Statistical Physics and Thermodynamics

万思扬

April, 25, 2024

Contents

Part I

Phenomenology

Chapter 1

systems composed of almost independent subsystems

- **近独立子系**：子系之间**几乎**没有相互作用，所以系统的能量为子系能量之和,

$$E(N, \epsilon_\lambda(y_l, N)) = \sum_i \epsilon_i \tag{1.0.1}$$

  – ϵ_λ 是子系处于 λ 能级时的能量，是广义坐标 y_l 的函数，注意温度 $\frac{1}{\beta}$ 是统计引入的，而 $\epsilon_\lambda(y_l, N)$ 是力学原理决定的，与统计原理无关，即,

$$\frac{\partial \epsilon_\lambda(y_l, N)}{\partial \beta} = 0 \tag{1.0.2}$$

  – 但系统要达到**平衡**，就要求子系之间必然**存在相互作用**。

- 粒子的能级分布 $\{a_\lambda\}$ 是每个能级上的子系统数量，满足,

$$\begin{cases} \sum_\lambda a_\lambda = N \\ \sum_\lambda \epsilon_\lambda a_\lambda = E \end{cases} \tag{1.0.3}$$

由于能级存在简并，简并度 (degeneracy) 为 $\{g_\lambda\}$ 所以微观状态数 $W(\{a_\lambda\})$ 不是一,

$$W(\{a_\lambda\}) = \frac{N!}{\prod_\lambda a_\lambda!} \prod_\lambda g_\lambda^{a_\lambda} \tag{1.0.4}$$

注意到，近独立子系**一定是可分辨**的，无论是否全同。

proof:

能级 ϵ_λ 中的 a_λ 个子系有 $g_\lambda^{a_\lambda}$ 种方式分布于不同的简并态中，然后由于可分辨，乘上前面的系数。

  – 使用 Stirling 近似,

$$\ln W(\{a_\lambda\}) \approx N \ln N - \sum_\lambda a_\lambda \ln \frac{a_\lambda}{g_\lambda} \tag{1.0.5}$$

  – 约束条件为,

$$\begin{cases} \delta E = \sum_\lambda \epsilon_\lambda \delta a_\lambda = 0 \\ \delta N = \sum_\lambda \delta a_\lambda = 0 \end{cases} \tag{1.0.6}$$

1.1 average distribution & most probable distribution

- 根据**等概率假设**，可知 $P(\{a_\lambda\}) \propto W(\{a_\lambda\})$，那么平均分布为，

$$\bar{a}_\lambda = \sum_{\{a_\lambda\}} a_\lambda P(\{a_\lambda\}) \tag{1.1.1}$$

- 最可几分布为，

$$\tilde{a}_\lambda = g_\lambda e^{-\alpha-\beta\epsilon_\lambda} = N g_\lambda \frac{e^{-\beta\epsilon_\lambda}}{Z} \tag{1.1.2}$$

其中 $e^\alpha = \frac{Z}{N}$

proof:

拉格朗日法求极值，

$$\begin{aligned} \frac{\partial W(\{a_\lambda\})}{\partial a_\lambda} &= \sum_\lambda \left(\ln \frac{a_\lambda}{g_\lambda} + 1\right) \\ \Longrightarrow \frac{\partial W}{\partial a_\lambda} &- \alpha \frac{\partial E}{\partial a_\lambda} - \beta \frac{\partial N}{\partial a_\lambda} = 0 \\ \Longrightarrow -\Big(\ln \frac{a_\lambda}{g_\lambda} &+ 1\Big) - \alpha\epsilon_\lambda - \beta = 0 \end{aligned} \tag{1.1.3}$$

且有，

$$\frac{\partial^2 W}{\partial a_{\lambda_1} \partial a_{\lambda_2}} = -\frac{1}{a_{\lambda_1}} \delta_{12} \le 0 \tag{1.1.4}$$

- 在 N 足够大的情况下，**最可几分布**等于**平均分布**，

$$\frac{W(\{\tilde{a}_\lambda + \delta a_\lambda\})}{W(\{\tilde{a}_\lambda\})} \approx \exp\Big(-\sum_\lambda \frac{\tilde{a}_\lambda}{2}\Big(\frac{\delta a_\lambda}{\tilde{a}_\lambda}\Big)^2\Big) \ll 1 \tag{1.1.5}$$

proof:

$$\ln \frac{W(\{\tilde{a}_\lambda + \delta a_\lambda\})}{W(\{\tilde{a}_\lambda\})} \approx \frac{1}{2} \sum_{\lambda_1,\lambda_2} \frac{\partial W}{\partial a_{\lambda_1} \partial a_{\lambda_2}} \delta a_{\lambda_1} \delta a_{\lambda_2} = -\sum_\lambda \frac{1}{2\tilde{a}_\lambda} (\delta a_\lambda)^2 \tag{1.1.6}$$

所以，

$$\frac{W(\{\tilde{a}_\lambda + \delta a_\lambda\})}{W(\{\tilde{a}_\lambda\})} \approx \exp\Big(-\sum_\lambda \frac{\tilde{a}_\lambda}{2}\Big(\frac{\delta a_\lambda}{\tilde{a}_\lambda}\Big)^2\Big) \ll 1 \tag{1.1.7}$$

所以，

$$\begin{aligned} & P(\{\tilde{a}_\lambda\}) \approx 1 \\ \Longrightarrow & P_\lambda \equiv \sum_{\{a_\lambda\}} P(\{a_\lambda\}) P(\lambda|\{a_\lambda\}) \approx P(\lambda|\{\tilde{a}_\lambda\}) = g_\lambda \frac{e^{-\beta\epsilon_\lambda}}{Z} \end{aligned} \tag{1.1.8}$$

或者，占据能级 λ 中某个简并态的概率为 $P_{i,\lambda} = \frac{e^{-\beta\epsilon_\lambda}}{Z}$

- 系统的**量子态总数**为，

$$\ln\Omega = \ln \sum_{\{a_\lambda\}} W(\{a_\lambda\}) \approx \ln W(\{\tilde{a}_\lambda\}) + O(\ln N) \tag{1.1.9}$$

proof:

$$\Omega \approx W(\{\tilde{a}_\lambda\}) \prod_\lambda \int_{-\epsilon}^{\epsilon} d(\delta a_\lambda) \exp\Big(-\frac{\tilde{a}_\lambda}{2}\Big(\frac{\delta a_\lambda}{\tilde{a}_\lambda}\Big)^2\Big) \tag{1.1.10}$$

where,

$$\int_{-\epsilon}^{\epsilon} d(\delta a_\lambda) \exp\Big(-\frac{\tilde{a}_\lambda}{2}\Big(\frac{\delta a_\lambda}{\tilde{a}_\lambda}\Big)^2\Big) \overset{x=\frac{\delta a_\lambda}{\tilde{a}_\lambda}}{\approx} \tilde{a}_\lambda \int_{-\infty}^{\infty} e^{-\frac{\tilde{a}_\lambda}{2}x^2} dx$$
$$= \tilde{a}_\lambda \sqrt{\frac{2\pi}{\tilde{a}_\lambda}} = \sqrt{2\pi \tilde{a}_\lambda} \tag{1.1.11}$$

so, we have,

$$\Omega \approx W(\{\tilde{a}_\lambda\}) \prod_\lambda \sqrt{2\pi\tilde{a}_\lambda}$$
$$\Longrightarrow \ln\Omega \approx \ln W(\{\tilde{a}_\lambda\}) + \underbrace{\frac{1}{2}\sum_\lambda \ln 2\pi\tilde{a}_\lambda}_{=O(\ln N)} \tag{1.1.12}$$

1.2 from partition function to everything

- recall that:
  - the constraints of the system are,

$$\begin{cases} \delta E = 0 & \text{in energy eigenstate} \\ \delta N = 0 \end{cases} \tag{1.2.1}$$

    with **almost independent** subsystem (and hence **distinguishable**), and, more strictly, the system is in an **eigenstate**.
  - the **energy level $\epsilon_\lambda(y_l)$**, which is determined by the law of mechanics, is **irrelevant to the temperature $\frac{1}{\beta}$**, which is introduced by statistics.
- summary:

$$\begin{cases} \text{entropy} & S = N\Big(\ln Z - \beta\frac{\partial}{\partial\beta}\ln Z\Big) \\ \text{internal energy} & E = -N\frac{\partial}{\partial\beta}\Big|_{y,N} \ln Z = \frac{1}{\beta}(S - N\ln Z) \\ \text{generalized force} & \langle Y_l\rangle = \sum_\lambda \tilde{a}_\lambda \frac{\partial\epsilon_\lambda}{\partial y_l} = \frac{N}{\beta}\frac{\partial}{\partial y_l}\Big|_{\beta,N} \ln Z \\ \text{chemical potential} & \mu = -\frac{1}{\beta}\frac{\partial}{\partial N}\Big|_{\beta,y} \ln Z^N \\ \text{Helmholtz free energy} & F = U - TS = -\frac{N}{\beta}\ln Z \end{cases} \tag{1.2.2}$$

- the **partition function** of the **subsystem** is,

$$Z(\beta, \epsilon_\lambda(y_l, N)) = \sum_\lambda g_\lambda e^{-\beta\epsilon_\lambda(y_l,N)} \tag{1.2.3}$$
$$\Longrightarrow E = -N\frac{\partial}{\partial\beta}\ln Z(\beta, y_l, N) \tag{1.2.4}$$

- the **entropy** is,

$$S = -\mathrm{tr}(\rho\ln\rho)$$
$$\approx N\ln Z + \beta E = N\Big(\ln Z - \beta\frac{\partial}{\partial\beta}\ln Z\Big) \tag{1.2.5}$$

proof:

the von Neumann entropy is,

$$\begin{cases} S = -\mathrm{tr}(\rho \ln \rho) \\ \rho = \sum_{\{a_{i,\lambda}\}} \underbrace{P(\{a_{i,\lambda}\})}_{\propto P(\{a_\lambda\})} |\{a_{i,\lambda}\}\rangle \langle \{a_{i,\lambda}\}| \end{cases} \tag{1.2.6}$$

so,

$$\begin{aligned} S &= -\sum_{\{a_{i,\lambda}\}} P(\{a_{i,\lambda}\}) \ln P(\{a_{i,\lambda}\}) \\ &\approx -\sum_{\tilde{a}_{i,\lambda}} P(\{\tilde{a}_{i,\lambda}\}) \ln P(\{\tilde{a}_{i,\lambda}\}) \\ &= \ln W(\{\tilde{a}_\lambda\}) \end{aligned} \tag{1.2.7}$$

where, the number of microstate is,

$$\begin{aligned} \ln W(\{\tilde{a}_\lambda\}) &\approx N \ln N - \sum_\lambda \tilde{a}_\lambda \ln \frac{\tilde{a}_\lambda}{g_\lambda} \\ &= N \ln N - N \sum_\lambda g_\lambda \frac{e^{-\beta\epsilon_\lambda}}{Z} \ln \left(N \frac{e^{-\beta\epsilon_\lambda}}{Z} \right) \\ &= N \ln Z + \beta E = N \Big(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \Big) \end{aligned} \tag{1.2.8}$$

- the energy of the system is,

$$E = \frac{1}{\beta}(S - N \ln Z) \Longleftrightarrow dE = \frac{1}{\beta}\Big(dS - N \frac{\partial \ln Z}{\partial y_l} dy_l - \frac{\partial \ln Z^N}{\partial N} dN \Big) \tag{1.2.9}$$

proof:

using the equation of entropy, $E = \frac{1}{\beta}(S - N \ln Z)$, so,

$$\begin{aligned} dE &= \frac{1}{\beta}\Big(dS \underbrace{-N \frac{\partial \ln Z}{\partial \beta}}_{=E} d\beta - N \frac{\partial \ln Z}{\partial y_l} dy_l - \frac{\partial N \ln Z}{\partial N} dN \Big) + \underbrace{(S - N \ln Z)}_{=\beta E} d\Big(\frac{1}{\beta}\Big) \\ &= \frac{1}{\beta}\Big(dS - N \frac{\partial \ln Z}{\partial y_l} dy_l - \frac{\partial \ln Z^N}{\partial N} dN \Big) \end{aligned} \tag{1.2.10}$$

  - notice that the **temperature** is $T = \frac{\partial E}{\partial S}\big|_{y_l,N} \Longrightarrow T = \frac{1}{\beta}$
  - the **generalized force** is defined to be,

$$\begin{cases} Y_l dy_l = dW = -\sum_\lambda a_\lambda d\epsilon_\lambda \\ \langle Y_l \rangle = \sum_{\{a_\lambda\}} P(\{a_\lambda\}) Y_l(\{a_\lambda\}) \end{cases} \Longrightarrow \langle Y_l \rangle \approx \frac{N}{\beta} \frac{\partial}{\partial y_l}\Big|_{\beta,N} \ln Z \tag{1.2.11}$$

proof:

since $P(\{\tilde{a}_\lambda\}) \approx 1$, we have,

$$\langle Y_l \rangle \approx -\sum_\lambda \tilde{a}_\lambda \frac{d\epsilon_\lambda}{dy_l} = -\sum_\lambda \underbrace{N g_\lambda \frac{e^{-\beta\epsilon_\lambda}}{Z}}_{=\tilde{a}_\lambda} \frac{d\epsilon_\lambda}{dy_l} \tag{1.2.12}$$

and,

$$\frac{\partial Z}{\partial y_l} = -\beta \sum_\lambda g_\lambda e^{-\beta\epsilon_\lambda} \frac{d\epsilon_\lambda}{dy_l} \implies \langle Y_l \rangle \approx \frac{N}{Z}\Big(\frac{1}{\beta}\frac{\partial Z}{\partial y_l}\Big) \tag{1.2.13}$$

$\langle Y_l \rangle$ is determined by both mechanic law and **statistic rules**.

- the **chemical potential** is,

$$\mu = -\frac{1}{\beta}\frac{\partial}{\partial N}\Big|_{\beta,y} \ln Z^N \tag{1.2.14}$$

- the heat,

$$dQ = \Big(\frac{E}{N} - \mu\Big)dN + \sum_\lambda \epsilon_\lambda N dP_\lambda \tag{1.2.15}$$

proof:

consider,

$$\langle dE \rangle = d\Big(\sum_\lambda \tilde{a}_\lambda \epsilon_\lambda\Big) = \sum_\lambda \Big(\tilde{a}_\lambda d\epsilon_\lambda + \epsilon_\lambda d\Big(N g_\lambda \frac{e^{-\beta\epsilon_\lambda}}{Z}\Big)\Big) \tag{1.2.16}$$

the heat is,

$$\begin{aligned} dQ &= \langle dE \rangle + \sum_l Y_l dy_l - \mu dN \\ &= \Big(\frac{E}{N} - \mu\Big)dN + \sum_\lambda \epsilon_\lambda N dP_\lambda \end{aligned} \tag{1.2.17}$$

restrict $dN = 0$, we have,

$$dQ = \sum_\lambda \epsilon_\lambda N dP_\lambda \tag{1.2.18}$$

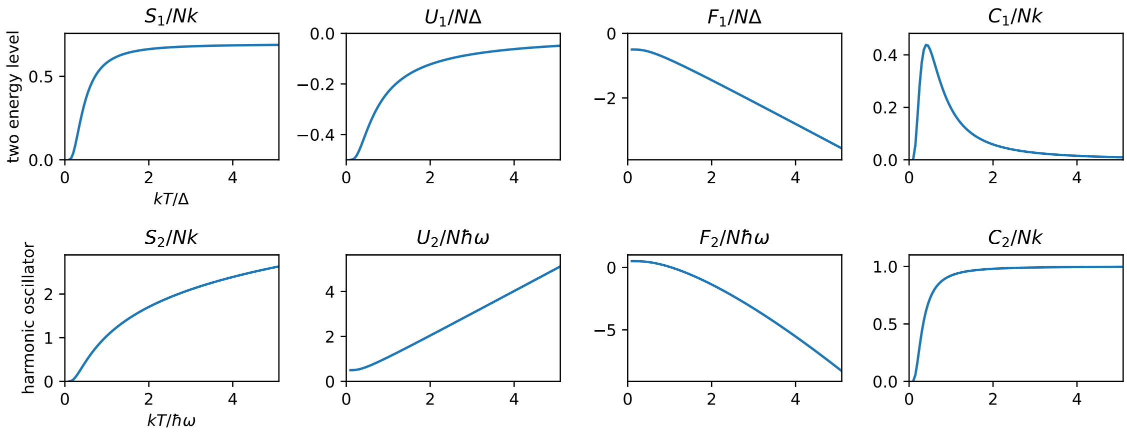
which implies that **adiabatic process** $\iff$ **preserves the most probable distribution**, $dN = dP_\lambda = 0$.

- the **Helmholtz free energy** is,

$$F = U - TS = -\frac{N}{\beta}\ln Z \tag{1.2.19}$$

1.3 two examples

- **二能级系统**与**谐振子系统**的热力学量随温度的变化如下图所示,



  – 二能级系统的热容在 $k_BT \sim \Delta$ 附近达到极大値，称为 Schottky 反常。

1.3.1 二能级系统，粒子数反转 & 负绝对温度

- N 个近独立子系统，子系统只有两个能级，$\epsilon_1 = -\frac{\Delta}{2}, \epsilon_2 = \frac{\Delta}{2}$，且不存在简并，$g_1 = g_2 = 1$
- the partition function is,

$$Z = \sum_{\lambda=1,2} g_\lambda e^{-\beta\epsilon_\lambda} = 2\cosh\frac{\beta\Delta}{2} \tag{1.3.1}$$

and the most probable distribution is,

$$\tilde{a}_\lambda = N g_\lambda \frac{e^{-\beta\epsilon_\lambda}}{Z}, \lambda = 1, 2 \tag{1.3.2}$$

- the entropy, energy and free energy of the system are,

$$\begin{cases} S = N\left(\ln\left(2\cosh\frac{\beta\Delta}{2}\right) - \frac{\beta\Delta}{2}\tanh\frac{\beta\Delta}{2}\right) \\ U = -\frac{N\Delta}{2}\tanh\frac{\beta\Delta}{2} \\ F = -\frac{N}{\beta}\ln\left(2\cosh\frac{\beta\Delta}{2}\right) \end{cases}$$

- the heat capacity is,

$$C = T\frac{\partial S}{\partial T}\Big|_N = N\left(\frac{\beta\Delta}{2}\right)^2 \cosh^{-2}\left(\frac{\beta\Delta}{2}\right) \tag{1.3.3}$$

calculation:

$$C = T\frac{\partial S}{\partial T}\Big|_N = -\beta\frac{\partial S}{\partial \beta}\Big|_N = \cdots \tag{1.3.4}$$

高温极限下 $\lim_{T\to\infty} C = \frac{N}{4}\left(\frac{\Delta}{k_B T}\right)^2 \sim \beta^2$，趋近于零。

粒子数反转 & 负绝对温度

- 二能级系统，熵与能量的关系为，

$$S = k_B\left(N\ln N - \frac{1}{2}\left(N - \frac{\overline{E}}{\epsilon}\right)\ln\frac{1}{2}\left(N - \frac{\overline{E}}{\epsilon}\right) - \frac{1}{2}\left(N + \frac{\overline{E}}{\epsilon}\right)\ln\frac{1}{2}\left(N + \frac{\overline{E}}{\epsilon}\right)\right) \tag{1.3.5}$$

其中 $\epsilon = \frac{\Delta}{2}$

proof:

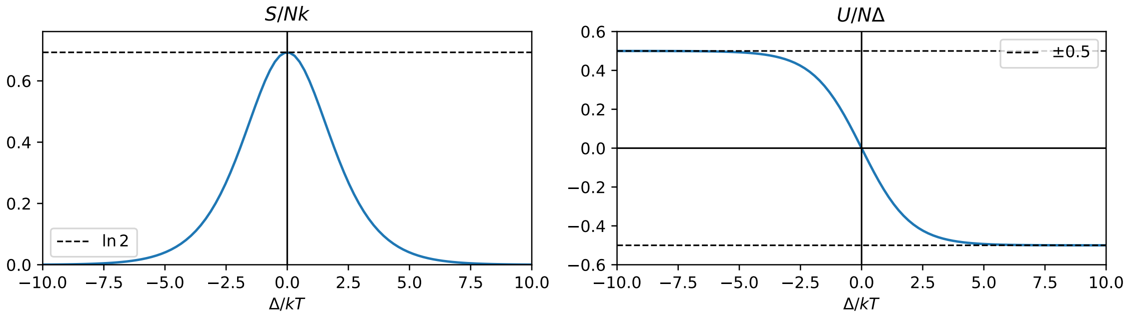
系统的微观状态数为，

$$\begin{cases} \overline{E} = \epsilon_1\overline{a}_1 + \epsilon_2\overline{a}_2 \\ N = \overline{a}_1 + \overline{a}_2 \\ W = C_N^{\overline{a}_1} = \frac{N!}{\overline{a}_1!(N-\overline{a}_1)!} \end{cases} \Longrightarrow \begin{cases} \overline{a}_1 = \frac{\overline{E} - N\epsilon_2}{\epsilon_1 - \epsilon_2} = \frac{N}{2} - \frac{\overline{E}}{\Delta} \\ \overline{a}_2 = \frac{\overline{E} - N\epsilon_1}{\epsilon_2 - \epsilon_1} = \frac{N}{2} + \frac{\overline{E}}{\Delta} \end{cases}$$
$$\Longrightarrow \ln W = N\ln N - \overline{a}_1\ln\overline{a}_1 - \overline{a}_2\ln\overline{a}_2 \tag{1.3.6}$$

所以，温度为，

$$\frac{1}{T} = \frac{\partial S}{\partial \overline{E}}\Big|_N = \frac{k_B}{\Delta}\ln\frac{N\epsilon - \overline{E}}{N\epsilon + \overline{E}} \tag{1.3.7}$$

  - 可见，$\overline{E} > 0$ 时，$T < 0$
  - $T = 0^-$ 对应最高能量，$\overline{E}_{\max} = N\epsilon$



- 实现负绝对温度的条件为：
  - 能量有上限，
  - 系统能达到平衡（能够具有温度），
  - 系统与环境隔绝。

  最后两个条件可以概括为 $\tau_s \ll \tau_E$，其中 τ_s 是系统内部达到平衡的弛豫时间，τ_E 是系统与环境达到平衡的弛豫时间。

1.3.2 谐振子系统

- 系统由 N 个近独立的谐振子组成，因此，子系统的能级不存在简并，为，

$$\epsilon_n = \hbar\omega(n + \frac{1}{2}) \tag{1.3.8}$$

- 配分函数为，

$$Z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} = \frac{1}{2\sinh\frac{\beta\hbar\omega}{2}} \tag{1.3.9}$$

- 系统的熵、内能和自由能为，

$$\begin{cases} S = N\Big(-\ln 2\sinh\dfrac{\beta\hbar\omega}{2} + \dfrac{\beta\hbar\omega}{2}\coth\dfrac{\beta\hbar\omega}{2}\Big) \\ U = N\dfrac{\hbar\omega}{2}\coth\dfrac{\beta\hbar\omega}{2} = N\hbar\omega\Big(\dfrac{1}{2} + \dfrac{1}{e^{\hbar\omega/k_BT} - 1}\Big) \\ F = \dfrac{N}{\beta}\ln 2\sinh\dfrac{\beta\hbar\omega}{2} \end{cases} \tag{1.3.10}$$

  高温极限下，$\lim_{T\to\infty} U = Nk_BT$

- 系统热容为，

$$C = -\beta\frac{\partial S}{\partial\beta}\Big|_N = N\Big(\frac{\frac{\beta\hbar\omega}{2}}{\sinh\frac{\beta\hbar\omega}{2}}\Big)^2 \tag{1.3.11}$$

  高温极限下，$\lim_{T\to\infty} C = Nk_B$

1.4 equipartition theorem

- 能均分定理 (equipartition theorem) 适用于**子系统的哈密顿量为二次型**的系统，

$$H = \sum_{ij}\Big(\frac{p_ip_j}{2m_{ij}} + \frac{1}{2}\frac{\partial^2 H}{\partial q_i\partial q_j}q_iq_j\Big) \tag{1.4.1}$$

  所以，

$$\begin{cases} \dfrac{\partial H}{\partial p_i} = \sum_j \dfrac{p_j}{m_{ij}} \\ \dfrac{\partial H}{\partial q_i} = \sum_j \dfrac{\partial^2 H}{\partial q_i\partial q_j}q_j \end{cases} \Longrightarrow H = \frac{1}{2}\sum_i\Big(p_i\frac{\partial H}{\partial p_i} + q_i\frac{\partial H}{\partial q_i}\Big) \tag{1.4.2}$$

- 考虑,
$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega} = \frac{1}{\beta}\delta_{ij} \tag{1.4.3}$$
其中，x_i 是相空间的坐标，$x = q_1, \cdots, q_r, p_1, \cdots, p_r$

proof:

$$\begin{aligned}\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega &= -\int x_i \frac{1}{\beta} \frac{\partial e^{-\beta H}}{\partial x_j} d\omega \\ &= -\frac{1}{\beta}\int \left(\frac{\partial}{\partial x_j}(x_i e^{-\beta H}) - \delta_{ij} e^{-\beta H} \right) d\omega \\ &= \frac{1}{\beta}\delta_{ij} Z_1 - \frac{1}{\beta}\int (x_i e^{-\beta H}) \Big|_{x_j=(x_j)_1}^{(x_j)_2} d\omega_{(j)}\end{aligned} \tag{1.4.4}$$

哈密顿量在边界处，$x_j = (x_j)_{1,2}$，为零，所以,

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\beta}\delta_{ij} \tag{1.4.5}$$

- 所以，能量的期望值为,
$$\langle H \rangle = \frac{1}{2}\sum_i \left(\langle p_i \frac{\partial H}{\partial p_i} \rangle + \langle q_i \frac{\partial H}{\partial q_i} \rangle \right) = \frac{N_f}{2} k_B T \tag{1.4.6}$$
其中，N_f 是系统的自由度，是 $\boldsymbol{2r}$ 减去循环坐标的数量。
- 能均分定理的适用条件：
  - 经典力学,
  - 哈密顿量为二次型。

1.4.1 virial theorem

- the virial theorem states that, for $H = T + V(q_1, \ldots, q_r)$ where the kinetic energy T is a quadratic form of $(p_1, \ldots, p_r)$ and V is independent of p's, then,
$$\langle T \rangle = \frac{1}{2}\sum_i \langle q_i \frac{\partial V}{\partial q_i} \rangle \tag{1.4.7}$$

proof:

consider,
$$G = \sum_i p_i q_i \Longrightarrow \frac{dG}{dt} = \sum_i \underbrace{\frac{dq_i}{dt}}_{=\frac{\partial H}{\partial p_i}} p_i + q_i \underbrace{\frac{dp_i}{dt}}_{=-\frac{\partial H}{\partial q_i}} = 2T - \sum_i q_i \frac{\partial V}{\partial q_i} \tag{1.4.8}$$
系统运动的范围有限，所以,
$$\langle \frac{dG}{dt} \rangle = 0 \Longrightarrow \langle T \rangle = \frac{1}{2}\sum_i \langle q_i \frac{\partial V}{\partial q_i} \rangle \tag{1.4.9}$$

- 结合能均分定理,
$$\mathcal{V} \equiv \sum_{i=1}^{3N} \langle q_i \dot{p}_i \rangle = -2\langle T \rangle = -3N k_B T \tag{1.4.10}$$
其中，N 是粒子数，$\mathcal{V}$ 称为位力 (virial)。
- 如果系统的势能为 $V(\lambda \vec{q}) = \lambda^n V(\vec{q})$，那么,
$$V = \frac{1}{n}\sum_i q_i \frac{\partial V}{\partial q_i} \Longrightarrow \mathcal{V} = -n\langle V \rangle \tag{1.4.11}$$

homogeneity relations:

- a function $f(x_1, \dots, x_n)$ satisfying $f(\alpha x_1, \dots, \alpha x_n) = \alpha^k f(x_i)$ is called a **homogeneous function of degree** $\boldsymbol{k}$
- **Euler's homogeneous function theorem**: $f(x_1, \dots, x_n)$ is homogeneous of degree k, then,

$$kf(\vec{x}) = \sum_{i=1}^{n} x_i \frac{\partial f(\vec{x})}{\partial x_i} \tag{1.4.12}$$

---

proof:

$$\frac{\partial f(\alpha\vec{x})}{\partial \alpha} = \sum_i x_i \frac{\partial f}{\partial x_i}\Big|_{\alpha\vec{x}} \tag{1.4.13}$$

and notice that,

$$\frac{\partial f(\alpha\vec{x})}{\partial \alpha} = \frac{\partial \alpha^k f(\vec{x})}{\partial \alpha} = k\alpha^{k-1} f(\vec{x}) \tag{1.4.14}$$

finally, set $\alpha = 1$, we have,

$$kf(\vec{x}) = \sum_i x_i \frac{\partial f}{\partial x_i}\Big|_{\vec{x}} \tag{1.4.15}$$

- 对谐振子，$\langle T \rangle = \langle V \rangle$
- 对引力或库仑系统，$-2\langle T \rangle = \langle V \rangle$

Chapter 2

ideal gases

2.1 monatomic gases

- **monatomic** means single atom.
- the partition function of the subsystem is,

$$Z_1 = \int \frac{d^3xd^3p}{h^3} e^{-\beta \frac{1}{2m}(p_x^2+p_y^2+p_z^2)} = V \underbrace{\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}}_{=n_Q} \tag{2.1.1}$$

  – 定义,

$$\begin{cases} n_Q = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} & \text{量子密度} \\ \lambda_{\text{th}} = n_Q^{-1/3} = \frac{h}{\sqrt{2\pi m k_B T}} & \text{特征长度} \end{cases} \tag{2.1.2}$$

- the partition function of the total system is,

$$Z_{\text{tot}} = \frac{1}{N!} Z_1^N \tag{2.1.3}$$

其中，系数 $\frac{1}{N!}$ 是因为子系统不可分辨，这与近独立系统子系统可分辨的性质不同。

- the energy, entropy, free energy, pressure and chemical potential of the system are,

$$\begin{cases} U = \frac{3}{2}k_BT \\ F = -Nk_BT\Big(\ln v + 1 + \frac{3}{2}\ln\frac{2\pi m k_B T}{h^2}\Big) = Nk_BT(\ln n\lambda_{\text{th}}^3 - 1) \\ S = Nk_B\Big(\ln v + \frac{5}{2} + \frac{3}{2}\ln\frac{2\pi m k_B T}{h^2}\Big) = Nk_B\Big(\frac{5}{2} - \ln n\lambda_{\text{th}}^3\Big) \\ p = \frac{1}{\beta}\frac{\partial}{\partial V}\Big|_{\beta,N} Z_{\text{tot}} = nk_BT \\ \mu = k_BT\ln n\lambda_{\text{th}}^3 \end{cases} \tag{2.1.4}$$

where $v = \frac{V}{N}, n = \frac{N}{V}$

2.2 diatomic gases

- the Hamiltonian of a diatomic molecule is,

$$H = \frac{1}{2m}(p_x^2+p_y^2+p_z^2) + \frac{1}{2\mu}p_r^2 + \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) + \frac{1}{2}\mu\omega^2 q_r^2 \tag{2.2.1}$$

where μ is the reduced mass, $I = \mu r_0^2$, $q_r = r - r_0$, and $p_\theta = I\dot\theta, p_\phi = I\sin^2\theta\dot\phi$

2.2.1 rotation and vibration

- treat the rotation and vibration as a subsystem.
- the wave function of the diatomic molecule is,

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi_R(\vec{R})\psi_r(\vec{r}) \tag{2.2.2}$$

  the energy eigenstates are,

$$\begin{cases} \psi^R_{\vec{p}}(\vec{R}) = e^{i\vec{p}\cdot\vec{R}} \\ \psi^r_{l,m}(r,\theta,\phi) = \dfrac{u_l(r)}{r} Y_{lm}(\theta,\phi) \end{cases} \tag{2.2.3}$$

  with the radial equation to be,

$$\Big(\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2}\Big(\epsilon^r_{n,l} - \frac{1}{2}\mu\omega^2 r^2\Big) - \frac{l(l+1)}{r^2}\Big)u_l(r) = 0 \tag{2.2.4}$$

- the degeneracy is,

$$g^r_{n,l} = 2l+1 \tag{2.2.5}$$

- 近似认为振动和转动自由度是独立的，那么，

$$\epsilon^r_{n,l} = \epsilon^{\text{vib}}_n + \epsilon^{\text{rot}}_l = \hbar\omega(n+\frac{1}{2}) + \underbrace{\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r_0^2}}_{=\frac{\hbar^2 l(l+1)}{2I}} \tag{2.2.6}$$

  简并度为 $g^{\text{vib}}_n = 1, g^{\text{rot}}_l = 2l+1$

- 所以，这两个自由度的配分函数为，

$$Z_r = Z_{\text{vib}}Z_{\text{rot}} = \underbrace{\sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}}_{=\frac{2}{\sinh\frac{\hbar\omega}{2k_BT}}} \sum_{l=0}^{\infty}(2l+1)e^{-\frac{\theta_r}{T}l(l+1)} \tag{2.2.7}$$

  其中，$\theta_r = \frac{\hbar^2}{2Ik_B}$ 是**转动的特征温度**。

  – 低温情况下，Z_{rot} 只需要保留前两项，

$$Z_{\text{rot}} \approx 1 + 3e^{-2\frac{\theta_r}{T}} \tag{2.2.8}$$

2.2.2 partition function and everything else

- the partition function of a diatomic molecule is,

$$Z = Z_R Z_r \overset{T\to 0}{\approx} V\Big(\frac{2\pi m}{h^2\beta}\Big)^{3/2}\frac{2}{\sinh\frac{\hbar\omega}{2k_BT}}(1+3e^{-2\frac{\theta_r}{T}}) \tag{2.2.9}$$

  and $Z_{\text{tot}} = \frac{Z^N}{N!}$

- the energy of the system is,

$$U = -\frac{\partial}{\partial\beta}\ln Z_{\text{tot}} \overset{T\to 0}{\approx} \frac{3}{2}Nk_BT + \underbrace{\frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2k_BT}}_{\approx\frac{\hbar\omega}{2}} + \underbrace{6Nk_B\theta_r\frac{1}{3+e^{2\frac{\theta_r}{T}}}}_{\approx 6Nk_B\theta_r e^{-2\frac{\theta_r}{T}}} \tag{2.2.10}$$

  – 可见，低温下转动、振动自由度均冻结，温度升高，转动自由度先激发，振动自由度随后再被激发。
  – 转动和振动的特征温度分别为 $\theta_r = \frac{\hbar^2}{2Ik_B}, \theta_v = \frac{\hbar\omega}{k_B}$

Part II

General Theory

Chapter 3

quantum statistics

3.1 number of microstates

- 考虑由全同粒子构成的系统，粒子的能级为 $\{\epsilon_\lambda\}$，能级的简并度为 $\{g_\lambda\}$，各能级占据粒子数为 $\{a_\lambda\}$，下面来计算系统的微观状态数。

3.1.1 system composed of Fermions

- 对于费米子系统，每个状态最多只能占据一个粒子，所以系统的微观状态数为，

$$W_{\text{F-D}}(\{a_\lambda\}) = \prod_\lambda C_{a_\lambda}^{g_\lambda} = \prod_\lambda \frac{g_\lambda!}{a_\lambda!(g_\lambda - a_\lambda)!} \tag{3.1.1}$$

即 g_λ 个相异元素（粒子状态）中取出 a_λ 个元素（由一个费米子占据）的组合数量（粒子全同）。

3.1.2 system composed of Bosons

- 对于玻色子系统，任何状态可以由任意多粒子占据，所以系统的微观状态数为，

$$W_{\text{B-E}}(\{a_\lambda\}) = \prod_\lambda \frac{(a_\lambda + g_\lambda - 1)!}{a_\lambda!(g_\lambda - 1)!} \tag{3.1.2}$$

利用“插板法”计算（见附录 B.1.3），$g_\lambda - 1$ 个全同的板插入 $a_\lambda + 1$ 个空隙，可以认为是 $g_\lambda - 1 + a_\lambda$ 个板和球的排列数 $(g_\lambda - 1 + a_\lambda)!$，除以板和球各自的排列数 $(g_\lambda - 1)!$ 和 $a_\lambda!$（因为板和球各自是全同的）。

3.2 Fermi-Dirac statistics

- 对于费米子系统，微观状态数的近似值为，

$$\ln W_{\text{F-D}}(\{a_\lambda\}) \approx \sum_\lambda g_\lambda \ln g_\lambda - a_\lambda \ln a_\lambda - (g_\lambda - a_\lambda)\ln(g_\lambda - a_\lambda) \tag{3.2.1}$$

约束条件为，

$$\begin{cases} E = \sum\limits_\lambda \epsilon_\lambda a_\lambda \\ N = \sum\limits_\lambda a_\lambda \end{cases} \tag{3.2.2}$$

- 微观状态数的极大值为，

$$\ln W(\{\tilde{a}_\lambda\}) = \sum_\lambda g_\lambda \Big(\frac{\ln(e^{\alpha+\beta\epsilon_\lambda} + 1)}{e^{\alpha+\beta\epsilon_\lambda} + 1} + \frac{\ln(e^{-\alpha-\beta\epsilon_\lambda} + 1)}{e^{-\alpha-\beta\epsilon_\lambda} + 1} \Big) \tag{3.2.3}$$

对应的最可几分布 $\approx$ 平均分布为，

$$\tilde{a}_\lambda = \frac{g_\lambda}{e^{\alpha+\beta\epsilon_\lambda} + 1} \approx \bar{a}_\lambda \tag{3.2.4}$$

proof:

first,

$$\frac{\partial \ln W_{\text{F-D}}}{\partial a_\lambda} = \ln(g_\lambda - a_\lambda) - \ln a_\lambda \tag{3.2.5}$$

now, use the method of Lagrangian multiplier,

$$\begin{aligned}\frac{\partial \ln W_{\text{F-D}}}{\partial a_\lambda} - \alpha - \beta\epsilon_\lambda = 0 \Longrightarrow \ln\left(\frac{g_\lambda - \tilde{a}_\lambda}{\tilde{a}_\lambda}\right) &= \alpha + \beta\epsilon_\lambda \\ \Longrightarrow \tilde{a}_\lambda &= \frac{g_\lambda}{e^{\alpha+\beta\epsilon_\lambda}+1}\end{aligned} \tag{3.2.6}$$

---

also,

$$\begin{aligned}\frac{\partial^2 \ln W_{\text{F-D}}}{\partial a_\lambda \partial a_{\lambda'}} &= \delta_{\lambda\lambda'}\frac{g_\lambda}{a_\lambda(a_\lambda - g_\lambda)} \\ \Longrightarrow \frac{\partial^2 \ln W_{\text{F-D}}}{\partial a_\lambda \partial a_{\lambda'}}\bigg|_{\{\tilde{a}_\lambda\}} &= -\frac{\delta_{\lambda\lambda'}}{g_\lambda}(e^{\alpha+\beta\epsilon_\lambda}+1)^2 e^{-(\alpha+\beta\epsilon_\lambda)} \le 0\end{aligned} \tag{3.2.7}$$

so,

$$\begin{aligned}\ln\frac{W_{\text{F-D}}(\{\tilde{a}_\lambda + \delta a_\lambda\})}{W_{\text{F-D}}(\{\tilde{a}_\lambda\})} &= -\sum_\lambda \frac{1}{2}\frac{g_\lambda \tilde{a}_\lambda}{g_\lambda - \tilde{a}_\lambda}\left(\frac{\delta a_\lambda}{\tilde{a}_\lambda}\right)^2 + O(\Delta^3) \\ \Longrightarrow \frac{W_{\text{F-D}}(\{\tilde{a}_\lambda + \delta a_\lambda\})}{W_{\text{F-D}}(\{\tilde{a}_\lambda\})} &\approx \exp\left(-\sum_\lambda \frac{1}{2}\frac{g_\lambda \tilde{a}_\lambda}{g_\lambda - \tilde{a}_\lambda}\left(\frac{\delta a_\lambda}{\tilde{a}_\lambda}\right)^2\right)\end{aligned} \tag{3.2.8}$$

which implies $\bar{a}_\lambda \approx \tilde{a}_\lambda$

- 系统处于 $\{a_\lambda\}$ 状态的概率为,

$$P_{\text{F-D}}(\{a_\lambda\}) = \frac{W_{\text{F-D}}(\{a_\lambda\})}{\Omega_{\text{F-D}}} \tag{3.2.9}$$

而系统的总微观状态数为,

$$\Omega_{\text{F-D}} \approx W_{\text{F-D}}(\{\tilde{a}_\lambda\}) \tag{3.2.10}$$

proof:

$$\begin{aligned}\Omega_{\text{F-D}} &= \sum_{\{a_\lambda\}} W_{\text{F-D}}(\{a_\lambda\}) \approx \left(\prod_\lambda \int da_\lambda\right) W_{\text{F-D}}(\{a_\lambda\}) \\ &\approx W_{\text{F-D}}(\{\tilde{a}_\lambda\}) \prod_\lambda \int d\delta a_\lambda \exp\left(-\sum_\lambda \frac{1}{2}\frac{g_\lambda \tilde{a}_\lambda}{g_\lambda - \tilde{a}_\lambda}\left(\frac{\delta a_\lambda}{\tilde{a}_\lambda}\right)^2\right) \\ &= W_{\text{F-D}}(\{\tilde{a}_\lambda\}) \prod_\lambda \tilde{a}_\lambda \sqrt{\frac{2\pi(g_\lambda - \tilde{a}_\lambda)}{g_\lambda \tilde{a}_\lambda}}\end{aligned} \tag{3.2.11}$$

so,

$$\ln \Omega_{\text{F-D}} \approx \ln W_{\text{F-D}}(\{\tilde{a}_\lambda\}) + \underbrace{\sum_\lambda \ln\left(\tilde{a}_\lambda \sqrt{\frac{2\pi(g_\lambda - \tilde{a}_\lambda)}{g_\lambda \tilde{a}_\lambda}}\right)}_{=O(\ln N)} \tag{3.2.12}$$

3.3 Bose-Einstein statistics

- 微观状态数近似为（注意 $g_\lambda \gg 1$）,

$$W_{\text{B-E}}(\{a_\lambda\}) \approx \sum_\lambda (g_\lambda + a_\lambda)\ln(g_\lambda + a_\lambda) - a_\lambda \ln a_\lambda - g_\lambda \ln g_\lambda \tag{3.3.1}$$

- 微观状态数的极大值为,

$$\ln W_{\text{B-E}}(\{\tilde{a}_\lambda\}) \approx \sum_\lambda g_\lambda \Big(\frac{\ln(e^{\alpha+\beta\epsilon_\lambda}-1)}{e^{\alpha+\beta\epsilon_\lambda}-1} - \frac{\ln(e^{-\alpha-\beta\epsilon_\lambda}-1)}{e^{-\alpha-\beta\epsilon_\lambda}-1} \Big) \tag{3.3.2}$$

对应的最可几分布 $\approx$ 平均分布为,

$$\tilde{a}_\lambda = \frac{g_\lambda}{e^{\alpha+\beta\epsilon_\lambda}-1} \approx \bar{a}_\lambda \tag{3.3.3}$$

proof:

first,

$$\frac{\partial W_{\text{B-E}}}{\partial a_\lambda} = \ln(g_\lambda + a_\lambda) - \ln a_\lambda \tag{3.3.4}$$

and use the method of Lagrangian multiplier,

$$\ln(g_\lambda + \tilde{a}_\lambda) - \ln \tilde{a}_\lambda - \alpha - \beta\epsilon_\lambda = 0 \Longrightarrow \tilde{a}_\lambda = \frac{g_\lambda}{e^{\alpha+\beta\epsilon_\lambda}-1} \tag{3.3.5}$$

---

and,

$$\frac{W_{\text{B-E}}(\{\tilde{a}_\lambda + \delta\epsilon_\lambda\})}{W_{\text{B-E}}(\{\tilde{a}_\lambda\})} = \exp\Big(-\sum_\lambda \frac{1}{2} \frac{g_\lambda \tilde{a}_\lambda}{g_\lambda + \tilde{a}_\lambda} \Big(\frac{\delta a_\lambda}{\tilde{a}_\lambda}\Big)^2 \Big) \tag{3.3.6}$$

- 系统处于 $\{a_\lambda\}$ 状态的概率为,

$$P_{\text{B-E}}(\{a_\lambda\}) = \frac{W_{\text{B-E}}(\{a_\lambda\})}{\Omega_{\text{B-E}}} \tag{3.3.7}$$

而系统的总微观状态数为,

$$\Omega_{\text{B-E}} \approx W_{\text{B-E}}(\{\tilde{a}_\lambda\}) \tag{3.3.8}$$

proof:

$$\begin{aligned} \Omega_{\text{B-E}} &\approx \Big(\prod_\lambda \int d\delta a_\lambda\Big) W_{\text{B-E}}(\{\tilde{a}_\lambda + \delta\epsilon_\lambda\}) \\ &= W_{\text{B-E}}(\{\tilde{a}_\lambda\}) \prod_\lambda \tilde{a}_\lambda \sqrt{\frac{2\pi(g_\lambda + \tilde{a}_\lambda)}{g_\lambda \tilde{a}_\lambda}} \end{aligned} \tag{3.3.9}$$

which means,

$$\ln \Omega_{\text{B-E}} \approx \ln W_{\text{B-E}}(\{\tilde{a}_\lambda\}) + O(\ln N) \tag{3.3.10}$$

3.4 summary (F-D, Maxwell-Boltzmann, & B-E statistics)

- the distribution, $\{a_\lambda\}$, of the subsystems is,

$$a_\lambda = \frac{g_\lambda}{e^{\alpha+\beta\epsilon_\lambda}+\eta} \quad \text{where} \quad \eta = \begin{cases} +1 & \text{F-D statistics} \\ 0 & \text{Maxwell-Boltzmann statistics} \\ -1 & \text{B-E statistics} \end{cases} \tag{3.4.1}$$

3.5 black body radiation

- 黑体辐射的能量密度分布为,

$$u(\nu, T) = \frac{\epsilon}{V} \frac{d\bar{a}}{d\epsilon}\Big|_{\epsilon=h\nu} \quad \text{and} \quad \begin{cases} \epsilon = \dfrac{ch}{2L}\sqrt{n_x^2 + n_y^2 + n_z^2} & n_i = 0, 1, 2, \cdots \\ g(\epsilon) \approx \dfrac{2 \times \frac{\pi}{2} n^2 dn}{d\epsilon} = \dfrac{8\pi L^3}{c^3 h^3}\epsilon^2 & \end{cases} \tag{3.5.1}$$

所以,

$$u(\epsilon, T) = \frac{8\pi}{c^3 h^3} \frac{\epsilon^3}{e^{\alpha+\beta\epsilon}-1} \quad \text{where} \quad \epsilon = h\nu \tag{3.5.2}$$

- 光子气体的粒子数不守恒，推导统计分布时去掉关于 N 的拉格朗日乘子，即 $\alpha=-\beta\mu=0$，所以，化学势为零，得到，

$$\begin{cases} u(\epsilon,T)=\dfrac{8\pi}{c^3h^3}\dfrac{\epsilon^3}{e^{\epsilon/k_BT}-1} \\ u(T)=\dfrac{8\pi^5k_B^4}{15h^3c^3}T^4 \\ p=N\langle-\dfrac{\partial\epsilon}{\partial V}\rangle=\dfrac{1}{3}u(T) \\ N=V\dfrac{16\pi k_B^3\zeta(3)}{c^3h^3}T^3 \\ \mu=0,G=0 \end{cases} \quad \text{and} \quad S=\frac{U+pV}{T}=\frac{4}{3}\frac{U}{T} \tag{3.5.3}$$

3.6 固体物理热容的量子理论（德拜 T^3 理论）

- 弹性波有横波和纵波，在 $\nu\sim\nu+d\nu$ 范围内的振动模式数量为,

$$g(\nu)=\underbrace{\frac{4\pi V}{3}\left(\frac{2}{c_t^3}+\frac{1}{c_l^2}\right)}_{=B}\nu^2 \tag{3.6.1}$$

其中 c_t,c_l 分别为横波和纵波的波速。

- 固体中有 N 个原子，自由度为 $3N$，德拜引入频率上限 ν_D，所以,

$$\int_0^{\nu_D}g(\nu)d\nu=3N\Longrightarrow\nu_D^3=\frac{9N}{B} \tag{3.6.2}$$

- 频率为 ν 的振子的平均能量为,

$$\bar{\epsilon}(\nu)=\sum_n nh\nu e^{-\beta nh\nu}=\frac{h\nu}{e^{\beta h\nu}-1} \tag{3.6.3}$$

所以，系统总能量为,

$$\bar{E}=\int_0^{\nu_D}\bar{\epsilon}(\nu)g(\nu)d\nu=3Nk_BTD(\frac{\Theta_D}{T}) \tag{3.6.4}$$

proof:

$$\bar{E}=\frac{B}{h^3}(k_BT)^4\int_0^{\frac{\Theta_D}{T}}\frac{y^3}{e^y-1}dy=3Nk_BTD(\frac{\Theta_D}{T}) \tag{3.6.5}$$

其中 $\Theta_D=\frac{h\nu_D}{k_B}$ 是德拜温度，且,

$$D(x)=\frac{3}{x^3}\int_0^x\frac{y^3}{e^y-1}dy \tag{3.6.6}$$

- 热容为,

$$\frac{C_V}{3Nk_B}=4D(\frac{\Theta_D}{T})-\frac{3\frac{\Theta_D}{T}}{e^{\frac{\Theta_D}{T}}-1} \tag{3.6.7}$$

  - 高温极限下，$C_V\to 3Nk_B$
  - 低温极限下，$\frac{C_V}{3Nk_B}\to\frac{4\pi^4}{5}\frac{T^3}{\Theta_D^3}$，称为德拜 T^3 定律。

Chapter 4

ensemble theory

4.1 the microscopic states

4.1.1 quantum description of the microscopic states

- the **Hilbert space** of $N = N_1 + N_2 + \cdots + N_k$ particles is,

$$\mathscr{H}^{(N)} = \bigotimes_{\nu=1}^{k} \mathscr{H}^{(N_\nu)} \tag{4.1.1}$$

where the ν-th kind of particles' Hilbert space is,

$$\begin{cases} \mathscr{H}_S^{(N_\nu)} = \mathscr{P}_S(\mathscr{H}^{\otimes N_\nu}) & \text{Bosons} \\ \mathscr{H}_A^{(N_\nu)} = \mathscr{P}_A(\mathscr{H}^{\otimes N_\nu}) & \text{Fermions} \end{cases} \tag{4.1.2}$$

where,

$$\mathscr{H}^{\otimes N} = \{|\psi_1(t)\rangle \otimes \cdots \otimes |\psi_N(t)\rangle \,|\, |\psi_{a=1,\cdots,N}(t)\rangle \in \mathscr{H}\} \tag{4.1.3}$$

- the **Hamiltonian** is,

$$H = \sum_\nu \left(\frac{1}{2m_\nu} \sum_{a=1}^{N_\nu} |\vec{p}_{\nu,a}|^2 \right) + V(\vec{q}_{1,1}, \cdots, \vec{q}_{\nu,a}, \cdots, \vec{q}_{k,N_k}) \tag{4.1.4}$$

4.1.2 classical description of the microscopic states

- N 粒子系统的相空间记作 Γ, 单粒子的相空间记作 μ, 有,

$$\Gamma^{(N)} = \mu^{\otimes N} \tag{4.1.5}$$

- N 粒子系统的相空间由所有粒子的坐标和动量张成,

$$q = (\vec{q}_1, \cdots, \vec{q}_N) \quad p = (\vec{p}_1, \cdots, \vec{p}_N) \tag{4.1.6}$$

这是一个 $2DN$ 维的空间.

- the Hamilton's equation of motion is,

$$\begin{cases} \dfrac{d\vec{q}_a}{dt} = \{\vec{q}_a, H(q,p)\}_{\text{PB}} \\ \dfrac{d\vec{p}_a}{dt} = \{\vec{p}_a, H(q,p)\}_{\text{PB}} \end{cases} \Longleftrightarrow \begin{cases} \dfrac{d\vec{q}_a}{dt} = \nabla_{\vec{p}_a} H(q,p) \\ \dfrac{d\vec{p}_a}{dt} = -\nabla_{\vec{q}_a} H(q,p) \end{cases} \tag{4.1.7}$$

where the Poisson bracket is,

$$\{A, B\}_{\text{PB}} = \sum_{a=1}^{N} \Big((\nabla_{\vec{q}_a} A) \cdot (\nabla_{\vec{p}_a} B) - (\nabla_{\vec{q}_a} B) \cdot (\nabla_{\vec{p}_a} A) \Big) \tag{4.1.8}$$

4.2 ensembles in classical statistics

- def.: **系综 (ensemble)** 代表一定条件下一个体系的大量可能状态的集合. 也就是说, 系综是系统状态的一个概率分布.

4.2.1 Liouville's theorem

- the Liouville's theorem states that in the phase space, the volume form, $\epsilon = dq_1 \wedge \cdots \wedge dq_N \wedge dp_1 \wedge \cdots \wedge dp_N$, doesn't evolve with time,

$$\frac{d}{dt}\epsilon = 0 \tag{4.2.1}$$

proof:

the coordinate system, $\{q_i, p_j\}$, of the phase space **evolve with time** (think of it as a **coordinate transformation**), and so do the cotangent vectors, $\{dq_i, dp_j\}$,

$$\begin{cases} q_i(t+dt) = q_i + \dfrac{\partial H}{\partial p_i}dt \\ p_i(t+dt) = p_i - \dfrac{\partial H}{\partial q_i}dt \end{cases}$$
$$\Longrightarrow \begin{pmatrix} dq_i(t+dt) \\ dp_j(t+dt) \end{pmatrix} = \begin{pmatrix} \delta_{ii'} + \frac{\partial^2 H}{\partial q_{i'}\partial p_i}dt & \frac{\partial^2 H}{\partial p_i \partial p_{j'}} \\ -\frac{\partial^2 H}{\partial q_j \partial q_{i'}} & \delta_{jj'} - \frac{\partial^2 H}{\partial q_j \partial p_{j'}} \end{pmatrix} \begin{pmatrix} dq_{i'}(t) \\ dp_{j'}(t) \end{pmatrix} \tag{4.2.2}$$

consequently, the volume form associated to this coordinate system evolves with time (or goes though a coordinate transformation), the **Jacobian determinant** of the transformation is,

$$\begin{aligned} \det \frac{\partial(q_1(t+dt), \cdots, p_1(t+dt), \cdots)}{\partial(q_1(t), \cdots, p_1(t), \cdots)} &= \begin{vmatrix} \delta_{ii'} + \frac{\partial^2 H}{\partial q_{i'}\partial p_i}dt & \frac{\partial^2 H}{\partial p_i \partial p_{j'}} \\ -\frac{\partial^2 H}{\partial q_j \partial q_{i'}} & \delta_{jj'} - \frac{\partial^2 H}{\partial q_j \partial p_{j'}} \end{vmatrix} \\ &= 1 + \sum_{i=1}^{N} \underbrace{\left(\frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial q_i \partial p_i}\right)}_{=0} dt + O(dt^2) \end{aligned} \tag{4.2.3}$$

i.e. $\frac{d}{dt}\epsilon = 0$

4.2.2 phase space, density function, and stationary ensemble

- the **density function**, $\rho(q_i, p_j, t)$, is the probability density of a single system or distribution of a large number of identical non-interacting systems.

- the **Liouville's equation** is,

$$\frac{d\rho}{dt} = 0 = \frac{\partial \rho}{\partial t} + \{\rho, H\}_{\mathrm{PB}} \tag{4.2.4}$$

where the Poisson bracket is,

$$\{\rho, H\}_{\mathrm{PB}} = \sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right) \tag{4.2.5}$$

proof:

the probability of a system located within ϵ is invariant under evolution,

$$\frac{d}{dt}(\rho\epsilon) = 0 \tag{4.2.6}$$

combining with Liouville's theorem, (4.2.1), we have Liouville's equation.

- if the density function satisfies,

$$\frac{\partial \rho}{\partial t} = 0 \tag{4.2.7}$$

then the ensemble is said to be **stationary**.

4.3 ensembles in quantum statistics

4.3.1 the density matrix for pure and mixed ensembles

- if an ensemble contains different states, we call it a **mixed ensemble**. the probability of state $|\psi_i\rangle$ is p_i, then the density matrix is,

$$\begin{cases} \rho = |\psi\rangle\langle\psi| & \text{pure ensemble} \\ \rho = \sum_i p_i |\psi_i\rangle\langle\psi_i| & \text{mixed ensemble} \end{cases} \tag{4.3.1}$$

notice that,

$$\mathrm{tr}\rho = 1, \rho^\dagger = \rho \quad \text{and} \quad \begin{cases} \rho^2 = \rho & \text{pure ensembles} \\ \rho^2 \neq \rho, \mathrm{tr}\rho^2 < 1 & \text{mixed ensembles} \end{cases} \tag{4.3.2}$$

---

and the density matrix is **positive semidefinite**, with,

$$\langle\psi|\rho|\psi\rangle = \sum_i p_i |\langle\psi|\psi_i\rangle|^2 \geq 0 \tag{4.3.3}$$

and in the basis of the eigenvectors of ρ (notice ρ is Hermitian, hence diagonalizable),

$$\rho|m\rangle = P_m|m\rangle \iff \rho = \sum_m P_m |m\rangle\langle m| \quad \text{with} \quad P_m \geq 0 \tag{4.3.4}$$

proof of $\mathrm{tr}\rho^2 < 1$:

$$\begin{aligned} \mathrm{tr}\rho^2 &= \sum_{ij} p_i p_j \langle\psi_i|\psi_j\rangle\langle\psi_j|\psi_i\rangle \\ &= \sum_{ij} p_i p_j |\langle\psi_i|\psi_j\rangle|^2 < \sum_i p_i \sum_j p_j = 1 \end{aligned} \tag{4.3.5}$$

alternatively, use the eigenvector basis,

$$\mathrm{tr}\rho^2 = \sum_m P_m^2 < 1 \tag{4.3.6}$$

4.3.2 von Neumann equation

- the time evolution of the density matrix is described by the **von Neumann equation**,

$$i\hbar\frac{\partial}{\partial t}\rho = [H, \rho] \tag{4.3.7}$$

calculation:

the Schrodinger's equation is,

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle \tag{4.3.8}$$

so,

$$\begin{aligned} \frac{\partial}{\partial t}\rho &= \sum_i p_i \Big(\frac{\partial|\psi_i\rangle}{\partial t}\langle\psi_i| + |\psi_i\rangle\frac{\partial\langle\psi_i|}{\partial t} \Big) \\ &= \sum_i p_i \Big(\frac{1}{i\hbar} H|\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\frac{1}{-i\hbar}\langle\psi_i| H \Big) = \frac{1}{i\hbar}[H, \rho] \end{aligned} \tag{4.3.9}$$

- compare the Heisenberg picture with the Schrodinger's picture, we have,

$$
\begin{cases}
|\psi(t)\rangle_S = U(t,0)\,|\psi(0)\rangle \\
\rho_S(t) = U(t,0)\rho(0)U^\dagger(t,0) \\
\langle O\rangle_t = \mathrm{tr}(\rho_S(t)O(0)) = \mathrm{tr}(\rho(0)\underbrace{U^\dagger(t,0)O(0)U(t,0)}_{=O_H(t)})
\end{cases}
\tag{4.3.10}
$$

Chapter 5

equilibrium ensembles

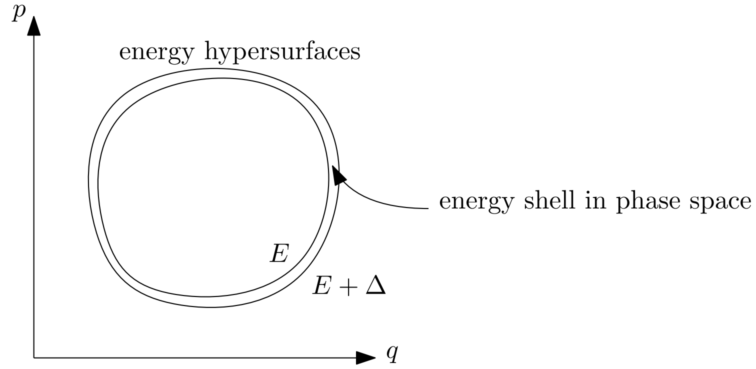
- notice that:
  - a **macroscopic system** consists of a **large number** of particles, and consequently has an **energy spectrum** with spacing of $\Delta E \sim e^{-N}$.
  - no system can be **strictly isolated** from its environment, thus cannot be characterized by a **single microstate**, but rather by **an ensemble of microstates**.
  - this statistical **ensemble of microstates** represents the **macrostate**, which is specified by the **macroscopic variables**, $E, V, N, \cdots$.
- in a **equilibrium state**,
$$\frac{\partial}{\partial t}\rho = 0 = -\frac{i}{\hbar}[H, \rho] \tag{5.0.1}$$
so, in equilibrium, the density matrix can only depend on the **conserved quantities**.
- five kinds of ensembles:

ensemble	macroscopic variables	density matrix, ρ
microcanonical	N, V, E	$\rho_{MC} = \frac{1}{\Omega(E)}\delta(H - E)$
canonical	N, V, T	$\rho_C = \frac{1}{Z}e^{-\beta H}$
grand canonical	μ, V, T	$\rho_G = \frac{1}{Z_G}e^{-\beta(H-\mu N)}$
Gibbs	N, p, T	不会
Enthalpy	N, p, H	不会

5.1 microcanonical ensembles

5.1.1 classical mechanically

- consider an isolated system with fixed N, V and an energy within $[E, E + \Delta]$ (and Δ is small),



- now, we want to prove (using (4.2.4) or (5.0.1)) that the regions within the energy shell have the same density function, $\rho(q, p, t)$, i.e. **the principle of equal a priori probabilities**.

proof:

we will prove that a uniform distribution leads to a stationary (or equilibrium) ensemble in **classical mechanics**.

- use the coordinate associated to the energy hypersurface, $\{k_\perp, s = (s_1, \cdots, s_{2DN-1})\}$.
- use the Liouville's equation,

$$\begin{aligned}\frac{\partial}{\partial t}\rho &= -\sum_i \Big(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}\Big) \\ &= -\frac{\partial \rho}{\partial k_\perp}\hat{k}_\perp \cdot \vec{v}\end{aligned} \tag{5.1.1}$$

- where the **velocity in phase space**, $\vec{v}$, is perpendicular to the gradient of the Hamiltonian, ∇H, i.e. tangential to the energy hypersurface,

$$\vec{v} = (\dot{q}, \dot{p}) = (\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q}) \quad \text{and} \quad |v| = |\nabla H| \tag{5.1.2}$$

- so, $\frac{\partial \rho}{\partial t} = 0$, it is indeed stationary.

- as long as the gradient of the density function, $\nabla\rho$, is perpendicular to the velocity $\vec{v}$, the ensemble is stationary.
- a special case is that $\nabla\rho \perp$ the energy hypersurface, i.e. $\nabla\rho \parallel \nabla H$.

- in the limit $\Delta \to 0$, the density function is,

$$\rho_{MC} = \frac{1}{\Omega(E)}\delta(E - H(q,p)) \tag{5.1.3}$$

where $\Omega(E)$ is the weighted area of the energy hypersurface, called the **phase surface**.

- $\Omega(E)$ is determined by the normalization condition,

$$\Omega(E) = \int \frac{dS}{h^{DN}N!}\frac{1}{|\nabla H(q,p)|} \tag{5.1.4}$$

proof:

the normalization condition is,

$$\int \frac{d^{DN}qd^{DN}p}{h^{DN}N!}\rho_{MC} = 1 \tag{5.1.5}$$

so,

$$\begin{aligned}\Omega(E) &= \int \frac{d^{DN}qd^{DN}p}{h^{DN}N!}\delta(E - H(q,p)) \\ &= \int \frac{dSdk_\perp}{h^{DN}N!}\delta(E - H(s_E) - |\nabla H|k_\perp) = \cdots\end{aligned} \tag{5.1.6}$$

where $\{k_\perp, s = (s_1, \cdots, s_{2DN-1})\}$ is the coordinate associated with the energy hypersurfaces.

- the **volume form** of the phase space is,

$$d\Gamma \equiv \frac{d^{DN}qd^{DN}p}{h^{DN}N!} \tag{5.1.7}$$

which is arbitrarily chosen at this stage, and is referred to **the limit found in quantum statistics**.

- the volume inside the energy shell is,

$$\overline{\Omega}(E) = \int \frac{d^{DN}qd^{DN}p}{h^{DN}N!}\Theta(E - H(q,p)) \Longrightarrow \Omega(E) = \frac{d\overline{\Omega}(E)}{dE} \tag{5.1.8}$$

proof:

$$\Theta(x) = \begin{cases} 0 & x < 0 \\ 1 & x > 0 \end{cases} \Longrightarrow \Theta'(x) = \delta(x) \tag{5.1.9}$$

5.1.2 quantum mechanically

- the density matrix of a microcanonical ensemble is,

$$\rho_{MC} = \sum_n \sum_{i=1}^{g_n} P(E_n, i) |E_n, i\rangle \langle E_n, i| \tag{5.1.10}$$

注意, 这里的能级是整个系统的能级, 与之前讨论中子系统的能级 ϵ_λ 不同.

- use the normalization,

$$\mathrm{tr}\rho_{MC} = 1 \Longrightarrow \sum_{n,i} P(E_n, i) = 1 \tag{5.1.11}$$

with the principle of equal a priori probabilities, the **density matrix** is,

$$P(E_n, i) = \begin{cases} \dfrac{1}{\Omega(E)\Delta} & E < E_n < E + \Delta \\ 0 & \text{otherwise} \end{cases} \Longleftrightarrow \boldsymbol{\rho_{MC} = \frac{1}{\Omega(E)}\delta_{H-E}} \tag{5.1.12}$$

proof:

first, let's prove $[H, \rho_{MC}] = 0$, which is obvious, because,

$$\rho_{MC} = \frac{1}{\Omega(E)}\delta_{H-E} \equiv \frac{1}{\Omega(E)}\int \frac{dk}{2\pi}e^{ik(H-E)} \text{ or } \frac{1}{\Omega(E)}\sum_i |E, i\rangle \langle E, i| \tag{5.1.13}$$

now, let's prove the $\Longleftrightarrow$ in (5.1.12), consider,

$$\begin{aligned}\langle E_n, i|\rho_{MC}|E_m, j\rangle &= \frac{1}{\Omega(E)}\int \frac{dk}{2\pi}\langle E_n, i|e^{ik(H-E)}|E_m, j\rangle \\ &= \frac{1}{\Omega(E)}\int \frac{dk}{2\pi}e^{ik(E_n-E)}\delta_{nm}\delta_{ij} = \frac{1}{\Omega(E)}\delta(E_n - E)\delta_{nm}\delta_{ij}\end{aligned} \tag{5.1.14}$$

or,

$$\langle E_n, i|\rho_{MC}|E_m, j\rangle = \frac{1}{\Omega(E)}\delta_{EE_n}\delta_{nm}\underbrace{\sum_k \delta_{ik}\delta_{kj}}_{=\delta_{ij}} \tag{5.1.15}$$

the normalization condition yields that,

$$\Omega(E) = \mathrm{tr}\delta(H - E) = g_E \tag{5.1.16}$$

where g_E is the degeneracy of energy level E of the total system, which we have calculated in chapter 1 (in the case of distinguishable subsystems) and 3 (in the case of Fermi system and Bose system).

proof:

$$\mathrm{tr}\rho_{MC} = \sum_{n,i} \langle E_n, i|\rho_{MC}|E_n, i\rangle = \frac{1}{\Omega(E)} \underbrace{\sum_{n,i} \delta_{EE_n}\delta_{ii}}_{=g_E} = 1 \tag{5.1.17}$$

5.2 canonical ensembles

- macroscopic variables: N, V, T.
- 考虑系统 1 嵌入在一个更大的系统 2 中 (热库), 两个系统的**相互作用能可以忽略**, 那么总 Hamiltonian 为,

$$H_0 = H + H_2 \tag{5.2.1}$$

- 在总能量为 E_0 的前提下, 系统 1 处于能量为 $E_n \ll E_0$ 的某一个态 i 的概率密度为,

$$\begin{aligned} P_1(E_n, i) &= \frac{\Omega_2(E_0 - E_n)}{\Omega_{\mathrm{tot}}(E_0)} \\ &= \frac{1}{\Omega_{\mathrm{tot}}(E_0)} e^{\ln \Omega_2(E_0 - E_n)} \end{aligned} \tag{5.2.2}$$

取近似 $\ln \Omega_2(E_0 - E_n) \approx \ln \Omega_2(E_0) - \frac{\partial \ln \Omega_2(E_0)}{\partial E} E_n$, 并注意到 $\frac{\partial \ln \Omega_2(E_0)}{\partial E} = \beta$, 所以,

$$P_1(E_n, i) = \underbrace{\frac{\Omega_2(E_0)}{\Omega_{\mathrm{tot}}(E_0)}}_{=\frac{1}{Z}} e^{-\beta E_n} \Longrightarrow P_1(E_n) = \frac{g_n}{Z} e^{-\beta E_n} \tag{5.2.3}$$

- the **density matrix** is,

$$\rho_C = \frac{1}{Z} e^{-\beta H} \tag{5.2.4}$$

- and the **partition function** can be calculated from normalization,

$$Z = \sum_n g_n e^{-\beta E_n} = \mathrm{tr}(e^{-\beta H}) \tag{5.2.5}$$

5.3 grand canonical ensembles

- macroscopic variables: μ, V, T.
- 依然考虑系统 1 嵌入在系统 2 中, 并满足,

$$H_0 = H + H_2 \quad N_0 = N + N_2 \tag{5.3.1}$$

- 系统 1 处于 $E_{N,n} \ll E_0, N \ll N_0$ 的某个状态 i 的概率为,

$$P_1(E_{N,n}, N, i) = \frac{\Omega_2(E_0 - E_{N,n}, N_0 - N)}{\Omega_{\mathrm{tot}}(E_0, N_0)} \approx \frac{\Omega_2(E_0, N_0)}{\Omega_{\mathrm{tot}}(E_0, N_0)} e^{-\beta(E_{N,n} - \mu N)} \tag{5.3.2}$$

其中**令**系数 μ, β 分别为,

$$\mu = -\frac{1}{\beta} \frac{\partial}{\partial N}\Big|_E \ln \Omega_2(E_0, N_0) \quad \text{and} \quad \beta = \frac{\partial}{\partial E}\Big|_N \ln \Omega_2(E_0, N_0) \tag{5.3.3}$$

- the **density matrix** is,

$$\rho_G = \frac{1}{\Xi} e^{-\beta(H - \mu N)} \tag{5.3.4}$$

$$= \frac{1}{\Xi} \sum_{N,n,i} |N, E_{N,n}, i\rangle\, e^{-\beta E_{N,n}} e^{\beta\mu N} \langle N, E_{N,n}, i| \tag{5.3.5}$$

where N is the **particle number operator**,

$$N = \sum_{N,n,i} |N, E_{N,n}, i\rangle\, N \,\langle N, E_{N,n}, i| \tag{5.3.6}$$

it is Hermitian and has the same eigenvector basis as H's, hence they commutes, $[H, N] = 0$.

- the **grand partition function** is,

$$\Xi = \mathrm{tr}(e^{-\beta(H-\mu N)}) = \sum_{N,n} g_{N,n} e^{-\beta(E_{N,n}-\mu N)} = \sum_{N} Z(N) e^{\beta\mu N} \tag{5.3.7}$$

5.3.1 thermodynamic quantities

- 通过巨正则配分函数 $\Xi(\beta, \mu, y_l)$ 可以得到系统的宏观量 (系统的能级 $E_{N,n}$ 是 y_l 的函数),

$$\begin{cases} \bar{E} - \mu\bar{N} = -\dfrac{\partial}{\partial\beta} \ln\Xi \\ \bar{N} = \dfrac{1}{\beta}\dfrac{\partial}{\partial\mu} \ln\Xi \\ \bar{Y}_l = \dfrac{1}{\beta}\dfrac{\partial}{\partial y_l} \ln\Xi \end{cases} \tag{5.3.8}$$

proof:

the energy is,

$$\bar{E} - \mu\bar{N} = \mathrm{tr}(\rho_G H) = \frac{1}{\Xi}\sum_{N,n} (E_{N,n} - \mu N) g_{N,n} e^{-\beta(E_{N,n}-\mu N)} = -\frac{1}{\Xi}\frac{\partial}{\partial\beta}\Xi \tag{5.3.9}$$

---

similarly, the particle number is,

$$\bar{N} = \frac{1}{\Xi}\sum_{N,n} N g_{N,n} e^{-\beta(E_{N,n}-\mu N)} = \frac{1}{\Xi}\frac{1}{\beta}\frac{\partial}{\partial\mu}\Xi \tag{5.3.10}$$

---

the generalized force is,

$$\bar{Y}_l = \frac{1}{\Xi}\sum_{N,n} \Big(-\frac{\partial E_{N,n}}{\partial y_l}\Big) g_{N,n} e^{-\beta(E_{N,n}-\mu N)} = \frac{1}{\Xi}\frac{1}{\beta}\frac{\partial}{\partial y_l}\Xi \tag{5.3.11}$$

- 巨正则系综的巨配分函数和熵为,

$$\begin{cases} \Phi_G = -\dfrac{1}{\beta} \ln\Xi \\ S = -k_B \langle \ln\rho_G \rangle = k_B \Big(\beta(\bar{E} - \mu\bar{N}) + \ln\Xi \Big) \end{cases} \tag{5.3.12}$$

proof:

the entropy is,

$$\begin{aligned} S/k_B &= -\mathrm{tr}(\rho_G \ln\rho_G) \\ &= -\frac{1}{\Xi}\sum_{N,n,{\color{red}i}} e^{-\beta(E_{N,n}-\mu N)} \Big(-\beta(E_{N,n} - \mu N) - \ln\Xi \Big) \\ &= \beta(\bar{E} - \mu\bar{N}) + \ln\Xi \end{aligned} \tag{5.3.13}$$

the grand potential is,

$$\Phi_G = U - TS - \mu N = -k_B T \ln \Xi \tag{5.3.14}$$

Part III

More Applications

Chapter 6

Bose and Fermi distribution

6.1 Bose and Fermi distribution

- 适用于: 近独立, 不可分辨的子系.
- define,

$$\eta = \begin{cases} -1 & \text{Bosons} \\ +1 & \text{Fermions} \end{cases} \tag{6.1.1}$$

- the density matrix of a grand canonical ensemble is,

$$\rho_G = \frac{1}{\Xi} e^{-\beta(H-\mu N)} \quad \text{and} \quad \boldsymbol{\Xi = \sum_{N=0}^{\infty} \sum_{n} g_{N,n} e^{-\beta(E_{N,n}-\mu N)}} \tag{6.1.2}$$

- use $|\{a_{\lambda,i}\}\rangle$ as basis (where i indicates the i-th degenerate state of energy level ϵ_λ),

$$\langle\{a_{\lambda,i}\}|\rho_G|\{a'_{\lambda,i}\}\rangle = \Big(\frac{1}{\Xi}\prod_\lambda e^{-\beta(\epsilon_\lambda-\mu)a_\lambda}\Big)\delta(\{a_{\lambda,i}\},\{a'_{\lambda,i}\}) \tag{6.1.3}$$

(微观态用处于不同状态, λ, i, 的子系统数量表示, $a_{\lambda,i}$)

- the grand partition function is,

$$\Xi = \prod_\lambda \Xi_\lambda = \prod_\lambda (1+\eta e^{-\beta\epsilon_\lambda-\alpha})^{\eta g_\lambda} \tag{6.1.4}$$

proof:

用子系统的分别情况, $\{a_\lambda\}$, 表示 Ξ 以及 $N, E_{N,n}, g_{N,n}$,

$$\begin{aligned} \Xi &= \sum_{\{a_\lambda=0\}}^{\{a_\lambda=\max\}} W(\{a_\lambda\}) \exp\Big(-\beta\Big(E(\{a_\lambda\})-\mu N(\{a_\lambda\})\Big)\Big) \\ &= \sum_{\{a_\lambda=0\}}^{\{a_\lambda=\max\}} \prod_\lambda W_\lambda(a_\lambda) e^{-\beta(\epsilon_\lambda-\mu)a_\lambda} = \prod_\lambda \underbrace{\sum_{a=0}^{\max} W_\lambda(a) e^{-\beta(\epsilon_\lambda-\mu)a}}_{:=\Xi_\lambda} \end{aligned} \tag{6.1.5}$$

其中 $W(\{a_\lambda\})$ 是 $\{a_\lambda\}$ 对应的微观态 $\{\sum_{i=1}^{g_\lambda} a_{\lambda,i} = a_\lambda\}$ 的数量,

$$\begin{cases} N(\{a_\lambda\}) = \sum_\lambda a_\lambda \\ E(\{a_\lambda\}) = \sum_\lambda \epsilon_\lambda a_\lambda \end{cases} \quad \text{and} \quad W_\lambda(a_\lambda) = \begin{cases} \dfrac{(a_\lambda+g_\lambda-1)!}{a_\lambda!(g_\lambda-1)!} & \text{Bosons} \\ \dfrac{g_\lambda!}{a_\lambda!(g_\lambda-a_\lambda)!} & \text{Fermions} \end{cases} \tag{6.1.6}$$

proof:

- 对于玻色子系统, 任何状态可以由任意多粒子占据, 所以系统的微观状态数为,

$$W_{\text{B-E}}(\{a_\lambda\}) = \prod_\lambda \frac{(a_\lambda + g_\lambda - 1)!}{a_\lambda!(g_\lambda - 1)!} \tag{6.1.7}$$

利用" 插板法" 计算 (见附录 B.1.3), $g_\lambda - 1$ 个全同的板插入 $a_\lambda + 1$ 个空隙, 可以认为是 $g_\lambda - 1 + a_\lambda$ 个板和球的排列数 $(g_\lambda - 1 + a_\lambda)!$, 除以板和球各自的排列数 $(g_\lambda - 1)!$ 和 $a_\lambda!$ (因为板和球各自是全同).

- 对于费米子系统, 每个状态最多只能占据一个粒子, 所以系统的微观状态数为,

$$W_{\text{F-D}}(\{a_\lambda\}) = \prod_\lambda C_{a_\lambda}^{g_\lambda} = \prod_\lambda \frac{g_\lambda!}{a_\lambda!(g_\lambda - a_\lambda)!} \tag{6.1.8}$$

即 g_λ 个相异元素 (粒子状态) 中取出 a_λ 个元素 (由一个费米子占据) 的组合数量 (粒子全同).

and,

$$\Xi_\lambda = \begin{cases} (1 - e^{-\beta(\epsilon_\lambda - \mu)})^{-g_\lambda} & \text{Bosons} \\ (1 + e^{-\beta(\epsilon_\lambda - \mu)})^{g_\lambda} & \text{Fermions} \end{cases} \tag{6.1.9}$$

proof:

- 对于玻色子, 考虑,

$$(1-x)^{-m} = \sum_{n=0}^{\infty} \frac{1}{n!} \underbrace{\left.\frac{d^n x^{-m}}{dx^n}\right|_{x=1}}_{=(-1)^n \frac{(m+n-1)!}{(m-1)!}} (-x)^n \tag{6.1.10}$$

so,

$$\Xi_{\lambda,\text{B-E}}(a) = \sum_{a=0}^{\infty} \frac{(a + g_\lambda - 1)!}{a!(g_\lambda - 1)!} e^{-\beta(\epsilon_\lambda - \mu)a} = (1 - e^{-\beta(\epsilon_\lambda - \mu)})^{-g_\lambda} \tag{6.1.11}$$

- 对于费米子,

$$(1+x)^m = \sum_{n=0}^{m} C_n^m x^n \tag{6.1.12}$$

so,

$$\Xi_{\lambda,\text{F-D}} = \sum_{a=0}^{g_\lambda} C_a^{g_\lambda} e^{-\beta(\epsilon_\lambda - \mu)a} = (1 + e^{-\beta(\epsilon_\lambda - \mu)})^{g_\lambda} \tag{6.1.13}$$

- summary,

$$\boldsymbol{\ln \Xi = \mp \sum_\lambda g_\lambda \ln(1 \mp e^{-\beta(\epsilon_\lambda - \mu)})} \quad \begin{cases} - & \text{Bosons} \\ + & \text{Fermions} \end{cases} \tag{6.1.14}$$

and,

$$\begin{aligned} \langle a_\lambda \rangle &= \frac{1}{\Xi} \text{tr}(a_\lambda e^{-\beta(H - \mu N)}) = \frac{1}{\Xi} \sum_{\{a_{\lambda,i}\}} a_\lambda e^{-\beta(\epsilon_\lambda - \mu)a_\lambda} \\ &= \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \Xi_\lambda = \frac{g_\lambda}{e^{\beta(\epsilon_\lambda - \mu)} \mp 1} \quad \begin{cases} - & \text{Bosons} \\ + & \text{Fermions} \end{cases} \end{aligned} \tag{6.1.15}$$

6.2 summary on grand canonical ensembles

- summary on grand canonical ensembles,

$$\begin{cases} \langle E_{N,n}, i|\rho_G|E_{N',n'}, j\rangle = \delta_{\dots}\dfrac{1}{\Xi}e^{-\beta(E_{N,n}-\mu N)} \\ \Xi(\beta, \alpha = -\beta\mu, y_l) = \displaystyle\sum_{N,n} g_{N,n}e^{-\beta E_{N,n}-\alpha N} \end{cases} \tag{6.2.1}$$

$$\begin{cases} \bar{E} = -\dfrac{\partial}{\partial\beta}\ln\Xi \\ \bar{N} = -\dfrac{\partial}{\partial\alpha}\ln\Xi \\ \bar{Y}_l = \dfrac{1}{\beta}\dfrac{\partial}{\partial y_l}\ln\Xi \end{cases} \quad \text{and} \quad \begin{cases} \Phi_G = -\dfrac{1}{\beta}\ln\Xi \\ S = k_B\Big(\beta(\bar{E}-\mu\bar{N}) + \ln\Xi\Big) \end{cases} \tag{6.2.2}$$

- 下面是关于近独立的玻色或费米子系.
- 巨正则配分函数为,

$$\Xi(\beta, \alpha, y_l) = \prod_\lambda (1+\eta e^{-\beta\epsilon_\lambda-\alpha})^{\eta g_\lambda} \iff \ln\Xi = \eta\sum_\lambda g_\lambda \ln(1+\eta e^{-\beta\epsilon_\lambda-\alpha}) \tag{6.2.3}$$

其中, y_l 是通过 ϵ_λ 依赖的外参量, 例如 V 或外加电磁场.

- 代入 (6.2.2), 得到,

$$\begin{cases} U \equiv \bar{E} = \displaystyle\sum_\lambda \frac{g_\lambda\epsilon_\lambda}{e^{\beta\epsilon_\lambda+\alpha}+\eta} \\ \bar{N} = \displaystyle\sum_\lambda \frac{g_\lambda}{e^{\beta\epsilon_\lambda+\alpha}+\eta} = \sum_\lambda \bar{a}_\lambda \\ \bar{Y}_l = -\displaystyle\sum_\lambda \frac{\partial\epsilon_\lambda}{\partial y_l}\bar{a}_\lambda \end{cases} \tag{6.2.4}$$

Chapter 7

degeneracy of ideal gases

- 本章沿用之前对 $\eta = \pm 1$ 的定义, 以及 $\alpha = -\beta\mu$.

7.1 非简并条件 & 经典极限

- 考虑玻色分布与费米分布的表达式,

$$\bar{a}_\lambda = \frac{g_\lambda}{e^{\beta\epsilon_\lambda + \alpha} + \eta} \overset{e^\alpha \gg 1}{\Longrightarrow} \bar{a}_\lambda = g_\lambda e^{-\beta\epsilon_\lambda - \alpha} \tag{7.1.1}$$

  $e^\alpha \gg 1$ 称为**非简并条件** (此时, 化学势 $\mu < 0$), 分布退化为玻尔兹曼分布.

- 非简并条件下,

$$\frac{\bar{a}_\lambda}{g_\lambda} \ll 1 \tag{7.1.2}$$

  每个量子态上占据的平均粒子数远小于 1, 所以费米子和玻色子的区别消失了.

- 在非简并条件下,

$$\begin{cases} \ln \Xi(\beta, \alpha, y_l) \approx \sum\limits_\lambda g_\lambda e^{-\beta\epsilon_\lambda - \alpha} = e^{-\alpha} Z(\beta, y_l) \\ \bar{N} = \ln \Xi = e^{-\alpha} Z \Longrightarrow \mu = -\dfrac{1}{\beta} \ln \dfrac{Z}{\bar{N}} \\ \bar{E} = -\dfrac{\partial}{\partial\beta} \ln \Xi = -\bar{N} \dfrac{\partial}{\partial\beta} \ln Z \\ \bar{Y}_l = \dfrac{1}{\beta} \dfrac{\partial}{\partial y_l} \ln \Xi = \dfrac{\bar{N}}{\beta} \dfrac{\partial}{\partial y_l} \ln Z \\ S = k_B \Big(\beta(\bar{E} - \mu\bar{N}) + \ln \Xi \Big) = k_B \Big(\overbrace{\bar{N} \Big(\ln Z - \beta \dfrac{\partial}{\partial\beta} \ln Z \Big)}^{\ln W_{\text{M-B,max}}} - \ln \bar{N}! \Big) \end{cases} \tag{7.1.3}$$

  其中, 熵里 $\ln \bar{N}!$ 项可以认为是子系非定域 (因此不可分辨) 引入的.

- 非定域子系的经典极限条件为,

$$\begin{cases} \dfrac{\Delta\epsilon_\lambda}{k_B T} \ll 1 & \textbf{能量量子化}\text{不起作用} \\ e^\alpha \gg 1 & \text{量子力学的}\textbf{粒子全同性原理}\text{不起作用} \end{cases} \tag{7.1.4}$$

7.1.1 决定非简并条件的物理参数

- 考虑体积为 V 的单原子理想气体,

$$\epsilon = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \quad n_i = 0, 1, 2, \cdots \Longrightarrow \frac{\Delta\epsilon}{k_B T} \approx \frac{\hbar^2\pi^2}{2mL^2 k_B T} \tag{7.1.5}$$

配分函数为,

$$Z=\int\frac{d^3xd^3p}{h^3}e^{-\beta\frac{1}{2m}(p_x^2+p_y^2+p_z^2)}=V\left(\frac{2\pi mk_BT}{h^2}\right)^{\frac{3}{2}}=\frac{V}{\lambda_T^3}\tag{7.1.6}$$

所以, 非简并条件为,

$$e^\alpha=\frac{Z}{\bar{N}}=\frac{1}{n\lambda_T^3}\gg 1\Longrightarrow n\lambda_T^3\ll 1\tag{7.1.7}$$

其中, n 是粒子数密度, 这表明粒子的平均间距要远大于 de Broglie 热波长 λ_T.

- 理想气体的各热力学量见 (2.1.4).

7.2 弱简并理想气体

- 考虑 $\frac{\Delta\epsilon}{k_BT}\ll 1$ 但 $e^\alpha>1$ 而非 $\gg$ 的情况.

7.2.1 Bose gases

- 考虑自旋为 0 的气体分子.
- 由于 $\frac{\Delta\epsilon}{k_BT}\ll 1$ 依然成立, 巨配分函数任然可以用积分计算 (只不过需要考虑对被积函数不能做近似),

$$\ln\Xi=\frac{V}{\lambda_T^3}g_{5/2}(z)\tag{7.2.1}$$

其中 $z=e^{-\alpha}$ 是**逸度** (fugacity), 而,

$$g_m(z)=\sum_{n=1}^{\infty}\frac{z^n}{n^m}\tag{7.2.2}$$

proof:

$$\begin{aligned}\ln\Xi&=-\int\frac{d\omega}{h^3}\ln(1-e^{-\beta\epsilon-\alpha})\\&=-\frac{V}{h^3}\int 4\pi(2m\epsilon)\frac{md\epsilon}{\sqrt{2m\epsilon}}\ln(1-e^{-\beta\epsilon-\alpha})\\&=-\frac{2\pi V}{h^3}\left(\frac{2m}{\beta}\right)^{\frac{3}{2}}\int_0^\infty\sqrt{x}dx\ln(1-e^{-x-\alpha})\end{aligned}\tag{7.2.3}$$

考虑,

$$\begin{aligned}\int_0^\infty\sqrt{x}dx\ln(1-e^{-x-\alpha})&=-\sum_{n=1}^\infty\int_0^\infty\sqrt{x}\frac{e^{-n(x+\alpha)}}{n}dx\\&=-\sum_{n=1}^\infty\frac{e^{-n\alpha}}{n}\int_0^\infty 2y^2e^{-ny^2}dy=-\frac{\sqrt{\pi}}{2}\sum_{n=1}^\infty\frac{e^{-n\alpha}}{n^{5/2}}\end{aligned}\tag{7.2.4}$$

代入,

$$\ln\Xi=\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}\sum_{n=1}^\infty\frac{e^{-n\alpha}}{n^{5/2}}\tag{7.2.5}$$

- 逸度 z 联系着 α, 热波长 λ_T 联系着 β.
- 各热力学量为,

$$\begin{cases}p=\dfrac{1}{\beta}\dfrac{\partial}{\partial V}\ln\Xi=k_BT\dfrac{g_{5/2}(z)}{\lambda_T^3}\\ \bar{E}=-\dfrac{\partial}{\partial\beta}\ln\Xi=\dfrac{3}{2}\dfrac{V}{\lambda_T^3}g_{5/2}(z)k_BT\\ \bar{N}=-\dfrac{\partial}{\partial\alpha}\ln\Xi=\dfrac{V}{\lambda_T^3}g_{3/2}(z)\end{cases}\tag{7.2.6}$$

- 物态方程和内能的修正公式为,

$$\frac{pV}{Nk_BT} = \frac{\bar{E}}{\frac{3}{2}Nk_BT} = \frac{g_{5/2}(z)}{g_{3/2}(z)} = 1 - 2^{-\frac{5}{2}}y + O(y^2) \tag{7.2.7}$$

其中 $y = n\lambda_T^3 < 1$.

calculation:

首先, 有 (注意 $z = e^{-\alpha} < 1$, 从数值计算可以看出, 实际上要求 $z < 0.7$ 左右),

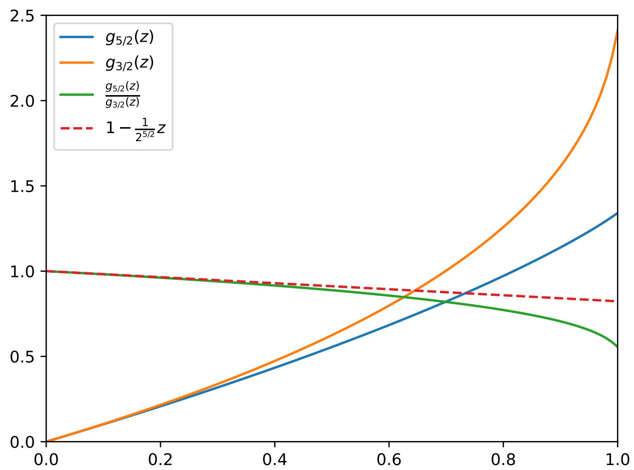
$$y = n\lambda_T^3 = g_{3/2}(z) = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots < 1 \tag{7.2.8}$$

设 $z = y + a_2y^2 + a_3y^3 + \cdots$, 代入,

$$y = y + a_2y^2 + a_3y^3 + \frac{y^2 + 2a_2y^3}{2^{3/2}} + \frac{y^3}{3^{3/2}} + O(y^4) \Longrightarrow \begin{cases} a_2 = -2^{-\frac{3}{2}} \\ a_3 = -3^{-\frac{3}{2}} + \frac{1}{4} \end{cases} \tag{7.2.9}$$

所以,

$$\begin{aligned} \frac{g_{5/2}(z)}{g_{3/2}(z)} &= \frac{z + \frac{z^2}{2^{5/2}} + \cdots}{z + \frac{z^2}{2^{3/2}} + \cdots} \\ &= \left(z + \frac{z^2}{2^{5/2}}\right)\left(\frac{1}{z} - \frac{1}{2^{3/2}}\right) + O(z^2) = 1 + \left(\frac{1}{2^{5/2}} - \frac{1}{2^{3/2}}\right)z + O(z^2) \\ &= 1 - \frac{1}{2^{5/2}}y + O(y^2) \end{aligned} \tag{7.2.10}$$



7.2.2 Fermi gases

- 考虑自旋为 $\frac{1}{2}$ 的气体分子.
- 巨配分函数为,

$$\ln \Xi = 2\int \frac{d\omega}{h^3}\ln(1 + e^{-\beta\epsilon-\alpha}) = 2\frac{V}{\lambda_T^3}f_{5/2}(z) \tag{7.2.11}$$

其中 2 来自于两个自旋态带来的简并度, z 依然是逸度, 而,

$$f_m(z) = \sum_{n=1}^{\infty}\frac{(-1)^{n-1}z^n}{n^m} = z - \frac{z^2}{2^m} + \frac{z^3}{3^m} - \cdots \tag{7.2.12}$$

proof:

$$
\begin{aligned}
\ln \Xi &= 2\int \frac{d\omega}{h^3}\ln(1+e^{-\beta\epsilon-\alpha}) \\
&= 2\frac{V}{h^3}\int 4\pi(2m\epsilon)\frac{md\epsilon}{\sqrt{2m\epsilon}}\ln(1+e^{-\beta\epsilon-\alpha}) \\
&= 4\pi\frac{V}{h^3}\left(\frac{2m}{\beta}\right)^{\frac{3}{2}}\int_0^\infty \sqrt{x}dx\ln(1+e^{-x-\alpha})
\end{aligned}
\tag{7.2.13}
$$

同样, 对 ln 进行展开,

$$
\begin{aligned}
\int_0^\infty \sqrt{x}dx\ln(1+e^{-x-\alpha}) &= \sum_{n=1}^\infty(-1)^{n+1}\frac{e^{-n\alpha}}{n}\int_0^\infty \sqrt{x}e^{-nx}dx \\
&= 2\sum_{n=1}^\infty(-1)^{n+1}\frac{e^{-n\alpha}}{n}\int_0^\infty y^2e^{-ny^2}dy \\
&= \frac{\sqrt{\pi}}{2}\sum_{n=1}^\infty(-1)^{n+1}\frac{e^{-n\alpha}}{n^{5/2}}
\end{aligned}
\tag{7.2.14}
$$

代入,

$$
\ln \Xi = 2\frac{V}{\lambda_T^3}\sum_{n=1}^\infty(-1)^{n+1}\frac{e^{-\alpha}}{n^{5/2}} \tag{7.2.15}
$$

其中 $\lambda_T = \frac{h^2}{2\pi m k_B T}$.

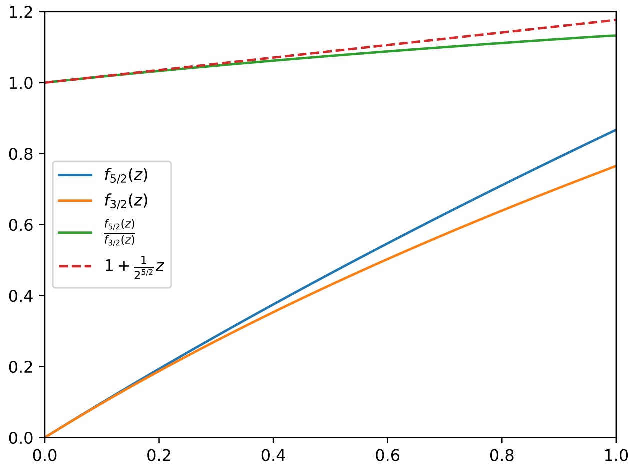
- 各热力学量为,

$$
\begin{cases}
p = \dfrac{1}{\beta}\dfrac{\partial}{\partial V}\ln\Xi = 2\dfrac{f_{5/2}(z)}{\lambda_T^3} \\
\bar{E} = -\dfrac{\partial}{\partial \beta}\ln\Xi = 3\dfrac{V}{\lambda_T^3}f_{5/2}(z)k_BT \\
\bar{N} = -\dfrac{\partial}{\partial \alpha}\ln\Xi = 2\dfrac{V}{\lambda_T^3}f_{3/2}(z)
\end{cases}
\tag{7.2.16}
$$

- 物态方程和内能的修正公式为,

$$
\frac{pV}{Nk_BT} = \frac{\bar{E}}{\frac{3}{2}Nk_BT} = \frac{f_{5/2}(z)}{f_{3/2}(z)} = 1+\frac{1}{2^{5/2}}y+O(y^2) \tag{7.2.17}
$$

其中 $y = \frac{1}{2}n\lambda_T^3$.



7.2.3 fugacity

- **逸度** (fugacity) 是实际气体的有效压强, 等于具有相同**温度**、**化学势**的理想气体对应的压强.

- 根据热力学方程,
$$d\mu = d\frac{G}{N} = -\frac{S}{N}dT + \frac{V}{N}dp \tag{7.2.18}$$
理想气体的化学势与压强的关系为,
$$\mu(T,p) = \mu^{\ominus}(T,p^{\ominus}) + k_BT\ln\frac{p}{p^{\ominus}} \Longrightarrow p = p^{\ominus}\exp\left(\frac{\mu-\mu^{\ominus}}{k_BT}\right) \tag{7.2.19}$$
相应的, 实际气体的逸度定义为,
$$f = f^{\ominus}\exp\left(\frac{\mu-\mu^{\ominus}}{k_BT}\right) \propto z = e^{-\alpha} \equiv \exp\left(\frac{\mu}{k_BT}\right) \tag{7.2.20}$$

7.2.4 summary & 统计关联

- 保留到最低阶,
$$\frac{pV}{Nk_BT} = \frac{\bar{E}}{\frac{3}{2}Nk_BT} = 1+\eta\frac{1}{2^{5/2}}y \quad \text{where} \quad \begin{cases} y = n\lambda_T^3 \quad \eta=-1 \quad \text{Bose gases} \\ y = \frac{1}{2}n\lambda_T^3 \quad \eta=+1 \quad \text{Fermi gases} \end{cases} \tag{7.2.21}$$
可见, 玻色气体存在**有效吸引**; 费米气体存在**有效排斥**.
- 这种有效相互作用称作**统计关联**, 是纯粹的量子力学效应, 区别与动力学关联.

7.3 strongly degenerate gases

- 强简并要求 $e^{\alpha} \lesssim 1$.

7.3.1 Bose gas: photon gas

- 参考 3.5, 注意 $\alpha = 0$, 我们有,
$$\ln\Xi = -\int_0^{\infty} g(\nu)\ln(1-e^{-\beta h\nu}) \tag{7.3.1}$$
其中,
$$\begin{cases} g(\nu)d\nu = 2\times\frac{4\pi}{8}n^2dn \\ \frac{h\nu}{c} = \frac{h}{2L}n \end{cases} \Longrightarrow g(\nu) = \frac{8\pi V}{c^3}\nu^2 \tag{7.3.2}$$
所以,
$$\ln\Xi = \frac{8\pi^5V}{45}\left(\frac{k_BT}{hc}\right)^3 \tag{7.3.3}$$

proof:

$$\begin{aligned}\ln\Xi &= -\frac{8\pi V}{c^3}\int\ln(1-e^{-\beta h\nu})\nu^2d\nu \\ &= -\frac{8\pi V}{(\beta hc)^3}\int_0^{\infty}\ln(1-e^{-x})x^2dx = \frac{8\pi V}{(\beta hc)^3}\sum_{n=1}^{\infty}\frac{1}{n}\int_0^{\infty}x^2e^{-nx}dx \\ &= \frac{16\pi V}{(\beta hc)^3}\underbrace{\sum_{n=1}^{\infty}\frac{1}{n^4}}_{=\frac{\pi^4}{90}} = \frac{8\pi^5}{45}\frac{V}{(\beta hc)^3}\end{aligned} \tag{7.3.4}$$

- 注意到 $\mu = 0$, 得到,
$$\begin{cases} \Phi_G = F = -k_BT\ln\Xi = -\frac{1}{3}aVT^4 \\ S = -\left.\frac{\partial F}{\partial T}\right|_V = \frac{4}{3}aVT^3 \end{cases} \quad \text{and} \quad \begin{cases} \bar{E} = aVT^4 = -3F \\ C_V = 3S \\ p = \frac{1}{3}aT^4 = \frac{\bar{E}}{3V} \end{cases} \tag{7.3.5}$$

其中 $a=\frac{8\pi^5k_B^4}{15(hc)^3}$, 以及,

$$\bar{N}=\frac{16\pi\zeta(3)V}{(\beta hc)^3} \tag{7.3.6}$$

7.3.2 strongly degenerate ideal gases: Bose-Einstein condensation

- 对于理想玻色气体, 能级上的粒子数非负,

$$\bar{a}_\lambda=\frac{g_\lambda}{e^{\beta\epsilon_\lambda+\alpha}-1}>0 \Longrightarrow \begin{cases} e^{\beta(\epsilon_\lambda-\mu)}>1 \Longrightarrow \mu<\epsilon_\lambda \Longrightarrow \mu<0 \\ \boldsymbol{e^{\alpha}>1} \end{cases} \tag{7.3.7}$$

(取最低能级为零), 所以一定有 $\alpha>0$ ($\mu<0$), 因此, 强简并条件为 $e^\alpha>1$ (或 $z<1$) 但接近 1.

- 可见**玻色**气体的化学势一定为**负** (或为**零**, 粒子数不守恒时); **费米**气体的化学势**可能为正**.

- 强简并时, 大多数粒子处于基态, 所以要单独考虑基态的贡献,

$$\ln\Xi=-g_0\ln(1-e^{-\alpha})-\int_{\epsilon_1}^{\infty}g(\epsilon)\ln(1-e^{-\beta\epsilon-\alpha})d\epsilon \tag{7.3.8}$$

g_0 取决于气体粒子的自旋等, 第二项积分在弱简并条件下已经计算过了, 见 (7.2.1).

- 粒子数为,

$$N=N_0+N_{\mathrm{exc}}=\frac{1}{e^\alpha-1}+\frac{V}{\lambda_T^3}g_{3/2}(z) \tag{7.3.9}$$

其中, $\lambda_T=\frac{h}{\sqrt{2\pi mk_BT}}$, 而 N_0 是基态的粒子数.

- 产生玻色爱因斯坦凝聚的临界温度为,

$$\begin{cases} N=N_{\mathrm{exc}} \\ z=1 \end{cases} \Longrightarrow T_c=\frac{h^2}{2\pi mk_B}\left(\frac{n}{g_{3/2}(1)}\right)^{\frac{2}{3}} \tag{7.3.10}$$

(因为温度再降低, 就必须考虑基态上的粒子数贡献了)

- 除了等体积地降温外, 我们还可以通过**等温压缩**得到凝聚, 临界体积 V_c 依然由下式决定,

$$n=\frac{1}{\lambda_T^3}g_{3/2}(1) \tag{7.3.11}$$

(通常用比容 v_c)

- 物理意义, 热波长 λ_T 与分子间距相当,

$$\frac{\lambda_T^3}{v}\begin{cases} <g_{3/2}(1) & \text{气相区} \\ >g_{3/2}(1) & \text{两相共存区} \end{cases} \tag{7.3.12}$$

- BEC 既是一阶, 也是三阶相变.

Chapter 8

相变的统计理论简介

Appendices

Appendix A

thermodynamics

A.1 heat capacity

- the relation between C_V and C_p is,

$$C_V - C_p = \left(p + \frac{\partial U}{\partial V}\Big|_T\right)\frac{\partial V}{\partial T}\Big|_p \tag{A.1.1}$$

proof:

$$\begin{aligned} C_V - C_p &= T\frac{\partial S}{\partial T}\Big|_V - T\frac{\partial S}{\partial T}\Big|_p \\ &= T\frac{\partial S}{\partial V}\Big|_T\frac{\partial V}{\partial T}\Big|_p \end{aligned} \tag{A.1.2}$$

consider $S(U(T,V),V)$,

$$\begin{aligned} \frac{\partial S}{\partial V}\Big|_T &= \frac{\partial S}{\partial V}\Big|_U + \frac{\partial S}{\partial U}\Big|_V\frac{\partial U}{\partial V}\Big|_T \\ &= \frac{p}{T} + \frac{1}{T}\frac{\partial U}{\partial V}\Big|_T \end{aligned} \tag{A.1.3}$$

- moreover,

$$C_V - C_p = TV\frac{\alpha^2}{\kappa_T} \quad \text{and} \quad \frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S} \tag{A.1.4}$$

where:

  - the isothermal compressibility, $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\big|_T$
  - the isentropic compressibility, $\kappa_S = -\frac{1}{V}\frac{\partial V}{\partial p}\big|_S$
  - the thermal expansion coefficient, $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\big|_p$

proof:

let's start from (A.1.2),

$$C_V - C_p = T\frac{\partial S}{\partial V}\Big|_T\frac{\partial V}{\partial T}\Big|_p \tag{A.1.5}$$

$$= T\frac{\partial p}{\partial T}\Big|_V(V\alpha) \tag{A.1.6}$$

and,

$$\frac{\partial p}{\partial T}\Big|_V = -\frac{\partial V}{\partial T}\Big|_p\frac{\partial p}{\partial V}\Big|_T = -(V\alpha)\frac{1}{-V\kappa_T} \tag{A.1.7}$$

---

now, let's prove the second equation:

$$
\begin{aligned}
&\frac{C_p}{C_V} \overset{?}{=} \frac{\kappa_T}{\kappa_S} \\
\Longrightarrow &\frac{\frac{\partial S}{\partial T}\big|_p}{\frac{\partial S}{\partial T}\big|_V} \overset{?}{=} \frac{\frac{\partial V}{\partial p}\big|_T}{\frac{\partial V}{\partial p}\big|_S} \Longrightarrow \frac{\partial S}{\partial T}\Big|_p \frac{\partial T}{\partial S}\Big|_V \overset{?}{=} \frac{\partial V}{\partial p}\Big|_T \frac{\partial p}{\partial V}\Big|_S
\end{aligned}
\tag{A.1.8}
$$

and,

$$
\begin{aligned}
&\frac{\partial(S,V)}{\partial(T,p)} = \begin{pmatrix} \frac{\partial S}{\partial T}\big|_p & \frac{\partial V}{\partial T}\big|_p = -a \\ \frac{\partial S}{\partial p}\big|_T = a & \frac{\partial V}{\partial p}\big|_T \end{pmatrix} \quad \frac{\partial(T,p)}{\partial(S,V)} = \begin{pmatrix} \frac{\partial T}{\partial S}\big|_V & \frac{\partial p}{\partial S}\big|_V = -b \\ \frac{\partial T}{\partial V}\big|_S = b & \frac{\partial p}{\partial V}\big|_S \end{pmatrix} \\
\Longrightarrow &\frac{\partial(S,V)}{\partial(T,p)} \frac{\partial(T,p)}{\partial(S,V)} = I = \begin{pmatrix} \frac{\partial S}{\partial T}\big|_p \frac{\partial T}{\partial S}\big|_V - ab & 0 \\ 0 & -ab + \frac{\partial V}{\partial p}\big|_T \frac{\partial p}{\partial V}\big|_S \end{pmatrix} \\
\Longrightarrow &\frac{\partial S}{\partial T}\Big|_p \frac{\partial T}{\partial S}\Big|_V = \frac{\partial V}{\partial p}\Big|_T \frac{\partial p}{\partial V}\Big|_S = 1 + ab
\end{aligned}
\tag{A.1.9}
$$

A.2 thermodynamic potentials

- summary:

名称	表达式	for homogeneous systems	微分
internal energy	U	$TS - yY + \mu N$	$dU = TdS - Ydy + \mu dN$
Helmholtz f.e.	$F = U - TS$	NA	$dF = -SdT - Ydy + \mu dN$
enthalpy	$H = U + yY$	NA	$dH = TdS + ydY + \mu dN$
Gibbs f.e.	$G = U - TS + yY$	μN	$dG = -SdT + ydY + \mu dN$
grand potential	$\Phi_G = U - TS - \mu N$	$-yY$	$d\Phi_G = -SdT - Ydy - Nd\mu$

A.3 thermal equilibrium

- summary:

name	precondition	inequality
principle of **maximal entropy**	$\delta Q = 0, dV = 0, dN = 0$	$dS \geq 0$
principle of **minimal free energy**	$dT = 0, dV = 0, dN = 0$	$dF \leq 0$
principle of **minimal Gibbs free energy**	$dT = 0, dp = 0, dN = 0$	$dG \leq 0$

Appendix B

a brief excursion into probability theory

B.1 combinations and permutations

B.1.1 combinations

- k 个元素的组合数 (number of k-combinations) 为,

$$C_k^n = \frac{n!}{k!(n-k)!} \tag{B.1.1}$$

是从 n 个相异元素中取出 k 个元素的组合数量。

B.1.2 permutations

- k 个元素的排列数 (number of k-permutations of n) 为,

$$P_k^n = \frac{n!}{(n-k)!} \tag{B.1.2}$$

是从 n 个相异元素中取出 k 个元素的排列数量。

B.1.3 stars and bars (combinatorics)

- stars and bars (插板法) is method to calculate how many ways there are to put n **indistinguishable balls** into k **distinguishable bins**.
- 具体方法是计算 n 个球和 $k-1$ 个隔板的总排列数，再除以球和隔板各自的排列数（因为它们各自是不可分辨的），所以小球的可能分布数为,

$$\frac{(n+k-1)!}{n!(k-1)!} = C_n^{n+k-1} \tag{B.1.3}$$

B.2 probability density and characteristic functions

- the **probability density** is $w(x_1, \cdots, x_n)$, and the average of a function, $F(X_1, \cdots, X_n)$, of the **random variables**, $X_1, \cdots, X_n$, is

$$\langle F(\vec{X})\rangle = \int d^n x\, w(\vec{x}) F(\vec{x}) \tag{B.2.1}$$

  - if $\vec{X}$ has **discrete values**, $\vec{\xi}_1, \vec{\xi}_2, \cdots$, then the probability density is,

$$w(\vec{x}) = p_1 \delta^{(n)}(\vec{x} - \vec{\xi}_1) + \cdots \tag{B.2.2}$$

- def.: $\mu_m \equiv \langle X^m \rangle$ is called **the m-th moment of** $w(x)$ (in the case of single random variable)
- def.: $(\Delta x_i)^2 = \langle X_i^2\rangle - \langle X_i\rangle^2$ is called the **mean square deviation**.

- def.: the **correlations** of X_i, X_j is,

$$K_{ij} = \langle (X_i - \langle X_i \rangle)(X_j - \langle X_j \rangle) \rangle \tag{B.2.3}$$

which describes how much the fluctuation between them are correlated.

  – if $w(\vec{x}) = w_i(x_i) w'(x_1, \cdots, x_{i-1}, x_{i+1}, \cdots, x_n)$, then $K_{ij} = 0$ for all $j \neq i$, i.e. X_i are not correlated to the rest of the variables.

- def.: the **characteristic function** is the Fourier transform of $w(x)$,

$$\chi(\vec{k}) = \int d^n x \, e^{-i\vec{k}\cdot\vec{x}} w(\vec{x}) \equiv \langle e^{-i\vec{k}\cdot\vec{x}} \rangle \iff w(\vec{x}) = \int \frac{d^n k}{(2\pi)^n} e^{i\vec{k}\cdot\vec{x}} \chi(\vec{k}) \tag{B.2.4}$$

if all the moments of the probability density exist, then,

$$\chi(\vec{k}) = \sum_{m=0}^{\infty} \frac{(-i)^m}{m!} \langle (\vec{k} \cdot \vec{X})^m \rangle \tag{B.2.5}$$

- treat $F(\vec{X})$ as a random variable, its probability density, $w_F(f)$, is,

$$w_F(f) = \langle \delta(F(\vec{X}) - f) \rangle \tag{B.2.6}$$

proof:

consider the characteristic function of w_F,

$$\begin{aligned} w_F(f) &= \int \frac{dk}{2\pi} e^{ikf} \chi_F(k) \\ &= \int \frac{dk}{2\pi} e^{ikf} \langle e^{-ikF} \rangle \\ &= \int \frac{dk}{2\pi} e^{ikf} \underbrace{\int d^n x \, w(x) e^{-ikF(\vec{x})}}_{=\langle e^{-ikf} \rangle} = \int d^n x \, w(\vec{x}) \delta(F(\vec{x}) - f) \end{aligned} \tag{B.2.7}$$

- def.: the probability density, $P_{n-1}(x_1, \cdots, x_{i-1}, x_{i+1}, \cdots, x_n)$, is,

$$P_{n-1}(x_1, \cdots, x_{i-1}, x_{i+1}, \cdots, x_n) = \int dx_i P_n(x_1, \cdots, x_n) \tag{B.2.8}$$

- def.: the **conditional probability density** is,

$$P_{k|n-k}(x_1, \cdots, x_k | x_{k+1}, \cdots, x_n) = \frac{P_n(x_1, \cdots, x_n)}{P_{n-k}(x_{k+1}, \cdots, x_n)} \tag{B.2.9}$$

which if the probability (density) of happening $x_1, \cdots, x_k$ after $x_{k+1}, \cdots, x_n$ happened.

B.3 the central limit theorem

B.3.1 the cumulants

- def.: the **cumulants**, κ_m, are defined by the logarithm of the characteristic function,

$$\ln \chi(k) = \ln \langle e^{-ikX} \rangle = \sum_{m=1}^{\infty} \kappa_m \frac{(-ik)^m}{m!} \tag{B.3.1}$$

- cheating sheet:

$$\begin{aligned} \kappa_1 &= \mu_1 \\ \kappa_2 &= (\Delta x)^2 = \mu_2 - \mu_1^2 \\ \kappa_3 &= \mu_3 - 3\mu_1\mu_2 + 2\mu_1^3 \\ \kappa_4 &= \mu_4 - 4\mu_1\mu_3 - 3\mu_2^2 + 12\mu_1^2\mu_2 - 6\mu_1^4 \end{aligned} \tag{B.3.2}$$

calculation:

the expansion of logarithm is $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$,

$$\begin{aligned}
&\ln\left(1 + (-ik)\mu_1 + \frac{(-ik)^2}{2}\mu_2 + \frac{(-ik)^3}{6}\mu_3 + O(k^4)\right) \\
=&(-ik)\mu_1 + \frac{(-ik)^2}{2}\mu_2 + \frac{(-ik)^3}{6}\mu_3 - \frac{1}{2}\left((-ik)^2\mu_1^2 + (-ik)^3\mu_1\mu_2\right) \\
&+ \frac{1}{3}(-ik)^3\mu_1^3 + O(k^4)
\end{aligned} \tag{B.3.3}$$

B.3.2 the central limit theorem and the Gaussian distribution

- **the central limit theorem**: consider a bunch of uncorrelated random variables, $X_1, X_2, \cdots, X_N$, with $w(x_1, \cdots, x_N) = w(x_1)\cdots w(x_N)$, then the probability distribution of $Y = X_1 + \cdots + X_N$ is,

$$\lim_{N\to\infty} w_Y(y) = \frac{1}{\sqrt{2\pi}\Delta y} e^{-\frac{(y-\langle y\rangle)^2}{2(\Delta y)^2}} \tag{B.3.4}$$

i.e. $w_Y(y)$ is a **Gaussian distribution** (when $N \to \infty$), and,

$$\langle y\rangle = N\langle x\rangle \qquad \Delta y = \sqrt{N}\Delta x \tag{B.3.5}$$

proof:

consider,

$$Z = \sum_i \frac{X_i - \langle X\rangle}{\sqrt{N}} = \frac{Y - \langle Y\rangle}{\sqrt{N}} \tag{B.3.6}$$

the probability distribution of Z is,

$$w_Z(z) = \int \frac{dk}{2\pi} e^{ikz} \chi_Z(k) \quad \text{and} \quad w_Y(y) = \frac{1}{\sqrt{N}} w_Z\left(\frac{y - \langle Y\rangle}{\sqrt{N}}\right) \tag{B.3.7}$$

and,

$$\chi_Z(k) = \int d^N x\, w(x_1)\cdots w(x_N) e^{-ik\sum_i \frac{x_i - \langle X\rangle}{\sqrt{N}}} = \chi^N\left(\frac{k}{\sqrt{N}}\right) \tag{B.3.8}$$

use the cumulants to expand the $\chi(\frac{k}{\sqrt{N}})$,

$$\chi\left(q = \frac{k}{\sqrt{N}}\right) = \exp\left(\kappa_1(-iq) + \kappa_2\frac{(-iq)^2}{2} + \kappa_3\frac{(-iq)^3}{6} + O(q^4)\right) \tag{B.3.9}$$

so,

$$\begin{aligned}
w_Z(z) &= \int \frac{dk}{2\pi} e^{ikz + N\left(-i\kappa_1\frac{k}{\sqrt{N}} - \kappa_2\frac{k^2}{2N} + i\kappa_3\frac{k^3}{6N^{3/2}} + O(\frac{1}{N^2})\right)} \\
&\overset{N\to\infty}{=} \int \frac{dk}{2\pi} e^{ikz - i\kappa_1\sqrt{N}k - \frac{\kappa_2}{2}k^2} \\
&\approx \int \frac{dk}{2\pi} e^{ikz - \frac{\kappa_2}{2}k^2} = \sqrt{\frac{1}{2\pi\kappa_2}} e^{-\frac{z^2}{2\kappa_2}} = \frac{1}{\sqrt{2\pi}\Delta x} e^{-\frac{z^2}{2(\Delta x)^2}}
\end{aligned} \tag{B.3.10}$$

and, finally,

$$w_Y(y) = \frac{1}{\sqrt{2\pi N}\Delta x} e^{-\frac{(y-\langle Y\rangle)^2}{2N(\Delta x)^2}} \tag{B.3.11}$$

the mean square deviation of Y is,

$$\begin{aligned}
(\Delta y)^2 &= \langle Y^2\rangle - \langle Y\rangle^2 = \langle (y - \langle Y\rangle)^2\rangle \\
&= \int dy'\, y'^2 \frac{1}{\sqrt{2\pi N}\Delta x} e^{-\frac{y'^2}{2N(\Delta x)^2}} \\
&= \frac{1}{\sqrt{2\pi N}\Delta x}\frac{1}{2}\sqrt{\pi(2N(\Delta x)^2)^3} = N(\Delta x)^2
\end{aligned} \tag{B.3.12}$$

- the **Gaussian distribution** is,

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad \text{with} \quad \overline{x} = \mu \quad \overline{(\Delta x)^2} = \sigma^2 \tag{B.3.13}$$

and,

$$\lim_{\sigma \to 0} p(x) = \delta(x - \mu) \tag{B.3.14}$$

- 二元高斯分布为,

$$p(x, y) = \frac{\sqrt{ac - b^2}}{\pi} e^{-ax^2 + 2bxy - cy^2} \tag{B.3.15}$$

and,

$$\begin{cases} \overline{x} = \overline{y} = 0 \\ \overline{x^2} = \dfrac{c}{2(ac - b^2)} \\ \overline{y^2} = \dfrac{a}{2(ac - b^2)} \\ \overline{xy} = \dfrac{b}{2(ac - b^2)} \end{cases} \tag{B.3.16}$$

Appendix C

mathematical preliminaries

C.1 Gaussian integral

- the Gaussian integral is,

$$\begin{cases} I_0 = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \\ I_1 = \int_{-\infty}^{\infty} x e^{-ax^2} dx = \frac{1}{2a} \end{cases} \tag{C.1.1}$$

with the recursive relation,

$$I_{n+2} = \int_{-\infty}^{\infty} x^{n+2} e^{-ax^2} dx = -\frac{\partial}{\partial a} \int_{-\infty}^{\infty} x^n e^{-ax^2} dx \tag{C.1.2}$$

and,

$$I_{2m} = (2m-1)!! \Big(\frac{1}{2a}\Big)^m \sqrt{\frac{\pi}{a}} \tag{C.1.3}$$

where $(2n-1)!! = 1 \times 3 \times 5 \times \cdots \times (2n-1)$

- cheating sheet:

$$I_n = \int_{-\infty}^{\infty} x^n e^{-ax^2} dx = \begin{cases} \frac{1}{2}\sqrt{\frac{\pi}{a^3}} & n=2 \\ \frac{1}{2a^2} & n=3 \\ \frac{3}{4}\sqrt{\frac{\pi}{a^5}} & n=4 \end{cases} \tag{C.1.4}$$

and,

$$\int e^{-ax^2+bx} dx = \int e^{-a(x-\frac{b}{2a})^2 + \frac{b^2}{4a}} dx = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}} \tag{C.1.5}$$

C.2 Dirac delta function

- some properties of the delta function:

$$\int f(x) \frac{d^n}{dx^n} \delta(x) dx = (-1)^n \frac{d^n}{dx^n}\Big|_0 f(x) \tag{C.2.1}$$

proof:

$$\begin{cases} \int f(x)\delta(x)dx = f(0) \\ \int f(x) \frac{d^{n+1}}{dx^{n+1}} \delta(x) dx = \underbrace{\int \frac{d}{dx}\Big(f(x)\frac{d^n}{dx^n}\delta(x)\Big)dx}_{=0} - \int \frac{df(x)}{dx}\frac{d^n}{dx^n}\delta(x)dx \end{cases} \tag{C.2.2}$$

$$\Longrightarrow \int f(x)\frac{d^n}{dx^n}\delta(x)dx = \int (-1)^n \frac{d^n f(x)}{dx^n}\delta(x)dx = (-1)^n \frac{d^n}{dx^n}\Big|_0 f(x) \tag{C.2.3}$$

and,

$$\delta(g(x)) = \sum_{i, x_i=0} \frac{\delta(x-x_i)}{|g'(x_i)|} \tag{C.2.4}$$

specially,

$$\delta(\alpha x) = \frac{\delta(x)}{|\alpha|} \tag{C.2.5}$$

C.3 Gamma function

- the Gamma function is,

$$\Gamma(z) = \int_0^\infty t^{z-1}e^{-t}dt \quad \text{and} \quad \Gamma(z+1) = z\Gamma(z) \tag{C.3.1}$$

proof:

$$\begin{aligned} \Gamma(z+1) &= \int_0^\infty t^z \overbrace{e^{-t}}^{=-\frac{d}{dt}e^{-t}} dt \\ &= -\underbrace{(t^z e^{-t})\Big|_0^\infty}_{=0} + \underbrace{\int z t^{z-1}e^{-t}dt}_{=z\Gamma(z)} \end{aligned} \tag{C.3.2}$$

- cheating sheet:

$$\begin{cases} \Gamma(1) = 1 & \Longrightarrow \Gamma(n+1) = n! \\ \Gamma(\frac{1}{2}) = \sqrt{\pi} & \Longrightarrow \Gamma(n+\frac{1}{2}) = \frac{(2n-1)!!}{2^n}\sqrt{\pi} \end{cases} \tag{C.3.3}$$

where $(2n-1)!! = 1 \times 3 \times 5 \times \cdots \times (2n-1)$

C.4 Riemann zeta function

- the Riemann ζ function is,

$$\zeta(n) = \sum_{k=1}^\infty \frac{1}{k^n} \tag{C.4.1}$$

当 $n > 1$ 时，函数值为有限的正实数。

- cheating sheet:

$$\zeta(2) = \frac{\pi^2}{6} \quad \zeta(3) \approx 1.202 \quad \zeta(4) = \frac{\pi^4}{90} \quad \zeta(\frac{3}{2}) \approx 2.612 \quad \zeta(\frac{5}{2}) \approx 1.341 \quad \zeta(\frac{7}{2}) \approx 1.127 \tag{C.4.2}$$

C.5 four integrals

- the integral A_n is,

$$A_n = \int_0^\infty \frac{x^n}{e^x - 1}dx = \zeta(n+1)\Gamma(n+1) \tag{C.5.1}$$

the integral won't diverge when $n > 1$

calculation:

notice that $\frac{1}{e^x-1} = \frac{e^{-x}}{e^{-x}-1} = e^{-x}\sum_{k=0}^{\infty} e^{-kx} = \sum_{k=0}^{\infty} e^{-(k+1)x}$, so,

$$\begin{aligned} A_n &= \int_0^\infty x^n \sum_{k=0}^{\infty} e^{-(k+1)x} dx \\ &= \underbrace{\sum_{k=0}^{\infty}(k+1)^{-(n+1)}}_{=\zeta(n+1)} \underbrace{\int_0^\infty t^n e^{-t} dt}_{=\Gamma(n+1)} \end{aligned} \tag{C.5.2}$$

where $t = (k+1)x$

- the integral B_n is,

$$B_n = \int_0^\infty \frac{x^n e^x}{(e^x-1)^2} dx = \zeta(n)\Gamma(n+1) \tag{C.5.3}$$

  the integral won't diverge when $n > 1$

- the integral C_n is,

$$C_n = \int_0^\infty \frac{x^n}{e^x+1} dx = (1-2^{-n})\zeta(n+1)\Gamma(n+1) \tag{C.5.4}$$

  notice $C_0 = \ln 2$ doesn't diverge.

- the integral D_n is,

$$D_n = \int_0^\infty \frac{x^n e^x}{(e^x+1)^2} dx = (1-2^{-(n-1)})\zeta(n)\Gamma(n+1) \tag{C.5.5}$$

  the integral won't diverge when $n > 1$

C.6 function $\mathscr{I}_n^{(\pm)}(\alpha)$

- the function is defined to be,

$$\mathscr{I}_n^{(\pm)}(\alpha) = \int_0^\infty \frac{x^n}{e^{x+\alpha} \pm 1} dx = \mp\Gamma(n+1)\mathrm{Li}_{n+1}(\mp e^{-\alpha}) \tag{C.6.1}$$

  where,

$$\mathrm{Li}_n(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^n} \quad \text{and} \quad \begin{cases} \mathrm{Li}_n(1) = \zeta(n) \\ \mathrm{Li}_1(z) = -\ln(1-z) \\ \dfrac{d}{dz}\mathrm{Li}_n(z) = \dfrac{\mathrm{Li}_{n-1}(z)}{z} \end{cases} \tag{C.6.2}$$

C.7 surface area of the unit $(D-1)$-sphere

- the surface area of the unit $(D-1)$-dimensional sphere embedded in D-dimensional Euclidean space is,

$$\mathscr{A}_{D-1} = \frac{2\pi^{D/2}}{\Gamma(\frac{D}{2})} \tag{C.7.1}$$

proof:

consider the integral,

$$\mathscr{Q} = \int (dx) e^{-\sum_i x_i^2} = \prod_i \int_{-\infty}^{\infty} dx_i\, e^{-x_i^2} = \pi^{D/2} \tag{C.7.2}$$

where $(dx) = \prod_i dx_i$, in another way,

$$\mathscr{Q} = \mathscr{A}_{D-1} \int_0^\infty r^{D-1} dr\, e^{-r^2} = \frac{1}{2}\mathscr{A}_{D-1}\Gamma(\frac{D}{2}) \tag{C.7.3}$$