Chapter 1 系综理论

研究对象： 宏观系统，由大量粒子组成 $\sim 10^{23}$ 个粒子的量级

描述 ↑ 宏观可测的物理量 [单组分，均相]

- 粒子数 N —— 化学势 μ
- 体积 V —— 压强 P
- 能量 E —— 温度 T
- 熵，Gibbs，Helmholtz，焓，…

→ 热力学平衡态，热力学关系

统计力学： 微观态 $\xrightarrow{\text{统计}}$ 宏观态

概率　平均　涨落

平衡态： 热力学上 A ~ B　A.B无能量传递

热力学第0定律 $\xrightarrow{\text{define}}$ 等价关系，"温度"

统计力学上：① 不产生宏观输运，演化停滞 ⟶ 相空间概率分布不变，$\frac{\partial \rho}{\partial t}=0$

② 混乱信息最少，信息熵最小 ⟵ 信息论

遍历假设：

宏观观测 $\frac{1}{T}\int_0^T \theta(T)\,dT = \langle\theta\rangle_\rho$ ⟵ 系综平均

宏观观测时间 T 内，系统在相空间内的演化轨迹，可以遍历相空间上任意一点

远大于微观状态动力学演化的时间尺度，近似认为无穷大

经典统计力学基础： "相空间" $\Gamma = \oplus_i \Omega_i$　$\Omega_i = P_i \oplus q_i$

$$\begin{cases}\dot q = \frac{\partial H}{\partial p}\\ \dot p = -\frac{\partial H}{\partial q}\end{cases}$$

相空间一个点 $a\in\Gamma$，代表体系的一个状态

系综：相空间 Γ 上的概率分布　[系统的众多"副本"在相空间不同点按相同动力学演化]

"流体"

流体：Euler 表述：
$$\begin{cases}\partial_t\rho + \vec\nabla\cdot\vec J = 0\\ \vec J = \vec v\cdot\rho \qquad \vec v = (\dot q, \dot p)\end{cases}$$

↓

Lagrange 表述：$\frac{d\rho}{dt}=0$

$$\longrightarrow \frac{\partial\rho}{\partial t} + \sum\left(\frac{\partial\rho}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial\rho}{\partial p}\frac{\partial H}{\partial q}\right) = 0 \longrightarrow \frac{\partial\rho}{\partial t} + \{H,\rho\} = 0$$

刘维尔方程

微正则系综： $N.\ V.\ E$ 固定

系统微观态总数 $\Omega = \Omega(N,V,E)$

等概率原理，每个态出现的概率为 $P_s = 1/\Omega$

熵： $S = k\ln\Omega$

$$\beta = \frac{1}{kT} = \left(\frac{\partial\ln\Omega}{\partial E}\right)_{N,V}$$
$$\beta\mu = \frac{\mu}{kT} = -\left(\frac{\partial\ln\Omega}{\partial N}\right)_{E,V}$$
$$\beta p = \frac{p}{kT} = \left(\frac{\partial\ln\Omega}{\partial V}\right)_{E,N}$$

态密度： $E\to E+dE$ 的态个数　$\bar\Omega(E)\,dE$

$\bar\Omega(E)$：态密度

$0\sim E$ 的态个数 $\phi(E)$ → $\bar\Omega = \frac{d\phi}{dE}$

eg. **理想气体**

(i) **单粒子**　三维势箱

$$\varepsilon_{\{n\}} = \frac{h^2}{8ma^2}(n_x^2+n_y^2+n_z^2) \qquad n_x.n_y.n_z \geq 1$$

$$\phi = \frac{1}{8}\frac{4}{3}\pi\left(\frac{8ma^2}{h^2}E\right)^{3/2} = \frac{\pi}{6}\left(\frac{8ma^2}{h^2}E\right)^{3/2}$$
$$\bar\Omega = \frac{\partial\phi}{\partial E} = \frac{\pi}{4}\left(\frac{8ma^2}{h^2}\right)^{3/2}E^{1/2}$$

(ii) **N个粒子**

$$\varepsilon_{\{n\}} = \frac{h^2}{8ma^2}\sum_{i=1}^{3N} n_i^2 \qquad n_i>0$$

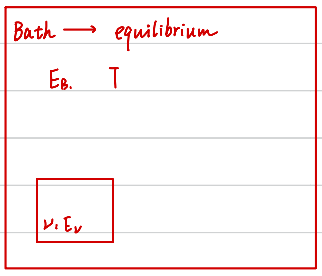
3N维球：$\phi = \left(\frac{1}{2}\right)^{3N}\frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2}+1)}\left(\frac{8ma^2}{h^2}E\right)^{\frac{3N}{2}}\frac{1}{N!}$ ⟵ N个粒子不可区分

$$\bar\Omega = \frac{d\phi}{dE} = \frac{1}{2^{3N}N!}\left(\frac{8\pi ma^2}{h^2}\right)^{3N/2}\frac{1}{(3N/2)!}\frac{3}{2}N E^{\frac{3N}{2}-1}$$
$$= \frac{V^N}{N!}\left(\frac{2\pi mE}{h^2}\right)^{3N/2}\frac{1}{(3N/2)!}\frac{3}{2}N\frac{1}{E}$$

$$\ln\Omega = \ln\bar\Omega\,dE = N\ln\frac{V}{N}\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2} + \frac{5}{2}N + \left[\ln\frac{3}{2}N + \ln\frac{dE}{E}\right]$$
$$= N\ln\frac{V}{N}\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2} + \frac{5}{2}N$$

$$\begin{cases}\frac{1}{kT} = \frac{3}{2}N\frac{1}{E} & \to E = \frac{3}{2}NkT\\ \frac{P}{kT} = \frac{N}{V} & \to PV = NkT\end{cases}$$

正则系综 $N.\ V.\ T$



system << Bath

系统处于 ν 的概率：　系统处于 ν 态，$\Omega_s = 1$

$P_\nu \propto \Omega_\nu(\text{Total}) = \Omega_B\cdot\Omega_s$　而 $E_{total} = E_B + E_\nu = \text{const}$

$= \Omega_B(E-E_\nu)$

而 $\ln\Omega_B = \ln\Omega_B(E) - \frac{\partial\ln\Omega_B}{\partial E}\cdot E_\nu$

$= \ln\Omega_B(E) - \beta_B E_\nu$　　$\beta_B = \beta = \frac{1}{kT}$

$\longrightarrow P_\nu \propto e^{-\beta E_\nu}$　而 $\sum_\nu P_\nu = 1$

$P_\nu = \frac{1}{Q}e^{-\beta E_\nu}$　$Q = \sum_\nu e^{-\beta E_\nu} = Q(N,V,T)$　正则配分函数。

连续化 $= \int dE\,\bar\Omega(E)\,e^{-\beta E}$　　$\bar\Omega(E)$：态密度 / 能级简并度

平均值与涨落

$$\langle E\rangle = \frac{1}{Z}\sum E_\nu e^{-\beta E_\nu} = \frac{1}{Q}\sum\frac{\partial}{\partial(-\beta)}e^{-\beta E_\nu} = \frac{1}{Q}\frac{\partial Q}{\partial(-\beta)} = \frac{\partial\ln Q}{\partial(-\beta)}$$
$$\langle(\delta E)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 = \frac{1}{Q}\sum E_\nu^2 e^{-\beta E_\nu} - \left(\frac{1}{Q}\sum E_\nu e^{-\beta E_\nu}\right)^2 = \frac{\partial\langle E\rangle}{\partial(-\beta)} = kT^2C_V$$

热力学： $dE = TdS - PdV + \mu dN$

$dF = -SdT - PdV + \mu dN$　　$F = E - TS$

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

$\longrightarrow F = -kT\ln Q + T f(N,V)$

而 $S = -\frac{\partial F}{\partial T} = k\ln Q + \frac{\langle E\rangle}{T} - f(N,V)$　取 $N.V=0 \longrightarrow Q=1\quad S=0\quad E=0 \longrightarrow f=0$

$$\boxed{\begin{cases}S = k\left(\ln Q - \beta\frac{\partial}{\partial\beta}\ln Q\right)\\ U = -\frac{\partial}{\partial\beta}\ln Q\\ F = -kT\ln Q\\ -\beta P = -\frac{\partial}{\partial V}\ln Q\\ \beta\mu = -\frac{\partial}{\partial N}\ln Q\end{cases}}$$

$$\sigma_E^2 = \frac{\langle(\delta E)^2\rangle}{\langle E\rangle^2} = \frac{kT^2C_V}{\langle E\rangle^2} \sim \frac{N}{N^2} = \frac{1}{N}$$

ideal gas：$\sigma_E^2 = \frac{kT^2\frac{3}{2}Nk}{(\frac{3}{2}NkT)^2} = \frac{2}{3N}$

分布： $P(E) = \Omega(E)e^{-\beta E}/Q$

$\ln P(E) = \ln\Omega(E) - \beta E - \ln Q$.　考察 $E = \langle E\rangle + \Delta E$ 的概率

$= \ln P(\langle E\rangle) + \frac{\partial\ln P}{\partial E}\Delta E + \frac{1}{2}\frac{\partial^2\ln P}{\partial E^2}(\Delta E)^2$

而 $\left.\frac{\partial\ln P}{\partial E}\right|_{\langle E\rangle} = \beta - \beta = 0$

$\frac{\partial^2\ln P}{\partial E^2} = \frac{\partial^2\ln\Omega}{\partial E^2} = \frac{\partial\beta}{\partial E} = -\frac{1}{\langle(\delta E)^2\rangle}$

$\longrightarrow \ln P(E) = \ln P(\langle E\rangle) - \frac{1}{2}\frac{(\Delta E)^2}{\langle(\delta E)^2\rangle} = \ln P(\langle E\rangle) - \frac{1}{2}\frac{(\Delta E/\langle E\rangle)^2}{\sigma_E^2}$

而 $\sigma_E^2 \sim \frac{1}{N} \sim 10^{-23}$　　$\Delta E/\langle E\rangle \sim 10^{-10}$

$\longrightarrow P(E) = P(\langle E\rangle)\,e^{-500} \ll 1$

偏离 $\langle E\rangle$，即使很小，也几乎不可能出现。

$P(\langle E\rangle)$ 最概然分布 = 真实分布

广义系综 $T,\ \zeta$ → $E,\ X$

$$\begin{cases}\text{巨正则}: X = N. & \zeta = -\beta\mu\\ \text{等压}: X = V, & \zeta = \beta P\end{cases}$$

同正则系综　$P_\nu = \frac{1}{\Xi}e^{-\beta E_\nu - \zeta X_\nu}$

$\Xi_1 = \sum_\nu e^{-\beta E_\nu - \zeta X_\nu} = \Xi_1(T,\zeta,\ldots)$

$$\langle E\rangle = -\frac{\partial\ln\Xi}{\partial\beta} \qquad \langle(\delta E)^2\rangle = -\frac{\partial\langle E\rangle}{\partial\beta} = \frac{\partial^2\ln\Xi}{\partial\beta^2}$$
$$\langle x\rangle = -\frac{\partial\ln\Xi}{\partial\zeta} \qquad \langle(\delta x)^2\rangle = -\frac{\partial\langle x\rangle}{\partial\zeta} = \frac{\partial^2\ln\Xi}{\partial\zeta^2}$$

$dE = TdS - pdV + \mu dN = TdS - kT\zeta dx$

而 $d\ln\Xi_1 = -Ed\beta - xd\zeta$

$\longrightarrow dS = \frac{1}{T}dE + k\zeta dx = d\left(\frac{E}{T} + k\zeta x\right) - Ed\left(\frac{1}{T}\right) - kxd\zeta$

$= d\left(k\ln\Xi_1 + \frac{E}{T} + k\zeta x\right)$

$\to S = k(\ln\Xi_1 + \beta E + \zeta x) = k\left(1 - \beta\frac{\partial}{\partial\beta} - \zeta\frac{\partial}{\partial\zeta}\right)\ln\Xi_1$

巨正则系综 $T.\ V.\ \mu$

$\Xi_1 = \sum_\nu e^{-\beta E_\nu + \beta\mu N_\nu} = \sum_\nu e^{-\beta E_\nu - \alpha N_\nu}$　　$\boxed{\alpha = -\beta\mu}$

$P_\nu = \frac{1}{\Xi_1}e^{-\beta E_\nu - \alpha N_\nu}$

热力学：

$$\begin{cases}J = U - TS - \mu N = -kT\ln\Xi_1 \qquad dJ = -SdT - PdV - Nd\mu\\ U = -\frac{\partial}{\partial\beta}\ln\Xi_1\\ S = k\left(1 - \beta\frac{\partial}{\partial\beta} - \alpha\frac{\partial}{\partial\alpha}\right)\ln\Xi_1\\ N = -\frac{\partial}{\partial\alpha}\ln\Xi_1 = \frac{\partial}{\partial(\beta\mu)}\ln\Xi_1\\ \beta P = \frac{\partial}{\partial V}\ln\Xi_1\end{cases}$$

等压系综 T, P, N

$$Z = \sum_\nu e^{-\beta E_\nu - \beta P V_\nu}$$

$$\boxed{\alpha = -\beta\mu}$$

$$P_\nu = \frac{1}{Z} e^{-\beta E_\nu - \beta P V_\nu}$$

热力学:

$$\begin{cases} G = U - TS + PV = -kT\ln Z \\ U = -\frac{\partial}{\partial\beta}\ln Z \\ S = k\left(1 - \beta\frac{\partial}{\partial\beta} - P\frac{\partial}{\partial P}\right)\ln Z \\ V = -\frac{\partial}{\partial(\beta P)}\ln Z \\ \mu = -\frac{\partial}{\partial(\beta N)}\ln Z \end{cases}$$

$$dZ = -SdT + VdP + \mu dN$$

涨落

$$\langle(\delta N)^2\rangle = -\frac{\partial\langle N\rangle}{\partial\alpha} = \frac{\partial\langle N\rangle}{\partial(\beta\mu)} = kT\frac{\partial N}{\partial\mu} = kTN^2\frac{\kappa}{V} \qquad \kappa = -\frac{1}{V}\frac{\partial V}{\partial P}$$

$$\sigma_N^2 = \langle(\delta N)^2\rangle / \langle N\rangle^2 = kT\kappa/V \sim \frac{1}{N}$$

$$\langle(\delta V)^2\rangle = -\frac{\partial\langle V\rangle}{\partial(\beta P)} = -kT\frac{\partial V}{\partial P} = kT\kappa V \qquad \kappa = -\frac{1}{V}\frac{\partial V}{\partial P}$$

$$\sigma_V^2 = \langle(\delta V)^2\rangle / \langle V\rangle^2 = kT\kappa/V \sim \frac{1}{N}$$

多组分

$$dE = TdS - pdV + \sum_i \mu_i dN_i$$

$$\begin{cases} \beta = \frac{\partial\ln\Omega}{\partial E} \\ \beta p = \frac{\partial\ln\Omega}{\partial V} \\ \beta\mu_i = -\frac{\partial\ln\Omega}{\partial N_i} \end{cases}$$

$$\Xi = \sum e^{-\beta E_\nu} e^{-\sum_i \alpha_i N_i}$$

关联