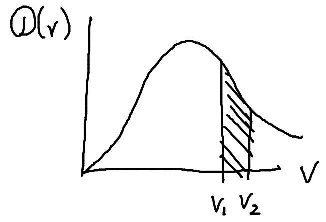
Maxwell Speed Distribution

What is probability that a gas molecule is moving at a certain speed v?



$\mathcal{D}(v)$ is a probability distribution

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

$$P(v \simeq v_1) = P(v_1 < v < v_1 + dv) = \mathcal{D}(v_1)\,dv$$

Normalized

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

For a particle in an ideal gas, ...

speed describes a macrostate

velocity $\vec{v}$ that describes a microstate

$V_x = 1\,m/s$, $V_y = 0\,m/s$ | $V_y = 1\,m/s$, $V_x = 0\,m/s$ | $V_x = -\sqrt{2}\,m/s$, $V_y = \sqrt{2}\,m/s$

different microstates

same speed macrostate $v = 1\,m/s$

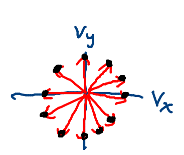
$$\mathcal{D}(v) = \begin{pmatrix}\text{probability that a}\\ \text{particle has a velocity}\\ \vec{v}\ \&\ |\vec{v}| = v\end{pmatrix} \times \begin{pmatrix}\text{number of vectors } \vec{v}\\ \text{with magnitude } v\end{pmatrix}$$

probability of a microstate via Boltzmann statistics × multiplicity of the macrostate

$$P = \frac{e^{-E/kT}}{Z}$$

$$e^{-mv^2/2kT} \times 4\pi v^2$$

surface area of sphere radius v



all $\vec{v}$ with a given $|\vec{v}| = v$

points is proportional to circumference of circle $2\pi v$

$$\mathcal{D} = C\, 4\pi v^2 e^{-mv^2/2kT}$$

$$1 = \int_0^{\infty} \mathcal{D}(v)\,dv = 4\pi C \int_0^{\infty} v^2 e^{-mv^2/2kT}\,dv$$

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

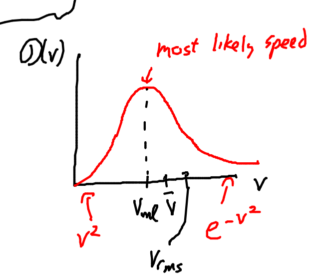
$$1 = 4\pi C \left(\frac{2kT}{m}\right)^{3/2} \underbrace{\int_0^{\infty} x^2 e^{-x^2}\,dx}_{\to \frac{\sqrt{\pi}}{4}}$$

$$C = \frac{1}{4\pi\left(\frac{2kT}{m}\right)^{3/2}\frac{\sqrt{\pi}}{4}}$$

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

Maxwell Speed Distribution

- for small v, $\mathcal{D}(v) \sim v^2$
- for large v, $\mathcal{D}(v) \sim e^{-v^2}$



most likely speed where $\mathcal{D}'(v) = 0$

$$v = \sqrt{\frac{2kT}{m}}$$

$$\langle v \rangle = \sum_v v P(v) = \int_0^{\infty} v\,\mathcal{D}(v)\,dv = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{2.55kT}{m}} > v_{ml}$$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = 1.22\,v_{ml} = 1.08\langle v \rangle$$

Z & F

- Z is like Ω
  so $\ln Z$ may be important too
- Natural variables of Z: T, V, N
  just like F!

Define $f = -kT \ln Z$

- $\frac{\partial f}{\partial T} = -k \ln Z - kT \frac{\partial \ln Z}{\partial T}$

$$\frac{\partial f}{\partial T} = +\frac{f}{T} - \cancel{kT} \frac{U\cancel{\beta}}{T}$$

$$\frac{\partial f}{\partial T} = \frac{f}{T} - \frac{U}{T} = \frac{f-U}{T}$$

Prove $f = F$.

$\beta = \frac{1}{kT}$

$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$ $\quad T = \frac{1}{k}\beta^{-1}$

$= -\frac{\partial \ln Z}{\partial T} \frac{\partial T}{\partial \beta}$

$= -\frac{\partial \ln Z}{\partial T}\left(-\frac{1}{k}\beta^{-2}\right)$

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

$\frac{\partial \ln Z}{\partial T} = \frac{\langle E \rangle \beta}{T}$

$\langle E \rangle = U$

$dF = -S\,dT + \dots$

Compare

$S = -\frac{\partial F}{\partial T}$

$$F = U - TS = U + T\frac{\partial F}{\partial T}$$

$$\rightarrow \frac{\partial F}{\partial T} = \frac{F-U}{T}$$

Same differential equation!