

Statistical Mechanics

Siyang Wan (万思扬)

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convention, notation, and units

- 使用 Planck units, 此时 $G, \hbar \equiv \frac{h}{2\pi}, c, k_B = 1$, 因此:

names/dimensions	expressions/values
Planck length (L)	$l_P = \sqrt{\frac{\hbar G}{c^3}} = 1.616 \times 10^{-35} \text{ m}$
Planck time (T)	$t_P = \frac{l_P}{c} = 5.391 \times 10^{-44} \text{ s}$
Planck mass (M)	$m_P = \sqrt{\frac{\hbar c}{G}} = 2.176 \times 10^{-8} \text{ kg} \simeq 10^{19} \text{ GeV}$
Planck temperature (Θ)	$T_P = \sqrt{\frac{\hbar c^5}{G k_B^2}} = 1.417 \times 10^{32} \text{ K}$

- 时空维度用 $d = D + 1$ 表示.

- 下面是 *Statistical Field Theory*, David Tong, 中引言的一部分.

... This phenomenon is known as *universality*.
All of this makes phase transitions interesting. They involve violence, universal truths and competition between rival states. The story of phase transitions is, quite literally, the song of fire and ice.
...
... This leads us to a paradigm which now underlies huge swathes of physics, far removed from its humble origin of a pot on a stove. This paradigm revolves around two deep facts about the Universe we inhabit: **Nature is organised by symmetry. And Nature is organised by scale.**

其中 symmetry 指 Landau's approach to phase transitions, scale 是指 renormalization group.

- 跳过的章节:
 - chapter 5 formulation of quantum statistics: eigenstate thermalization hypothesis.
 - chapter 7 ideal Bose systems: ^4He .
 - chapter 8 ideal Fermi systems: the electron gas in metals; ultracold atomic Fermi gases; statistical model of the atom.

Part I

basic theory

Chapter 1

the statistical basis of thermodynamics

1.1 statistics and thermodynamics

- macrostates vs. microstates.
- the postulate of "equal *a priori* probabilities": 对于一个孤立 (具有确定的 E, V, N) 的热平衡系统, 任何可能的 microstate 的概率相同.
- 通过考虑 two physical systems, A_1, A_2 , brought into thermal contact, 达到平衡态时 $\Omega_1 \Omega_2$ 处于最大值, 得到

$$\begin{cases} S = k_B \ln \Omega(E, V, N) \\ TdS = dU + PdV - \mu dN \end{cases} \quad (1.1.1)$$

其中 $U = \langle E \rangle$.

- 对于 homogeneous systems, 有

$$TdT = VdP - Nd\mu \iff TS = U + PV - \mu N. \quad (1.1.2)$$

homogeneity relations:

对于 homogeneous systems, 有

$$S(\alpha U, \alpha V, \alpha N) = \alpha S(U, V, N) \implies TS = \dots \quad (1.1.3)$$

a function $f(x_1, \dots, x_n)$ satisfying

$$f(\alpha x_1, \dots, \alpha x_n) = \alpha^k f(x_1, \dots, x_n) \quad (1.1.4)$$

is called a homogeneous function of degree k .

consider

$$\frac{\partial f(\alpha \vec{x})}{\partial \alpha} = \sum_i x_i \frac{\partial f}{\partial x_i} \Big|_{\alpha \vec{x}} = \frac{\partial \alpha^k f(\vec{x})}{\partial \alpha} = k \alpha^{k-1} f(\vec{x}), \quad (1.1.5)$$

and by setting $\alpha = 1$, we have Euler's homogeneous function theorem,

$$k f(\vec{x}) = \sum_i x_i \frac{\partial f}{\partial x_i} \Big|_{\vec{x}}. \quad (1.1.6)$$

- 可以定义各种 free energies 如下:

names	expressions	for homogeneous sys.	differentials
internal energy	U	$U = TS - PV + \mu N$	$dU = TdS - PdV + \mu dN$
Helmholtz f.e.	$F = U - TS$	N/A	$dF = -SdT - PdV + \mu dN$
enthalpy	$H = U + PV$	N/A	$dH = TdS + VdP + \mu dN$
Gibbs f.e.	$G = U - TS + PV$	$G = \mu N$	$dG = -SdT + VdP + \mu dN$
grand potential	$\Phi_G = U - TS - \mu N$	$\Phi_G = -PV$	$d\Phi_G = -SdT - PdV - Nd\mu$

- $S = k_B \ln \Omega$ 源于 microcanonical ensemble.
- $F = -k_B T \ln Z_C$ 源于 canonical ensemble.
- $\Phi_G = -k_B T \ln Z_{GC}$ 源于 grand canonical ensemble.

- the specific heats are

$$C_V \equiv T \left(\frac{\partial S}{\partial T} \right)_{V,N} = \left(\frac{\partial U}{\partial T} \right)_{V,N}, \quad C_P \equiv T \left(\frac{\partial S}{\partial T} \right)_{P,N} = \left(\frac{\partial H}{\partial T} \right)_{P,N}, \quad (1.1.7)$$

并存在关系

$$\begin{cases} C_V - C_P = \left(P + \left(\frac{\partial U}{\partial V} \right)_{T,N} \right) \left(\frac{\partial V}{\partial T} \right)_{P,N} = TV \frac{\alpha^2}{\kappa_T}, \\ \frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S} \end{cases}, \quad (1.1.8)$$

其中

$$\begin{cases} \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N} & \text{isothermal compressibility} \\ \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{S,N} & \text{isentropic compressibility} \\ \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N} & \text{thermal expansion coefficient} \end{cases}. \quad (1.1.9)$$

1.2 classical ideal gas

- consider a classical (粒子波包不重叠) system composed of noninteracting particles.

- 这两个条件导致每个粒子的分布不受其它粒子的影响, 所以

$$\Omega(E, V, N) = f(E, N) V^N \implies \left(\frac{\partial \ln \Omega}{\partial V} \right)_{E,N} = \frac{N}{V}, \quad (1.2.1)$$

得到 equation of state,

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = k_B \frac{N}{V}. \quad (1.2.2)$$

- 考虑方形势阱 ($L^3 = V$) 中的能量本征值,

$$E = \sum_{i=1}^{3N} \epsilon_i, \quad \text{where } \epsilon_i = \frac{h^2}{8mL^2} n_i^2, n_i = 1, 2, \dots, \quad (1.2.3)$$

那么

$$\begin{aligned} \Gamma(E - \Delta E, E, V, N) &\equiv \sum_{E-\Delta E}^E \Omega(E, V, N) = \frac{1}{2^{3N+1}} \frac{3N \pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} \left(\frac{8mV^{2/3}}{h^2} \right)^{\frac{3N}{2}} E^{\frac{3N}{2}-1} \Delta E \\ &= \frac{\frac{3N}{2}}{\left(\frac{3N}{2}\right)!} (2\pi m E)^{\frac{3N}{2}} \left(\frac{V}{h^3} \right)^N \frac{\Delta E}{E}, \end{aligned} \quad (1.2.4)$$

因此 (忽略 $O(\ln N), O(\ln \frac{\Delta E}{E})$ 项)

$$\ln \Gamma \approx \frac{3N}{2} + N \ln \left(\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right). \quad (1.2.5)$$

- 注意, 计算中认为每个粒子都是可区分的 (distinguishable).
- 这个结果与 homogeneous system 的性质矛盾.

calculation:

用到 n -sphere 的面积和体积公式,

$$V_n = \frac{\pi^{n/2}}{(n/2)!}, \quad S_{n-1} = \frac{n\pi^{n/2}}{(n/2)!}, \quad (1.2.6)$$

其中

$$(z)! \equiv \Gamma(z+1) = z\Gamma(z), \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}. \quad (1.2.7)$$

Stirling's formula is

$$\ln N! \approx N \ln N - N. \quad (1.2.8)$$

1.3 Gibbs paradox

- 我们已经注意到 (1.2.5) 与 homogeneous system 的性质矛盾.
- Gibbs 为解决这个问题修改了 number of microstates,

$$\Omega(E, V, N) \mapsto \frac{\Omega(E, V, N)}{N!}, \quad (1.3.1)$$

因此, 得到 Sackur–Tetrode equation,

$$S(E, V, N) = k_B \left(N \ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right) + \frac{5}{2} N \right). \quad (1.3.2)$$

- 结论: ideal gas 中的粒子是 identical and indistinguishable.
 - 系数 $\frac{1}{N!}$ 只有在所有粒子都处于不同状态时才正确, 这种条件称为 classical limit.

- 理想气体的化学势为

$$\mu = E \left(\frac{5}{3N} - \frac{2S}{3N^2 k_B} \right) = k_B T \ln \left(\underbrace{\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2}}_{=n\lambda^3 \ll 1} \right) \ll 0. \quad (1.3.3)$$

- 理想气体的 partition function 见 subsection 3.3.1.

Chapter 2

elements of ensemble theory

- 本章从经典力学角度讨论 ensemble theory.

2.1 phase space of a classical system and Liouville's theorem

- classical system 的 microstates 用 phase space 中的一个点 (p_i, q_i) 描述.
- the canonical equation of motion is

$$\begin{cases} \dot{p}_i = -\frac{\partial H}{\partial q_i} \\ \dot{q}_i = \frac{\partial H}{\partial p_i} \end{cases}. \quad (2.1.1)$$

- an ensemble of systems 就是一个系统在某个 macrostate (和其它条件) 下, 其 microstate 的概率分布, 用 $\rho(p, q, t)$ 描述.
- 如果

$$\frac{\partial \rho}{\partial t} = 0, \quad (2.1.2)$$

则称 the ensemble is stationary or equilibrium.

- 一类热平衡系综为 $\rho(p, q) = \rho(H(p, q))$.

-
- Liouville's theorem: $p_i(t), q_i(t) : s \mapsto \mathbb{R}$ 是 phase space 中的标量场 (state, s , 是 phase space 中的点), 体元 $\epsilon = dp_1 \wedge \cdots \wedge dp_\nu \wedge dq_1 \wedge \cdots \wedge dq_\nu$ 不随时间变化,

$$\frac{d\epsilon}{dt} = 0. \quad (2.1.3)$$

proof:

注意到

$$\begin{pmatrix} dp_1(t+dt) \\ \vdots \\ dp_\nu(t+dt) \\ dq_1(t+dt) \\ \vdots \\ dq_\nu(t+dt) \end{pmatrix} = \begin{pmatrix} \delta_{ij} - \frac{\partial^2 H}{\partial q_i \partial p_j} dt & -\frac{\partial^2 H}{\partial q_i \partial q_j} dt \\ \frac{\partial^2 H}{\partial p_i \partial p_j} dt & \delta_{ij} + \frac{\partial^2 H}{\partial p_i \partial q_j} dt \end{pmatrix} \begin{pmatrix} dp_1(t) \\ \vdots \\ dp_\nu(t) \\ dq_1(t) \\ \vdots \\ dq_\nu(t) \end{pmatrix}, \quad (2.1.4)$$

因此

$$\epsilon(t+dt) = \begin{vmatrix} \delta_{ij} - \frac{\partial^2 H}{\partial q_i \partial p_j} dt & -\frac{\partial^2 H}{\partial q_i \partial q_j} dt \\ \frac{\partial^2 H}{\partial p_i \partial p_j} dt & \delta_{ij} + \frac{\partial^2 H}{\partial p_i \partial q_j} dt \end{vmatrix} \epsilon(t)$$

$$= \left(1 + \sum_{i=1}^{\nu} \underbrace{\left(-\frac{\partial^2 H}{\partial q_i \partial p_i} + \frac{\partial^2 H}{\partial p_i \partial q_i} \right)}_{=0} dt + O(dt^2) \right) \epsilon(t). \quad (2.1.5)$$

- Liouville's equation:

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}_{\text{BP}} \equiv \sum_{i=1}^{\nu} \left(\frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} \right). \quad (2.1.6)$$

proof:

注意到

$$\frac{d(\rho(p, q, t) \epsilon(t))}{dt} = 0, \quad (2.1.7)$$

结合 Liouville's theorem, 可知

$$\frac{d\rho(p, q, t)}{dt} = 0 \implies \dots \quad (2.1.8)$$

2.2 the microcanonical ensemble

- the microcanonical ensemble 的概率密度为

$$\rho(H(p, q)) = \begin{cases} \frac{1}{\Gamma} & E - \Delta E \leq H(p, q) \leq E \\ 0 & \text{otherwise} \end{cases}, \quad (2.2.1)$$

其中

$$\Gamma = \frac{\omega}{\omega_0}, \quad (2.2.2)$$

其中 ω 是 $E - \Delta E \leq H(p, q) \leq E$ 所占相空间的体积, ω_0 是一个状态所占相空间的体积.

- 在 section 1.2 中, $\omega_0 = h^{3N}$.
- 实验发现, 一般地, $\omega_0 = h^\nu$, 其中 ν 是 degree of freedom, 这在经典和极端相对论 (光子气) 情况下都成立.

Chapter 3

the canonical ensemble

3.1 equilibrium between a system and a heat reservoir

- 系统 A 与 heat reservoir A_{HR} 存在热交换, 它们组成整体系统 A_0 ,

$$E_0 = E + E_{\text{HR}}, \quad \Omega_0 = \sum_{E=0}^{E_0} \Omega(E) \Omega_{\text{HR}}(E_0 - E). \quad (3.1.1)$$

- 系统 A 处于能量 E 的某个 microstate 的概率为

$$P = \frac{\Omega_{\text{HR}}(E_0 - E)}{\Omega_0}, \quad (3.1.2)$$

有近似

$$\Omega_{\text{HR}}(E_0 - E) \approx \Omega_{\text{HR}}(E_0) e^{-\beta E}. \quad (3.1.3)$$

因此, canonical ensemble 的概率密度为

$$\rho(p, q) = \frac{e^{-\beta H(p, q)}}{Z_C}. \quad (3.1.4)$$

3.2 a system in the canonical ensemble

- 考虑一个由 \mathcal{N} 个 identical subsystems 组成的系统 (heat reservoir), 总能量为 \mathcal{E} , 每个子系统 (其中一个就是系统 A) 可能处于 $N_{\text{EL}} + 1$ 个 energy level,

$$\begin{cases} \sum_{i=0}^{N_{\text{EL}}} n_i = \mathcal{N} \\ \sum_{i=0}^{N_{\text{EL}}} n_i E_i = \mathcal{E} \end{cases}, \quad (3.2.1)$$

其中 n_i 表示处于第 i 个 energy level 的子系统数量.

- 系统处于 $\{n_i\}$ 的 number of microstate 为

$$W\{n_i\} = \frac{\mathcal{N}!}{n_0! \cdots n_{N_{\text{EL}}}!} \implies \ln W\{n_i\} \approx \mathcal{N} \ln \mathcal{N} - \sum_{i=0}^{N_{\text{EL}}} n_i \ln n_i. \quad (3.2.2)$$

- 能级 i 上的子系统数量的期望值为

$$\langle n_i \rangle = \frac{\sum_{\{n_i\}} n_i W\{n_i\}}{\sum_{\{n_i\}} W\{n_i\}}. \quad (3.2.3)$$

3.2.1 the method of most probable values

- the most probable microstate $\{n_i\}$ 对应 $W\{n_i\}$ 取最大值, 此时

$$\frac{n_i}{\mathcal{N}} = \frac{e^{-\beta E_i}}{Z_C}, \quad (3.2.4)$$

其中 β 满足

$$\frac{\mathcal{E}}{\mathcal{N}} \equiv U = \frac{\sum_{i=0}^{N_{\text{EL}}} E_i e^{-\beta E_i}}{Z_C}. \quad (3.2.5)$$

– 此时

$$\begin{aligned} \max(\ln W\{n_i\}) &= \beta \mathcal{E} + \mathcal{N} \ln Z_C \\ &= \mathcal{N} \left(1 - \beta \frac{\partial}{\partial \beta} \right) \ln Z_C. \end{aligned} \quad (3.2.6)$$

proof:

用 the method of Lagrange multipliers 求 $\ln W\{n_i\}$ 的极大值点, 并满足约束条件 (3.2.1),

$$\begin{aligned} \frac{\partial \ln W\{n_i\}}{\partial n_i} - \alpha - \beta E_i &= 0 \\ \implies -(\ln n_i + 1) - \alpha - \beta E_i &= 0 \\ \implies n_i &= e^{-1-\alpha} e^{-\beta E_i}. \end{aligned} \quad (3.2.7)$$

- 可见, 这个由 \mathcal{N} 个 identical subsystems 组成的系统是一个 heat reservoir, 其中每个 subsystem 都处于 canonical ensemble.

3.2.2 the method of mean values

- 本 subsection 我们直接计算 (3.2.3).
- 定义新函数

$$\tilde{W}\{n_i\} := \frac{\mathcal{N}!}{n_0! \cdots n_{N_{\text{EL}}}!} \omega_0^{n_0} \cdots \omega_{N_{\text{EL}}}^{n_{N_{\text{EL}}}}, \quad (3.2.8)$$

和 (总系统的总微观态数)

$$\Gamma(\mathcal{N}, U) := \sum_{\{n_i\}} \tilde{W}\{n_i\}. \quad (3.2.9)$$

– 那么

$$\langle n_i \rangle = \frac{\partial}{\partial \omega_i} \Big|_{\omega_0, \dots, \omega_{N_{\text{EL}}}=1} \ln \Gamma(\mathcal{N}, U). \quad (3.2.10)$$

notice:

注意到

$$(\omega_1 + \cdots + \omega_M)^N = \sum_{\{n_i\}} \frac{N!}{n_1! \cdots n_M!} \omega_1^{n_1} \cdots \omega_M^{n_M}, \quad (3.2.11)$$

但是这里求和只需要满足 $\sum_{i=1}^M n_i = N$, 与 $\Gamma(\mathcal{N}, U)$ 中的求和需要满足的两条约束条件 (3.2.1) 不同.

- 引入 generating function $G(\mathcal{N}, z)$,

$$\begin{aligned} G(\mathcal{N}, z) &:= \sum_{U=0}^{\infty} \Gamma(\mathcal{N}, U) z^{\mathcal{N}U} \\ &= \sum_{U=0}^{\infty} \left(\sum_{\{n_i\}} \frac{\mathcal{N}!}{n_0! \cdots n_{N_{\text{EL}}}!} (\omega_0 z^{E_0})^{n_0} \cdots (\omega_{N_{\text{EL}}} z^{E_{N_{\text{EL}}}})^{n_{N_{\text{EL}}}} \right) \\ &= \left(\omega_0 z^{E_0} + \cdots + \omega_{N_{\text{EL}}} z^{E_{N_{\text{EL}}}} \right)^{\mathcal{N}}, \end{aligned} \quad (3.2.12)$$

令 $f(z) := \omega_0 z^{E_0} + \cdots + \omega_{N_{\text{EL}}} z^{E_{N_{\text{EL}}}}$.

- 选取合适的单位使得 E_i 都是整数, 且最低能级的能量 $E_0 = 0$.
- 此时, $\Gamma(\mathcal{N}, U)$ 就是 $G(\mathcal{N}, z)$ 对 z 作 Taylor expansion 的系数, 因此

$$\Gamma(\mathcal{N}, U) = \frac{1}{2\pi i} \oint \frac{G(\mathcal{N}, z)}{z^{\mathcal{N}U+1}} dz \simeq \exp \left(\mathcal{N}(\ln f(z_0) - U \ln z_0) \right), \quad (3.2.13)$$

其中 z_0 满足

$$U \approx \frac{\sum_{i=0}^{N_{\text{EL}}} \omega_i E_i z_0^{E_i}}{\sum_{i=0}^{N_{\text{EL}}} \omega_i z_0^{E_i}}. \quad (3.2.14)$$

calculation:

考虑 $f_1(z) = \frac{1}{z} + z$, $f_2(z) = \frac{1}{z} - z$, $f_3(z) = \frac{1}{z^2} + \frac{1}{z} + z + z^2$, $f_4(z) = \frac{1}{z^2} + \frac{1}{z} + z - z^2$, 分别如下图所示.

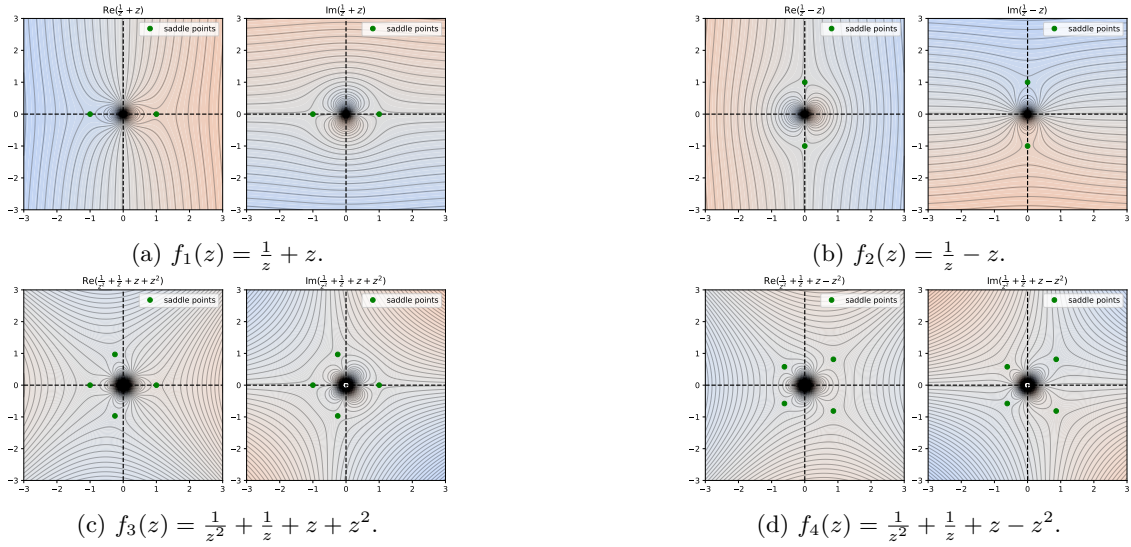


Figure 3.1: plots of $f_1(z)$, $f_2(z)$, $f_3(z)$, $f_4(z)$.

让 the contour of integration 正好穿过鞍点, 积分结果由 integrand 在鞍点附近的取值决定 (?). 因此, 我们首先需要确定鞍点的位置. 将 integrand 写作如下形式,

$$\frac{(f(z))^{\mathcal{N}}}{z^{\mathcal{N}U+1}} = e^{\mathcal{N}g(z)} \implies g(z) = \ln f(z) - \left(U + \frac{1}{\mathcal{N}} \right) \ln z, \quad (3.2.15)$$

鞍点 z_0 位于 (考虑到 $\mathcal{N}U \gg 1$)

$$\frac{dg(z=z_0)}{dz} = 0 \implies U \approx U + \frac{1}{\mathcal{N}} = \frac{\sum_{i=0}^{N_{\text{EL}}} \omega_i E_i z_0^{E_i}}{\sum_{i=0}^{N_{\text{EL}}} \omega_i z_0^{E_i}}, \quad (3.2.16)$$

此时

$$g''(z_0) = \frac{f''(z_0)}{f(z_0)} - \frac{(U + \frac{1}{\mathcal{N}})^2 - (U + \frac{1}{\mathcal{N}})}{z_0^2}, \quad (3.2.17)$$

在 $g(z_0)$ 附近展开

$$g(z_0 + \Delta z) = g(z_0) + \frac{1}{2} g''(z_0) (\Delta z)^2 + O((\Delta z)^3), \quad (3.2.18)$$

因此积分可以近似为

$$\begin{aligned} \Gamma(\mathcal{N}, U) &\simeq \frac{1}{2\pi i} \frac{(f(z_0))^{\mathcal{N}}}{z_0^{\mathcal{N}U+1}} \int_{-\pi}^{\pi} \exp \left(\frac{\mathcal{N}}{2} g''(z_0) (z_0 e^{i\theta} - z_0)^2 \right) i z_0 e^{i\theta} d\theta \\ &\simeq \frac{1}{2\pi i} \frac{(f(z_0))^{\mathcal{N}}}{z_0^{\mathcal{N}U+1}} \int_{-\infty}^{\infty} \exp \left(-\frac{\mathcal{N}}{2} g''(z_0) (z_0 \theta)^2 \right) i z_0 d\theta \end{aligned}$$

$$= \frac{(f(z_0))^{\mathcal{N}}}{z_0^{\mathcal{N}U+1}} \frac{1}{\sqrt{2\pi\mathcal{N}g''(z_0)}}, \quad (3.2.19)$$

或者

$$\begin{aligned} \ln \Gamma(\mathcal{N}, U) &\simeq \mathcal{N}(\ln f(z_0) - U \ln z_0) - \left(\ln z_0 + \frac{1}{2} \ln(2\pi\mathcal{N}g''(z_0)) \right) \\ &\simeq \mathcal{N}(\ln f(z_0) - U \ln z_0) \end{aligned} \quad (3.2.20)$$

- 取 $\omega_1, \dots, \omega_{N_{\text{EL}}} = 1$, 此时 $z_0 \in \mathbb{R}$, 令

$$z_0 = e^{-\beta}, \quad (3.2.21)$$

那么

$$\begin{cases} \ln \Gamma(\mathcal{N}, U) = \mathcal{N}(\ln Z_C + \beta U) \\ Z_C = \sum_{i=0}^{N_{\text{EL}}} e^{-\beta E_i} \end{cases}. \quad (3.2.22)$$

- 还可以得到

$$\frac{\langle (\Delta n_i)^2 \rangle}{\langle n_i \rangle^2} = \frac{1}{\langle n_i \rangle} - \frac{1}{\mathcal{N}} \left(1 + \frac{(E_i - U)^2}{\langle (E - U)^2 \rangle} \right), \quad (3.2.23)$$

其中

$$\langle E^2 \rangle = \frac{\sum_{i=1}^{N_{\text{EL}}} E_i^2 e^{-\beta E_i}}{\sum_{i=1}^{N_{\text{EL}}} e^{-\beta E_i}}, \quad U \equiv \langle E \rangle. \quad (3.2.24)$$

- 注意 (3.2.5), U 是 subsystem 的能量期望值, 不是总系统 (heat reservoir) 的.
- 用 grand partition function 算更简单, 见 (6.2.2).

3.3 the partition function and the Helmholtz free energy and more

- the partition function is

$$Z_C(T, V, N) = \sum_{i=0}^{N_{\text{EL}}} e^{-\beta E_i} = \int \frac{d^{\nu} p d^{\nu} q}{h^{\nu}} e^{-\beta H(p, q)}, \quad (3.3.1)$$

and the Helmholtz free energy is

$$F = U - TS = -k_B T \ln Z_C. \quad (3.3.2)$$

- $Z_C(T, V, N)$ 对 V, N 的依赖源于 $E_i(V, N)$.

- 另外, 求和可以转化为积分 (使用 Laplace transform)

$$\begin{cases} Z_C(T, V, E) = \int_0^{\infty} g(E) e^{-\beta E} dE \\ g(E) \equiv \frac{\Omega(N, V, E)}{\Delta E} = \frac{1}{2\pi i} \int_{-\infty}^{\infty} e^{(x+iy)E} Z_C(T = \frac{1}{k_B(x+iy)}, V, E) dy, \end{cases} \quad (3.3.3)$$

其中 $x > 0$ 是任意正实数, ΔE 是能级间隙.

3.3.1 the partition function of the classical ideal gas

- 系统由全同不可区分粒子组成, 那么

$$\begin{aligned} Z_C(T, V, N) &= \int \frac{d^{3N} p d^{3N} q}{N! h^{3N}} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} \\ &= \frac{1}{N!} \left(\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right)^N. \end{aligned} \quad (3.3.4)$$

- 观察可见

$$Z_C(T, V, N) = \frac{(Z_C(T, V, 1))^N}{N!}, \quad (3.3.5)$$

这对于任何由全同不可分辨无相互作用粒子组成的系统都成立 (无论这些粒子是否有 internal degrees of freedom).

3.4 energy fluctuations in the canonical ensemble

- 通过 canonical ensemble 和 microcanonical ensemble 计算出的热力学量必须一致, 这种一致性的来源如下.
- canonical ensemble 和 microcanonical ensemble 的主要区别在于能量的取值范围, 考虑能量的方差

$$\begin{aligned}\langle(\Delta E)^2\rangle &= \langle E^2\rangle - \langle E\rangle^2 = \frac{1}{Z_C} \frac{\partial^2}{\partial \beta^2} Z_C - \left(-\frac{\partial}{\partial \beta} \ln Z_C\right)^2 \\ &= \frac{\partial^2}{\partial \beta^2} \ln Z_C = \left(\frac{\partial U}{\partial \beta}\right)_{V,N} = k_B T^2 C_V,\end{aligned}\quad (3.4.1)$$

因此

$$\frac{\sqrt{\langle(\Delta E)^2\rangle}}{U} = \frac{k_B T}{U} \sqrt{\frac{C_V}{k_B}} \sim N^{-\frac{1}{2}}, \quad (3.4.2)$$

可见能量涨落很小, canonical ensemble 和 microcanonical ensemble 的差异可以忽略.

- 在 canonical ensemble 中, 最概然能量 E^* 为

$$\left.\frac{\partial \Omega(E, V, N) e^{-\beta E}}{\partial E}\right|_{E^*} = 0 \implies \left.\left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}\right|_{E^*} = \frac{1}{k_B T}, \quad (3.4.3)$$

对比热力学中的公式 $\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$, 可见

$$E^* = U, \quad (3.4.4)$$

能量的 most probable value 等于其 mean value (这显然是 $N \rightarrow \infty$ 情况下的近似结果).

- 系统处于能量 E 的概率是

$$P(E) = \frac{\Omega(E) e^{-\beta E}}{Z_C} \approx \frac{1}{Z_C} e^{-\beta(U-TS)} e^{-\frac{(E-U)^2}{2k_B T^2 C_V}}. \quad (3.4.5)$$

calculation:

对 $\ln(\Omega(E) e^{-\beta E})$ 在 $E = U$ 附近展开,

$$\left.\frac{\partial^2}{\partial E^2}\right|_U \ln(\Omega(E) e^{-\beta E}) = -\frac{1}{k_B T^2 C_V}. \quad (3.4.6)$$

因此, partition function 为

$$Z_C(T, V, N) \simeq e^{-\beta(U-TS)} \sqrt{2\pi k_B T^2 C_V}, \quad (3.4.7)$$

注意到

$$-k_B T \ln Z_C \equiv F = (U - TS) - \underbrace{\frac{k_B T}{2} \ln(2\pi k_B T^2 C_V)}_{\sim O(\ln N)}, \quad (3.4.8)$$

第二项可以忽略, 因此 $F \approx U - TS$.

3.5 the equipartition theorem and the virial theorem

3.5.1 the equipartition theorem

- 能均分定理 (equipartition theorem, or classical theorem of equipartition of energy) 适用于哈密顿量为二次型的系统,

$$H = \sum_{i,j} \left(\frac{p_i p_j}{2m_{ij}} + \frac{1}{2} \frac{\partial^2 H}{\partial q_i \partial q_j} q_i q_j \right), \quad (3.5.1)$$

所以,

$$\begin{cases} \frac{\partial H}{\partial p_i} = \sum_j \frac{p_j}{m_{ij}} \\ \frac{\partial H}{\partial q_i} = \sum_j \frac{\partial^2 H}{\partial q_i \partial q_j} q_j \end{cases} \implies H = \frac{1}{2} \sum_i \left(p_i \frac{\partial H}{\partial p_i} + q_i \frac{\partial H}{\partial q_i} \right). \quad (3.5.2)$$

- 考虑

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega} = \frac{1}{\beta} \delta_{ij}, \quad (3.5.3)$$

其中, x_i 是相空间的坐标, $x = (p_1, \dots, p_\nu, q_1, \dots, q_\nu)$.

proof:

$$\begin{aligned} \int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega &= - \int x_i \frac{1}{\beta} \frac{\partial e^{-\beta H}}{\partial x_j} d\omega \\ &= -\frac{1}{\beta} \int \left(\frac{\partial}{\partial x_j} (x_i e^{-\beta H}) - \delta_{ij} e^{-\beta H} \right) d\omega \\ &= \frac{1}{\beta} \delta_{ij} Z_C - \frac{1}{\beta} \int (x_i e^{-\beta H}) \Big|_{x_j=(x_j)_1}^{(x_j)_2} d\omega_{(j)} \end{aligned} \quad (3.5.4)$$

哈密顿量在边界处, $x_j = (x_j)_{1,2}$, 为零, 所以...

- 所以, 能量的期望值为,

$$\langle H \rangle = \frac{1}{2} \sum_i \left(\langle p_i \frac{\partial H}{\partial p_i} \rangle + \langle q_i \frac{\partial H}{\partial q_i} \rangle \right) = \frac{f}{2} k_B T \quad (3.5.5)$$

其中, f 是系统的 number of nonvanishing coefficients, 是 2ν 减去循环坐标的数量.

- 能均分定理的适用条件:

1. 经典力学,
2. 哈密顿量为二次型.

3.5.2 the virial theorem

- the virial theorem: 对于哈密顿量, $H = T + V(q)$, 的动能项为二次型, 且势能项与 p 无关的情况, 有

$$\langle T \rangle = -\frac{1}{2} \mathcal{V}, \quad (3.5.6)$$

其中

$$\mathcal{V} := \sum_i \langle q_i \dot{p}_i \rangle \quad (3.5.7)$$

被称作系统的 virial.

proof:

考虑,

$$G = \sum_i p_i q_i \implies \frac{dG}{dt} = \sum_i \underbrace{\dot{q}_i}_{=\frac{\partial H}{\partial p_i}} p_i + q_i \dot{p}_i = 2T + \sum_i q_i \dot{p}_i, \quad (3.5.8)$$

系统运动的范围有限, 所以,

$$\langle \frac{dG}{dt} \rangle = 0 \implies \langle T \rangle = -\frac{1}{2} \sum_i \langle q_i \dot{p}_i \rangle. \quad (3.5.9)$$

3.5.3 classical ideal gas and nonideal gas

- 对于理想气体, 其 virial 为

$$\begin{aligned} \mathcal{V} &= \sum_{i=1}^N \langle \vec{x}_i \cdot \vec{F}_i \rangle = \oint_S \vec{x} \cdot (-P d\vec{S}) \\ &= -P \oint \nabla \cdot \vec{x} dV = -3PV, \end{aligned} \quad (3.5.10)$$

结合 equipartition theorem 可知 $\langle T \rangle = \frac{3}{2}Nk_B T$, 所以

$$\frac{3}{2}Nk_B T = -\frac{1}{2}(-3PV) \implies PV = Nk_B T. \quad (3.5.11)$$

- 对于粒子间存在 two-body interaction potential $u(r)$ 的 nonideal gas, 利用相同的办法可得 virial equation of state,

$$\begin{aligned} \mathcal{V} &= \sum_{i=1}^N \langle \vec{x}_i \cdot \vec{F}_i \rangle = -3PV - \sum_{i < j} \left\langle \frac{\partial u(r=r_{ij})}{\partial r} r_{ij} \right\rangle \\ \implies \frac{PV}{Nk_B T} &= 1 - \frac{1}{D} \frac{1}{Nk_B T} \sum_{i < j} \left\langle \frac{\partial u(r=r_{ij})}{\partial r} r_{ij} \right\rangle, \end{aligned} \quad (3.5.12)$$

其中 $D = 3$ 是空间维数.

3.6 a system of harmonic oscillators

- 考虑一个由 practically independent harmonic oscillators 组成的系统. 两个重要的例子是:
 1. 黑体辐射理论 (光子的统计力学),
 2. lattice vibration 理论 (phonons 的统计力学).

3.6.1 classically

- 系统的 partition function 为

$$\begin{aligned} Z_C(T, V, N=1) &= \int \frac{dp dq}{h} e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2)} = \frac{k_B T}{\hbar\omega} \\ \implies Z_C(T, V, N) &= \left(\frac{k_B T}{\hbar\omega} \right)^N, \end{aligned} \quad (3.6.1)$$

注意谐振子是 distinguishable, 因为每个谐振子代表 photons 或 phonons 的一个能级, 可区分.

- 得到

$$\begin{cases} U = Nk_B T \\ S = Nk_B \left(1 + \ln \frac{k_B T}{\hbar\omega} \right) \\ \mu = -k_B T \ln \frac{k_B T}{\hbar\omega} \\ \Omega(E \geq 0) = \frac{1}{(\hbar\omega)^N} \frac{E^{N-1}}{(N-1)!} \end{cases}. \quad (3.6.2)$$

3.6.2 quantum mechanically

- 每个谐振子有如下能级,

$$\epsilon_n = \hbar\omega \left(n + \frac{1}{2} \right), \quad (3.6.3)$$

因此

$$\begin{aligned} Z_C(T, V, N=1) &= \frac{1}{2 \sinh \frac{\hbar\omega}{2k_B T}} \\ \implies Z_C(T, V, N) &= \left(\frac{1}{2 \sinh \frac{\hbar\omega}{2k_B T}} \right)^N. \end{aligned} \quad (3.6.4)$$

- 得到

$$\begin{cases} U = N\hbar\omega \left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right) \\ S = Nk_B \left(\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega}) \right) \\ \mu = \frac{1}{2}\hbar\omega + k_B T \ln(1 - e^{-\beta\hbar\omega}) \\ C_P = C_V = Nk_B (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \end{cases}, \quad (3.6.5)$$

以及

$$\Omega(E = \hbar\omega(\frac{N}{2} + M)) = \binom{N+M-1}{M} \equiv \frac{(N+M-1)!}{M!(N-1)!}. \quad (3.6.6)$$

3.7 the statistics of paramagnetism

- 首先回顾一下 magnetization.
- magnetization field \vec{M} 是介质单位体积的磁矩 (magnetic moment).
- $\vec{B}, \vec{H}, \vec{M}$ 的关系为

$$\vec{B} = \mu_0(\vec{H} + \vec{M}), \quad (3.7.1)$$

对于线性介质

$$\vec{M} = \chi\vec{H}, \quad \vec{B} = \mu\vec{H} = \mu_0(1 + \chi)\vec{H}. \quad (3.7.2)$$

3.7.1 classically (Langevin paramagnetism)

- 考虑一个由 N 个 distinguishable magnetic dipoles $\vec{\mu}$ 组成的系统.
- 系统的能量为

$$E = - \sum_{i=1}^N \mu_0 \vec{\mu} \cdot \vec{H}, \quad (3.7.3)$$

其中 \vec{H} 是 external magnetic field. 系统的 partition function 为

$$Z_C(T, V, N) = \left(\int \sin\theta d\theta d\phi e^{\beta\mu_0\mu H \cos\theta} \right)^N = \left(4\pi \frac{\sinh \frac{\mu_0\mu H}{k_B T}}{\frac{\mu_0\mu H}{k_B T}} \right)^N. \quad (3.7.4)$$

- 得到

$$\langle \mu_z \rangle = \frac{VM_z}{N} = \mu \left(\coth \frac{\mu_0\mu H}{k_B T} - \frac{k_B T}{\mu_0\mu H} \right), \quad (3.7.5)$$

其中 M_z 是系统的 magnetization field \vec{M} 在 z 方向 (外加磁场的方向) 的分量,

– 当 $\mu_0\mu H \ll k_B T$ 时,

$$M_z \simeq \frac{N}{V} \frac{\mu_0\mu^2}{3k_B T} H \implies \chi = \frac{C}{T}, \quad (3.7.6)$$

其中 $C = \frac{N}{V} \frac{\mu_0\mu^2}{3k_B}$ 称为介质的 Curie constant.

3.7.2 quantum mechanically (Brillouin paramagnetism)

- 磁矩 μ 由轨道磁矩 μ_L 和自旋磁矩 μ_S 构成, 在总角动量 J 的投影方向

$$\vec{\mu} \cdot \vec{J} |s, l, j, m_j\rangle = -\frac{g(s, l, j)\mu_B}{\hbar} J^2 |s, l, j, m_j\rangle, \quad (3.7.7)$$

其中系数 $\frac{g\mu_B}{\hbar}$ 称作 gyromagnetic ratio, $\mu_B = \frac{e\hbar}{2m}$ 是 Bohr magneton, g 是 Lande's g -factor,

calculation:

磁矩 μ 由自旋磁矩 μ_S 和轨道磁矩 μ_L 构成,

$$\begin{cases} \vec{\mu} = \vec{\mu}_S + \vec{\mu}_L \\ \vec{\mu}_S = -\frac{g_S\mu_B}{\hbar} \vec{S} \\ \vec{\mu}_L = -\frac{g_L\mu_B}{\hbar} \vec{L} \end{cases}, \quad \text{with} \quad \begin{cases} g_S \approx 2 \\ g_L = 1 \end{cases}, \quad (3.7.8)$$

并且

$$\begin{cases} [L_i, L_j] = i\hbar\epsilon_{ijk}L_k \\ L_z |l, m\rangle = m\hbar |l, m\rangle \\ L^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle \end{cases}, \quad \begin{cases} \vec{J} = \vec{S} + \vec{L} \\ [J^2, S_z] = i\hbar(S_1 \otimes L_2 - S_2 \otimes L_1) \neq 0 \\ J^2 |s, l, j, m_j\rangle = j(j+1)\hbar^2 |s, l, j, m_j\rangle \end{cases}, \quad (3.7.9)$$

其中 $j = |s - l|, \dots, s + l$ (详见笔记 [Lie Groups and Lie Algebras](#)).
最后

$$\begin{aligned}\vec{\mu} \cdot \vec{J} |s, l, j, m_j\rangle &= -\mu_B \hbar \left(\frac{g_S - g_L}{2} s(s+1) - \frac{g_S - g_L}{2} l(l+1) + \frac{g_L + g_S}{2} j(j+1) \right) |s, l, j, m_j\rangle \\ &= -\frac{g(s, l, j) \mu_B}{\hbar} J^2 |s, l, j, m_j\rangle,\end{aligned}\quad (3.7.10)$$

因此

$$g(s, l, j) = \frac{g_L + g_S}{2} + (g_S - g_L) \frac{s(s+1) - l(l+1)}{2j(j+1)}.\quad (3.7.11)$$

- 单个磁矩的 Hamiltonian 为

$$\hat{H} = -\mu_0 \mu_z H \quad (3.7.12)$$

可见 $|s, m_s\rangle \otimes |l, m_l\rangle$ 是能量本征态, 而非 $|s, l, j, m_j\rangle$.

- 但垂直于 \vec{J} 的磁矩在时间平均下没有贡献, 所以可以认为有效的磁矩为

$$\vec{\mu}_{\text{eff}} = -\frac{g(s, l, j) \mu_B}{\hbar} \vec{J}, \quad (3.7.13)$$

此时, 系统的能级为

$$\epsilon_{m_j} = g(s, l, j) \mu_0 \mu_B H m_j, \quad (3.7.14)$$

注意: 系统中所有粒子的量子数 s, l, j 都一样.

- 系统的 partition function 为

$$Z_C(T, V, N) = \left(\sum_{m_j=-j}^j e^{-\beta g(s, l, j) \mu_0 \mu_B H m_j} \right)^N = \frac{\sinh(1 + \frac{1}{2j})x}{\sinh \frac{1}{2j}x}, \quad (3.7.15)$$

其中 $x = \beta g(s, l, j) \mu_0 \mu_B H j$.

- 得到

$$\langle \mu_z \rangle = g(s, l, j) \mu_B j B_j(x), \quad (3.7.16)$$

其中 $B_j(x)$ 是 Brillouin function of order j ,

$$B_j(x) = \left(1 + \frac{1}{2j}\right) \coth \left(\left(1 + \frac{1}{2j}\right)x \right) - \frac{1}{2j} \coth \left(\frac{1}{2j}x \right). \quad (3.7.17)$$

- 高温极限下, $x \rightarrow 0$, 有

$$\chi \equiv \frac{H}{M_z} \Big|_{\beta \rightarrow 0} = \frac{C_j}{T}, \quad C_j = \frac{N \mu_0 g^2 \mu_B^2 j(j+1)}{3k_B}, \quad (3.7.18)$$

和经典方法得到的结果一致.

3.8 thermodynamics of two-state systems: negative temperature

- 考虑一个由 $j = \frac{1}{2}, g = 2$ 的磁矩构成系统, 磁矩只有两个能级 $\pm\epsilon, \epsilon = \mu_B \mu_0 H$
- 系统的 partition function 为

$$Z_C(T, V, N) = \left(2 \cosh(\beta\epsilon) \right)^N. \quad (3.8.1)$$

- 得到

$$\begin{cases} U = -N\epsilon \tanh \frac{\epsilon}{k_B T} \iff \frac{1}{T} = \frac{k_B}{2\epsilon} \ln \frac{N\epsilon - U}{N\epsilon + U} \\ S = Nk_B \left(\ln \left(2 \cosh \frac{\epsilon}{k_B T} \right) - \frac{\epsilon}{k_B T} \tanh \frac{\epsilon}{k_B T} \right) \\ M_z = \frac{N}{V} \mu_B \tanh \frac{\epsilon}{k_B T} \\ C_{V,H} = Nk_B \left(\frac{\epsilon}{k_B T} \right)^2 \cosh^{-2} \frac{\epsilon}{k_B T} \end{cases}. \quad (3.8.2)$$

- 如果 $T < 0$, 那么 E 必须有上限, 否则 $Z_C \rightarrow \infty$.

3.8.1 negative temperature in a more general case

- 考虑一个具有能量上限的系统, 考虑其在 $\beta = 0$ 附近的行为.
- 系统的 partition function 为

$$Z_C(T, V, N) = \left(\sum_{i=0}^{N_{\text{EL}}} e^{-\beta \epsilon_i} \right)^N$$

$$\stackrel{\beta \rightarrow 0}{\simeq} \left(\sum_{i=0}^{N_{\text{EL}}} \left(1 - \beta \epsilon_i + \frac{1}{2} (\beta \epsilon_i)^2 \right) \right)^N = N_{\text{EL}}^N \left(1 - \beta \bar{\epsilon} + \frac{1}{2} \beta^2 \bar{\epsilon}^2 \right)^N, \quad (3.8.3)$$

因此

$$\ln Z_C(T, V, N) \simeq N \left(\ln N_{\text{EL}} - \beta \bar{\epsilon} + \frac{1}{2} \beta^2 (\bar{\epsilon}^2 - \bar{\epsilon}^2) \right). \quad (3.8.4)$$

- 得到

$$\begin{cases} U \simeq N \left(\bar{\epsilon} - \beta (\bar{\epsilon} - \bar{\epsilon})^2 \right) \\ S \simeq N k_B \left(\ln N_{\text{EL}} - \frac{1}{2} \beta^2 (\bar{\epsilon} - \bar{\epsilon})^2 \right) \\ C_V \simeq N k_B \beta^2 (\bar{\epsilon} - \bar{\epsilon})^2 \end{cases} \quad (3.8.5)$$

- 注意到, 两个系统具有温度 $\beta_1 > \beta_2$, 那么 A_2 向 A_1 传热.
 - 一个例子是负温度系统会向正温度系统传热, (这符合直觉, 因为负温度系统中的粒子平均能量更高, (这种说法当然不准确)).

proof:

考虑 A_1 向 A_2 传热 ΔQ , 那么

$$\Delta S_0 = \Delta S_1 + \Delta S_2 = k_B \Delta Q (-\beta_1 + \beta_2), \quad (3.8.6)$$

可见 $\Delta Q < 0$.

Chapter 4

the grand canonical ensemble

4.1 equilibrium between a system and a particle–energy reservoir

- 系统 A 和 particle–energy reservoir A_{PER} 存在能量和粒子交换,

$$\begin{cases} E_0 = E + E_{\text{PER}} \\ N_0 = N + N_{\text{PER}} \end{cases}, \quad \Omega_0(E_0, N_0) = \sum_{E, N} \Omega(E, N) \Omega_{\text{PER}}(E_0 - E, N_0 - N). \quad (4.1.1)$$

- 系统 A 处于 E, N 下的某一个 microstate 的概率为

$$P = \frac{\Omega_{\text{PER}}(E_0 - E, N_0 - N)}{\Omega_0} \simeq \frac{e^{-\beta(E - \mu N)}}{Z_{\text{GC}}}. \quad (4.1.2)$$

4.2 a system in the grand canonical ensemble

- 考虑一个由 \mathcal{N} 个全同子系统组成的系统, 总能量为 $\mathcal{E} = \mathcal{N} \langle E \rangle$, 总粒子数为 $N_{\text{GCE}} = \mathcal{N} \langle N \rangle$, 其中 $\langle E \rangle \equiv U, \langle N \rangle$ 分别是子系统能量和粒子数的期望值.
- $n_{i,N}$ 表示处于能级 E_i 且有 N 个粒子的子系统数量, 那么

$$\begin{cases} \sum_{i,N} n_{i,N} = \mathcal{N} \\ \sum_{i,N} n_{i,N} E_i = \mathcal{E} \\ \sum_{i,N} n_{i,N} N = N_{\text{GCE}} \end{cases}. \quad (4.2.1)$$

- $\{n_{i,N}\}$ 的微观态数量为

$$W\{n_{i,N}\} = \frac{\mathcal{N}!}{n_{0,1}! \cdots n_{N_{\text{EL}}, N_{\text{GCE}}}!} \implies \ln W\{n_{i,N}\} = \mathcal{N} \ln \mathcal{N} - \sum_{i,N} n_{i,N} \ln n_{i,N}. \quad (4.2.2)$$

- 最概然分布为

$$n_{i,N}^* = \mathcal{N} \frac{e^{-\beta(E_i - \mu N)}}{Z_{\text{GC}}} \approx \langle n_{i,N} \rangle. \quad (4.2.3)$$

- 并且有

$$\begin{cases} \langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{\text{GC}} \\ \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_{\text{GC}} \end{cases}. \quad (4.2.4)$$

4.3 the partition function and the grand potential

- 定义 fugacity,

$$z := e^{\beta\mu}. \quad (4.3.1)$$

- the partition function of the grand canonical ensemble 为

$$Z_{GC}(T, V, z) = \sum_{i, N} z^N e^{-\beta E_i} = \sum_{N=1}^{\infty} z^N Z_C(E, V, N), \quad (4.3.2)$$

and the grand potential is

$$\Phi_G(T, V, \mu) = -k_B T \ln Z_{GC}(T, V, z). \quad (4.3.3)$$

4.4 particle number fluctuations in the grand canonical ensemble

- grand canonical ensemble 中的系统的粒子数和能量的方差是

$$\begin{cases} \langle (\Delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \ln Z_{GC} = \frac{1}{\beta} \left(\frac{\partial N}{\partial \mu} \right)_{T, V}, \\ \langle (\Delta E)^2 \rangle = \frac{\partial^2}{\partial \beta^2} \ln Z_{GC} = - \left(\frac{\partial U}{\partial \beta} \right)_{V, z} \end{cases}, \quad (4.4.1)$$

因此

$$\begin{cases} \frac{\sqrt{\langle (\Delta N)^2 \rangle}}{\langle N \rangle} = \sqrt{\frac{k_B T}{V} \kappa_T} \\ \langle (\Delta E)^2 \rangle = \langle (\Delta E)^2 \rangle_C + \left(\left(\frac{\partial U}{\partial N} \right)_{T, V} \right)^2 \langle (\Delta N)^2 \rangle \end{cases}, \quad (4.4.2)$$

通常 $\kappa_T \sim \frac{1}{P}$, 因此

$$\begin{cases} \frac{\sqrt{\langle (\Delta N)^2 \rangle}}{\langle N \rangle} \sim N^{-\frac{1}{2}} \\ \frac{\sqrt{\langle (\Delta E)^2 \rangle}}{U} \sim N^{-\frac{1}{2}} \end{cases}. \quad (4.4.3)$$

calculation:

考虑 $N(T, V, \mu)$, 注意对 homogeneous system $SdT = VdP - Nd\mu$,

$$dN = \left(\frac{\partial N}{\partial \mu} \right)_{T, V} \underbrace{\left(-\frac{S}{N} dT + \frac{V}{N} dP \right)}_{=d\mu} + \left(\frac{\partial N}{\partial T} \right)_{V, \mu} dT + \left(\frac{\partial N}{\partial V} \right)_{T, \mu} dV, \quad (4.4.4)$$

因此

$$\left(\frac{\partial N}{\partial \mu} \right)_{T, V} \frac{V}{N} = \left(\frac{\partial N}{\partial P} \right)_{T, V} = - \frac{\left(\frac{\partial V}{\partial P} \right)_{T, N}}{\left(\frac{\partial V}{\partial N} \right)_{T, P}}, \quad (4.4.5)$$

对 homogeneous system

$$\left(\frac{\partial V}{\partial N} \right)_{T, P} = \frac{V}{N}, \quad (4.4.6)$$

因此

$$\left(\frac{\partial N}{\partial \mu} \right)_{T, V} = - \frac{N^2}{V^2} \left(\frac{\partial V}{\partial P} \right)_{T, N} = \frac{N^2}{V} \kappa_T \implies \frac{\langle (\Delta N)^2 \rangle}{N^2} = \frac{k_B T}{V} \kappa_T. \quad (4.4.7)$$

代入 $z = e^{\beta\mu}$,

$$\langle (\Delta E)^2 \rangle = - \left(\frac{\partial U}{\partial \beta} \right)_{V, z} = k_B T^2 \left(\frac{\partial U}{\partial T} \right)_{V, \mu} + k_B T \mu \left(\frac{\partial U}{\partial \mu} \right)_{T, V}, \quad (4.4.8)$$

且

$$\left(\frac{\partial U}{\partial T} \right)_{V, \mu} + \left(\frac{\partial U}{\partial \mu} \right)_{T, V} \left(\frac{\partial \mu}{\partial T} \right)_{V, N} = \left(\frac{\partial U}{\partial T} \right)_{V, N} = C_V, \quad (4.4.9)$$

代入,

$$\langle(\Delta E)^2\rangle = k_B T^2 C_V + k_B T \left(\mu - T \left(\frac{\partial \mu}{\partial T} \right)_{V,N} \right) \left(\frac{\partial U}{\partial \mu} \right)_{T,V}, \quad (4.4.10)$$

注意 $\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$, 因此

$$\begin{aligned} \mu - T \left(\frac{\partial \mu}{\partial T} \right)_{V,N} &= \left(\frac{\partial F}{\partial N} \right)_{T,V} - T \frac{\partial}{\partial T} \Big|_{V,N} \left(\frac{\partial F}{\partial N} \right)_{T,V} \\ &= \left(\frac{\partial F}{\partial N} \right)_{T,V} - T \frac{\partial}{\partial N} \Big|_{T,V} \underbrace{\left(\frac{\partial F}{\partial T} \right)_{V,N}}_{=-S} \\ &= \left(\frac{\partial(F+TS)}{\partial N} \right)_{T,V} = \left(\frac{\partial U}{\partial N} \right)_{T,V}, \end{aligned} \quad (4.4.11)$$

所以

$$\langle(\Delta E)^2\rangle = \underbrace{k_B T^2 C_V}_{=\langle(\Delta E)^2\rangle_C} + k_B T \left(\frac{\partial U}{\partial N} \right)_{T,V} \left(\frac{\partial U}{\partial \mu} \right)_{T,V}, \quad (4.4.12)$$

最后注意到

$$\left(\frac{\partial U}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial \mu} \right)_{T,V} = \left(\frac{\partial U}{\partial \mu} \right)_{T,V}, \quad (4.4.13)$$

得到

$$\langle(\Delta E)^2\rangle = \langle(\Delta E)^2\rangle_C + \left(\left(\frac{\partial U}{\partial N} \right)_{T,V} \right)^2 \langle(\Delta N)^2\rangle. \quad (4.4.14)$$

4.5 examples

4.5.1 classical ideal gas

- 现在来考虑更一般的理想气体 (粒子可能有 internal degrees of motion), 此时

$$Z_C(T, V, N) = \frac{(Z_C(T, V, 1))^N}{N!}, \quad (4.5.1)$$

而

$$Z_C(T, V, 1) = V \phi(T). \quad (4.5.2)$$

- 理想气体的 Z_{GC} 为

$$Z_{GC}(T, V, z) = \sum_{N=1}^{\infty} z^N \frac{(V \phi(T))^N}{N!} = e^{z V \phi(T)}, \quad (4.5.3)$$

因此

$$\begin{cases} \Phi_G = -k_B T z V \phi(T) \\ U = k_B T^2 z V \phi'(T) \\ N = z V \phi(T) \\ P = \frac{N k_B T}{V} \\ S = N k_B \left(-\ln z + z \frac{V}{N} (T \phi'(T) + \phi(T)) \right) \end{cases}. \quad (4.5.4)$$

4.5.2 solid: a system of harmonic oscillators

- 固体的 Einstein model.
- 系统的 partition function 为 (固体每个粒子有 $D = 3$ 个振动方向, 对 $\phi(T)$ 作相应改动)

$$Z_C(T, V, N) = (Z_C(T, V, 1))^N, \quad Z_C(T, V, 1) = \phi(T) = \begin{cases} \frac{1}{2 \sinh \frac{\hbar \omega}{2 k_B T}} & \text{quantum mechanically} \\ \frac{k_B T}{\hbar \omega} & \text{classically} \end{cases}. \quad (4.5.5)$$

- 系统 Z_{GC} 为

$$Z_{GC} = \sum_{N=1}^{\infty} z^N \phi^N(T) = \frac{1}{1 - z\phi(T)}, \quad (4.5.6)$$

因此

$$\begin{cases} N = \frac{z\phi(T)}{1 - z\phi(T)} \Rightarrow z\phi(T) \simeq 1 - \frac{1}{N} \iff \beta\mu \simeq -\frac{1}{N} - \ln \phi(T) \\ U = Nk_B T^2 \frac{\phi'(T)}{\phi(T)} \\ S = Nk_B \left(\ln \pi(T) + T \frac{\phi'(T)}{\phi(T)} + O\left(\frac{\ln N}{N}\right) \right) \end{cases}. \quad (4.5.7)$$

4.5.3 solid-vapor equilibrium

- 考虑一个由固态和气态组成的系统, 具有温度 T 和体积 V .
- 固态和液态具有相同的 fugacity, 结合 (4.5.4) 和 (4.5.7),

$$\frac{N_g}{V_g \phi_g(T)} = z_g = z_s \simeq \frac{1}{\phi_s(T)} \Rightarrow \frac{N_g}{V_g} = \frac{P_{\text{vapor}}}{k_B T} = \frac{\phi_g(T)}{\phi_s(T)}, \quad (4.5.8)$$

代入单原子气体的 $\phi_g(T)$ 和 Einstein model 的 $\phi_s(T)$, 得到

$$P_{\text{vapor}} = k_B T \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \left(2 \sinh \frac{\hbar\omega}{2k_B T} \right)^3 e^{-\frac{\epsilon}{k_B T}} \\ \underset{\text{classically}}{\simeq} k_B T \left(\frac{m\omega^2}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{\epsilon}{k_B T}}, \quad (4.5.9)$$

其中 $\epsilon = \epsilon_g - \epsilon_s$ 是粒子处于固态和气态的能量差.

4.6 thermodynamic phase diagram

- 一个典型的 P - V - T phase diagram 如下 (来自 Wikipedia):

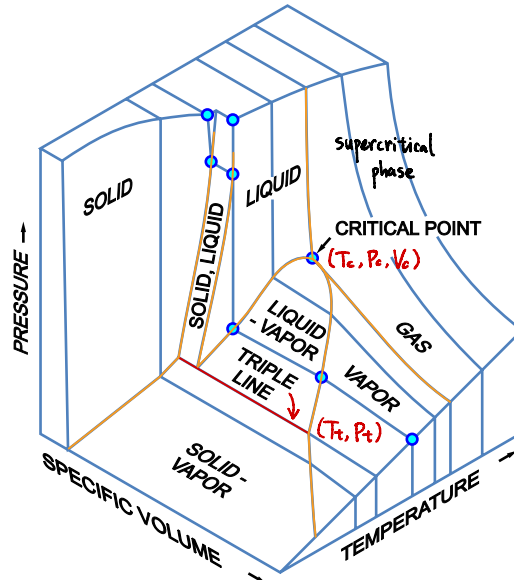


Figure 4.1: P - V - T phase diagram

- 几个重要的特征:
 - triple line & triple point.
 - critical point.
 - two-phase coexistence planes.

4.7 phase equilibrium and the Clausius–Clapeyron equation

- $P_\sigma(T)$ 描述 P - T 面上的 phase boundary between two phases, 有 Clausius–Clapeyron equation,

$$\frac{dP_\sigma}{dT} = \frac{s_B - s_A}{v_B - v_A} = \frac{L}{T\Delta v}, \quad (4.7.1)$$

其中 s 是 entropy per particle, v 是 specific volume, L 是 latent heat per particle (即 A 相转化为 B 相的吸热).

proof:

两相共存要求 $\mu_A = \mu_B$, 对于 homogeneous systems,

$$sdT = vdP - d\mu \implies d\mu = -sdT + vdP, \quad (4.7.2)$$

因此

$$-s_A dT + v_A dP = -s_B dT + v_B dP \implies \dots \quad (4.7.3)$$

- 在 triple point, 3 条两相共存线的斜率保证任何一条共存线 (比如 A - B 相共存线) 指向第三个相 (C 相), 如下图所示.

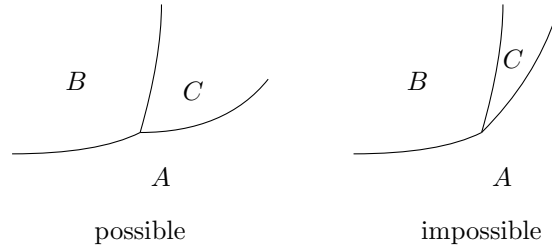


Figure 4.2: the slopes of 3 coexistence lines.

proof:

注意到

$$\Delta s_{AB} + \Delta s_{BC} + \Delta s_{CA} \equiv 0, \quad \Delta v_{AB} + \Delta v_{BC} + \Delta v_{CA} \equiv 0, \quad (4.7.4)$$

为了方便, 接下来分别用指标 1, 2, 3 替代 AB, BC, CA .

我们需要证明 $u_i = (\Delta v_i, \Delta s_i), i = 1, 2, 3$ 满足

$$\sum_{i=1}^3 \alpha_i u_i = 0, \quad \text{with } \alpha_i > 0, \quad (4.7.5)$$

显然成立, $\alpha_i = 1$.

Chapter 5

formulation of quantum statistics

5.1 quantum mechanical ensemble theory: the density matrix

- 用 density matrix 描述一个 ensemble,

$$\rho = \sum_i p_i |\psi_i\rangle \langle \psi_i|, \quad (5.1.1)$$

在 Schrödinger 绘景下

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]. \quad (5.1.2)$$

- density matrix 满足

$$\text{Tr } \rho = 1, \quad \text{Tr } \rho^2 \leq 1, \quad (5.1.3)$$

其中第二个等号在 pure state 下成立.

- the von Neumann entropy is

$$S = -\text{Tr } \rho \ln \rho. \quad (5.1.4)$$

- stationary ensemble 的定义与 chapter 2 中一样, 见 (2.1.2).

5.2 statistics of the various ensembles

5.2.1 the microcanonical ensemble

- microcanonical ensemble 的 density matrix 为

$$\rho = \sum_{\text{some } i} \frac{1}{\Omega} |i\rangle \langle i|, \quad (5.2.1)$$

其中 $|i\rangle$ 是能量本征态, 对所有 accessible states 求和.

5.2.2 the canonical ensemble

- canonical ensemble 的 density matrix 为

$$\rho = \frac{e^{-\beta H}}{Z_C}, \quad Z_C = \text{Tr } e^{-\beta H}. \quad (5.2.2)$$

- 各热力学量为

$$\begin{cases} F = -k_B T \ln Z_C(T, V, N) \\ S = -\left(\frac{\partial F}{\partial T}\right)_{V, N} = k_B \left(\ln Z_C + T \frac{\partial}{\partial T} \ln Z_C \right) \end{cases}. \quad (5.2.3)$$

5.2.3 the grand canonical ensemble

- grand canonical ensemble 的 density matrix 为

$$\rho = \frac{e^{-\beta(H-\mu N)}}{Z_{GC}}. \quad (5.2.4)$$

- 各热力学量为

$$\begin{cases} \Phi_G = k_B T \ln Z_{GC}(T, V, \mu) \\ S = \left(\frac{\partial \Phi_G}{\partial T} \right)_{V, \mu} = k_B \left(\ln Z_{GC} + T \frac{\partial}{\partial T} \ln Z_{GC} \right) \end{cases} \quad (5.2.5)$$

5.3 example: an electron in a magnetic field

- 电子自旋为 $\frac{\hbar}{2}\vec{\sigma}$, 那么电子在磁场中的 Hamiltonian 为

$$\hat{H} = -\mu_0(-\mu_B \vec{\sigma}) \cdot \vec{H} = \mu_0 \mu_B H \sigma_z, \quad (5.3.1)$$

其中 Bohr magneton $\mu_B = \frac{e\hbar}{2m}$.

- density matrix in the canonical ensemble is

$$\rho = \frac{e^{-\beta \hat{H}}}{Z_C} = \frac{1}{2 \cosh(\beta \mu_0 \mu_B H)} \begin{pmatrix} e^{-\beta \mu_0 \mu_B H} & 0 \\ 0 & e^{\beta \mu_0 \mu_B H} \end{pmatrix}. \quad (5.3.2)$$

- 得到

$$\langle \sigma_z \rangle = \text{Tr}(\sigma_z \rho) = \tanh(\beta \mu_0 \mu_B H). \quad (5.3.3)$$

5.4 the thermal de Broglie wavelength and the statistical potential

- 考虑一个由 2 个 indistinguishable 粒子组成的系统.
- 在 \vec{x}_1, \vec{x}_2 分别发现一个粒子的概率密度为

$${}_{\text{F or B}} \langle \vec{x}_1, \vec{x}_2 | \rho_C | \vec{x}_1, \vec{x}_2 \rangle_{\text{F or B}} \approx \frac{1}{V^2} \left(1 + \eta e^{-2\pi \frac{|\vec{x}_1 - \vec{x}_2|^2}{\lambda^2}} \right), \quad \eta = \begin{cases} +1 & \text{Bosons} \\ -1 & \text{Fermions} \end{cases}, \quad (5.4.1)$$

其中

$$\lambda = \left(\frac{2\pi\beta\hbar^2}{m} \right)^{\frac{1}{2}} = \frac{h}{\sqrt{2\pi m k_B T}} \quad (5.4.2)$$

称为 thermal de Broglie wavelength, 如果 $n\lambda^3 \ll 1$, 量子效应不明显, 可以使用 Boltzmann statistics.

calculation:

$$\begin{aligned} {}_{\text{F}} \langle \vec{x}_1, \vec{x}_2 | e^{-\beta H} | \vec{x}_1, \vec{x}_2 \rangle_{\text{F}} &= \int \frac{d^3 k_1}{(2\pi)^3} \frac{d^3 k_2}{(2\pi)^3} e^{-\beta \left(\frac{k_1^2}{2m} + \frac{k_2^2}{2m} \right)} \frac{1}{2} \left(1 - \text{Re} e^{i(\vec{x}_1 - \vec{x}_2) \cdot (\vec{k}_1 - \vec{k}_2)} \right) \\ &= \frac{1}{2} \frac{1}{(2\pi)^6} \left(\frac{2\pi m}{\beta \hbar^2} \right)^3 - \frac{1}{2} \frac{1}{(2\pi)^6} \left(\frac{2\pi m}{\beta \hbar^2} \right)^3 \text{Re} \exp \left(-\frac{m}{\beta \hbar^2} |\vec{x}_1 - \vec{x}_2|^2 \right) \\ &= \frac{1}{2\lambda^6} \left(1 - e^{-2\pi \frac{|\vec{x}_1 - \vec{x}_2|^2}{\lambda^2}} \right), \end{aligned} \quad (5.4.3)$$

那么

$$\begin{aligned} Z_C &= \int d^3 x_1 d^3 x_2 {}_{\text{F}} \langle \vec{x}_1, \vec{x}_2 | e^{-\beta H} | \vec{x}_1, \vec{x}_2 \rangle_{\text{F}} \\ &= \frac{V^2}{2\lambda^6} - \frac{1}{2\lambda^6} \int d^3 x_1 d^3 x_2 e^{-2\pi \frac{|\vec{x}_1|^2 + |\vec{x}_2|^2 - 2\vec{x}_1 \cdot \vec{x}_2}{\lambda^2}} \\ &= \frac{V^2}{2\lambda^6} - \frac{1}{2\lambda^6} \int d^3 x_2 e^{-2\pi \frac{|\vec{x}_2|^2}{\lambda^2}} \left(\frac{\pi \lambda^2}{2\pi} \right)^{\frac{3}{2}} e^{\frac{\lambda^2}{8\pi} \left(\frac{4\pi}{\lambda^2} \vec{x}_2 \right)^2} \end{aligned}$$

$$= \frac{V^2}{2\lambda^6} \left(1 - \frac{1}{2^{3/2}} \frac{\lambda^3}{V}\right) \approx \frac{V^2}{2\lambda^6}, \quad (5.4.4)$$

Bosons 的情况类似.

- 如果两个粒子可区分,

$$\langle \vec{x}_1, \vec{x}_2 | \rho_C | \vec{x}_1, \vec{x}_2 \rangle = \frac{1}{V^2}. \quad (5.4.5)$$

- 因此, (5.4.1) 中的 correlation 可以用一个势能 $v_s(r)$ 替代, 从而用经典力学的方法模拟这种量子统计效应,

$$v_s(r) = -k_B T \ln \left(1 + \eta e^{-2\pi \frac{|\vec{x}_1 - \vec{x}_2|^2}{\lambda^2}} \right), \quad (5.4.6)$$

函数图像如下:

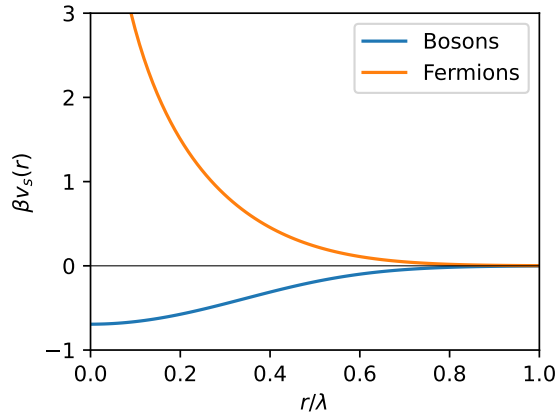


Figure 5.1: statistical potential.

proof:

只需要在 canonical ensemble 中引入一个 Boltzmann factor

$$e^{-\beta v_s(r)} = 1 + \eta e^{-2\pi \frac{|\vec{x}_1 - \vec{x}_2|^2}{\lambda^2}}. \quad (5.4.7)$$

5.5 eigenstate thermalization hypothesis

- ergodicity of classical systems 要求几乎所有初始态都演化到均匀覆盖相空间中的等能面.
 - integrable systems 一定不是 ergodic, 因为它们有 ν 个 constants of motion, 无法覆盖 $\nu - 1$ 维 energy surface.
 - ergodic hypothesis 只在几个特例里被证明, 如 hard sphere gas.
- 因为量子系统的演化有么正性, 所以即便对应的经典系统有遍历性, 这个量子系统也不可能出现 ergodic-like behavior, 因此孤立的量子系统不可能热化.

- 如果一个可观测量 $\langle O \rangle$ 从 a wide range of possible initial values, 在实验时间尺度内, 演化到一个 unique time-independent value (with small fluctuations), 则称 O 表现出 equilibrium behavior,

$$O \text{ displays equilibrium behavior} \iff \lim_{t \rightarrow \infty} \langle O(t) \rangle = \text{Const.} \quad (5.5.1)$$

- 一般来说, 这样的 O 不可能存在, 因为

$$\langle \psi(t) | O | \psi(t) \rangle = \sum_{m,n} c_m^* O_{mn} c_n e^{-i(E_n - E_m)t/\hbar}, \quad (5.5.2)$$

其时间平均值为

$$\text{time average of } \langle O(t) \rangle = \sum_n |c_n|^2 O_{nn} + \sum_{E_m=E_n, m \neq n} c_m^* O_{mn} c_n, \quad (5.5.3)$$

永远依赖于初始条件.

- 但是, 可能存在一些多体系统, 它们的 a large but restricted set of pure states and a large but restricted set of observables will thermalize.
- 注意到:
 - 对于 homogeneous systems, $S \propto \nu$, (ν 是 degrees of freedom), 因此能量本征态的数量正比于 $e^{\alpha\nu}$.
 - 能级简并数可以忽略, (比如理想气体 $\Omega(E) \propto \left(\frac{e^{\alpha'}}{\nu}\right)^\nu$).

- 此时

$$\text{time average of } \langle O(t) \rangle \simeq \sum_n |c_n|^2 O_{nn}, \quad (5.5.4)$$

考虑 pure state with energy eigenvalue E ,

$$c_n \neq 0 \quad \text{when} \quad E_n = E, \quad (5.5.5)$$

令

$$O_{nn} = O(E) + \delta O_n, \quad E_n = E, \quad (5.5.6)$$

且如果 δO_n 满足

$$\sum_n |c_n|^2 \delta O_n \ll O(E), \forall c_n, \quad (5.5.7)$$

那么 $\langle O(t) \rangle$ 的时间平均就与初始条件 (即 c_n) 的选取无关了.

- 最后, 还要求 $\langle O(t=0) \rangle$ 可以明显偏离 $O(E)$, 但是随后 $t > 0$ 时的涨落却可以忽略.

- 满足这些条件的 local operator 具有如下形式

$$O_{mn} \approx O(E_n) \delta_{mn} + \frac{O_2(E_m, E_n)}{\sqrt{\Gamma}} R_{mn}, \quad (5.5.8)$$

其中 $\{R_{mn}\}$ 是一个 $\Gamma \times \Gamma$ real symmetric Gaussian random matrix, $O(\cdot), O_2(\cdot, \cdot)$ 是光滑函数.

- random matrix R 具有以下特征:

- 对角元平均值为 0, and variance $\sigma^2 = 2$.
- 满足

$$\begin{cases} \frac{1}{\Gamma} \langle \text{Tr } R \rangle = 0 \\ \frac{1}{\Gamma} \langle \text{Tr } R^2 \rangle = \Gamma + 1 \end{cases}, \quad (5.5.9)$$

其中 $\langle \cdot \rangle$ 表示对矩阵元的 normal distribution 的期望值.

- 对于 $\Gamma \gg 1$, R 的本征值 λ 的概率分布函数呈半圆形

$$\rho(x = \frac{\lambda}{\sqrt{\Gamma}}) = \frac{1}{2\pi} \sqrt{4 - x^2}, x \in [-2, 2], \quad (5.5.10)$$

因此 $\langle (\Delta\lambda)^2 \rangle = \Gamma$, 与 (5.5.9) 相符 ($\Gamma \gg 1$).

- 还有一些性质, 见 Pathria, Beale, *Statistical Mechanics*, page 147.

- ...

Chapter 6

the theory of simple gases

6.1 an ideal gas in various quantum-mechanical ensembles

6.1.1 in a microcanonical ensemble

- 用能级 ϵ_i (不是能量本征态) 上的粒子数 n_i 表示系统的状态 $\{n_i\}$, 有

$$\begin{cases} \sum_i n_i = N \\ \sum_i n_i \epsilon_i = E \end{cases}, \quad (6.1.1)$$

系统的微观状态数为

$$\begin{cases} W_B\{n_i\} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \\ W_F\{n_i\} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \quad n_i \leq g_i \end{cases}, \quad (6.1.2)$$

其中 g_i 表示粒子的 ϵ_i 能级的 degeneracy.

- 用 Stirling 公式作近似,

$$\begin{cases} \ln W_B\{n_i\} \approx \sum_i \left((n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i \right) \\ \ln W_F\{n_i\} \approx \sum_i \left(g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i) \right) \end{cases}. \quad (6.1.3)$$

calculation:

对于 Bose-Einstein statistics, 往 g_i 个格子中放 n_i 个 indistinguishable 小球, 有

$$\begin{cases} \frac{g_i^{n_i}}{n_i!} & \text{一个格子放多个球的情况可忽略时, 即 } g_i \gg n_i \\ \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} & \text{插板法} \end{cases} \quad (6.1.4)$$

种放法. 插板法: 球 (n_i 个) 和板 ($g_i - 1$ 个) 都是 indistinguishable, 它们各自可以放在 $(n_i + g_i - 1)!$ 个位置...

对于 Fermi-Dirac statistics, 每个格子最多一个小球, 有

$$\frac{g_i!}{n_i!(g_i - n_i)!} \quad (6.1.5)$$

种放法.

- 最概然分布为

$$\begin{cases} n_i^* = \frac{g_i}{e^{\alpha+\beta\epsilon_i} - 1} & \text{Bose-Einstein} \\ n_i^* = \frac{g_i}{e^{\alpha+\beta\epsilon_i} + 1} & \text{Fermi-Dirac} \end{cases}, \quad (6.1.6)$$

此时

$$\ln W\{n_i^*\} = \alpha N + \beta E - \frac{1}{\eta} \sum_i g_i \ln(1 - \eta e^{-\alpha-\beta\epsilon_i}), \quad \text{with } \eta = \begin{cases} +1 & \text{Bose-Einstein} \\ -1 & \text{Fermi-Dirac} \\ \rightarrow 0 & \text{Boltzmann} \end{cases}, \quad (6.1.7)$$

其中 $\alpha = -\beta\mu$.

- 注意 $PV = TS - U + \mu N$, 得到

$$PV = -\frac{1}{\eta} k_B T \sum_i g_i \ln(1 - \eta e^{-\alpha-\beta\epsilon_i}) \xrightarrow{\eta \rightarrow 0} N k_B T. \quad (6.1.8)$$

6.1.2 in a canonical ensemble

- 系统的 partition function 为

$$Z_C = \sum_{\{n_i\}} W\{n_i\} e^{-\beta E\{n_i\}}, \quad (6.1.9)$$

求和需要满足 $\sum_i n_i = N$ 的约束条件, 不方便处理, 这个约束在 grand canonical ensemble 中不存在.

6.1.3 in a grand canonical ensemble

- 系统的 grand partition function 为

$$Z_{GC} = \prod_i \exp\left(-\frac{g_i}{\eta} \ln(1 - \eta e^{-\alpha-\beta\epsilon_i})\right) = \begin{cases} \prod_i (1 - e^{-\alpha-\beta\epsilon_i})^{-g_i} & \text{Bose-Einstein} \\ \prod_i (1 + e^{-\alpha-\beta\epsilon_i})^{g_i} & \text{Fermi-Dirac} \\ \prod_i \exp(g_i e^{-\alpha-\beta\epsilon_i}) & \text{Boltzmann} \end{cases}, \quad (6.1.10)$$

它们的函数图像分别为如下图 (观察到 ϵ 越大 (等价于 β 越大), 三种统计的差别越小; g 显然没有影响):

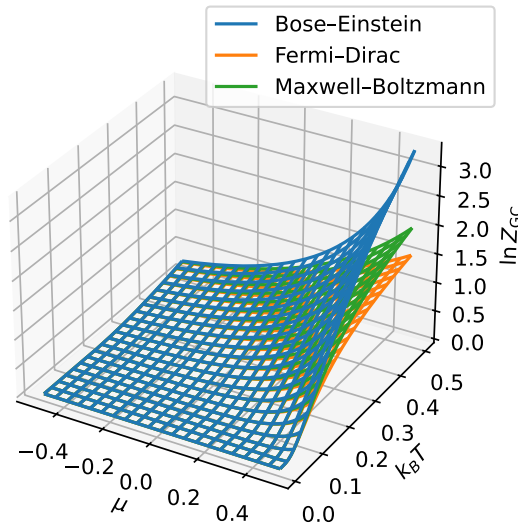


Figure 6.1: grand partition functions with $g = 3, \epsilon = 0.7$.

calculation:

麻烦的方法是

$$Z_{\text{GC}} = \sum_{\{n_i=0\}}^{\{n_i=\max\}} W\{n_i\} e^{-\beta E\{n_i\} - \alpha N\{n_i\}}. \quad (6.1.11)$$

对 Bose–Einstein statistics,

$$Z_{\text{GC}} = \prod_i \sum_{n_i=0}^{\infty} \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} (e^{-\alpha - \beta \epsilon_i})^{n_i}, \quad (6.1.12)$$

注意到 Taylor expansion

$$\frac{1}{(1-x)^n} = \sum_{m=0}^{\infty} \frac{1}{m!} \frac{(n+m-1)!}{(n-1)!} x^m, \quad (6.1.13)$$

所以

$$Z_{\text{GC}} = \prod_i (1 - e^{-\alpha - \beta \epsilon_i})^{-g_i}. \quad (6.1.14)$$

对于 Fermi–Dirac statistics,

$$Z_{\text{GC}} = \prod_i \sum_{n_i=0}^{g_i} \frac{g_i!}{n_i! (g_i - n_i)!} (e^{-\alpha - \beta \epsilon_i})^{n_i}, \quad (6.1.15)$$

注意到

$$(1+x)^n = \sum_{m=1}^n \frac{1}{m!} \frac{n!}{(n-m)!} x^m, \quad (6.1.16)$$

所以

$$Z_{\text{GC}} = \prod_i (1 + e^{-\alpha - \beta \epsilon_i})^{g_i}. \quad (6.1.17)$$

对于 Maxwell–Boltzmann statistics,

$$Z_{\text{GC}} = \prod_i \sum_{n_i=0}^{\infty} \frac{g_i^{n_i}}{n_i!} (e^{-\alpha - \beta \epsilon_i})^{n_i} = \prod_i \exp(g_i e^{-\alpha - \beta \epsilon_i}). \quad (6.1.18)$$

实际上, 用每个能量本征态 (而不是能级) 上的粒子数计算更方便, 只需要把 (6.1.12) ~ (6.1.18) 中的 $g_i \mapsto 1$ 即可.

– 注意到这里没有用 $n_i, g_i \gg 1$ 的条件.

• 得到

$$\begin{cases} \Phi_{\text{G}} = -k_B T \ln Z_{\text{GC}} \\ U = \sum_i \frac{g_i \epsilon_i}{e^{\alpha + \beta \epsilon_i} - \eta} \\ N = \sum_i \frac{g_i}{e^{\alpha + \beta \epsilon_i} - \eta} \\ \langle n_i \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \ln Z_{\text{GC}} = \frac{g_i}{e^{\alpha + \beta \epsilon_i} - \eta} \\ S = k_B (\beta U + \alpha N + \ln Z_{\text{GC}}) \end{cases}. \quad (6.1.19)$$

6.2 statistics of the occupation numbers

• 能级 ϵ_i 上的粒子数为

$$\langle n_i \rangle = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} - \eta}, \quad (6.2.1)$$

其函数图像如下:

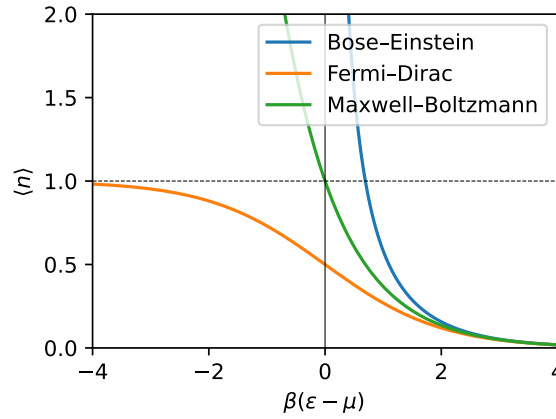


Figure 6.2: plot of $\langle n \rangle$ with $g = 1$.

- n_i 的方差为

$$\frac{\langle (\Delta n_i)^2 \rangle}{\langle n_i \rangle^2} = \frac{1}{\langle n_i \rangle} + \frac{\eta}{g_i}. \quad (6.2.2)$$

calculation:

$$\begin{aligned} \langle (\Delta n_i)^2 \rangle &= \langle n_i^2 \rangle - \langle n_i \rangle^2 = \frac{1}{Z_{GC}} \frac{1}{\beta^2} \frac{\partial^2}{\partial \epsilon_i^2} Z_{GC} - \frac{1}{\beta^2} \left(\frac{\partial}{\partial \epsilon_i} \ln Z_{GC} \right)^2 \\ &= \frac{1}{\beta^2} \frac{\partial^2}{\partial \epsilon_i^2} \ln Z_{GC} = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \langle n_i \rangle = \dots \end{aligned} \quad (6.2.3)$$

- 更进一步, 根据 (6.1.10), 能量本征态 (不是能级) 占有 n_i 个粒子的概率是

$$p(n_i) = \begin{cases} \frac{\langle n_i \rangle^{n_i}}{(\langle n_i \rangle + 1)^{n_i+1}} & \text{Bose-Einstein} \\ \begin{cases} \langle n_i \rangle & n_i = 1 \\ 1 - \langle n_i \rangle & n_i = 0 \end{cases} & \text{Fermi-Dirac} \\ \frac{\langle n_i \rangle^{n_i}}{n_i!} e^{-\langle n_i \rangle} & \text{Boltzmann} \end{cases} \quad (6.2.4)$$

calculation:

能级占有 n_i 个粒子的概率是

$$p(n_i) = \begin{cases} \frac{\frac{(n_i+g_i-1)!}{n_i!(g_i-1)!} (e^{-\alpha-\beta\epsilon_i})^{n_i}}{(1 - e^{-\alpha-\beta\epsilon_i})^{-g_i}} = \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!} \frac{g_i^{g_i} \langle n_i \rangle^{n_i}}{(\langle n_i \rangle + g_i)^{g_i+n_i}} & \text{Bose-Einstein} \\ \frac{\frac{g_i!}{n_i!(g_i-n_i)!} (e^{-\alpha-\beta\epsilon_i})^{n_i}}{(1 + e^{-\alpha-\beta\epsilon_i})^{g_i}} = \frac{g_i!}{n_i!(g_i-n_i)!} \frac{\langle n_i \rangle^{n_i} (g_i - \langle n_i \rangle)^{g_i-n_i}}{g_i^{g_i}} & \text{Fermi-Dirac} \\ \frac{\frac{g_i^{n_i}}{n_i!} (e^{-\alpha-\beta\epsilon_i})^{n_i}}{\exp(g_i e^{-\alpha-\beta\epsilon_i})} = \frac{\langle n_i \rangle^{n_i}}{n_i!} e^{-\langle n_i \rangle} & \text{Boltzmann} \end{cases} \quad (6.2.5)$$

6.3 kinetic considerations

- 气体的压强和 rate of effusion 分别为

$$\begin{cases} P = \frac{1}{3} \frac{N}{V} \langle |\vec{p}| |\vec{u}| \rangle \\ R = \frac{1}{4} \frac{N}{V} \langle |\vec{u}| \rangle \end{cases}, \quad (6.3.1)$$

其中 \vec{u} 是分子速度, 上式与统计方法无关.

calculation:

都是直接从动力学计算, 令粒子速度分布为 $f(|\vec{u}|)$, ...

6.4 gaseous systems composed of molecules with internal motion

- 本 section 在经典统计极限下 ($n\lambda^3 \ll 1$) 计算.
- 令粒子的能级为

$$\epsilon = \underbrace{\frac{|\vec{p}|^2}{2m}}_{=\epsilon_K} + \epsilon_{\text{in}}, \quad (6.4.1)$$

其中 ϵ_{in} 是 internal motion 的能量.

- 系统的 grand partition function 为

$$\frac{PV}{k_B T} = \ln Z_{\text{GC}} = \frac{V}{\lambda^3} z j(T), \quad (6.4.2)$$

其中 internal partition function 为

$$j(T) = \sum_{\text{internal}} g_{\text{in}}(\epsilon_{\text{in}}) e^{-\beta \epsilon_{\text{in}}}. \quad (6.4.3)$$

calculation:

$$\begin{aligned} \ln Z_{\text{GC}} &= \sum_i g_i z e^{-\beta \epsilon_i} = z \sum_{\epsilon_K} g_K(\epsilon_K) e^{-\beta \epsilon_K} \sum_{\text{internal}} g_{\text{in}}(\epsilon_{\text{in}}) e^{-\beta \epsilon_{\text{in}}} \\ &= \frac{V}{\lambda^3} z \sum_{\text{internal}} g_{\text{in}}(\epsilon_{\text{in}}) e^{-\beta \epsilon_{\text{in}}}. \end{aligned} \quad (6.4.4)$$

- 得到

$$\begin{cases} N = z \frac{\partial}{\partial z} \ln Z_{\text{GC}} = \frac{V}{\lambda^3} z j(T) \iff \mu = k_B T (\ln n \lambda^3 - \ln j(T)) \\ U = -\frac{\partial}{\partial \beta} \ln Z_{\text{GC}}(T, V, z) = N \left(\frac{3}{2} k_B T + k_B T^2 \frac{\partial}{\partial T} \ln j(T) \right) \\ S = N k_B \left(\frac{5}{2} - \beta \mu + T \frac{\partial}{\partial T} \ln j(T) \right) \end{cases}. \quad (6.4.5)$$

- 分子的 internal energy 由以下四种因素决定:

1. the electronic state,
2. the state of nuclei,
3. the vibrational state,
4. the rotational state,

严格说, these four excitation modes mutually interact, 但大多数情况下, 他们可以单独处理.

- 因此 $j(T)$ 可以写作

$$j(T) = j_{\text{elec}}(T) j_{\text{nuc}}(T) j_{\text{vib}}(T) j_{\text{rot}}(T), \quad (6.4.6)$$

当 nuclei state 和 rotational state 的相互作用不可忽略时,

$$j(T) = j_{\text{elec}}(T) j_{\text{nuc-rot}}(T) j_{\text{vib}}(T). \quad (6.4.7)$$

6.4.1 monatomic molecules

- 考虑温度远低于 ionization energy 的单原子气体, $T \ll \epsilon_{\text{ion}}/k_B \sim 10^4\text{-}10^5$ K, 此时, (几乎) 所有原子都处于 (electronic) ground state.
- nuclei state 有 spin- S_n , 因此 $j_{\text{nuc}}(T) = g_{\text{nuc}} = 2S_n + 1$.
- 得到

$$j(T) = (2S_n + 1) \sum_{J=|L-S|}^{L+S} (2J+1)e^{-\beta\epsilon_{L,S,J}}, \quad (6.4.8)$$

其中 L, S 分别是电子的 orbital angular momentum 和 spin, 因为原子处于 electronic ground state, L, S 是常数, (通常 $L = S = 0$), 可以简写 $\epsilon_J \equiv \epsilon_{L,S,J}$.

– 如果 $\epsilon_J \ll k_B T$, 那么

$$j_{\text{elec}}(T) \simeq \sum_{J=|L-S|}^{L+S} (2J+1) = (2L+1)(2S+1). \quad (6.4.9)$$

– 如果 $\epsilon_J \gg k_B T$, 那么

$$j_{\text{elec}}(T) \simeq (2J_0 + 1)e^{-\beta\epsilon_0}, \quad (6.4.10)$$

下标 0 表示 fine structure 中的 lowest energy state.

- 系统的能量为

$$U = \begin{cases} \frac{3}{2}Nk_B T & \epsilon_J \ll k_B T \\ \frac{3}{2}Nk_B T + N\epsilon_0 & \epsilon_J \gg k_B T \end{cases}. \quad (6.4.11)$$

- 可见, 无论在高温还是低温极限下, 气体的 specific heat 都是 $\frac{3}{2}Nk_B$, 只有 entropy 和 chemical potential 受到影响.
- specific heat 在 $T \sim \Delta\epsilon_J/k_B$ 时达到极大, $\Delta\epsilon_J$ 是 separation of the fine structure levels.

6.4.2 diatomic molecules

- 同样, 考虑温度远低于 energy of dissociation, $T \ll \epsilon_{\text{diss}}/k_B \sim 10^4\text{-}10^5$ K, 此时, 所有分子处于 lowest electronic state.
- 考虑

$$j_{\text{elec}}(T) = g_0 + g_1 e^{-\beta\Delta}, \quad (6.4.12)$$

那么

$$\begin{cases} U_{\text{elec}} = N\Delta \frac{(g_1/g_0)e^{-\beta\Delta}}{1 + (g_1/g_0)e^{-\beta\Delta}} \\ (C_V)_{\text{elec}} = Nk_B \left(\frac{\Delta}{k_B T}\right)^2 \frac{(g_1/g_0)e^{-\beta\Delta}}{(1 + (g_1/g_0)e^{-\beta\Delta})^2} \end{cases}, \quad (6.4.13)$$

得到 $T-(C_V)_{\text{elec}}$ 关系如下图:

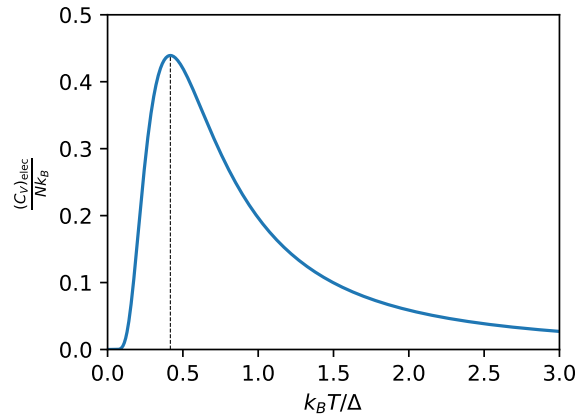


Figure 6.3: plot of $T-(C_V)_{\text{elec}}$.

- 考虑分子振动频率 ω (更高频未激发), 参考 subsection 3.6.2, harmonic oscillator 的 specific heat 为

$$(C_V)_{\text{vib}} = Nk_B \left(\frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}, \quad \Theta_v = \frac{\hbar\omega}{k_B}, \quad (6.4.14)$$

其图像见 figure 6.4a.

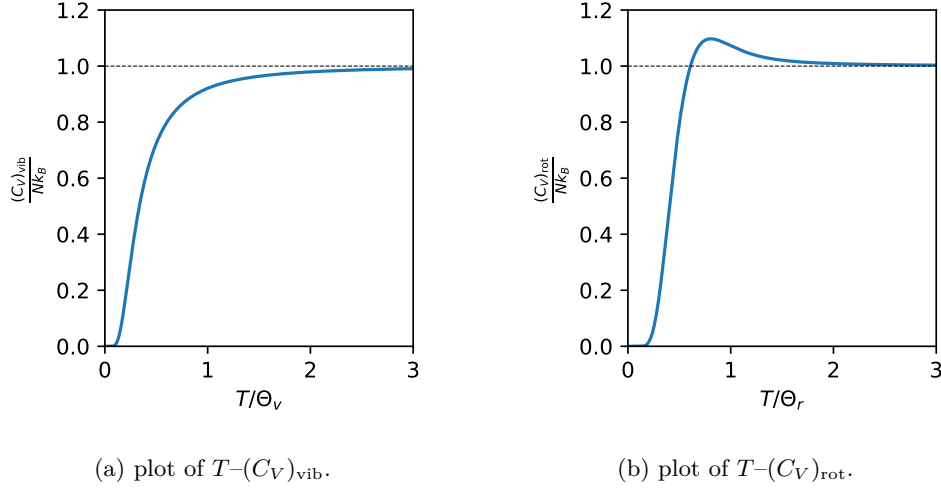


Figure 6.4

- nuclei states 和 rotational states 之间的相互作用在 heteronuclear molecules 中可以忽略, 但在 homonuclear molecules 中不能.
- 首先考虑 heteronuclear 的情况, rotational partition function 为

$$j_{\text{rot}}(T) = \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)\hbar^2/(2I)}$$

$$\approx \begin{cases} \frac{T}{\Theta_r} + \frac{1}{3} + \frac{1}{15} \frac{\Theta_r}{T} + \frac{4}{315} \left(\frac{\Theta_r}{T} \right)^2 + \dots & T \gg \Theta_r, \\ 1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + \dots & T \ll \Theta_r \end{cases}, \quad (6.4.15)$$

其中 $I = \frac{m_1 m_2}{(m_1 + m_2)} r_0^2$ 是分子的 moment of inertia, $\Theta_r = \frac{\hbar^2}{2Ik_B}$.

- 由此引入的 specific heat 为

$$(C_V)_{\text{rot}} \approx \begin{cases} Nk_B \left(1 + \frac{1}{45} \left(\frac{\Theta_r}{T} \right)^2 + \frac{16}{945} \left(\frac{\Theta_r}{T} \right)^3 \dots \right) & T \gg \Theta_r, \\ 12Nk_B \left(\frac{\Theta_r}{T} \right)^2 e^{-2\Theta_r/T} & T \ll \Theta_r \end{cases}, \quad (6.4.16)$$

其图像见 figure 6.4b.

- homonuclear 的情况下...

6.4.3 polyatomic molecules

- 经典近似下, rotational partition function 为

$$j_{\text{rot}}(T) \simeq \int_{-\infty}^{\infty} \frac{d\Omega dL_1 dL_2 dL_3}{h^3} e^{-\beta(L_1^2/(2I_1) + L_2^2/(2I_2) + L_3^2/(2I_3))}$$

$$= \frac{8\pi^2}{h^3} \prod_{i=1,2,3} \sqrt{\frac{2I_i \pi}{\beta}} = \sqrt{\pi} \prod_{i=1,2,3} \sqrt{\frac{2I_i k_B T}{\hbar^2}}. \quad (6.4.17)$$

- 此时

$$(C_V)_{\text{rot}} = \frac{3}{2} N k_B. \quad (6.4.18)$$

- 振动与 (6.4.14) 类似, 只是多了几个振动模式.

6.5 chemical equilibrium

- 对于 chemical reaction



系统达到 chemical equilibrium 的条件是

$$\nu_A \mu_A + \nu_B \mu_B = \nu_X \mu_X + \nu_Y \mu_Y. \quad (6.5.2)$$

- 如果系统是 ideal gas 或 dilute solution, 系统的 free energy 是各成分的和, 那么

$$F = N \langle \epsilon \rangle + N k_B T \ln(n \lambda^3) - N k_B T - N k_B T \ln j(T), \quad (6.5.3)$$

因此

$$\mu_A = \left(\frac{\partial F}{\partial N_A} \right)_{T,V} = \langle \epsilon_A \rangle + k_B T \ln(n_A \lambda_A^3) - k_B T \ln j_A(T), \quad (6.5.4)$$

那么 (6.5.2) 化为

$$\frac{\prod [X]^{\nu_X}}{\prod [A]^{\nu_A}} = e^{-\beta \Delta \mu^{(0)}(T)}, \quad (6.5.5)$$

其中 $[A] = n_A/n_0$, n_0 可以任取, 且

$$\begin{cases} \Delta \mu^{(0)} = \nu_X \mu_X^{(0)} + \nu_Y \mu_Y^{(0)} - \nu_A \mu_A^{(0)} - \nu_B \mu_B^{(0)} \\ \mu_A^{(0)}(T) = \mu_A(n_A = n_0, T) \end{cases}. \quad (6.5.6)$$

calculation:

注意到

$$e^{\nu_A \beta \mu_A} = \left(\frac{n_A \lambda_A^3}{j_A(T)} \right)^{\nu_A} e^{\nu_A \beta \langle \epsilon_A \rangle}, \quad (6.5.7)$$

代入,

$$\prod_A [A]^{\nu_A} \left(\frac{n_0 \lambda_A^3}{j_A(T)} \right)^{\nu_A} e^{\nu_A \beta \langle \epsilon_A \rangle} = \prod_X [X]^{\nu_X} \left(\frac{n_0 \lambda_X^3}{j_X(T)} \right)^{\nu_X} e^{\nu_X \beta \langle \epsilon_X \rangle} \Rightarrow \frac{\prod [X]^{\nu_X}}{\prod [A]^{\nu_A}} = \dots \quad (6.5.8)$$

Chapter 7

ideal Bose systems

- 根据 (5.4.2), 如果 $n\lambda^3 \ll 1$ 的条件不再满足, 就需要考虑量子效应.
 - 需要分别讨论可以对 $n\lambda^3 \lesssim 1$ 作级数展开的区间, 和 $n\lambda^3 \gtrsim 1$ 系统完全偏离经典统计的情况.
- $g_n(z)$ 是 Bose-Einstein function,

$$g_n(z) \equiv \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{z^{-1}e^x - 1} dx = z + \frac{z^2}{2^n} + \frac{z^3}{3^n} + \cdots, \quad \text{and} \quad g'_n(z) = \frac{1}{z} g_{n-1}(z), \quad (7.0.1)$$

是单调递增函数, $-1 < z < 1$, 且 $g_n(1) = \zeta(n)$.

7.1 thermodynamic behavior of an ideal Bose gas

- ideal Bose gas 的 grand partition function 为

$$\frac{PV}{k_B T} = \ln Z_{GC} = N_s \left(\frac{V}{\lambda^3} g_{5/2}(z) - \underbrace{\ln(1-z)}_{\text{negligible}} \right), \quad (7.1.1)$$

其中 $z = e^{\beta\mu} < 1$ 是 fugacity (见 (1.3.3)), N_s 是粒子的自旋状态数.

calculation:

注意到粒子能量 ϵ 的简并度为 (根据 (1.2.3))

$$g(\epsilon) = N_s 2\pi \frac{V/\lambda^3}{(\pi k_B T)^{3/2}} \epsilon^{1/2}, \quad (7.1.2)$$

所以 (另外 $g_0 = N_s \neq 0$, 而 $g(0) = 0$, 需要把 $\epsilon = 0$ 单独拿出来)

$$\begin{aligned} \ln Z_{GC} &= -N_s \ln(1-z) - N_s 2\pi \frac{V/\lambda^3}{(\pi k_B T)^{3/2}} \int_0^\infty \ln(1 - ze^{-\beta\epsilon}) \epsilon^{1/2} d\epsilon \\ &= -N_s \ln(1-z) - N_s \frac{2\pi}{\pi^{3/2}} \frac{V}{\lambda^3} \int_0^\infty \ln(1 - ze^{-x}) x^{1/2} dx = \cdots, \end{aligned} \quad (7.1.3)$$

注意 $\ln(1-z)$ 在 $z=1$ 处有一个极点, 所以 Taylor 展开收敛的条件是

$$ze^{-x} < 1 \implies z < 1. \quad (7.1.4)$$

- 基态贡献的 $N_s \ln(1-z)$ 可以忽略 (但其导数不一定能忽略).

proof:

注意到

$$N_0 = N_s \frac{1}{z^{-1} - 1} \implies -N_s \ln(1-z) = N_s \ln(N_0/N_s + 1) \leq O(\ln N), \quad (7.1.5)$$

而 $\ln Z_{GC} \sim N$, 因此可以忽略.

- 得到 (框起来的公式在 T_c 两侧都成立)

$$\boxed{\begin{cases} N = N_s \frac{V}{\lambda^3} g_{3/2}(z) + N_s \frac{1}{z^{-1} - 1} \\ U = \frac{3N_s}{2} k_B T \frac{V}{\lambda^3} g_{5/2}(z) \end{cases}}, \quad (7.1.6)$$

和 equation of state (in the form of virial expansion, 见 (3.5.12)),

$$\boxed{\frac{PV}{Nk_B T} = \frac{1}{n\lambda^3/N_s} g_{5/2}(z)} = \begin{cases} \frac{g_{5/2}(z)}{g_{3/2}(z)} = \sum_{l=1}^{\infty} a_l (n\lambda^3/N_s)^{l-1} & T \gg T_c, \text{ virial expansion} \\ \frac{1}{n\lambda^3/N_s} \zeta(\frac{5}{2}) & T < T_c \end{cases}, \quad (7.1.7)$$

($T \gg T_c$ 指要求级数收敛), 其中 virial coefficients are

$$\begin{aligned} a_1 &= 1, \quad a_2 = -\frac{1}{4\sqrt{2}} \approx -0.177, \quad a_3 = -\left(\frac{2}{9\sqrt{3}} - \frac{1}{8}\right) \approx -0.0033, \\ a_4 &= -\left(\frac{3}{32} + \frac{5}{32\sqrt{2}} - \frac{1}{2\sqrt{6}}\right) \approx -0.00011. \end{aligned} \quad (7.1.8)$$

- 注意到 $U = \frac{3}{2}PV$ ($T < T_c$ 时也成立), 系统的 specific heat 为

$$\frac{C_V}{Nk_B} = \begin{cases} \overbrace{\frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)}}^{\text{忽略了 } N_0} = \frac{3}{2} \sum_{l=1}^{\infty} \frac{5-3l}{2} a_l (n\lambda^3/N_s)^{l-1} & T \gg T_c \\ \frac{15}{4} \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} \left(\frac{T}{T_c}\right)^{\frac{3}{2}} & T < T_c \end{cases}. \quad (7.1.9)$$

- 得到 T - PV 和 T - C_V 曲线, 如下图:

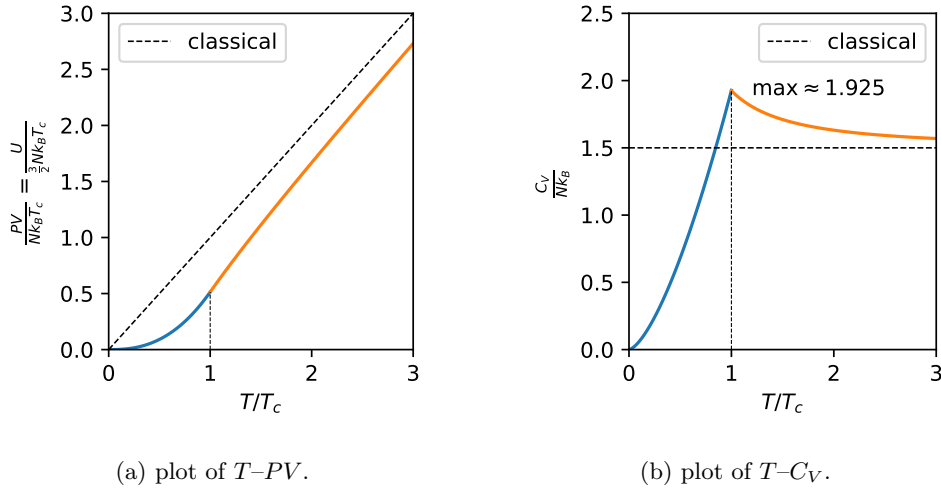


Figure 7.1

可见 $T = T_c$ 时存在相变.

- 系统的熵为

$$S = U + PV - \mu N = \begin{cases} Nk_B \left(\frac{5}{2} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \ln z \right) & T > T_c \\ \frac{5}{2} k_B \frac{V}{\lambda^3/N_s} \zeta(\frac{5}{2}) = \frac{5}{2} k_B N_e \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} & T < T_c \end{cases}, \quad (7.1.10)$$

可见 $S \propto N_e$, 处于基态的粒子不贡献熵, as expected.

7.1.1 normal phase and condensed phase

- grand partition function 计算方法的前提条件是 (7.1.4), (代入 N - z 关系式) 等价于

$$N_e < N_s \frac{V}{\lambda^3} \underbrace{\zeta(\frac{3}{2})}_{\approx 2.612}, \quad (7.1.11)$$

其中 N_e 表示激发态上的粒子数量.

- 当 z 接近 1 时, $N_0 = N_s \frac{1}{z-1-1} \gg 1$, 此时,

$$\begin{cases} z = 1 - \frac{N_s}{N_0} \\ N_0 = N - N_s \frac{V}{\lambda^3} \zeta(\frac{3}{2}) \gg 1 \end{cases}, \quad (7.1.12)$$

几乎所有粒子都处于基态, 称为 Bose-Einstein condensation.

- 发生 Bose-Einstein condensation 的条件是 $N > N_s \frac{V}{\lambda^3} \zeta(\frac{3}{2})$, 或者

$$n\lambda^3/N_s > \zeta(\frac{3}{2}) \iff T < T_c = \frac{h^2}{2\pi m k_B} \left(\frac{N/N_s}{V\zeta(\frac{3}{2})} \right)^{\frac{2}{3}}, \quad (7.1.13)$$

此时, 系统可以认为处于两相混合态: 由 N_e 个处于激发态的粒子 (in the normal phase), 和 N_0 个处于基态的粒子 (in the condensed phase) 组成.

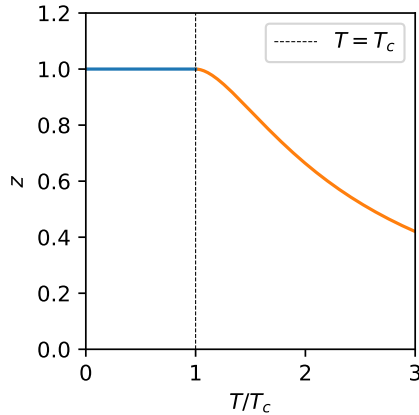
- 一个对化简有用的公式,

$$\frac{T}{T_c} = \left(\frac{\zeta(\frac{3}{2})}{n\lambda^3/N_s} \right)^{\frac{2}{3}}. \quad (7.1.14)$$

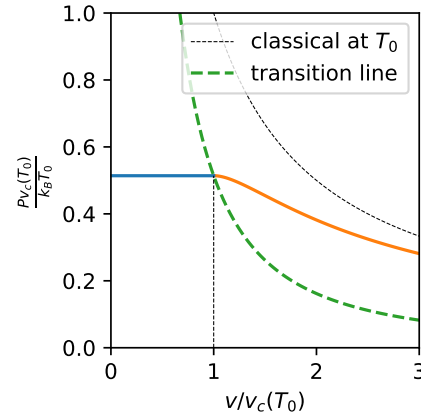
- $T < T_c$ 时,

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c} \right)^{\frac{3}{2}} \underset{T=T_c-0^+}{\approx} \frac{3}{2} \frac{T_c - T}{T_c}. \quad (7.1.15)$$

- 综上, z 随 T 变化曲线如 figure 7.2a.



(a) plot of T - z .



(b) plot of an isotherm at T_0 .

Figure 7.2

7.1.2 isotherms and adiabats of the ideal Bose gas

- 等温线上, 相变发生在 characteristic volume,

$$v_c = \frac{\lambda^3}{N_s \zeta(\frac{3}{2})}, \quad (7.1.16)$$

因此, v - P 曲线如 figure 7.2b, 其中 transition line 为

$$P v^{5/3} = \frac{h^2}{2\pi m} \frac{1}{N_s^{2/3}} \frac{\zeta(\frac{5}{2})}{\zeta^{5/3}(\frac{3}{2})}, \quad (7.1.17)$$

是一条特殊的绝热线.

- 可逆绝热过程中, 根据 (7.1.10),

$$\begin{cases} z = \text{Const.} \implies n\lambda^3 = \text{Const.} & T > T_c \\ n\lambda^3 = \text{Const.} & T < T_c \end{cases}$$

$$\implies n\lambda^3 = \text{Const.} \quad \text{or} \quad \frac{P}{T^{5/2}} = \text{Const.} \quad \text{or} \quad Pv^{5/3} = \text{Const.}, \quad (7.1.18)$$

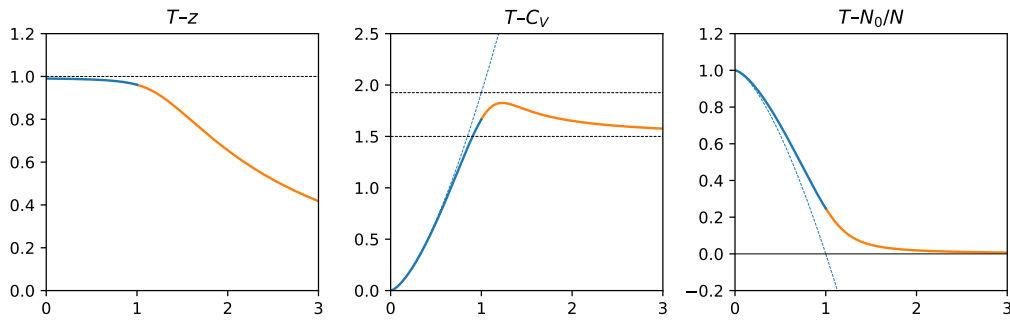
与 ideal classical gas 中的情况完全一样, 但是

$$\gamma \equiv \frac{C_P}{C_V} = \frac{5}{3} \frac{g_{5/2}(z)g_{1/2}(z)}{g_{3/2}^2(z)}, \quad (7.1.19)$$

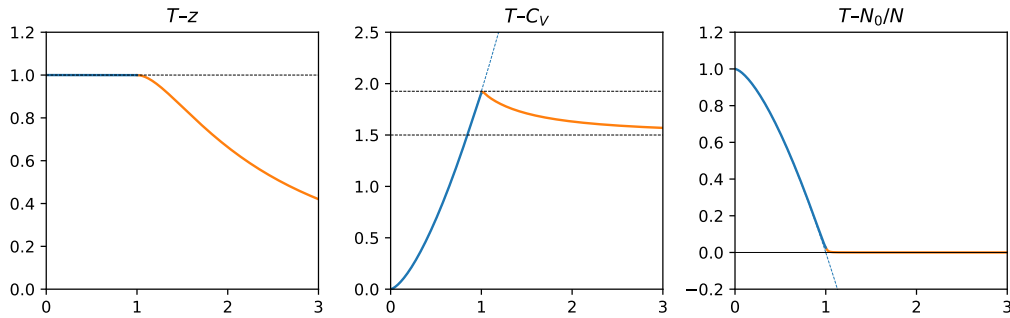
与 ideal classical gas 中不一样.

7.1.3 numerical results

- 用数值方法计算 ideal Bose gas 的 thermodynamic functions, 得到结果如下:



(a) thermodynamic functions of an ideal Bose gas by numerical method with $N/N_s = 100$.



(b) thermodynamic functions of an ideal Bose gas by numerical method with $N/N_s = 10^5$.

Figure 7.3

7.2 Bose–Einstein condensation in ultracold atomic gases

- 考虑单个粒子的 Hamiltonian 为

$$H = \frac{|\vec{p}|^2}{2m} + V(\vec{r}), \quad V(\vec{r}) = \frac{1}{2}m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2), \quad (7.2.1)$$

粒子的能级为

$$\epsilon = \sum_i \hbar \omega_i \left(n_i + \frac{1}{2} \right). \quad (7.2.2)$$

- 系统的 grand partition function 为

$$\ln Z_{\text{GC}} = -N_s \left(\frac{1}{2(\beta \hbar \omega_0)^3} g_4(z) + \underbrace{\ln(1 - ze^{-\beta \epsilon_0})}_{\text{negligible}} \right). \quad (7.2.3)$$

calculation:

注意到

$$\int_0^\epsilon g(\epsilon') d\epsilon' = N_s \int \theta(\epsilon - \epsilon(\vec{n})) d^3 n, \quad (7.2.4)$$

因此, 能级 $\epsilon \gg \epsilon_0$ 的简并为

$$\begin{aligned} g(\epsilon) &= N_s \int_0^\infty dn_1 \int_0^\infty dn_2 \int_0^\infty dn_3 \delta(\epsilon - \epsilon(n_1, n_2, n_3)) \\ &= N_s \int_0^\infty dn_1 \int_0^\infty dn_2 \frac{1}{\hbar\omega_3} \theta(\epsilon - \epsilon(n_1, n_2, 0)) \\ &= N_s \frac{1}{\hbar\omega_3} \int_0^{\frac{(\epsilon - \epsilon_0)}{\hbar\omega_1}} dn_1 \int_0^{\frac{(\epsilon - \epsilon_0) - \hbar\omega_1 n_1}{\hbar\omega_2}} dn_2 = N_s \frac{(\epsilon - \epsilon_0)^2}{2(\hbar\omega_0)^3}, \end{aligned} \quad (7.2.5)$$

其中 $\omega_0 = (\omega_1\omega_2\omega_3)^{1/3}$, 且基态能量 ϵ_0 可以忽略. 代入 (6.1.10),

$$\begin{aligned} \ln Z_{GC} &= -N_s \ln(1 - ze^{-\beta\epsilon_0}) - \int_0^\infty \ln(1 - ze^{-\beta\epsilon}) g(\epsilon) d\epsilon \\ &= -N_s \ln(1 - ze^{-\beta\epsilon_0}) - N_s \frac{1}{2(\beta\hbar\omega_0)^3} \int_0^\infty \ln(1 - ze^{-x}) x^2 dx = \dots \end{aligned} \quad (7.2.6)$$

- 得到

$$\begin{cases} N = N_s \frac{1}{(\beta\hbar\omega_0)^3} g_3(z) + N_s \frac{1}{z^{-1} - 1} \Rightarrow \frac{k_B T_c}{\hbar\omega_0} = \left(\frac{N/N_s}{\zeta(3)} \right)^{\frac{1}{3}} \\ U = 3 \frac{(k_B T)^4}{(\hbar\omega_0)^3} g_4(z) \\ \frac{C_\omega}{Nk_B} = \begin{cases} \frac{12\zeta(4)}{\zeta(3)} \left(\frac{T}{T_c} \right)^3 \\ \frac{1}{\zeta(3)} \left(\frac{T}{T_c} \right)^3 \left(12g_4(z) - \frac{9g_3^2(z)}{g_2(z)} \right) \end{cases} \end{cases}, \quad (7.2.7)$$

其中 C_ω 不连续, 与 section 7.1 中不同.

7.3 thermodynamics of the blackbody radiation: the photon gas

- section 4.1 中的推导前提是 heat reservoir 粒子数守恒, photon gas 没有这个约束条件, 因此 $\mu = 0$.
- photon 的能级为

$$\epsilon = \frac{\hbar c}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2}. \quad (7.3.1)$$

- photon gas 的 grand partition function 为

$$\frac{PV}{k_B T} = \ln Z_{GC} = 16\pi \frac{V}{h^3 c^3} (k_B T)^3 g_4(z) \Big|_{z=1} = \frac{8\pi^5 V}{45 h^3 c^3} (k_B T)^3, \quad (7.3.2)$$

虽然 $z = 1$, 但 $\ln Z_{GC}(T, V, z)$ 对 z 的偏导数依然有用.

calculation:

能级简并为

$$\begin{aligned} g(\epsilon) &= 2 \int_0^\infty dn_1 \int_0^\infty dn_2 \int_0^\infty dn_3 \delta(\epsilon - \epsilon(n_1, n_2, n_3)) \\ &= 2 \int_0^\infty dn_1 \int_0^\infty dn_2 \left(\frac{\hbar c}{2L} \frac{n_3}{\sqrt{n_1^2 + n_2^2 + n_3^2}} \Big|_{\epsilon=\epsilon(\vec{n})} \right)^{-1} \theta(\epsilon - \epsilon(n_1, n_2, 0)) \\ &= 2\epsilon \left(\frac{2L}{\hbar c} \right)^2 \int_0^\infty dn_1 \int_0^\infty dn_2 \frac{1}{\sqrt{n_\epsilon^2 - n_1^2 - n_2^2}} \theta(\epsilon - \epsilon(n_1, n_2, 0)) = 8\pi \frac{V}{h^3 c^3} \epsilon^2, \end{aligned} \quad (7.3.3)$$

代入 (6.1.10),

$$\begin{aligned}\ln Z_{\text{GC}} &= -2 \ln(1-z) - \int_0^\infty \ln(1 - ze^{-\beta\epsilon}) g(\epsilon) d\epsilon \\ &= -2 \ln(1-z) + 16\pi \frac{V}{h^3 c^3} (k_B T)^3 g_4(z),\end{aligned}\quad (7.3.4)$$

忽略第一项, 令 $z = 1, \zeta(4) = \frac{\pi^4}{90}$, 得到...

- 得到

$$\begin{cases} N = \frac{\partial}{\partial \alpha} \Big|_{\alpha=0} \ln Z_{\text{GC}} = \int_0^\infty \frac{g(\epsilon)}{e^{\beta\epsilon} - 1} d\epsilon = 16\pi \zeta(3) \frac{V}{h^3 c^3} (k_B T)^3 \\ \frac{U}{V} = 3P = \frac{8\pi^5}{15} \frac{1}{h^3 c^3} (k_B T)^4 \\ S = \frac{4}{3} \frac{U}{T} \\ C_V = 3S, C_P \rightarrow \infty \end{cases}, \quad (7.3.5)$$

以及

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle^2} = \frac{1}{\langle N \rangle^2} \frac{\partial^2}{\partial \alpha^2} \Big|_{\alpha=0} \ln Z_{\text{GC}} = \frac{1}{\langle N \rangle} \frac{\pi^2}{6\zeta(3)}, \quad (7.3.6)$$

与 (4.4.2) 不同 (注意到 photon gas 的 $\kappa_T \rightarrow \infty$).

7.4 the field of sound waves: the phonon gas

- 固体的 Hamiltonian 为

$$H = \frac{m}{2} \sum_{i=1}^{3N} \dot{x}_i^2 + \Phi_0 + \frac{1}{2} \sum_{i,j} \underbrace{\frac{\partial^2 \Phi}{\partial x_i \partial x_j}}_{=\alpha_{ij}} x_i x_j + O(x^3), \quad (7.4.1)$$

其中 x 是固体中的原子相对平衡位置的偏离, 保留二阶项称作 harmonic approximation. 对 x 作正交变换得到 normal coordinates q , 得到

$$H = \Phi_0 + \sum_{i=1}^{3N} \frac{1}{2} m (\dot{q}_i^2 + \omega_i^2 q_i^2), \quad (7.4.2)$$

where ω_i are the characteristic frequencies of the normal modes.

- 固体的能级为

$$E\{n_i\} = \Phi_0 + \sum_{i=1}^{3N} \hbar \omega_i \left(n_i + \frac{1}{2} \right). \quad (7.4.3)$$

- 可以认为 $\hbar \omega_i$ 是 phonon 的能级, n_i 是这个能级上的声子数, 那么声子是 indistinguishable Boson, 且粒子数不守恒, $\mu = 0$.
- 系统的 grand partition function 为

$$\ln Z_{\text{GC}} = - \sum_{i=1}^{3N} \ln(1 - ze^{-\beta \hbar \omega_i}) \Big|_{z=1}. \quad (7.4.4)$$

- 得到

$$\begin{cases} N_{\text{phonons}} = \sum_{i=1}^{3N} \frac{1}{e^{\beta \hbar \omega_i} - 1} \\ U = \left(\Phi_0 + \sum_{i=1}^{3N} \frac{1}{2} \hbar \omega_i \right) + \sum_{i=1}^{3N} \frac{\hbar \omega_i}{e^{\beta \hbar \omega_i} - 1} \\ C_V = k_B \sum_{i=1}^{3N} \frac{e^{\beta \hbar \omega_i}}{(e^{\beta \hbar \omega_i} - 1)^2} (\beta \hbar \omega_i)^2 \end{cases} \quad (7.4.5)$$

- 进一步的研究依靠固体的 frequency spectrum, Einstein 假设 $\omega_1 = \dots = \omega_{3N} = \omega_E$, Debye 假设固体有 continuous spectrum of frequencies.

7.4.1 Einstein solid model

- 代入 $\omega_i = \omega_E$, 令 $\hbar\omega_E = k_B\Theta_E$, 得到

$$C_V = 3Nk_B \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} (\Theta_E/T)^2. \quad (7.4.6)$$

7.4.2 Debye solid model

- Debye 假设 phonon 的能级简并为

$$g(\omega) \equiv g(\epsilon) \frac{d\epsilon}{d\omega} = \begin{cases} 9N \frac{\omega^2}{\omega_D^3} & \omega \leq \omega_D \\ 0 & \omega > \omega_D \end{cases}, \quad \omega_D^3 = 18\pi^2 \frac{N}{V} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right)^{-1}, \quad (7.4.7)$$

其中 c_L, c_T 分别是固体中 longitude modes 和 transverse modes 的声速.

calculation:

声子在固体中形成驻波,

$$\frac{\omega_i L}{c} = \pi \sqrt{n_{i,x}^2 + n_{i,y}^2 + n_{i,z}^2} \Rightarrow g(\omega) = \frac{N_s}{2\pi^2} \frac{V}{c^3} \omega^2, \quad (7.4.8)$$

注意到横波有两个偏振,

$$g(\omega) = \frac{V}{2\pi^2} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) \omega^2, \quad (7.4.9)$$

总状态为 $3N$, 所以需要有一个截至频率 ω_D ,

$$\int_0^{\omega_D} g(\omega) d\omega = 3N \Rightarrow \frac{V}{2\pi^2} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) \frac{\omega_D^3}{3} = 3N. \quad (7.4.10)$$

- 代入, 令 $\hbar\omega_D = k_B\Theta_D$, 得到

$$C_V = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \stackrel{T \ll \Theta_D}{\approx} \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D} \right)^3. \quad (7.4.11)$$

- 实验表明固体 (aluminum) 的频谱在低频接近 Debye 的假设, Cu 的 $T-C_V$ 曲线在整个实验区间都与 Debye 的预测符合良好.
- 令 $\omega_E \approx \omega_D$, 固体的比热如下图:

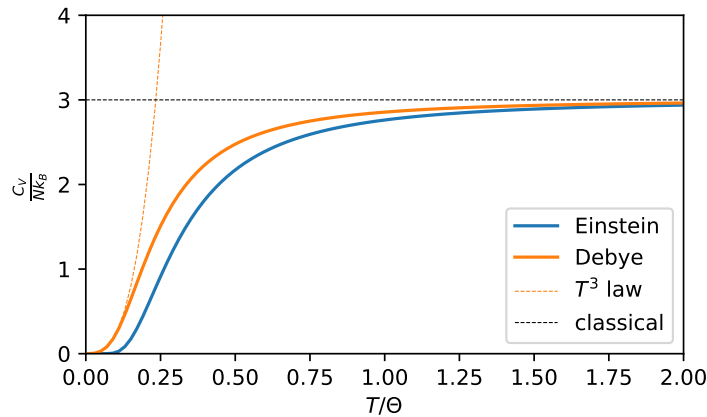


Figure 7.4: the specific heat of a solid.

7.5 something about helium-4

- about ${}^4\text{He}$...

Chapter 8

ideal Fermi systems

- $f_n(z)$ 是 Fermi–Dirac function,

$$f_n(z) \equiv \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{z^{-1}e^x + 1} dx = z - \frac{z^2}{2^n} + \frac{z^3}{3^n} - \cdots, \quad \text{and} \quad f'_n(z) = \frac{1}{z} f_{n-1}(z), \quad (8.0.1)$$

是单调递增函数 (当 $n > 0$), $-1 < z < 1$, 且 $f_n(1) = (1 - 2^{1-n})\zeta(n)$.

- 与 Bose–Einstein statistics 不同, $f_n(z)$ 在 $z = 1$ 没有极点, 只是它的级数展开在 $z > 1$ 发散 (因为 $z = -1$ 处有极点).
- $g_n(z) = -f_n(-z) = \text{Li}_n(z)$, 称为 **Polylogarithm**, 见下图:

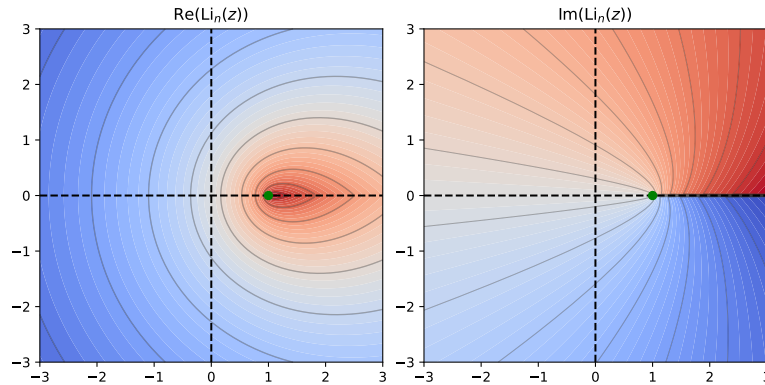


Figure 8.1: plot of $\text{Li}_n(z)$ with $n = \frac{3}{2}$.

8.1 thermodynamic behavior of an ideal Fermi gas

- ideal Fermi gas 的 grand partition function 为

$$\frac{PV}{k_B T} = \ln Z_{\text{GC}} = N_s \left(\frac{V}{\lambda^3} f_{5/2}(z) + \underbrace{\ln(1+z)}_{\text{always negligible}} \right), \quad (8.1.1)$$

对 μ 的取值范围没有限制.

calculation:

粒子能量的简并度见 (7.1.2), 所以

$$\ln Z_{\text{GC}} = N_s \ln(1+z) + \int_0^\infty \ln(1 + ze^{-\beta\epsilon}) g(\epsilon) d\epsilon = \cdots, \quad (8.1.2)$$

且

$$N_0 = \frac{N_s}{z^{-1} + 1} < N_s \implies \ln(1+z) = -\ln(1 - N_0/N_s) \sim N_0/N_s \ll N. \quad (8.1.3)$$

- 得到

$$\begin{cases} N = N_s \frac{V}{\lambda^3} f_{3/2}(z) \\ U = \frac{3}{2} N_s k_B T \frac{V}{\lambda^3} f_{5/2}(z) \\ S = N k_B \left(\frac{5}{2} \frac{f_{5/2}(z)}{f_{3/2}(z)} - \ln z \right) \\ \frac{C_V}{N k_B} = \frac{15}{4} \frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4} \frac{f_{3/2}(z)}{f_{1/2}(z)} \end{cases}, \quad (8.1.4)$$

注意到 $U = \frac{3}{2} PV$ 依然成立.

- 经典极限 $n\lambda^3 \ll 1$ 对应 $z \ll 1$, 此时 $f_n(z) \simeq z$, 代入可以得到理想气体的各热力学量.
- 对 equation of state 作 virial expansion,

$$\begin{cases} \frac{PV}{N k_B T} = \sum_{l=1}^{\infty} (-1)^{l-1} a_l (n\lambda^3/N_s)^{l-1} \\ \frac{C_V}{N k_B} = \frac{3}{2} \sum_{l=1}^{\infty} (-1)^{l-1} \frac{5-3l}{2} a_l (n\lambda^3/N_s)^{l-1} \end{cases}, \quad (8.1.5)$$

其中系数 a_l 见 (7.1.8), 展开适用于 $n\lambda^3/N_s \ll 1$.

8.1.1 degenerate ideal Fermi gas

ground state of the system: $T \rightarrow 0$

- 当 $n\lambda/N_s \rightarrow \infty, z \rightarrow \infty$ 时 ($T \rightarrow 0$), mean occupation number 变成 step function,

$$\langle n_i \rangle = \begin{cases} g_i & \epsilon < \mu_0 \\ 0 & \epsilon > \mu_0 \end{cases}, \quad (8.1.6)$$

其中 $\mu_0 \equiv \epsilon_F \equiv \frac{p_F^2}{2m}$ 称为 Fermi energy, p_F 称为 Fermi momentum, $k_B T_F \equiv \epsilon_F$ 称为 Fermi temperature,

$$\epsilon_F \equiv k_B T_F = \left(6\pi^2 n / N_s \right)^{\frac{2}{3}} \frac{\hbar^2}{2m}, \quad p_F = \left(6\pi^2 n / N_s \right)^{\frac{1}{3}} \hbar. \quad (8.1.7)$$

calculation:

$$N = \int_0^{\mu_0} g(\epsilon) d\epsilon = N_s 2\pi \frac{V/\lambda^3}{(\pi k_B T)^{3/2}} \frac{2}{3} \mu_0^{3/2} \implies \mu_0 = \left(\frac{3}{4\pi} n \lambda^3 / N_s \right)^{\frac{2}{3}} \pi k_B T = \dots \quad (8.1.8)$$

- 此时, Fermi gas 处于能量基态,

$$\frac{E_0}{V} = \frac{3}{2} P_0 = N_s \frac{2\pi}{5 m \hbar^3} p_F^5 = \frac{3}{5} n \epsilon_F = \frac{3}{5} \left(6\pi^2 / N_s \right)^{\frac{2}{3}} \frac{\hbar^2}{2m} n^{5/3}, \quad (8.1.9)$$

可见 $P_0 \propto n^{5/3}$.

with finite temperature

- 将 Fermi-Dirac function 关于 $\ln z = \beta\mu$ 展开, 得到

$$\begin{cases} N = N_s \frac{4\pi}{3} V \left(\frac{2m}{\hbar^2} \beta \ln z \right)^{\frac{3}{2}} \left(1 + \frac{\pi^2}{8} (\ln z)^{-2} + \dots \right) \implies \mu \simeq \epsilon_F \left(1 - \frac{\pi^2}{12} (\beta \epsilon_F)^{-2} \right) \\ U = \frac{3}{2} PV = \frac{3}{5} N \epsilon_F \left(1 + \frac{5\pi^2}{12} (\beta \epsilon_F)^{-2} + \dots \right) \\ \frac{C_V}{N k_B} = \frac{\pi^2}{2} \frac{1}{\beta \epsilon_F} + \dots \\ S = N k_B \left(\frac{\pi^2}{2} (\beta \epsilon_F)^{-2} + \dots \right) \end{cases}, \quad (8.1.10)$$

可见 $T \rightarrow 0$ 时 $S \rightarrow 0$, 符合预期.

- ideal Fermi gas 的 specific heat 和 T - PV 关系如下图所示:

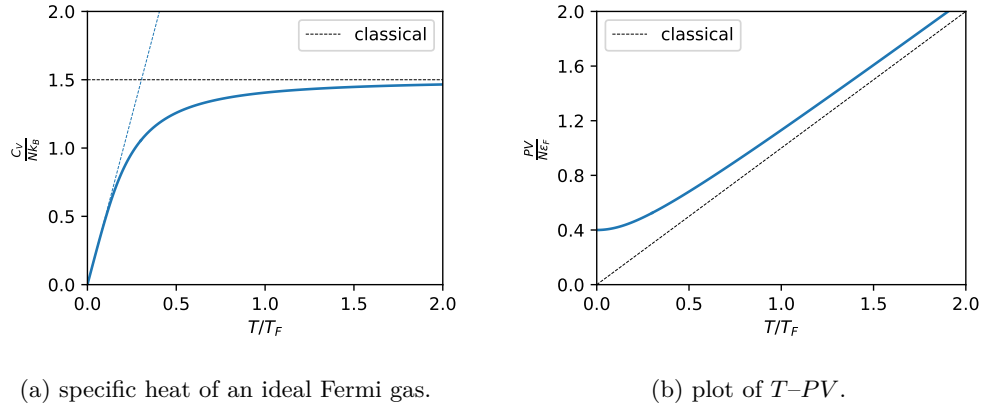


Figure 8.2

8.2 magnetic behavior of an ideal Fermi gas

- Maxwell-Boltzmann statistics 给出的结果见 section 3.7.

8.2.1 Pauli paramagnetism

- Pauli 将 alkali metal 中的 conducting electrons 视为 highly degenerate Fermi gas.
- 电子的 Hamiltonian 为

$$H = \frac{|\vec{p}|^2}{2m} - \mu_0 \vec{\mu}^* \cdot \vec{H}, \quad (8.2.1)$$

其中 $\vec{\mu}^* = -\mu_B \vec{\sigma}$ (见 (5.3.1)). 因此, 系统的 grand partition function 为

$$\ln Z_{GC} = \frac{V}{\lambda^3} \left(f_{5/2}(ze^{-\beta\epsilon_{M,+}}) + f_{5/2}(ze^{-\beta\epsilon_{M,-}}) \right). \quad (8.2.2)$$

calculation:

将电子的能量分成 $\epsilon = \epsilon_K + \epsilon_M$, 其中 $\epsilon_M = \pm\mu_0\mu_B H$, 所以

$$\begin{aligned} \ln Z_{GC} &= \sum_{\epsilon_K, \epsilon_M} g_K(\epsilon_K) \ln(1 + ze^{-\beta(\epsilon_K + \epsilon_M)}) \\ &= \frac{V}{\lambda^3} \left(f_{5/2}(ze^{-\beta\epsilon_{M,+}}) + f_{5/2}(ze^{-\beta\epsilon_{M,-}}) \right). \end{aligned} \quad (8.2.3)$$

- 得到

$$N_{\pm} = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_{M,\pm}} \ln Z_{GC} = \frac{V}{\lambda^3} f_{3/2}(ze^{-\beta\epsilon_{M,\pm}}) \simeq \frac{V}{6\pi^2} \left(\frac{2m}{\hbar^2} (\epsilon_F - \epsilon_{M,\pm}) \right)^{\frac{3}{2}}, \quad (8.2.4)$$

因此

$$\begin{aligned} V \langle M_z \rangle &= N \langle \mu_z^* \rangle = N_+(-\mu_B) + N_- (+\mu_B) \\ &\simeq \frac{4\pi^2 V \mu_B}{3} \left(\left(\frac{2m}{\hbar^2} (\epsilon_F + \mu_0 \mu_B H) \right)^{\frac{3}{2}} - \left(\frac{2m}{\hbar^2} (\epsilon_F - \mu_0 \mu_B H) \right)^{\frac{3}{2}} \right), \end{aligned} \quad (8.2.5)$$

系统的 low-field magnetic susceptibility is

$$\chi_0 = \lim_{H \rightarrow 0} \frac{M_z}{H} = 4\pi\mu_0\mu_B^2 \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \epsilon_F^{1/2} = \left[\frac{3}{2} \frac{N}{V} \frac{\mu_0 \mu_B^2}{\epsilon_F} \right], \quad \epsilon_F(n, H=0) = \frac{\hbar^2}{2m} \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}}, \quad (8.2.6)$$

其中, 用 (8.2.4) 得到 ϵ_F 的表达式, 下标 0 表示 $T \rightarrow 0$ (again, highly degenerate).

- 对比高温极限 (3.7.18) ($g = 2, j = \frac{1}{2}$),

$$\chi_\infty = \frac{N}{V} \frac{\mu_0 \mu_B^2}{k_B T}. \quad (8.2.7)$$

- 有限温度下,

$$\begin{aligned} V \langle M_z \rangle &= N_+(-\mu_B) + N_- (+\mu_B) \stackrel{H \rightarrow 0}{=} \left(\frac{V}{\lambda^3} f'_{3/2}(z) 2z \beta \mu_0 \mu_B H \right) \mu_B \\ &= 2 \frac{V}{\lambda^3} f_{1/2}(z) \frac{\mu_0 \mu_B^2}{k_B T} H = N \frac{f_{1/2}(z)}{f_{3/2}(z)} \frac{\mu_0 \mu_B^2}{k_B T} H. \end{aligned} \quad (8.2.8)$$

- 在有限 (但依然简并, $T \ll T_c$) 温度下, 参考 (8.1.10),

$$V \langle M_z \rangle \stackrel{H \rightarrow 0}{=} \left(2 \frac{V}{\lambda^3} f_{1/2}(z) \beta \mu_0 \mu_B H \right) \mu_B \simeq V \langle M_z \rangle_{T=0} \left(1 - \frac{\pi^2}{12} \frac{1}{(\beta \epsilon_F)^2} \right), \quad (8.2.9)$$

因此

$$\chi \stackrel{T \ll T_F}{\simeq} \chi_0 \left(1 - \frac{\pi^2}{12} \frac{1}{(\beta \epsilon_F)^2} \right). \quad (8.2.10)$$

- 高温极限下, $z \ll 1 \implies f_n(z) \simeq z - \frac{z^2}{2^n}$,

$$\begin{aligned} V \langle M_z \rangle &\simeq \chi_\infty \left(1 - \left(\frac{1}{2^{1/2}} - \frac{1}{2^{3/2}} \right) z \right) H \simeq \chi_\infty \left(1 - \frac{1}{2^{5/2}} n \lambda^3 \right) H \\ &\implies \chi \stackrel{T \gg T_F}{\simeq} \chi_\infty \left(1 - \frac{1}{2^{5/2}} n \lambda^3 \right). \end{aligned} \quad (8.2.11)$$

8.2.2 Landau diamagnetism

- 单个电子的 Hamiltonian, 及其能级和能级简并度 $g(\epsilon)$ 见 appendix A.
- 系统的 grand partition function 为

$$\begin{aligned} \ln Z_{\text{GC}} &= V \frac{Be}{h^2} \sqrt{2\pi m k_B T} \sum_{j=0}^{\infty} f_{3/2}(z e^{-\beta 2\hbar \omega_L (j + \frac{1}{2})}) \\ &= \frac{V}{\lambda^3} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{3/2}} \frac{x}{\sinh nx}, \end{aligned} \quad (8.2.12)$$

其中 $x = \beta \hbar \omega_L = \beta \mu_{\text{eff}} B$.

calculation:

$$\begin{aligned} \ln Z_{\text{GC}} &= L_x L_y \frac{Be}{h} \sum_{j, n_z=0}^{\infty} \ln \left(1 + z e^{-\beta(2\hbar \omega_L (j + \frac{1}{2}) + \frac{\hbar^2}{8m L_z^2} n_z^2)} \right) \\ &\simeq L_x L_y \frac{Be}{h} \sum_{j=0}^{\infty} \int_{-\infty}^{\infty} \frac{L_z dp_z}{h} \ln \left(1 + z e^{-\beta(2\hbar \omega_L (j + \frac{1}{2}) + \frac{p_z^2}{2m})} \right) \\ &= V \frac{Be}{h^2} \sqrt{2\pi m k_B T} \sum_{j=0}^{\infty} \int_0^{\infty} \ln \left(1 + z e^{-\beta 2\hbar \omega_L (j + \frac{1}{2})} e^{-x} \right) x^{-1/2} dx, \end{aligned} \quad (8.2.13)$$

令 $z_j = z e^{-\beta 2\hbar \omega_L (j + \frac{1}{2})}$, 积分部分为

$$I(z_j) = 2 \int_0^{\infty} \frac{x^{1/2}}{z_j^{-1} e^x + 1} dx = \sqrt{\pi} f_{3/2}(z_j). \quad (8.2.14)$$

- 注意, $B \rightarrow 0$ 时, $\frac{x}{\sinh nx} \rightarrow \frac{1}{n}$, 代入,

$$\ln Z_{\text{GC}} \rightarrow \frac{V}{\lambda^3} f_{5/2}(z), \quad (8.2.15)$$

符合预期.

at high temperature

- 高温极限下 $z \ll 1$, 系统的 partition function 化为

$$\ln Z_{\text{ZG}} \simeq V \frac{Be}{h^2} \sqrt{2\pi m k_B T} \sum_{j=0}^{\infty} z e^{-\beta 2\hbar\omega_L(j+\frac{1}{2})} = V \frac{Be}{h^2} \sqrt{2\pi m k_B T} z \left(2 \sinh \beta \hbar \omega_L\right)^{-1}. \quad (8.2.16)$$

- 得到

$$\begin{cases} N = \frac{zV}{\lambda^3} \frac{x}{\sinh x} \\ VM = -\frac{\partial U}{\partial B} = \frac{1}{\beta} \frac{\partial}{\partial B} \ln Z_{\text{GC}}(T, V, z) = -N \mu_{\text{eff}} \left(\coth x - \frac{1}{x} \right) \end{cases}, \quad (8.2.17)$$

其中 $x = \beta \hbar \omega_L = \beta \mu_{\text{eff}} B$,

$$\mu_{\text{eff}} = \frac{e\hbar}{2m}. \quad (8.2.18)$$

– 结果类似于 Langevin paramagnetism, 见 section 3.7, 但负号是 quantization 的结果.

- 注意到 $\mu_{\text{eff}} B \ll k_B T \implies B \approx \mu_0 H$, 得到

$$\chi_{\infty} \simeq -\frac{N}{V} \frac{\mu_0 \mu_{\text{eff}}^2}{3 k_B T}, \quad (8.2.19)$$

结合 (8.2.7), 高温下 electron gas 的 susceptibility 为

$$\chi_{\infty} = \frac{N}{V} \frac{\mu_0}{k_B T} \left(\mu_B^2 - \frac{1}{3} \left(\frac{e\hbar}{2m} \right)^2 \right). \quad (8.2.20)$$

at all temperature with weak magnetic field

- 不再要求 z 是小量, 但依然有 $\mu_0 \mu_{\text{eff}} H \approx \mu_{\text{eff}} B \ll k_B T$.
- 有

$$\begin{cases} VM = \frac{1}{\beta} \frac{\partial}{\partial B} \ln Z_{\text{GC}} \\ = \frac{1}{\beta} \frac{V}{\lambda^3} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{3/2}} \beta \mu_{\text{eff}} \frac{\partial}{\partial x} \frac{x}{\sinh nx} \\ = \frac{V}{\lambda^3} \mu_{\text{eff}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{3/2}} \left(1 - \frac{nx}{\tanh nx} \right) \frac{1}{\sinh nx} \\ N = z \frac{\partial}{\partial z} \ln Z_{\text{GC}} = \frac{V}{\lambda^3} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{1/2}} \frac{x}{\sinh nx} \stackrel{x \rightarrow 0}{=} \frac{V}{\lambda^3} f_{3/2}(z) \end{cases}, \quad (8.2.21)$$

那么

$$\begin{aligned} \chi &\approx \beta \mu_0 \mu_{\text{eff}} \lim_{x \rightarrow 0} \frac{M}{x} \\ &= \frac{1}{\lambda^3} \frac{\mu_0 \mu_{\text{eff}}^2}{k_B T} \lim_{x \rightarrow 0} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{3/2}} \underbrace{\frac{1}{x} \left(1 - \frac{nx}{\tanh nx} \right) \frac{1}{\sinh nx}}_{\rightarrow -\frac{2}{3}} \\ &= -\frac{1}{3} \frac{1}{\lambda^3} \frac{\mu_0 \mu_{\text{eff}}^2}{k_B T} f_{1/2}(z). \end{aligned} \quad (8.2.22)$$

- 低温 ($T \ll T_F$) 情况下,

$$\begin{cases} f_{1/2} \simeq \frac{2}{\sqrt{\pi}} (\ln z)^{1/2} \\ f_{3/2} \simeq \frac{4}{3\sqrt{\pi}} (\ln z)^{3/2} \\ \epsilon_F \simeq k_B T \ln z \end{cases} \implies \boxed{\chi_0 = -\frac{1}{2} \frac{N}{V} \frac{\mu_0 \mu_{\text{eff}}^2}{\epsilon_F}}. \quad (8.2.23)$$

8.3 the electron gas in metals

- 用 Maxwell-Boltzmann statistics 描述 electron gas 的理论称为 Drude-Lorentz model, 用 Fermi-Dirac statistics 的理论由 Sommerfeld 提出, 称为 free electron model.
- 以 Na 为例,

$$(\epsilon_F)_{\text{Na}} = \left(3\pi^2 \frac{n_a n_e}{a^3}\right)^{\frac{2}{3}} \frac{\hbar^2}{2m} = 3.14 \text{ eV}, \quad (T_F)_{\text{Na}} = 3.64 \times 10^4 \text{ K}, \quad (8.3.1)$$

其中 n_a 一个 unit cell 中的原子数, n_e 是每个 Na 原子的 conduction electron 数, a 是 lattice constant, $m = 0.98m_e$ 是电子的 effective mass.

- 因此, the conduction electrons in sodium constitute a highly degenerate Fermi system.

- 金属的 specific heat 分别来自 lattice vibration (见 figure 7.4) 和 electron gas (见 figure 8.2a).
– 极低温, 电子主导 ($\propto T/T_F$); 常温, 晶格振动主导; 高温, 两者都有.

8.4 relativistic electron gas: white dwarf stars

- white dwarf stars 中, nucleons 和 electrons 的数量比约为 2, 因此, 具有 N 个电子的星质量为

$$M \simeq N(m_e + 2m_p) \simeq 2m_p \implies n = \frac{N}{V} \simeq \frac{\rho}{2m_p} \sim 10^{36} \text{ m}^{-3}, \quad (8.4.1)$$

其中 m_p 表示 proton mass, $\rho \sim 10^{10} \text{ kg/m}^3$ 是白矮星密度.

- 代入 (8.1.7), 得到 electron gas 的 Fermi energy,

$$\epsilon_F \sim O(0.36) \text{ MeV}, \quad T_F \sim 10^{10} \text{ K}, \quad (8.4.2)$$

与电子质量 $m_e c^2 \approx 0.51 \text{ MeV}$ 相近.

- white dwarf 温度为 $T \sim 10^7 \text{ K}$.
- 可见, white dwarf 中的 electron gas 是相对论性的, 且 (almost) completely degenerate.
– 接下来的计算忽略了 nuclei 和 radiation 产生的压力, 并近似认为系统均匀.
– 以上是对 white dwarf 的一系列估算, 正式内容现在开始.

- 由于电子是相对论性的, section 8.1 中的内容不能直接使用.
- 我们只计算 $T/T_F \rightarrow 0$ 的情况, electron gas 的 Fermi momentum 为

$$\frac{p_F}{mc} = \frac{1}{mc} \left(\frac{3n}{8\pi}\right)^{\frac{1}{3}} \hbar \simeq \left(\frac{9\pi M}{8m_p}\right)^{\frac{1}{3}} \frac{\hbar/mc}{R}, \quad (8.4.3)$$

这依然成立, 其中 M, R 分别是 white dwarf 的质量和半径.

- 电子的动能和速度为

$$\epsilon = mc^2 \left(\sqrt{1 + \frac{p^2}{m^2 c^2}} - 1 \right) \implies u = \frac{d\epsilon}{dp} = \frac{p/m}{\sqrt{1 + \frac{p^2}{m^2 c^2}}}, \quad (8.4.4)$$

因此, electron gas 的 P_0 为

$$P_0 = \frac{1}{3} \frac{N}{V} \langle up \rangle_0 = \frac{1}{3} \frac{N}{V} \left(\frac{1}{N} \int_{|\vec{p}|=0}^{|\vec{p}|=p_F} u(p) p \frac{2V d^3 p}{h^3} \right) = \frac{m^4 c^5}{3h^3} A\left(\frac{p_F}{mc}\right), \quad (8.4.5)$$

其中

$$A(x) = x\sqrt{1+x^2}(-3+2x^2) + 3 \operatorname{arcsinh} x. \quad (8.4.6)$$

8.4.1 Chandrasekhar limit

- electron degeneracy pressure 和 white dwarf 引力平衡的条件是

$$-P_0(R)4\pi R^2 dR + \alpha \frac{GM^2}{R^2} dR = 0 \implies P_0(R) = \frac{\alpha}{4\pi} \frac{GM^2}{R^4}, \quad (8.4.7)$$

其中 $\alpha \sim 1$.

- 联立 (8.4.3), (8.4.5), (8.4.7), 得到

$$A\left(\left(\frac{9\pi M}{8m_p}\right)^{\frac{1}{3}} \frac{\hbar/mc}{R}\right) = 6\pi\alpha \left(\frac{\hbar/mc}{R}\right)^3 \frac{GM^2/R}{mc^2}. \quad (8.4.8)$$

- 注意到 $M \sim 10^{30}$ kg, 那么

$$\left(\frac{9\pi M}{8m_p}\right)^{\frac{1}{3}} \frac{\hbar}{mc} \sim 10^6 \text{ m}, \quad (8.4.9)$$

分别讨论 R 远大于和远小于 10^6 m 两种情况.

- $R \gg 10^6$ m, 此时 $x \rightarrow 0$, $A(x) \simeq \frac{8}{5}x^5$, 得到

$$R \simeq \frac{3(9\pi)^{2/3}}{40\alpha} \frac{\hbar^2}{Gm_em_p^{5/3}} M^{-1/3}. \quad (8.4.10)$$

- $R \ll 10^6$ m, 此时 $x \rightarrow \infty$, $A(x) \simeq 2x^4 - 2x^2$, 得到

$$R \simeq \frac{(9\pi)^{1/3}}{2} \frac{\hbar}{m_ec} \left(\frac{M}{m_p}\right)^{\frac{1}{3}} \sqrt{1 - \left(\frac{M}{M_0}\right)^{\frac{2}{3}}}, \quad (8.4.11)$$

其中

$$M_0 = \frac{9}{64} \left(\frac{3\pi}{\alpha^3}\right)^{\frac{1}{2}} \frac{(\hbar c/G)^{3/2}}{m_p^2} \simeq 1.44\odot, \quad (8.4.12)$$

其中, 取 $\alpha \approx 0.676$, 且 mass of the sun $\odot \simeq 1.989 \times 10^{30}$ kg.

- 得到 white dwarfs 的 mass-radius relationship, 如下图:

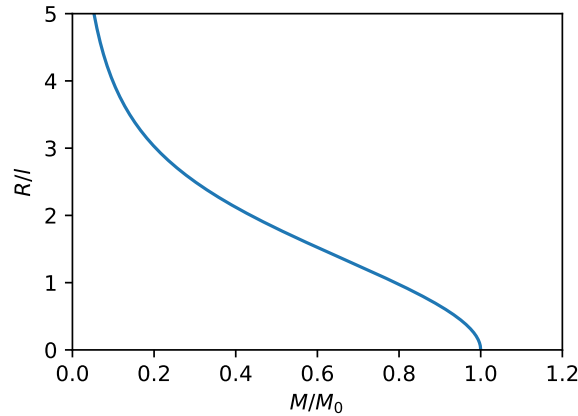


Figure 8.3: the mass-radius relationship for white dwarfs.

Part II

more advanced topics

Chapter 9

thermodynamics of the early universe

Part III

phase transition

Chapter 10

phase transitions: criticality, universality, and scaling

- 热力学系统可以分为两类: noninteracting & interacting.
- noninteracting 的系统包括: the specific heat of gases (section 1.2 and 6.4); the specific heat of solids (section 7.4); chemical equilibrium in an ideal gas or a dilute solution (section 6.5); condensation of an ideal Bose gas (section 7.1 and 7.2); spectral distribution of the blackbody radiation (section 7.3); the free electron theory of metals (section 8.3); the phenomenon of paramagnetism (section 3.7 and 8.2).
 - 除了 Bose–Einstein condensation 之外, 所有这些系统的 thermodynamic functions 都是光滑的.
- interacting 的系统包括: the condensation of gases; the melting of solids; the coexistence of phases (especially near a critical point); mixtures and solutions (包括 the onset of phase separation); ferromagnetism and antiferromagnetism; the order–disorder transitions in alloys; the superfluid transition from liquid He I to liquid He II; transition from a normal to a superconducting material.
 - interacting 的系统, 经常会遇到 thermodynamic functions 具有 analytic discontinuities or singularities 的情况, 相应地, 会遇到各种 phase transitions.

10.1 general remarks on the problem of condensation

- 对任何热力学系统, 都有

$$\left(\frac{\partial P'}{\partial v}\right)_{v,T} = -\frac{k_B T}{v^2} \frac{\langle N \rangle}{\langle (\Delta N)^2 \rangle} \leq 0, \quad (10.1.1)$$

其中 P' 定义为

$$P' := \frac{k_B T}{V} \ln Z_{GC} \equiv -\frac{\Phi_G}{V}, \quad (10.1.2)$$

对于 homogeneous system (注意 multiphase systems 也可以是 homogeneous, 但要忽略表面效应) 有 $P' = P$.

calculation:

注意到

$$-\frac{V}{N^2} \left(\frac{\partial P'}{\partial v}\right)_{T,V} = \left(\frac{\partial P'}{\partial N}\right)_{T,V} = -\frac{1}{V} \left(\frac{\partial \Phi_G}{\partial N}\right)_{T,V}, \quad (10.1.3)$$

且

$$\left(\frac{\partial \Phi_G}{\partial N}\right)_{T,V} = -N \left(\frac{\partial \mu}{\partial N}\right)_{T,V} = -\frac{N}{\left(\frac{\partial N}{\partial \mu}\right)_{T,V}} = -\frac{N}{\beta \langle (\Delta N)^2 \rangle}, \quad (10.1.4)$$

最后一个等号用到了 (4.4.1).

- 注意到, 在某些区间, $\langle (\Delta N)^2 \rangle \sim O(N^2)$, 此时

$$\left(\frac{\partial P'}{\partial v}\right)_{v,T} \sim O(N^{-1}) \simeq 0. \quad (10.1.5)$$

10.2 condensation of a van der Waals gas

10.2.1 mean field estimate

- 考虑气体分子之间具有相互作用, 那么系统的 partition function 为

$$Z_C(T, V, N) = \frac{1}{N!} \int \frac{d^{3N} p d^{3N} q_i}{h^{3N}} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} e^{-\beta \sum_{i<j} u(q_i - q_j)} \\ \simeq \frac{1}{N! \lambda^{3N}} \left(V - \frac{N\Omega}{2} \right)^N e^{\beta \frac{V}{2v^2} u}. \quad (10.2.1)$$

calculation:

考虑

$$\sum_{i<j} u(\vec{q}_i - \vec{q}_j) = \frac{1}{2} \int d^3 r_1 d^3 r_2 n(\vec{r}_1) n(\vec{r}_2) u(\vec{r}_1 - \vec{r}_2), \quad (10.2.2)$$

其中

$$n(\vec{r}) = \sum_{i=1}^N \delta^{(3)}(\vec{r} - \vec{q}_i) \Rightarrow \int d^3 r n(\vec{r}) = N, \quad (10.2.3)$$

作 approximation of uniform density, 那么

$$n(\vec{r}) \simeq \frac{N}{V} \Rightarrow \sum_{i<j} u(\vec{q}_i - \vec{q}_j) \simeq \frac{V}{2v^2} \int d^3 r u(\vec{r}), \quad (10.2.4)$$

注意到

$$u(\vec{r}) = u(r) = \begin{cases} \infty & r < \sigma \\ < 0 & r > \sigma \end{cases} \quad \text{and} \quad \int_{\sigma}^{\infty} u(r) 4\pi r^2 dr = -u < 0, \quad (10.2.5)$$

代入

$$\sum_{i<j} u(\vec{q}_i - \vec{q}_j) \simeq -\frac{V}{2v^2} u, \quad (10.2.6)$$

最后, 注意到 (其中 $\Omega = \frac{4\pi}{3}(2\sigma)^3$)

$$\int d^{3N} q \simeq V(V - \Omega) \cdots (V - (N-1)\Omega) \simeq V^N - \frac{N^2}{2} \Omega V^{N-1} \simeq \left(V - \frac{N\Omega}{2} \right)^N, \quad (10.2.7)$$

所以...

- 得到

$$\begin{cases} F = -k_B T \ln Z_C = N k_B T \left(-1 + \ln \frac{n \lambda^3}{1 - \frac{n\Omega}{2}} \right) - \frac{N^2}{2V} u \\ P = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T \left(\frac{\partial \ln Z_C}{\partial V} \right)_{T,N} = \frac{k_B T}{v - \frac{\Omega}{2}} - \frac{u}{2v^2} \\ S = N k_B \left(\frac{5}{2} - \ln \frac{n \lambda^3}{1 - \frac{n\Omega}{2}} \right) \\ U = \frac{3}{2} N k_B T - \frac{N^2}{2V} u \end{cases}. \quad (10.2.8)$$

10.2.2 the van der Waals equation

- van der Waals gas 满足 equation of state 为

$$P = \frac{k_B T}{v - b} - \frac{a}{v^2} \quad \text{or} \quad P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}, \quad (10.2.9)$$

其中 $P_r = \frac{P}{P_c}$, $v_r = \frac{v}{v_c}$, $T_r = \frac{T}{T_c}$, 且

$$P_c = \frac{a}{27b^2}, \quad v_c = 3b, \quad k_B T_c = \frac{8a}{27b}. \quad (10.2.10)$$

- van der Waals gas 的 isotherms 如下图所示:

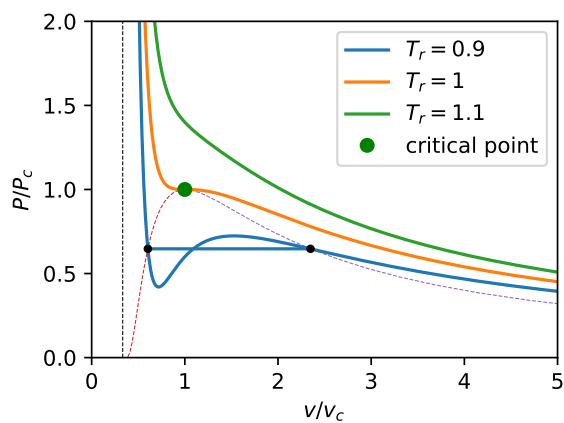


Figure 10.1: isotherms of the van der Waals gas.

- 具体的计算细节可以参考 Wikipedia page: [van der Waals equation: saturation](#).

10.3 a dynamical model of phase transitions

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Appendices

Appendix A

Landau levels

A.1 separation of variables method

- Landau 考虑了电子在磁场 $\vec{B} = B\hat{e}_z$, $\vec{A} = \frac{1}{2}(-By\hat{e}_x + Bx\hat{e}_y)$ 中的运动, 但忽略自旋, 电子的 Hamiltonian 为

$$H = \frac{1}{2m}(\vec{p} + e\vec{A})^2 = \frac{|\vec{p}|^2}{2m} + \frac{eB}{2m}\hat{L}_z + \frac{e^2}{2m}|\vec{A}|^2. \quad (\text{A.1.1})$$

- 使用 cylindrical coordinates,

$$\begin{cases} r = \sqrt{x^2 + y^2} \\ \tan \phi = \frac{y}{x} \\ z = z \end{cases} \implies \begin{cases} \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}, \\ \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \end{cases}, \quad (\text{A.1.2})$$

因此, 本征值方程为

$$\left(-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2} \right) - i\hbar\omega_L \frac{\partial}{\partial \phi} + \frac{1}{2}m\omega_L^2 r^2 - \epsilon \right) \psi(r, \phi, z) = 0, \quad (\text{A.1.3})$$

其中 $\omega_L = \frac{eB}{2m}$ 是 Larmor frequency.

- 分离变量 $\psi(r, \phi, z) = e^{ip_z z/\hbar} e^{il\phi} R_{l,p_z}(r)$, $l \in \mathbb{Z}$, 并令

$$\begin{cases} \frac{\hbar^2 \kappa_l^2}{2m} = \epsilon - \hbar\omega_L l - \frac{p_z^2}{2m} \\ \frac{1}{\kappa_l^4} \left(\frac{m\omega_L}{\hbar} \right)^2 = \alpha^2 \\ \rho = \kappa_l r \end{cases}, \quad (\text{A.1.4})$$

那么, radial equation 为

$$\rho^2 R'' + \rho R' + (\rho^2 - l^2 - \alpha^2 \rho^4) R = 0. \quad (\text{A.1.5})$$

A.1.1 asymptotic solution

- 考虑 $\rho \gg |l|$ 的区间,

$$\rho^2 R'' + \rho R' - \alpha^2 \rho^4 R \simeq 0, \quad (\text{A.1.6})$$

试探解 $R \sim e^{-k_\alpha \rho^2}$, 代入

$$(4k_\alpha^2 - \alpha^2)\rho^4 - 4k_\alpha \rho^2 \simeq 0, \quad (\text{A.1.7})$$

忽略 $O(\rho^2)$, 得到

$$R \sim e^{-\frac{\alpha}{2}\rho^2}. \quad (\text{A.1.8})$$

- 再考虑 $\rho \ll |l|$ 的区间,

$$\rho^2 R'' + \rho R' - l^2 R = 0, \quad (\text{A.1.9})$$

试探解 $R \sim \rho^m$, 代入

$$m^2 - l^2 = 0 \implies m = \pm l, \quad (\text{A.1.10})$$

舍去非物理的解,

$$R \sim \rho^{|l|}. \quad (\text{A.1.11})$$

A.1.2 solve the radial equation

- 令 $R = \rho^{|l|} e^{-\frac{\alpha}{2}\rho^2} u(\rho^2)$, 代入, 并令 $x = \alpha\rho^2$, 那么

$$xu'' + (|l| + 1 - x)u' + \frac{1}{4\alpha}(1 - 2\alpha - 2\alpha|l|)u = 0, \quad (\text{A.1.12})$$

如果 $\frac{1}{4\alpha}(1 - 2\alpha - 2\alpha|l|) = n_r \geq 0 \in \mathbb{Z}$, 那么可以得到精确解,

$$R = \rho^{|l|} e^{-\frac{\alpha}{2}\rho^2} L_{n_r}^{(|l|)}(\alpha\rho^2), \quad (\text{A.1.13})$$

其中 $L_{n_r}^{(|l|)}(x)$ 是 **generalized Laguerre polynomial**.

- 对应的 energy eigenvalue 为

$$\epsilon = 2\hbar\omega_L \left(n_r + \theta(l)l + \frac{1}{2} \right) + \frac{p_z^2}{2m}, \quad \text{with} \quad \begin{cases} n_r \in \mathbb{Z}_{\geq 0} \\ l \in \mathbb{Z} \end{cases}. \quad (\text{A.1.14})$$

A.2 ladder operator method

- 令

$$\begin{cases} a = \frac{1}{\sqrt{2}}(a_x - ia_y) \\ b = \frac{1}{\sqrt{2}}(a_x + ia_y) \end{cases}, \quad \text{where} \quad a_i = \sqrt{\frac{m\omega_L}{2\hbar}} \left(x_i + \frac{i}{m\omega_L} p_i \right), \quad i = x, y, \quad (\text{A.2.1})$$

那么 a, b 满足

$$[a, a^\dagger] = [b, b^\dagger] = 1, \quad [a, b] = [a, b^\dagger] = 0. \quad (\text{A.2.2})$$

calculation:

$$\begin{cases} [a, a^\dagger] = \frac{1}{2}([a_x, a_x^\dagger] + [a_y, a_y^\dagger]) = 1 \\ [b, b^\dagger] = \frac{1}{2}([a_x, a_x^\dagger] + [a_y, a_y^\dagger]) = 1 \\ [a, b^\dagger] = \frac{1}{2}([a_x, a_x^\dagger] - [a_y, a_y^\dagger]) = 0 \end{cases} \quad (\text{A.2.3})$$

- 角动量算符 \hat{L}_z 可以写作

$$\hat{L}_z = -i\hbar(a_x^\dagger a_y - a_x a_y^\dagger) = \hbar(a^\dagger a - b^\dagger b). \quad (\text{A.2.4})$$

- 电子的 Hamiltonian (通过因式分解) 可以写作

$$\begin{aligned} H &= \frac{|\vec{p}|^2}{2m} + \omega_L(xp_y - yp_x) + \frac{1}{2}m\omega_L^2(x^2 + y^2) \\ &= \frac{p_z^2}{2m} + \left(\frac{p_x^2 + p_y^2}{2m} + \omega_L(xp_y - yp_x) + \frac{1}{2}m\omega_L^2(x^2 + y^2) \right) \\ &= \frac{p_z^2}{2m} + \left(\frac{p_x + ip_y}{\sqrt{2m}} + i\sqrt{\frac{m}{2}}\omega_L(x + iy) \right) \left(\frac{p_x - ip_y}{\sqrt{2m}} - i\sqrt{\frac{m}{2}}\omega_L(x - iy) \right) + \hbar\omega_L \\ &= \frac{p_z^2}{2m} + 2\hbar\omega_L \left(a^\dagger a + \frac{1}{2} \right). \end{aligned} \quad (\text{A.2.5})$$

- 因此, 系统的能量本征态为

$$|p_z\rangle \otimes (a^\dagger)^{n_a} |0\rangle_a \otimes (b^\dagger)^{n_b} |0\rangle_b, \quad \text{with} \quad \begin{cases} n_a \in \mathbb{Z}_{\geq 0} \\ n_b \in \mathbb{Z}_{\geq 0} \end{cases}, \quad (\text{A.2.6})$$

其本征值为

$$\begin{cases} \text{energy} & 2\hbar\omega_L \left(n_a + \frac{1}{2} \right) + \frac{p_z^2}{2m} \\ \text{angular momentum} & \hbar l = \hbar(n_a - n_b) \end{cases} \quad (\text{A.2.7})$$

— 与 (A.1.14) 有对应关系

$$\begin{cases} n_a = n_r + \theta(l)l \geq n_r \\ n_b = n_r - \theta(-l)l \geq n_r \end{cases}. \quad (\text{A.2.8})$$

A.3 energy level degeneracy

- 电子能级的简并度为

$$g(\epsilon) \simeq 2\pi V \frac{(2m)^{3/2}}{h^3} \epsilon^{1/2}, \quad (\text{A.3.1})$$

但是, 要注意直接拿 $\epsilon \gg 2\hbar\omega_L$ 计算 partition function, 等价于 $B \rightarrow 0$ (duh).

calculation:

注意到 $\frac{p_z^2}{2m} = \frac{\hbar^2}{8mL_z^2} n_z^2$, (其中 L_z 是 z 方向的长度, 不要与角动量算符 \hat{L}_z 混淆)

$$\begin{aligned} g(\epsilon) &= \int_0^\infty dn_r \int_{-\infty}^\infty dl \int_0^\infty dn_z \delta(\epsilon - \epsilon(n_r, l, n_z)) \\ &= \frac{1}{2} \sqrt{\frac{8mL_z^2}{h^2}} \int_0^\infty dn_r \int_{-\infty}^\infty dl \frac{1}{\sqrt{\epsilon - \epsilon(n_r, l, 0)}} \theta(\epsilon - \epsilon(n_r, l, 0)) \\ &= \frac{1}{2} \sqrt{\frac{8mL_z^2}{h^2}} \frac{1}{\sqrt{2\hbar\omega_L}} \int_0^\infty dn_r \int_{-\infty}^{\frac{\epsilon}{2\hbar\omega_L} - (n_r + \frac{1}{2})} dl \frac{1}{\sqrt{\frac{\epsilon}{2\hbar\omega_L} - (n_r + \frac{1}{2}) - \frac{l+|l|}{2}}} \\ &= L_z \sqrt{\frac{m}{\hbar^3\omega_L}} \int_0^\infty dn_r \left(\frac{l_{\max}}{\sqrt{\frac{\epsilon}{2\hbar\omega_L} - (n_r + \frac{1}{2})}} + 2\sqrt{\frac{\epsilon}{2\hbar\omega_L} - (n_r + \frac{1}{2})} \right) \theta(\epsilon - \epsilon(n_r, 0, 0)) \\ &= L_z \sqrt{\frac{2\pi m}{\hbar^3\omega_L}} \left(2l_{\max} \sqrt{\frac{\epsilon}{2\hbar\omega_L} - \frac{1}{2}} + \frac{4}{3} \left(\frac{\epsilon}{2\hbar\omega_L} - \frac{1}{2} \right)^{\frac{3}{2}} \right), \end{aligned} \quad (\text{A.3.2})$$

用经典力学估算 l_{\max} , (注意 $\vec{p} = m\vec{v} - e\vec{A}$),

$$\hbar l_{\max} = m\omega_L R_{\max}^2 \implies l_{\max} = \frac{eB}{h} S_{xy}, \quad (\text{A.3.3})$$

其中 $S_{xy} = \pi R_{\max}^2$, 对于

$$l_{\max} \gg \frac{\epsilon}{2\hbar\omega_L} \gg 1, \quad (\text{A.3.4})$$

近似有

$$g(\epsilon) \simeq 2\pi l_{\max} L_z \frac{\sqrt{2m}}{\hbar^2\omega_L} \epsilon^{1/2} = 2\pi V \frac{(2m)^{3/2}}{h^3} \epsilon^{1/2}. \quad (\text{A.3.5})$$

ladder operator 的方法与 Pathria 的方法一样,

$$\max(n_b) = l_{\max} = L_x L_y \frac{eB}{h}, \quad (\text{A.3.6})$$

结果一致.

按照 Pathria 的讲法, $\epsilon = 2\hbar\omega_L(j + \frac{1}{2}) + \frac{p_z^2}{2m}$, $j \in \mathbb{Z}_{\geq 0}$, 那么,

$$\begin{aligned} \frac{g(\epsilon)}{L_x L_y \frac{eB}{h}} &= \int_0^\infty dj \int_0^\infty dn_z \delta(\epsilon - \epsilon(j, n_z)) \\ &= \frac{1}{2} \sqrt{\frac{8mL_z^2}{h^2}} \int_0^\infty dj \frac{1}{\sqrt{\epsilon - \epsilon(j, 0)}} \theta(\epsilon - \epsilon(j, 0)) \\ &= \frac{1}{2} \sqrt{\frac{8mL_z^2}{h^2}} \frac{1}{\sqrt{2\hbar\omega_L}} \int_0^{\frac{\epsilon}{2\hbar\omega_L} - \frac{1}{2}} dj \frac{1}{\sqrt{\frac{\epsilon}{2\hbar\omega_L} - \frac{1}{2} - j}} \\ &= L_z \sqrt{\frac{2\pi m}{\hbar^3\omega_L}} 2\sqrt{\frac{\epsilon}{2\hbar\omega_L} - \frac{1}{2}} \simeq 2\pi L_z \frac{\sqrt{2m}}{\hbar^2\omega_L} \epsilon^{1/2}. \end{aligned} \quad (\text{A.3.7})$$