Last time:

Z for ideal gas:

$$Z_1 = \frac{1}{\left(\frac{\hbar}{2}\right)^3} \int e^{-\left(\frac{p_x^2+p_y^2+p_z^2}{2mkT}\right)} dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$

$$= \frac{1}{\left(\frac{\hbar}{2}\right)^3} V \int e^{\frac{-p_x^2+p_y^2+p_z^2}{2mkT}} dp_x\,dp_y\,dp_z$$

$$= \frac{V}{\left(\frac{\hbar}{2}\right)^3} \left[\int_{-\infty}^{\infty} e^{\frac{-p^2}{2mkT}} dp\right]^3$$

$$= \frac{V}{\left(\frac{\hbar}{2}\right)^3} \left[\sqrt{2mkT} \int_{-\infty}^{\infty} e^{-x^2} dx\right]^3$$

$$Z_1 = \frac{V}{\left(\frac{\hbar}{2}\right)^3} (2mkT)^{3/2} \pi^{3/2}$$

$$Z_1 = V\left(\frac{2\pi m k T}{\hbar^2}\right)^{3/2} \qquad \left(\frac{h}{2} \to \hbar\right)$$

$$Z_N = \frac{V^N \left(\frac{2\pi m k T}{\hbar^2}\right)^{\frac{3N}{2}}}{N!}$$

What is $\frac{2\pi m k T}{\hbar^2}$?

Dimensions: $\frac{M \cdot E}{E^2 \cdot T^2} = \frac{M}{E \cdot T^2} = \frac{M}{M \frac{L^2}{T^2} T^2} = \frac{1}{L^2}$

$\sqrt{\frac{\hbar^2}{2\pi m k T}}$ is a length

Call it the thermal de Broglie wavelength

$$\lambda_T = \sqrt{\frac{\hbar^2}{2\pi m k T}}$$

de Broglie wavelength

$\lambda = \frac{h}{p}$, wavelength of ψ (distance over which matter is wavelike)

For an ideal gas, $\frac{p^2}{2m} = E \longrightarrow p = \sqrt{2mE}$

$$\lambda = \frac{h}{\sqrt{2mE}}$$

$$U = NE = \frac{3}{2}NkT$$

$$E = \frac{3}{2}kT$$

$$\lambda = \frac{h}{\sqrt{3mkT}}$$

compare to: $\lambda_T = \sqrt{\frac{\hbar^2}{2\pi mkT}}$

Interpretation: λ_T is the average de Broglie wavelength

$$Z_N = \frac{1}{N!}\frac{V^N}{\lambda_T^{3N}}, \quad \lambda_T = \sqrt{\frac{\hbar^2}{2\pi mkT}}$$

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

$$\frac{\partial}{\partial\beta} Z = \frac{1}{N!} V^N \frac{\partial}{\partial\beta}\left(\lambda_T^{-3N}\right)$$

$$= \frac{V^N}{N!}(-3N)\lambda_T^{-3N-1} \frac{\partial}{\partial\beta}\lambda_T$$

$$= -3N \frac{V^N}{N!}\lambda_T^{-(3N+1)} \frac{\partial}{\partial\beta}\left(\frac{\hbar^2\beta}{2\pi m}\right)^{1/2}$$

$$= -3N \frac{V^N}{N!}\lambda_T^{-(3N+1)} \cdot \frac{1}{2}\left(\frac{\hbar^2\beta}{2\pi m}\right)^{-\frac{1}{2}}\left(\frac{\hbar^2}{2\pi m}\right)$$

$$= -\frac{3N}{2}\frac{V^N}{N!}\lambda_T^{-(3N+1)} \frac{1}{\lambda_T} \frac{\lambda_T^2}{\beta}$$

$$= -\frac{3}{2}N \frac{V^N}{N!}\frac{\lambda_T^{-3N}}{\beta}$$

$$\frac{\partial}{\partial\beta} Z = -\frac{3}{2}N\frac{1}{\beta} Z$$

$$U = -\frac{1}{Z}\frac{\partial}{\partial\beta} Z = \frac{3}{2}N\beta = \frac{3}{2}NkT$$

$S, \quad P, \quad \mu ?$

Use $\quad F = -kT \ln Z$

$$Z_N = \frac{1}{N!} \frac{V^N}{\lambda_T^{3N}}$$

$$\ln Z = \ln V^N - \ln N! - \ln \lambda_T^{3N}$$

$$F = -kT \left[N \ln V - \ln N! - 3N \ln \lambda_T \right]$$

$p = ?$ (ask)

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$-\left(\frac{\partial F}{\partial V}\right)_{T,N} = P$$

$$\boxed{P = \frac{kTN}{V}}$$

$S: \quad F = U - TS$

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

A few more interesting results before we move on

Way back in chapter 1, we used equipartition to estimate the average speed of a gas molecule

$$U = \frac{3}{2} NKT$$

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

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

$$V_{rms} \neq V_{avg}$$

5, 7, 4, 9, 2

$$\sqrt{\frac{25+49+16+81+4}{5}} = 5.92$$

vs

$$\frac{5+7+4+9+2}{5} = 5.4$$

Of course, we could find $\langle v \rangle$ very easily

(Ask)

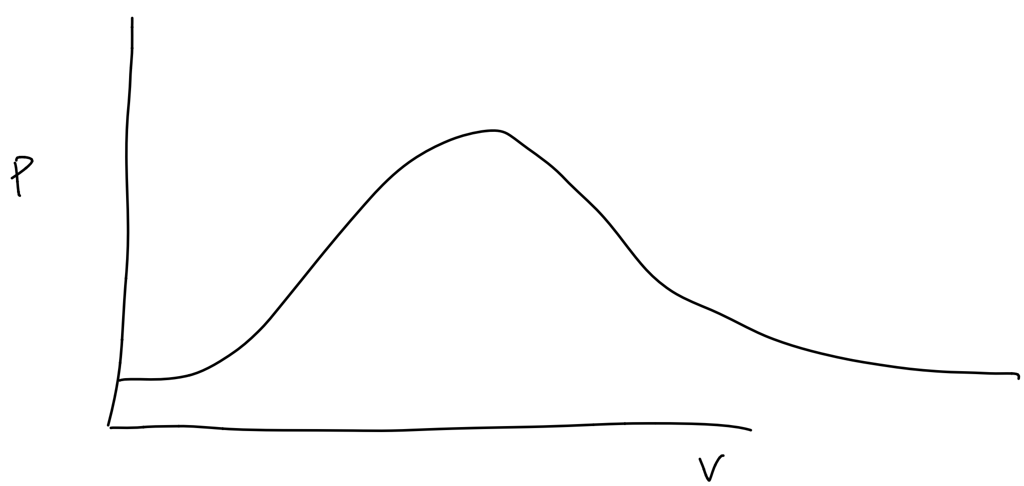
$$\langle v \rangle = \sum_{s} \frac{v e^{\frac{-mv^2}{2kT}}}{Z}$$

$$\langle v \rangle = \frac{1}{Z} \frac{1}{h^3} \int v e^{\frac{-mv^2}{2kT}} \, dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$

We want to take this a step further

We want the probability distribution for the speed

If I pick a molecule at random, what is the probability its speed is v?



Since v is continuous, it doesn't make sense to ask what is $P(\text{exactly } v)$

Instead, we want $P(v_1 < v < v_2)$

P that v is with (v_1, v_2)

$$= P(v = v_1 \text{ or } v = v_1 + dv \text{ or } v = v_1 + 2dv \text{ or } \ldots)$$

$$= P(v = v_1) + P(v = v_1 + dv) + \ldots$$

$$= \frac{1}{Z} \sum_{v_1 \to v_2} e^{-\frac{mv^2}{2kT}}$$

$$\sum e^{-\frac{mv^2}{2kT}} \longrightarrow \frac{1}{h^3} \underbrace{\int e^{-\frac{mv^2}{2kT}} dx\,dy\,dz\,dp_x\,dp_y\,dp_z}_{\text{integrate over } \vec{r}}$$

$$= \frac{V}{h^3} m^3 \int e^{-\frac{mv^2}{kT}} dv_x\,dv_y\,dv_z$$

v_x, v_y, v_z are not independent, since what we want is $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$

So switch to spherical coords

$$dv_x\,dv_y\,dv_z \longrightarrow v^2 \sin\theta \, dv\, d\theta\, d\phi$$

$$P(v_1 < v < v_2) = \frac{1}{Z}\frac{V}{\hbar^3}m^3 \int_0^{2\pi} \phi\, d\phi \int_0^{\frac{\pi}{2}} \sin\theta\, d\theta \int_{v_1}^{v_2} v^2 e^{\frac{-mv^2}{2kT}}\, dv$$

$$P(v_1 < v < v_2) = \frac{1}{Z}\frac{Vm^3 4\pi}{\hbar^3} \int_{v_1}^{v_2} v^2 e^{\frac{-mv^2}{2kT}}\, dv$$

$$= \frac{\lambda_T^3}{V}\frac{Vm^3 4\pi}{\hbar^3} \int_{v_1}^{v_2} v^2 e^{\frac{-mv^2}{2kT}}\, dv$$

$$\frac{\lambda_T}{\hbar^3} = \left(\frac{\hbar^2}{2\pi mkT}\right)^{3/2} = \left(\frac{1}{2\pi mkT}\right)^{3/2}$$

$$P(v_1 < v < v_2) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_{v_1}^{v_2} v^2 e^{\frac{-mv^2}{2kT}}\, dv$$

Note: $\int_0^{\infty} (\ ) = 1$

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

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

$$\langle v \rangle = \sum_v v D(v) \rightarrow \int_0^\infty v D(v)\,dv$$

$$\langle v \rangle = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}}\,dv$$

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

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

$$dv = \sqrt{\frac{2kT}{m}}\, dx$$

$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT}{m}\right)^2 \int_0^\infty x^3 e^{-x^2}\,dx$$

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

$$\int_0^\infty x^3 e^{-x^2}\,dx$$

To understand how to integrate, first consider

$$\int_0^\infty x^2 e^{-x^2}\,dx$$

$$= \int_0^\infty x^2 e^{-sx^2}\,dx, \quad s=1$$

$$= \int_0^\infty -\frac{\partial}{\partial s}\left(e^{-sx^2}\right) dx$$

$$= -\frac{\partial}{\partial s}\int_0^\infty e^{-sx^2}\,dx$$

$f(x) = e^{-sx^2}$ is an <u>even</u> function

$$f(x) = f(-x)$$

$$\int_0^\infty e^{-sx^2}\,dx = \int_{-\infty}^0 e^{-sx^2}\,dx; \quad \int_{-\infty}^\infty e^{-sx^2}\,dx = \int_{-\infty}^0 + \int_0^\infty$$

$$\int_{-\infty}^{\infty} e^{-sx^2}\,dx = 2\int_{-\infty}^{0} e^{-sx^2}\,dx = 2\int_{0}^{\infty} e^{-sx^2}\,dx$$

$$\int_{0}^{\infty} x^2 e^{-x^2}\,dx = -\frac{\partial}{\partial s}\int_{0}^{\infty} e^{-sx^2}\,dx = \frac{-1}{2}\frac{\partial}{\partial s}\int_{-\infty}^{\infty} e^{-sx^2}\,dx$$

$$\int_{-\infty}^{\infty} e^{-sx^2}\,dx$$

$$\chi = \sqrt{s}\,x$$

$$\int_{-\infty}^{\infty} e^{-sx^2}\,dx = \frac{1}{\sqrt{s}}\int_{-\infty}^{\infty} e^{-\chi^2}\,d\chi = \sqrt{\frac{\pi}{s}}$$

$$\int_{0}^{\infty} x^2 e^{-sx^2}\,dx = -\frac{1}{2}\frac{\partial}{\partial s}\left(\frac{\pi}{s}\right)^{1/2}$$

$$= \left(-\frac{1}{2}\right)\left(\frac{1}{2}\right)\left(\frac{\pi}{s}\right)^{-\frac{1}{2}}\left(\frac{-\pi}{s^2}\right)$$

$$= \frac{1}{4}\sqrt{\frac{s}{\pi}}\left(\frac{\pi}{s^2}\right)\Bigg|_{s=1}$$

$$= \frac{\sqrt{\pi}}{4}$$

$$\langle v \rangle = \frac{4}{\sqrt{\pi}} \left(\frac{2kT}{m} \right)^{1/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv$$

$$\Big\downarrow \; x = \sqrt{\frac{m}{2kT}}\, v$$

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

$$\int_0^\infty x^3 e^{-x^2} dx = \int_0^\infty -x \frac{\partial}{\partial s} e^{-sx^2} dx$$

$$= -\frac{\partial}{\partial s} \int_0^\infty x e^{-sx^2} dx$$

$u = x^2$

$du = 2x\,dx$

$$= -\frac{\partial}{\partial s} \int_0^\infty \frac{1}{2} e^{-su} du = -\frac{1}{2}\frac{\partial}{\partial s}\left[\frac{-1}{s}(0-1) \right]$$

$$= \frac{1}{2s^2} = \frac{1}{2}$$

$$\int_0^\infty x^3 e^{-x^2} dx = \frac{1}{2}$$

$$\langle v \rangle = \frac{4}{\sqrt{\pi}} \left(\frac{2KT}{m}\right)^{1/2} \int_0^\infty x^3 e^{-x^2} dx$$

$$= \frac{2}{\sqrt{\pi}} \left(\frac{2KT}{m}\right)^{\frac{1}{2}}$$

$$\boxed{\langle v \rangle = \left(\frac{8KT}{\pi m}\right)^{1/2}}$$

$$\langle v^2 \rangle = \left(\frac{m}{2\pi KT}\right)^{3/2} 4\pi \int_0^\infty v^4 e^{-\frac{mv^2}{2KT}} dv$$

$$\langle v^2 \rangle = \frac{3KT}{m} \longrightarrow \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3KT}{m}}$$

$$\sigma_v^2 = \left(\langle v^2 \rangle - \langle v \rangle^2 \right)$$

$$\sigma_v^2 = \left(3 - \frac{8}{\pi}\right) \frac{KT}{m}$$

$$\sigma_v = \sqrt{\left(3 - \frac{8}{\pi}\right) \frac{KT}{m}}$$

N_2: $m = \frac{28\,g}{mol} = 4.6 \times 10^{-26}\,kg$

$K = 1.38 \times 10^{-23} \frac{J}{K}$

$T = 293\ K$

$$V_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3KT}{m}} = 514\ \frac{m}{s}$$

$$V_{avg} = \langle v \rangle = \sqrt{\frac{8}{\pi}\frac{KT}{m}} = 473\ \frac{m}{s}$$

$$E = c_1 q_1^2 + c_2 q_2^2 + \dots$$

$$= \sum_1^f c_i q_i^2$$

$$Z = \sum_{\vec{s}} e^{-\frac{1}{kT}\sum c_i q_i^2}$$

$$Z = \frac{1}{\Delta q^f} \int e^{-\frac{1}{kT}\sum_1^f c_i q_i^2} dq_1 dq_2 \cdots dq_f$$

$$= \frac{1}{\Delta q^f} \int e^{-\frac{1}{kT} c_1 q_1^2} e^{-\frac{1}{kT} c_2 q_2^2} \cdots e^{-\frac{1}{kT} c_f q_f^2} dq_1 dq_2 \cdots dq_f$$

$$= \frac{1}{\Delta q^f} \left[\int e^{-\frac{1}{kT} c q^2} dq \right]^f$$

$$x = \sqrt{\frac{c}{kT}}\, q$$

$$dx = \sqrt{\frac{c}{kT}}\, dq$$

$$Z = \frac{1}{\Delta q^f} \left[\sqrt{\frac{kT}{c}} \int_{-\infty}^{\infty} e^{-x^2} dx \right]^f$$

$$Z = \frac{1}{\Delta q^f} \left(\sqrt{\frac{\pi kT}{c}} \right)^f = \frac{1}{\Delta q^f} \left(\frac{\pi kT}{c} \right)^{\frac{f}{2}}$$

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

$$\frac{\partial}{\partial \beta} Z = \frac{1}{\Delta q^f}\frac{\partial}{\partial \beta}\left(\frac{\pi}{c\beta}\right)^{\frac{f}{2}}$$

$$= \frac{1}{\Delta q^f}\frac{f}{2}\left(\frac{\pi}{c\beta}\right)^{\frac{f}{2}-1}\left(\frac{-\pi}{c\beta^2}\right)$$

$$= \frac{-1}{\Delta q^f}\frac{f}{2}\left(\frac{\pi}{c\beta}\right)^{\frac{f}{2}}\left(\frac{1}{\beta}\right)$$

$$\langle E \rangle = \frac{1}{Z}\frac{1}{\Delta q^f}\frac{f}{2}\left(\frac{\pi}{c\beta}\right)^{\frac{f}{2}}\left(\frac{1}{\beta}\right)$$

$$Z = \frac{1}{\Delta q^f}\left(\frac{\pi}{c\beta}\right)^{\frac{f}{2}}$$

$$\langle E \rangle = \frac{1}{Z}\cdot\frac{f}{2}\cdot Z\cdot\frac{1}{\beta}$$

$$\langle E \rangle = \frac{1}{2} f \frac{1}{\beta} = \frac{1}{2} f k T$$

$$\langle E \rangle = \frac{1}{2} f k T$$

$$U = N\langle E \rangle = \frac{1}{2} N f k T$$