_B T$$

量子 Rotational modes

$$Z = \sum_{l=0}^{\infty} e^{-\frac{\beta \hbar^2 l(l+1)}{2I}} (2l+1) \quad \theta_{\text{rotational}} = \frac{\hbar^2}{2Ik_B}$$

$$\text{when } T \gg \theta_{\text{rot}}, T \rightarrow \infty \quad \lim_{T \rightarrow \infty} Z = \int_0^\infty dx (2x+1) e^{-\frac{\theta_{\text{rot}} x(x+1)}{T}} = \frac{T}{\theta_{\text{rot}}}$$

2.6 量子系综的应用

Microcanonical ensemble: ideal gas

$$N = n_1 + n_2 + \cdots = \sum_i n_i \quad \sum_i E_i n_i = E$$

Ferminous: n_i 个粒子, g_i 个态中, 每个态中只能有一个费米子

$$\omega_i = \binom{g_i}{n_i} = \frac{g_i!}{n_i!(g_i - n_i)!}$$

Bosons:

$$\omega_i = \binom{n_i + g_i - 1}{g_i} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

$$\Omega(E, V, N) = \begin{cases} \sum_{\{n_i\}} \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} & \text{fermions} \\ \sum_{\{n_i\}} \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} & \text{bosons} \end{cases}$$

In the limits $n_i/g_i \ll 1$, 能量相同的态很多, 对应温度较高, 态的个数远大于粒子个数。

$$\prod_i \frac{g_i!}{n_i!(g_i - n_i)!} = \prod_i \frac{g_i(g_i - 1) \cdots (g_i - n_i + 1)}{n_i!} \simeq \prod_i \frac{g_i^{n_i}}{n_i!}$$

$$\prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} = \prod_i \frac{(n_i + g_i - 1)(n_i + g_i - 2) \cdots g_i}{n_i!} = \prod_i \frac{g_i^{n_i}}{n_i!}$$

1. 补充: $\vec{L} = m\vec{r} \times \vec{v} = mr^2(\dot{\theta}\hat{\phi} - \dot{\phi}\sin\theta\hat{\theta}) \quad L = I\omega \quad E = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$

最概然分布

定义. $\sum_{\{n_i\}} \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} = \ln \mathcal{W}(\{n_i\})$

$$\delta \ln \mathcal{W}(\{n_i\}) - \left[\alpha \sum_i \delta n_i + \beta \sum_i E_i \delta n_i \right] = 0$$

$$\ln \mathcal{W}(\{n_i\}) \approx \left\{ \begin{array}{ll} \sum_i g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i) & \text{fermions} \\ \sum_i (n_i + g_i - 1) \ln (n_i + g_i - 1) - n_i \ln n_i - (g_i - 1) \ln (g_i - 1) & \text{bosons} \end{array} \right\}$$

$$\text{Fermions} \quad \sum_i [-\ln n_i + \ln (g_i - n_i) - \alpha - \beta E_i] \delta n_i = 0 \Rightarrow \frac{\bar{n}_i}{g_i} = \frac{1}{e^{\alpha + \beta E_i} + 1}$$

$$\text{bosons} \quad \sum_i [-\ln n_i + \ln (g_i + n_i) - \alpha - \beta E_i] \delta n_i = 0 \Rightarrow \frac{\bar{n}_i}{g_i} = \frac{1}{e^{\alpha + \beta E_i} - 1}$$

$$\text{Boltzmann} \quad \frac{\bar{n}_i}{g_i} = \frac{1}{e^{\alpha + \beta E_i}}$$

巨正则系综（理想气体）

$$\langle O \rangle = \text{Tr } \hat{\rho} \hat{O}$$

$$\text{密度算符 } \hat{\rho} = e^{\beta(\mu \hat{N} - \hat{H})}$$

$$Z = \text{Tr } e^{\beta(\mu \hat{N} - \hat{H})} = \sum_{\{\mu_s\}} e^{\beta(\mu \hat{N}_s - E_s)} = \sum_{N_s=0}^{\infty} (e^{\beta \mu})^{N_s} Z_{N_s} = \sum_{N=0}^{\infty} \sum'_{\{n_i\}} e^{\beta \sum_i (\mu - E_i) n_i}$$

$$\text{其中 } Z_{N_s} = \sum'_{\{n_i\}} e^{-\beta \sum_i n_i E_i}, \quad \sum_i n_i = N_s$$

$$Z = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \prod_i e^{\beta(\mu - E_i) n_i} = \prod_i^N \left[\sum_{n_i} e^{\beta(\mu - E_i) n_i} \right]$$

$$\left\{ \begin{array}{ll} \text{对于费米子} & n_i = 0/1 \quad Z = \prod_i^N [1 + e^{\beta(\mu - E_i)}] \\ \text{对于玻色子} & n_i = 0, 1, \dots \quad Z = \prod_i \frac{1}{1 - e^{\beta(\mu - E_i)}} \end{array} \right\} \Rightarrow Z = \prod_i (1 - \zeta e^{-\beta(E_i - \mu)})^{-\zeta}$$

其中, $\zeta = -1 \Leftrightarrow \text{fermions}$ $\zeta = +1 \Leftrightarrow \text{bosons}$

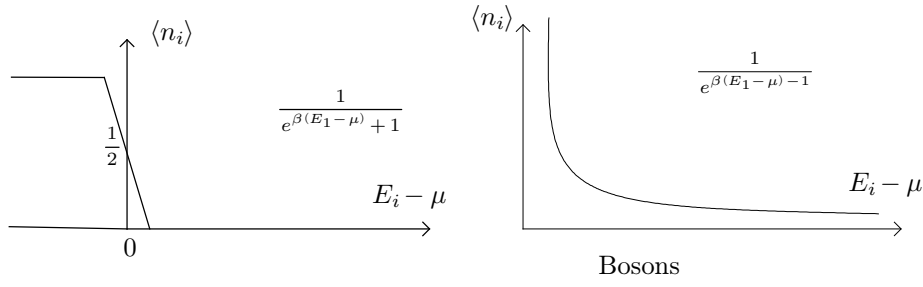
Occupation number 布居数

巨正则系综中的粒子数不确定，但可以计算平均值

$$\langle N \rangle = - \left(\frac{\partial \Phi}{\partial \mu} \right)_{V, T} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = \sum_i \frac{e^{-\beta(E_i - \mu)}}{1 - \zeta e^{-\beta(E_i - \mu)}} = \sum_i \frac{1}{e^{\beta(E_i - \mu)} - \zeta} \quad (\text{考试})$$

在高温极限下，均退化为经典分布

$$\langle E \rangle = \sum_i \langle n_i \rangle E_i = \sum_i \frac{E_i}{e^{\beta(E_i - \mu)} - \zeta} \quad \langle E \rangle - \mu \langle N \rangle = - \frac{\partial}{\partial \mu} \ln Z$$



$$\sum_{\vec{k}} \rightarrow V \int \frac{d^3k}{(2\pi)^3} = \frac{V}{h^3} \int d^3p = \frac{1}{h^3} \int d^3p d^3q$$

$$\ln Z = -\zeta \sum_i \ln \left(1 - \zeta e^{\beta \left(\mu - \frac{\hbar^2 k^2}{2m} \right)} \right)$$

因为 $p = - \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu}$

$$\frac{p}{k_B T} = \frac{\ln Z}{V} = -\zeta \int \frac{d^3k}{(2\pi)^3} \ln \left(1 - \zeta e^{\beta \left(\mu - \frac{\hbar^2 k^2}{2m} \right)} \right)$$

$$\frac{N}{V} = g \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta \left(\frac{\hbar^2 k^2}{2m} - \mu \right)} - \zeta} \quad 2$$

$$\frac{E}{V} = g \int \frac{d^3k}{(2\pi)^3} \frac{\hbar^2 k^2 / 2m}{e^{\beta \left(\frac{\hbar^2 k^2}{2m} - \mu \right)} - \zeta}$$

$$x = \beta \hbar^2 k^2 / 2m \Rightarrow k = \frac{\sqrt{2m k_B T}}{\hbar} \sqrt{x} = \frac{2\sqrt{\pi x}}{\lambda} \quad dk = \frac{\sqrt{\pi}}{\lambda} \frac{dx}{x}$$

$$\begin{aligned} \frac{p}{k_B T} &= -\zeta g \int \frac{d^3k}{(2\pi)^3} \ln \left(1 - \zeta e^{\beta \left(\mu - \frac{\hbar^2 k^2}{2m} \right)} \right) \\ &= -\zeta \frac{g}{(2\pi)^3} \int \frac{\sqrt{\pi}}{\lambda} \frac{dx}{\sqrt{x}} \frac{4\pi x}{\lambda^2} (4\pi) \ln(1 - \zeta z e^{-x}) \\ &= \frac{4g}{3\sqrt{\pi}} \frac{2}{\lambda^3} \int_0^\infty dx x^{\frac{1}{2}} \ln(1 - \zeta z e^{-x}) \\ &= \frac{4g}{3\sqrt{\pi}} \frac{1}{\lambda^3} \int_0^\infty dx \frac{x^{\frac{3}{2}} z e^{-x}}{1 - \zeta z e^{-x}} \\ &= \frac{4g}{3\sqrt{\pi}} \frac{1}{\lambda^3} \int_0^\infty dx \frac{x^{\frac{3}{2}}}{z^{-1} e^x - \zeta} \end{aligned}$$

分别代回 $\frac{N}{V}$, $\frac{E}{V}$

$$\frac{N}{V} = \frac{2g}{\sqrt{\pi}} \frac{1}{\lambda^3} \int_0^\infty dx \frac{x^{\frac{1}{2}}}{z^{-1} e^x - \zeta}$$

$$\frac{E}{V} = \frac{2g}{\sqrt{\pi}} \frac{1}{\lambda^3} \int_0^\infty dx \frac{x^{\frac{3}{2}}}{z^{-1} e^x - \zeta}$$

2. $g = 2s + 1$ (好像是简并度), λ 为热波长 $\lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}}$

$$g_v(z) = \frac{1}{\Gamma(v)} \int_0^\infty dx \frac{x^{v-1}}{z^{-1}e^x - 1} \quad f_v = \frac{1}{\Gamma(v)} \int_0^\infty dx \frac{x^{v-1}}{z^{-1}e^x + 1}$$

$$\frac{p}{k_B T} = \left\{ \begin{array}{l} \frac{g}{\lambda^3} g_{\frac{5}{2}}(z) \\ \frac{g}{\lambda^3} f_{\frac{5}{2}}(z) \end{array} \right\} \quad \frac{N}{V} = \left\{ \begin{array}{l} \frac{g}{\lambda^3} g_{\frac{3}{2}}(z) \\ \frac{g}{\lambda^3} f_{\frac{3}{2}}(z) \end{array} \right\} \quad \frac{E}{k_B T V} = \left\{ \begin{array}{ll} \frac{3}{2} \frac{g}{\lambda^3} g_{\frac{5}{2}}(z) & \text{bosons} \\ \frac{3}{2} \frac{g}{\lambda^3} f_{\frac{5}{2}}(z) & \text{fermions} \end{array} \right\} \Rightarrow E = \frac{3}{2} p V \quad (1)$$

重点背记。

Classical limit : j

$$\left\{ \begin{array}{l} g_v(z) \\ f_v(z) \end{array} \right\} \Rightarrow \frac{1}{\Gamma(v)} \int_0^\infty dx x^{v-1} e^{-x} z \sum_{k'=0}^\infty (\pm 1)^{k'} e^{-x k'} z^{k'} = \sum_{k=1}^\infty \frac{(\pm 1)^{k+1} z^k}{k^v}$$

$$\frac{N}{V} = \frac{g}{\lambda^3} \left(z + \zeta \frac{z^2}{2^{\frac{3}{2}}} + O(z^3) \right) \Rightarrow z + \zeta \frac{z^2}{2^{\frac{3}{2}}} + O(z^3) = \frac{\lambda^3 N}{g V} \equiv \epsilon$$

而我们既可以将 z 的不同次方展开，还可以反向按照 ϵ 的不同次方展开。assume $z = \epsilon + A_1 \epsilon^2 + \dots$

$$\epsilon + A_1 \epsilon^2 + \zeta \frac{\epsilon^2}{2^{\frac{3}{2}}} + \dots = \epsilon \Rightarrow A_1 = -\zeta \frac{1}{2^{\frac{3}{2}}} \Rightarrow z = \frac{\lambda^3 N}{g V} - \zeta \frac{1}{2^{\frac{3}{2}}} \left(\frac{\lambda^3 N}{g V} \right)^2$$

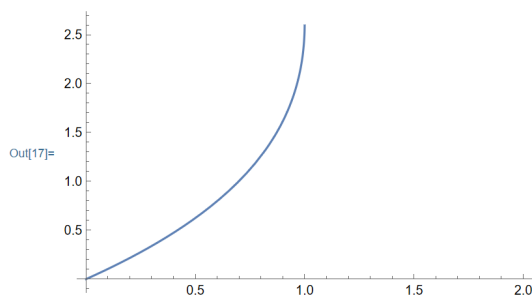
$$\begin{aligned} \frac{p}{k_B T} &= \frac{g}{\lambda^3} \left(z + 3 \frac{z^2}{2^{\frac{5}{2}}} + \dots \right) \\ &= \frac{g}{\lambda^3} \left[\frac{\lambda^3 N}{g V} - \zeta \frac{1}{2^{\frac{3}{2}}} \left(\frac{\lambda^3 N}{g V} \right) + \zeta \frac{1}{2^{\frac{5}{2}}} \left(\frac{\lambda^3 N}{g V} \right)^2 + \dots \right] \\ \Rightarrow p V &= N k_B T \left[1 - \zeta \frac{1}{2^{\frac{5}{2}}} \left(\frac{N \lambda^3}{V g} \right) + \dots \right] \end{aligned}$$

多对数函数：

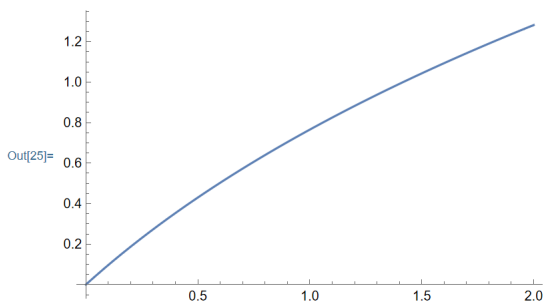
$$g_v(z) = \frac{1}{\Gamma(v)} \int_0^\infty dx \frac{x^{v-1}}{z^{-1}e^x - 1} \equiv \text{PolyLog}[v, z]$$

$$f_v = \frac{1}{\Gamma(v)} \int_0^\infty dx \frac{x^{v-1}}{z^{-1}e^x + 1} = -\text{PolyLog}[v, -z]$$

In[17]:= `Plot[PolyLog[3/2, z], {z, 0, 2}]`
[绘图] [多对数函数]



In[25]:= `Plot[-PolyLog[3/2, -z], {z, 0, 2}]`
[绘图] [多对数函数]



Ground states $T=0$,对于量子力学而言，电子全部处于基态。 $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$

$$\frac{1}{e^{\beta(E_i - \mu)} + 1} \xrightarrow{\beta \rightarrow \infty} \begin{cases} 1 & \text{if } E_i < \mu \equiv E_F \\ 0 & \text{if } E_i > \mu \equiv E_F \end{cases}$$

$$E_F = \frac{p_F^2}{2m} \quad p_F = \hbar k_F$$

$$\begin{aligned} N &= g \sum_{p \leq p_F} 1 \\ &= g \frac{V}{(2\pi\hbar)^3} \int d^3p \delta(p_F - p) \\ &= \frac{g V p_F^2}{6\pi^2 \hbar^3} \end{aligned}$$

$$p_F = \hbar \left(\frac{6\pi^2}{g} \frac{N}{V} \right)^{\frac{1}{3}} \quad E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{g} \frac{N}{V} \right)^{\frac{2}{3}}$$

Ground-state energy

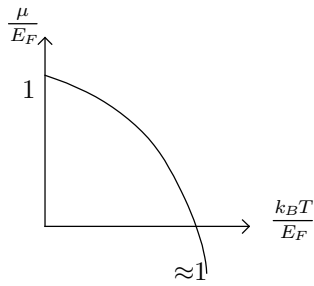
$$E = \frac{gV}{6\pi^2 \hbar^3} \int d^3p \frac{p^2}{2m} \delta(p_F - p) = \frac{g V p_F^5}{20\pi^2 \hbar^3 m}$$

$$\text{费米简并压} \quad p = \frac{2}{3} \frac{E}{V} = \frac{g V p_F^5}{30\pi^2 \hbar^3 m} = \frac{2}{5} \frac{N}{V} E_F \neq 0 = \frac{\hbar^2}{5m} \left(\frac{6\pi^2}{g} \right)^{\frac{2}{3}} \left(\frac{N}{V} \right)^{\frac{5}{3}}$$

$$\text{费米温度: } T_F = \frac{E_F}{k_B} \quad \text{当温度远小于费米温度时，可以等效为0K}$$

温度较低但不为0时。

The limit of complete degeneracy, $Z \gg 1$



$$\begin{aligned} f_\nu(z) &= \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^x + 1} \\ x = \xi + \ln Z &\implies \frac{1}{\Gamma(\nu)} \int_{-\ln Z}^\infty d\xi \frac{(\xi + \ln Z)^{\nu-1}}{e^\xi + 1} \\ &= \frac{1}{\Gamma(\nu)} \int_{-\ln Z}^\infty \frac{1}{\nu} \frac{d}{d\nu} (\xi + \ln Z)^\nu \frac{1}{e^\xi + 1} \\ &= \frac{1}{\Gamma(\nu+1)} \int_{-\infty}^\infty \left(1 + \frac{\xi}{\ln Z}\right)^\nu \frac{e^\xi}{(e^\xi + 1)^2} d\xi \end{aligned}$$

$$f_\nu(z) = \frac{(\ln Z)^\nu}{\Gamma(\nu+1)} \int_{-\infty}^{\infty} \left(\underset{A}{1} + \frac{v\xi}{\underset{B}{\ln Z}} + \frac{\nu(\nu-1)\xi^2}{\underset{C}{2(\ln z)^2}} + \dots \right) \frac{e^\xi}{(e^\xi+1)^2} d\xi$$

$$A = \frac{(\ln Z)^\nu}{\Gamma(\nu+1)} \int_{-\infty}^{\infty} \frac{e^\xi}{(e^\xi+1)^2} d\xi = \frac{(\ln z)^\nu}{\Gamma(\nu+1)} \times 1$$

B 部分奇函数积分, 为0

$$C = \int_{-\infty}^{\infty} \frac{\nu(\nu-1)\xi^2}{2(\ln z)^2} \times \frac{e^\xi}{(e^\xi+1)^2} d\xi = \frac{\nu(\nu-1)}{2(\ln z)^2} \zeta(2) = \frac{\pi^2}{3} \frac{\nu(\nu-1)}{2(\ln z)^2}$$

其中, $\zeta(n)$ 为Riemann zeta function, 上式中使用 $\zeta(2)$ 存疑, 因为mathematica中的四个函数似乎都不是这个函数, 没有 $\zeta(2) = \frac{\pi^2}{6}$ 的。但对于加粗部分积分, 确实是 $\frac{\pi^2}{3}$

$$f_\nu(z) \approx \frac{(\ln z)^\nu}{\Gamma(\nu+1)} \left[1 + \frac{\pi^2}{3} \frac{\nu(\nu-1)}{2(\ln z)^2} + \dots \right]$$

$$\begin{aligned} \frac{N}{V} &= \frac{g}{\lambda^3} \frac{(\ln Z)^{\frac{3}{2}}}{\Gamma\left(\frac{5}{2}\right)} \left[1 + \frac{\pi^2}{3} \frac{3}{8(\ln Z)^2} + \dots \right] \\ \frac{\lambda^3}{g} \frac{N}{V} \Gamma\left(\frac{5}{2}\right) &= (\ln Z)^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8(\ln Z)^2} + \dots \right] \end{aligned}$$

而 $Z = e^{\beta\mu}$

$$\text{仅仅取第一项 } (\beta\mu)^{\frac{3}{2}} = \frac{3}{4} \sqrt{\pi} \frac{N}{gV} \left(\frac{h}{\sqrt{2\pi m k_B T}} \right)^3 = \frac{N}{gV} \frac{3h^2 \beta^{\frac{3}{2}}}{(2m)^{\frac{3}{2}} 4\pi}$$

$$\Rightarrow \mu = \frac{\hbar^2}{2m} \left(\frac{6\pi}{g} \frac{N}{V} \right)^{\frac{2}{3}} = E_F$$

$$\text{取到第二项乃至以后: } (E_F)^{\frac{3}{2}} = \mu^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \dots \right]$$

2.7 Ideal fermi gas

huang 14 16

$$\frac{p}{k_B T} = \frac{g}{\lambda^3} f_{\frac{5}{2}}(z) \quad \frac{N}{V} = \frac{g}{\lambda^3} f_{\frac{3}{2}}(z) \quad \frac{E}{k_B T V} = \frac{3}{2} \frac{g}{\lambda^3} f_{\frac{5}{2}}(z)$$

$$E = \frac{3}{2} p V$$

$$1. \quad \frac{N}{V} \approx \frac{g}{\lambda^3} \frac{(\ln Z)^{\frac{3}{2}}}{\Gamma\left(\frac{5}{2}\right)} \left[1 + \frac{\pi^2}{8} \frac{1}{(\ln Z)^2} \right]$$

$$2. \quad E_F = \mu \left[1 + \frac{2}{3} \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right] \quad \mu = E_F \left(1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right)$$

$$3. \quad \frac{E}{k_B T V} = \frac{3}{2} \frac{g}{\lambda^3} \frac{(\ln Z)^{\frac{5}{2}}}{\Gamma\left(\frac{7}{2}\right)} \left[1 + \frac{\pi^3}{3} \frac{15}{8(\ln Z)^2} + \dots \right]$$

$$\Rightarrow \frac{E}{V} = \frac{3}{5} \frac{N}{V} E_F \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{E_F} \right) + \dots \right]$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \approx N k_B \frac{\pi^2}{2} \frac{T}{T_F}$$

4. Gibbs - Duhe, relations

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$$

$$\frac{\partial E}{\partial \lambda S} S + \frac{\partial E}{\partial \lambda V} V + \frac{\partial E}{\partial \lambda N} N \Big|_{\lambda=1} = E$$

$$dE = \left(\frac{\partial E}{\partial S} \right)_{V,N} dS + \left(\frac{\partial E}{\partial V} \right)_{S,N} dV + \left(\frac{\partial E}{\partial N} \right)_{S,V} dN$$

$$E = TS - pV + \mu N$$

$$S = \frac{1}{T} (E + pV - \mu N) = k_B N \frac{\pi^2}{2} \frac{T}{T_F} \text{ (和 } C_V \text{ 相等)}$$

2.7.1 朗道铁磁相变理论

$$H = \frac{(\vec{p} - e \vec{A})^2}{2m} \text{ Landau diamagnetism}$$

$$H = \frac{p^2}{2m} - \mu_0 \vec{\sigma} \cdot \vec{B}$$

$$Z_n = \sum_{\{n_p^+, n_p^-\}} \exp(-\beta E_n)$$

$$\text{Pauli paramagnetism } E_n = \sum_p (\varepsilon_{p,+1} n_{p,+1} - \varepsilon_{p,-1} n_{p,-1}) \quad \varepsilon_{p,\pm 1} = \frac{p^2}{2m} \mp \mu_0 B$$

$$\text{记 } \sum_p n_p^+ = N_+, \quad \sum_p n_p^- = N_-, \quad N_- + N_+ = N$$

$$\begin{aligned} Z_n &= \sum_{N_+=0}^N e^{\beta \mu_0 B (2N_+ - N)} \sum_{\{n_p^+\}} e^{-\beta \sum_p \frac{p^2}{2m} n_p^+} \sum_{\{n_p^-\}} e^{-\beta \sum_p \frac{p^2}{2m} n_p^-} \\ &= e^{-\beta \mu_0 B N} \sum_{N_+=0}^N e^{2\beta \mu_0 B N_+} Z_{N_+}^{(0)} Z_{N-N_+}^{(0)} \end{aligned}$$

为了去 \sum , 我们可以选择取极大分布的情况代替所有情况求和。

$$Z_N^{(0)} = \sum_{\sum_p n_p = N} e^{-\beta \sum_p \frac{p^2}{2m} n_p} \equiv e^{-\beta F(N)}$$

$$\Rightarrow \frac{1}{N} \ln Z_N = -\beta \mu_0 B + \frac{1}{N} \ln \sum_{N_+=0}^N e^{2\beta \mu_0 B N_+ - \beta F(N_+) - \beta F(N-N_+)}$$

$$\frac{1}{N} \ln Z_N = \beta f(\bar{N}_+) + O\left(\frac{1}{N} \ln N\right)$$

$$f(\bar{N}_+) = \max_{N_+} [f(N_+)]$$

$$f(N_+) = \mu_0 B \left(\frac{2N_+}{N} - 1 \right) - \frac{1}{N} [F(N_+) - F(N - N_+)]$$

为了得到最概然的分布情况，我们需要取 $f(N_+)$ 的最大值。

$$\begin{aligned}\frac{\partial f(N_+)}{\partial N_+} \Big|_{N_+=\bar{N}_+} &= 0 \Rightarrow 2\mu_0 B - \left[\frac{\partial F(N')}{\partial N'} \right]_{N'=\bar{N}_+} - \left[\frac{\partial F(N-N')}{\partial N'} \right]_{N'=\bar{N}_+} = 0 \\ &\Rightarrow \mu^{(0)}(\bar{N}_+) - \mu^{(0)}(N - \bar{N}_+) = 2\mu_0 B \\ &\Rightarrow \mu^{(0)}\left(\frac{1+r}{2}N\right) - \mu^{(0)}\left(\frac{1-r}{2}N\right) = 2\mu_0 B\end{aligned}$$

$$\text{磁化强度 } M = \mu_0(\bar{N}_+ - \bar{N}_-) = \mu_0 N r, \quad r = \frac{2\bar{N}_+}{N} - 1 = \frac{\bar{N}_+ - \bar{N}_-}{N}.$$

$B=0$ 时, r 也应该很小。当 r 很小时, r 可以近似为

$$\begin{aligned}r &\simeq \frac{2\mu_0 B}{\left(\frac{\partial \mu^{(0)}(x_N)}{\partial x}\right)_{x=\frac{1}{2}}} \\ x &= \frac{1}{V} \frac{\partial M}{\partial B} = \frac{2\mu_0^2 N/V}{\left(\frac{\partial \mu^{(0)}(x_N)}{\partial x}\right)_{x=\frac{1}{2}}}\end{aligned}$$

For $T \rightarrow 0$

$$\mu^{(0)}(xN) \Big|_{x=\frac{1}{2}} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{g} \frac{xN}{V} \right)$$

$$\Rightarrow \frac{\partial \mu^{(0)}}{\partial x} \Big|_{xN} = \frac{2^{\frac{4}{3}}}{3} \left(\frac{3N}{4\pi V} \right)^{\frac{2}{3}} \frac{\hbar^2}{2m}$$

$$E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{2} \frac{N}{V} \right)^{\frac{2}{3}}$$

$$\Rightarrow {}^{(1)}x \Big|_{T \rightarrow 0} \equiv x_0 = \frac{3\mu_0^2 N}{2E_F V}$$

$${}^{(2)}x = x_0 \left(1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 + \dots \right)$$

$$\mu = E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 + \dots \right], \quad \frac{\partial \mu(xN)}{\partial x} = \frac{\partial E_F(xN)}{\partial x} + \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \frac{\partial E_F(xN)}{\partial x}$$

For $T \rightarrow \infty$

$$\frac{N}{V} = \frac{g}{\lambda^3} f_{\frac{3}{2}}(z) = \frac{g}{\lambda^3} \left(z - \frac{z^2}{2^{3/2}} + \dots \right) \Rightarrow z = \frac{\lambda^3 N}{g V} + \frac{1}{2^{3/2}} \left(\frac{\lambda^3 N}{g V} \right) + \dots$$

$$\Rightarrow \mu^{(0)}(N) \simeq k_B T \ln \left(\frac{N \lambda^3}{V} \right) \Rightarrow x_\infty = \frac{\mu_0^2 N/V}{k_B T} \quad (1)$$

$$x = x_\infty \left(1 - \frac{\lambda^3 N/V}{2^{5/2}} \right)$$

$$\frac{\partial \mu^{(0)}}{\partial x} \Big|_{x=\frac{1}{2}} = 2k_B T$$

2.8 理想玻色系统

2.8.1 光子

photons 光子 $\left(n + \frac{1}{2}\right) \hbar \omega$ $\hbar \omega = h\nu = \hbar c k = \hbar c \frac{2\pi}{\lambda} = \frac{hc}{\lambda}$

$$H = \frac{1}{2} \sum_{\vec{k}, \alpha} \left[|\tilde{p}_{\vec{k}, \alpha}|^2 + \omega_{\alpha}^2(\vec{k}) |\tilde{u}_{\alpha}(\vec{k})|^2 \right]$$

$$H^q = \sum_{\vec{k}, \alpha} \hbar c k \left(n_{\alpha}(\vec{k}) + \frac{1}{2} \right)$$

Energy $\hbar \omega$. Momentum $\hbar \vec{k}$. Potential vector $\vec{\epsilon}$, $|\vec{\epsilon}| = 1$, $\vec{k} \cdot \vec{\epsilon} = 0$

$$Z = \sum_{\{n_{\alpha}(\vec{k})\}} e^{-\beta H_q} = \sum_{\{n_{\alpha}(\vec{k})\}} \prod_{k, \alpha} e^{\left[-\beta \hbar \omega(\vec{k}) \left(n_{\alpha}(\vec{k}) + \frac{1}{2} \right) \right]} = \prod_{\vec{k}, \alpha} \frac{e^{-\beta \hbar c k / 2}}{1 - e^{-\beta \hbar c k}}$$

$$Z = \prod_{\vec{k}, \alpha} \left[\frac{1}{1 - e^{-\beta \hbar c k}} \right] \text{ (不考虑零点能)}$$

$$\langle n_{\alpha}(k) \rangle = -\frac{1}{\beta} \frac{\partial}{\partial (\hbar \omega)} \ln Z = \frac{1}{e^{\beta \hbar \omega} - 1}$$

$$E = \langle H^q \rangle = \sum_{\vec{k}, \alpha} \hbar c k \left(\frac{e^{-\beta \hbar c k}}{1 - e^{-\beta \hbar c k}} + \frac{1}{2} \right)$$

$$\langle H^q \rangle = -\frac{\partial}{\partial \beta} \ln Z = V E_0 + \frac{2V}{(2\pi)^3} \int d^3 \vec{k} \frac{\hbar c k}{e^{\beta \hbar c k} - 1}$$

$$F = -k_B T \ln Z, p = -\frac{\partial F}{\partial V} = p_0 + \frac{1}{3} \frac{E}{V}$$

2023.12.29

能量流密度(黑体辐射):

$$\phi = \langle c_{\perp} \rangle \frac{E}{V}$$

φ : escaping energy flux per unit area and per unit time

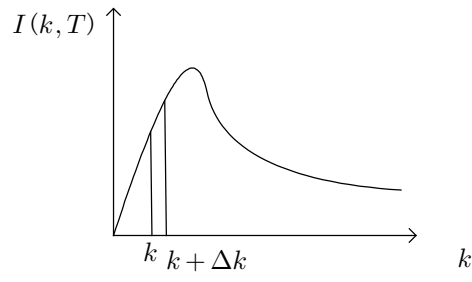
$$\langle c_{\perp} \rangle = c \times \frac{1}{4\pi} \int_0^{\frac{\pi}{2}} 2\pi \sin \theta d\theta \cdot \cos \theta = \frac{c}{4}$$

$$\begin{aligned} \phi &= \frac{cE}{4V} \\ &= \frac{1}{4} c \cdot \frac{1}{V} \frac{\pi^2}{15} V \left(\frac{k_B T}{\hbar c} \right)^3 k_B T = \frac{\pi^2 k_B^4 T^4}{60 \hbar^3 c^2} = \sigma T^4 \end{aligned}$$

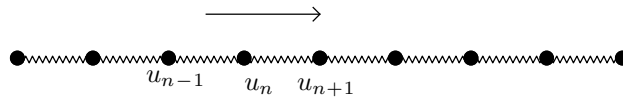
$$\frac{E}{V} = \int dk \varepsilon(k, T)$$

$$\varepsilon(k, T) = \frac{\hbar c}{\pi^2} \frac{k^3}{e^{\beta \hbar \omega} - 1}$$

$$I(k, T) = \frac{c}{4} \varepsilon(k, T) \text{ 表示 } k \sim k + \Delta k \text{ 之间的能量流}$$



2.8.2 Phonon.声子



$$C(u_{n+1} - u_n) - C(u_n - u_{n-1}) = m \frac{d^2 u_n}{dt^2}$$

$$\text{形式解 } u_n = \sum_k Q_k e^{ikna}$$

$$2C(\cos(ka) - 1)Q_k = m \frac{d^2 Q_k}{dt^2}$$

$$Q_k = A_k e^{i\omega_k t}$$

$$\omega_k = \sqrt{\frac{2C}{m}(1 - \cos ka)} = \sqrt{\frac{4C}{m}} \left| \sin \frac{ka}{2} \right|$$

Quantum version

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 \sum_{i=j+1}^N (x_i - x_j)^2$$

这里使用 $\sum_{i=j+1}$ 是为了保证 i, j 相邻且不计算两边。

定义

$$Q_k = \frac{1}{\sqrt{N}} \sum_l e^{ikal} x_l, \quad \Pi_k = \frac{1}{\sqrt{N}} \sum_l e^{-ikal} p_l$$

$$[x_l, p_m] = i\hbar \delta_{l,m} \Rightarrow \left[Q_k, \Pi_{k'} \right] = i\hbar \delta_{k,k'}$$

$$[Q_k, Q_{k'}] = [\Pi_k, \Pi_{k'}] = 0$$

$$\sum_l x_l, x_{l+m} = \sum_k Q_k Q_{-k} e^{iamk}, \quad \sum_l p_l^2 = \sum_k \Pi_k \Pi_{k'}$$

$$\frac{1}{2} m \omega^2 \sum_j (x_j - x_{j+1})^2 = \frac{1}{2} m \omega^2 \sum_k Q_k Q_{-k} (2 - e^{ika} - e^{-ika}) = \frac{1}{2} \sum_k m \omega_k^2 Q_k Q_{-k}$$

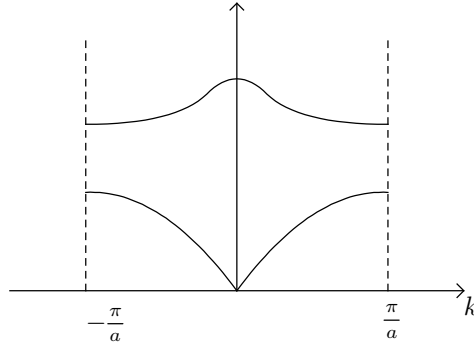
$$\omega_k = \sqrt{2\omega^2(1 - \cos ka)} = 2\omega \left| \sin \frac{ka}{2} \right|$$

$$H = \frac{1}{2m} \sum_k (\Pi_k \Pi_{-k} + m^2 \omega_k^2 Q_k Q_{-k})$$

$$b_k = \sqrt{\frac{m\omega}{2\hbar}} \left(Q_k + \frac{i}{m\omega_k} \Pi_k \right) \quad [b_k, b_{k'}^+] = \delta_{k,k'} \quad [b_k, b_{k'}] = [b_k^+, b_{k'}^+] = 0$$

$$Q_k = \sqrt{\frac{\hbar}{2m\omega_k}} (b_k^+ + b_{-k}) \quad \Pi_k = i\sqrt{\frac{\hbar m \omega_k}{2}} (b_k^+ - b_{-k})$$

$$\Rightarrow H = \sum_k \hbar \omega_k \left(b_k^+ b_k + \frac{1}{2} \right)$$



$$\omega(\vec{k}) = ck$$

Einstein model: all oscillators are assumed to have the same frequency ω_E

震荡的频率全相同

$$\text{total Energy} \quad E = 3N \frac{\hbar \omega_E}{e^{\beta \hbar \omega} - 1}$$

$$C_v = \frac{dE}{dT} = 3N K_B \left(\frac{T_E}{T} \right)^2 \frac{e^{-T_E/T}}{(1 - e^{-T_E/T})^2}$$

高温情况下: $C_v = 3N K_B$

Debye model:

$$\omega(\vec{k}) = ck$$

$$f(\omega) d\omega = \frac{3V}{(2\pi)^3} 4\pi k^2 dk, \quad 3 \text{ 是指三种震动模式。} \quad f(\omega) = \frac{1}{c} \frac{3V}{(2\pi^2)} k^2$$

$[\omega, \omega + d\omega]$ 之间的频率可以与 $[k, k + dk]$ 范围内的频率

对于含有 N 个粒子的系统，最多只有 $3N$ 个震动模式。

$$\int_0^{\omega_m} f(\omega) d\omega = 3N \quad \text{截断条件} \quad (\omega \text{ 为截止频率})$$

$$\Rightarrow \omega_m = c \left(\frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} = ck_m \text{---Debye 频率, } \lambda_m = \frac{2\pi c}{\omega_m} = \left(\frac{4\pi}{3} \frac{V}{N} \right)^{\frac{1}{3}}$$

$$E(\{n_i\}) = \sum_{i=1}^{3N} \hbar\omega_i \cdot n_i, \quad Z = \sum_{\{n_i\}} e^{-\beta E(\{n_i\})} = \prod_{i=1}^{3N} \frac{1}{1 - e^{-\beta\hbar\omega_i}}$$

$$\Rightarrow \langle n_i \rangle = -\frac{1}{\beta} \frac{\partial}{\partial (\hbar\omega_i)} \ln Z = \frac{1}{e^{\beta\hbar\omega} - 1}$$

$$E = -\frac{\partial}{\partial \beta} \ln Z = \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1} = \frac{3V}{2\pi^2 c^3} \int_0^{\omega_m} \omega^2 \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

$$\frac{E}{N} = \frac{9(k_B T)^4}{(\hbar\omega)^3} \int_0^{\beta\hbar\omega_m} dt \frac{t^3}{e^t - 1}$$

Debye function

$$D \equiv \frac{3}{x^3} \int_0^x dt \frac{t^3}{e^t - 1} = \begin{cases} 1 - \frac{3}{8}x + \frac{1}{20}x^2 + \dots & x \ll 1 \\ \frac{\pi^4}{15x^3} + O(e^{-x}) & x \gg 1 \end{cases}$$

$$\Rightarrow \frac{E}{N} = 3k_B T D(\lambda) = \begin{cases} 3k_B T \left(1 - \frac{3}{8} \frac{T_D}{T} \right) & T \gg T_D \\ 3k_B T \left[\frac{\pi^4}{15} \left(\frac{T}{T_D} \right)^3 + \dots \right] & T \ll T_D \end{cases}$$

$$\frac{C_V}{Nk_B} = 3D(\lambda) + 3T \frac{dD(\lambda)}{dT} = \begin{cases} 3 \left[1 - \frac{1}{20} \left(\frac{T_D}{T} \right)^2 + \dots \right] & T \gg T_D \\ \frac{12\pi^4}{15} \left(\frac{T}{T_D} \right)^3 + \dots & T \ll T_D \end{cases}$$

2.8.3 玻色-爱因斯坦凝聚

Bose - Einstein Condensation 是一种宏观量子效应

色散关系不同导致 $f(\omega) d\omega = \frac{3V}{(2\pi)^3} 4\pi k^2 dk$ 对应的转换关系也不同 ($\frac{d\omega}{dk}$ 不同)。

以下讨论的是理想玻色气体 (不考虑粒子间的相互作用)

每种模式的平均粒子数为 $\frac{1}{e^{\beta(E_i - \mu)} - 1}$ (粒子数一定要大于零, 因此 E_i 一定大于等于 μ , for any i), $\Rightarrow \mu \leq 0$ ($\mu \leq 0$ 是从这里为了满足自洽引入的)。而 $0 \leq z = e^{\beta\mu} \leq 1$ 。

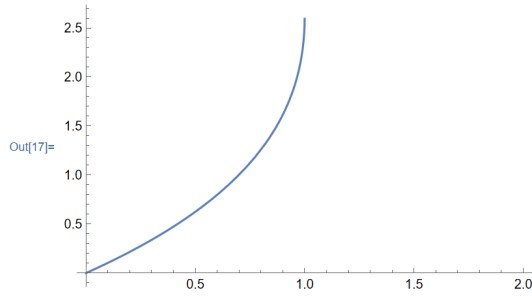
由

$$\text{粒子数密度: } \frac{N}{V} = \frac{g}{\lambda^3} g_{\frac{3}{2}}(z)$$

$$g_{\frac{3}{2}}(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty dx \frac{x^{\frac{1}{2}}}{z^{-1}e^x - 1} = \sum_{k=1}^\infty \frac{z^k}{k^{\frac{3}{2}}}$$

$$g_{\frac{3}{2}}(z) = \text{PolyLog}\left[\frac{3}{2}, z\right], z=1 \text{ 时, } g_{\frac{3}{2}}(1) \approx 2.612$$

In[17]:= Plot[PolyLog[$\frac{3}{2}$, z], {z, 0, 2}]



而 $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$, $g_{\frac{3}{2}} \leq g_{\frac{3}{2}}(1)$, $\frac{N}{V} \leq \frac{g}{\lambda^3} \xi\left(\frac{3}{2}\right) \sim T^{\frac{3}{2}}$, 当温度有高温降低到一定温度时, $\frac{N}{V} \leq T^{\frac{3}{2}}$ 一定要满足, 但是 $\frac{N}{V}$ 不可能无穷的小, 在低温下不太现实。

$$\frac{N}{V} = \int \frac{dk^3}{(2\pi)^3} \frac{g}{e^{\beta(\hbar^2 k^2/2m - \mu)} - 1} = \frac{g}{\hbar^3} \frac{m^{\frac{3}{2}}}{\sqrt{2}\pi^2} \int_0^\infty dE \frac{\sqrt{E}}{e^{\beta(E-\mu)} - 1}$$

$$N = \sum_i \frac{1}{e^{\beta(E_i - \mu)} - 1} = \sum_i \frac{1}{z^{-1} e^{\beta E_i} - 1} = \frac{1}{z^{-1} - 1} + \sum_i' \frac{1}{z^{-1} e^{\beta \hbar \omega} - 1} = \frac{1}{z^{-1} - 1} + \frac{g}{\lambda^3} V g_{\frac{3}{2}}(z)$$

Critical temperature

$$\frac{N}{V} = \frac{1}{\lambda^3} g_{\frac{3}{2}}(1) \quad \lambda_c = \frac{h}{\sqrt{2\pi m k_B T}}$$

2024.1.5

Bose-Einstein Condensation

理想玻色气体, 无相互作用, 低温条件产生玻色爱因斯坦凝聚

存在相互作用时, 会产生超流动性。

$$\frac{1}{e^{\beta(E, -\mu)} - 1} \rightarrow \mu \leq 0 \Rightarrow 0 \leq z \leq 1$$

状态方程: $\frac{N}{V} = \frac{g}{\lambda^3} g_{\frac{3}{2}}(z)$ $\frac{N}{V} \leq \frac{g}{\lambda^3} \frac{\xi(\frac{3}{2})}{g_{\frac{3}{2}}(1)} \sim T^{\frac{3}{2}}$, 温度低的时候不等式总会有不成立的情况发生。

$$g = 1, g_{\frac{3}{2} \max}(z) = g(1)$$

$$\text{不成立的临界温度 } T_C, \frac{N}{V} = \frac{1}{\lambda^3} g_{\frac{3}{2}}(1)$$

$$\lambda_C = \frac{h}{\sqrt{2\pi m k_B T_C}} \Rightarrow \lambda_C = \left(\frac{g_{\frac{3}{2}}(1) V}{N} \right)^{\frac{1}{3}}$$

$$\Rightarrow k_B T_C = \frac{2\pi \frac{\hbar^2}{m}}{\left[V g_{\frac{3}{2}}(1) / N \right]^{\frac{2}{3}}}$$

$$\begin{aligned} N &= \sum_i \frac{1}{e^{\beta(E_i - \mu)} - 1} = \frac{V}{\hbar^3} \frac{m^{\frac{3}{2}}}{\sqrt{2}\pi^2} \int_0^\infty dE \frac{\sqrt{E}}{e^{\beta(E - \mu)} - 1} \\ &= \frac{1}{z^{-1} - 1} + \sum_i' dE \frac{1}{e^{\beta(E_i - \mu)}} \\ &= \frac{1}{z^{-1} - 1} + \frac{V}{\lambda^3} g_{\frac{3}{2}}(z) \end{aligned}$$

设凝聚的粒子数为 N_0 ,下面求解凝聚的粒子数所占总粒子数的比例

$$N = \frac{1}{z^{-1}-1} + N \left(\frac{T}{T_C} \right)^{\frac{3}{2}} \frac{g_{\frac{3}{2}}(z)}{g_{\frac{3}{2}}(1)}$$

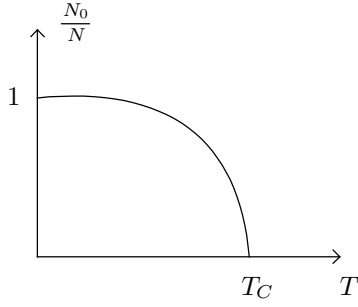
$$N_0 \Rightarrow z = \frac{N_0}{N_0 + 1}$$

将 $\frac{V}{\lambda^3} g_{\frac{3}{2}}(z)$ 代换出来³

1. $T > T_C$, $z < 1$ 对应高温情况, 不产生凝聚只要 z 不接近1, $\frac{1}{z^{-1}-1}$ 就可以看作是一个小的常量, 可以忽略不计。

2. $T < T_C$, $z = 1 - O\left(\frac{1}{N}\right)$, z 接近1, $N \left(\frac{T}{T_C} \right)^{\frac{3}{2}} \frac{g_{\frac{3}{2}}(z)}{g_{\frac{3}{2}}(1)} \approx N \left(\frac{T}{T_C} \right)^{\frac{3}{2}} \times 1$ 。

$$N = N_0 + N \left(\frac{T}{T_C} \right)^{\frac{3}{2}}, \frac{N_0}{N} = \begin{cases} 0, & T > T_C \\ 1 - \left(\frac{T}{T_C} \right)^{\frac{3}{2}}, & T < T_C \end{cases}$$



状态方程

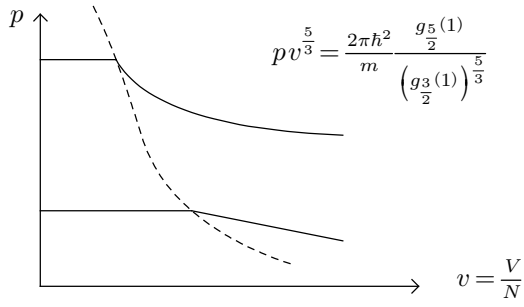
$$Z = \prod_i \frac{1}{1 - z e^{-\beta E_i}}$$

$$\begin{aligned} \frac{pV}{k_B T} &= \ln Z = - \sum_i \ln(1 - z e^{-\beta E_i}) \\ &= -V \int \frac{d^3 k}{(2\pi)^3} \ln(1 - z e^{-\beta \frac{\hbar^2 k^2}{2m}}) - \ln(1 - z) \\ &= \frac{V}{\lambda^3} g_{\frac{5}{2}}(z) - \ln(1 - z) \end{aligned}$$

$$-\frac{1}{V} \ln(1 - z) = \frac{1}{V} \ln(N_0 + 1),$$

$$\frac{p}{k_B T} = \frac{1}{\lambda^3} g_{\frac{5}{2}}(z) = \begin{cases} \frac{1}{\lambda^3} g_{\frac{5}{2}}(z), & T > T_C \\ \frac{1}{\lambda^3} g_{\frac{5}{2}}(1), & T < T_C \end{cases}$$

3. $\frac{V}{\lambda^3} g_{\frac{3}{2}}(z) = \frac{V}{\lambda_C^3} \frac{\lambda_C^3}{\lambda^3} \frac{g_{\frac{3}{2}}(z)}{g_{\frac{3}{2}}(1)} g_{\frac{3}{2}}(1)$

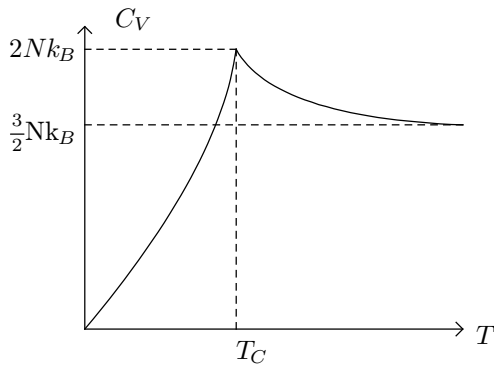
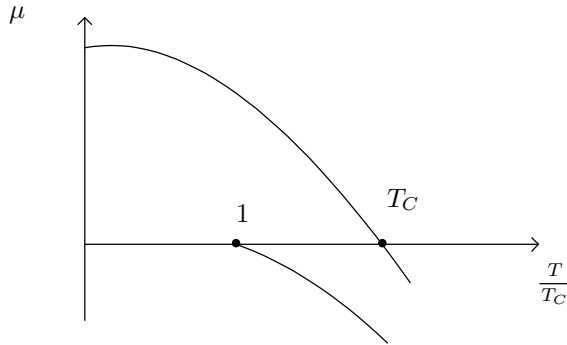


$$\frac{E}{k_B T V} = \frac{3}{2} \frac{1}{\lambda^3} g_{\frac{5}{2}}(z) \Rightarrow \frac{E}{N} = \frac{3}{2N} p V$$

$$\frac{C_V}{N k_B} = \frac{3V}{2N k_B} \left(\frac{\partial p}{\partial T} \right)_{V, N} = \begin{cases} \frac{15}{4} \frac{V}{\lambda^3} g_{\frac{5}{2}}(z) - \frac{9}{4} \frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)} & (T > T_C) \\ \frac{15}{4} \frac{V}{\lambda^3} g_{\frac{5}{2}}(1) & (T < T_C) \end{cases}$$

$$\frac{d}{dz} g_v(z) = \frac{1}{z} g_{v-1}(z)$$

$$\left\{ \begin{array}{l} \left(\frac{dN}{dT} \right)_{V, N} = 0 \\ \frac{N}{V} = \frac{1}{\lambda^3} g_{\frac{3}{2}}(z) \end{array} \right\} \Rightarrow \frac{3}{2T} \frac{g_{\frac{3}{2}}(z)}{\lambda^3} + \frac{1}{\lambda^3} \frac{1}{z} g_{\frac{1}{2}}(z) \left(\frac{\partial z}{\partial T} \right)_{V, N} = 0 \text{ 考试不要求}$$



本文档记录了许志芳老师秋季学期部分板书内容，由孙全超同学记录。感谢张竞予同学为本文档进行的大量纠错工作。如果您发现本文档仍存在错误，请您通过邮箱与笔者联系，我们进行检查并为您提供最新的文档。