Physics 301 Fall 2019

Lecture #8 - Boltzman Statistics

Ch. 6

In lecture #3 we found that for a system in equilibrium at temp T, the probability to be in microstate s with energy E_s ($\tilde{p}$ for probability)

$$\boxed{\tilde{p}_s = \frac{1}{Z} e^{-\beta E_s} \qquad \beta \equiv \frac{1}{kT}}$$

with normalization factor Z "the partition function"

$$\boxed{Z = \sum_{s \text{ microstates}} e^{-E_s \beta}}$$

Very general $e^{-\beta E_s}$ called Boltzmann factor.

<u>Example</u> atomic excitation ratio of probabilities

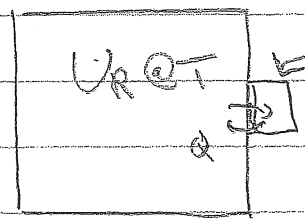
$$\frac{\tilde{p}_n}{\tilde{p}_m} = \frac{D_n}{D_m} e^{-(E_N - E_m)\beta}$$

$n=1$ is lowest energy state "groundstate"

D_n = degeneracy factor of state with energy E_N for hydrogen $D_n = 2n+1$

from Lec 3-8
#8-2

Boltzmann factor and Entropy



system state ψ_j, E_j

$U = U_R + E_j = \text{const.}$

"reservoir" (T = const) big chunk of Cu.

Every joint state of system of sample plus reservoir is equally probable. With sample energy E_j, the reservoir multiplicity is with U-E_j. Thus probability of state E_j is proportional to that multiplicity.

$$P_j = \text{Const} \times \Omega_R(U - E_j)$$

$$= \text{Const} \times \exp\left(\frac{1}{k} S_R(U - E_j)\right)$$

S_R changes very slowly because it is so large and E_j so small. Taylor expand

$$S_R(U - E_j) = S_R(U) + \left(\frac{\partial S_R}{\partial U}\right)(-E_j)$$

$$= S_R(U) - \frac{E_j}{T}$$

$$P_j = \text{Const}' \times e^{-E_j/kT}$$

for hydrogen, $E_2 - E_1 = 10.2$ eV

and $kT\big|_{298} = \frac{1}{39}$ eV so $\beta \Delta E \simeq 400$

and $\frac{\tilde{P}_2}{\tilde{P}_1} = 0$ at room temp.

Atoms absorb light (photon) if $hf \approx \Delta E$ and rapidly ($\sim$ns) de-excite by re-emitting photon.

Early evidence for CMB temperature came from observation of CN clouds (see p6.12). cyanogen

$\bar{E}$ is easy to compute from Z using a trick.

$$\bar{E} = \sum \tilde{P}_s E_s$$

energy weighted average

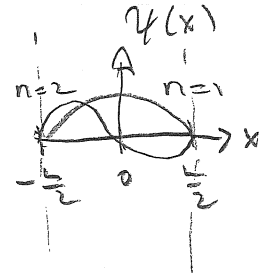
trick

$$= \frac{1}{Z} \sum_s E_s e^{-\beta E_s} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_s e^{-\beta E_s}$$

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

Partition function for ideal gas

recall in lec #2, counting of states for single particle in box of side L



∞ P.E.

momentum $P_i = \left(\frac{h}{2L}\right) n_i$ $\quad n_i = 1, 2, 3, \ldots$

quantum number $\quad i = x, y, z$

Number of states for 1 particle

$$\Omega_1 = \int_{n_x, n_y, n_z > 0} dn_x\, dn_y\, dn_z = \int_{-\infty}^{\infty} \left(\frac{1}{8}\right) \left(\frac{2L}{h}\right)^3 d^3\vec{p}$$

only one octant

$$= \frac{L^3}{h^3} \int d^3\vec{p} = \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} = \frac{V V_p}{h^3}$$

then partition function for $E = \frac{|\vec{p}|^2}{2m}$ (translational)

$$Z_{tr} = \frac{V}{h^3} \int d^3\vec{p}\, e^{-\frac{\beta}{2m}|\vec{p}|^2} \qquad V \equiv L^3$$

$$= \frac{V}{h^3} \int_{-\infty}^{\infty} dP_x\, e^{-\frac{\beta}{2m}P_x^2} \int_{-\infty}^{\infty} dP_y\, e^{-\frac{\beta}{2m}P_y^2} \int_{-\infty}^{\infty} dP_z\, e^{-\frac{\beta}{2m}P_z^2}$$

in Cartesian coordinates

$$= \frac{V}{h^3} \left[\int_{-\infty}^{\infty} dP_x\, e^{-\frac{\beta}{2m}P_x^2}\right]^3 = \frac{V}{h^3}\left(\frac{2m}{\beta}\right)^{3/2} \left[\int_{-\infty}^{\infty} dx\, e^{-x^2}\right]^3$$

let $x = \sqrt{\frac{\beta}{2m}}\, P_x$

single molecule translational degrees of freedom

Gaussian integral $\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\pi}$

$$\boxed{Z = V\left(\frac{2m\pi kT}{h^2}\right)^{3/2} \equiv \frac{V}{l_Q^3}} \qquad l_Q^3 \equiv V_Q$$

Where we have defined "thermal deBroglie wavelength" or "quantum length"

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{3}{2} kT$$

$$\sqrt{\langle p^2 \rangle} = \sqrt{3mkT} \quad \text{thermal momentum}$$

so $$\boxed{l_Q = \sqrt{\frac{h^2}{2\pi m kT}} = \sqrt{\frac{3}{2\pi}}\,\frac{h}{\sqrt{\langle p^2 \rangle}}}$$

Numerically, for Nitrogen gas N_2

$$m(N_2) = 2(14)u$$
$$uc^2 = 0.9315 \times 10^9\ eV$$
$$hc = 2\pi\,(197\ eV \cdot nm)$$
$$kT\big|_{298} = \frac{1}{38.9}\ eV$$

$$l_Q^{N_2} = \frac{2\pi\,(197\ eV \cdot nm)}{\left[2\pi\left(\frac{1}{38.9}\ eV\right) 28 \times 0.9315 \times 10^9\ eV\right]^{1/2}}$$

$$l_Q^{N_2} = 1.97 \left[\frac{(2\pi)(38.9)}{28\,(9.315)} \right] \times 10^{-2}\ \text{nm}$$

$$= 0.0191\,\text{nm} \approx 0.2\,\text{Å}$$

So at room temperature $l_Q <$ size of atom and atoms behave as classical <u>perfectly</u> <u>elastic</u> <u>particles</u>.

min excitation energy of hydrogen of $10.2\,\text{eV} \gg kT$ @ $298\,\text{K}$

<u>Note</u>: $l_Q = \sqrt{\frac{28}{m}}\, l_Q^{N_2}$

where m is molar mass of some other gas.

Rotational states of diatomic molecule

recall specific heat of gas –

$$C_V = \frac{f}{2} \underbrace{NK}_{nR} \qquad f = 3 \text{ monatomic}$$

$$= 5 \text{ diatomic}$$

$$C_p = C_V + nR = \frac{7}{2} R \text{ for diatomic gas}$$

$$= 29 \text{ J/K} \qquad \text{see Table in book}$$

While internal atomic excitation and to good degree vibrational excitation very improbable at room temp. ("frozen") molecular rotations are not.

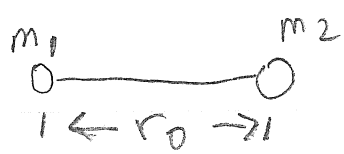
rotational kinetic energy

$$E_{rot} = \frac{|\vec{J}|^2}{2I}$$

$\vec{J}$ is angular momentum

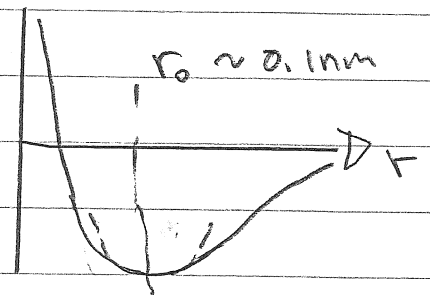
I = moment of inertia $= \mu r_0^2$ ← reduced mass

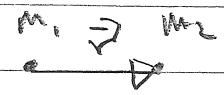
$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2$$



"rigid rotor" $r_0 = \text{const}$

A bit on diatomic molecule, quantum angular momentum





$$\vec{L} = \vec{r} \times (\mu \dot{\vec{r}}) \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$V(r) \cong V(r_0) + \frac{1}{2}\mu\omega^2 (r - r_0)^2 \quad \text{quadratic}$$

<u>Vibrational energy</u> $\quad E_{n_v} = \left(n_v + \frac{1}{2}\right)\hbar\omega \quad n_v = 0, 1, 2, \ldots$

$$\Delta E_v = \hbar\omega \cong \frac{1}{10}\,eV \sim \tfrac{1}{4} \times kT \text{ @ room temp.}$$

rigid rotor approximation

<u>rotational</u> $\quad I = \mu r_0^2$

$$E_\ell = \frac{\langle |\hat{L}|^2 \rangle}{2I} = \frac{\hbar^2}{2I} j(j+1) \qquad j = 0, 1, 2, \ldots$$

$$\Delta E_\ell = \frac{\ell \hbar^2}{I} \sim (10^{-2} \sim 10^{-3})\,eV \quad \text{excited at room temp.}$$

degeneracy $D_j = 2j+1$ corresponding to integer m_j, $-j \le m_j \le j$ integer steps

$$\langle \hat{J}_z \rangle = m_j \hbar$$

<u>note</u> electron angular momentum. $\langle \hat{S}_z \rangle = \pm \frac{\hbar}{2}$ "spin half"

$$\langle |\hat{S}|^2 \rangle = \hbar^2 \tfrac{1}{2}\left(\tfrac{1}{2}+1\right) \qquad -\tfrac{1}{2} \le m_s \le \tfrac{1}{2}$$

"Intrinsic" – no classical degree of freedom

magnetic moment –

$$E = \pm \mu_B B \qquad \text{Bohr } \mu_B = \frac{e\hbar}{2m_e c} = 0.6 \times 10^{-8}\,eV/G$$

predicted by Dirac.

In Q.M., rigid rotor angular momentum is "quantized" taking only certain values given in terms of integer $j = 0, 1, 2$ quantum number

$$|\vec{J}|^2 = \hbar^2 j(j+1) \qquad \hbar = \frac{h}{2\pi} \quad \text{"h-bar"}$$

where degeneracy of each j $D_j = 2j+1$

$-j \le m_j < +j$ or $-j, -(j-1) \ldots 0 \ldots (j-1), j$

so

$$E_{rot} = \frac{\hbar^2}{2I} j(j+1) \equiv \epsilon\, j(j+1)$$

for CO, $\epsilon = 0.00024\,eV = 2.4 \times 10^{-4}\,eV$

$$\frac{\epsilon}{k} = 2.8$$

$$\frac{\tilde{p}_1}{\tilde{p}_0} = 3\, e^{-\beta \epsilon \overbrace{2}^{j(j+1) \text{ for } j=1}} \Big|_{300} = 3\, e^{\underbrace{-2(2.4 \times 10^{-4}\,eV)/(1/40)\,eV}_{0.98}}$$

$$= 2.94 \quad \text{easily excited}$$

$\boxed{\text{p6.29}}$

from p6.28 estimate freeze-out $\frac{kT}{\epsilon} \cong \frac{1}{2}$

for HD (D = deuterium) $\epsilon = 0.0057$

$$T_{\substack{\text{freeze}\\\text{out}}} = \frac{\epsilon}{2k} = \frac{0.0057}{2(8.62 \times 10^{-5}\,eV/K)} = 33\,K$$

Partition function Z_{rot}

$$\boxed{Z_{rot} = \sum_{j=0}^{\infty} D_j \, e^{-\beta \varepsilon j(j+1)}}$$

$D_j = (2j+1)$ degeneracy factor

We can approximate as an integral for $\varepsilon\beta \ll 1$ in this case, only large values of j contribute

differential of continuous variable $j \gg 1$

$$Z_{rot} \cong \int_0^{\infty} dj \, (2j+1) \, e^{-\beta \varepsilon j(j+1)}$$

let $x = \beta \varepsilon j(j+1) \approx \beta \varepsilon j^2$

$$dj\,(2j+1) \cong 2j\,dj = dj^2 = \frac{1}{\beta\varepsilon}\,dx$$

$$Z_{rot} \cong \int_0^{\infty} \frac{dx}{\beta\varepsilon} e^{-x} = \frac{1}{\beta\varepsilon} = \left(\frac{kT}{\varepsilon}\right) \quad (kT \gg \varepsilon)$$

$$\bar{E}_{rot} = -\frac{1}{Z_{rot}} \frac{\partial Z_{rot}}{\partial \beta} = -\beta\varepsilon\left(\frac{-1}{\varepsilon\beta^2}\right) = \frac{1}{\beta} = kT$$

$$C_V^{rot} = \frac{\partial \bar{E}}{\partial T} = k$$

Corresponding to 2 degrees of freedom!

<u>Density of states</u> return to $Z_{tr}^{(1)}$, single molecule

$$Z_{tr}^{(1)} = \frac{V}{h^3} \int \underbrace{d^3p}_{4\pi p^2 dp} e^{-\beta p^2/2m}$$ spherical coordinates

let $\varepsilon = p^2/2m$ $\quad d\varepsilon/dp = p/m$

$p^2 dp = \sqrt{2m\varepsilon}\, m\, d\varepsilon$

$$Z_{tr}^{(1)} = \int g_1(\varepsilon)\, e^{-\beta\varepsilon}\, d\varepsilon$$ <u>Boltzmann factor</u>

density of states g_1 = # energy states between ε, $\varepsilon + d\varepsilon$ is

$$g_1(\varepsilon) = \frac{V}{h^3} 4\pi \sqrt{2m^3}\, \sqrt{\varepsilon}$$ See Lec 2 p.15

$$= \frac{1}{4} \frac{V}{h^3} \pi (8m)^{3/2} \sqrt{\varepsilon}$$

for electron gas, $D_{\frac{1}{2}} = 2(\frac{1}{2}) + 1 = 2$ multiplicity

$$g_e(\varepsilon) = 2 g_1(\varepsilon) \quad (\text{eg } 7.51)$$

doing integral with sustitution $\varepsilon = x^2$ gives as before

$$Z_{tr}^{(1)} = \frac{V}{l_Q^3} \qquad l_Q = \sqrt{\frac{h^2}{2\pi m k T}}$$

Recall from phys 330

phys 330, lec 15-7

Maxwell velocity distribution

molecular velocities of gas at temperature T

$$d^3\vec{v} \equiv dv_x\, dv_y\, dv_z$$

probability g to have speed $\vec{v}$ can only depend on v^2 by symmetry. Must have:

$$v^2 = |\vec{v}|^2 = v_x^2 + v_y^2 + v_z^2$$

$$g(v^2) = h(v_x^2)\, h(v_y^2)\, h(v_z^2)$$

Functional equation has solution

$$h(v_x^2) = \text{const}\; e^{-v_x^2/2\sigma^2}$$

$2\sigma^2$ some constant

$$g(v^2) = \left(\frac{1}{\sqrt{2\pi}\,\sigma}\right)^3 \exp\left\{-\frac{1}{2}\frac{v^2}{\sigma^2}\right\}$$

normalized Gaussian. Kinetic theory for 3 degrees of freedom

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT = \frac{1}{2} m\, 3\sigma^2$$

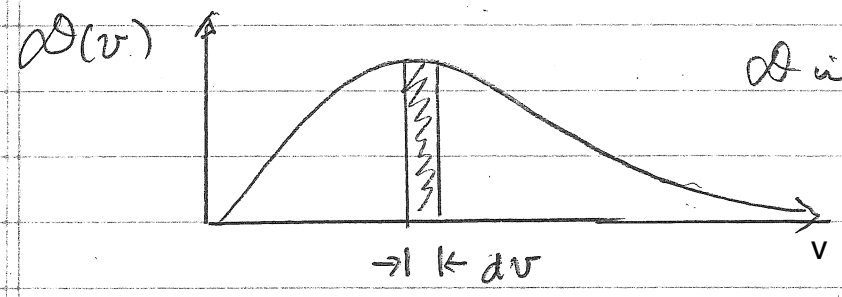
Gaussian $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\sigma^2$

$$\sigma^2 = kT/m$$

$$g(v^2) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\left(\frac{\frac{1}{2}mv^2}{kT}\right)\right\}$$

Boltzmann factor

<u>Maxwell speed distribution</u> Molecular speeds in gas



$\mathcal{D}$ is probability density function (PDF)

$$d\tilde{P}(v, v+dv) = \mathcal{D}(v)\, dv$$

with speed v, probability $\propto e^{-\beta\left(\frac{m}{2}v^2\right)}$

integrating $d\tilde{P}$ over all velocities in 3 dimensions we get $\int d\tilde{P} = 1$.

$$1 = \int_0^\infty \mathcal{D}(v)\, dv = \underset{\text{normalization}}{C} \int d^3v\, e^{-\beta\left(\frac{m}{2}v^2\right)}$$

since speeds are symmetric in space, $\int d^3v = 4\pi \int v^2 dv$

$$1 = C \int_0^\infty 4\pi v^2 e^{-\beta\left(\frac{m}{2}v^2\right)} dv$$

let $x = \sqrt{\frac{\beta m}{2}}\, v$

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

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

then

$$\mathcal{D}(v) = \left(\frac{m\beta}{2\pi}\right)^{3/2} 4\pi v^2 e^{-\beta m v^2/2}$$

this is Maxwell speed PDF

most probable speed (max in PDF)
v_{max} :

$$\frac{d}{dv}\mathcal{D}(v)\Big|_{v_{max}} = 0$$

gives $v_{max} = \sqrt{\frac{2}{m\beta}}$

mean speed

$$\bar{v} = \langle v \rangle = \int_0^\infty v\,\mathcal{D}(v)\,dv = \sqrt{\frac{8}{\pi}\frac{1}{m\beta}}$$

slightly larger than v_{max} since distribution has long tail.

Relation of Helmholtz F to Z

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S = \frac{F-U}{T} = k\beta(F-U)$$

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

$$\frac{\partial F}{\partial T} = \frac{\partial F}{\partial \beta}\frac{\partial \beta}{\partial T} = -k\beta^2\frac{\partial F}{\partial \beta}$$, get diff. eq. for F as

$$-k\beta^2\frac{\partial F}{\partial \beta} = k\beta F - k\beta\left(-\frac{\partial}{\partial \beta}\ln Z\right)$$

$$\beta\frac{\partial F}{\partial \beta} + F = -\frac{\partial}{\partial \beta}(\ln Z)$$

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

$$\boxed{F = -\frac{1}{\beta}\ln Z}$$

And since we can get all thermodynamic quantities from F, we can get <u>everything from Z</u>.

Partition function for ideal gas

$$\boxed{Z = \frac{1}{N!}\left(\frac{V Z_{int}}{V_Q}\right)^N}$$

$$V_Q = l_Q^3$$

$$V_Q = l_Q^3 = \left(\frac{h^2\beta}{2\pi m}\right)^{3/2}$$

$$Z_{int} = Z_e Z_{rot}$$

int= "internal"

Z_e is degeneracy of electronic ground state

Note. $Z_e = 1$ for N_2 and $Z_e = 1$ for monatomic gas.

$$N! \cong N^N e^{-N}$$

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

and $F = -kT \ln Z$

$$= -NRT\left[\ln V - \ln N - \ln V_Q + 1\right] + F_{int}$$

$$F_{int} = -NRT \ln Z_{int}$$

<u>for monatomic ideal gas</u> $\ln N!$

$$\ln Z = N\left[\ln V - \ln N - \ln V_Q + 1\right]$$

$$\ln V_Q = \ln\left(l_Q^3\right) = \ln\left(\frac{h^2\beta}{2\pi m}\right)^{3/2}$$

$$= \frac{3}{2}\ln\beta + \text{const}$$

$$\ln Z = N\left[\ln V - \ln N - \frac{3}{2}\ln\beta\right] + \text{const}$$

$$\boxed{\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2}kT}$$

$$\boxed{P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = kT\frac{N}{V}}$$ E.O.S.

<u>entropy</u> $F = U - TS$

$$\boxed{S = \frac{1}{T}(U - F) = \frac{\langle E\rangle}{T} + k\ln Z}$$

$$= \frac{3}{2}kN + k\ln\left[\left(\frac{V}{l_Q^3}\right)^N \frac{1}{N!}\right]$$

$$\ln N! = N\ln N - N = N\ln(N/e)$$

$\frac{3}{2} = \ln e^{3/2}$, then

$$S = kN\ln\left[\frac{V}{N l_Q^3}e^{5/2}\right]$$

Sackur-Tetrode
eq 2.49

circa 1912

Gibbs free Energy

$$G = F + PV$$

for ideal gas, $PV = NkT$ so for ideal gas

$$G = -NkT\left[\ln\left(\frac{NkT}{P}\right) - \ln N - \ln V_Q\right] + F_{int}$$

$$\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu = \frac{G}{N} - NkT\frac{\partial}{\partial N}\left[\ \ \right]$$

$$\frac{\partial}{\partial N}\left[\ \ \right] = \frac{P}{NkT}\left(\frac{kT}{P}\right) - \frac{1}{N} = 0$$

so $$\boxed{\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu = \frac{G}{N}}$$

Another way to think about entropy (P. 6.43)

$$S = -k \sum_s \tilde{P}(s) \ln \tilde{P}(s)$$

for an isolated system $P(s) = \frac{1}{\Omega}$

since all accessible states are equally probable. Then

$$S = -k \ln\left(\frac{1}{\Omega}\right) \underbrace{\sum_s \frac{1}{\Omega}}_{1} = +k \ln \Omega$$

For $\tilde{P}(s) = \frac{1}{Z} e^{-\beta E_s}$ For a system in thermal equilibrium with reservoir at temperature T

$$\ln \tilde{P}(s) = -\beta E_s - \ln Z$$

$$S = -k \sum_s \frac{1}{Z} e^{-\beta E_s} \left[-\beta E_s - \ln Z\right]$$

$$= k\beta \underbrace{\sum_s E_s e^{-\beta E_s}}_{U} + \underbrace{k \ln Z}_{-k\beta F}$$

$$\boxed{S = \frac{1}{T}\left[U - F\right]}$$