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

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21.3 very good

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

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

22.3 Grand Partition Function (巨配分函数)

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

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

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

...
grand partition function

$$\Xi = \sum_{N=0}^{\infty} \sum_{s} \mathrm{e}^{\beta(\mu N - E_s)} \tag{22.3.3}$$

or

$$\Xi = \sum_{N=0}^{\infty} \sum_{s} \mathrm{e}^{\alpha N - \beta E_s} \quad (\alpha = \beta\mu) \tag{22.3.4}$$

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$$\begin{aligned} \langle N \rangle &= \frac{1}{\Xi} \sum_{N} \sum_{s} N \, \mathrm{e}^{\alpha N - \beta E_s} \\ &= \frac{1}{\Xi} \sum_{N} \sum_{s} \left(-\frac{\partial}{\partial \alpha}\right) \mathrm{e}^{\alpha N - \beta E_s} = -\frac{\partial}{\partial \alpha} \ln \Xi \end{aligned} \tag{22.3.5}$$

$$\begin{aligned} U = \langle E \rangle &= \frac{1}{\Xi} \sum_{N} \sum_{s} E_s \, \mathrm{e}^{\alpha N - \beta E_s} \\ &= \frac{1}{\Xi} \sum_{N} \sum_{s} \left(-\frac{\partial}{\partial \beta}\right) \mathrm{e}^{\alpha N - \beta E_s} = -\frac{\partial}{\partial \beta} \ln \Xi \end{aligned} \tag{22.3.6}$$

$$X = \tag{22.3.7}$$

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.