

3. Boltzmann Distribution and Helmholtz Free Energy

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- Total energy is $U_o = U_{\mathcal{R}} + U_{\mathcal{S}}$ for a closed combined system of a reservoir \mathcal{R} and a system \mathcal{S} .
- The ratio of the probability that the system is in quantum state 1 at energy ϵ_1 to the probability that the system is in quantum state 2 at energy ϵ_2 is the ratio of the two multiplicities:

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{\text{Multiplicity of } \mathcal{R} \text{ at energy } U_o - \epsilon_1}{\text{Multiplicity of } \mathcal{R} \text{ at energy } U_o - \epsilon_2} = \frac{g_{\mathcal{R}}(U_o - \epsilon_1)}{g_{\mathcal{R}}(U_o - \epsilon_2)} \quad (1)$$

- Rewrite eq. (1) in terms of the entropy and use Taylor expansion (derivation shown on KK p.60), we arrive at:

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{\exp(-\epsilon_1/\tau)}{\exp(-\epsilon_2/\tau)}$$

- A term of the form $\exp(-\epsilon/\tau)$ is known as a **Boltzmann factor**.
- Partition function (summation over the Boltzmann factor for all states s of the system):

$$Z(\tau) = \sum_s \exp(-\epsilon_s/\tau)$$

- Probability $P(\epsilon_s)$:

$$P(\epsilon_s) = \frac{\exp(-\epsilon_s/\tau)}{Z}$$

- $\langle \dots \rangle =$ thermal average:

$$U = \langle \epsilon \rangle = \frac{\sum \epsilon_s \exp(-\epsilon_s/\tau)}{Z} = \tau^2 (\partial \log Z / \partial \tau)$$

- Average pressure $\langle p \rangle$, usually written as p :

$$p = - \left(\frac{\partial U}{\partial V} \right)_{\sigma}$$

where $U \equiv \langle \epsilon \rangle$

- At constant U :

$$p = \tau \left(\frac{\partial \sigma}{\partial V} \right)_U$$

- Substitute p into the differential of the entropy:

$$d\sigma(U, V) = \left(\frac{\partial \sigma}{\partial U} \right)_V dU + \left(\frac{\partial \sigma}{\partial V} \right)_U dV$$

we get

$$d\sigma = \frac{1}{\tau} dU + \frac{p}{\tau} dV$$

which is known as the **thermodynamic identity** Rearrange:

$$dU = \tau d\sigma - p dV$$

where we can identify $\tau d\sigma$ as the heat added to the system and $-p dV$ as the work done on the system

- **Heat**: the transfer of energy between two systems brought into thermal contact
- Helmholtz free energy - the free energy tells us how to balance the conflicting demands of a system for minimum energy and maximum entropy:

$$F \equiv U - \tau \sigma$$

- Differential relations:

$$\left(\frac{\partial F}{\partial \tau} \right)_V = -\sigma; \left(\frac{\partial F}{\partial V} \right)_\tau = -p$$

- Calculation of F from Z :

$$F = -\tau \log Z$$

- One atom in a box (check pg. 72): its partition function is

$$Z_1 = n_Q / n$$

where

$$n_Q \equiv (M\tau/2\pi\hbar^2)^{3/2}$$

is called the **quantum concentration**

- When $n/n_Q \ll 1$, the gas is in the **classical regime**.
- An ideal gas is defined as a gas of noninteracting atoms in the classical regime.
- For an ideal gas of one atom:

$$U = \frac{3}{2} \tau$$

- Ideal gas law:

$$pV = N\tau$$

- A process is reversible if the system remains infinitesimally close to the equilibrium state at all times during the process.