

1. For the equation:

$$f(v_x) = Ae^{-\gamma v_x^2}$$

determine whether γ must be strictly positive, strictly negative, or either by considering limits.

As speed $v_x \rightarrow \pm\infty$ $f(v_x) \rightarrow 0$ since the probability must be finite. If $\gamma < 0$, then exponent is positive, and the limit diverges. Therefore $\gamma > 0$

2. Without looking at the slides for the result, evaluate $\langle v_x^+ \rangle$ and $\langle v_x \rangle$. $\langle v_x^+ \rangle$ denotes the average of positive values of v_x . Potentially useful integrals:

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-Mv_x^2/2RT}$$

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}} \quad \int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a} \quad \text{for } a > 0$$

$$\begin{aligned} \langle v_x^+ \rangle &= \int_0^{\infty} v_x f(v_x) dv_x = \left(\frac{M}{2\pi RT}\right)^{1/2} \int_0^{\infty} v_x e^{-Mv_x^2/2RT} dv_x \quad \left(a = \frac{M}{2RT}\right) \\ &= \left(\frac{M}{2\pi RT}\right)^{1/2} \cdot \frac{1}{2\left(\frac{M}{2RT}\right)} = \left(\frac{M}{2\pi RT}\right)^{1/2} \cdot \frac{RT}{M} \\ &= \left(\frac{RT}{2\pi M}\right)^{1/2} \end{aligned}$$

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dv_x = \left(\frac{M}{2\pi RT}\right)^{1/2} \int_{-\infty}^{\infty} v_x e^{-Mv_x^2/2RT} dv_x = 0$$

v_x is odd function, e^{-x^2} is an even function. Odd \times even is odd, and integral of odd is 0.

3. For the speed distribution, show that $\langle u \rangle = \sqrt{\frac{8RT}{\pi M}}$. Potentially useful integral:

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

$$\begin{aligned} \langle u \rangle &= \int_0^{\infty} u F(u) du = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^{\infty} u^3 e^{-Mu^2/2RT} du \quad \left(a = \frac{M}{2RT}\right) \\ \int_0^{\infty} u^3 e^{-au^2} du &= \frac{1}{2a^2} = \frac{1}{2} \left(\frac{2RT}{M}\right)^2 \\ \langle u \rangle &= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \cdot \frac{1}{2} \left(\frac{2RT}{M}\right)^2 \\ &= 2\pi \cdot M^{-1/2} \cdot (2RT)^{1/2} \cdot (2\pi)^{-3/2} \\ &= \sqrt{\frac{8RT}{\pi M}} \end{aligned}$$

4. (a) Derive an expression for u_{probable} .

$$\frac{dF}{du} = 0$$

The constant terms disappear when we take the derivative and set to 0

$$\begin{aligned} F(u) &= \cancel{4\pi} u^2 \left(\frac{M}{\cancel{2\pi RT}} \right)^{3/2} e^{-Mu^2/2RT} \\ &= u^2 e^{-Mu^2/2RT} \\ \frac{dF}{du} &= 2u e^{-Mu^2/2RT} + u^2 \left(-\frac{M}{RT} \right) u e^{-Mu^2/2RT} \\ \frac{dF}{du} &= u e^{-Mu^2/2RT} \left(2 - \frac{Mu^2}{RT} \right) \\ 0 &= 2 - \frac{Mu_p^2}{RT} \implies u_{\text{probable}} = \sqrt{\frac{2RT}{M}} \end{aligned}$$

- (b) Rank the characteristic speeds u_{rms} , u_{probable} and $\langle u \rangle$ in ascending order.

$$u_{\text{probable}} = \sqrt{\frac{2RT}{M}} < \langle u \rangle = \sqrt{\frac{8RT}{\pi M}} < u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

- (c) Compute u_{rms} , u_{probable} and $\langle u \rangle$ numerically for N_2 at 298 K and rank them in ascending order. Does this match our expectations?

Watch for units on molar mass!

$$\begin{aligned} M_{\text{N}_2} &= 28.02 \times 10^{-3} \frac{\text{kg}}{\text{mol}} & R &= 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} & T &= 298 \text{ K} \\ u_{\text{probable}} &= \sqrt{\frac{2(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298 \text{ K})}{0.02802 \frac{\text{kg}}{\text{mol}}}} = 421 \frac{\text{m}}{\text{s}} \\ \langle u \rangle &= \sqrt{\frac{8(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298 \text{ K})}{\pi(0.02802 \frac{\text{kg}}{\text{mol}})}} = 475 \frac{\text{m}}{\text{s}} \\ u_{\text{rms}} &= \sqrt{\frac{3(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298 \text{ K})}{0.02802 \frac{\text{kg}}{\text{mol}}}} = 515 \frac{\text{m}}{\text{s}} \\ 421 \frac{\text{m}}{\text{s}} &< 475 \frac{\text{m}}{\text{s}} < 515 \frac{\text{m}}{\text{s}} \implies u_p < \langle u \rangle < u_{\text{rms}} \checkmark \end{aligned}$$

Homework Problem 31

1. Compute $\langle v_x^2 \rangle$ to verify the result from lecture, $\langle v_x^2 \rangle = \frac{RT}{M}$.

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$