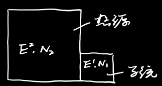
• 巨正则系综

宏观状态：(T, V, μ). 允许能量、粒子数的交换



$$E = E_n^1 + E^2 \qquad (E_n^1, N_1)：量子态 |n\rangle$$
$$N = N_1 + N_2$$

总微观状态数：

$$\Omega(E,N,V) = \sum_{E_n^1, N_1} \underbrace{\Omega_1(E_n^1, N_1)}_{1} \cdot \Omega_2(E - E_n^1, N - N_1)$$

对 $\ln\Omega_2$ 展开：

$$\ln\Omega_2(E - E_1^n, N - N_1) \simeq \ln\Omega_2(E, N) - \underbrace{\frac{\partial\ln\Omega_2}{\partial E}}_{\frac{1}{k_BT}} \cdot E_n^1 - \underbrace{\frac{\partial\ln\Omega_2}{\partial N}}_{-\frac{\mu}{k_BT}} \cdot N_1$$

$$= \ln\Omega_2(E, N) - \beta E_n^1 + \beta\mu N_1 .$$

代入：

$$\Omega(E,N,V) = \sum_{E_1^n, N_1} \Omega_2(E,N,V) \cdot e^{-\beta(E_n^1 - \mu N_1)}$$

• 根据微正则系综的概率分布，得到：

$$p(E_n, N) = \frac{e^{-\beta(E_n - \mu N)}}{\sum\limits_{E_n, N} e^{-\beta(E_n - \mu N)}} = \frac{1}{Q} e^{-\beta(E_n - \mu N)}$$

$$Q = \sum_{E_n, N} e^{-\beta(E_n - \mu N)}，\quad 巨配分函数（教科书中的 \Xi）$$

注：有的书上会定义 $\alpha = -\beta\mu$. $\Rightarrow e^{-\beta E - \alpha N}$. (T, μ) 是独立变量，故可取 (α, β) 为独立变量.

后面会定义 $e^{\beta\mu} = z$. 逸度. fugacity.

回到巨配分函数.

$$Q = \sum_N e^{\beta\mu N} \cdot \sum_{E_n} e^{-\beta E_n(N)} = \sum_N e^{\beta\mu N} \cdot \underbrace{Z(T,V,N)}_{正则配分函数}. \qquad \left[对比：Z = \sum_E \Omega(E) e^{-\beta E}\right]$$

• [乍看之下回到了正则系综，但这只是形式上的，
真正的简化是操作层面的]

与正则系综同理，求和可用极值来代表：

$$Q \simeq e^{\beta\mu N^*} \cdot Z(T,V,N^*) = e^{\beta\mu N^*} e^{-\beta F^*}$$

$$= e^{-\beta(F^* - \mu N^*)} = e^{-\beta\Phi^*}.$$

$\Phi = F - \mu N$ 巨热力势. $\Phi = E - TS - \mu N = -pV$.

此处：$\Phi = -k_BT\ln Q$.

热力学量

$$\langle E\rangle = -\left(\frac{\partial}{\partial\beta}\ln Q\right)_z . \quad （要保证 z = e^{\beta\mu} 不变，否则会拿下来 \mu N）$$

$$\langle N\rangle = \left(\frac{\partial}{\partial(\beta\mu)}\ln Q\right)_\beta .$$

由

$$d\Phi = -SdT - pdV - Nd\mu.$$

可以求出其他的热力学函数. [$\Phi = -pV$. 因此 p 已经知道了]

• 理想气体

$$Z(T,V,N) = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N.$$

$$Q = \sum_{N=0}^{\infty} z^N \cdot \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N = \exp\left(\frac{zV}{\lambda_T^3}\right).$$

$$\ln Q = \frac{zV}{\lambda_T^3}.$$

$$\Phi = -k_BT\ln Q = -k_BT\frac{zV}{\lambda_T^3}.$$

$$p = -\frac{\Phi}{V} = \frac{k_BT}{V} \cdot \frac{z}{\lambda_T^3}. \qquad N = ?$$

$$\langle N\rangle = \frac{\partial}{\partial(\beta\mu)}\ln Q = \frac{V}{\lambda_T^3}\frac{\partial}{\partial(\beta\mu)}(e^{\beta\mu}) = \frac{zV}{\lambda_T^3}.$$

$$\Rightarrow p = \langle N\rangle \cdot k_BT.$$

注：由 $N = \frac{zV}{\lambda_T^3}$：$e^{\beta\mu} = \frac{N}{V}\lambda_T^3 = n\lambda_T^3$.

$\mu = \frac{1}{\beta}\ln(n\lambda_T^3)$. 又得到了这个结论.

$$\langle E\rangle = -\left(\frac{\partial}{\partial\beta}\ln Q\right)_z = -zV\frac{\partial}{\partial\beta}(\lambda_T^{-3}).$$

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} = \sqrt{\frac{\beta}{2\pi m}}\,h,\quad \frac{\partial}{\partial\beta}(\lambda_T^{-3}) = -\frac{3}{2}\lambda_T^{-3}\cdot\frac{1}{\beta}$$

$$\Rightarrow \langle E\rangle = \frac{3}{2}zV\cdot\frac{1}{\beta\lambda_T^3} = \frac{3}{2}\langle N\rangle\cdot k_B T.$$

- 能量与粒子数的涨落

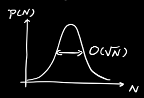
严格来说是 $\left(\frac{\partial N}{\partial\mu}\right)_{T,V}$

$$\langle N^2\rangle_c = \left(\frac{\partial^2}{\partial(\beta\mu)^2}\ln Q\right)_\beta = \frac{\partial N}{\partial(\beta\mu)}\bigg|_\beta = k_B T\left(\frac{\partial N}{\partial\mu}\right)_T \propto N.$$

$\Rightarrow \frac{\langle N^2\rangle_c}{N} \propto \frac{1}{\sqrt{N}}$. [问：热力学极限怎么体现？]

$\langle N^n\rangle_c \propto N$.

故 N 的分布也是极窄的高斯：



[严格来说，$p(N)$ 满足泊松分布，但 $\langle N\rangle\to\infty$ 时与高斯一致]

问：$\left(\frac{\partial N}{\partial\mu}\right)_{T,V} = ?$　想法：与某个响应函数联系到一起.

$$d\mu = -s\,dT + v\,dp$$

$$\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = \left(\frac{\partial\mu}{\partial p}\right)_{T,V}\cdot\left(\frac{\partial p}{\partial N}\right)_{T,V} = \frac{V}{N}\left(\frac{\partial p}{\partial N}\right)_{T,V}$$

又

$$\left(\frac{\partial p}{\partial N}\right)_V\cdot\left(\frac{\partial N}{\partial V}\right)_p\cdot\left(\frac{\partial V}{\partial p}\right)_N = -1 \quad [T\ \text{不变}]$$

代入得

$$\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = -\left(\frac{V}{N}\right)^2\cdot\left(\frac{\partial p}{\partial V}\right)_{N,T}$$

$$\Rightarrow \langle N^2\rangle_c = -k_B T\cdot\left(\frac{N}{V}\right)^2\left(\frac{\partial V}{\partial p}\right)_{N,T}$$

$$= k_B T\cdot\frac{N^2}{V}\cdot\underbrace{\kappa_T}_{\text{压缩系数}} = n k_B T\cdot N\kappa_T \propto N.$$

一般来说，κ_T 有限. 但在临界点附近，κ_T 发散!!

这表明粒子数 N 的涨落是剧烈的！ → 临界乳光现象.

$$\langle E^2\rangle_c = \left(\frac{\partial^2}{\partial\beta^2}\ln Q\right)_z = -\left(\frac{\partial E}{\partial\beta}\right)_{z,N} = k_B T^2\left(\frac{\partial E}{\partial T}\right)_{z,V}.$$

[注：$\left(\frac{\partial E}{\partial T}\right)_{z,V} \neq C_V$. 后者是 $\left(\frac{\partial E}{\partial T}\right)_{N,V}$]

结果：$\langle E^2\rangle_c = \underbrace{k_B T^2 C_V}_{\text{原有项}} + k_B T\left(\frac{\partial E}{\partial N}\right)^2\cdot\underbrace{\langle N^2\rangle_c}_{\text{粒子数涨落}}$.