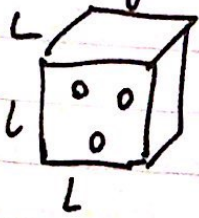


From last time:

Ideal gas



$$E = \frac{\hbar^2 \pi^2}{2mL^2} \left((n_x^2)_1 + (n_y^2)_1 + (n_z^2)_1 + (n_y^2)_2 + \dots \right)$$

$$= \frac{\hbar^2 \pi^2}{2mL^2} n^2 \quad n^2 = (n_x^2)_1 + (n_y^2)_1 + (n_z^2)_1$$

$$N(n) = \frac{1}{2^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} n^{3N}$$

$$N(E) = \frac{1}{2^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} \left(\frac{2mL^2}{\hbar^2 \pi^2} E \right)^{3N/2}$$

$N!$ indistinguishable

$$g(E) = \frac{\partial}{\partial E} N(E) \quad \Omega(E) \approx g(E) \Delta E$$

$$S(N, E, V) = k_B \left\{ \frac{3N}{2} \ln \pi - 3N \ln 2 - \ln \left(\left(\frac{3N}{2} \right)! \right) - \ln N! + \frac{3N}{2} \ln \left| \frac{2m}{\hbar^2 \pi^2} \right| + N \ln V + \ln \frac{3N}{2} + \left(\frac{3N}{2} + 1 \right) \ln E + \ln \Delta E \right\}$$

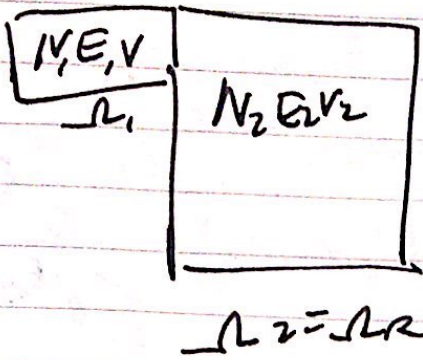
$$\rightarrow N k_B \left\{ \frac{3}{2} \ln \frac{E}{N} - \ln \frac{N}{V} + \frac{3}{2} \ln \left(\frac{m}{3\pi \hbar^2} \right) + \frac{5}{2} \right\} \quad \text{Sakur-Tetrode energy}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N, V} \Rightarrow E = \frac{3}{2} N k_B T$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E, N} \Rightarrow P = N k_B T$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N} \right)_{E, V} \Rightarrow -\frac{\mu}{T} = \frac{3}{2} k_B \ln \left(\frac{E}{N} \right) - k_B \ln \left(\frac{N}{V} \right) + \frac{3}{2} k_B \ln \frac{m}{3\pi \hbar^2}$$

Reservoir + Microsystem



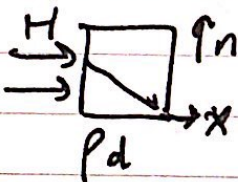
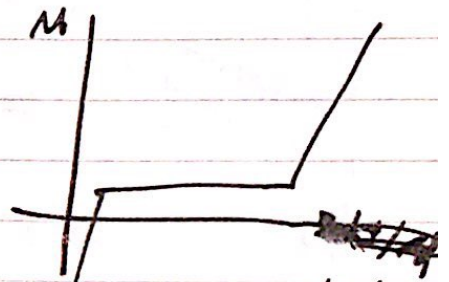
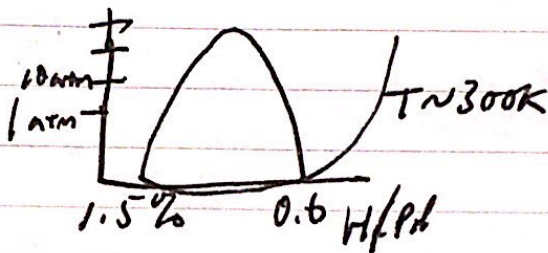
$$\Omega(N, E, V) = \sum_{N_1, E_1, V_1} \Omega_1(N_1, E_1, V_1) \Omega_R(N-N_1, E-E_1, V-V_1)$$

$$P(N, E, V) = \frac{\Omega_1(N_1, E_1, V_1) \Omega_R(N-N_1, E-E_1, V-V_1)}{\sum_{N', E', V'} \Omega_1(N', E', V') \Omega_R(N-N', E-E', V-V')}$$

Set $\frac{\partial S_R}{\partial N} = \frac{\partial S_R}{\partial E} = \frac{\partial S_R}{\partial V} = \frac{1}{k_B T}$

$$\begin{aligned} S_R(N-N_1, E-E_1, V-V_1) &= S_R(N, E, V) \\ &- N_1 \left(\frac{\partial S_R}{\partial N} \right)_{E, V} - E_1 \left(\frac{\partial S_R}{\partial E} \right)_{N, V} \\ &- V_1 \left(\frac{\partial S_R}{\partial V} \right)_{N, E} \end{aligned}$$

$$\begin{aligned} \vec{J}_0 &= -D \nabla_n \\ \vec{J}_0 &= -B \nabla_n \end{aligned}$$



hydrogen potential

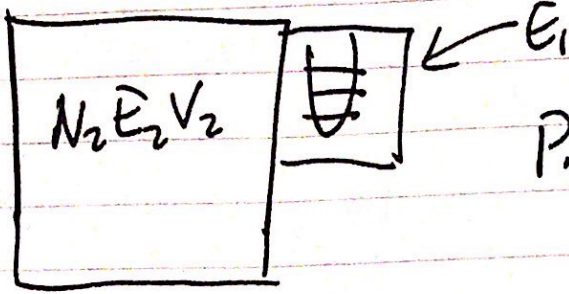
How do we tell the difference? $\frac{S_R(N, E, V)}{k_B} = \Omega_2(N, E, V) e^{\dots}$

$$P(N, E, V) = \Omega_1(N_1, E_1, V_1) e^{\dots}$$

$$\sum_{N', E', V'} \Omega_1(N', E', V') e^{-E'/k_B T} e^{-N'/k_B T} e^{-V'/k_B T}$$

$$P(N, E, V) = \Omega_1(N, E, V) e^{-E/k_B T} e^{-N/k_B T} e^{-V/k_B T}$$

$$\sum_{N', E', V'} \Omega_1(N', E', V') e^{-E'/k_B T} e^{-N'/k_B T} e^{-V'/k_B T}$$



$$P_n(T) = \frac{1 \cdot e^{-E_n/k_B T} e^0 \cdot e^0}{\sum_{n'} e^{-E_{n'}/k_B T}}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m \omega^2 x^2 \quad \frac{e^{-E_n}}{\sum_{n'} e^{-E_{n'}/k_B T}}$$

$$E_n = \hbar \omega_0 (n + \frac{1}{2})$$

$$P_n(T) = \frac{e^{-\frac{\hbar \omega_0 (n + \frac{1}{2})}{k_B T}}}{\sum_{n'} e^{-\frac{\hbar \omega_0 (n' + \frac{1}{2})}{k_B T}}} = \frac{e^{-\frac{\hbar \omega_0}{k_B T} n}}{\sum_{n'} e^{-\frac{\hbar \omega_0}{k_B T} n'}}$$

$$\langle \langle \hat{H} \rangle \rangle = \langle \langle \frac{\hat{p}^2}{2m} + \frac{1}{2} m \omega^2 x^2 \rangle \rangle_{n'}$$

$$= \langle \langle \hbar \omega_0 (\hat{a}^\dagger \hat{a} + \frac{1}{2}) \rangle \rangle \rightarrow \frac{1}{1 - e^{-\hbar \omega_0 / (k_B T)}}$$

↑ quantum mechanical
↑ thermal avg

$$= \sum_n E_n P_n(T) = \frac{\sum_n E_n e^{-E_n/k_B T}}{\sum_n e^{-E_n/k_B T}}$$

$$= \sum_n \hbar \omega_0 (n + \frac{1}{2}) e^{-\hbar \omega_0 / (k_B T) (n + \frac{1}{2})}$$

$$\frac{\sum_n e^{-\frac{\hbar \omega_0}{k_B T} (n + \frac{1}{2})}}{\sum_n e^{-\frac{\hbar \omega_0}{k_B T} (n + \frac{1}{2})}}$$

$$= \frac{1}{2} \hbar \omega_0 + \hbar \omega_0 \frac{\sum_n n e^{-\frac{\hbar \omega_0}{k_B T} n}}{\sum_n e^{-\frac{\hbar \omega_0}{k_B T} n}}$$

$$F(\beta) = \sum_{n=0}^{\infty} e^{-\beta n} = 1 + e^{-\beta} + (e^{-\beta})^2 + \dots = \frac{1}{1 - e^{-\beta}} \quad |e^{-\beta}| < 1$$

$$\beta = \frac{\hbar \omega_0}{k_B T} \quad \sum_{n=0}^{\infty} n e^{-\beta n} = \frac{d}{d\beta} F(\beta) = \frac{d}{d\beta} \frac{1}{1 - e^{-\beta}} = \frac{e^{-\beta}}{(1 - e^{-\beta})^2}$$

$$\langle \langle \hat{H} \rangle \rangle = \frac{1}{2} \hbar \omega_0 + \hbar \omega_0 \frac{e^{-\hbar \omega_0 / k_B T}}{(1 - e^{-\hbar \omega_0 / k_B T})^2} = \frac{e^{-\hbar \omega_0 / k_B T}}{1 - e^{-\hbar \omega_0 / k_B T}} + \frac{1}{2} \hbar \omega_0$$

$$= \frac{\hbar \omega_0}{e^{\hbar \omega_0 / k_B T} - 1} + \frac{1}{2} \hbar \omega_0$$

$$\langle \langle \hat{H} \rangle \rangle = \left\langle \left\langle \int \frac{1}{2} \epsilon_0 \hat{\mathbf{E}} \cdot \hat{\mathbf{E}} + \frac{1}{2} \mu_0 \hat{\mathbf{H}} \cdot \hat{\mathbf{H}} d^3r \right\rangle \right\rangle$$

$$= \left\langle \left\langle \sum_{\mathbf{k}\sigma} \frac{\epsilon}{k\sigma} \hbar \omega_{\mathbf{k}} \left(\hat{N}_{\mathbf{k}\sigma} + \frac{1}{2} \right) \right\rangle \right\rangle$$

$$= \sum_{\mathbf{k}\sigma} \hbar \omega_{\mathbf{k}} \left(\langle \langle \hat{N}_{\mathbf{k}\sigma} \rangle \rangle + \frac{1}{2} \right)$$

$$\langle \langle \hat{N}_{\mathbf{k}\sigma} \rangle \rangle = \sum_{\mathbf{k}\sigma} \left(\frac{\hbar \omega_{\mathbf{k}}}{e^{\frac{\hbar \omega_{\mathbf{k}}}{k_B T}} - 1} + \frac{\hbar \omega_{\mathbf{k}}}{2} \right)$$

$$\langle \langle \hat{H} \rangle \rangle = \sum_{\mathbf{k}\sigma} \frac{\hbar \omega_{\mathbf{k}}}{2} + \int_{-\infty}^{\infty} P(E) \frac{E}{e^{E/k_B T} - 1} dE$$

$$P(E) = \begin{cases} 0 & E < 0 \\ \frac{L^3 \epsilon^2}{\pi^2 \hbar^3 c^3} & E > 0 \end{cases} \int_0^{\infty} \frac{L^3 \epsilon^3}{\pi^2 \hbar^3 c^3} \frac{1}{e^{E/k_B T} - 1} dE$$

$$\frac{\langle \langle \hat{H} \rangle \rangle - Z_1 P_1}{L^3} = \int_0^{\infty} \frac{(h\nu)^3}{\pi^2 \left(\frac{h}{2\pi}\right)^3 c^3} \frac{1}{e^{h\nu/k_B T} - 1} h d\nu$$

$$= \int_0^{\infty} \frac{8\pi\nu^3}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1} d\nu$$

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}$$

Planck's formula