

Boltzmann Distribution and Helmholtz Free Energy

Michael Brodskiy

Professor: A. Stepanyants

October 3, 2023

- 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

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

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

$$sQ = dU = sW$$

- 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:

$$\begin{aligned}z_1 &= n_Q V \\ n_Q &<< n\end{aligned}$$

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

* We can predict the expected number of particles in state s , using:

$$\langle N_s \rangle = N \frac{e^{-\frac{\epsilon_s}{\tau}}}{z_1} = \frac{N}{n_Q V} = \frac{n}{n_Q}$$

Many particles in a box

- Particles are distinguishable because of different masses
 - The N -particle partition function becomes:

$$z_N = z_1 z_2 \cdots Z_N$$

- With two particles in two distinguishable quantum states, with the same mass:
 - * This gives us:

$$\begin{aligned}z_1 &= e^{-\frac{\epsilon_1}{\tau}} + e^{-\frac{\epsilon_2}{\tau}} \\ z_2 &= e^{-\frac{\epsilon_1}{\tau}} + e^{-\frac{\epsilon_2}{\tau}}\end{aligned}$$

- * This means distinguishable particles of same mass give us:

$$z_N = z_1^N$$

- For identical particles

$$z_N = \frac{z_1^N}{N!}$$

- * This formula is correct only in the classical regime
- * Applying this to what we know:

$$F = -\tau \ln(z_N) = -\tau \ln\left(\frac{(n_Q V)^N}{N!}\right) = -\tau (N \ln(n_Q V) - \ln(N!))$$

- * Using the Stirling approximation, we get:

$$F = -\tau (N \ln(n_Q V) - N \ln(N) + N)$$

$$F = -\tau N \left(\ln\left(\frac{n_Q}{n}\right) + 1 \right)$$

- * The Sackur-Tetrode formula is:

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N} = N \left(\ln\left(\frac{n_Q}{n}\right) + \frac{5}{2} \right)$$

- * Obtaining energy, we find:

$$U = F + \tau \sigma = \frac{3}{2} \tau N \text{ or } \tau^2 \left(\frac{\partial \ln(z_N)}{\partial \tau} \right)_{V,N}$$

- * If we derive with respect to volume:

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

$$PV = N\tau$$

Thermal Radiation

- $I(\lambda)$ is the radiant intensity, i.e. intensity per unit wavelength in units of $\left[\frac{\text{J}}{\text{s m}^3}\right]$
- Using an experiment with a detector tuned to a variety of wavelengths, it was determined that:
 - λ_{max} shifts to lower wavelengths as T increases (Wien's Law)
 - Area under the curve is approximately T^4
- This developed the Blackbody model of thermal radiation
 - A blackbody absorbs all external radiation
 - A blackbody emits thermal equilibrium radiation at temperature T

- Properties of a photon:
 - The mass is negligible; that is, $m = 0$
 - $s = 1$ (spin)
 - $s_z = \pm 1$
 - Has momentum p
 - Has energy ε
 - Has wavelength λ
 - Has frequency f, ω
 - Has wave number, K
- Relationships:

$$\lambda = \frac{h}{p}$$

$$f = \frac{\varepsilon}{h}$$

$$k = \frac{2\pi}{\lambda}$$

$$\boxed{\varepsilon = \hbar\omega}$$

- Modes of radiation describe different solutions of Maxwell's equations (e.g. TEM mode, E, B are \perp to propagation direction)
- The thermal average # of photons in a mode of frequency ω :

$$P(s) = \frac{e^{-\frac{\varepsilon s}{\tau}}}{z}; \quad z = \sum_{s=0}^{\infty} e^{-\frac{\varepsilon s}{\tau}} = \frac{1}{1 - e^{-\frac{\hbar\omega}{\tau}}}$$

$$\langle s \rangle = \sum_{s=0}^{\infty} sP(s) = \frac{1}{z} \sum_{s=0}^{\infty} s e^{-\frac{s\hbar\omega}{\tau}} = \frac{1}{z} \frac{\partial}{\partial \left(-\frac{\hbar\omega}{\tau}\right)} \frac{1}{1 - e^{-\frac{\hbar\omega}{\tau}}}$$

$$\langle s \rangle = \frac{1}{e^{\frac{\hbar\omega}{\tau}} - 1}$$