

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

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

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

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

- Reviewing some important formulas:

- Entropy:

$$\sigma(u, v) = \ln(g(u, v))$$

- Fundamental Temperature:

$$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_V$$

- Probability:

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

- Partition Function:

$$z(\tau, V) = \sum_s e^{-\frac{\varepsilon_s}{\tau}}$$

- Energy:

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

- Pressure:

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

- Note: there may be other ways to derive some of these quantities; however, these are the critical functions we have learned so far.

- Back to the total differential, we get:

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

- For $\sigma = c$, a constant, $d\sigma = 0$, known as an isentropic process

$$\frac{\partial U}{\partial V}_\sigma = -\frac{(\partial\sigma)_U}{\partial V}$$

$$\overline{\left(\frac{\partial\sigma}{\partial U}\right)_V = -\tau \left(\frac{\partial\sigma}{\partial V}\right)_U}$$

Thus, we see:

$$P = \tau \left(\frac{\partial \sigma}{\partial V} \right)_U^1$$

Thermodynamic Identity

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

$\underbrace{\tau}_{\text{heat added}^2} d\sigma = \underbrace{dU}_{\Delta \text{internal energy}} + P \underbrace{dV}_{\text{work done by gas}}$

$$sQ = dU = sW$$

- This is the first law
- Helmholtz Free Energy, $F(\tau, V)$
 - For a Reservoir (\mathcal{R}) and System (S) placed in thermal contact:

$$U_{\mathcal{R}} + U_S = U_o$$

$$\sigma_{\mathcal{R}+S} = \sigma_{\mathcal{R}}(U_{\mathcal{R}}) + \sigma_S(U_S)$$

$$\sigma_{\mathcal{R}+S} = \sigma_{\mathcal{R}}(U_o - U_S) + \sigma_S(U_S)$$

- Using Taylor Expansion:

$$\sigma_{\mathcal{R}} - \frac{1}{\tau_{\mathcal{R}}} (U_s - \tau_{\mathcal{R}} \cdot \sigma_S)$$

- As $\sigma_{\mathcal{R}+s}$ increases,

$$F_S \equiv U_s - \tau_{\mathcal{R}} \sigma_S$$

decreases, assuming that $\tau_{\mathcal{R}}, V_s, N_s$ are constant

- To summarize this process, we can say: If S is brought into thermal contact with \mathcal{R} at $\tau_{\mathcal{R}}, V_s, N_s$ constant, then F_S will decrease and S will come into a new equilibrium state in which F_S is minimal, F_S^{min}
 - $F_S - F_S^{min}$ — The maximum amount of work S can perform
 - This is because, at the same time as the system is minimizing the free energy, it is also trying to maximize entropy (as seen in the subtracted term of the formula)
- Identities Related to Helmholtz Free Energy

$$F(\tau, V) = U - \tau \sigma$$

$$dF = dU - \sigma d\tau - \tau d\sigma$$

$$= \cancel{\tau d\sigma} - PdV - \sigma d\tau - \cancel{\tau d\sigma}$$

$$= -\sigma d\tau - PdV$$

¹Note: the negative sign is dropped because entropy can only increase, and pressure is always positive

- This gives us:

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_v \quad P = - \left(\frac{\partial F}{\partial V} \right)_\tau$$

- Maxwell Relations

- Consider $f(x, y)$ which is twice continuously differentiable in x and y

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

$$\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x = \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y$$

- Applying this to the above, we get:

$$\frac{\partial}{\partial \tau} \left(\frac{\partial F}{\partial V} \right) = \frac{\partial}{\partial \tau} (-P)$$

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

$$\left(\frac{\partial P}{\partial \tau} \right)_V = \left(\frac{\partial \sigma}{\partial V} \right)_\tau$$

- Calculation of F from z :

$$F = -\tau \ln(z)$$

$$z = e^{-\frac{F}{\tau}}$$

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

- Ideal Gas:

- A gas of non-interacting quantum particles in a classical regime
- Considering a single quantum particle in a box:

$$-\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = \varepsilon \psi(x, y, z)$$

$$\varepsilon_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2ML^2} (n_x^2 + n_y^2 + n_z^2), \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

$$\psi_{n_x, n_y, n_z}(x, y, z) = A \sin \left(\frac{\pi n_x}{L} x \right) \sin \left(\frac{\pi n_y}{L} y \right) \sin \left(\frac{\pi n_z}{L} z \right)$$

$$z_1 = \sum_{n_x n_y n_z=1}^{\infty} e^{-\frac{\hbar^2 \pi^2}{2ML^2 \tau} (n_x^2 + n_y^2 + n_z^2)}$$

$$\iiint_0^\infty dn_x dn_y dn_z e^{-\alpha^2 (n_x^2 + n_y^2 + n_z^2)} \quad \alpha \equiv \sqrt{\frac{\hbar^2 \pi^2}{2ML^2 \tau}} \ll 1$$

* These become Gaussian integrals:

$$\begin{aligned}\int_{-\infty}^{\infty} e^{-x^2} dx &\equiv \sqrt{\pi} \\ \int_0^{\infty} e^{-x^2} dx &\equiv \frac{\sqrt{\pi}}{2} \\ \frac{1}{2} \int_0^{\infty} e^{-\alpha^2 n_x^2} dn_x &\equiv \frac{\sqrt{\pi}}{2\alpha}\end{aligned}$$

* Thus, we get:

$$z_1 = \left(\frac{\sqrt{\pi}}{2\alpha} \right)^3 = \left(\frac{\sqrt{\pi}}{2\sqrt{\frac{\hbar^2 \pi^2}{2ML^2\tau}}} \right)^3 = \left(\frac{M\tau}{2\pi\hbar^2} \right)^{\frac{3}{2}} V$$

* The following value is known as the quantum concentration

$$\begin{aligned}n_Q &\equiv \left(\frac{M\tau}{2\pi\hbar^2} \right)^{\frac{3}{2}} \\ n_Q &= \frac{1}{\lambda_D^3}\end{aligned}$$

where λ_D is the de Broglie wavelength

* Finally, we are left with:

$$z_1 = n_Q V$$

$$n_Q \ll n$$

$$\text{Classical regime: } n_Q \gg n = \frac{N}{V}$$