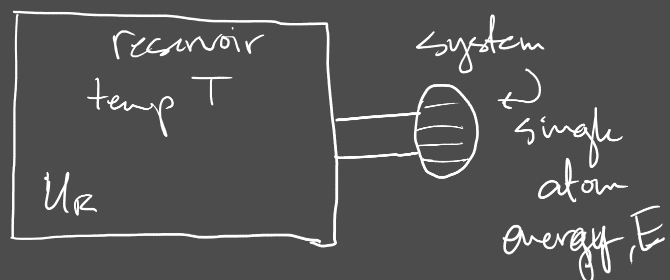
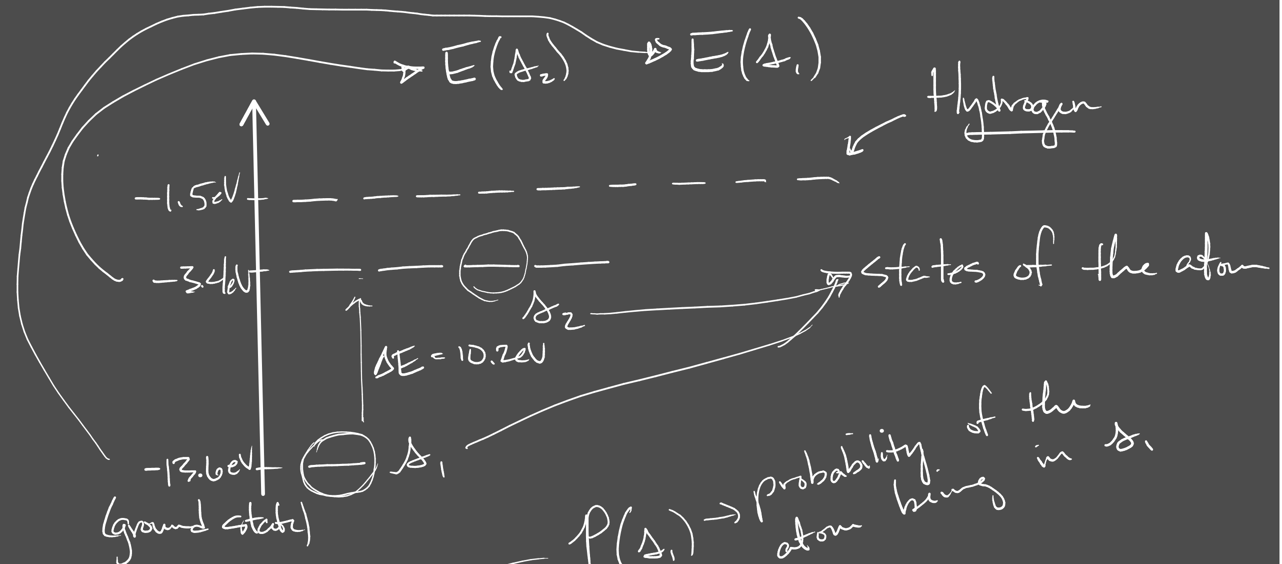
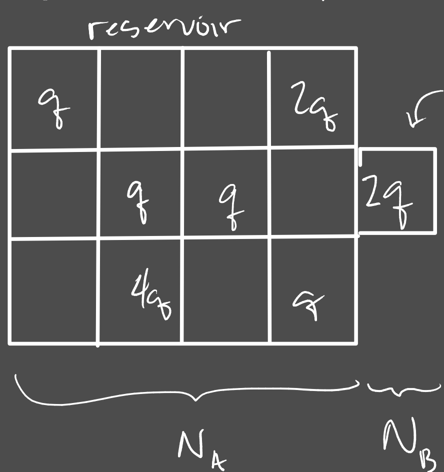
Chapter 6 - Boltzmann Statistics





$P(s_1) \rightarrow$ probability of the atom being in s_1

Einstein solid



The probability of finding the atom in any particular state is proportion to the number microstates that are accessible to the reservoir.

when the atom is in state s_1 it has energy $E(s_1)$ and the reservoir has $\Omega_R(s_1)$

atom $\rightarrow s_2 \rightarrow E(s_2) \longrightarrow$ reservoir $\Omega_R(s_2)$

$E(s_2) > E(s_1)$ then $\Omega_R(s_1) > \Omega_R(s_2)$

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{\ln \Omega_R(s_2)}}{e^{\ln \Omega_R(s_1)}} = \frac{e^{S_R(s_2)/k_B}}{e^{S_R(s_1)/k_B}} = e^{[S_R(s_2)-S_R(s_1)]/k_B}.$$

$$dS_R = \frac{1}{T}\left(dU_R + \underbrace{P\,dV_R}_{dV_R \ll dU_R} - \cancel{\mu\, dN_R} \to 0\right)$$

$$S_R(s_2) - S_R(s_1) = \frac{1}{T}\underbrace{\left[U_R(s_2) - U_R(s_1)\right]}_{-\left[E(s_2)-E(s_1)\right]}$$

$$\frac{P(s_2)}{P(s_1)} = e^{-[E(s_2)-E(s_1)]/k_BT}$$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/k_BT}}{e^{-E(s_1)/k_BT}}$$

Boltzmann factor

$$\frac{P(s_2)}{e^{-E(s_2)/k_BT}} = \frac{P(s_1)}{e^{-E(s_1)/k_BT}} = \frac{1}{Z}$$

$$\boxed{P(s) = \frac{1}{Z} e^{-E(s)/k_B T}}$$

$Z \rightarrow$ partition function

$$\sum_s P(s) = 1 = \sum_s \frac{1}{Z} e^{-E(s)/k_B T} = \frac{1}{Z} \sum_s e^{-E(s)/k_B T}$$

over all state

$$Z = \sum_s e^{-E(s)/k_B T}$$

What is the probability of a H atom being in the first excited state, relative to the ground state, in sun's atmosphere, where T = 5800K.

$$\frac{P(s_2)}{P(s_1)} = e^{-[E(s_2) - E(s_1)]/k_B T} = e^{-10.2\,eV/0.5\,eV} = e^{-20.4} = 1.4 \cdot 10^{-9}$$

$\times 4$ degeneracy

$\boxed{5.5 \cdot 10^{-9}}$ $\times 10^9$ H's

eV $\rightarrow$ energy

$\Delta K = -\Delta U = -q\Delta V = 1.6 \cdot 10^{-19}\,C \cdot 1\,V = 1.6 \cdot 10^{-19}\,J$

$1\,eV = 1.6 \cdot 10^{-19}\,J$

$k_B T = 1.38 \cdot 10^{-23} \cdot 5800\,K$

$k_B T = 8 \cdot 10^{-20}\,J \cdot \frac{1\,eV}{1.6 \cdot 10^{-19}\,J} = 0.5\,eV$

expect 5.5 of them to be in 1^{st} excited state

6.2

$$P(E) = \frac{1}{Z} e^{-F/k_B T}$$

$$F = E - TS$$

"entropy" $\rightsquigarrow k_B \ln(\underbrace{\text{degeneracy}}_{d(E)})$

earlier $P(s) = \frac{1}{Z} e^{-E(s)/k_B T}$

$P(s) \propto \Omega_R$

$e^{\ln \Omega_R} = e^{S}$

$$P(E) = d(E) \cdot P(s)$$

$$= d(E) \cdot \frac{1}{Z} e^{-E(s)/k_B T}$$

$$= e^{\ln d(E)} \cdot \frac{1}{Z} \cdot e^{-E(s)/k_B T}$$

$$= \frac{1}{Z} e^{\ln d(E) - E(s)/k_B T}$$

$$= \frac{1}{Z} e^{-[E(s) - T \underbrace{k_B \ln(d(E))}_{S}] / k_B T}$$

$$\to P(E) = \frac{1}{Z} e^{-F/k_B T}$$

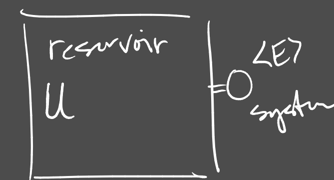
Average Values

$$P(s) = \frac{1}{Z} e^{-E(s)/k_B T} \leftarrow \frac{1}{k_B T} = \beta$$

$$P(s) = \frac{1}{Z} e^{-\beta E(s)}$$

$$Z = \sum_s e^{-\beta E(s)}$$

canonical ensemble



→ average energy

$$\langle E \rangle = \sum_s E(s) \cdot P(s) = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)}$$

"average energy"

"expectation value"

$$\langle E \rangle = \int E(s) \cdot \rho(s)\, ds$$

energy function

probability density

small space between states

total energy?

$$U = N \langle E \rangle$$

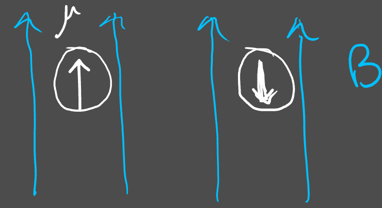
Any quantity can be averaged in this

$$\langle X \rangle = \sum_s X(s) P(s)$$

$$\langle X \rangle = \int_s X(s) \rho(s)\, ds$$

2 state paramagnet

$$E_{\uparrow} = -\mu \cdot B$$



$$E_{\downarrow} = +\mu \cdot B$$

μ ↳ magnetic dipole moment

$$Z = \sum_s e^{-\beta E(s)} = e^{-\beta(-\mu B)} + e^{-\beta(+\mu B)}$$

$$\cosh(x) = \frac{e^x + e^{-x}}{2}$$

$$Z = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B)$$

$$\sinh(x) = \frac{e^x - e^{-x}}{2}$$

$$P_{\uparrow} = \frac{e^{\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}} \qquad P_{\downarrow} = \frac{e^{-\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}$$

$$P_{\uparrow} + P_{\downarrow} \stackrel{?}{=} 1 \quad \checkmark\checkmark$$

Average energy

$$\langle E \rangle = \sum_s E(s) P(s) = \frac{1}{Z}\sum_s E(s)\, e^{-\beta E(s)} = \frac{1}{2\cosh\beta\mu B}\left(-\mu B\, e^{\beta\mu B} + \mu B \cdot e^{-\beta\mu B}\right)$$

$$= -\frac{\mu B}{2\cosh\beta\mu B} \cdot \underbrace{\left(e^{\beta\mu B} - e^{-\beta\mu B}\right)}_{2\sinh\beta\mu B}$$

$$\langle E \rangle = \frac{-\mu B}{\cancel{Z} \cosh \beta \mu B} \cdot \cancel{Z} \sinh \beta \mu B$$

$$\frac{\sin \theta}{\cos \theta} = \tan \theta$$

$$\frac{\sinh \theta}{\cosh \theta} = \tanh \theta$$

$$\langle E \rangle = -\mu B \tanh(\beta \mu B)$$

total energy $U = N \langle E \rangle$

$$\boxed{U = -\mu B N \tanh\left(\mu B / k_B T\right)}$$ ← compare to ch. 3 notes

Problem 6.16

$$\underbrace{\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}}_{Z = \sum_s e^{-\beta E(s)}} = -\frac{\partial (\ln Z)}{\partial \beta}$$

$$\langle E \rangle = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)}$$

$$\frac{\partial \sum_s e^{-\beta E(s)}}{\partial \beta} = \sum_s \frac{\partial e^{-\beta E(s)}}{\partial \beta} = -\sum_s E(s) e^{-\beta E(s)}$$

$$\langle E \rangle = \frac{\sum_s E(s) e^{-\beta E(s)}}{\sum_s e^{-\beta E(s)}} \leftarrow$$

$$= \frac{-\frac{\partial Z}{\partial \beta}}{Z} = \boxed{-\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \langle E \rangle}$$

$$\boxed{\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial(\ln Z)}{\partial \beta}}$$

$$\frac{\partial f(y)}{\partial x} = \underbrace{\frac{\partial f(y)}{\partial y}}_{\frac{1}{y}} \cdot \frac{\partial y}{\partial x}$$

$$\frac{1}{y} \Rightarrow f(y) = \ln y$$

back to the paramagnet

$$\langle E\rangle = -\frac{1}{\cancel{2}\cosh\beta\mu B}\cdot\frac{\partial(\cancel{2}\cosh\beta\mu B)}{\partial\beta}$$

$$= -\frac{1}{\cosh\beta\mu B}\cdot\sinh(\beta\mu B)\cdot\mu B$$

$$\frac{d\cos x}{dx} = -\sin x$$

$$\frac{d\cosh x}{dx} = \sinh x$$

$$\langle E\rangle = -\mu B\tanh(\beta\mu B)$$

even easier!

Diatomic Gas + Rotational Energy

$$E(j) = j(j+1)\cdot \epsilon$$

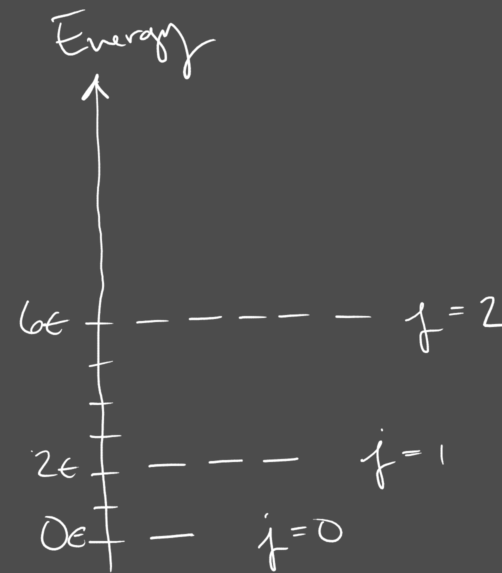
↳ energy constant

$$j = 0, 1, 2, 3 \ldots$$

degeneracy $= 2j + 1$

molecules w/ distinguishable atoms

CO, CN



$$Z = \sum_{j=0}^{\infty} \underbrace{(2j+1)}\cdot e^{-j(j+1)\epsilon/k_B T}$$

← convert to an integral

need to multiply by the degeneracy of each state to count all Boltzmann factors

For "high" temperatures $\rightarrow kT >> \epsilon$

$$Z = \int_0^\infty (2j+1) e^{-j(j+1)\epsilon/k_BT} dj = \frac{kT}{\epsilon}$$

$$Z = \frac{kT}{\epsilon} = \frac{1}{\beta \cdot \epsilon}$$

$$\langle E_{rot} \rangle = -\frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = +\cancel{\beta} \cdot \cancel{\epsilon} \cdot \frac{+1}{\cancel{\epsilon} \beta^{\cancel{2}}} = \frac{1}{\beta} = k_B T$$

$U_{rot} = N\langle E_{rot} \rangle = N k_B T$ equipartition $U = \frac{f}{2} N k_B T$

$f = 2$, two rotational degrees of freedom for diatomic gas

$$U_{total} = U_{trans} + U_{rot} = \frac{5}{2} N k_B T$$

For indistinguishable atoms, O_2, N_2

half as many state (in the high temperature limit)

$$Z_{rot} = \frac{kT}{2\epsilon}$$

Equipartion Theorem

$$U_{thermal} = \frac{f}{2} N k_B T$$

true for all quadratic degrees of freedom

$$\frac{1}{2}mv_x^2, \quad \frac{1}{2}I\omega_x^2, \quad \frac{1}{2}kx^2$$

$$E(q) = cq^2$$

↳ some variable (coordinate, momentum)

$$Z = \sum_q e^{-\beta E(q)} = \sum_q e^{-\beta c q^2}$$

nearly continuous

$$Z = \frac{1}{\Delta q} \underbrace{\sum_q e^{-\beta c q^2} \Delta q}$$

for small Δq this sum is approximated by an integral

this assumption is important.

Einstein solid only works w/ equipartion at high temps

Ch 3 p3 of notes & problems 3.24, 3.25

$$Z = \frac{1}{\Delta q}\int_{-\infty}^{\infty} e^{-\beta c q^2}\,dq$$

$$x^2 = \beta c q^2$$

$$x = q\sqrt{\beta c}$$

$$dx = dq\,\sqrt{\beta c}$$

$$Z = \frac{1}{\Delta q}\,\frac{1}{\sqrt{\beta c}}\underbrace{\int_{-\infty}^{\infty} e^{-x^2}\,dx}_{\sqrt{\pi}}$$

$$Z = \frac{1}{\Delta q}\cdot\frac{1}{\sqrt{\beta c}}\cdot\sqrt{\pi}$$

$$\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= -\frac{\cancel{\Delta q}\sqrt{\beta \cancel{c}}}{\cancel{\sqrt{\pi}}}\cdot\frac{\cancel{\sqrt{\pi}}}{\cancel{\Delta q}}\cdot\left(-\frac{1}{2}\right)\frac{\beta^{-3/2}}{\cancel{\sqrt{c}}}$$

$$\langle E\rangle = \frac{1}{2}\beta^{-1}$$

$$\beta = \frac{1}{k_B T}$$

$$\boxed{\langle E\rangle = \frac{1}{2}k_B T}$$

Maxwell-Boltzmann Speed Distribution

From equipartion,

$$\frac{3}{2}k_BT = \frac{1}{2}m\langle v^2\rangle$$

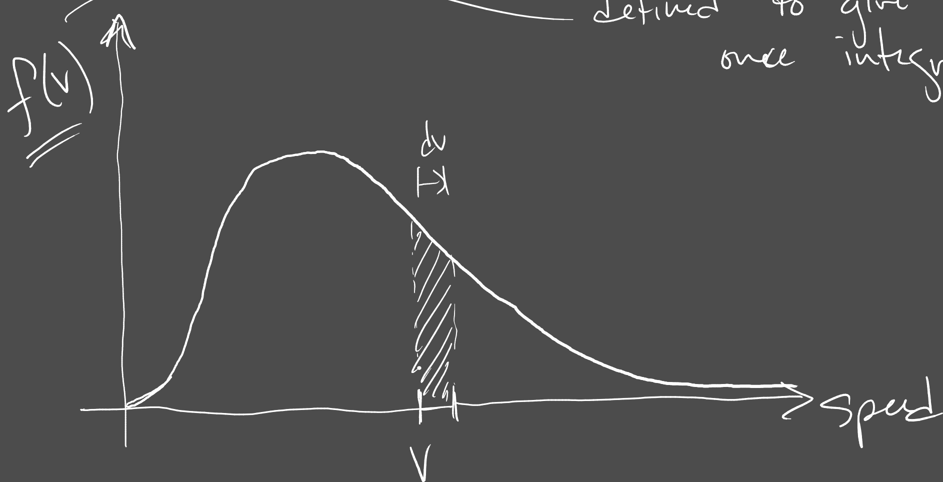
$$\langle v^2\rangle = \frac{3k_BT}{m}$$

$$\underbrace{\sqrt{\langle v^2\rangle}}_{V_{rms}} = \sqrt{\frac{3k_BT}{m}}$$

V_{rms} → average-ish

→ how many molecules have velocity between $\underbrace{v \text{ and } v+dv}_{\text{"around } v\text{"}}$

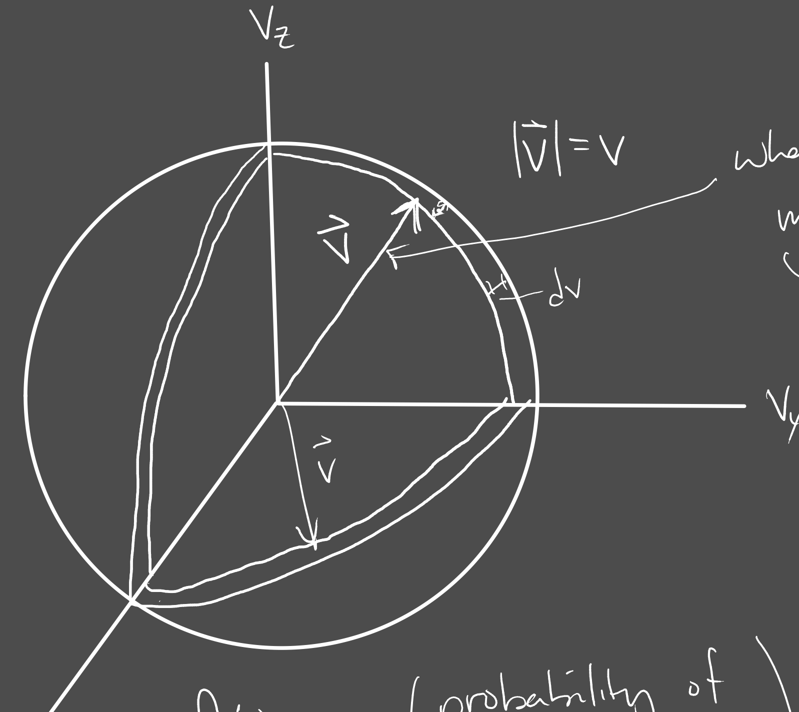
defined to give a probability once integrated



$$\begin{pmatrix}\text{probability of molecule} \\ \text{having a speed between} \\ v \text{ and } v+dv\end{pmatrix} = f(v)\,dv$$

↑ probability density

$$\begin{pmatrix}\text{probability of molecule} \\ \text{having a speed between} \\ v_1 \text{ \& } v_2\end{pmatrix} = \int_{v_1}^{v_2} f(v)\,dv$$



V_x

$|\vec{v}| = v$

$$\underbrace{\text{what is the probability of a molecule having velocity } \vec{v}\text{ ?}}_{\text{multiply by the degeneracy of all the vectors having speed } v.}$$

$$f(v) \propto \underbrace{\begin{pmatrix}\text{probability of} \\ \text{having velocity} \\ \vec{v}\end{pmatrix}}_{e^{-\beta E(\vec{v})}} \cdot \underbrace{\begin{pmatrix}\text{number of } \vec{v} \\ \text{that have} \\ \text{a speed } v\end{pmatrix}}_{4\pi v^2 \cdot dv}$$

$$\text{prob. of } E(\vec{v}) \propto e^{-\beta E(\vec{v})}$$

$$\propto e^{-mv^2/2k_BT}$$

$$f(v) = C \cdot 4\pi v^2 \cdot e^{-mv^2/2k_BT}$$

$$1 = \int_0^\infty f(v)\,dv = C\cdot 4\pi \underbrace{\int_0^\infty v^2 e^{-mv^2/2k_BT}\,dv}_{\text{change variables}} = C\cdot 4\pi \int_0^\infty \left(\sqrt{\frac{2k_BT}{m}}\right)^2 x^2 \cdot e^{-x^2} \sqrt{\frac{2k_BT}{m}}\,dv$$

$$x^2 = \frac{mv^2}{2k_BT}$$

$$x = v\sqrt{\frac{m}{2k_BT}}$$

$$dx = dv\sqrt{\frac{m}{2k_BT}}$$

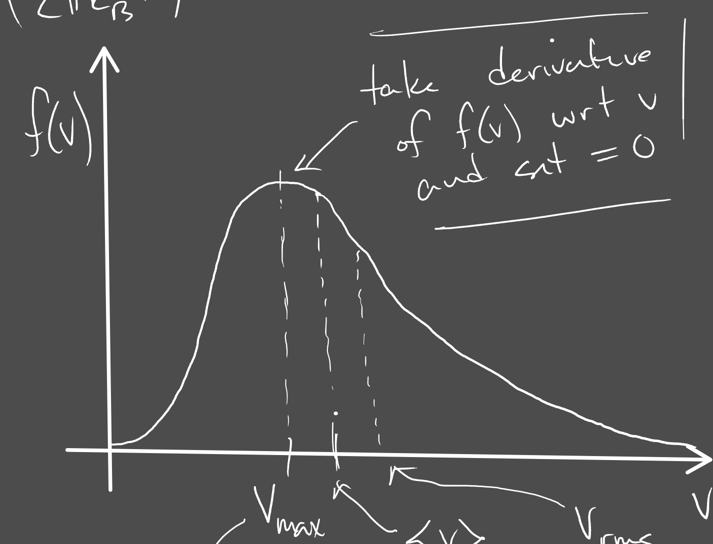
$$1 = C\cancel{4}\pi\left(\frac{2k_BT}{m}\right)^{3/2}\cdot \underbrace{\int_0^\infty x^2 e^{-x^2}\,dx}_{\frac{\sqrt{\pi}}{\cancel{4}}}$$

$$1 = C\cdot\left(\frac{2\pi k_BT}{m}\right)^{3/2}$$

$$C = \left(\frac{m}{2\pi k_BT}\right)^{3/2}$$

$$\boxed{f(v) = \left(\frac{m}{2\pi k_BT}\right)^{3/2}\cdot 4\pi v^2 \cdot e^{-mv^2/2k_BT}}$$

Maxwell-Boltzmann speed distribution



most probable speed

$$V_{max} = \sqrt{\frac{2k_BT}{m}}$$

$$\langle v \rangle = \sum_v v \cdot \underbrace{f(v) \cdot dv}_{\text{probability}}$$

$$\downarrow$$

$$\langle v \rangle = \int_0^\infty v \cdot f(v) \cdot dv$$

$$\langle v^2 \rangle = \int_0^\infty v^2 \cdot f(v)\, dv$$

$$\hookrightarrow x = \frac{v}{v_{max}}$$

grand canonical ensemble

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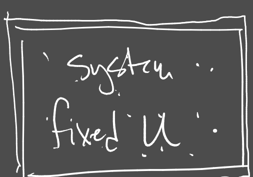
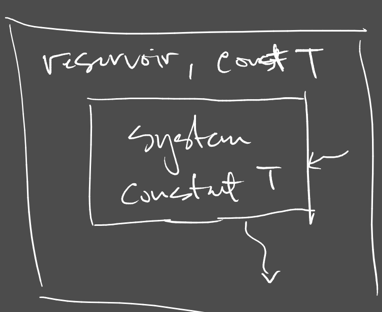
partition function → ideal gas law



$\Omega \to k_B \ln \Omega = S$ always increase

← microcanonical ensemble

canonical ensemble



Z =ish to the number of microstates available to the system at T

$$Z = \sum_s e^{-\beta E(s)}$$

$$k_B \ln Z = -F$$

always increase

wrong units

$$-\frac{F}{T} = k_B \ln Z$$

$$\boxed{F = -k_B T \ln Z}$$ TRUE!

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}$$

Two particle partition function?

$$Z_{total} = \sum_{s} e^{-\beta[E_1(s) + E_2(s)]}$$

particle 1

particle 2

non-interacting particles

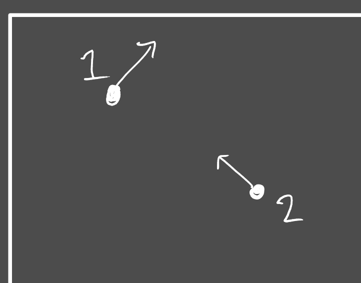
→ if distinguishable

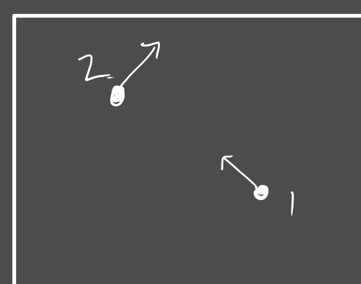
$$Z_{total} = \sum_{s_1}\sum_{s_2} e^{-\beta E_1(s_1)}\, e^{-\beta E_2(s_2)}$$

$$= Z_1 Z_2$$

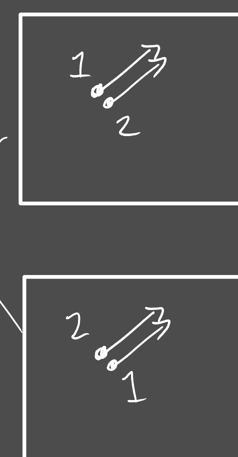
→ if not distinguishable

system is in the same state, but the particles are in different states





$$\frac{\text{same system state}}{\text{same particle state}}$$



$$Z_{total} = \frac{1}{2} Z_1 Z_2$$

for low density gas, this is no problem

For many particles

$$Z_{total} = Z_1 Z_2 Z_3 Z_4 \cdots Z_N \leftarrow \text{distinguishable}$$

indistinguishable

$$Z_{total} = \frac{1}{N!} Z_1^N$$

N! number of ways of exchanging particles w/ each other!

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now for ideal gas

rotational, vibrational, other

$$Z_1 = \sum_s e^{-\beta E(s)} = \sum_s e^{-\beta E_{tr}(s)} \cdot e^{-\beta E_{int}(s)}$$

$$Z_1 = \sum_{\substack{\text{translational}\\ \text{states}}} e^{-\beta E_{tr}} \sum_{\substack{\text{internal}\\ \text{states}}} e^{-\beta E_{int}}$$

$$Z_1 = \underbrace{Z_{tr}} \cdot \underbrace{Z_{int}}$$

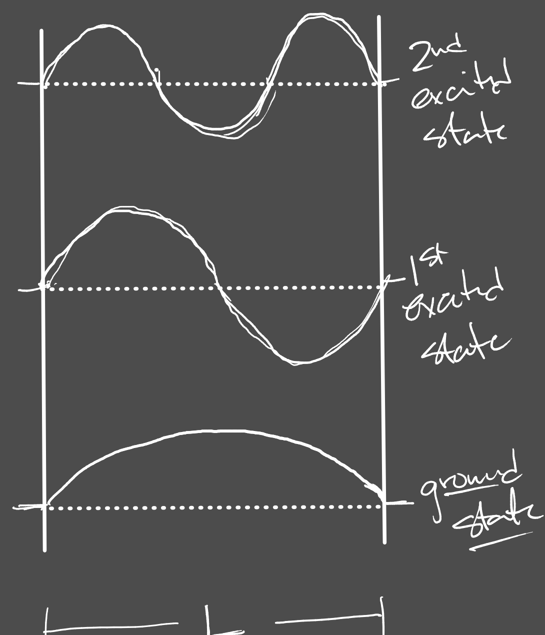
- vibrating ✓
- rotation ✓
- also electronic states
  - ↳ ground states are degenerate and so they contribute a factor to the Z_{int} Ex. $O_2 \rightarrow d=3$

$$Z = \sum_{s} e^{-\beta E_{tr}(s)} = \sum_{p} e^{-p^2/2mk_BT}$$

$$E(s) \to E(\vec{p}) = \frac{p^2}{2m}$$

$\to$ what is the momentum of a particle in a 1-D box?

Recall: $p \to$ quantized



p_3

p_2

p_1

how are wavelength + momentum related

de Broglie relation

$$p_n = \frac{h}{\lambda_n}$$

$$\left.\begin{aligned} \lambda_1 &= 2L = \frac{2L}{1} \\ \lambda_2 &= L = \frac{2L}{2} \\ \lambda_3 &= \frac{2}{3}L = \frac{2L}{3} \end{aligned}\right\} \lambda_n = \frac{2L}{n}$$

$$E_n = \frac{p_n^2}{2m}, \quad p_n = \frac{h}{\lambda_n}, \quad \lambda_n = \frac{2L}{n}$$

$$p_n = \frac{nh}{2L}$$

$$\boxed{E_n = \frac{n^2h^2}{8L^2m}}$$

$$Z_{1D} = \underbrace{\sum_n e^{-n^2h^2/8L^2mk_BT}}_{\substack{\text{for large } L \text{ and } T \\ \text{this can be approximated} \\ \text{by an integral}}} \longrightarrow Z_{1D} = \underbrace{\int_0^\infty e^{-n^2h^2/8L^2mk_BT}\,dn}_{\text{another Gaussian-like integral}}$$

$$Z_{1D} = \frac{\sqrt{\pi}}{2} \cdot \sqrt{\frac{8L^2mk_BT}{h^2}} = L \cdot \underbrace{\sqrt{\frac{2\pi mk_BT}{h^2}}}_{\frac{1}{l_Q}}$$

$$Z_{1D} = \frac{L}{l_Q} \qquad l_Q = \frac{h}{\sqrt{2\pi mk_BT}}$$

moving to 3-D

$$Z_{tr} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-h^2n_x^2/8L_x^2mk_BT} \cdot e^{-h^2n_y^2/8L_y^2mk_BT} \cdot e^{-h^2n_z^2/8L_z^2mk_BT}$$

$$Z_{tr} = \frac{L_x}{l_Q} \cdot \frac{L_y}{l_Q} \cdot \frac{L_z}{l_Q} = \frac{V}{v_Q} \qquad v_Q = \left(\frac{h}{\sqrt{2\pi mk_BT}}\right)^3$$

$$Z_1 = Z_{tr} Z_{int} = \frac{V}{v_Q} \cdot Z_{int}$$

$$Z_{total} = \frac{1}{N!}\left(\frac{V}{v_Q} \cdot Z_{int}\right)^N$$

$$\ln Z_{total} = N\left[\ln V + \ln Z_{int} - \ln N - \ln v_Q + 1\right]$$

Stirling's Approx

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

$$\langle E_{int}\rangle = -\frac{\partial(\ln Z)}{\partial \beta}$$

$$U = \underbrace{\underbrace{-N\frac{\partial(\ln Z_{int})}{\partial \beta}}_{-\langle E_{int}\rangle}}_{U_{int}} + \underbrace{N\frac{\partial(\ln v_Q)}{\partial \beta}}_{\frac{N}{v_Q}\cdot\frac{\partial v_Q}{\partial \beta} = N\cdot\frac{3}{2}\cdot\frac{1}{\beta}}$$

$$U = U_{int} + \frac{3}{2}Nk_BT \longrightarrow$$ just like equipartition says

$$C_v = \frac{\partial U}{\partial T} = \underbrace{\frac{\partial U_{int}}{\partial T}}_{\text{for rotation}} + \frac{3}{2} N k_B$$

$$U_{int} = N \langle E_{int} \rangle$$

$$= N k_B T$$

$$\frac{\partial U_{int}}{\partial T} = N k_B \Rightarrow R \text{ per mole}$$

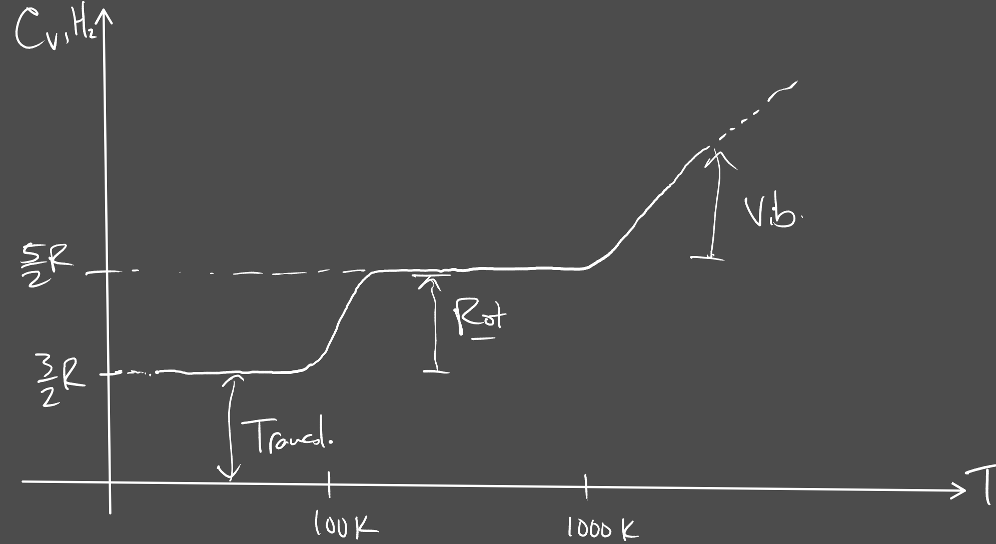


figure 1.13

Now Helmholtz Free Energy

$$F = -k_B T \ln Z$$

$$F = -N k_B T \left[\ln V + \ln Z_{int} - \ln N - \ln v_Q + 1 \right]$$

$$F = -N k_B T \left[\ln V - \ln N - \ln v_Q + 1 \right] \underbrace{- N k_B T \ln Z_{int}}_{+F_{int}}$$

$$p = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{N k_B T}{V} \longleftarrow \text{ideal gas law!}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \underbrace{Nk_B\left[\ln\left(\frac{V}{Nv_Q}\right) + \frac{5}{2}\right]}_{\text{Sackur Tetrode}} - \frac{\partial F_{int}}{\partial T}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln\left(\frac{V Z_{int}}{N v_Q}\right)$$