

# OVERVIEW

- Molecular speeds
- Maxwell distribution
- Boltzmann distribution

# MOLECULAR SPEEDS I

Temperature is the measure of the average (translational) kinetic energy of the molecules

$$\frac{m\langle v^2 \rangle}{2} = \frac{3}{2} k_B T$$

Define the so-called *root mean square* (rms) speed

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

$v_{\text{rms}}$

- increases with temperature
- is smaller for heavier molecules

# MOLECULAR SPEEDS II

What exactly is  $\langle \dots \rangle$ ?

For  $N$  molecules

$$\langle v_x^2 \rangle \equiv \frac{1}{N} \underbrace{(v_{x;1}^2 + v_{x;2}^2 + \dots + v_{x;N}^2)}_{N \text{ terms}}$$

where the sum is over all the molecules.

**Q:** How many molecules have a given value of  $v_x$ ?

**A:** Can't really tell,  $v_x$  is a continuous variable

**Q:** How many molecules have  $v_x$  in a certain interval  $dv_x$ ?

# VELOCITY DISTRIBUTION

The number of molecules with  $v_x$  between  $v_x$  and  $v_x + dv_x$ :

$$dN = Nf(v_x) dv_x$$

where  $f(v_x)$  is the *distribution function*.

Two equivalent interpretations:  $f(v_x) dv_x$  is

- the fraction of molecules with  $x$ -projections of velocity between  $v_x$  and  $v_x + dv_x$
- the *probability* that a randomly chosen molecule has  $v_x$  in this interval

# VELOCITY DISTRIBUTION II

Normalization (the probabilities sum to unity):

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1$$

$$\int_{v_1}^{v_2} f(v_x) dv_x = \text{fraction of molecules with } v_x \text{ between } v_1 \text{ and } v_2$$

Averages:

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dv_x$$

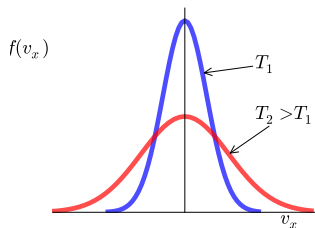
$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x) dv_x$$

By symmetry  $f(-v_x) = f(v_x) \Rightarrow \langle v_x \rangle = 0$ , but  $\langle v_x^2 \rangle \neq 0$

# MAXWELL DISTRIBUTION

Ideal gas *only*

Maxwell distribution (for *velocity projection*):

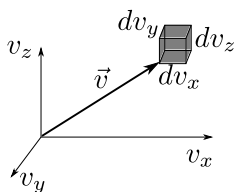


$$f(v_x) = \left( \frac{m}{2\pi k_B T} \right)^{1/2} \exp \left( -\frac{mv_x^2}{2k_B T} \right)$$

- is symmetric around zero
- the width is given by the temperature

# MAXWELL DISTRIBUTION

**Q:** What is the distribution of the *velocity*, rather than velocity *projection*?



$$v = |\vec{v}| = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

Need to: (i) find probability that all three projections of  $\vec{v}$  are within a cube  $d\Omega$ , and then (ii) integrate over the possible directions of  $\vec{v}$ .

$$\begin{aligned}\text{Prob}(v_x, v_y, v_z \in d\Omega) &= f(v_x) dv_x \cdot f(v_y) dv_y \cdot f(v_z) dv_z \\ &\propto \exp\left(-\frac{mv^2}{2k_B T}\right) dv_x dv_y dv_z\end{aligned}$$

# MAXWELL DISTRIBUTION

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Since this does not have any angular dependence, integrating over the directions is easy:

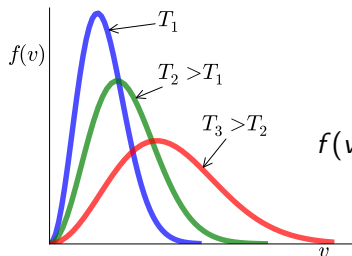
$$\int\int_{\text{angles}} (\dots) dv_x dv_y dv_z = 4\pi v^2 dv$$

Finally,

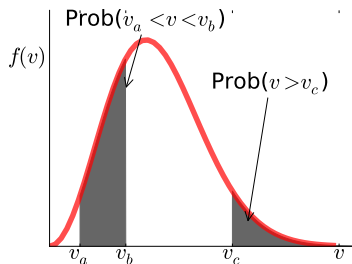
$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$



# MAXWELL DISTRIBUTION



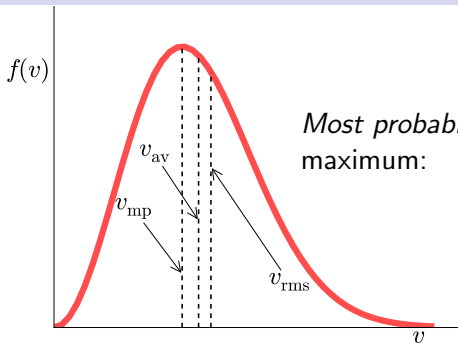
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Normalization:

$$\int_0^{\infty} f(v) dv = 1$$

# CHARACTERISTIC VELOCITIES OF THE MAXWELL DISTRIBUTION



*Most probable speed:*  $v$  at which  $f(v)$  has maximum:

$$v_{\text{mp}} = \sqrt{\frac{2k_B T}{m}}$$

*Average speed:*  $v_{\text{av}} = \langle v \rangle = \int_0^\infty v f(v) dv = \sqrt{\frac{8k_B T}{\pi m}}$

*rms speed:*  $v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \left( \int_0^\infty v^2 f(v) dv \right)^{1/2} = \sqrt{\frac{3k_B T}{m}}$

## MAXWELL DISTRIBUTION

$$\mathbf{Prob}(v_x \in [u, u + dv_x]) \propto \exp\left(-\frac{mu^2/2}{k_B T}\right) dv_x$$

## GIBBS DISTRIBUTION

In fact, a more general result holds: if the energy of a system depends on some variable  $\xi$ , then in thermal equilibrium

$$\mathbf{Prob}(\xi \in [\xi, \xi + d\xi]) \propto \exp\left(-\frac{E(\xi)}{k_B T}\right) d\xi$$

For ideal gases, this was first derived by L. Boltzmann, later generalized by J. Gibbs.

# EXAMPLE: MAXWELL-BOLTZMANN DISTRIBUTION

ISOTHERMAL ATMOSPHERE:  $T = \text{const}$

The energy of a single molecule is  $E = \frac{mv^2}{2} + mgh$ , hence the *joint distribution* of  $v$  and  $h$ ,

$$f(v, h) \propto v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \exp\left(-\frac{mgh}{k_B T}\right)$$

Intuitively,  $f(v, h)$  is a fraction of molecules with velocities around  $v$  at altitudes around  $h$ .

Formally:

$$f(v) = \int_0^\infty f(v, h) dh \quad (\text{Maxwell distribution})$$

$$f(h) = \int_0^\infty f(v, h) dv \quad \text{gives density variation with the altitude}$$

Real atmosphere is  
a little more  
complicated.

Image credits:  
NOAA.

