Rotational motion of carbon monoxide

$$E_j = j(j+1)\varepsilon \quad j = 0, 1, 2, \ldots$$

$$Z = \frac{kT}{\varepsilon} \qquad kT \gg \varepsilon$$

low-T limit is harder

fortunately room T <u>is</u> high T

for all diatomic gases except H_2.

This applies for all diatomic gases except for one thing

O_2 : $O = O$

$$Z = \frac{kT}{2\varepsilon}$$

($\frac{kT}{\varepsilon}$ overcounts by a factor of 2)

b/c O atoms are identical

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

CO: $-\frac{1}{kT/\varepsilon}\frac{\partial \frac{kT}{\varepsilon}}{\partial \beta}$

O_2: $-\frac{1}{kT/\cancel{2}\varepsilon}\frac{\partial \frac{kT}{\cancel{2}\varepsilon}}{\partial \beta}$

Overall constant factors in Z don't have physical significance – it's like an energy baseline

for both $\langle E \rangle = kT = \frac{2}{2}kT$

equipartition theorem for $f = 2$

Proof of the Equipartition Theorem

Let q be a position or a momentum

$$E = cq^2 \qquad c\text{: constant}$$

$$Z = \sum_s e^{-\beta E_s} = \sum_q e^{-\beta c q^2}$$

if $\Delta E << kT$, $\quad Z = \int_{-\infty}^{\infty} e^{-\beta c q^2}\, dq$

spacing in energy levels

Let $s = \sqrt{\beta c}\, q$

$ds = \sqrt{\beta c}\, dq \rightarrow dq = \frac{ds}{\sqrt{\beta c}}$

$$Z = \int_{-\infty}^{\infty} e^{-s^2} \frac{ds}{\sqrt{\beta c}}$$

$$= \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-s^2}\, ds = C\beta^{-1/2}$$

for some constant C

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\overset{0}{\cancel{\ln C}} - \frac{1}{2}\ln\beta\right]$$

$$= \frac{1}{2}\frac{\partial}{\partial\beta}\ln\beta = \frac{1}{2}\frac{1}{\beta} = \frac{1}{2}kT \; \blacksquare$$

For

$$E = c_1 q_1^2 + c_2 q_2^2 + \cdots + c_n q_n^2$$

$$Z = \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} e^{-\beta c_1 q_1^2} e^{-\beta c_2 q_2^2} \cdots e^{-\beta c_n q_n^2}\, dq_1\, dq_2 \cdots dq_n$$

$$= \int_{-\infty}^{\infty} e^{-\beta c_1 q_1^2} dq_1 \int_{-\infty}^{\infty} e^{-\beta c_2 q_2^2} dq_2 \cdots \int_{-\infty}^{\infty} e^{-\beta c_n q_n^2} dq_n$$

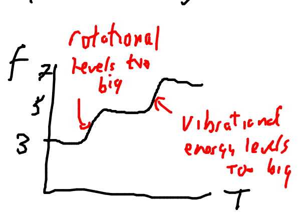
$$C_1 \beta^{-1/2} \qquad C_2 \beta^{-1/2} \qquad \cdots \qquad C_n \beta^{-1/2}$$

$$Z = \mathbb{C}\, \beta^{-n/2}$$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial\beta}\left[\ln \mathbb{C} - \frac{n}{2}\ln\beta\right]$$

$$= \frac{n}{2}\frac{1}{\beta} = \frac{1}{2}nkT \; \blacksquare$$

We've seen that f can be fractional in practice.



This is when

$kT << \Delta E$

level energy spacing

for some types of d.o.f.

eg. Maxwell Speed Distribution

What is the average speed of a molecule in a gas?

One possibility: root-mean-square speed

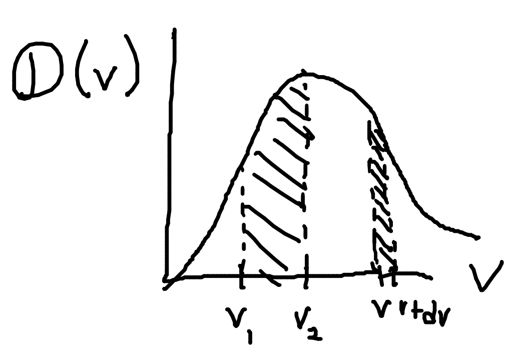
$$\langle \tfrac{1}{2} m \underbrace{v^2}_{} \rangle = \tfrac{3}{2} kT \qquad (v_x^2+v_y^2+v_z^2)$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

$\langle v^2 \rangle \neq \langle v \rangle^2$

• Probability that N_2 molecule has $v = 3\ m/s$ exactly?
0% (speed is continuous)

Define a probability distribution



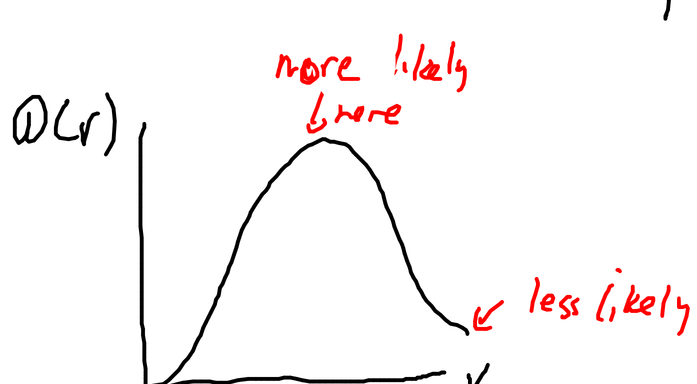
$P(v_1 < v < v_2)$ = area under $D(v)$ between v_1 & v_2

$$P = \int_{v_1}^{v_2} D(v)\, dv$$

Distributions are meant to be integrated
e.g. Dirac delta "function" $\delta(x)$
(really, distribution)

Probability that speed is between v & $v+dv$

$$P = D(v)\, dv$$



$$\int_{-\infty}^{\infty} D(v)\, dv = 1$$