3. Boltzmann Distribution and Helmholtz Free Energy

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October 16, 2017

- Total energy is $U_o = U_{\mathscr{R}} + U_{\mathscr{S}}$ for a closed combined system of a reservoir $\mathscr{R}$ and a system $\mathscr{S}$.

- 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:

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

- 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 $P(\epsilon_s)$:

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

- $< \cdots > = $ thermal average:

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

- Average pressure $< p >$, usually written as p:

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

where $U \equiv < \epsilon >$

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

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

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