

Boltzmann Distribution and Helmholtz Free Energy

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- For a system (S) in reservoir (\mathcal{R}), we can assume:

- $S + \mathcal{R}$ is closed
- S and \mathcal{R} are in thermal equilibrium; that is:

$$\tau_S = \tau_{\mathcal{R}} \cong \tau$$

- $U_s + U_{\mathcal{R}} \cong U_o$ (the total energy)
- $U_s \ll U_{\mathcal{R}}, U_o$
- S is in a quantum state, s , of energy ε_s

$$U_{\mathcal{R}} = \langle \varepsilon_s \rangle$$

- The probability $P(\varepsilon_s)$ to observe S in a quantum state s is:

$$g_{\mathcal{R}+S} = \sum_{\varepsilon_s} g_{\mathcal{R}}(U_o - \varepsilon_s, V_{\mathcal{R}}) g_S(\varepsilon_s, V_s) = g_{\mathcal{R}}(U_o - \varepsilon_s, V_{\mathcal{R}})$$

$$P(\varepsilon_s) \approx g_{\mathcal{R}}(U_o - \varepsilon_s) = e^{\ln(g_{\mathcal{R}}(U_o - \varepsilon_s))} = e^{\sigma_{\mathcal{R}}(U_o - \varepsilon_s)}$$

Using expansion we can transform this to:

$$e^{\sigma_{\mathcal{R}}(U_o - \varepsilon_s)} \approx e^{\overbrace{\sigma_{\mathcal{R}}(U_o)}^{\text{constant}} - \frac{\partial \sigma_{\mathcal{R}}}{\partial U_{\mathcal{R}}} \varepsilon_s} \approx e^{-\frac{\partial \sigma_{\mathcal{R}}}{\partial U_{\mathcal{R}}} \varepsilon_s} = e^{-\frac{\varepsilon_s}{\tau}}$$

$$P(\varepsilon_s) \approx e^{-\frac{\varepsilon_s}{\tau}}$$

$$P(\varepsilon_s) = \frac{1}{z} e^{-\frac{\varepsilon_s}{\tau}}$$

This is known as the Boltzmann factor; the z is known as the partition function. Given statistical definitions, we know:

$$\sum_s P(\varepsilon_s) = \frac{1}{z} \sum_s e^{-\frac{\varepsilon_s}{\tau}} = 1$$

This gets us:

$$z = \sum_s e^{-\frac{\varepsilon_s}{\tau}}$$

– Ensemble or thermal average energy of S , U :

$$U = \langle \varepsilon_s \rangle = \sum_s \varepsilon_s P(\varepsilon_s) = \sum_s \varepsilon_s \frac{e^{-\frac{\varepsilon_s}{\tau}}}{z}$$

$$\frac{1}{z} \frac{\partial z}{\partial \tau} = \frac{\partial \ln(z)}{\partial \tau} = \frac{1}{\tau^2} \sum_s \varepsilon_s \frac{e^{-\frac{\varepsilon_s}{\tau}}}{z} \rightarrow U = \tau^2 \frac{\partial \ln(z)}{\partial \tau}$$

Thus, the formula is finalized to:

$$U(\tau, V) = \tau^2 \left(\frac{\partial \ln(z(\tau, V))}{\partial \tau} \right)_V$$

- Pressure

- Consider once more a similar configuration of a reservoir and system
- We can change the volume such that $S : V \rightarrow V - \Delta V$; compression is done slowly, and S remains in the same quantum state, s ; therefore, $\sigma(\varepsilon_s)$ remains unchanged. This means it is an isentropic, reversible process
- The work done on S :

$$W = \underbrace{P}_{\text{pressure}} \cdot \underbrace{A}_{\text{area}} \cdot \underbrace{\Delta x}_{\text{displacement}} = P \Delta V$$

From conservation of energy:

$$W_{on} = U(V - \Delta V) - U(V)$$

$$P \Delta V = - \frac{\partial U}{\partial V} \Delta V$$

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

- Thermodynamic Identity

$$\sigma = \sigma(U, V)$$

$$d\sigma = \frac{\partial\sigma}{\partial U}dU + \frac{\partial\sigma}{\partial V}dV$$

$$\text{If } d\sigma = 0 \text{ (isentropic)} \rightarrow \left(\frac{\partial U}{\partial V}\right)_\sigma = -\frac{\frac{\partial\sigma}{\partial V}}{\frac{\partial\sigma}{\partial U}}$$