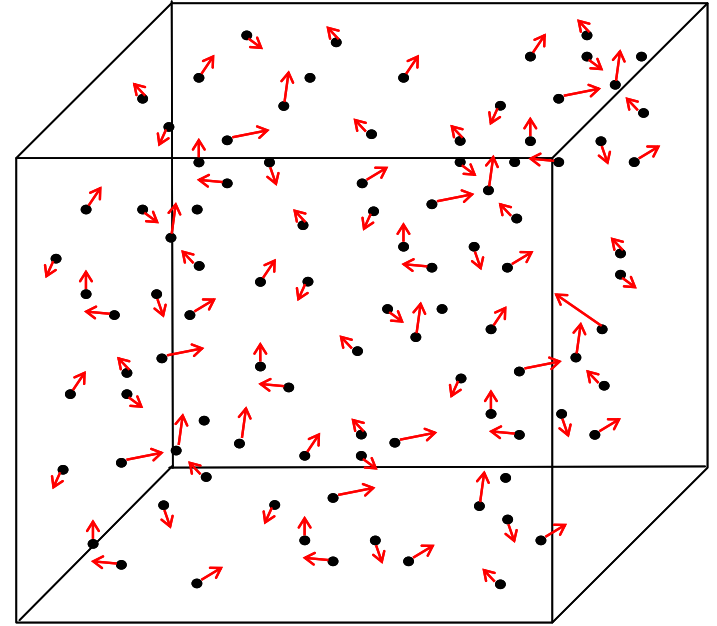# Maxwell – Boltzmann distribution for molecular velocities

James Clerk Maxwell
(1831-1879)

Ludwig Boltzmann
(1844 – 1906)

The velocity distribution is derived for an ideal gas based on very simple assumptions:

• The distribution of velocity is isotropic in all directions (spatial homogeneity)

• The velocity distributions in the x, y, and z directions are independent and identical

• External factors enter into the distribution function for the velocity

• We later derive the distribution function using statistical mechanics

Kinetic Theory of Gases: A Mechanistic Viewpoint of Gas Properties

Ideal Gas Model:
- Atoms are small hard spheres which only interact upon collision
- The volume of the atoms is much smaller than the volume of the gas
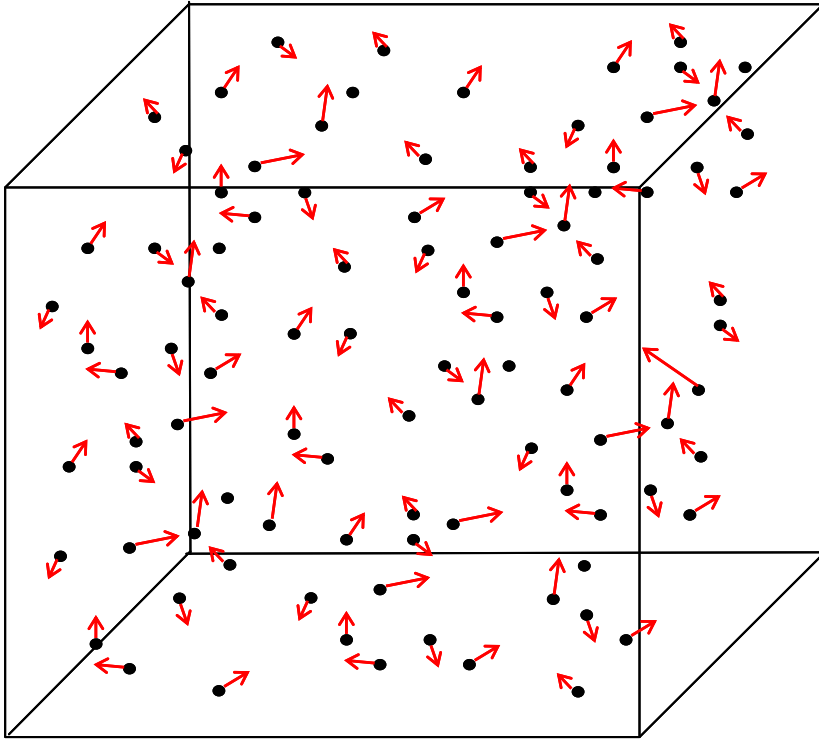
v : speed of the gas molecules

v_x, v_y, v_z: components of velocity of the gas molecules

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

- We assume there is no bias in the distribution of the velocity components v_x, v_y, v_z
- The choice of coordinate system is arbitrary

The average of the square of the velocity components is identical in all directions

$$\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle = \left\langle v^2 \right\rangle / 3$$

Why not state the average of the velocity components?

Preamble: Relating velocity distribution to macroscopic pressure of an ideal gas
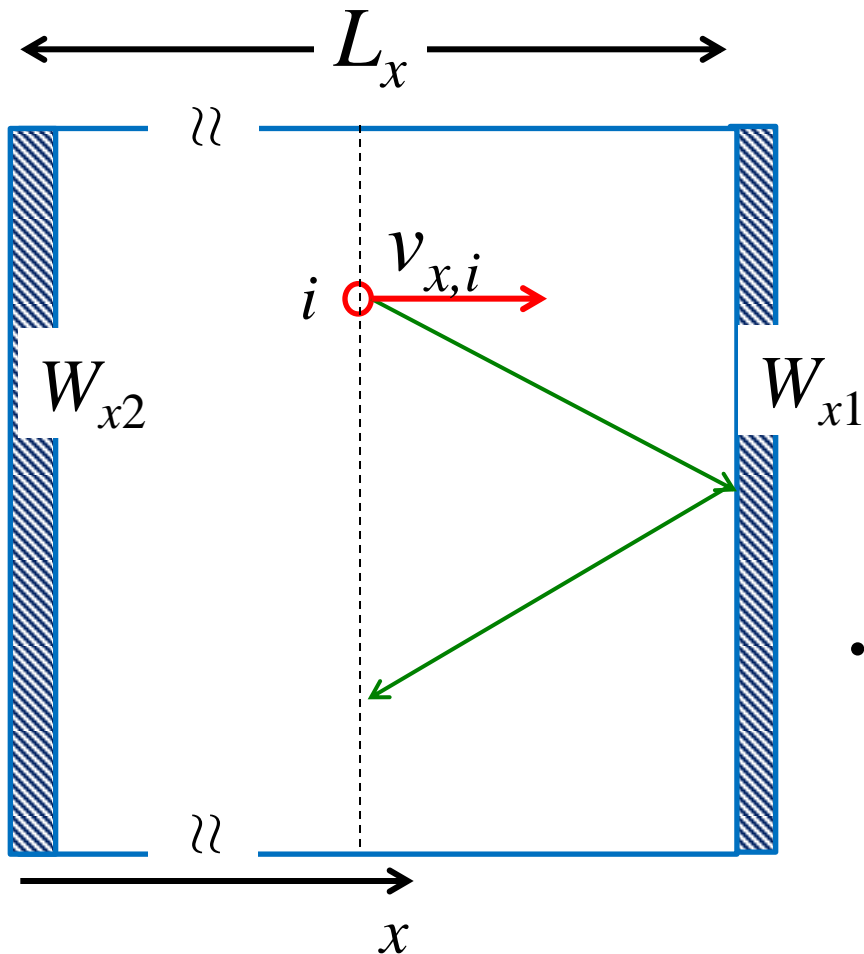
- The collision of molecule i with the wall results in a momentum change and a force exerted on the wall.

Change in momentum

$$f_{x,i} = \frac{\Delta p_{x,i}}{\Delta t} = \frac{2mv_{x,i}}{2L/v_{x,i}}$$

Time between consecutive collisions with the wall

- Contribution to pressure from molecule i with velocity $v_{x,i}$

$$P_{x,i} = \frac{f_i}{A} = \frac{mv_{x,i}^2}{AL} = \frac{mv_{x,i}^2}{V}$$

Total gas pressure from all molecules in x-direction

$$P_x = \sum_{i=1}^{N} P_{x,i} = \sum_{i=1}^{N} \frac{mv_{x,i}^2}{V} = \frac{Nm\langle v_x^2 \rangle}{V} = \frac{Nm\langle v^2 \rangle}{3V}$$

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Mechanical expression for pressure of an ideal gas - 2

- From microscopic mechanical analysis

$$P_{micro} = \frac{Nm\langle v^2 \rangle}{3V} = \frac{2N\langle E_K \rangle}{3V}$$

- From experimental macroscopic study of ideal gases

$$P_{expt} = \frac{nRT}{V} = \frac{NkT}{V}$$

$P_{expt} = P_{micro}$

$$\Longrightarrow \quad kT = \frac{m}{3}\langle v^2 \rangle = \frac{2}{3}\langle E_K \rangle$$

Result: Temperature is related to the average kinetic energy of molecules in an ideal gas!

- A macroscopic thermodynamic variable T is related to the average microscopic kinetic energy of the molecules;
- The average squared speed of molecules in the system is proportional to the temperature;
- Can we find the probability distribution of speed and kinetic energy?

Assumptions used to derive the Maxwell – Boltzmann distribution for velocities

1) The probability distributions in x, y, z directions have identical mathematical form and are independent of each other.

$$P(v_x) = P(v_y) = P(v_z) \implies P(v_x, v_y, v_z) = P(v_x)P(v_y)P(v_z)$$

2) The probability distribution of the molecule only depends on the speed and not individual Cartesian components of the velocity, which are arbitrary (why?)

$$P(v_x, v_y, v_z) = P(v) \qquad v^2 = v_x^2 + v_y^2 + v_z^2$$

Combining 1) and 2) $\qquad \therefore P(v) = P(v_x)P(v_y)P(v_z)$

Taking the derivative of both sides with respect to v_x (using the chain rule),

$$\frac{dP(v)}{dv_x} = P(v_y)P(v_z)\frac{dP(v_x)}{dv_x} \implies \frac{1}{P(v)}\frac{dP(v)}{dv}\frac{dv}{dv_x} = \frac{1}{P(v_x)}\frac{dP(v_x)}{dv_x}$$

$$\frac{1}{vP(v)}\frac{dP(v)}{dv} = \frac{1}{v_x P(v_x)}\frac{dP(v_x)}{dv_x} = const. \implies P(v_x) = Ae^{-Cv_x^2}$$

A Gaussian distribution! 5

Maxwell – Boltzmann distribution for molecular velocities

The probability distribution has two unknown factors, A and C:

$$P(v_x) = Ae^{-Cv_x^2}$$

- The A factor is determined by the normalization condition of the probability:

$$\int_{-\infty}^{+\infty} P(v_x)\,dv_x = 1 \Rightarrow P(v_x) = \left(\frac{C}{\pi}\right)^{1/2} e^{-Cv_x^2} \qquad I_0 = \int_{-\infty}^{+\infty} e^{-\alpha x^2}\,dx = \left(\frac{\pi}{\alpha}\right)^{1/2}$$

Note that the range of the velocity components is from $-\infty$ to $+\infty$

- The C factor is determined from the kinetic theory of gases result:

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \frac{1}{2}kT \qquad\qquad \frac{1}{2}m\int_{-\infty}^{+\infty} v_x^2 P(v_x)\,dv_x = \frac{1}{2}kT$$
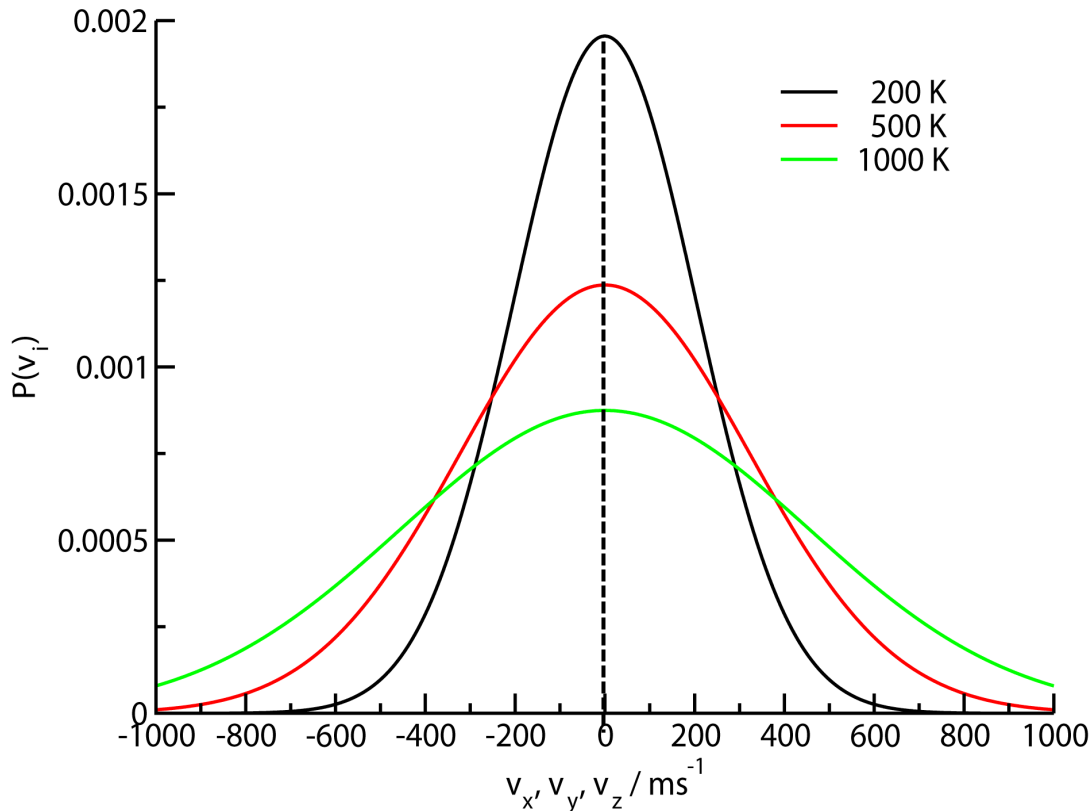
$$I_n = \int_{-\infty}^{\infty} x^n e^{-ax^2}\,dx = \frac{1\cdot 3\cdot 5\cdot\ldots\cdot(n-1)}{(2\alpha)^{n/2}}\left(\frac{\pi}{\alpha}\right)^{1/2} \qquad n \text{ even}$$

The probability distribution for Cartesian components

$$P(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}$$

Maxwell – Boltzmann distribution for molecular velocity components

$$P_1(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}$$

- Distribution is symmetric w.r.t. positive and negative directions;

- Average velocity component is 0;

$$\langle v_x \rangle = 0$$

- Most probable value for the component of velocity is 0,

- The standard deviation is:

$$\sqrt{(v_x - \langle v_x \rangle)^2} = \sigma = \left(\frac{kT}{m}\right)^{1/2}$$

- Distribution is broad!

- Distribution becomes broader at higher temperature

https://phet.colorado.edu/en/simulation/gas-properties

Maxwell – Boltzmann distribution for molecular speed

Combining the three components of the velocity distribution

$$P_1(v)dv_x dv_y dv_z = P_1(v_x)P_1(v_y)P_1(v_z)dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2kT} dv_x dv_y dv_z$$

Change the velocities from Cartesian coordinates to spherical polar coordinates:

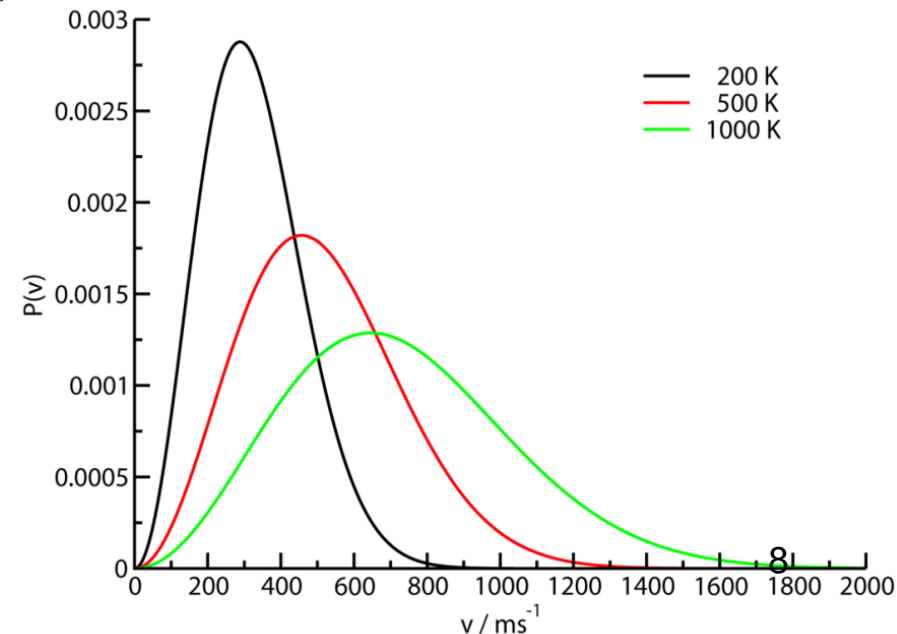$$v^2 \sin\theta\, dv\, d\theta\, d\phi = dv_x dv_y dv_z = d\mathbf{v}$$

The probability distribution does not depend on angles θ and ϕ

$$P_1(v)d\mathbf{v} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} v^2 dv \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi$$

Giving a distribution function for speed:

$$P_1(v)dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} dv$$

The speed distribution is not Gaussian!

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The Maxwell – Boltzmann distribution for speed of one molecule

The probability distribution for speed:
$$P_1(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$
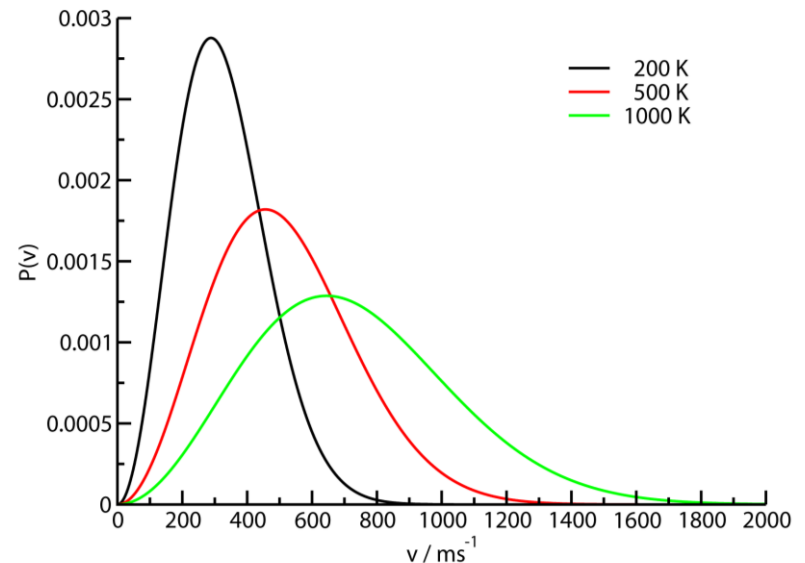
Most probable speed:

$$\frac{dP_1(v)}{dv} = 0 \Rightarrow 2v_P e^{-mv_P^2/2kT} - \frac{m}{kT} v_P^3 e^{-mv_P^2/2kT} = 0 \Rightarrow v_P = \sqrt{\frac{2kT}{m}}$$
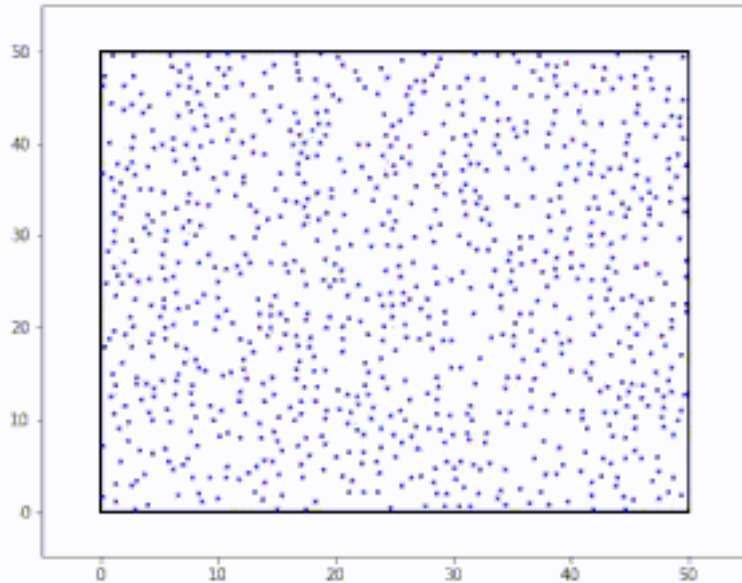
Average speed:

$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{+\infty} v^3 e^{-mv^2/2kT} \, dv = \sqrt{\frac{8kT}{\pi m}}$$

$$I_n = \int_0^\infty x^{2n+1} e^{-ax^2} \, dx = \frac{n!}{2\alpha^{n+1}} \qquad n \text{ odd}$$

• The probability distribution is broad!
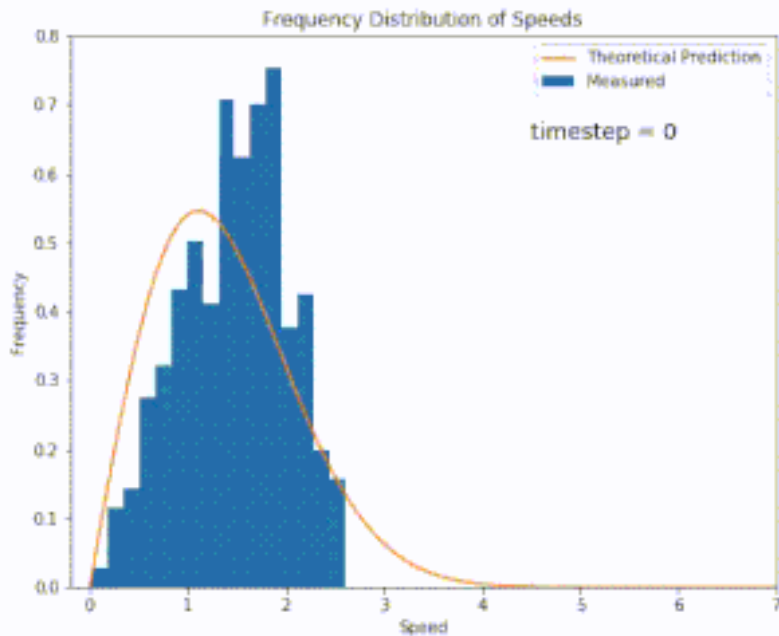• Distribution becomes broader at higher temperature

The Maxwell – Boltzmann distribution for speed of one molecule

$$P_1(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$

Molecular dynamics simulation of ideal gas and determining the velocity distribution one molecule

Maxwell – Boltzmann distribution for single molecule energy

We can determine an energy distribution for a single ideal gas molecule by changing the variable from v to ε

$$\varepsilon = mv^2/2 \Rightarrow d\varepsilon = mv\,dv$$

- Distribution function for the energy of one molecule:

$$P_1(\varepsilon)d\varepsilon = \frac{2}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{3/2}\varepsilon^{1/2}e^{-\varepsilon/kT}d\varepsilon$$

- Most probable energy

$$\frac{dP_1(\varepsilon)}{d\varepsilon} = 0 \Rightarrow \frac{1}{2}\varepsilon_P^{-1/2}e^{-\varepsilon_P/kT} - \frac{1}{kT}\varepsilon_P^{1/2}e^{-\varepsilon_P/kT} = 0 \Rightarrow \varepsilon_P = \frac{kT}{2}$$

- Average energy

$$\langle\varepsilon\rangle = \bar{\varepsilon} = \int_0^\infty \varepsilon P_1(\varepsilon)d\varepsilon = \tfrac{3}{2}kT$$

- Variance (spread) of the energy distribution?

$$\int_0^\infty x^n e^{-\alpha x}dx = \frac{n(n-1)\cdots\left(\frac{1}{2}\right)\sqrt{\pi}}{\alpha^{n+1}}$$

$$\langle(\varepsilon-\langle\varepsilon\rangle)^2\rangle = \frac{2}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{3/2}\int_0^\infty(\varepsilon-\langle\varepsilon\rangle)^2\varepsilon^{1/2}e^{-\varepsilon/kT}d\varepsilon$$

$$= \frac{2}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{3/2}\left(\frac{15\sqrt{\pi}(kT)^{7/2}}{8} - \frac{18\sqrt{\pi}(kT)^{7/2}}{8} + \frac{9\sqrt{\pi}(kT)^{7/2}}{8}\right) = \frac{3}{2}(kT)^2$$

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Maxwell – Boltzmann distribution for a single molecule energy

$$\varepsilon_P = \frac{1}{2}kT$$

$$\langle\varepsilon\rangle = \frac{3}{2}kT$$

$$P_1(\varepsilon)d\varepsilon = \frac{2}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{3/2}\varepsilon^{1/2}e^{-\varepsilon/kT}d\varepsilon$$

$$\sigma = (3/2)^{1/2}kT = 1.22kT$$

- The distribution of energy for a single ideal gas molecule is broad

$$\frac{\sigma}{\langle\varepsilon\rangle} = \frac{\sqrt{3/2}kT}{3/2kT} = \sqrt{\frac{2}{3}}$$

Y axis: $P_1(\varepsilon/kT)$

X axis: ε/kT
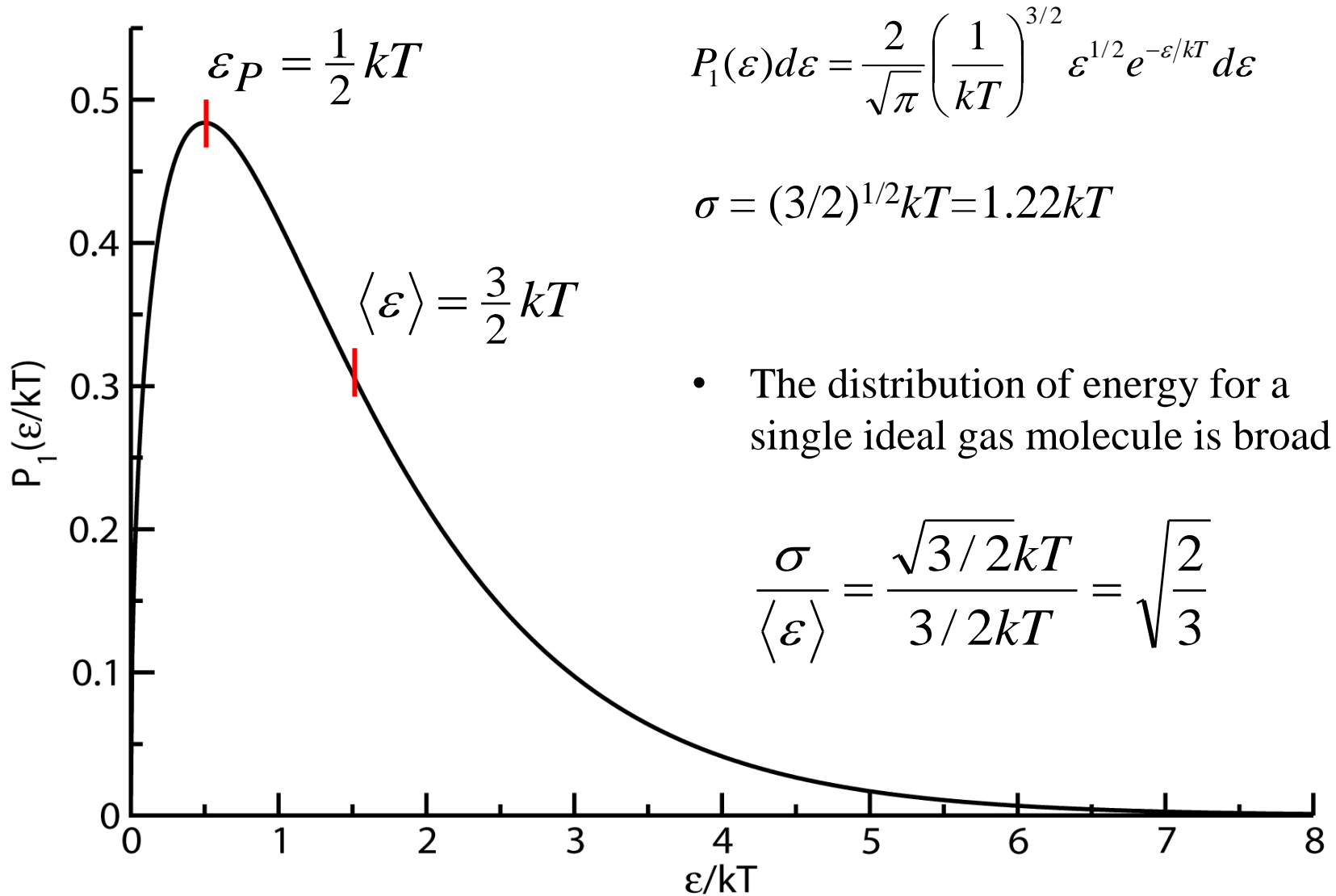
Convolution: Maxwell – Boltzmann distribution for the energy of 2 molecules

In an ideal gas, the total energy is the sum of one-molecule energies and the probabilities for energies in different molecules are uncorrelated

$$E = \varepsilon_I + \varepsilon_{II} \qquad P_2(\varepsilon_I, \varepsilon_{II}) = P_1(\varepsilon_I)P_1(\varepsilon_{II})$$

Convolution of two one-molecule energy probability distributions

$$P_2(E) = \iint_{\varepsilon_I + \varepsilon_{II} = E} P_1(\varepsilon_I)P_1(\varepsilon_{II})d\varepsilon_I d\varepsilon_{II} = \int_0^E P_1(\varepsilon_I)P_1(E - \varepsilon_I)d\varepsilon_I$$

$$P_2(E) = \frac{4}{\pi(kT)^3} \int_0^\infty \varepsilon^{1/2}(E - \varepsilon)^{1/2} e^{-E/kT} d\varepsilon$$

The integral can be evaluated (see Chapter 5) to give

$$P_2(E) = \frac{1}{2(kT)^3} E^2 e^{-E/kT}$$

Maxwell – Boltzmann distribution for energy of two molecules

$$P_2(E) = \frac{1}{2(kT)^3} E^2 e^{-E/kT}$$

Most probable two-molecule energy:

$$\frac{dP_2(E)}{dE} = 0 \Rightarrow 2E_P e^{-E_P/kT} - \frac{1}{kT} E_P^2 e^{-E_P/kT} = 0 \Rightarrow E_P = 2kT$$

Average:

$$\langle E \rangle = \frac{1}{2(kT)^3} \int_0^\infty E^3 e^{-E/kT} dE = \frac{1}{2(kT)^3} \frac{6}{(1/kT)^4} = 3kT$$

Variance:

$$\sigma^2 = \frac{1}{2(kT)^3} \int_0^\infty \left(E - \langle E \rangle\right)^2 E^2 e^{-E/kT} dE$$

$$= \frac{1}{2(kT)^3} \left[24(kT)^5 - 12\langle E \rangle (kT)^4 + 2(kT)^3 \langle E \rangle^2 \right] = 3(kT)^2$$

$$\frac{\sigma}{\langle E \rangle} = \frac{\sqrt{3}kT}{3kT} = \frac{1}{\sqrt{3}}$$

Maxwell – Boltzmann distribution for energy of *N*-molecules

We can continue the convolution process to get probability for energies of *N* molecules:

$$E = \varepsilon_I + \varepsilon_{II} + \cdots + \varepsilon_N \qquad P_N(E) = \frac{1}{\left(\frac{3N}{2}-1\right)!(kT)^{3N/2}} E^{[(3N/2)-1]} \exp(-E/kT)$$

Most probable: $\dfrac{dP_N(E)}{dE} = 0 \Rightarrow E_P = (3N/2-1)kT$

Average: $\langle E \rangle = \dfrac{1}{\left(\frac{3N}{2}-1\right)!(kT)^{3N/2}} \displaystyle\int_0^\infty E^{(3N/2)} \exp(-E/kT)dE = \frac{3N}{2}kT$

Variance:

$$\left\langle \left(E - \langle E \rangle\right)^2 \right\rangle = \frac{1}{\left(\frac{3N}{2}-1\right)!(kT)^{3N/2}} \int_0^\infty \left[E^2 - 3NkTE + \left(\tfrac{3}{2}NkT\right)^2 \right] E^{(3N/2)-1} \exp(-E/kT)dE = \frac{3N}{2}(kT)^2$$

$$\therefore \frac{\sigma}{\langle E \rangle} = \sqrt{\frac{2}{3N}}$$

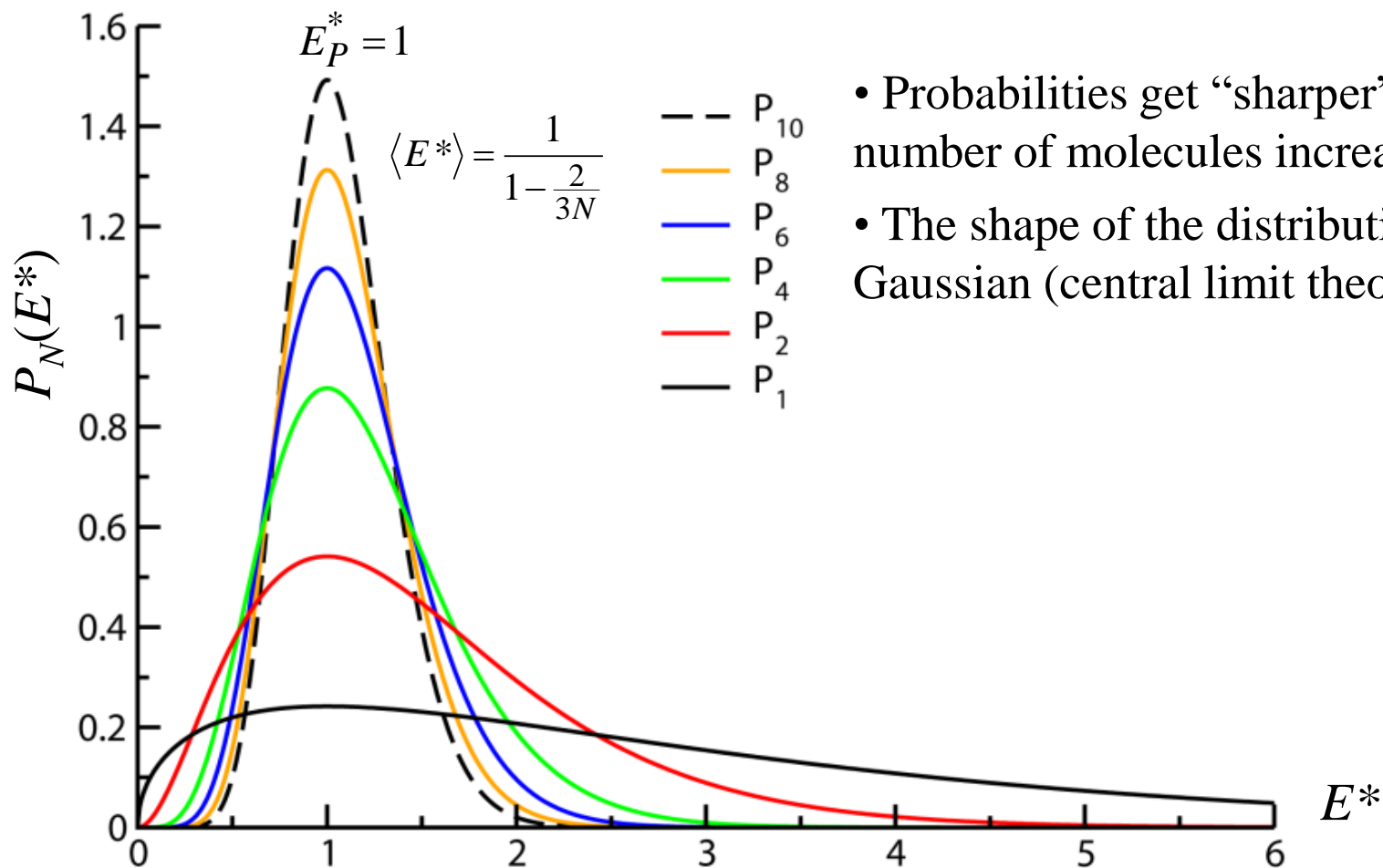• Change of variables to energy relative to the maximum $E/E_P = E^*$

$$P_N(E)dE = \frac{(3N/2-1)^{3N/2}}{(3N/2-1)!} E^{*[(3N/2)-1]} \exp\left[-(3N/2-1)E^*\right]dE^* = P_N(E^*)dE^*$$

Maxwell – Boltzmann distribution for energy of N-molecules

$$E = \varepsilon_I + \varepsilon_{II} + \cdots + \varepsilon_N \qquad P_N(E^*) = \frac{(3N/2-1)^{3N/2}}{(3N/2-1)\,!} E^{*[(3N/2)-1]} \exp\left[-(3N/2-1)E^*\right]$$

"Reduced energy" $E^* = E/E_P$

Probability distributions for 1 to 10 molecule energies

$E_P^* = 1$

$\langle E^* \rangle = \dfrac{1}{1-\dfrac{2}{3N}}$

- - - P_{10}
——— P_8
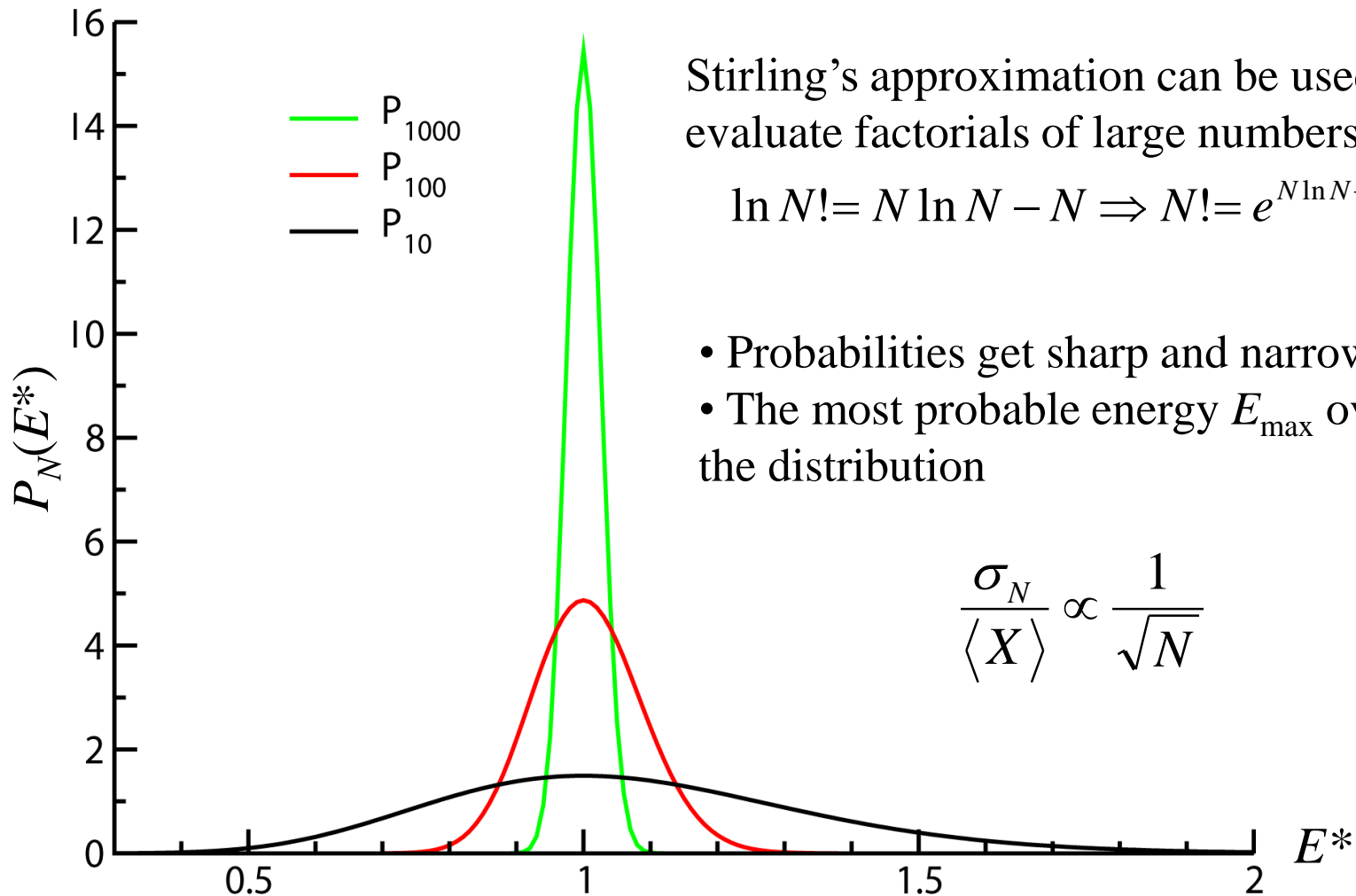——— P_6
——— P_4
——— P_2
——— P_1

- Probabilities get "sharper" as the number of molecules increases

- The shape of the distribution becomes Gaussian (central limit theorem)!

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Energy distributions for large collections of molecules

$$P_N(E^*) = \frac{(3N/2-1)^{3N/2}}{(3N/2-1)!} E^{*[(3N/2)-1]} \exp[-(3N/2-1)E^*]$$

Probability distributions for 10 to 1000 molecule energies

Stirling's approximation can be used to evaluate factorials of large numbers:

$$\ln N! = N \ln N - N \Rightarrow N! = e^{N \ln N - N}$$

- Probabilities get sharp and narrow for large N
- The most probable energy E_{max} overwhelms the distribution

$$\frac{\sigma_N}{\langle X \rangle} \propto \frac{1}{\sqrt{N}}$$

Central limit theorem applies for the energy distribution of for large collections of molecules

$$P_N(E_N) = \frac{1}{\left(\frac{3N}{2}-1\right)!(kT)^{3N/2}} E_N^{[(3N/2)-1]} \exp(-E_N/kT)$$

Simplify the notation using $n = 3N/2 - 1$ and $\beta = 1/kT$ to define:
$x = (E_N - n/\beta)/(n/\beta)$

$$P_N(E_N)dE_N = P(x)dx = \frac{n^{n+1}e^{-n}}{n!}(1+x)^n e^{-nx}dx$$

Using the logarithm approximation for small x: $\quad \lim_{x \to 0}(1+x)^n \approx e^{nx}e^{nx^2/2}$

$$P(x) = \frac{n^{n+1}e^{-n}}{n!}e^{nx^2/2} = \boxed{\frac{\sqrt{2\pi n}\,n^n e^{-n}}{n!}}\sqrt{\frac{n}{2\pi}}e^{nx^2/2}$$

= 1 from the relation for the factorial of large numbers

The energy distribution for the N molecule system becomes Gaussian!

$$P(x)dx = \sqrt{\frac{n}{2\pi}}e^{-nx^2/2}dx \Rightarrow P_N(E_N)dE_N = \frac{1}{\sqrt{2\pi\sigma_N^2}}e^{-(E_N - E_{N,P})^2/2\sigma_N^2}dE_N$$