Statistical Mechanics

Siyang Wan (万思扬)

April 20, 2025

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 $\Omega_1\Omega_2$ 处于最大値, 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	$\Phi_{\mathrm{G}} = U - TS - PV$	$\Phi_{\mathrm{G}} = -PV$	$d\Phi_{\mathrm{G}} = -SdT - PdV - Nd\mu$

– S 源于 microcanonical ensemble, F 源于 canonical ensemble.

- the specific heats are

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

并存在关系

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

其中

$$\begin{cases} \kappa_T = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_{T,N} \\ \kappa_S = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_{S,N} \\ \alpha = \frac{1}{V}\Big(\frac{\partial V}{\partial T}\Big)_{P,N} \end{cases}. \tag{1.1.9}$$

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

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

得到 equation of state,

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

- 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

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

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

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

– 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,

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

- 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

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

- 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,

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

- 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,

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

  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 $W\{n_i\}$ 取最大値, 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 $\ln W\{n_i\}$ 的极大値点, 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

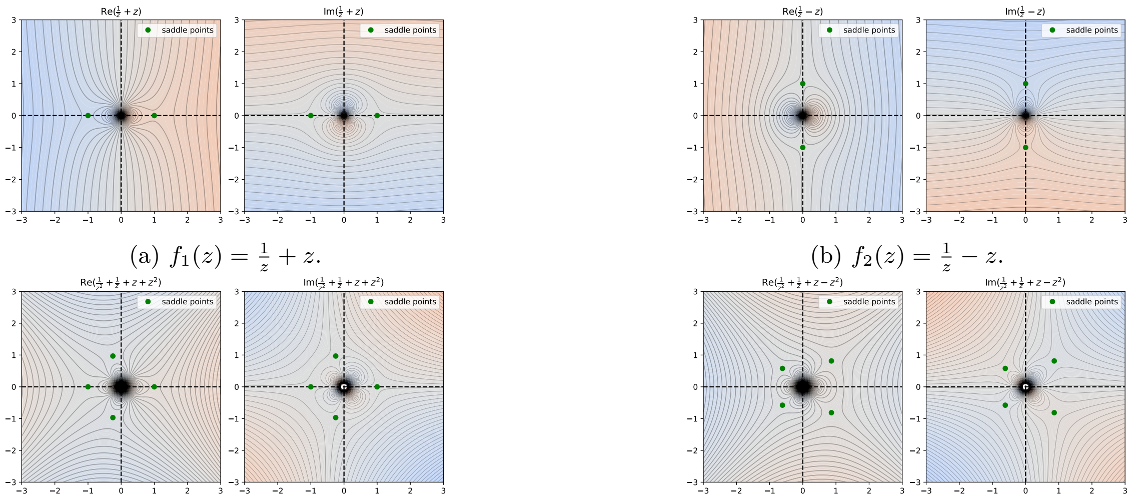
$$\Gamma(\mathcal{N},U)=\frac{1}{2\pi i}\oint\frac{G(\mathcal{N},z)}{z^{\mathcal{N}U+1}}dz\simeq\exp\Big(\mathcal{N}(\ln f(z_0)-U\ln z_0)\Big), \tag{3.2.13}$$

其中 z_0 满足

$$U\approx\frac{\sum_{i=0}^{N_{\mathrm{EL}}}\omega_iE_iz_0^{E_i}}{\sum_{i=0}^{N_{\mathrm{EL}}}\omega_iz_0^{E_i}}. \tag{3.2.14}$$

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 $\mathcal{N}U\gg1$)

$$\frac{dg(z=z_0)}{dz}=0\Longrightarrow U\approx U+\frac{1}{\mathcal{N}}=\frac{\sum_{i=0}^{N_{\mathrm{EL}}}\omega_iE_iz_0^{E_i}}{\sum_{i=0}^{N_{\mathrm{EL}}}\omega_iz_0^{E_i}}, \tag{3.2.16}$$

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

$$\begin{aligned}\Gamma(\mathcal{N},U)&\simeq\frac{1}{2\pi i}\frac{(f(z_0))^{\mathcal{N}}}{z_0^{\mathcal{N}U+1}}\int_{-\pi}^{\pi}\exp\Big(\frac{\mathcal{N}}{2}g''(z_0)(z_0e^{i\theta}-z_0)^2\Big)iz_0e^{i\theta}d\theta\\&\simeq\frac{1}{2\pi i}\frac{(f(z_0))^{\mathcal{N}}}{z_0^{\mathcal{N}U+1}}\int_{-\infty}^{\infty}\exp\Big(-\frac{\mathcal{N}}{2}g''(z_0)(z_0\theta)^2\Big)iz_0d\theta\end{aligned}$$

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

或者

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

- 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

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

  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 的能量期望值, 不是总系统 (heat reservoir) 的.

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 transformation)

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

  其中 $x > 0$ 是任意正实数.

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

$$\begin{aligned}Z_{\mathrm{C}}(T,V,N) &= \int \frac{d^{3N}pd^{3N}q}{N!h^{3N}} e^{-\beta\sum_{i=1}^{N}\frac{p_i^2}{2m}} \\ &= \frac{1}{N!}\Big(\frac{V}{h^3}\sqrt{2\pi m k_B T}\Big)^N.\end{aligned} \tag{3.3.4}$$

- 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

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

因此

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

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

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

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

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

calculation:

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

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

因此, partition function 为

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

注意到

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

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,

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

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

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Part II

more advanced topics

Part III

phase transition