Notes of JU Guoxing TD&SP

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19 Equipartition of Energy

19.1 Equipartition Theorem

20 Partition Function

Energy Fluctuation:
$\langle (E - \langle E \rangle)^2 \rangle$
Relative fluctuation:

$$\frac{\langle (E - \langle E \rangle)^2 \rangle}{\langle E \rangle^2} \propto \frac{1}{N} \tag{20.0.1}$$

20.1

20.2 Obtain functions of State

20.2.1 Internal E

$$U = \frac{\sum_i E_i \, \mathrm{e}^{-\beta E_i}}{\sum_i \mathrm{e}^{-\beta E_i}} = \frac{\sum_i E_i \, \mathrm{e}^{-\beta E_i}}{Z} \tag{20.2.1}$$

while

$$-\frac{\mathrm{d}Z}{\mathrm{d}\beta} = \sum_i E_i \, \mathrm{e}^{-\beta E_i} \tag{20.2.2}$$

thus

$$U = -\frac{1}{Z}\frac{\mathrm{d}Z}{\mathrm{d}\beta} = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta} \tag{20.2.3}$$

20.2.2 Entropy

E.g. 20.3
a) 2-evel system. Energy level $-\Delta/2, \Delta/2$.

$$Z = \tag{20.2.4}$$

Find U, F, S
Discussion:
Def: characteristic temperature (特征温度) $k_B T_{ch} = E$
1) High temperature limit: $\beta\Delta = \dfrac{\Delta}{k_B T} << 1$
i.e. $T >> T_{ch}$
2) Low temperature limit: $\beta\Delta = \dfrac{\Delta}{k_B T} >> 1$

$$U = -\frac{\Delta}{2} \tag{20.2.5}$$

ground state occupied.
特征温度附近，热容量有极大值，称为Schottky反常。

b) simple harmonic oscillator

$$Z = \tag{20.2.6}$$

Discussion:
Def: Einstein characteristic Temp $k_B \theta_E = \hbar\omega$
1) $T >> \theta_E$

20.3

20.4 Combining Partition Functions

21 Statistical Mechanics for Ideal Gas

21.1 Density of States

box $V = L \times L \times L$
wave vector

$$\mathbf{k} = \frac{\mathbf{p}}{\hbar} \tag{21.1.1}$$

wave fxn

$$\psi(x, y, z) = \left(\frac{2}{3}\right)^{3/2} \sin(k_x x)\sin(k_y y)\sin(k_z z) \tag{21.1.2}$$

PBC:

$$\psi(x, y, z) = \psi(x + L, y, z) = ... \tag{21.1.3}$$

$$k_x = \frac{2\pi n_x}{L} \tag{21.1.4}$$

$$k_y = ... \tag{21.1.5}$$

$$E = \frac{1}{2m}p^2 = \frac{2\pi^2\hbar^2}{mL^2}(n_x^2 + n_y^2 + n_z^2) \tag{21.1.6}$$

in k space, every state occupy a volume $(2\pi/L)^3$, (in n space, vol = 1)
thus in momentum space, the volume of a state

$$\left(\frac{2\pi\hbar}{L}\right)^3 = \frac{h^3}{V} \tag{21.1.7}$$

thus density of state

$$g(\mathbf{p})\mathrm{d}^3\mathbf{p} = \frac{V}{h^3}\mathrm{d}^3\mathbf{p} \tag{21.1.8}$$

$$g(\mathbf{k})\mathrm{d}^3\mathbf{k} = \frac{V}{(2\pi)^3}\mathrm{d}^3\mathbf{k} \tag{21.1.9}$$

in spheric coord

$$g(p,\theta,\phi)\mathrm{d}p\mathrm{d}\theta\mathrm{d}\phi = \frac{Vp^2\sin\theta}{h^3}\mathrm{d}p\mathrm{d}\theta\mathrm{d}\phi \tag{21.1.10}$$

$$g(p)\mathrm{d}p = \frac{Vp^2}{h^3}\mathrm{d}p\int_0^\pi \sin\theta\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi = \frac{4\pi V}{h^3}p^2\mathrm{d}p \tag{21.1.11}$$

$$\begin{aligned} g(k)\mathrm{d}k = g(p)\mathrm{d}p = g(p)\frac{\mathrm{d}p}{\mathrm{d}k}\mathrm{d}k = \frac{4\pi V}{h^3}p^2\hbar\mathrm{d}k \\ = \frac{V}{2\pi^2}k^2\mathrm{d}k \end{aligned} \tag{21.1.12}$$

$\because$

$$\mathrm{d}E = \frac{p\mathrm{d}p}{m} \tag{21.1.13}$$

$$g(E)\mathrm{d}E = g(p)\mathrm{d}p = \frac{4\pi V}{h^3}\sqrt{2mE}m\mathrm{d}E \tag{21.1.14}$$

21.2 Quantum Density

single-particle parti fxn of ideal gas

$$\begin{aligned} Z_1 &= \int_0^\infty \mathrm{e}^{-\beta E(k)}\, g(k)\mathrm{d}k \\ &= \frac{V}{2\pi^2}\int_0^\infty \mathrm{e}^{-\beta\hbar^2k^2/2m}\, k^2\mathrm{d}k \\ &= \frac{V}{\hbar^3}\left(\frac{m}{2\pi\beta}\right)^{3/2} \end{aligned} \tag{21.2.1}$$

def: quantum density

$$n_Q = \frac{Z_1}{V} = \frac{1}{\hbar^3}\left(\frac{m}{2\pi\beta}\right)^{3/2} \tag{21.2.2}$$

thermal wavelength (热波长)

$$\lambda_{th} = \hbar\sqrt{\frac{2\pi\beta}{m}} = h\sqrt{\frac{\beta}{2\pi m}} \tag{21.2.3}$$

$$Z_1 = \frac{V}{\lambda_{th}} \tag{21.2.4}$$

21.3 Distinguishability (可分辨性)

for distinguishable particles

$$Z_N = (Z_1)^N \tag{21.3.1}$$

indistinguishable but non-degenerate (非简并)

$$Z_N = \frac{Z_1^N}{N!} \tag{21.3.2}$$

for ideal gas, non-degeneracy requires

$$N << \text{number of } E_\ell \tag{21.3.3}$$

or number density

$$n << n_Q \tag{21.3.4}$$

that's a good approximation in room temp, but not good for electron in metals.

21.4 State Functions of Ideal Gas

$$\begin{aligned}\ln Z_N &= N(\ln V - 3\ln\lambda_{th}) - \ln N! \\ &= N\ln V + \frac{3}{2}N\ln T + Cons. = N\ln V - \frac{3}{2}N\ln\beta + Cons.\end{aligned} \tag{21.4.1}$$

$$U = -\frac{\mathrm{d}\ln Z_N}{\mathrm{d}\beta} = \frac{3}{2}\frac{N}{\beta} \tag{21.4.2}$$

$$C_V = \frac{3}{2}k_B \tag{21.4.3}$$

$$\begin{aligned}F &= -\frac{1}{\beta}\ln Z_N \\ &= -\frac{N}{\beta}\ln V - \frac{3N}{2\beta}\ln T - \frac{Cons.}{\beta} \\ &= -Nk_BT\ln V - \frac{3N}{2}k_BT\ln T - Cons.\cdot k_BT\end{aligned} \tag{21.4.4}$$

$$p = -\left(\frac{\partial F}{\partial T}\right)_T = \frac{Nk_BT}{V} \tag{21.4.5}$$

$$\ln Z_N = N \ln V - 3N \ln \lambda_{th}) - N \ln N + N$$
$$= N\left(1 + \ln \frac{V}{N\lambda^3}\right) \tag{21.4.6}$$

$$F = ... \tag{21.4.7}$$

$$S = ... \tag{21.4.8}$$

$$G = ... \tag{21.4.9}$$

21.5 Gibbs Paradox

21.6 Heat Capacity of Diatomic Gas

22 Chemical Potential

22.1 Definition

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu \mathrm{d}N \tag{22.1.1}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{22.1.2}$$

22.2 Meaning of CP

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{N,V} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{N,U} \mathrm{d}V + \left(\frac{\partial S}{\partial N}\right)_{U,V} \mathrm{d}N \tag{22.2.1}$$

$$\mathrm{d}S = \frac{\mathrm{d}U}{T} + \frac{p\mathrm{d}V}{T} - \frac{\mu \mathrm{d}N}{T} \tag{22.2.2}$$

$\therefore$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T} \tag{22.2.3}$$

22.3 Grand Partition Function (巨配分函数)

system ϵ, N, V
reservoir $U >> \epsilon, \mathcal{N} >> N$
thus, entropy of reservoir

$$S(U - \epsilon, \mathcal{N} - N) = S(U, \mathcal{N}) - \frac{1}{T}\epsilon + \frac{\mu}{T}N \tag{22.3.1}$$

$$\Omega = \mathrm{e}^{S/k_B} = \mathrm{e}^{S(U,\mathcal{N})} \tag{22.3.2}$$

$$\ln \Omega(U - \epsilon, \mathcal{N} - N) = \ln \Omega(U, \mathcal{N}) - \left(\frac{\partial \ln \Omega}{\partial N}\right)(-N) + \left(\frac{\partial \ln \Omega}{\partial E}\right)(-\epsilon) \tag{22.3.3}$$

$$\alpha = \left(\frac{\partial \ln \Omega}{\partial N}\right) = -\frac{\mu}{k_B T} \tag{22.3.4}$$

$$\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right) = \frac{1}{k_B T} \tag{22.3.5}$$

$$P = \frac{1}{\Xi}\,\mathrm{e}^{-\alpha N - \beta E_s} \tag{22.3.6}$$

grand partition function

$$\Xi = \sum_{N=0}^{\infty}\sum_{s} \mathrm{e}^{\beta(\mu N - E_s)} \tag{22.3.7}$$

or

$$\Xi = \sum_{N=0}^{\infty}\sum_{s} \mathrm{e}^{\alpha N - \beta E_s} \quad (\alpha = \beta\mu) \tag{22.3.8}$$

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$$\begin{aligned}\langle N\rangle &= \frac{1}{\Xi}\sum_{N}\sum_{s} N\,\mathrm{e}^{\alpha N - \beta E_s} \\ &= \frac{1}{\Xi}\sum_{N}\sum_{s}\left(-\frac{\partial}{\partial\alpha}\right)\mathrm{e}^{\alpha N - \beta E_s} = -\frac{\partial}{\partial\alpha}\ln\Xi\end{aligned} \tag{22.3.9}$$

$$\begin{aligned}U = \langle E\rangle &= \frac{1}{\Xi}\sum_{N}\sum_{s} E_s\,\mathrm{e}^{\alpha N - \beta E_s} \\ &= \frac{1}{\Xi}\sum_{N}\sum_{s}\left(-\frac{\partial}{\partial\beta}\right)\mathrm{e}^{\alpha N - \beta E_s} = -\frac{\partial}{\partial\beta}\ln\Xi\end{aligned} \tag{22.3.10}$$

$$X = \tag{22.3.11}$$

22.4 Grand Potential

$$\Phi_G = -k_B T \ln \Xi \tag{22.4.1}$$

Since

$$S = k_B\left(\ln\Xi - \alpha\frac{\partial}{\partial\alpha}\ln\Xi - \beta\frac{\partial}{\partial\beta}\ln\Xi\right) \tag{22.4.2}$$

$$\langle N\rangle = -\frac{\partial}{\partial\alpha}\ln\Xi \tag{22.4.3}$$

$$U = -\frac{\partial}{\partial\beta}\ln\Xi \tag{22.4.4}$$

thus

$$S = k_B(\ln\Xi + \alpha\langle N\rangle + \beta U) = k_B\ln\Xi - \frac{\mu}{T}\langle N\rangle + \frac{1}{T}U \tag{22.4.5}$$

$$\Phi_G = U - TS - \mu\langle N\rangle = F - \mu\langle N\rangle \tag{22.4.6}$$

$$\mathrm{d}\Phi_G = -S\mathrm{d}T - p\mathrm{d}V - \langle N\rangle\mathrm{d}\mu \tag{22.4.7}$$

22.5

$$S = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N \tag{22.5.1}$$

i.e.

$$U - TS + pV = \mu N \tag{22.5.2}$$

thus

$$G = \mu N \tag{22.5.3}$$

(μ - single particle Gibbs function)

$$\Phi_G = F - \mu N = F - G = -pV \tag{22.5.4}$$

Differentiate (22.5.3)

$$\mathrm{d}G = \mu \mathrm{d}N + N\mathrm{d}\mu \tag{22.5.5}$$

while

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N \tag{22.5.6}$$

thus

$$S\mathrm{d}T - V\mathrm{d}p + N\mathrm{d}\mu = 0 \tag{22.5.7}$$

which is Gibbs-Duhem Equation.

Fluctuation ...

22.6

22.7 Conservation of Number of Particle