Problem Set 3. Note questions not in order on Q sheet.

9. The kinetic energy for a molecule confined to 2-D is

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 .$$

In thermal equilibrium at a temperature T, the velocity will have a Boltzmann distribution

$$\underbrace{P(v_x, v_y)\, dv_x dv_y}_{\text{Probability velocity is } v_x \to v_x + dv_x \ \& \ v_y \to v_y + dv_y} \propto e^{-\frac{1}{2} m (v_x^2 + v_y^2)/k_B T} dv_x dv_y$$

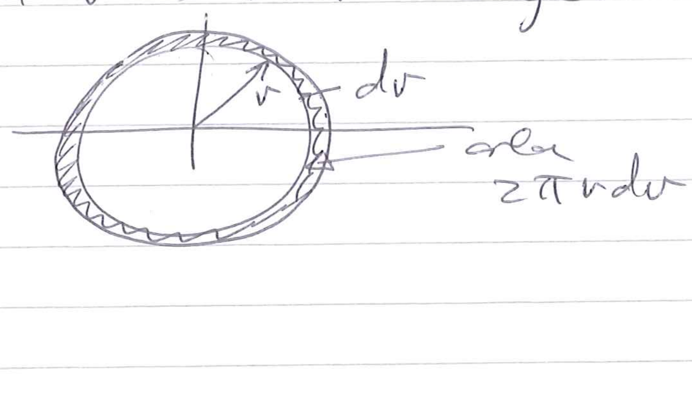
If we instead represent the velocity as a magnitude (v) & an angle (θ), then integrate over all θ

$$\Rightarrow \quad P(v)\, dv \propto e^{-\frac{1}{2} m v^2 / k_B T} \, v\, dv .$$

Boltzmann factor

c.f. $r\, dr\, d\theta$ in polar coordinates

Size of velocity space in $v \to v + dv$ range:



We can normalise this as follows:

$$\int_0^\infty N v\, e^{-\frac{1}{2}mv^2/k_BT}\, dv = 1$$

$$\Rightarrow \quad N = \left(\int_0^\infty v e^{-\frac{1}{2}mv^2/k_BT}\, dv\right)^{-1}$$

$$= \cancel{2} \cdot \frac{m}{\cancel{2} k_B T}$$

$$\therefore \quad P(v) = \left(\frac{m}{k_B T}\right) v\, e^{-\frac{mv^2}{2k_BT}}.$$

The average kinetic energy is:

(1) $$\langle \tfrac{1}{2}mv^2 \rangle = \int_0^\infty \frac{1}{2}mv^2 P(v)\, dv = \frac{1}{2} m . \frac{m}{k_BT} . \underbrace{\int_0^\infty v^3 e^{-\frac{mv^2}{2k_BT}}}_{\frac{1}{2\left(\frac{m}{2k_BT}\right)^2}}$$

(formula book)

$$= \frac{\cancel{1}}{\cancel{2}} \frac{m^2}{k_BT} . \frac{\cancel{1}}{\cancel{2}} \frac{\cancel{4}(k_BT)^{\cancel{2}}}{m^2} = k_B T.$$

(2) $$\langle \tfrac{1}{2}mv_x^2 \rangle = \int_0^\infty \frac{1}{2}mv_x^2 P(v_x)\, dv_x = \frac{1}{2}k_B T.$$

2x degrees of freedom $\Rightarrow$ $k_B T$ in total.

10.

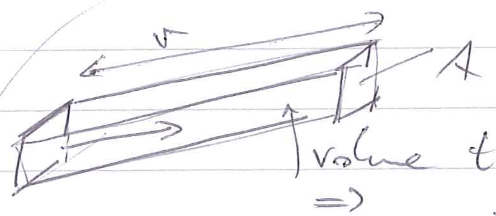
$$\int_0^N dN' = N = \int_0^\infty \frac{1}{\cancel{4}} n v \cdot \cancel{4}\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_BT}} dv.$$

$$= n\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_0^\infty v^3 e^{-\frac{mv^2}{2k_BT}} dv.$$

$$= n\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \cdot \frac{1}{2} \cdot \left(\frac{2k_BT}{m}\right)^2$$

$$= \frac{n (k_BT)^{\frac{1}{2}}}{m^{\frac{1}{2}} \pi^{\frac{1}{2}} 2^{\frac{1}{2}}} = \underline{\underline{n\sqrt{\frac{k_BT}{2\pi m}}}}$$

Note: $dN = \frac{1}{4} n v \underbrace{P(v)\, dv.}_{\substack{\text{fraction} \\ v \to dv + v}}$ # per area per time



volume that can strike area
$\Rightarrow$ $A.v.n$ total # particles

only $\frac{1}{2}$ are to the left $\frac{1}{2}$ & $\frac{1}{2}$ have +ve velocity

$$\int_0^\infty \frac{1}{2} m v^2 \frac{1}{4} n v \cdot 4\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_BT}} dv.$$

$$= \frac{mn\pi}{2} \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_0^\infty v^5 e^{-\frac{mv^2}{2k_BT}} dv.$$

$$= \frac{mn\pi}{2} \cdot \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \left(\frac{2k_BT}{m}\right)^3 = \sqrt{\frac{2}{\pi}}\, n \frac{(k_BT)^{\frac{3}{2}}}{m^{\frac{1}{2}}}.$$

Hence $\langle \frac{1}{2} m v^2 \rangle = \dfrac{\sqrt{\frac{2}{\pi}}\, n \,\frac{(k_B T)^{3/2}}{m^{1/2}}}{n \sqrt{\frac{k_B T}{2\pi m}}}$

$= 2 k_B T.$

The fast particles are more likely to escape, & hence push up the average kinetic energy of the particles that leave.

1 ~~8~~. The temperature of the gas follows from the average kinetic energy:

$$1 eV = \frac{3}{2} k_B T \Rightarrow T \simeq 7730 K.$$

$$\text{or } (k_B T = \tfrac{2}{3} eV)$$

$$P(n=3) = \frac{1}{Z} e^{-\epsilon_3/k_B T} . (2.3^2)$$

$$P(n=1) = \frac{1}{Z} e^{-\epsilon_1/k_B T} . (2.1^2).$$

$$\Rightarrow \frac{P(n=3)}{P(n=1)} = 9 . e^{-(\epsilon_3 - \epsilon_1)/k_B T}.$$

$$= 9 . \exp\left\{ - \frac{13.6 eV}{\frac{2}{3} eV} . \left(-\frac{1}{3^2} + \frac{1}{1^2} \right) \right\}$$

$$= 9 . \exp(-18.1) = 1.2 \times 10^{-7}.$$

2

ϵ ——— $P(\epsilon) \propto e^{-\epsilon/k_BT}$

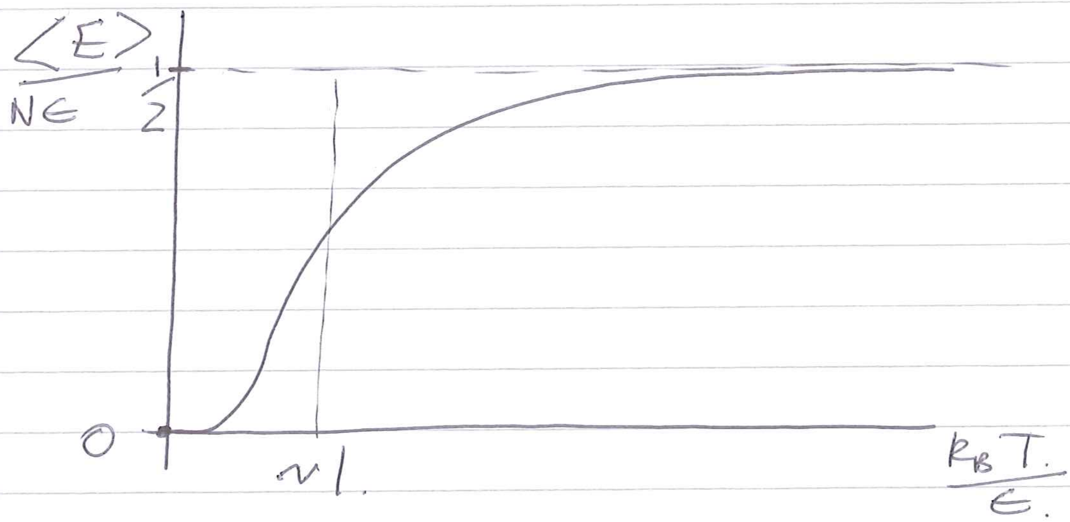
0 ——— $P(0) \propto 1$ (Boltzmann factor)

$\therefore \quad Z = 1 + e^{-\epsilon/k_BT}$

& $\quad P(0) = \dfrac{1}{1+e^{-\epsilon/k_BT}} \qquad P(\epsilon) = \dfrac{1}{1+e^{-\epsilon/k_BT}} \cdot e^{-\epsilon/k_BT}$

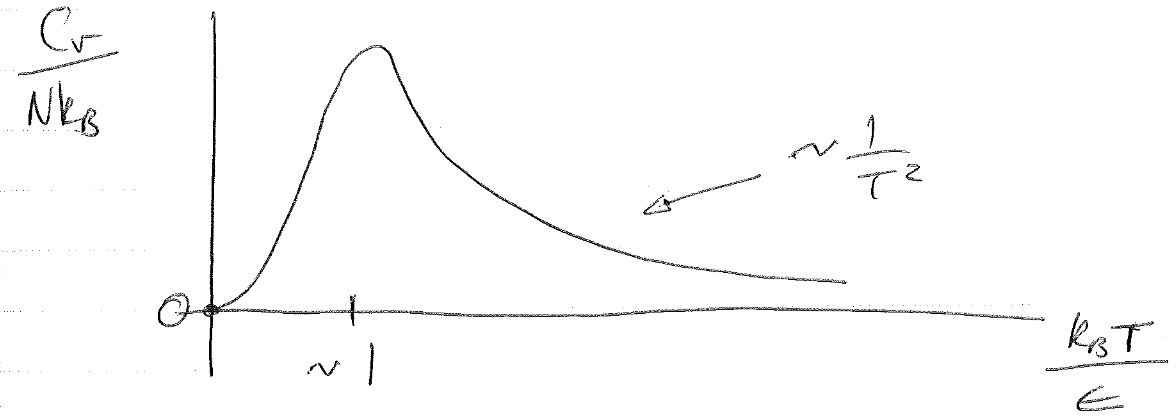
a) $\langle E \rangle = N\big(P(0).0 + P(\epsilon).\epsilon\big)$

$$= \frac{N\epsilon\, e^{-\epsilon/k_BT}}{1+e^{-\epsilon/k_BT}} = \frac{N\epsilon}{e^{\epsilon/k_BT}+1}.$$



b) $C_v = \left.\dfrac{\partial \langle E \rangle}{\partial T}\right|_v$

$$= N\epsilon.\ \frac{1}{(e^{\epsilon/k_BT}+1)^2}\ \frac{\epsilon}{k_BT^2} = Nk_B\left(\frac{\epsilon}{k_BT}\right)^2 \cdot \frac{1}{(e^{\epsilon/k_BT}+1)^2}$$



Energy — for $k_B T \lesssim \epsilon$ there is not enough thermal energy to excite any of the particles $\Rightarrow \langle E \rangle \sim 0$. when $k_B T \sim \epsilon$ the particles have enough thermal energy for some of them to occupy the excited state. $k_B T \gg \epsilon$ the particles are evenly distributed between 0 & ϵ levels.

Heat capacity — • $k_B T \lesssim \epsilon$ — all particles in lowest level & can't absorb heat energy
• $k_B T \sim \epsilon$ — particles excited across gap of ϵ $\Rightarrow$ large heat capacity (Schottky anomaly)
• $k_B T \gg \epsilon$ — particles evenly distributed & no further excitation possible $\Rightarrow C_v \to 0$.

4.

$$Z_{cl} = c \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \; e^{-\left(\frac{p^2}{2m} + \frac{fx^2}{2}\right)\frac{1}{k_B T}}$$

$$= c \sqrt{\frac{\pi}{\left(\frac{1}{2mk_BT}\right)}} \cdot \sqrt{\frac{\pi}{\left(\frac{f}{2k_BT}\right)}}$$

$$= c\,\pi\, 2k_BT \sqrt{\frac{m}{f}} \qquad \text{NB } \omega^2 = \frac{f}{m}$$

$$= c\,\pi\, 2k_BT \frac{1}{\omega}$$

The quantum version (from lectures) is

$$Z_{QM} = e^{-\frac{\hbar\omega}{2}\frac{1}{k_BT}} \frac{1}{1 - e^{-\hbar\omega/k_BT}}$$

Z_{cl} & Z_{QM} are quite different. Z_{QM} should be similar to Z_{cl} at high temperature

for large T:

$$Z_{QM} \simeq \left(1 - \frac{\hbar\omega}{2k_BT}\right) \cdot \frac{k_BT}{\hbar\omega}$$

(expanding exponentials)

$$\simeq \frac{k_BT}{\hbar\omega}$$

$\therefore$ If $2\pi c = \frac{1}{\hbar}$ i.e. $c = \frac{1}{h}$

$\Rightarrow$ the two versions are in agreement at high temperature.

5. If $C_v = 5k_B$ then the system has

$$\frac{5k_B}{\frac{1}{2}k_B} = 10$$ quadratic degrees of freedom

with energy spacing $\epsilon \lesssim k_B T$.

(It may have more that are 'quenched' because the energy levels are 'very widely spaced').

6. For an oxygen molecule

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_B T \simeq 40\ \text{meV}$$

$(T = 300\,\text{K})$.

$$\Rightarrow \langle v^2 \rangle \sim 250 \times 10^3\ \text{m s}^{-1}$$

$$\therefore\ v \sim 500\ \text{m s}^{-1}$$

If $T_0 \longrightarrow 2T_0$

$$\sqrt{\langle v^2 \rangle} \longrightarrow \sqrt{2}\sqrt{\langle v^2 \rangle}$$

3. From lectures

$$P(n=1) = \frac{e^{-\frac{3\hbar\omega}{2k_BT}}}{\left(\frac{e^{-\hbar\omega/2k_BT}}{1-e^{-\hbar\omega/k_BT}}\right)}$$

Boltzmann factor

$$= e^{-\hbar\omega/k_BT} \cdot \left(1 - e^{-\hbar\omega/k_BT}\right).$$

At $T = 1K$

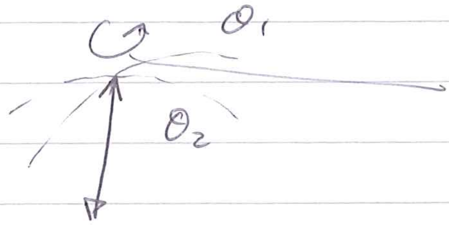
$$\Rightarrow \quad \frac{\hbar\omega}{k_B T} = 1.014$$

$$\therefore \quad p(n=1) \simeq e^{-1}(1 - e^{-1}) = 0.231$$
$$\simeq 23.1\%$$

7. If ϵ is the energy level spacing for the rotational modes

$$\left(\epsilon \sim \frac{\hbar^2}{2I} \text{ in lectures} \right)$$

Then for $k_B T >> \epsilon$ we can use the equipartition theorem. The diatomic molecule has 2 degrees of freedom



these rotations are irrelevant.

$\Rightarrow$ Heat capacity is k_B per molecule.

8. By the equipartition theorem

$$C_V \simeq \frac{1}{2} k_B \times \# \text{d.o.f.}$$

$$= \frac{1}{2} k_B \times (\underbrace{3}_{\text{translation}} + \underbrace{3}_{\text{rotation}} + \underbrace{6}_{\text{vibrational modes}})$$

$$= 6 k_B.$$

Typically the rotational modes are more widely spaced than translational modes. The vibrational modes are more widely spaced still.