

# Chapter 03

## Kinetic Theory of Gases

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Chem. 4300

## History of ideal gas law

- 1662: **Robert Boyle** discovered with changing pressure at constant temperature that product of pressure and volume of a gas at equilibrium is constant,

$$pV = \text{constant at constant } T$$

- 1780s: **Jacques Charles** found that ratio of volume to temperature was also invariant when temperature was changed with pressure kept constant,

$$V/T = \text{constant at constant } p$$

- 1811: **Amedeo Avogadro** found ratio of volume to amount remained constant with changing amount at fixed pressure and temperature,

$$V/n = \text{constant at constant } p \text{ and } T$$

- 1834: **Emile Clapeyron** combined gas laws of Boyle, Charles, and Avogadro into ideal gas equation of state,

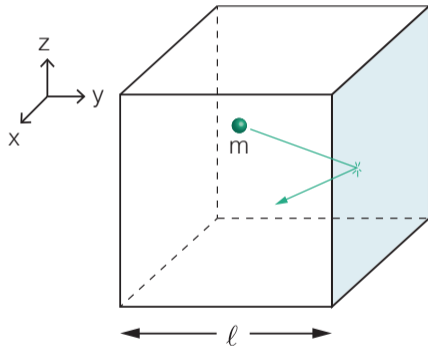
$$pV = nRT$$

where  $R$  is gas constant.

## Bernoulli's derivation of Boyle's law, $pV = \text{constant}$ .

As early as 1738 **Daniel Bernoulli** proposed a microscopic kinetic explanation of Boyle's law, but only after Clapeyron's work did Bernoulli's kinetic theory gain widespread acceptance.

*Bernoulli's derivation*



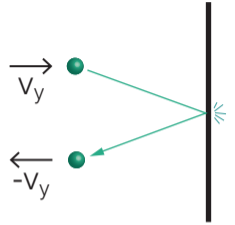
Remember pressure is defined as force per unit area.

What is the force of one gas molecule hitting a wall?

## Force on wall is momentum change when a molecule hits it.

Force along  $y$  is given by ratio of change in momentum to time between collisions.

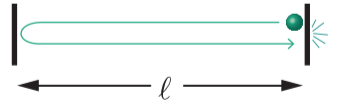
$$F_y = \frac{\Delta p_y}{\Delta t}$$



Linear momentum is conserved in collision with wall

$$\Delta p_y = p_{y,\text{final}} - p_{y,\text{initial}} = (-mv_y) - (mv_y) = -2mv_y$$

Time to travel length of box, hit wall, and travel back is  $\Delta t = 2\ell / v_y$



Average force of 1 molecule hitting 1 wall of box is  $F_y = \frac{\Delta p_y}{\Delta t} = \frac{-2mv_y}{2\ell / v_y} = -\frac{mv_y^2}{\ell}$

## Force of $N$ molecules hitting all walls of the box.

Sum over  $N$  molecules hitting one wall is

$$F_{yN} = -\frac{m}{\ell} \sum_{\alpha=1}^N v_{y\alpha}^2$$

Add **magnitude** (i.e., ignore signs) of all forces on all 6 walls (top, bottom, left, right, front, back)

$$F_{\text{total}} = 2\frac{m}{\ell} \sum_{\alpha=1}^N v_{x\alpha}^2 + 2\frac{m}{\ell} \sum_{\alpha=1}^N v_{y\alpha}^2 + 2\frac{m}{\ell} \sum_{\alpha=1}^N v_{z\alpha}^2 = 2\frac{m}{\ell} \sum_{\alpha=1}^N \underbrace{(v_{x\alpha}^2 + v_{y\alpha}^2 + v_{z\alpha}^2)}_{v_{\alpha}^2} = 2\frac{m}{\ell} \sum_{\alpha=1}^N v_{\alpha}^2$$

Define mean square velocity as

$$\overline{v^2} = \frac{1}{N} \sum_{\alpha=1}^N v_{\alpha}^2 \quad \text{or} \quad N\overline{v^2} = \sum_{\alpha=1}^N v_{\alpha}^2$$

and write total force on all 6 walls of box as

$$F_{\text{total}} = 2\frac{m}{\ell} N\overline{v^2}$$

## Pressure from $N$ molecules inside the box.

Pressure is force per unit area. Total area of box walls is 6 times area of 1 wall:  $A_{\text{total}} = 6A_{\text{wall}}$ .

$$p = F_{\text{total}}/A_{\text{total}} = F_{\text{total}}/(6A_{\text{wall}}) \quad \text{Substituting previous result: } F_{\text{total}} = 2\frac{m}{\ell}N\overline{v^2}$$

gives

$$p = 2\frac{m}{\ell}N\overline{v^2}/(6A_{\text{wall}}) = \frac{Nm\overline{v^2}}{3A_{\text{wall}}\ell} = \frac{Nm\overline{v^2}}{3V} \quad \text{where } V = A_{\text{wall}}\ell \text{ is volume of box}$$

Rearranging gives Boyle's law ( $pV = \text{constant}$ )

$$pV = \frac{Nm\overline{v^2}}{3} = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{2}{3}N\overline{\epsilon}_k, \quad \text{where } \overline{\epsilon}_k \text{ is mean kinetic energy of molecule}$$

Rewriting in terms of moles, i.e.,  $N = nN_A$  where  $N_A$  is Avogadro constant,

$$pV = \frac{2}{3}nN_A\overline{\epsilon}_k = \frac{2}{3}nE_k \quad \text{where } E_k \text{ is kinetic energy of 1 mole of gas}$$

## Temperature is a quantity derived from energy

Finally connect to Ideal gas law:

$$pV = nRT = \frac{2}{3}nE_k$$

and we discover

$$E_k = \frac{3}{2}RT$$

translational kinetic energy of 1 mole of ideal gas

- Equation reveals true nature of temperature—reflects translational kinetic energy of atoms and molecules.
- Can't have negative temperatures because can't have negative kinetic energy.
- Raising gas temperature increases kinetic energy of gas molecules and vice versa.
- Dividing by  $N_A$  we obtain relationship on per molecule basis

$$\bar{e}_k = \frac{E_k}{N_A} = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} k_B T$$

$k_B = R/N_A = 1.38064852 \times 10^{-23}$  J/K is defined as Boltzmann constant.

## Average molecular speed

Given

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

define root mean square speed,  $c_{\text{rms}} = \sqrt{\overline{v^2}}$ , and obtain

$$c_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

$c_{\text{rms}}$  is related to temperature and molecular mass,  $m$ , or molar mass,  $M$

- Molecular speeds increase with increasing temperature.
- Molecular speeds decrease with increasing molecular mass.



## Average molecular speed

### Example

Calculate the rms speed for a mole of vanillin molecules at room temperature.

### Solution

Since Vanillin has chemical formula  $C_8H_8O_3$  with a molecular weight of 152.1 g/mol we obtain

$$c_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R(300 \text{ K})}{152.1 \text{ g/mol}}} \approx 221 \text{ m/s} \approx 500 \text{ mph}$$

If vanillin has such a high speed why does it take so long for the scent to travel across a room?

# Maxwell Distribution Laws



James Clerk Maxwell  
1831-1879

What is parent probability distribution function for

- molecular velocities,  $p(\vec{v})$
- molecular speeds,  $p(c)$
- molecular energies,  $p(E)$ ?

## Maxwell Distribution Laws

In 1859 James Clerk Maxwell worked out the probability distribution of molecular velocities,  $f(\vec{v})$ , for gas molecules as perfectly elastic spheres.

Maxwell assumed that distribution of velocities in each direction were uncorrelated, that is,  $f(\vec{v})$  can be written as product of 3 independent distributions

$$f(\vec{v}) = f(v_x) f(v_y) f(v_z)$$

He also reasoned that distribution of velocities is independent of direction, implying that  $f(\vec{v})$  should only depend on magnitude of velocities,

$$f(v_x) f(v_y) f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2)$$

This is an example of a *functional equation*: an equation in which the unknowns are functions.

## How do we solve this functional equation?

$$f(v_x) f(v_y) f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2)$$

Product of functions on left must give sum of their variables as function argument on right.

A function,  $f(v_i)$ , that satisfies this functional equation is

$$f(v_i) = a e^{-b v_i^2}$$

Putting this function into functional equation gives

$$\phi(v_x^2 + v_y^2 + v_z^2) = a^3 e^{-b(v_x^2 + v_y^2 + v_z^2)}$$

Need to determine  $a$  and  $b$ .

## Normalizing Maxwell's distribution for molecular velocities

As the  $f(v_i)$  are probability distributions we require them to be normalized,

$$\int_{-\infty}^{\infty} f(v_i) dv_i = 1 \quad \text{so} \quad \int_{-\infty}^{\infty} a e^{-bv_i^2} dv_i = 1$$

requires that  $a = \sqrt{b/\pi}$  and

$$f(v_i) = \sqrt{\frac{b}{\pi}} e^{-bv_i^2}$$

Taken together Maxwell's probability distribution then becomes

$$f(\vec{v}) = f(v_x) f(v_y) f(v_z) = \left(\frac{b}{\pi}\right)^{3/2} e^{-b(v_x^2 + v_y^2 + v_z^2)}$$

Still need to determine  $b$ .

## Maxwell's distribution law for molecular velocities

From Bernoulli's kinetic theory we learned that  $\overline{v^2} = 3k_B T/m$ .

This mean square speed should also be obtained from probability distribution

$$\overline{v^2} = \int (v_x^2 + v_y^2 + v_z^2) f(\vec{v}) d\vec{v} = 3k_B T/m$$

Substituting our normalized solution for  $f(\vec{v})$  we obtain

$$\overline{v^2} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (v_x^2 + v_y^2 + v_z^2) \left(\frac{b}{\pi}\right)^{3/2} e^{-b(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z = 3k_B T/m$$

Solving this 3D integral equation requires  $b = m/(2k_B T)$ , and finally obtain

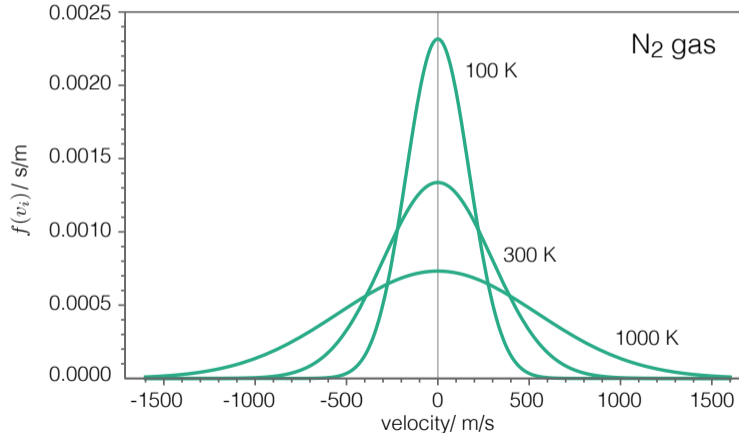
$$f(\vec{v}) = \frac{1}{\sqrt{(2\pi)^3}} \left(\frac{m}{k_B T}\right)^{3/2} e^{-\frac{1}{2}(v_x^2 + v_y^2 + v_z^2)/(k_B T/m)}$$

This is *Maxwell's distribution law for molecular velocities*: A 3D Gaussian probability distribution with a standard deviation of  $\sqrt{k_B T/m}$ .

## Maxwell's distribution law for molecular velocities

Maxwell's distribution law is a 3D Gaussian distribution centered on  $\vec{v} = 0$ .

Distribution for one component of velocity vector for  $\text{N}_2$  gas at 3 different temperatures.



# Maxwell's distribution law for molecular speeds



## Maxwell's distribution law for molecular speeds

Speed is magnitude of velocity vector. To get speed distribution transform Maxwell's velocity distribution into spherical coordinates,

$$c = \sqrt{v_x^2 + v_y^2 + v_z^2}, \quad \cos \theta = \frac{v_z}{c}, \quad \tan \phi = \frac{v_y}{v_x}.$$

With this change of variables we find

$$f(\vec{v}) = f(c, \theta, \phi) = \frac{1}{\sqrt{(2\pi)^3}} \left( \frac{m}{k_B T} \right)^{3/2} e^{-\frac{1}{2}c^2/(k_B T/m)}$$

This is independent of  $\theta$  and  $\phi$  so if we put it into the normalization

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} f(c, \theta, \phi) c^2 dc \sin \theta d\theta d\phi = 1$$

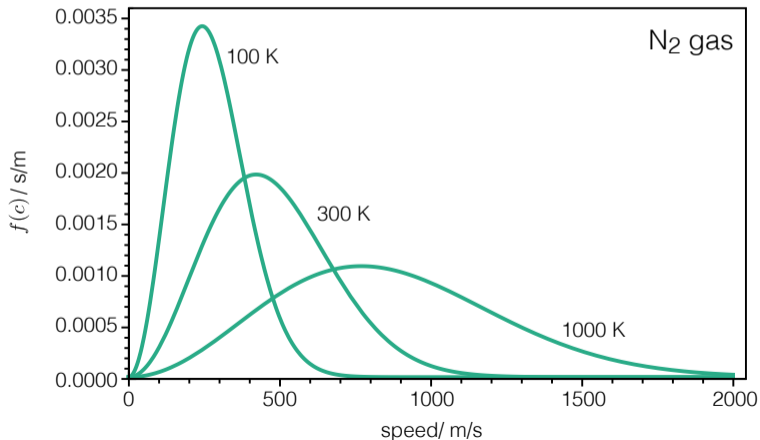
we can integrate away  $\theta$  and  $\phi$  and obtain

$$f(c) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$

*Maxwell's distribution law for molecular speeds.*

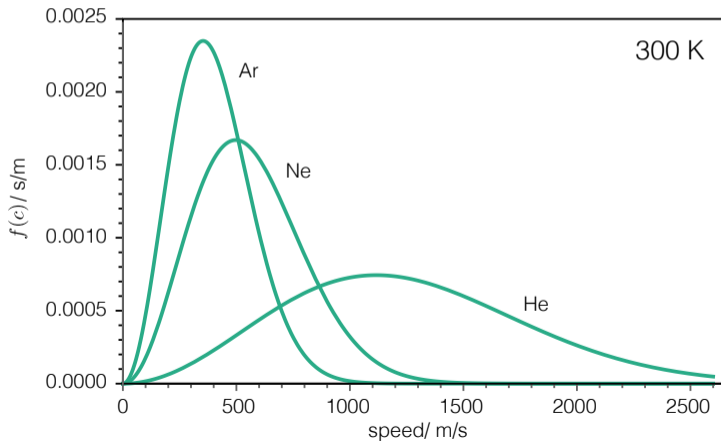
# Maxwell's distribution law for molecular speeds

$$f(c) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$



# Maxwell's distribution law for molecular speeds

$$f(c) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$



## Mean speed

With Maxwell's distribution law for molecular speeds

$$f(c) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$

we can calculate the mean speed

$$\bar{c} = \int_0^{\infty} cf(c)dc = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} \cdot \frac{1}{2} \left( \frac{2k_B T}{m} \right)^2$$

which simplifies to

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

Note, mean speed,  $\bar{c}$ , is smaller than root mean square speed,  $c_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$ .

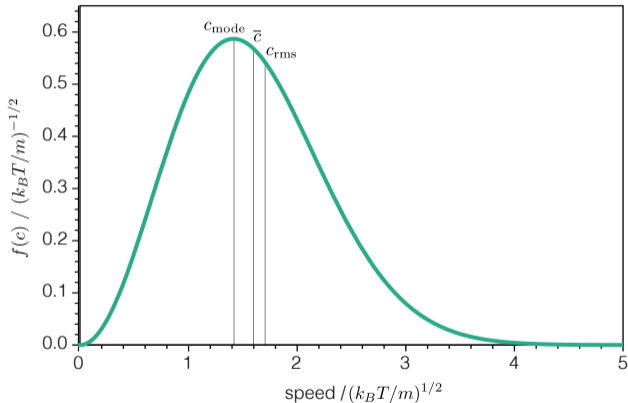
## Most probable speed

$$f(c) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$

To calculate most probable speed need to find  $c$  value where  $f(c)$  is maximum.

Set  $df(c)/dc = 0$ , solve for  $c$  to obtain

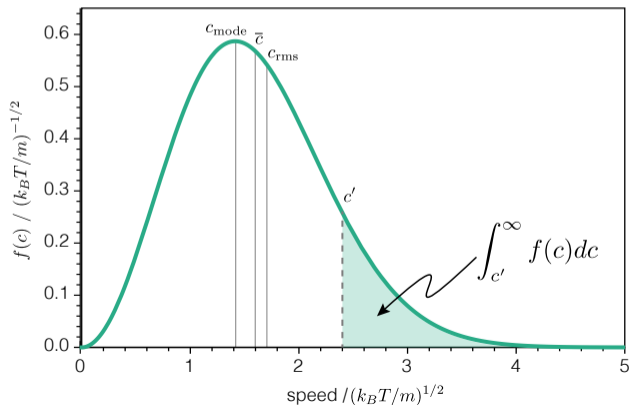
$$c_{\text{mode}} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$$



## Fraction of molecules with speeds between $c_1$ and $c_2$ .

Fraction of molecules with speeds between  $c_1$  and  $c_2$  is obtained by integrating Maxwell speed distributions between these two limits,

$$\frac{\delta N}{N} = \int_{c_1}^{c_2} f(c)dc$$

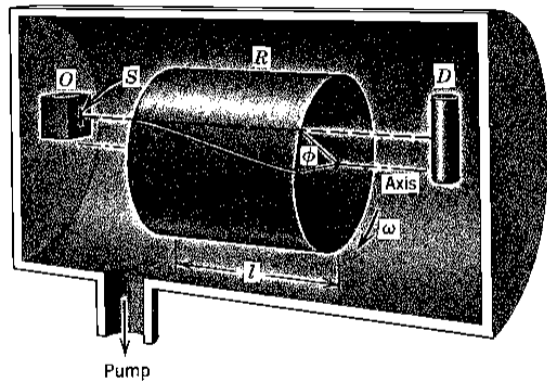


## Kinetic Theory of Gases Simulation

1955 - Miller and Kusch experimentally verify Maxwell's molecular speed distribution.

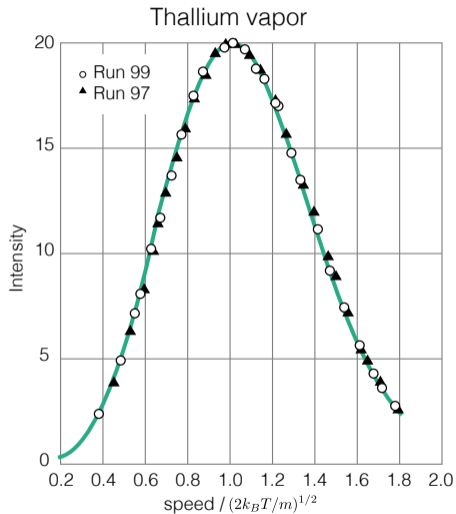
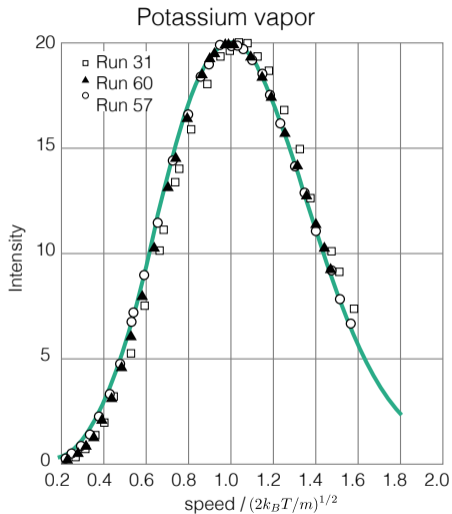


## Miller and Kusch experiments



- In 1955 Miller and Kusch published first convincing measurements of speed distribution for K and Tl atoms in gas phase.
- For each fixed rotation speed only molecules with a small range of speeds can travel from the furnace to the detector.
- With dimensions given in instrument diagram the selected speed is  $v_0 = \omega l / \phi$ .
- Measuring intensity as a function of rotation speed gives the atomic speed distribution.

# Miller and Kusch experiments



## Miller and Kusch experiments

Beam	Run	Oven Tempera- ture deg K	Oven pressure in mm of mercury	Velocity of $I_{\max}$ in m/sec	
				From oven temp	From exp distr
K	57	$466 \pm 2$	$4.5 \times 10^{-3}$	$628 \pm 2$	$630 \pm 3$
K	60	$544 \pm 3$	$1.2 \times 10^{-1}$	$678 \pm 3$	$679 \pm 3$
K	31	$489 \pm 2$	$1.4 \times 10^{-2}$	$644 \pm 2$	$682 \pm 3$
Tl	99	$870 \pm 4$	$3.2 \times 10^{-3}$	$376 \pm 1$	$376 \pm 2$
Tl	97	$944 \pm 5$	$2.1 \times 10^{-2}$	$392 \pm 1$	$395 \pm 2$

# Distribution of kinetic energies

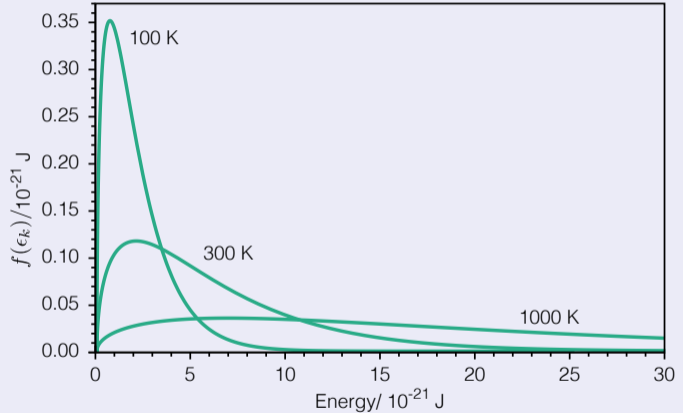
## Homework

Given

$$f(c) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2} c^2 / (k_B T / m)}$$

derive distribution of kinetic energies,

$$f(\epsilon_k) = \frac{2}{\sqrt{\pi}} \left( \frac{1}{k_B T} \right)^{3/2} \epsilon_k^{1/2} e^{-\epsilon_k / (k_B T)}$$



Hint: start with  $f(c) dc = f(\epsilon_k) d\epsilon_k$  and  $\epsilon_k = \frac{1}{2} mc^2$ .