Review - Partition Function

- For N non-interacting, distinguishable molecules

$$Z_{\text{total}} = Z_1 Z_2 \cdots Z_N$$

- For N non-interacting, indistinguishable molecules

$$Z_{\text{total}} \approx \frac{Z_1 Z_2 \cdots Z_N}{N!} = \frac{(Z_1)^N}{N!}$$

- We will apply this to an ideal gas
  – Rotational, vibrational, translational energies

Ideal Gas Revisited

- Partition function for N molecules (all identical) $Z_{\text{total}} = \dfrac{1}{N!} Z_1^{\,N}$
- To get Z_1 need to add up Boltzmann factors for all available microstates of single molecule
- Each one has this form:

$$e^{-E(s)/kT} = e^{-E_{\text{tr}}(s)/kT} e^{-E_{\text{int}}(s)/kT}$$

- So, partition function is:

$$Z_1 = Z_{\text{tr}} Z_{\text{int}}$$

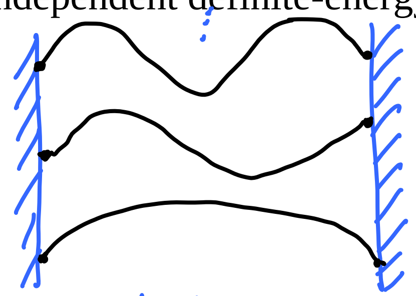
$$Z_{\text{tr}} = \sum_{\substack{\text{translational}\\ \text{states}}} e^{-E_{\text{tr}}/kT} \qquad Z_{\text{int}} = \sum_{\substack{\text{internal}\\ \text{states}}} e^{-E_{\text{int}}/kT}$$

$$E_{\text{int}} = E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

Ideal Gas Translation

- Start with simplest case
  - 1 particle of mass *m*, in a 1-dimensional box of size *L*

- Need to compute all translational states for this particle
  - Use a quantum mechanical approach to count the independent definite-energy wavefunctions



$\lambda_3 = \frac{2L}{3}$ $n=3$

$\lambda_2 = \frac{2L}{2}$ $n=2$

$\lambda_1 = 2L$ $n=1$

de Broglie relation

$p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$

wavefunctions describe possible states of system

Ideal Gas Translation

- Need to compute all translational states for this particle
  - Quantum mechanically allowed states (momentum states):

$$p_n = \frac{h}{2L} n \qquad (n = 1, 2, 3, \ldots)$$

  - Energy levels (states):

$$E(n) = \frac{p^2}{2m} = \frac{h^2 n^2}{8mL^2} \qquad (n = 1, 2, 3, \ldots)$$

Consider N_2 in $L = 1$ cm

$$\frac{h^2}{8mL^2} = \frac{(6.62\times10^{-34}\,J\cdot s)^2}{8\cdot(28\times1.6\times10^{-27}\,kg)(0.01\,m)^2}$$

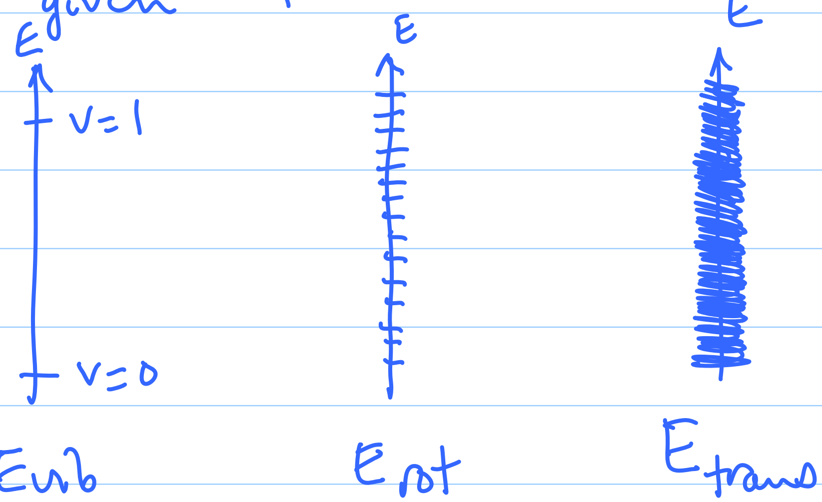
$\approx 10^{-38} J \qquad \approx 10^{-19} eV$

consider

$E_{rot} \sim 10^{-4}$ eV

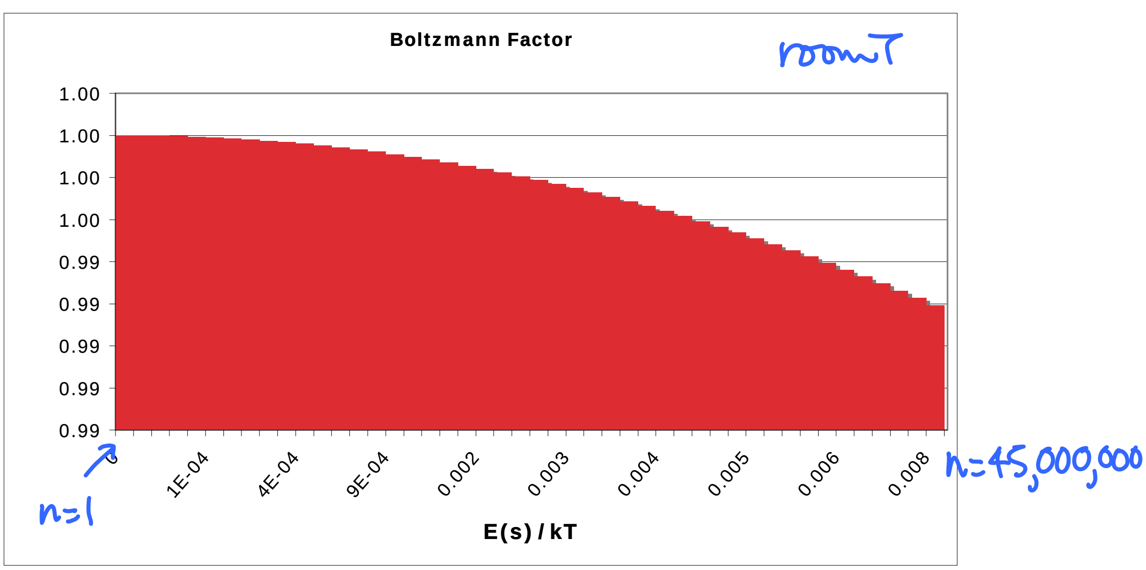
$E_{vib} \sim 10^{-1}$ eV

for given T



some liberty taken in drawing

Boltzmann Factor for Translation



$e^{-h^2 n^2 / 8mL^2 kT}$

$kT \approx 250\times10^{-4}$ eV

1-D Translational Partition Function

- Starting from $Z_{1D} = \sum_n e^{-E_n/kT}$

$$Z_{1D} = \sum_n e^{-h^2 n^2/(8mL^2kT)}$$

$$= \int_0^\infty e^{-h^2n^2/8mL^2kT}\, dn$$

$$x^2 \equiv \frac{h^2 n^2}{8mL^2kT} \qquad dx \equiv dn\sqrt{\frac{h^2}{8mL^2kT}}$$

$$Z_{1D} = \underbrace{\int_0^\infty e^{-x^2} dx}\,\sqrt{\frac{8mL^2kT}{h^2}}$$

$$= \frac{\sqrt{\pi}}{2}\cdot\sqrt{\frac{8mL^2kT}{h^2}} = \sqrt{\frac{2\pi mkT}{h^2}}\,L = \frac{L}{l_Q}$$

quantum length

3D box is $L \times L \times L$

$$E(n_x, n_y, n_z) = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

$$= \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$Z_{3D} = \sum_{n_x, n_y, n_z} e^{-\frac{h^2}{8mL^2kT}(n_x^2 + n_y^2 + n_z^2)}$$

$$= \underbrace{\sum_{n_x} e^{-\frac{h^2}{8mL^2kT}n_x^2}}\;\underbrace{\sum_{n_y} e^{-\frac{h^2}{8mL^2kT}n_y^2}}\;\underbrace{\sum_{n_z} e^{-\frac{h^2}{8mL^2kT}n_z^2}}$$

$$Z_{3D} = \left(\frac{L}{l_Q}\right)^3 = \frac{V}{l_Q^3} = \frac{V}{v_Q}$$

v_Q quantum volume

$$l_Q^3 = v_Q = \left(\sqrt{\frac{h^2}{2\pi mkT}}\right)^3$$

for N indistinguishable particles

$$Z_N = \frac{1}{N!}\left(\frac{V}{v_Q}\right)^N$$ translations only

Thermodynamic Properties

Remember that we are only including translations so far

- Then, $\ln Z = N\ln V - N\ln \upsilon_Q - N\ln N + N$

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z$$

$$= N\frac{\partial}{\partial \beta}\ln\left(\frac{h}{\sqrt{2\pi m k T}}\right)^3 \rightarrow$$ think of as $\ln C\beta^{3/2}$

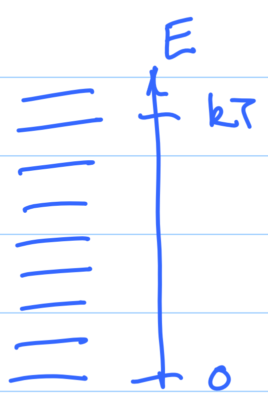
$$= \frac{3N}{2}\frac{1}{\beta} = \frac{3}{2}NkT$$

for entropy

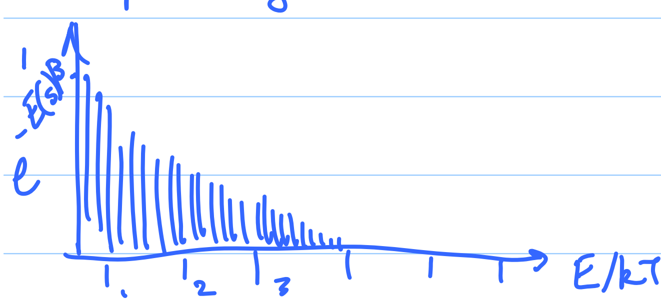
$$S = \frac{U-F}{T} = \frac{3}{2}Nk + Nk\left[\ln V - \ln v_Q - \ln N + 1\right]$$

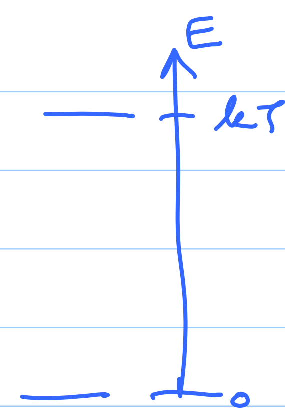
$$S = Nk\left[\ln\left(\frac{V}{v_Q N}\right) + \frac{5}{2}\right]$$

Sackur-Tetrode equation

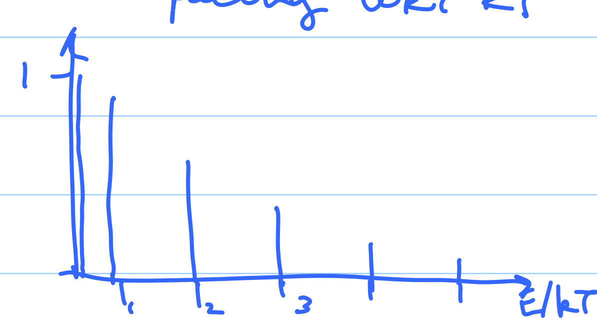


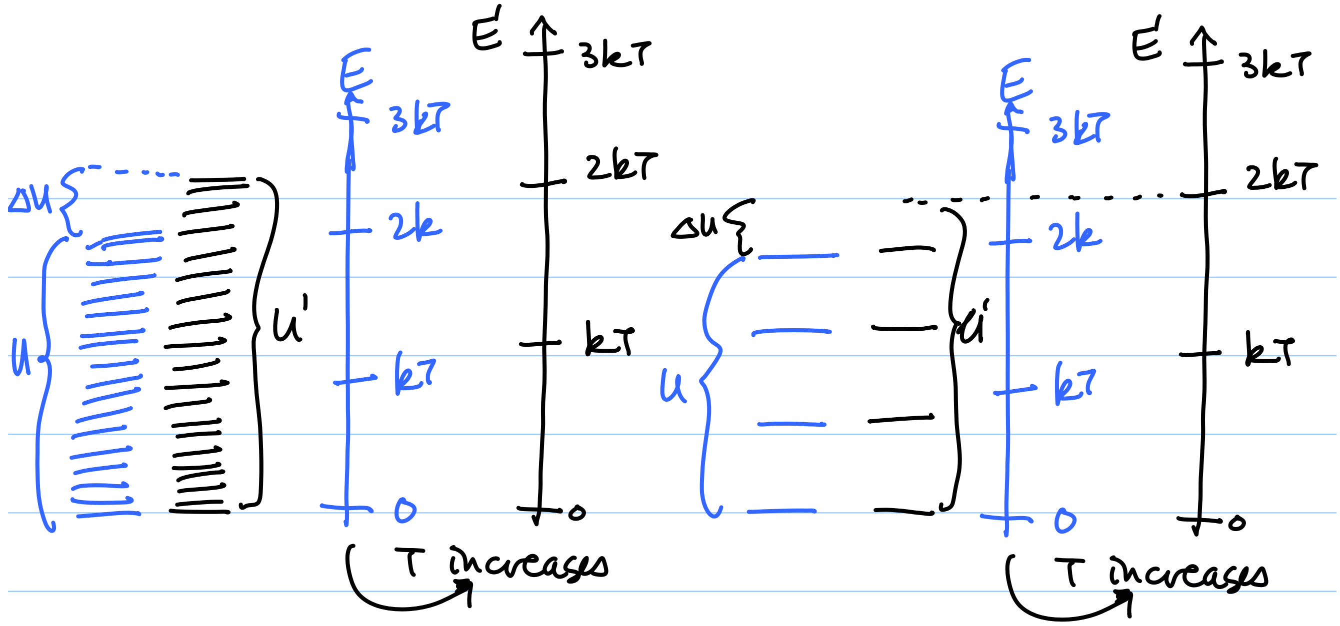
high T limit
small energy spacing WRT kT





low T limit
large energy spacing WRT kT





$C_V = \frac{dU}{dT} \approx \frac{\Delta U}{\Delta T}$

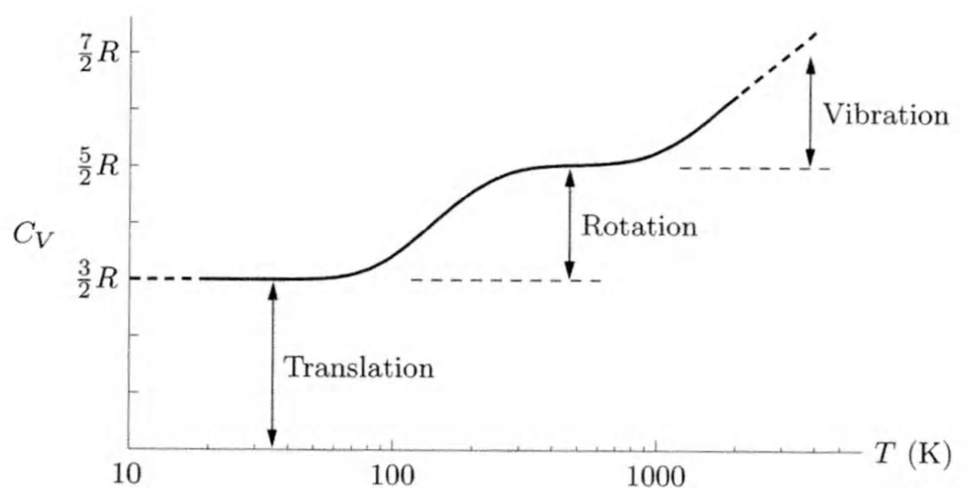
high T limit

$C_V \sim \frac{\Delta U}{\Delta T} = 0$

no state available
so no ΔU increase
low T limit

Frozen degrees of freedom

- Example of H_2 molecule



- Need Quantum and Statistical Mechanics!