Statistical Mechanics

Siyang Wan (万思扬)

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Contents

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

- 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.

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
$$\begin{cases} S = k_B \ln \Omega(E, V, N) \\ TdS = dU + PdV - \mu dN \end{cases}, \tag{1.1.1}$$
其中 $U = \langle E \rangle$.
- 对于 homogeneous systems, 有
$$SdT = VdP - Nd\mu \iff TS = U + PV - \mu N. \tag{1.1.2}$$

homogeneity relations:

对于 homogeneous systems, 有
$$S(\alpha U, \alpha V, \alpha N) = \alpha S(U, V, N) \Longrightarrow TS = \cdots \tag{1.1.3}$$

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a function $f(x_1, \cdots, x_n)$ satisfying
$$f(\alpha x_1, \cdots, \alpha x_n) = \alpha^k f(x_1, \cdots, x_n) \tag{1.1.4}$$
is called a homogeneous function of degree k.
consider
$$\frac{\partial f(\alpha\vec{x})}{\partial \alpha} = \sum_i x_i \frac{\partial f}{\partial x_i}\Big|_{\alpha\vec{x}} = \frac{\partial \alpha^k f(\vec{x})}{\partial \alpha} = k\alpha^{k-1} f(\vec{x}), \tag{1.1.5}$$
and by setting $\alpha = 1$, we have Euler's homogeneous function theorem,
$$kf(\vec{x}) = \sum_i x_i \frac{\partial f}{\partial x_i}\Big|_{\vec{x}}. \tag{1.1.6}$$

- 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 源于 microcanonical ensemble, F 源于 canonical ensemble.

- the specific heats are

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

并存在关系

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

其中

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

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

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

得到 equation of state,

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

- 考虑方形势阱 ($L^3 = V$) 中的能量本征值,

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

那么

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

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

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

  – 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,

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

其中

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

Stirling's formula is

$$\ln N! \approx N \ln N - N. \tag{1.2.8}$$

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,

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

  因此, 得到 Sackur-Tetrode equation,

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

- 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

$$\mu = E\left(\frac{5}{3N} - \frac{2S}{3N^2 k_B} \right) = k_B T \ln \left(\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right). \tag{1.3.3}$$

- 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

$$\begin{cases} \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \\ \dot{q}_i = \dfrac{\partial H}{\partial p_i} \end{cases}. \tag{2.1.1}$$

- 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

$$\frac{\partial \rho}{\partial t} = 0, \tag{2.1.2}$$

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,

$$\frac{d\epsilon}{dt} = 0. \tag{2.1.3}$$

proof:

注意到

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

因此

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

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

- Liouville's equation:

$$\frac{\partial \rho}{\partial t} = \{H,\rho\}_{\mathrm{BP}} \equiv \sum_{i=1}^{\nu}\Big(\frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} - \frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i}\Big). \tag{2.1.6}$$

proof:

注意到

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

结合 Liouville's theorem, 可知

$$\frac{d\rho(p,q,t)}{dt} = 0 \Longrightarrow \cdots \tag{2.1.8}$$

2.2 the microcanonical ensemble

- the microcanonical ensemble 的概率密度为

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

其中

$$\Gamma = \frac{\omega}{\omega_0}, \tag{2.2.2}$$

其中 ω 是 $E-\Delta E \le H(p,q) \le E$ 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,

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

- 系统 A 处于能量 E 的**某个 microstate** 的概率为

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

  有近似

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

  因此, canonical ensemble 的概率密度为

$$\rho(p, q) = \frac{e^{-\beta H(p,q)}}{Z_{\mathrm{C}}}. \tag{3.1.4}$$

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 $N_{\mathrm{EL}} + 1$ 个 energy level,

$$\begin{cases} \sum_{i=0}^{N_{\mathrm{EL}}} n_i = \mathcal{N} \\ \sum_{i=0}^{N_{\mathrm{EL}}} n_i E_i = \mathcal{E} \end{cases}, \tag{3.2.1}$$

  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

$$W\{n_i\} = \frac{\mathcal{N}!}{n_0! \cdots n_{N_{\mathrm{EL}}}!} \Longrightarrow \ln W\{n_i\} \approx \mathcal{N} \ln \mathcal{N} - \sum_{i=0}^{N_{\mathrm{EL}}} n_i \ln n_i. \tag{3.2.2}$$

- 能级 i 上的子系统数量的期望值为

$$\langle n_i \rangle = \frac{\sum_{\{n_i\}} n_i W\{n_i\}}{\sum_{\{n_i\}} W\{n_i\}}. \tag{3.2.3}$$

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

$$\frac{n_i}{\mathcal{N}} = \frac{e^{-\beta E_i}}{Z_{\mathrm{C}}}, \tag{3.2.4}$$

其中 β 满足

$$\frac{\mathcal{E}}{\mathcal{N}} \equiv U = \frac{\sum_{i=0}^{N_{\mathrm{EL}}} E_i e^{-\beta E_i}}{Z_{\mathrm{C}}}. \tag{3.2.5}$$

  – 此时

$$\begin{aligned} \max(\ln W\{n_i\}) &= \beta\mathcal{E} + \mathcal{N}\ln Z_{\mathrm{C}} \\ &= \mathcal{N}\Big(1-\beta\frac{\partial}{\partial\beta}\Big)\ln Z_{\mathrm{C}}. \end{aligned} \tag{3.2.6}$$

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),

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

- 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

$$\tilde{W}\{n_i\} := \frac{\mathcal{N}!}{n_0!\cdots n_{N_{\mathrm{EL}}}!}\omega_0^{n_0}\cdots\omega_{N_{\mathrm{EL}}}^{n_{N_{\mathrm{EL}}}}, \tag{3.2.8}$$

和 (总系统的总微观态数)

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

  – 那么

$$\langle n_i\rangle = \frac{\partial}{\partial\omega_i}\Big|_{\omega_{0,\cdots,N_{\mathrm{EL}}}=1} \ln\Gamma(\mathcal{N}, U). \tag{3.2.10}$$

notice:

注意到

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

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 $G(\mathcal{N}, z)$,

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

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

- 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

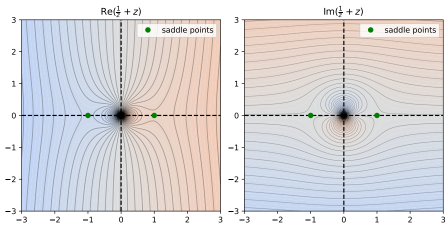
$$\Gamma(\mathcal{N}, U) = \frac{1}{2\pi i} \oint \frac{G(\mathcal{N}, z)}{z^{\mathcal{N}U+1}} dz \simeq \exp\Big(\mathcal{N}(\ln f(z_0) - U \ln z_0)\Big), \tag{3.2.13}$$

其中 z_0 满足

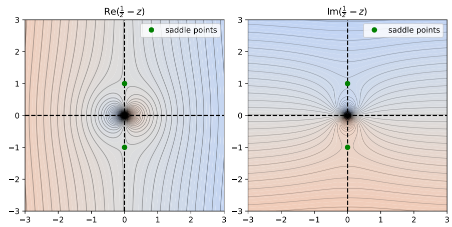
$$U \approx \frac{\sum_{i=0}^{N_{\text{EL}}} \omega_i E_i z_0^{E_i}}{\sum_{i=0}^{N_{\text{EL}}} \omega_i z_0^{E_i}}. \tag{3.2.14}$$

calculation:

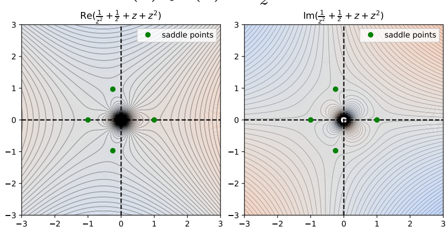
考虑 $f_1(z) = \frac{1}{z} + z, f_2(z) = \frac{1}{z} - z, f_3(z) = \frac{1}{z^2} + \frac{1}{z} + z + z^2, f_4(z) = \frac{1}{z^2} + \frac{1}{z} + z - z^2$, 分别如下图所示.



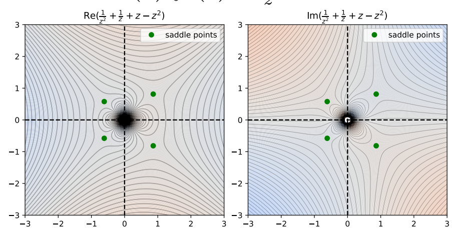
(a) $f_1(z) = \frac{1}{z} + z$.



(b) $f_2(z) = \frac{1}{z} - z$.



(c) $f_3(z) = \frac{1}{z^2} + \frac{1}{z} + z + z^2$.



(d) $f_4(z) = \frac{1}{z^2} + \frac{1}{z} + z - z^2$.

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,

$$\frac{(f(z))^{\mathcal{N}}}{z^{\mathcal{N}U+1}} = e^{\mathcal{N}g(z)} \Longrightarrow g(z) = \ln f(z) - \Big(U + \frac{1}{\mathcal{N}}\Big) \ln z, \tag{3.2.15}$$

鞍点 z_0 位于 (考虑到 $\mathcal{N}U \gg 1$)

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

此时

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

在 $g(z_0)$ 附近展开

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

因此积分可以近似为

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

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

或者

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

- 取 $\omega_{1,\cdots,N_{\mathrm{EL}}} = 1$, 此时 $z_0 \in \mathbb{R}$, 令
$$z_0 = e^{-\beta}, \tag{3.2.21}$$
那么
$$\begin{cases}\ln\Gamma(\mathcal{N},U) = \mathcal{N}(\ln Z_{\mathrm{C}} + \beta U) \\ Z_{\mathrm{C}} = \sum_{i=0}^{N_{\mathrm{EL}}} e^{-\beta E_i}\end{cases}. \tag{3.2.22}$$
- 还可以得到
$$\frac{\langle(\Delta n_i)^2\rangle}{\langle n_i\rangle^2} = \frac{1}{\langle n_i\rangle} - \frac{1}{\mathcal{N}}\left(1 + \frac{(E_i - U)^2}{\langle(E-U)^2\rangle}\right), \tag{3.2.23}$$
其中
$$\langle E^2\rangle = \frac{\sum_{i=1}^{N_{\mathrm{EL}}} E_i^2 e^{-\beta E_i}}{\sum_{i=1}^{N_{\mathrm{EL}}} e^{-\beta E_i}}, \quad U \equiv \langle E\rangle\,. \tag{3.2.24}$$
  - 注意 (3.2.5), U 是 subsystem 的能量期望値, 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
$$Z_{\mathrm{C}}(T,V,N) = \sum_{i=0}^{N_{\mathrm{EL}}} e^{-\beta E_i} = \int \frac{d^\nu p d^\nu q}{h^\nu} e^{-\beta H(p,q)}, \tag{3.3.1}$$
and the Helmholtz free energy is
$$F = U - TS = -k_B T\ln Z_{\mathrm{C}}. \tag{3.3.2}$$
  - $Z_{\mathrm{C}}(T,V,N)$ 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)
$$\begin{cases} Z_{\mathrm{C}}(T,V,E) = \int_0^\infty g(E)e^{-\beta E}dE \\ g(E) \equiv \frac{\Omega(N,V,E)}{\Delta E} = \frac{1}{2\pi i}\int_{-\infty}^{\infty} e^{(x+iy)E} Z_{\mathrm{C}}(T = \frac{1}{k_B(x+iy)}, V, E)dy, \end{cases} \tag{3.3.3}$$
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
$$\begin{aligned} Z_{\mathrm{C}}(T,V,N) &= \int \frac{d^{3N}pd^{3N}q}{N!h^{3N}} e^{-\beta\sum_{i=1}^N \frac{p_i^2}{2m}} \\ &= \frac{1}{N!}\left(\frac{V}{h^3}(2\pi m k_B T)^{3/2}\right)^N. \end{aligned} \tag{3.3.4}$$
- 观察可见
$$Z_{\mathrm{C}}(T,V,N) = \frac{(Z_{\mathrm{C}}(T,V,1))^N}{N!}, \tag{3.3.5}$$
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

$$\begin{aligned}\langle(\Delta E)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 &= \frac{1}{Z_{\mathrm{C}}}\frac{\partial^2}{\partial\beta^2}Z_{\mathrm{C}} - \Big(-\frac{\partial}{\partial\beta}\ln Z_{\mathrm{C}}\Big)^2 \\ &= \frac{\partial^2}{\partial\beta^2}\ln Z_{\mathrm{C}} = \Big(\frac{\partial U}{\partial\beta}\Big)_{V,N} = k_B T^2 C_V,\end{aligned} \tag{3.4.1}$$

因此

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

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

$$\frac{\partial\Omega(E,V,N)e^{-\beta E}}{\partial E}\Big|_{E^*} = 0 \Longrightarrow \Big(\frac{\partial\ln\Omega}{\partial E}\Big)_{V,N}\Big|_{E^*} = \frac{1}{k_B T}, \tag{3.4.3}$$

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

$$E^* = U, \tag{3.4.4}$$

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

- 系统处于能量 E 的概率是

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

calculation:

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

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

因此, partition function 为

$$Z_{\mathrm{C}}(T,V,N) \simeq e^{-\beta(U-TS)}\sqrt{2\pi k_B T^2 C_V}, \tag{3.4.7}$$

注意到

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

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,

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

所以,

$$\begin{cases}\dfrac{\partial H}{\partial p_i} = \displaystyle\sum_j \frac{p_j}{m_{ij}} \\ \dfrac{\partial H}{\partial q_i} = \displaystyle\sum_j \frac{\partial^2 H}{\partial q_i\partial q_j}q_j\end{cases} \Longrightarrow H = \frac{1}{2}\sum_i\Big(p_i\frac{\partial H}{\partial p_i} + q_i\frac{\partial H}{\partial q_i}\Big). \tag{3.5.2}$$

- 考虑
$$\langle x_i \frac{\partial H}{\partial x_j}\rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega} = \frac{1}{\beta}\delta_{ij}, \tag{3.5.3}$$
其中, x_i 是相空间的坐标, $x = (p_1, \cdots, p_\nu, q_1, \cdots, q_\nu)$.

proof:

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

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,
$$\langle H\rangle = \frac{1}{2}\sum_i \Big(\langle p_i \frac{\partial H}{\partial p_i}\rangle + \langle q_i \frac{\partial H}{\partial q_i}\rangle \Big) = \frac{f}{2} k_B T \tag{3.5.5}$$
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
$$\langle T\rangle = -\frac{1}{2}\mathcal{V}, \tag{3.5.6}$$
其中
$$\mathcal{V} := \sum_i \langle q_i \dot{p}_i\rangle \tag{3.5.7}$$
被称作系统的 virial.

proof:

考虑,
$$G = \sum_i p_i q_i \Longrightarrow \frac{dG}{dt} = \sum_i \underbrace{\dot{q}_i}_{=\frac{\partial H}{\partial p_i}} p_i + q_i \dot{p}_i = 2T + \sum_i q_i \dot{p}_i, \tag{3.5.8}$$
系统运动的范围有限, 所以,
$$\langle \frac{dG}{dt}\rangle = 0 \Longrightarrow \langle T\rangle = -\frac{1}{2}\sum_i \langle q_i \dot{p}_i\rangle. \tag{3.5.9}$$

3.5.3 classical ideal gas and nonideal gas

- 对于理想气体, 其 virial 为
$$\begin{aligned}\mathcal{V} = \sum_{i=1}^N \langle \vec{x}_i \cdot \vec{F}_i\rangle &= \oint_S \vec{x}\cdot(-P d\vec{S}) \\ &= -P \oint \nabla\cdot\vec{x}\, dV = -3PV,\end{aligned} \tag{3.5.10}$$

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

$$\frac{3}{2}Nk_BT = -\frac{1}{2}(-3PV) \Longrightarrow PV = Nk_BT. \tag{3.5.11}$$

- 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,

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

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

$$\begin{aligned} Z_{\mathrm{C}}(T,V,N=1) &= \int \frac{dpdq}{h}\, e^{-\beta(\frac{p^2}{2m}+\frac{1}{2}m^2\omega^2q^2)} = \frac{k_BT}{\hbar\omega} \\ \Longrightarrow Z_{\mathrm{C}}(T,V,N) &= \Big(\frac{k_BT}{\hbar\omega}\Big)^N, \end{aligned}\tag{3.6.1}$$

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

$$\begin{cases} U = Nk_BT \\ S = Nk_B\Big(1+\ln\dfrac{k_BT}{\hbar\omega}\Big) \\ \mu = -k_BT\ln\dfrac{k_BT}{\hbar\omega} \\ \Omega(E\geq 0) = \dfrac{1}{(\hbar\omega)^N}\dfrac{E^{N-1}}{(N-1)!} \end{cases}. \tag{3.6.2}$$

3.6.2 quantum mechanically

- 每个谐振子有如下能级,

$$\epsilon_n = \hbar\omega\Big(n+\frac{1}{2}\Big), \tag{3.6.3}$$

因此

$$\begin{aligned} Z_{\mathrm{C}}(T,V,N=1) &= \frac{1}{2\sinh\frac{\hbar\omega}{2k_BT}} \\ \Longrightarrow Z_{\mathrm{C}}(T,V,N) &= \Big(\frac{1}{2\sinh\frac{\hbar\omega}{2k_BT}}\Big)^N. \end{aligned}\tag{3.6.4}$$

- 得到

$$\begin{cases} U = N\hbar\omega\Big(\dfrac{1}{e^{\beta\hbar\omega}-1}+\dfrac{1}{2}\Big) \\ S = Nk_B\Big(\dfrac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ln(1-e^{-\beta\hbar\omega})\Big) \\ \mu = \dfrac{1}{2}\hbar\omega + k_BT\ln(1-e^{-\beta\hbar\omega}) \\ C_P = C_V = Nk_B(\beta\hbar\omega)^2\dfrac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} \end{cases}, \tag{3.6.5}$$

以及

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

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

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

  对于线性介质

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

3.7.1 classically

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

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

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

$$Z_{\mathrm{C}}(T,V,N)=\Big(\int\sin\theta d\theta d\phi\, e^{\beta\mu_0\mu H\cos\theta}\Big)^N=\Big(4\pi\frac{\sinh\frac{\mu_0\mu H}{k_BT}}{\frac{\mu_0\mu H}{k_BT}}\Big)^N. \tag{3.7.4}$$

- 得到

$$\langle\mu_z\rangle=\frac{VM_z}{N}=\mu\Big(\coth\frac{\mu_0\mu H}{k_BT}-\frac{k_BT}{\mu_0\mu H}\Big), \tag{3.7.5}$$

  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 $\mu_0\mu H\ll k_BT$ 时,

$$M_z\simeq\frac{N}{V}\frac{\mu_0\mu^2}{3k_BT}H\Longrightarrow\chi=\frac{C}{T}, \tag{3.7.6}$$

    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

- 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

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

  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,

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

并且

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

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

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

因此

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

- 单个磁矩的 Hamiltonian 为
$$\hat{H}=-\mu_0\mu_z H \tag{3.7.12}$$
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
$$\vec{\mu}_{\text{eff}}=-\frac{g(s,l,j)\mu_B}{\hbar}\vec{J}, \tag{3.7.13}$$
此时, 系统的能级为
$$\epsilon_{m_j}=g(s,l,j)\mu_0\mu_B H m_j, \tag{3.7.14}$$
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
$$Z_{\rm C}(T,V,N)=\Big(\sum_{m_j=-j}^{j}e^{-\beta g(s,l,j)\mu_0\mu_B H m_j}\Big)^N=\frac{\sinh(1+\frac{1}{2j})x}{\sinh\frac{1}{2j}x}, \tag{3.7.15}$$
其中 $x=\beta g(s,l,j)\mu_0\mu_B Hj$.
- 得到
$$\langle\mu_z\rangle=g(s,l,j)\mu_B j B_j(x), \tag{3.7.16}$$
其中 $B_j(x)$ 是 Brillouin function of order j,
$$B_j(x)=\Big(1+\frac{1}{2j}\Big)\coth\Big(\Big(1+\frac{1}{2j}\Big)x\Big)-\frac{1}{2j}\coth\Big(\frac{1}{2j}x\Big). \tag{3.7.17}$$
- 高温极限下, $x\to 0$, 有
$$\chi\equiv\frac{H}{M_z}\Big|_{\beta\to 0}=\frac{C_j}{T},\quad C_j=\frac{N}{V}\frac{\mu_0 g^2\mu_B^2 j(j+1)}{3k_B}, \tag{3.7.18}$$
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
$$Z_{\rm C}(T,V,N)=\Big(2\cosh(\beta\epsilon)\Big)^N. \tag{3.8.1}$$
- 得到
$$\begin{cases} U=-N\epsilon\tanh\dfrac{\epsilon}{k_BT} \iff \dfrac{1}{T}=\dfrac{k_B}{2\epsilon}\ln\dfrac{N\epsilon-U}{N\epsilon+U} \\ S=Nk_B\Big(\ln\Big(2\cosh\dfrac{\epsilon}{k_BT}\Big)-\dfrac{\epsilon}{k_BT}\tanh\dfrac{\epsilon}{k_BT}\Big) \\ M_z=\dfrac{N}{V}\mu_B\tanh\dfrac{\epsilon}{k_BT} \\ C_{V,H}=Nk_B\Big(\dfrac{\epsilon}{k_BT}\Big)^2\cosh^{-2}\dfrac{\epsilon}{k_BT} \end{cases}. \tag{3.8.2}$$
- 如果 $T<0$, 那么 E 必须有上限, 否则 $Z_{\rm C}\to\infty$.

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

$$
\begin{aligned}
Z_{\mathrm{C}}(T, V, N) &= \Big(\sum_{i=0}^{N_{\mathrm{EL}}} e^{-\beta\epsilon_i}\Big)^N \\
&\overset{\beta\to 0}{\simeq} \Big(\sum_{i=0}^{N_{\mathrm{EL}}} \Big(1 - \beta\epsilon_i + \frac{1}{2}(\beta\epsilon_i)^2\Big)\Big)^N = N_{\mathrm{EL}}^N\Big(1 - \beta\bar{\epsilon} + \frac{1}{2}\beta^2\overline{\epsilon^2}\Big)^N,
\end{aligned} \tag{3.8.3}
$$

  因此

$$
\ln Z_{\mathrm{C}}(T, V, N) \simeq N\Big(\ln N_{\mathrm{EL}} - \beta\bar{\epsilon} + \frac{1}{2}\beta^2(\overline{\epsilon^2} - \bar{\epsilon}^2)\Big). \tag{3.8.4}
$$

- 得到

$$
\begin{cases}
U \simeq N\Big(\bar{\epsilon} - \beta\overline{(\epsilon - \bar{\epsilon})^2}\Big) \\
S \simeq Nk_B\Big(\ln N_{\mathrm{EL}} - \frac{1}{2}\beta^2\overline{(\epsilon - \bar{\epsilon})^2}\Big) \\
C_V \simeq Nk_B\beta^2\overline{(\epsilon - \bar{\epsilon})^2}
\end{cases}. \tag{3.8.5}
$$

- 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

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

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,

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

- 系统 A 处于 E, N 下的某一个 microstate 的概率为

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

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 $N_{\mathrm{GCE}} = \mathcal{N}\langle N\rangle$, 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

$$\begin{cases} \displaystyle\sum_{i,N} n_{i,N} = \mathcal{N} \\ \displaystyle\sum_{i,N} n_{i,N} E_i = \mathcal{E} \\ \displaystyle\sum_{i,N} n_{i,N} N = N_{\mathrm{GCE}} \end{cases}. \tag{4.2.1}$$

- $\{n_{i,N}\}$ 的微观态数量为

$$W\{n_{i,N}\} = \frac{\mathcal{N}!}{n_{0,1}! \cdots n_{N_{\mathrm{EL}},N_{\mathrm{GCE}}}!} \Longrightarrow \ln W\{n_{i,N}\} = \mathcal{N}\ln\mathcal{N} - \sum_{i,N} n_{i,N}\ln n_{i,N}. \tag{4.2.2}$$

- 最概然分布为

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

- 并且有

$$\begin{cases} \langle N\rangle = \dfrac{1}{\beta}\dfrac{\partial}{\partial\mu}\ln Z_{\mathrm{GC}} \\ \langle E\rangle = -\dfrac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}} \end{cases}. \tag{4.2.4}$$

4.3 the partition function and the grand potential

- 定义 fugacity:
$$f := e^{\beta\mu}. \tag{4.3.1}$$
- the partition function of the grand canonical ensemble 为
$$Z_{\mathrm{GC}}(T,V,f) = \sum_{i,N} f^N e^{-\beta E_i} = \sum_{N=1}^{\infty} f^N Z_{\mathrm{C}}(E,V,N), \tag{4.3.2}$$
and the grand potential is
$$\Phi_{\mathrm{G}}(T,V,\mu) = -k_B T \ln Z_{\mathrm{GC}}(T,V,f). \tag{4.3.3}$$

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
$$\begin{cases} \langle(\Delta N)^2\rangle = \langle N^2\rangle - \langle N\rangle^2 = \dfrac{1}{\beta^2}\dfrac{\partial^2}{\partial\mu^2}\ln Z_{\mathrm{GC}} = \dfrac{1}{\beta}\Big(\dfrac{\partial N}{\partial\mu}\Big)_{T,V} \\ \langle(\Delta E)^2\rangle = \dfrac{\partial^2}{\partial\beta^2}\ln Z_{\mathrm{GC}} = -\Big(\dfrac{\partial U}{\partial\beta}\Big)_{V,f} \end{cases}, \tag{4.4.1}$$
因此
$$\begin{cases} \dfrac{\sqrt{\langle(\Delta N)^2\rangle}}{\langle N\rangle} = \sqrt{\dfrac{k_B T}{V}\kappa_T} \\ \langle(\Delta E)^2\rangle = \langle(\Delta E)^2\rangle_{\mathrm{C}} + \left(\Big(\dfrac{\partial U}{\partial N}\Big)_{T,V}\right)^2 \langle(\Delta N)^2\rangle \end{cases}, \tag{4.4.2}$$
通常 $\kappa_T \sim \frac{1}{P}$, 因此
$$\begin{cases} \dfrac{\sqrt{\langle(\Delta N)^2\rangle}}{\langle N\rangle} \sim N^{-\frac{1}{2}} \\ \dfrac{\sqrt{\langle(\Delta E)^2\rangle}}{U} \sim N^{-\frac{1}{2}} \end{cases}. \tag{4.4.3}$$

calculation:

考虑 $N(T,V,\mu)$, 注意对 homogeneous system $SdT = VdP - Nd\mu$,
$$dN = \Big(\frac{\partial N}{\partial\mu}\Big)_{T,V}\underbrace{\Big(-\frac{S}{N}dT + \frac{V}{N}dP\Big)}_{=d\mu} + \Big(\frac{\partial N}{\partial T}\Big)_{V,\mu}dT + \Big(\frac{\partial N}{\partial V}\Big)_{T,\mu}dV, \tag{4.4.4}$$
因此
$$\Big(\frac{\partial N}{\partial\mu}\Big)_{T,V}\frac{V}{N} = \Big(\frac{\partial N}{\partial P}\Big)_{T,V} = -\frac{\big(\frac{\partial V}{\partial P}\big)_{T,N}}{\big(\frac{\partial V}{\partial N}\big)_{T,P}}, \tag{4.4.5}$$
对 homogeneous system
$$\Big(\frac{\partial V}{\partial N}\Big)_{T,P} = \frac{V}{N}, \tag{4.4.6}$$
因此
$$\Big(\frac{\partial N}{\partial\mu}\Big)_{T,V} = -\frac{N^2}{V^2}\Big(\frac{\partial V}{\partial P}\Big)_{T,N} = \frac{N^2}{V}\kappa_T, \Longrightarrow \frac{\langle(\Delta N)^2\rangle}{N^2} = \frac{k_B T}{V}\kappa_T. \tag{4.4.7}$$

代入 $f = e^{\beta\mu}$,
$$\langle(\Delta E)^2\rangle = -\Big(\frac{\partial U}{\partial\beta}\Big)_{V,f} = k_B T^2\Big(\frac{\partial U}{\partial T}\Big)_{V,\mu} + k_B T\mu\Big(\frac{\partial U}{\partial\mu}\Big)_{T,V}, \tag{4.4.8}$$
且
$$\Big(\frac{\partial U}{\partial T}\Big)_{V,\mu} + \Big(\frac{\partial U}{\partial\mu}\Big)_{T,V}\Big(\frac{\partial\mu}{\partial T}\Big)_{V,N} = \Big(\frac{\partial U}{\partial T}\Big)_{V,N} = C_V, \tag{4.4.9}$$

代入,

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

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

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

所以

$$\langle(\Delta E)^2\rangle = \underbrace{k_B T^2 C_V}_{=\langle(\Delta E)^2\rangle_{\mathrm{C}}} + k_B T\Big(\frac{\partial U}{\partial N}\Big)_{T,V}\Big(\frac{\partial U}{\partial\mu}\Big)_{T,V}, \tag{4.4.12}$$

最后注意到

$$\Big(\frac{\partial U}{\partial N}\Big)_{T,V}\Big(\frac{\partial N}{\partial\mu}\Big)_{T,V} = \Big(\frac{\partial U}{\partial\mu}\Big)_{T,V}, \tag{4.4.13}$$

得到

$$\langle(\Delta E)^2\rangle = \langle(\Delta E)^2\rangle_{\mathrm{C}} + \bigg(\Big(\frac{\partial U}{\partial N}\Big)_{T,V}\bigg)^2\langle(\Delta N)^2\rangle\,. \tag{4.4.14}$$

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

$$Z_{\mathrm{C}}(T,V,N) = \frac{(Z_{\mathrm{C}}(T,V,1))^N}{N!}, \tag{4.5.1}$$

而

$$Z_{\mathrm{C}}(T,V,1) = V\phi(T). \tag{4.5.2}$$

- 理想气体的 Z_{GC} 为

$$Z_{\mathrm{GC}}(T,V,f) = \sum_{N=1}^{\infty} f^N\frac{(V\phi(T))^N}{N!} = \exp\Big(fV\phi(T)\Big), \tag{4.5.3}$$

因此

$$\begin{cases}\Phi_G = -k_B T f V\phi(T)\\ U = k_B T^2 f V\phi'(T)\\ N = fV\phi(T)\\ P = \dfrac{Nk_BT}{V}\\ S = Nk_B\Big(-\ln f + f\dfrac{V}{N}(T\phi'(T)+\phi(T))\Big)\end{cases}. \tag{4.5.4}$$

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)

$$Z_{\mathrm{C}}(T,V,N) = (Z_{\mathrm{C}}(T,V,1))^N, \quad Z_{\mathrm{C}}(T,V,1) = \phi(T) = \begin{cases}\dfrac{1}{2\sinh\frac{\hbar\omega}{2k_BT}} & \text{quantum mechanically}\\ \dfrac{k_BT}{\hbar\omega} & \text{classically}\end{cases}. \tag{4.5.5}$$

- 系统 Z_{GC} 为

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

因此

$$\begin{cases} N=\dfrac{f\phi(T)}{1-f\phi(t)}\implies f\phi(T)\simeq 1-\dfrac{1}{N}\iff\beta\mu\simeq-\dfrac{1}{N}-\ln\phi(T)\\ U=Nk_BT^2\dfrac{\phi'(T)}{\phi(T)}\\ S=Nk_B\Big(\ln\pi(T)+T\dfrac{\phi'(T)}{\phi(T)}+O(\frac{\ln N}{N})\Big)\end{cases}. \tag{4.5.7}$$

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),

$$\frac{N_{\mathrm{g}}}{V_{\mathrm{g}}\phi_{\mathrm{g}}(T)}=f_{\mathrm{g}}=f_{\mathrm{s}}\simeq\frac{1}{\phi_{\mathrm{s}}(T)}\implies\frac{N_{\mathrm{g}}}{V_{\mathrm{g}}}=\frac{P_{\mathrm{vapor}}}{k_BT}=\frac{\phi_{\mathrm{g}}(T)}{\phi_{\mathrm{s}}(T)}, \tag{4.5.8}$$

代入单原子气体的 $\phi_{\mathrm{g}}(T)$ 和 Einstein model 的 $\phi_{\mathrm{s}}(T)$, 得到

$$\begin{aligned}P_{\mathrm{vapor}}&=k_BT\Big(\frac{2\pi mk_BT}{h^2}\Big)^{\frac{3}{2}}\Big(2\sinh\frac{\hbar\omega}{2k_BT}\Big)^3e^{-\frac{\epsilon}{k_BT}}\\ &\overset{\text{classically}}{\simeq}k_BT\Big(\frac{m\omega^2}{2\pi k_BT}\Big)^{\frac{3}{2}}e^{-\frac{\epsilon}{k_BT}},\end{aligned} \tag{4.5.9}$$

其中 $\epsilon=\epsilon_{\mathrm{g}}-\epsilon_{\mathrm{s}}$ 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):

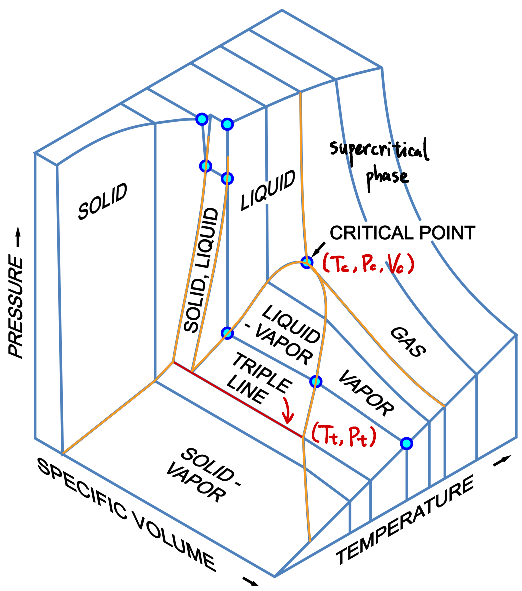


Figure 4.1: P-V-T phase diagram

- 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,

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

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,

$$sdT = vdP - d\mu \Longrightarrow d\mu = -sdT + vdP, \tag{4.7.2}$$

因此

$$-s_A dT + v_A dP = -s_B dT + v_B dP \Longrightarrow \cdots \tag{4.7.3}$$

- 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.

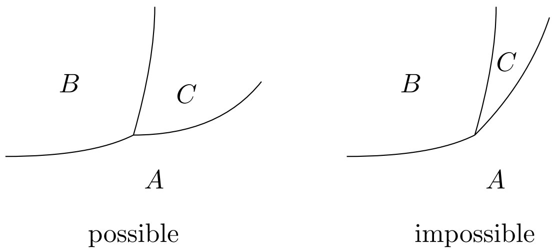


Figure 4.2: the slopes of 3 coexistence lines.

proof:

注意到

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

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

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

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,
$$\rho = \sum_i p_i \left|\psi_i\right\rangle \left\langle\psi_i\right|, \tag{5.1.1}$$
在 Schrödinger 绘景下
$$i\hbar\frac{\partial\rho}{\partial t} = [H, \rho]. \tag{5.1.2}$$
  - density matrix 满足
$$\operatorname{Tr}\rho = 1, \quad \operatorname{Tr}\rho^2 \le 1, \tag{5.1.3}$$
其中第二个等号在 pure state 下成立.
- the von Neumann entropy is
$$S = -\operatorname{Tr}\rho\ln\rho. \tag{5.1.4}$$
- 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
$$\rho = \sum_{\text{some } i} \frac{1}{\Omega} \left|i\right\rangle \left\langle i\right|, \tag{5.2.1}$$
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
$$\rho = \frac{e^{-\beta H}}{Z_{\mathrm{C}}}, \quad Z_{\mathrm{C}} = \operatorname{Tr} e^{-\beta H}. \tag{5.2.2}$$
- 各热力学量为
$$\begin{cases} F = -k_B T \ln Z_{\mathrm{C}}(T, V, N) \\ S = -\left(\dfrac{\partial F}{\partial T}\right)_{V,N} = k_B\left(\ln Z_{\mathrm{C}} + T\dfrac{\partial}{\partial T}\ln Z_{\mathrm{C}}\right) \end{cases}. \tag{5.2.3}$$

5.2.3 the grand canonical ensemble

- grand canonical ensemble 的 density matrix 为

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

- 各热力学量为

$$\begin{cases} \Phi_{\mathrm{G}} = k_B T \ln Z_{\mathrm{GC}}(T,V,\mu) \\ S = \Big(\dfrac{\partial \Phi_{\mathrm{G}}}{\partial T}\Big)_{V,\mu} = k_B\Big(\ln Z_{\mathrm{GC}} + T\dfrac{\partial}{\partial T}\ln Z_{\mathrm{GC}}\Big) \end{cases}. \tag{5.2.5}$$

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

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

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

- density matrix in the canonical ensemble is

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

- 得到

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

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

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

其中

$$\lambda = \Big(\frac{2\pi\beta\hbar^2}{m}\Big)^{\frac{1}{2}} \tag{5.4.2}$$

称为 thermal de Broglie wavelength.

calculation:

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

那么

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

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

Bosons 的情况类似.

- 如果两个粒子可区分,

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

- 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,

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

函数图像如下:

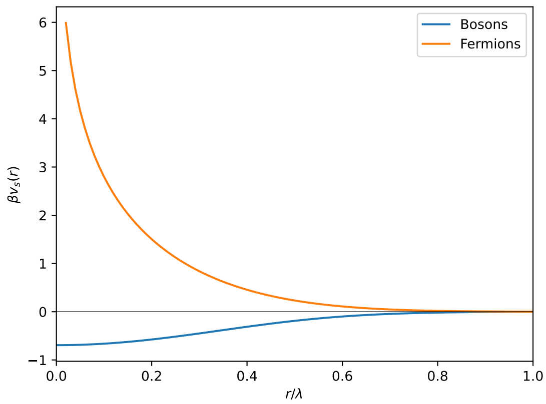


Figure 5.1: statistical potential.

proof:

只需要在 canonical ensemble 中引入一个 Boltzmann factor

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

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幺正性, 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,

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

  - 一般来说, 这样的 O 不可能存在, 因为

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

其时间平均值为

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

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 $\Omega(E) \propto (\frac{e^{\alpha'}}{\nu})^{\nu}$).
- 此时

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

考虑 pure state with energy eigenvalue E,

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

令

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

且如果 δO_n 满足

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

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

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

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

$$\begin{cases} \frac{1}{\Gamma}\langle \mathrm{Tr}\, R\rangle = 0 \\ \frac{1}{\Gamma}\langle \mathrm{Tr}\, R^2\rangle = \Gamma + 1 \end{cases}, \tag{5.5.9}$$

  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

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

  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

$$\begin{cases} \sum_i n_i = N \\ \sum_i n_i \epsilon_i = E \end{cases}, \tag{6.1.1}$$

系统的微观状态数为

$$\begin{cases} W_{\mathrm{B}}\{n_i\} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \\ W_{\mathrm{F}}\{n_i\} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} & n_i \le g_i \end{cases}, \tag{6.1.2}$$

其中 g_i 表示粒子的 ϵ_i 能级的 degeneracy.

  – 用 Stirling 公式作近似,

$$\begin{cases} \ln W_{\mathrm{B}}\{n_i\} \approx \sum_i \Big((n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i \Big) \\ \ln W_{\mathrm{F}}\{n_i\} \approx \sum_i \Big(g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i) \Big) \end{cases}. \tag{6.1.3}$$

calculation:

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

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

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

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

种放法.

- 最概然分布为

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

此时

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

其中 $\alpha = -\beta\mu$.

- 注意 $PV = TS - U + \mu N$, 得到

$$PV = -\frac{1}{\eta}k_B T \sum_i g_i \ln\left(1-\eta e^{-\alpha-\beta\epsilon_i}\right) \overset{\eta\to 0}{=} Nk_B T. \tag{6.1.8}$$

6.1.2 in a canonical ensemble

- 系统的 partition function 为

$$Z_{\mathrm{C}} = \sum_{\{n_i\}} W\{n_i\} e^{-\beta E\{n_i\}}, \tag{6.1.9}$$

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

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

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):

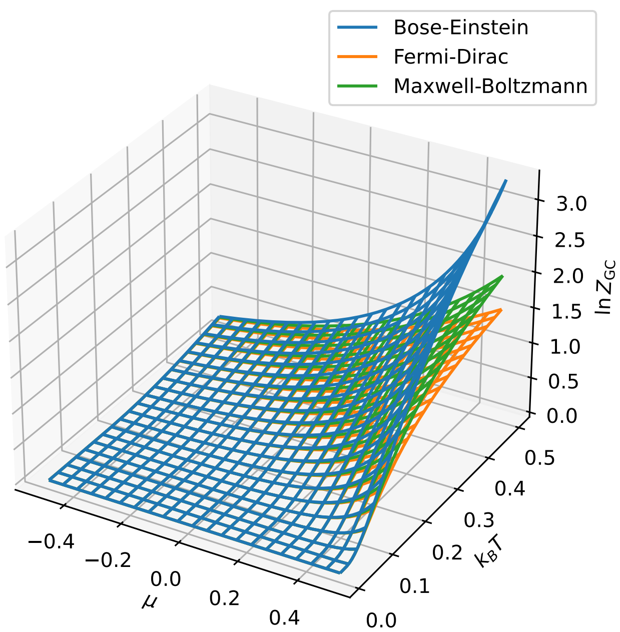


Figure 6.1: grand partition functions with $g = 3, \epsilon = 0.7$.

calculation:

麻烦的方法是

$$Z_{\mathrm{GC}} = \sum_{\{n_i=0\}}^{\{n_i=\max\}} W\{n_i\} e^{-\beta E\{n_i\} - \alpha N\{n_i\}}. \tag{6.1.11}$$

对 Bose-Einstein statistics,

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

注意到 Taylor expansion

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

所以

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

对于 Fermi-Dirac statistics,

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

注意到

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

所以

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

对于 Maxwell-Boltzmann statistics,

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

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

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

6.2 statistics of the occupation numbers

- 能级 ϵ_i 上的粒子数为

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

其函数图像如下:

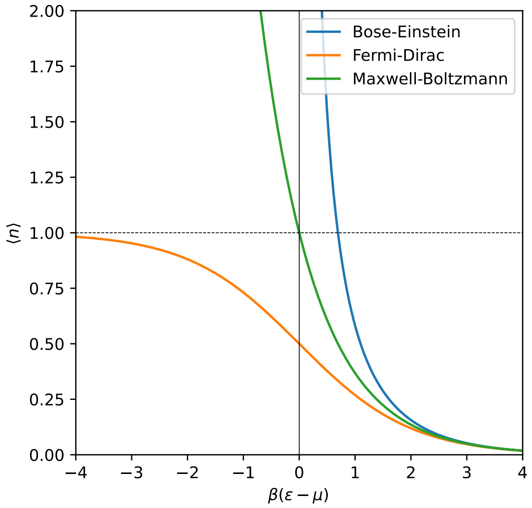


Figure 6.2: plot of $\langle n\rangle$ with $g = 1$.

- n_i 的方差为

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

calculation:

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

- 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

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

calculation:

能级占有 n_i 个粒子的概率是

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

Part II

more advanced topics

Part III

phase transition