• 理想气体的热力学性质.

$$S(E,V,N) = Nk_B \ln\left[\frac{V}{N}\cdot\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}Nk_B.$$

$$dS = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN.$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{3}{2}\frac{Nk_B}{E} \Rightarrow E = \frac{3}{2}Nk_BT.$$

(对于这两个量, $h^{3N}N!$ 无影响)

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{Nk_B}{V} \Rightarrow pV = Nk_BT.$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{5}{2}k_B + k_B\ln\left[\frac{V}{N}\cdot\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right] - Nk_B\cdot\frac{5}{2}\cdot\frac{1}{N}$$

$$= k_B\ln\left[\frac{V}{N}\cdot\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right]$$

这里可见, 除以 $N!$ 保证了 μ 是强度量.

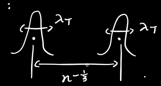
代入 $E=\frac{3}{2}Nk_BT$:

$$\mu = k_BT\cdot\ln\left[\frac{N}{V}\cdot\left(\frac{h^2}{2\pi mk_BT}\right)^{3/2}\right]$$

定义 $\lambda_T = \frac{h}{\sqrt{2\pi mk_BT}}$ 热波长. ($\lambda\sim\frac{h}{p}$, $p\sim\sqrt{2mE}\sim\sqrt{2mk_BT}$)

$$= k_BT\cdot\ln[n\cdot\lambda_T^3].$$

$n\cdot\lambda_T^3$:



$$n\lambda_T^3\begin{cases}\gg 1: \text{粒子重叠, 量子效应显著.}\\ \ll 1: \text{量子效应可忽略.} \Rightarrow \text{经典极限. } (T\to\infty)\end{cases}$$

或: $\frac{\mu}{k_BT} = \ln[n\cdot\lambda_T^3]$.

经典极限 $T\to\infty$

$$\frac{\mu}{k_BT} = \ln[n\lambda_T^3] \xrightarrow{T\to\infty} -\infty.$$

$\mu<0$ 经典理想气体, 化学势为负, 而且非常负!!! $(\sim T\cdot\ln T)$ 比 k_BT 还快!!

[之后在讨论 $\frac{\mu}{k_BT}$ 的时候还会涉及, 这里先mark一下]

理解: $\mu=\left(\frac{\partial E}{\partial N}\right)_{S,V}$ N增加, S必然增加 $\Rightarrow$ 为了保持S, 只能让E减小.

• 麦克斯韦-玻尔兹曼分布

$$P(\vec{p}_1,\cdots,\vec{p}_n,\vec{q}_1,\cdots,\vec{q}_n) = \frac{1}{\Omega(E,V,N)}$$

↳ 联合概率密度

问: 粒子1 动量为 $\vec{p}_1$ 的概率?

$$P(\vec{p}_1) = \frac{1}{h^{3N}N!}\int d^3q_1\cdot\prod_{i=2}^{N}d^3p_id^3q_i\cdot P(\vec{p}_1,\cdots,\vec{p}_n;\vec{q}_1,\cdots,\vec{q}_n)$$

$$= \frac{1}{\Omega(E,V,N)\cdot h^{3N}\cdot N!}\cdot V\cdot\underbrace{\int\prod_{i=2}^{N}d^3p_id^3q_i}_{\Omega(E-\frac{p_1^2}{2m},V,N-1)\cdot h^{3(N-1)}\cdot(N-1)!}$$

$$= \frac{V\cdot\Omega(E-\frac{p_1^2}{2m},V,N-1)\cdot h^{3(N-1)}\cdot(N-1)!}{\Omega(E,V,N)\cdot h^{3N}\cdot N!}$$

$$\Omega = \left(\frac{V}{h^3}\right)^N\cdot\frac{(2\pi mE)^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2})\cdot N!}\cdot\left(\frac{\Delta}{E}\right)$$

$$= \frac{\Gamma(\frac{3N}{2})}{\Gamma(\frac{3}{2}(N-1))}\cdot\left(\frac{E-\frac{p_1^2}{2m}}{E}\right)^{\frac{3}{2}(N-1)}\cdot\frac{1}{(2\pi mE)^{3/2}}\cdot\frac{E}{E-\frac{p_1^2}{2m}}$$

$$\simeq \left(\frac{3N}{2}\right)^{\frac{3}{2}}\cdot\frac{1}{(2\pi mE)^{3/2}}\cdot\left(1-\frac{p_1^2}{2mE}\right)^{\frac{3N}{2}}$$

↳ 不重要了, 要取极限: $(1-\frac{\alpha}{x})^x\to e^{\alpha}$, $x\to\infty$.

$$\simeq \left(\frac{3N}{4\pi mE}\right)^{3/2}\cdot\exp\left(-\frac{3Np_1^2}{4mE}\right)$$

$$\Rightarrow P(\vec{p}_1) = \frac{1}{(2\pi mk_BT)^{3/2}}\cdot e^{-\frac{p_1^2}{2mk_BT}}$$

麦克斯韦分布律.

• 伊辛磁体 (二能级系统)

$\sigma_\mu=\pm1$ $\{\sigma_i\}_{i=1}^{N}$: 描述系统状态.

$$H = -\mu_0B\sigma = \begin{cases}\varepsilon_+ = -\mu_0B\\ \varepsilon_- = +\mu_0B\end{cases}$$

微观状态数 $\Omega(E,N)$:

n_+ $\sigma=+1$; n_- $\sigma=-1$

$$\Omega(E,N) = \binom{N}{n_+} = \frac{N!}{n_+!\,n_-!}$$

$$S(E,N) = k_B\ln\Omega$$

$$\simeq k_B(N\ln N - n_+\ln n_+ - n_-\ln n_-)$$

$$E(n_+) = -\mu_0 B(n_+ - n_-) = -\mu_0 B(2n_+ - N).$$

故 $n_+ = \frac{1}{2}\left(N - \frac{E}{\mu_0 B}\right).$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k_B\left[\frac{\partial n_+}{\partial E}(-\ln n_+ - 1) + \frac{\partial n_-}{\partial E}(-\ln n_- - 1)\right]$$

$$= \frac{k_B}{2\mu_0 B}\ln\frac{n_+}{n_-}.$$

$$\Rightarrow \frac{n_-}{n_+} = e^{-\frac{2\mu_0 B}{k_B T}}.$$

$$p(n_+) = \frac{e^{\frac{\mu_0 B}{k_B T}}}{\underbrace{e^{-\frac{\mu_0 B}{k_B T}} + e^{\frac{\mu_0 B}{k_B T}}}}, \quad p(n_-) = \frac{e^{-\frac{\mu_0 B}{k_B T}}}{e^{-\frac{\mu_0 B}{k_B T}} + e^{\frac{\mu_0 B}{k_B T}}}.$$

配分函数：把所有的东西加起来.