

# Chapter 16. Kinetic Theory of Gases

## Summary

- **molecular interpretation of the pressure** and  $pV = nRT$
- the importance of **molecular motions**
- **velocities and speeds** of gas molecules
- **distribution functions** for molecular speeds and velocities
- application to **effusion** (gas leak through a pin hole)
- **molecular collision rates** – important for chemical kinetics

# Section 16.1 Kinetic Theory of Gas Pressure and Energy

What is “Kinetic Theory” ?

- gases are treated as a collection of moving particles
- kinetic theory applies if the average distance between molecules is very large compared to the molecular size
- useful for gases at low pressures
- many applications to physical and chemical processes
- one of the most successful scientific theories

# Key assumptions of the **Kinetic Theory of Gases**

- the gas consists of particles of mass  $m$  in ceaseless **random motion**\*
- the size of the particles is negligible compared to the average distance between collisions
- the particles do not interact, except for perfectly **elastic collisions**\*\*

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\*random motion – not organized motion, as in bulk flow through a tube

\*\*translation kinetic energy unchanged by collisions – no internal energy modes (such as vibrations or rotations) are excited

**Example: Argon gas at 300 K and 1 bar**

(No internal rotations or vibrations. *Why?*)

**volume per mole:**  $V_m \approx 25 \text{ L mol}^{-1} = 0.025 \text{ m}^3 \text{ mol}^{-1}$

Divide  $V_m$  by Avogadro's number to get

**volume per argon atom:**  $\approx 4.1 \times 10^{-26} \text{ m}^3 = 41 \text{ nm}^3$

Use the argon atom diameter ( $\approx 0.29 \text{ nm}$ ) to calculate

**volume occupied by one Ar atom:**  $\approx (4/3)\pi r^3 = 0.013 \text{ nm}^3$

**Conclusion**

Only about 0.03 % of the container volume is occupied by argon atoms. The system is mostly “empty space”.

# Kinetic Theory of Gas Pressure

**Experiment results** for gases at low pressures

- pressure at fixed  $n$ ,  $V$  is proportional to  $T$
- pressure at fixed  $n$ ,  $T$  is inversely proportional to  $V$
- pressure at fixed  $T$ ,  $V$  is proportional to  $n$

combine to give the **empirical** ideal gas law:

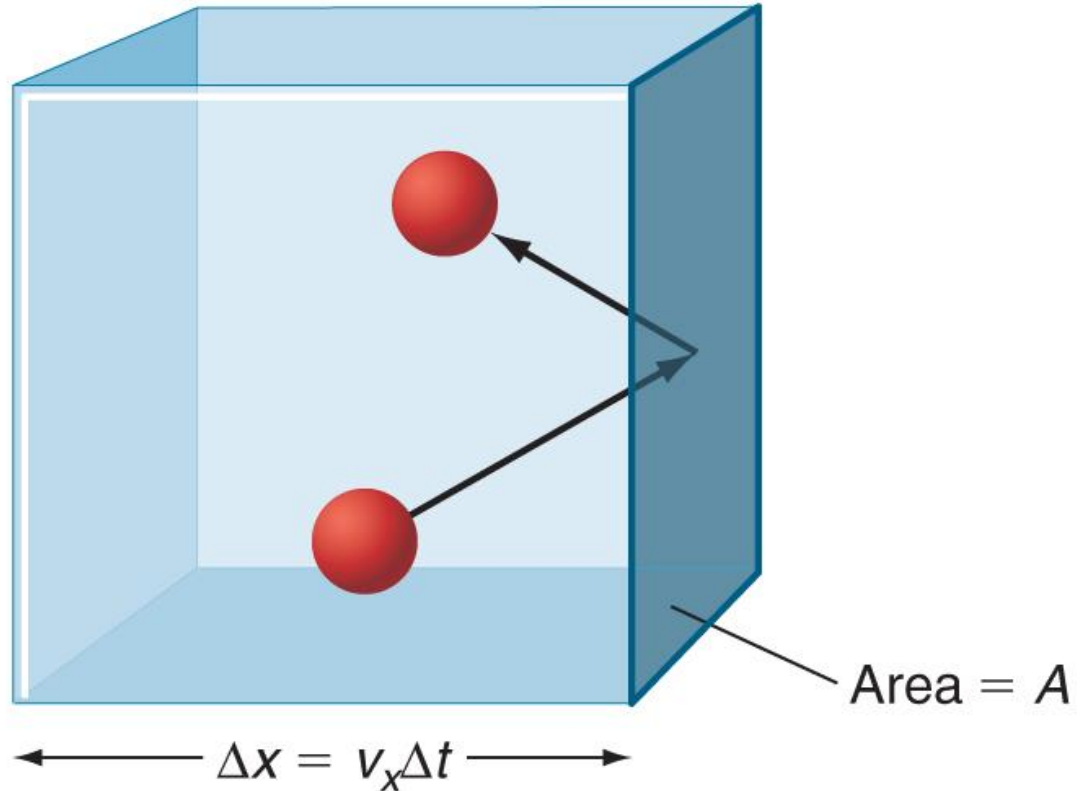
$$p = \frac{nRT}{V}$$

But is there a **theoretical interpretation** of the ideal gas law?

A particle of mass  $m$  with  $x$ -component velocity  $v_x$  collides with a wall of area  $A$ .

The collision changes the  $x$ -component of the velocity from  $v_x$  to  $-v_x$ .

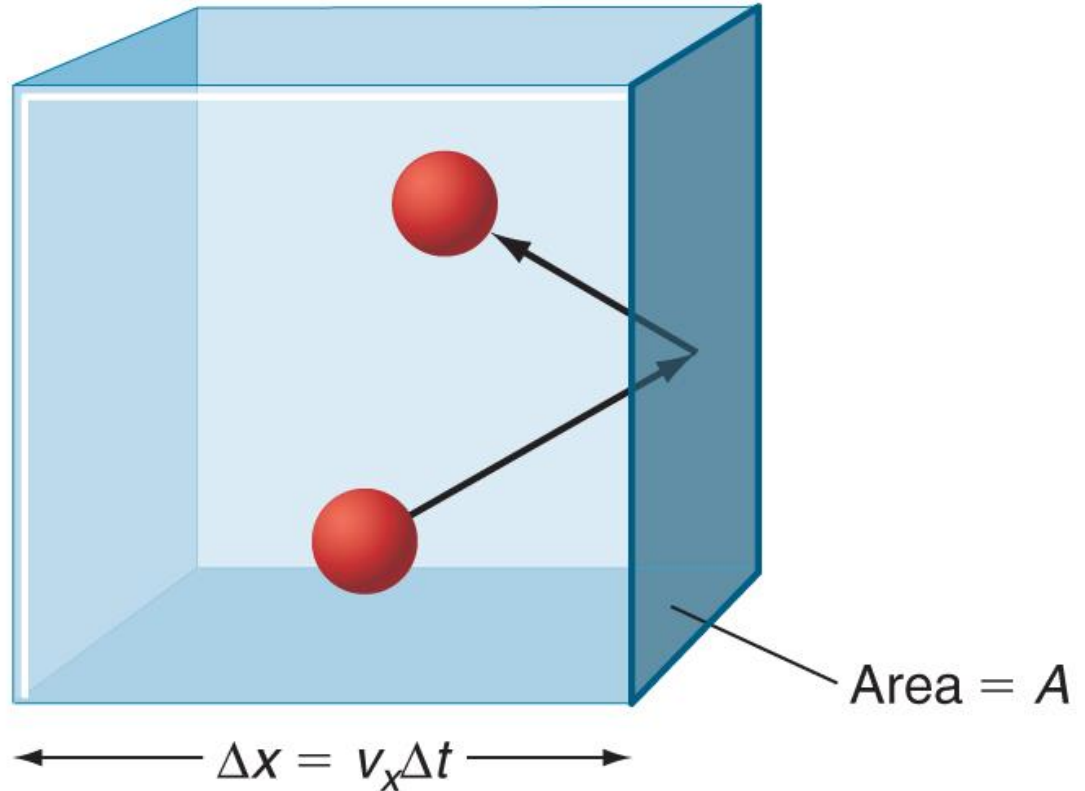
**Momentum change per collision:**  $mv_x - m(-v_x) = 2mv_x$



Next, calculate the number of particles colliding with the wall in the time interval  $\Delta t$ .

All particles within the distance  $v_x \Delta t$  from the wall will hit it in the time interval  $\Delta t$  if they are moving toward the wall.

One half of the particles in the **volume**  $A v_x \Delta t$  (the ones moving right) hit the wall in the time interval  $\Delta t$ .



For a container of volume  $V$  filled with  $n$  moles of particles, the number of particles in volume  $Av_x\Delta t$  is

$$nN_A \frac{Av_x\Delta t}{V}$$

One half of these molecules hit the wall, so the momentum change in time interval  $\Delta t$  is

(number of collisions)  $\times$  (momentum change per collision)

$$= \left( \frac{1}{2} nN_A \frac{Av_x\Delta t}{V} \right) \times (2mv_x) = \frac{nN_A mAv_x^2\Delta t}{V}$$



The pressure on the wall is the force (rate of change of momentum) divided by the wall area.

Divide by  $\Delta t$  and  $A$  to get

$$p = \frac{nN_A m A v_x^2 \Delta t}{V} \frac{1}{A \Delta t} = \frac{nN_A m v_x^2}{V} = \frac{nM v_x^2}{V}$$

using  $M = N_A m$  for the particle molar mass.

**This kinetic theory result is starting to resemble the ideal gas law!**

$$p = \frac{nRT}{V}$$

Not all of the molecules travel with the same velocity. As a result, the pressure is the **average value** of  $nMv_x^2/V$ . Using angular brackets  $\langle v_x^2 \rangle$  to denote the average value of  $v_x^2$  gives

$$p = \frac{nM \langle v_x^2 \rangle}{V}$$

Because molecules are moving randomly,  $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$  and the average particle speed squared  $c^2$  is

$$c^2 = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle$$

**Important kinetic theory result:**

$$p = \frac{1}{3} \frac{nMc^2}{V}$$

# Comparison of the Kinetic Theory and Ideal Gas Pressure Equations

$$p = \frac{1}{3} \frac{nMc^2}{V} = \frac{nRT}{V}$$

**Mean (Average) Particle Speed Squared:**

$$c^2 = \frac{3RT}{M}$$

**Root Mean Squared (rms) Particle Speed:**

$$c = \sqrt{\frac{3RT}{M}}$$

# Comparison of the Kinetic Theory and Ideal Gas Pressure Equations

**Mean (Average) Particle Translational Kinetic Energy (per mole):**

$$\frac{1}{2}Mc^2 = \frac{1}{2}M(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle) = \frac{3}{2}RT$$

**Equipartition Theorem for the Mean Translational Kinetic Energy for Each of the  $x$ ,  $y$ , and  $z$  Dimensions (per mole):**

$$\frac{1}{2}M \langle v_x^2 \rangle = \frac{1}{2}M \langle v_y^2 \rangle = \frac{1}{2}M \langle v_z^2 \rangle = \frac{1}{2}RT$$

Important interpretation of the **temperature  $T$**

→ a measure of average molecular kinetic energy

## Comparison of the Kinetic Theory and Ideal Gas Equations

**Mean (Average) Translational Kinetic Energy (per mole):**

$$\frac{1}{2}Mc^2 = \frac{3}{2}RT$$

**Pressure:**

$$p = \frac{nRT}{V} = \frac{2}{3} \left( \frac{3}{2} \frac{RT}{V} \right) = \frac{2}{3} \left( \frac{\text{translational kinetic energy}}{\text{volume}} \right)$$

*A new interpretation of the pressure of a gas!*

→ 2/3 of the translational kinetic energy per unit volume

## Example: Argon gas at 300 K

**Mean argon atom speed squared:**

$$c^2 = \frac{3RT}{M} = \frac{3 (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{0.03995 \text{ kg mol}^{-1}} = 187,300 \text{ m}^2 \text{ s}^{-2}$$

**Mean molar translational kinetic energy:**

$$\frac{1}{2}Mc^2 = \frac{3}{2}RT = 3741 \text{ J mol}^{-1}$$

**Root-mean-squared (rms) argon atom speed:**

$$\begin{aligned} c &= \sqrt{187,300 \text{ m}^2 \text{ s}^{-2}} = 432.8 \text{ m s}^{-1} \\ &= 1558 \text{ km/hr} = 968.1 \text{ miles/hr} \end{aligned}$$

# The Speed of Sound $c_{\text{sound}}$ (*another important speed*)

from Chem 231:

$$c_{\text{sound}} = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_S} = \sqrt{\frac{1}{\rho \kappa_S}} = \sqrt{\frac{C_{pm}}{C_{Vm}} \frac{1}{\rho \kappa_T}}$$

$p$  = gas pressure

$\rho$  = gas density

$C_{Vm}$  = molar heat capacity at constant volume

$C_{pm}$  = molar heat capacity at constant pressure

**adiabatic compressibility  $\kappa_S$**

(at constant entropy)

$$\kappa_S = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p}\right)_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S$$

**isothermal compressibility  $\kappa_T$**

(at constant temperature)

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p}\right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

## Example: The Speed of Sound for Argon

assuming ideal-gas behavior  $\kappa_T = 1/p$  and:

$$p = nRT/V$$

$$\rho = nM/V$$

$$C_{Vm} = 3R/2 \text{ (for monatomic gases)}$$

$$C_{pm} = 5R/2 \text{ (for monatomic gases)}$$

Exercise: Show

$$c_{\text{sound}} = \sqrt{\frac{5}{3} \frac{RT}{M}}$$

for monatomic gases

For **argon at 300 K** the speed of sound is  $c_{\text{sound}} = 322.6 \text{ m s}^{-1}$

**Points to ponder:** the speed of sound is

- independent of pressure
- proportional to  $T^{1/2}$
- proportional to  $M^{-1/2}$



## Section 16.2 Velocity Distribution in One Dimension

Detailed mechanical description of macroscopic systems.

Need to specify:

- $x_i, y_i, z_i$  coordinates for the positions of  $\approx 10^{23}$  molecules?
- $v_{xi}, v_{yi}, v_{zi}$  velocity components for  $\approx 10^{23}$  molecules (constantly changing due to molecular collisions)?

**Mission Impossible!**

# Impossible to Calculate the Positions and Velocities of Molecules in Macroscopic Systems.

What to do? Give up?

***No! Plan B:***

Huge numbers ( $\approx 10^{23}$ ) of molecules are moving in random directions with different velocities – use **statistics**.

Calculate the velocity **distribution function** giving the **probability** of different molecular velocities, from  $-\infty$  to  $+\infty$

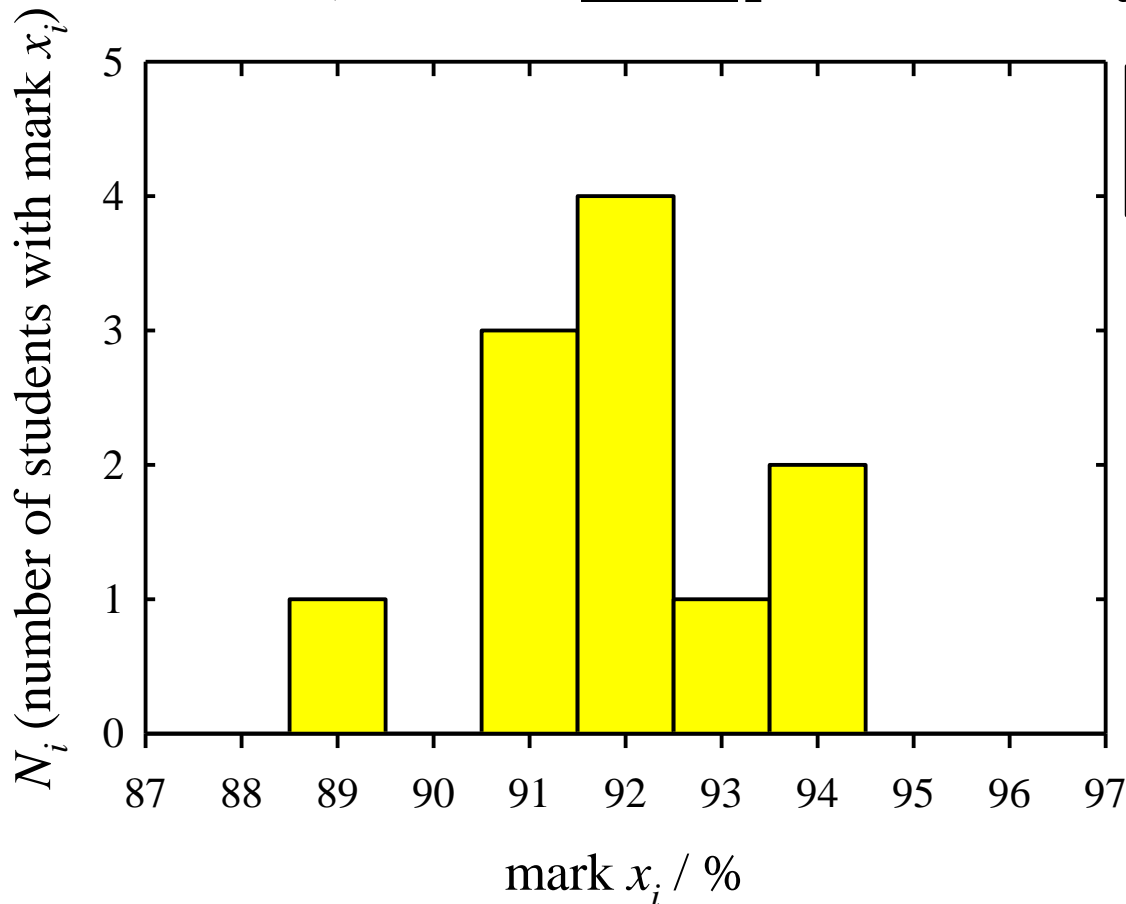
Average velocities, average speeds, average energies and other useful information can then be obtained.

# Distribution Functions

- What are they?
- Why are they important?
- How can we use them?

# An Example of a Distribution Function

- histogram plot of final-exam marks for Chem 232
- number  $N_i$  of students with mark  $x_i$  plotted against mark  $x_i$
- *a clear, concise visual presentation of the data*



a discrete distribution

*Why?*

$N_i$  and  $x_i$  are  
not continuous

$$N_i = 0, 1, 2, 3, 4$$

$$x_i = 89, 91, 92, 93, 94$$

## What is the average mark?

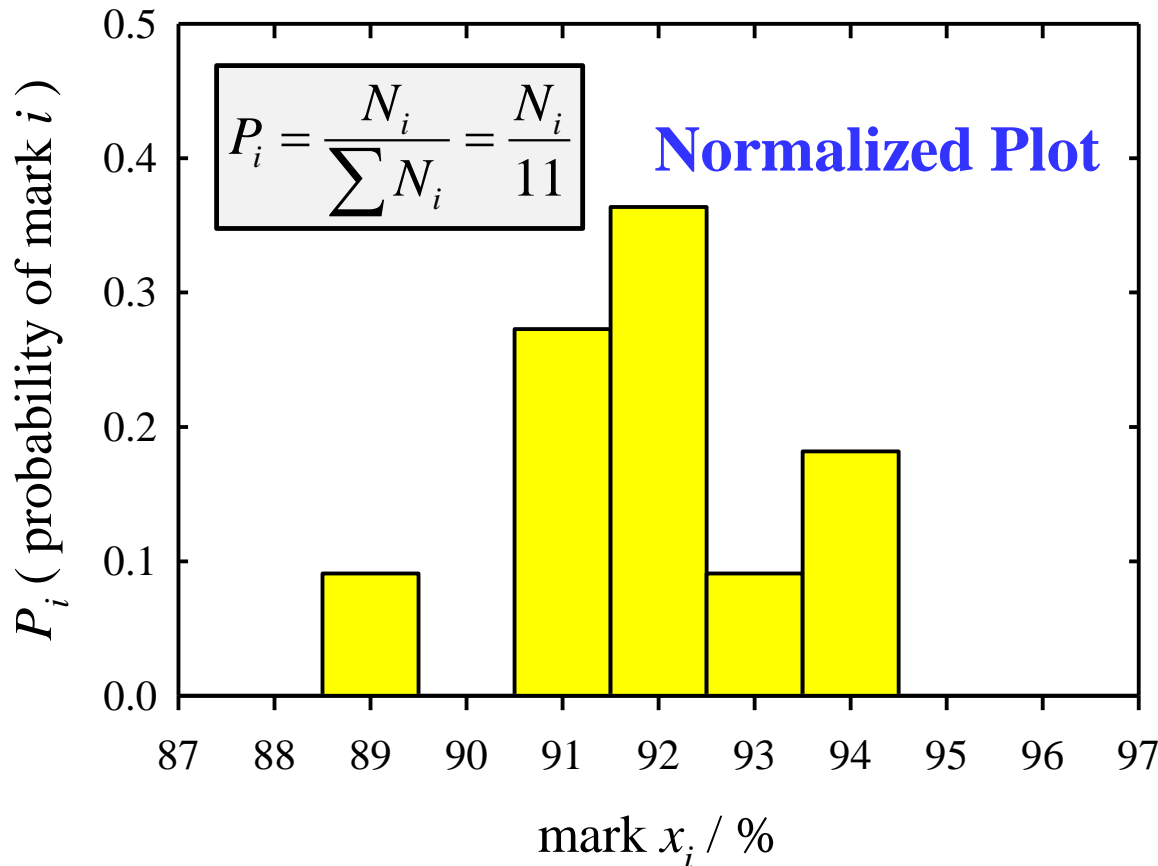
$$\langle x \rangle = \frac{\sum_i N_i x_i}{\sum_i N_i} = \frac{\text{total marks}}{\text{total number of students}}$$

$$\langle x \rangle = \frac{(1)(89) + (3)(91) + (4)(92) + (1)(93) + (2)(94)}{1 + 3 + 4 + 1 + 2}$$

$$\langle x \rangle = \frac{1101}{11} = 91.90 \%$$

## another way to calculate the average mark:

- the area under the histogram plot is  $\sum N_i = 11$
- Dividing by  $\sum N_i = 11$  gives  $P_i =$  **the probability of mark  $x_i$**
- the **normalized histogram** is the **mark probability distribution**



**Area = 1** under  
 $P_i$  plotted vs.  $N_i$

**Why?**

The area represents  
the sum of all possible  
probabilities.

## Calculating average values for a discrete probability distribution

$$P_i = \frac{N_i}{\sum N_i}$$

$$\langle x \rangle = \sum_i P_i x_i$$

$$= P_1 x_1 + P_2 x_2 + P_3 x_3 + P_4 x_4 + P_5 x_5 + P_6 x_6 + P_7 x_7 + P_8 x_8 + P_9 x_9 + P_{10} x_{10} + P_{11} x_{11}$$

$$= \frac{1}{11} 89 + \frac{0}{11} 90 + \frac{3}{11} 91 + \frac{4}{11} 92 + \frac{1}{11} 93 + \frac{2}{11} 94$$

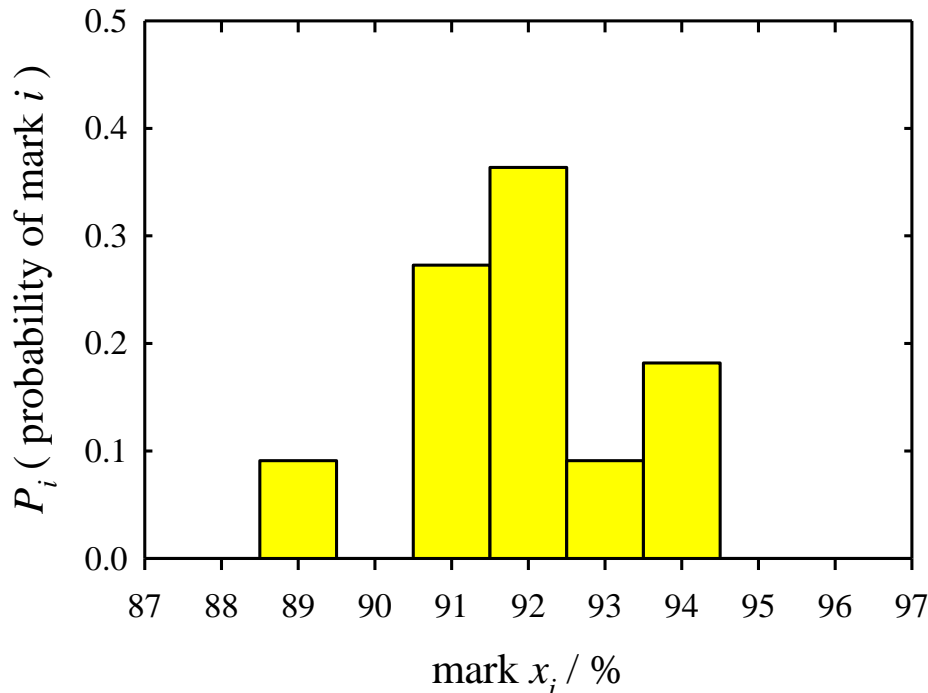
$$\langle x \rangle = 91.90 \% \quad \text{average mark}$$

# Calculating average values from a discrete probability distribution

$$P_i = \frac{N_i}{\sum N_i}$$

$$\langle x \rangle = \sum_i P_i x_i$$

The probability  $P_i$  of mark  $x_i = 0, 1, 2, \dots, 97, 98, 99, 100$  is the area of a rectangle of height  $P_i$  and width  $\Delta x = 1$ .





Average of discrete  $x_0, x_1, x_2, \dots$  values:

$$\langle x \rangle = \sum_i P_i x_i$$

What about averages of **continuous** values, such as velocities, speeds, translational kinetic energies, ...?

1. Use **probability distribution function  $P(x)$**  to give the probability  $x$  is between  $x$  and  $x + dx$
2. Instead of adding discrete  $x_i P_i$  values, integrate  $xP(x)dx$  values:

**replace discrete  $x_i P_i$   
with continuous  $P(x)dx$**

$$\langle x \rangle = \int xP(x)dx$$

## Example: Molecular Speeds

**Distribution function:**

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

gives the probability  $F(v)dv$  of molecules with speeds in the range from  $v$  to  $v + dv$ .

**Average speed:**

$$\langle v \rangle = \int_0^{\infty} v F(v) dv = \sqrt{\frac{8kT}{\pi m}}$$

# Distribution Functions

- applications in every branch of science and technology

## Important Example: Electron Probability Distributions $\psi^* \psi$

Solving Schrodinger's equation  $\hat{H}\psi = E\psi$  gives quantum mechanical wave functions  $\psi(x, y, z)$  describing 1s, 2s, 2p, 3s, 3p, 3d, ... electron orbitals.

The **probability** of finding an electron at coordinates  $x$  to  $x + dx$ ,  $y$  to  $y + dy$ ,  $z$  to  $z + dz$  in volume element  $dx dy dz$  is:

$$\psi^2(x, y, z) dx dy dz \quad \text{or} \quad \psi^*(x, y, z) \psi(x, y, z) dx dy dz$$

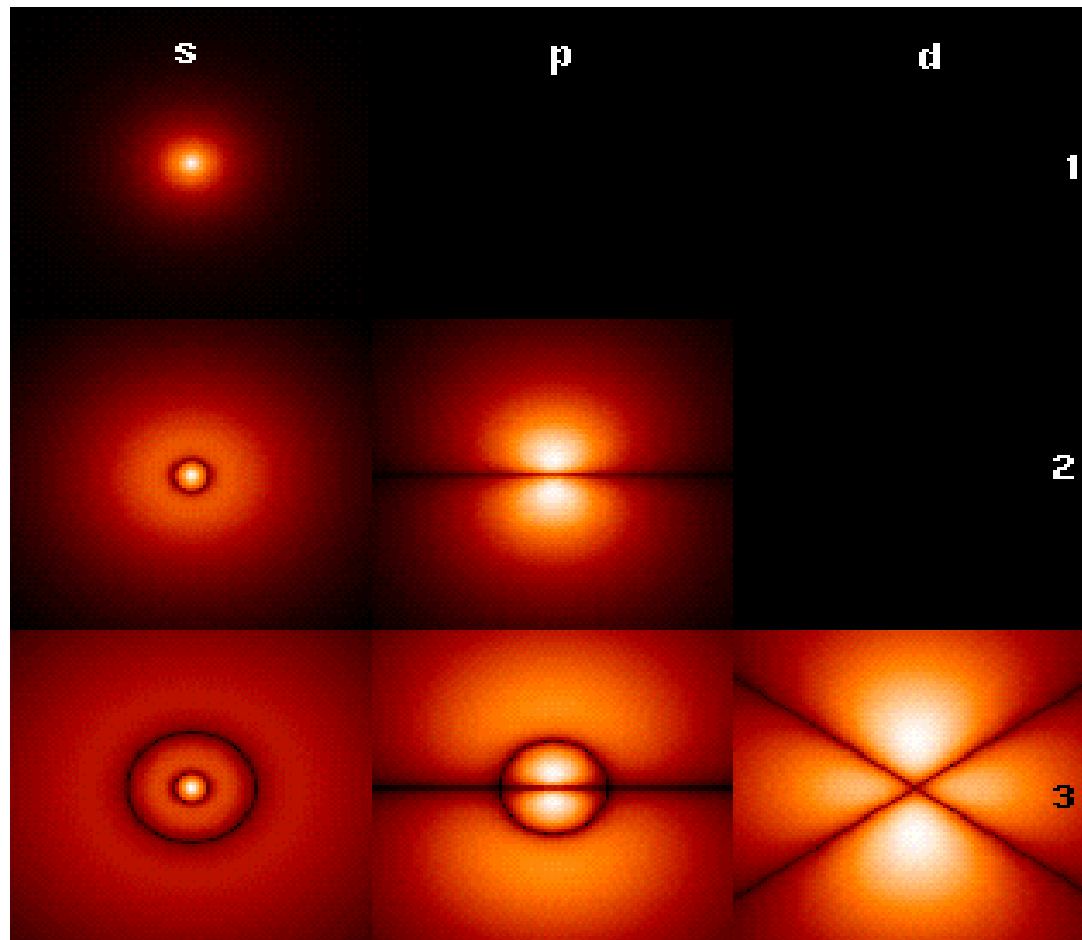
[ if  $\psi(x, y, z)$  is *real* ]

[ if  $\psi(x, y, z)$  is *complex* ]

**Probability distribution functions  $\psi^*(x, y, z)\psi(x, y, z)$**

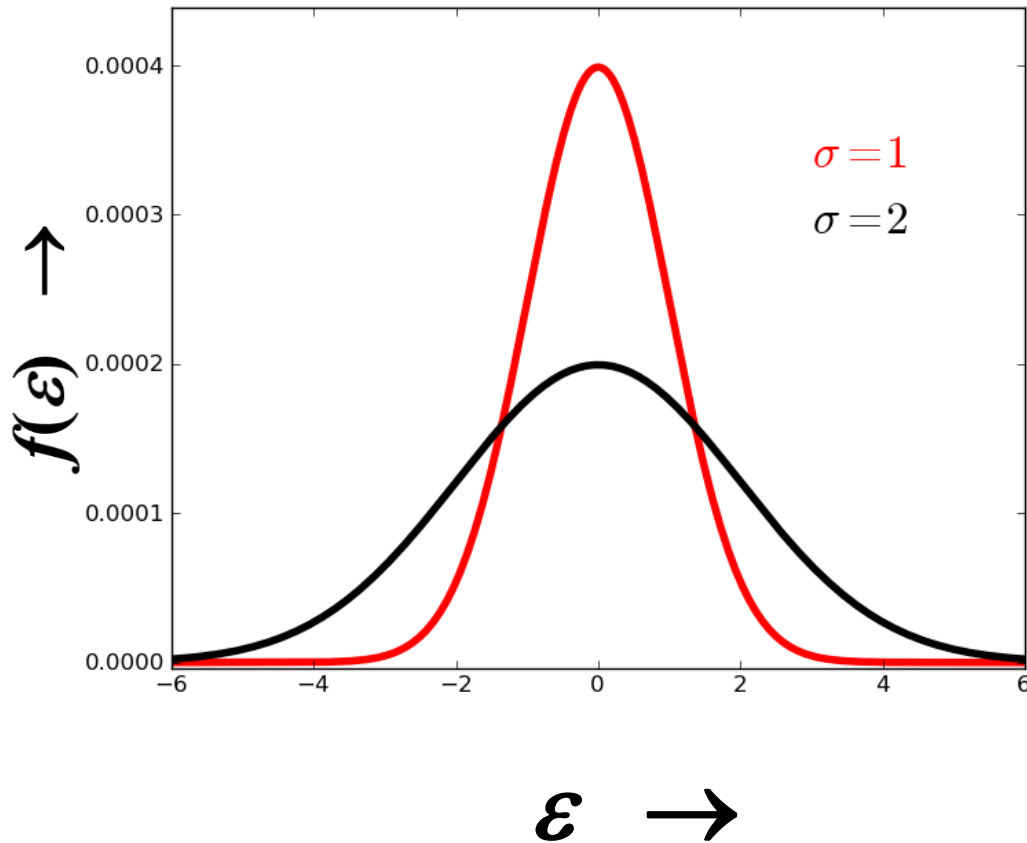
**for electrons in 1s, 2s, 2p, 3s, 3p, 3d orbitals**

(higher probability density in the brighter regions)



## Another important example of a distribution function:

### Normal (Gaussian) Distribution of Random Errors



$$f(\varepsilon) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\varepsilon^2/2\sigma^2}$$

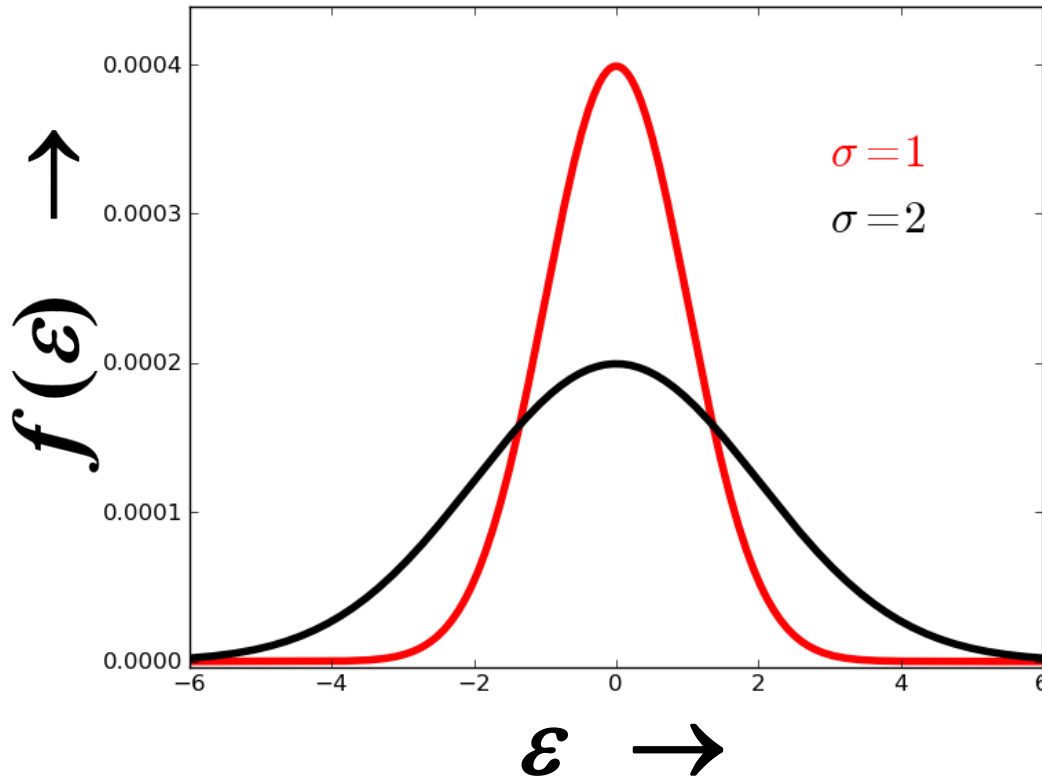
$\sigma$  = the **variance**  
(average value of  $\varepsilon^2$ )

narrow distribution: small  $\sigma$   
(high precision)

wide distribution: large  $\sigma$   
(low precision)

# Normal (Gaussian) Distribution of Random Errors $\varepsilon$

$$f(\varepsilon) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\varepsilon^2/2\sigma^2}$$



$f(\varepsilon)$  is normalized:

$$1 = \int_{-\infty}^{+\infty} f(\varepsilon) d\varepsilon$$

**Why?**

average value of  $\varepsilon$  is zero:

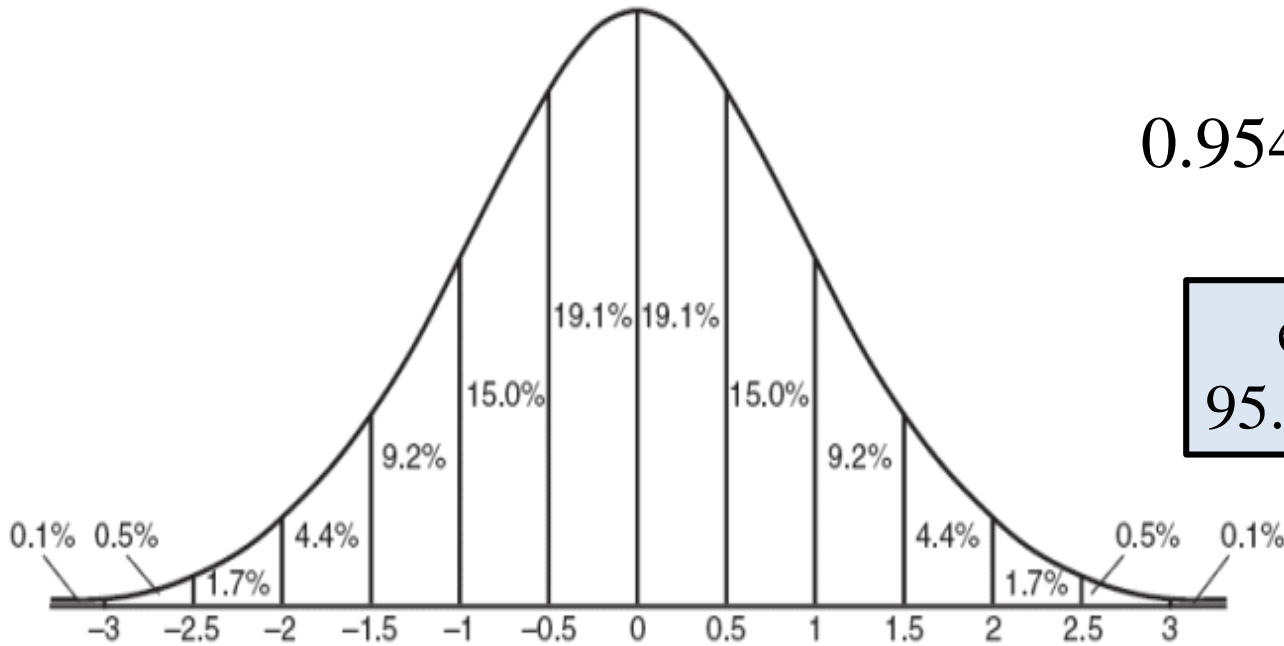
$$\langle \varepsilon \rangle = 0 = \int_{-\infty}^{+\infty} \varepsilon f(\varepsilon) d\varepsilon$$

**Why?**

average value of  $\varepsilon^2$  :  
(the variance  $\sigma^2$ )

$$\langle \varepsilon^2 \rangle = \sigma^2 = \int_{-\infty}^{+\infty} \varepsilon^2 f(\varepsilon) d\varepsilon$$

# Normal (Gaussian) Distribution of Random Errors $\varepsilon$



$$0.954 = \int_{-2\sigma}^{+2\sigma} f(\varepsilon) d\varepsilon$$

error  $\pm 2\sigma$   
95.5 % probability

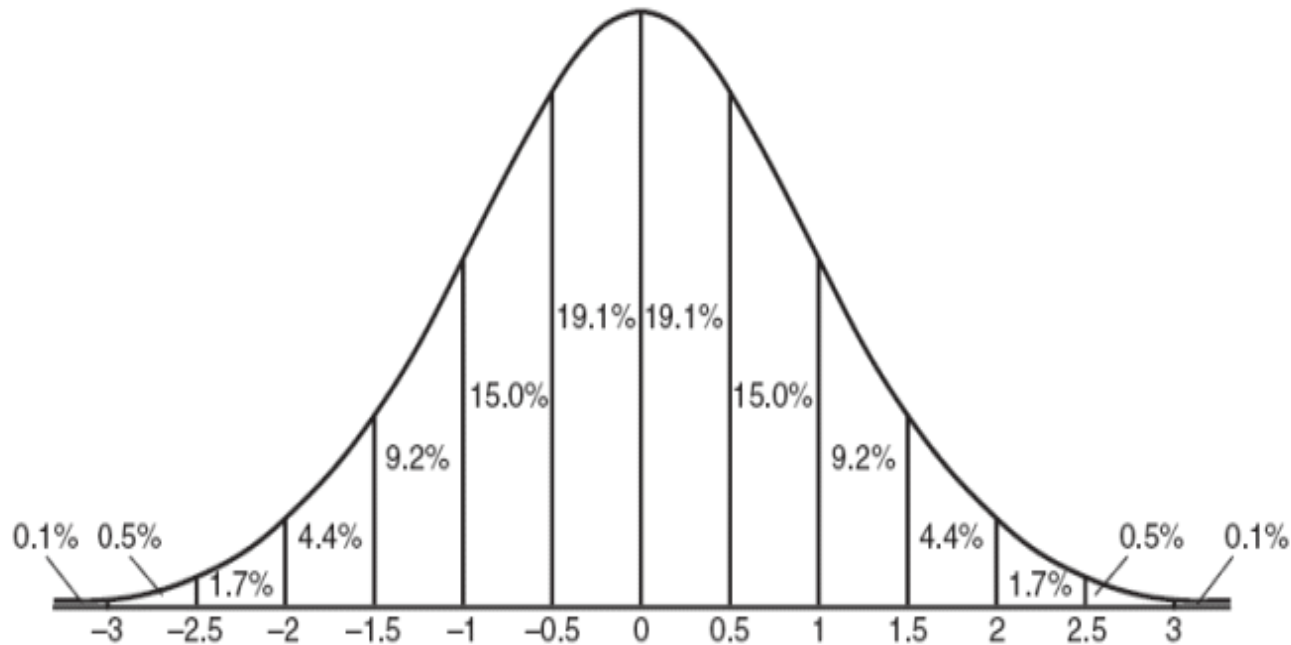
$$0.682 = \int_{-\sigma}^{+\sigma} f(\varepsilon) d\varepsilon$$

error  $\pm \sigma$   
68.2 % probability

$$0.998 = \int_{-3\sigma}^{+3\sigma} f(\varepsilon) d\varepsilon$$

error  $\pm 3\sigma$   
99.8 % probability

# Normal (Gaussian) Distribution of Random Errors $\varepsilon$



$$0.500 = \int_{-\infty}^0 f(\varepsilon) d\varepsilon$$

negative error:  
50 % probability

$$0.500 = \int_0^{+\infty} f(\varepsilon) d\varepsilon$$

positive error:  
50 % probability



## Another Example:

### Boltzmann Distribution over Molecular Energy Levels

The probability that a molecule is in energy level  $E_i$  is proportional to the **Boltzmann factor**  $\exp(-E_i/kT)$

$$f(E_i) \text{ proportional to } e^{-E_i/kT}$$

$$f(E_i) = Ae^{-E_i/kT}$$

$A$  is a normalization factor

# Barometric Equation: Boltzmann Distribution of Molecules in a Gravity Field

A molecule at elevation  $h$  above sea level has **gravitational potential energy  $mgh$**

The probability that a molecule is at elevation  $h$  is proportional to the Boltzmann factor  $\exp(-mgh/kT)$

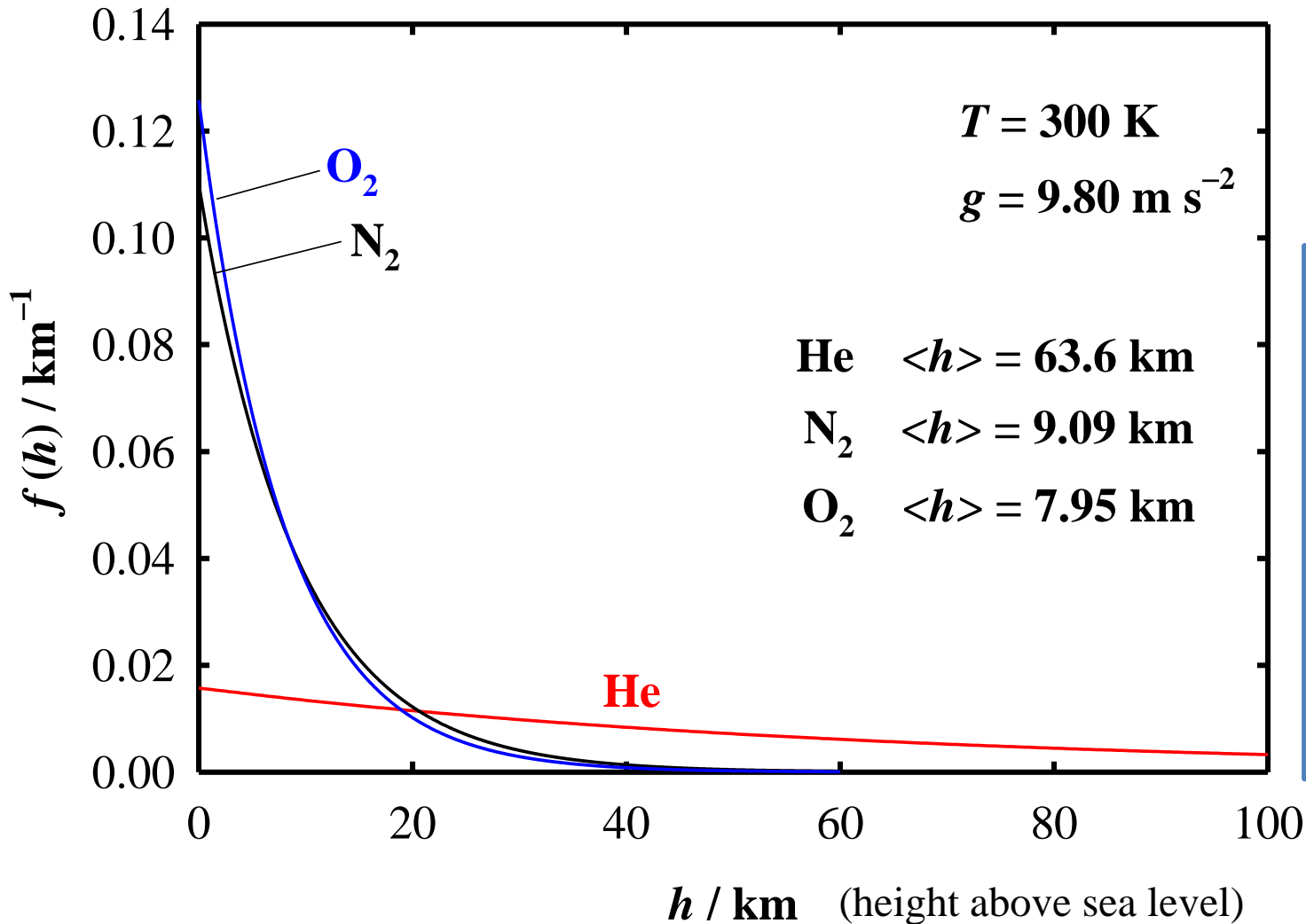
find:

$$f(h) = \frac{mg}{kT} e^{-mgh/kT} = \frac{1}{\langle h \rangle} e^{-h/\langle h \rangle}$$

average elevation:

$$\langle h \rangle = \frac{kT}{mg} = \int_0^{+\infty} hf(h)dh$$

# Barometric Distribution of He, N<sub>2</sub> and O<sub>2</sub>



$$1 = \int_0^{+\infty} f(h) dh$$

H<sub>2</sub> and He are by far the most abundant elements in the Universe.

Why is there  
 ≈ no H<sub>2</sub> and  
 ≈ no He in our  
 atmosphere?

*Back to Section 16.2:*

## Velocity Distribution $f(v_x)$ in One Dimension

A molecule of mass  $m$  moving in the  $x$ -direction with velocity  $v_x$  has translational kinetic energy:

$$E_{vx} = \frac{1}{2}mv_x^2$$

The Boltzmann distribution gives

$$f(v_x) = Ae^{-E_{vx}/kT} = Ae^{-mv_x^2/2kT}$$

with normalization constant  $A$

## Velocity Probability Distribution $f(v_x)$ in One Dimension

$$f(v_x) = Ae^{-E_{vx}/kT}$$

The pre-exponential normalization factor  $A$  is evaluated using:

$$1 = \int_{-\infty}^{+\infty} f(v_x) dv_x = A \int_{-\infty}^{+\infty} e^{-mv_x^2/2kT} dv_x = A \sqrt{\frac{2\pi kT}{m}}$$

use a **table of definite integrals** to evaluate this term

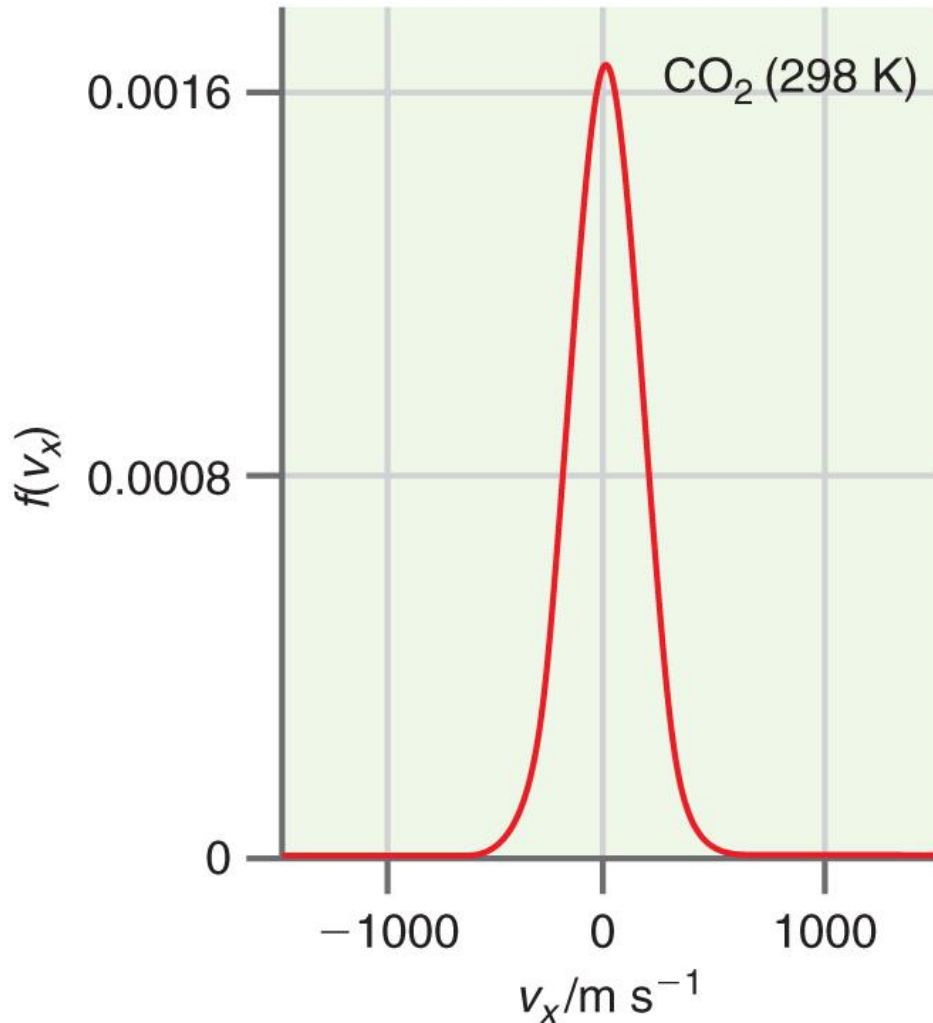
Find:

$$A = \sqrt{\frac{m}{2\pi kT}}$$

and

$$f(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT}$$

# Velocity Distribution Function in One Dimension



$$f(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT}$$

**What is  $f(v_x)$ ?**

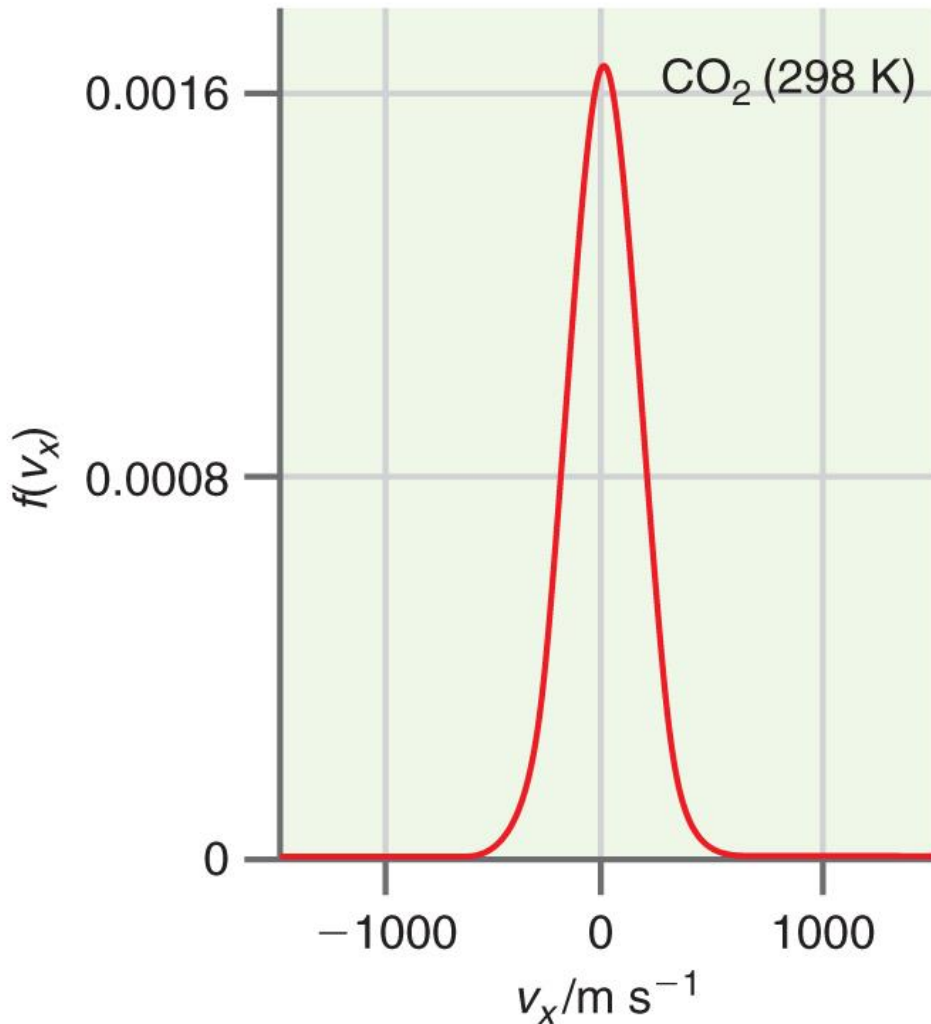
$f(v_x)dv_x$  is the probability molecular velocity  $v_x$  is in the range  $v_x$  to  $v_x + dv_x$

$m$  = molecular mass

$k = R/N_{\text{Avogadro}}$  = Boltzmann constant

$T$  = temperature

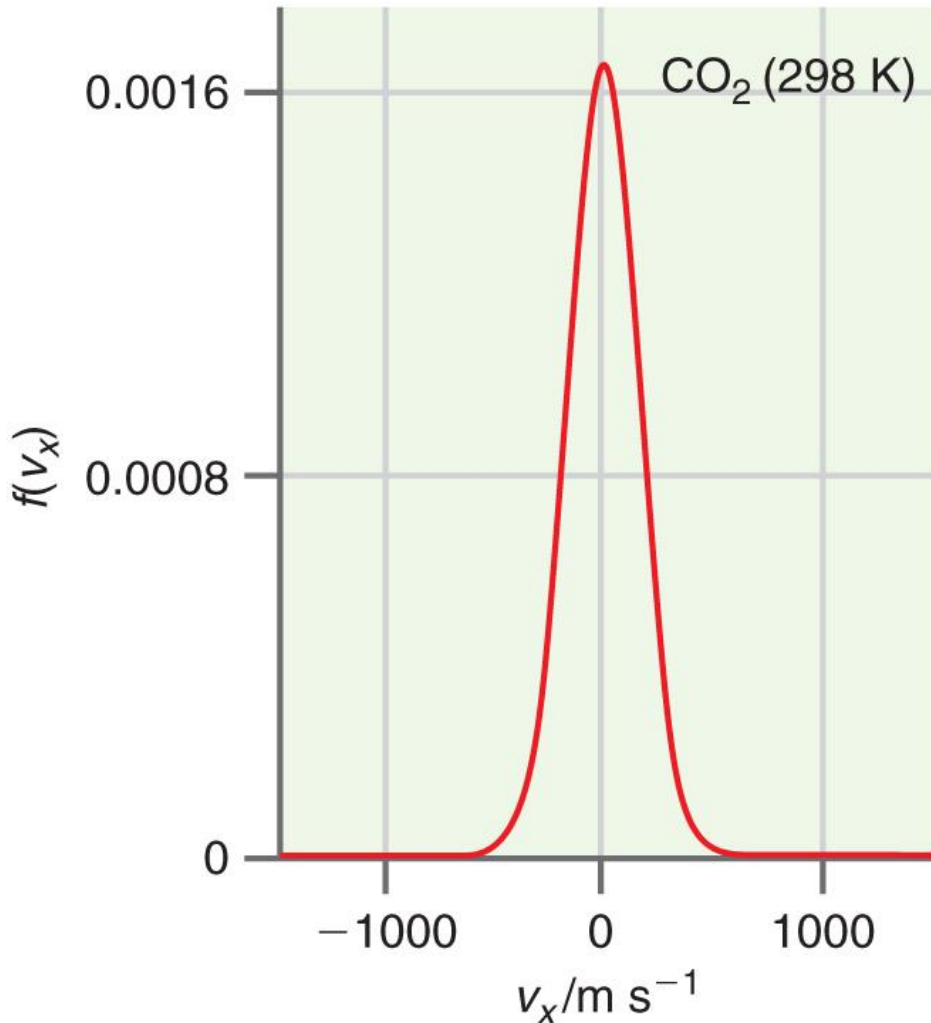
# Velocity Distribution Function in One Dimension



$$f(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT}$$

- Most probable value of  $v_x$ ? **Why?**  
(*hint*: there is no bulk flow)
- Why is  $f(v_x)$  symmetrical?  
 $f(v_x) = f(-v_x)$
- $f(v_x) \rightarrow 0$  as  $v_x \rightarrow \pm\infty$  **Why?**
- Same distribution for  $v_y$  and  $v_z$ ?

# Velocity Distribution Function in One Dimension



$$f(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT}$$

Compare  $f(v_x)$  with the normal distribution of random errors:

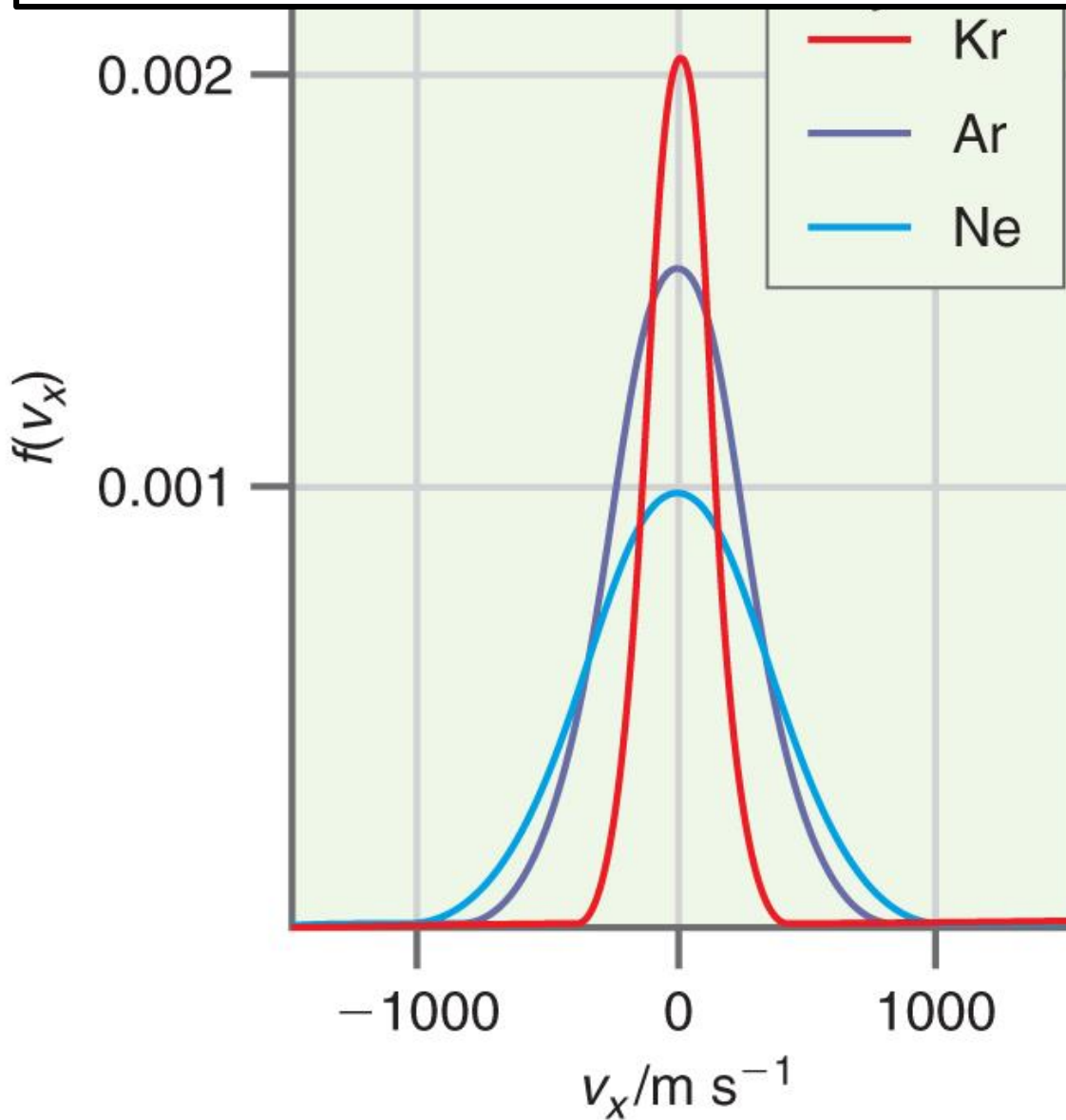
$$f(\varepsilon) = \frac{1}{\sqrt{2\pi} \sigma} e^{-\varepsilon^2/2\sigma^2}$$

**Notice** *(it's no accident!)*:

$f(v_x)$  is a normal distribution with variance  $\sigma^2 = \langle v_x^2 \rangle = kT/m$



# Velocity Distribution Functions for Neon, Argon and Krypton



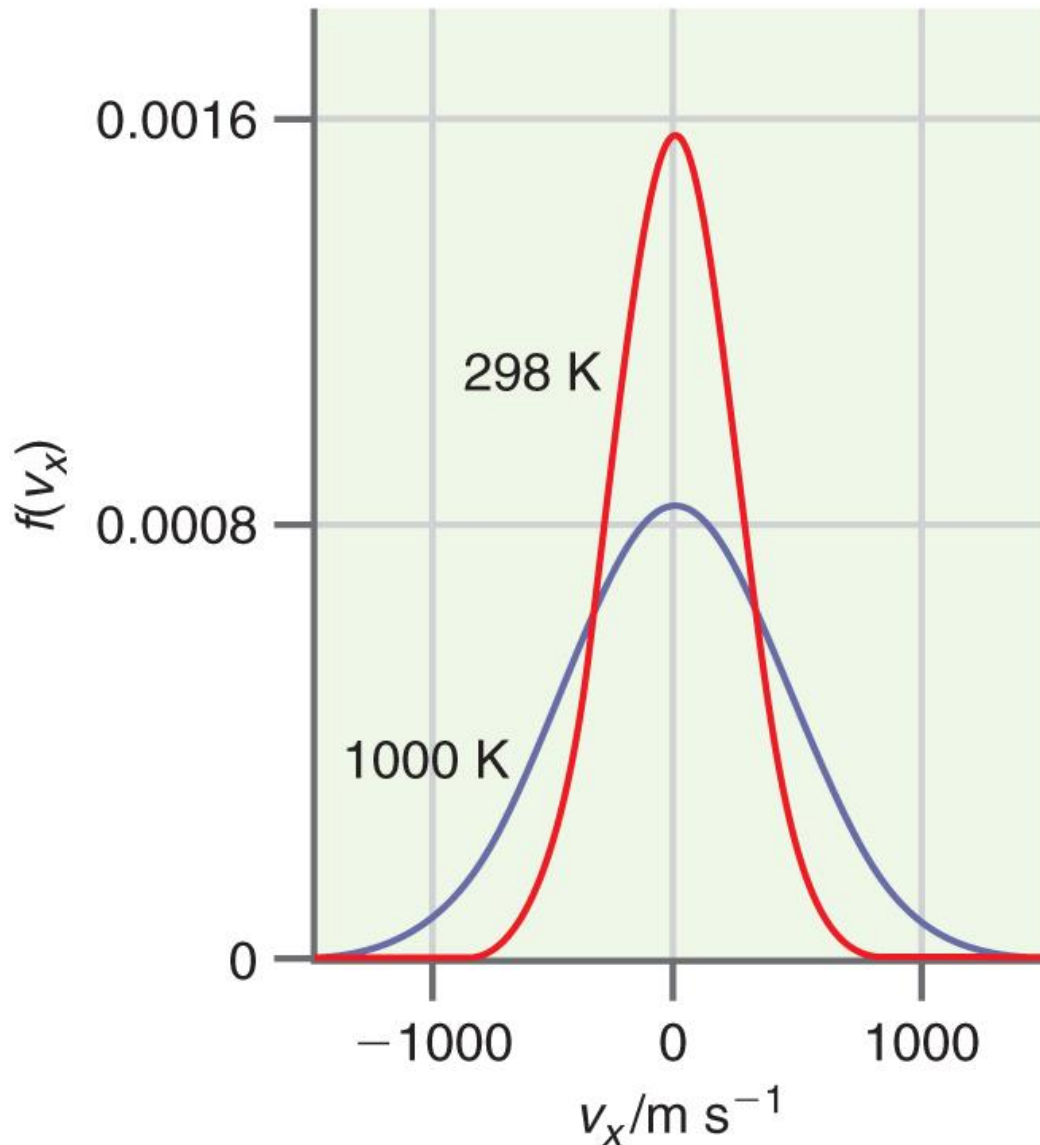
$$T = 298 \text{ K}$$

As the molecular mass increases, the velocity distributions get:

- narrower
- taller

Does this make sense?

# Velocity Distribution for Ar at 298 K and 1000 K



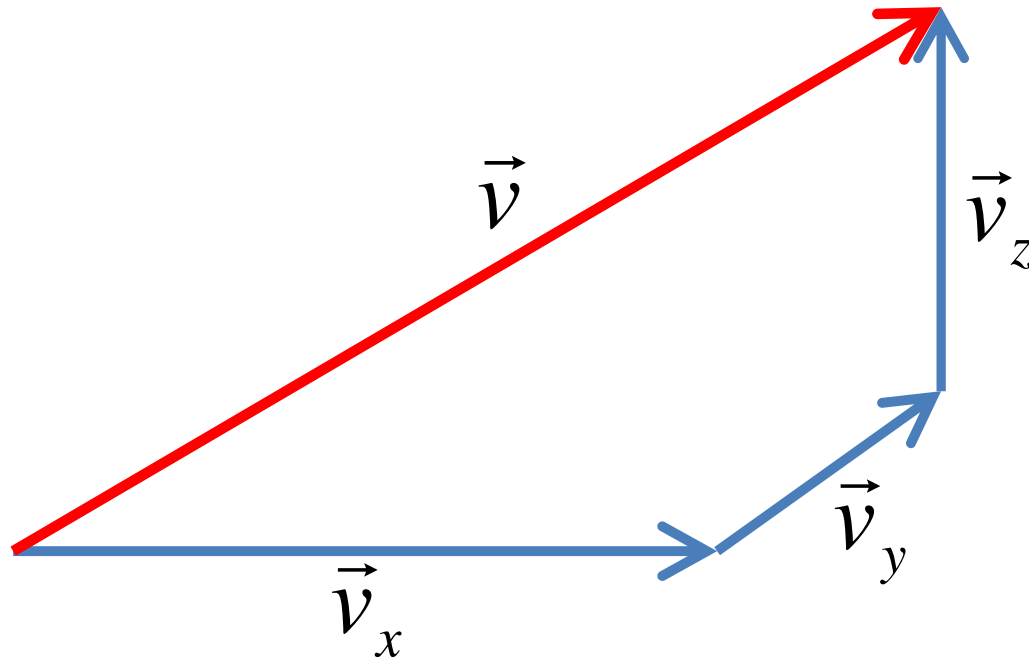
## Temperature Effects

As the temperature decreases, velocity distributions get taller and narrower.

Does this make sense?

## Section 16.3 Distribution of Molecular Speeds

A **molecular velocity**  $\vec{v}$  is the **vector** sum of the velocity components in the  $x$ ,  $y$  and  $z$  directions.



$$\vec{v} = \vec{v}_x + \vec{v}_y + \vec{v}_z$$

magnitude  
*and*  
direction

## Section 16.3 Distribution of Molecular Speeds

A **molecular speed**  $v$  is the magnitude (no direction) of the velocity vector.

(Pythagoras Theorem)

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

Notice that different velocity vectors can give the same speed (*important later*). Example:

$$\vec{v}_x = 100 \text{ m s}^{-1} \quad \vec{v}_y = 350 \text{ m s}^{-1} \quad \vec{v}_z = -200 \text{ m s}^{-1}$$

and

$$\vec{v}_x = 350 \text{ m s}^{-1} \quad \vec{v}_y = 200 \text{ m s}^{-1} \quad \vec{v}_z = 100 \text{ m s}^{-1}$$

Probability of a velocity vector with  $x$ ,  $y$  and  $z$  components

$v_x$  to  $v_x + dv_x$

$v_y$  to  $v_y + dv_y$

$v_z$  to  $v_z + dv_z$

$$= f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$$

$$= \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT} \sqrt{\frac{m}{2\pi kT}} e^{-mv_y^2/2kT} \sqrt{\frac{m}{2\pi kT}} e^{-mv_z^2/2kT} dv_x dv_y dv_z$$

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

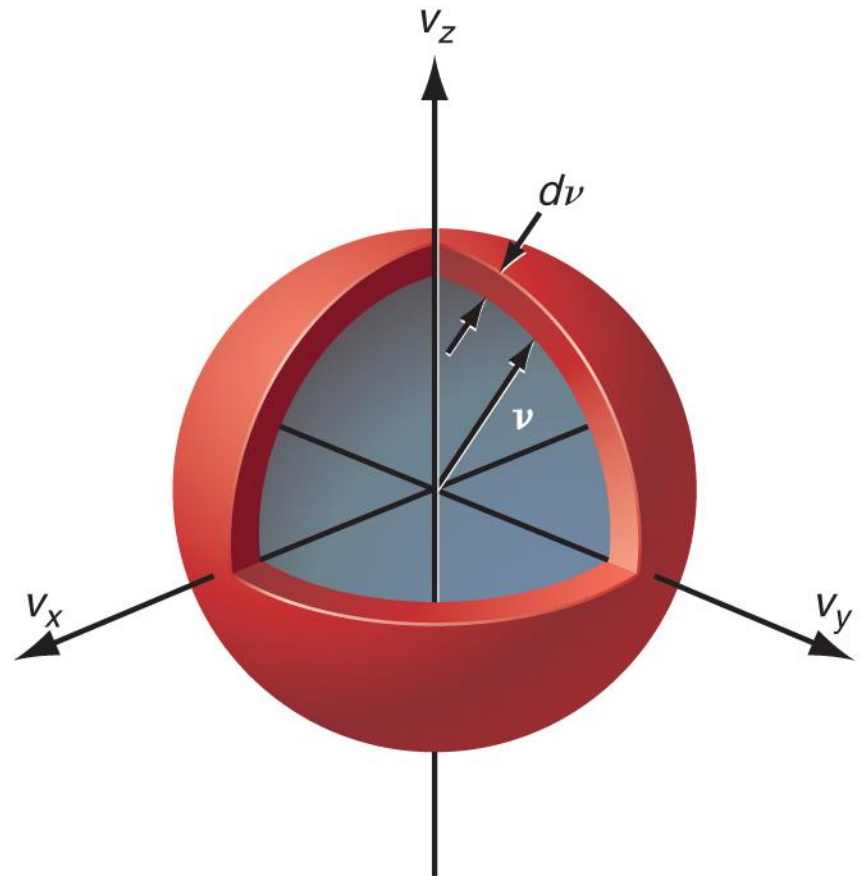
$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} dv_x dv_y dv_z$$

$dv_x dv_y dv_z$  can be pictured as a “tiny cube” in three-dimensional velocity space with edges  $dv_x$  and  $dv_y$  and  $dv_z$ .

To calculate the probability a given molecular speed, add up the volumes  $dv_x dv_y dv_z$  of cubes in a spherical shell that give the same speed **in any direction**

A “speed shell” from  $v$  to  $v + dv$  has area  $4\pi v^2$ , thickness  $dv$  and “volume”  $4\pi v^2 dv$ .

The sum of  $dv_x dv_y dv_z$  values that gives speeds from  $v$  to  $v + dv$  is  $4\pi v^2 dv$ .



Show the volume of a speed-shell of radius  $v$  and differential thickness  $dv$  is  $4\pi v^2 dv$

**shell volume** = volume of sphere(radius  $v + dv$ ) – volume of sphere(radius  $v$ )

$$= (4/3)\pi(v + dv)^3 - (4/3)\pi(v)^3$$

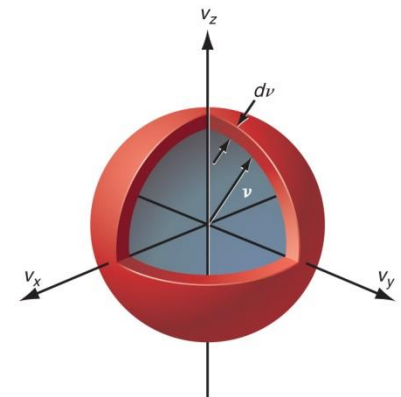
$$= (4/3)\pi [ (v + dv)^3 - (v)^3 ]$$

negligible 2<sup>nd</sup>-order and 3<sup>rd</sup>-order differential terms

$$= (4/3)\pi [ \cancel{v^3} + 3v^2dv + 3v(dv)^2 + (dv)^3 - \cancel{v^3} ]$$

$$= (4/3)\pi [ 3v^2dv ]$$

$$= 4\pi v^2 dv$$



# Maxwell Speed Distribution Function $F(v)$

Important result: the probability of a **molecular speed** in the range from  $v$  to  $v + dv$  is

in terms of molecular mass  $m$ :

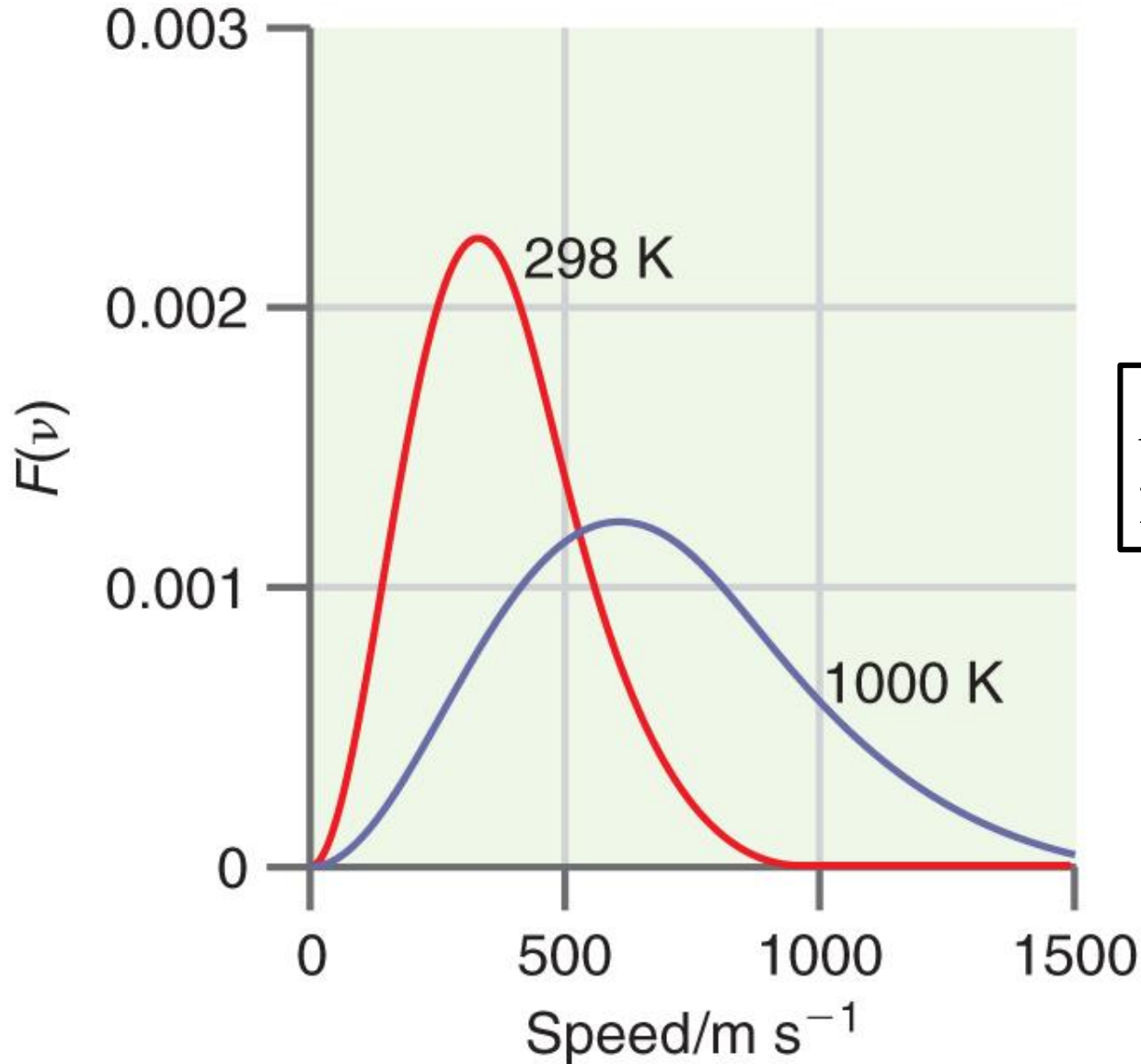
$$F(v)dv = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv$$

in terms of molar mass  $M$ :

$$F(v)dv = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT} dv$$

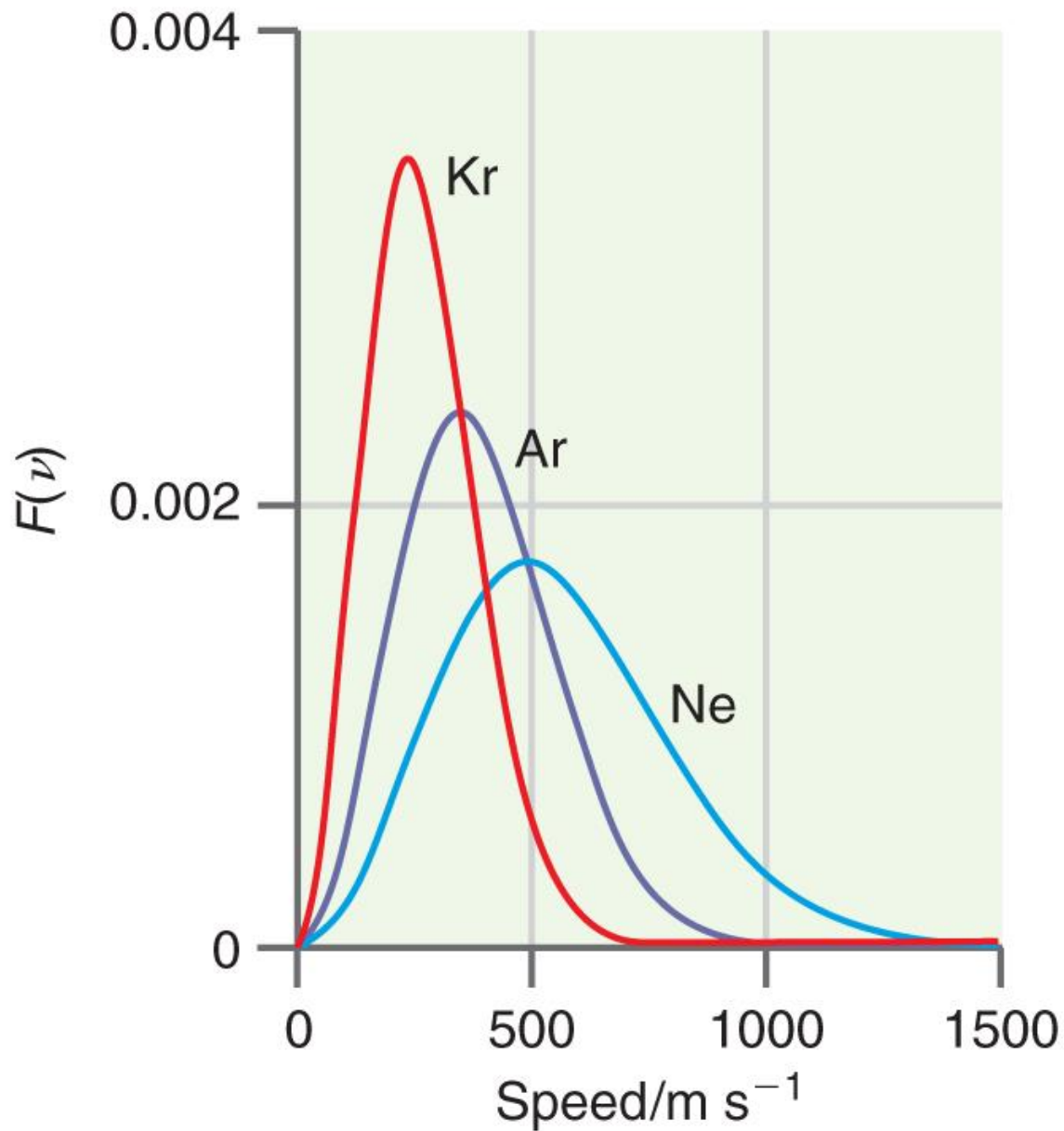


What do speed distribution functions “look like”?



temperature effects

$F(v)$  for argon at  
298 K and 1000 K



mass effects

$$m_{\text{Ne}} < m_{\text{Ar}} < m_{\text{Kr}}$$

Speed distribution functions at 298 K for Ne, Ar and Kr

## Maxwell Speed Distribution Function $F(v)$

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

The probability of a molecule with a speed in the range  $v_1$  to  $v_2$  is the area under the  $F(v)$  curve plotted from  $v_1$  to  $v_2$

$F(v) \rightarrow 0$  as  $v \rightarrow 0$  and as  $v \rightarrow \infty$ . This means very few molecules have very low or very high speeds

The fraction of molecules with speeds larger than 10 times the most probable speed (calculated next) is  $9 \times 10^{-42}$ .  
No molecules have speeds this high!

## Section 16.4 Most Probable, Average and Root-Mean-Square (rms) Molecular Speeds

### Most Probable Molecular Speed ( $v_{\text{mp}}$ )

Gas molecules move with a wide range of different speeds.

What is the most probable molecular speed?

Find  $v_{\text{mp}}$  that maximizes  $F(v)$ . Solve:

$$\frac{dF(v)}{dv} = \frac{d}{dv} \left[ 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \right] = 0$$

$$4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \left[ 2v - \frac{mv^3}{kT} \right] = 0$$

Find ( *try it!* ):

$$v_{\text{mp}} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

## Average Molecular Speed ( $v_{\text{ave}}$ )

What is the average molecular speed? Solve:

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

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

$$= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2} \left( \frac{2kT}{m} \right)^2$$

use a **table of definite integrals**  
to evaluate this term

Find (*try it!*):

$$v_{\text{ave}} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

## Root-Mean-Squared Speed ( $v_{\text{rms}}$ )

Root-mean-squared speed sounds complicated, but it's just the square root of the average squared speed\* (the variance):

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

This might look familiar!

$v_{\text{rms}}$  is identical to the square root of the average squared speed calculated from equipartition theory:

$$\frac{1}{2}m \langle v^2 \rangle = \frac{1}{2}m(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle) = 3 \frac{kT}{2}$$

## Root-Mean-Squared Speed ( $v_{\text{rms}}$ )

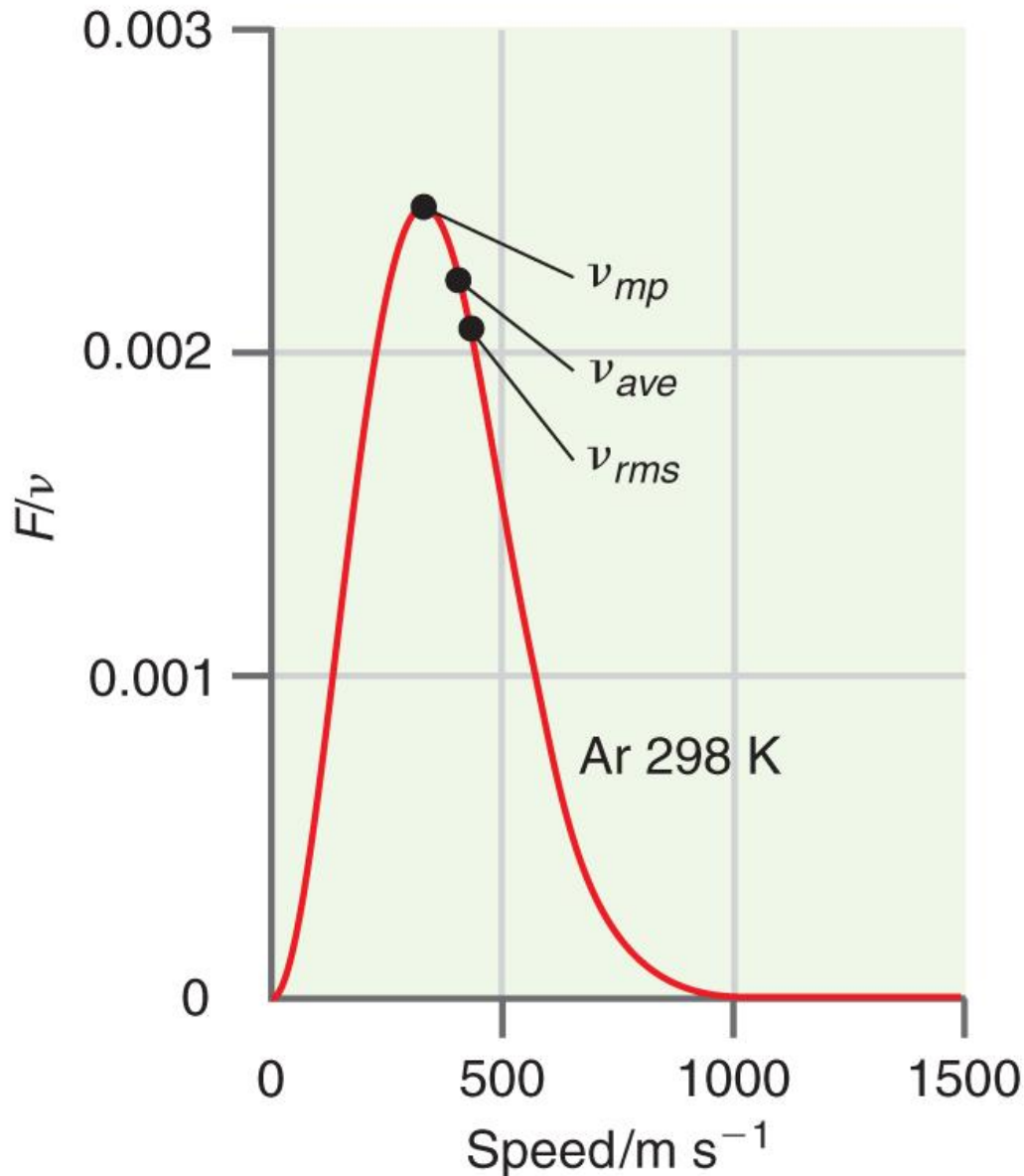
\*Note that the root-mean-squared speed  $v_{\text{rms}}$   
(first square  $v$ , then average, then take the square root)

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

differs from the root-squared-mean speed  
(first average  $v$ , then square, then take the square root)  
which is just the average speed

$$v_{\text{rsm}} = \sqrt{\langle v \rangle^2} = \langle v \rangle = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

# Most Probable, Average, and Root-Mean-Square Speeds



Argon at 25 °C

The most probable speed is smaller than the average speed.

Also, the average speed is smaller than the rms speed.

**Why?**

**Hint:** Notice that  $F(v)$  is not symmetrical.

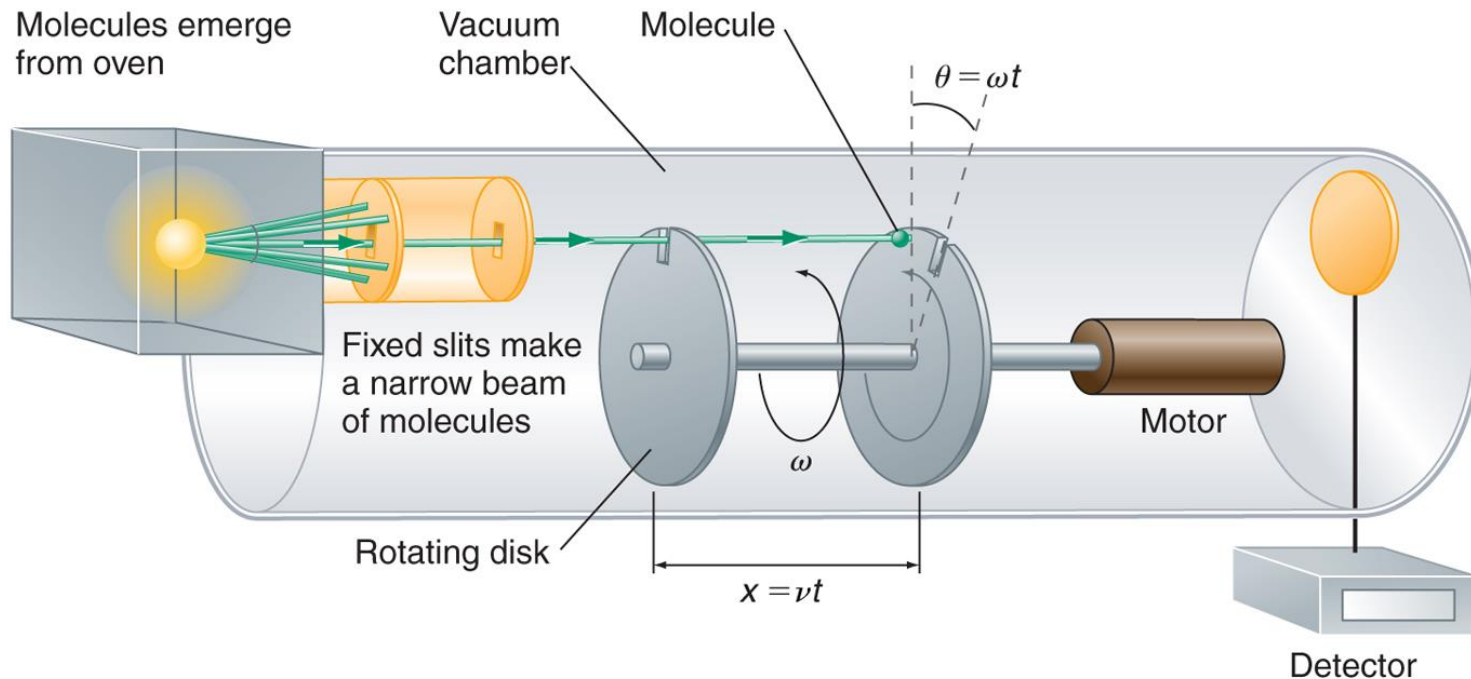


Theory is fine, but can speed distributions *be measured* ?

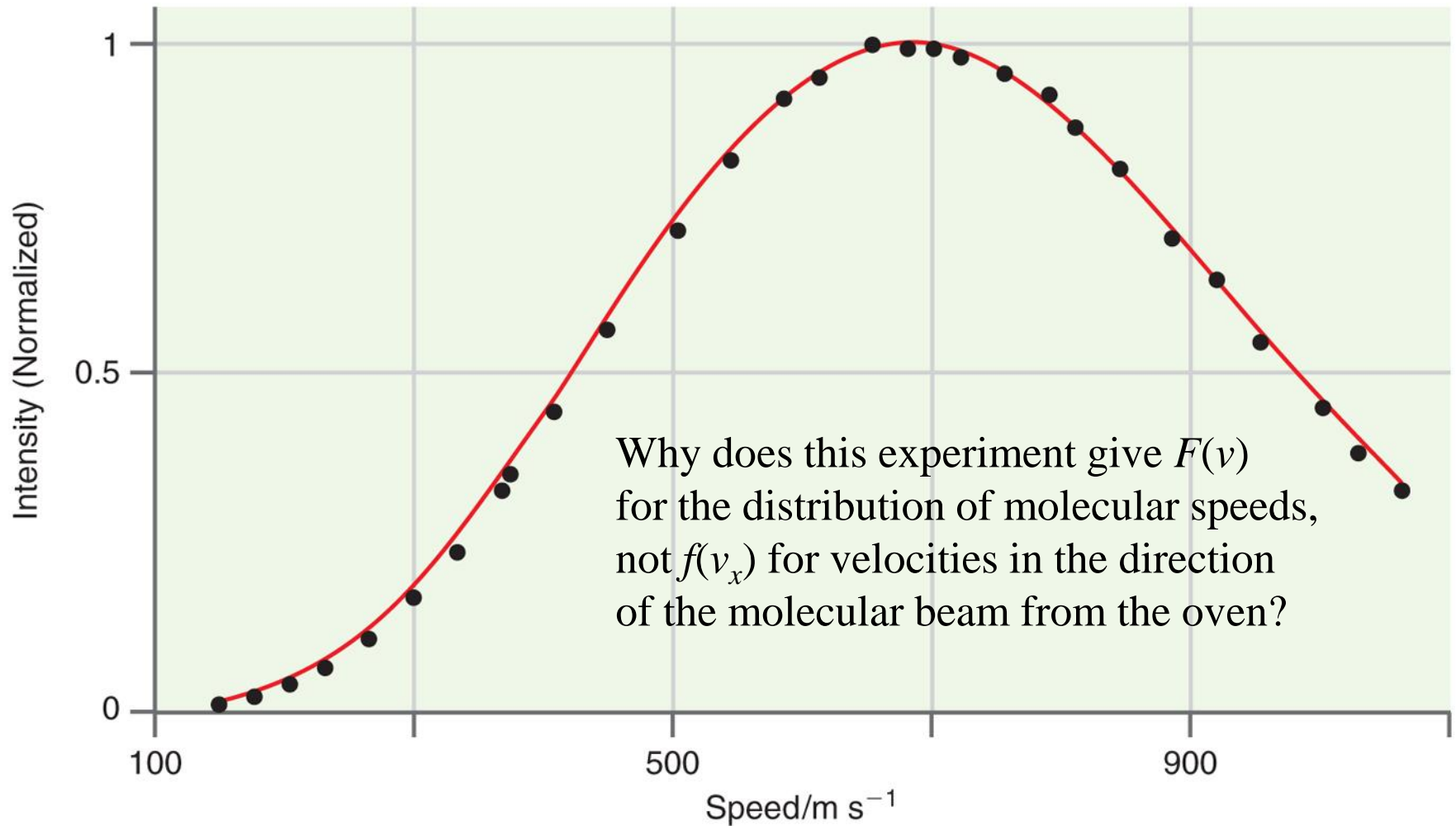
**One approach:** Use a **molecular beam** and **velocity selector**

An oven with a pinhole and collimating slits emits a narrow beam of gas molecules. The molecules pass through a pair of slots offset by angle  $\theta$  in rotating metal discs.

Discs separated by distance  $L$  rotating at angular velocity  $\omega$  provide  $L = t v$  and  $\theta = \omega t$  which selects molecules with speed  $v = \omega L / \theta$ . Molecules with other speeds hit the discs and do not reach the detector.



**Figure 16.8** Measured (●) and predicted (—) speed distributions for potassium vapor at 466 K. Miller and Kusch. *Phys. Rev.* **1955**, 99, 1314.



## Distribution of Translational Kinetic Energies $E$

For some applications it is important to know the probability **distribution of molecular energies**.

The probability  $F(E)dE$  of a molecule with translational kinetic energy in the range  $E$  to  $E + dE$  is calculated from the probability  $F(v)dv$  of molecular speeds

The kinetic energy of a molecule is  $E = mv^2/2$ , which gives

$$v = (2E/m)^{1/2}$$

$$dv = dE/(2mE)^{1/2}$$

for the molecular speed and its differential.

## Distribution of Translational Kinetic Energies $E$

Substitution of  $v = (2E/m)^{1/2}$  and  $dv = dE/(2mE)^{1/2}$  into

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

for the probability of molecular speeds gives (*try it!*)

$$F(E)dE = \frac{2\pi\sqrt{E}}{(\pi kT)^{3/2}} e^{-E/kT} dE$$

$F(E)dE$  is independent of the molecular mass. *Why?*

The average translational kinetic energy is

$$\langle E \rangle = \int_0^{\infty} EF(E)dE = \frac{3}{2}kT$$

# Distribution of Translational Kinetic Energies $E$

Probability of molecular translational energies:

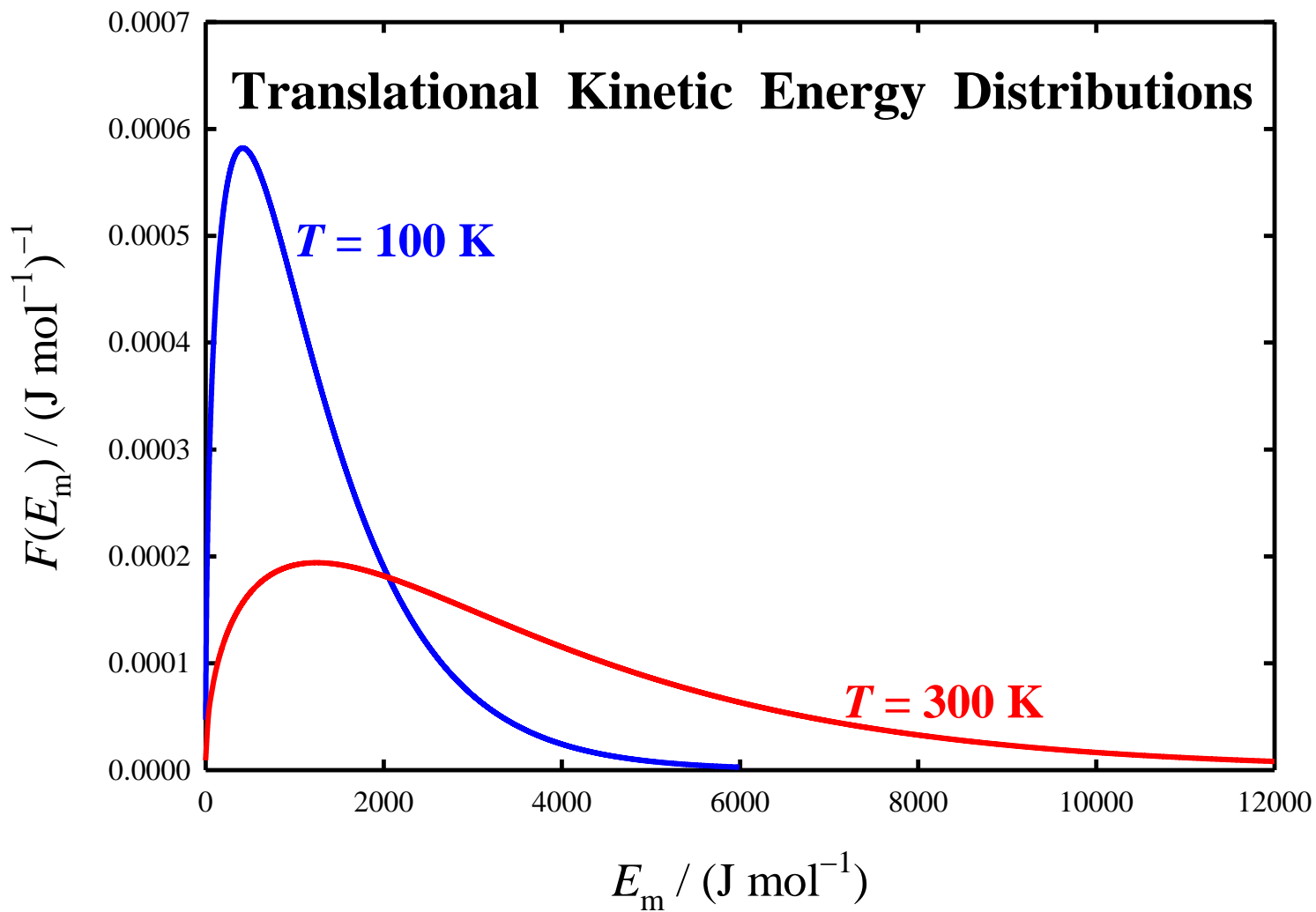
$$F(E)dE = \frac{2\pi\sqrt{E}}{(\pi kT)^{3/2}} e^{-E/kT} dE$$

Probability of molar translational energies (use  $E_m = N_A E$  and  $R = N_A k$ ):

$$F(E_m)dE_m = \frac{2\pi\sqrt{E_m}}{(\pi RT)^{3/2}} e^{-E_m/RT} dE_m$$

$F(E)dE$  and  $F(E_m)dE_m$  are independent of molecular mass.

*Why?*



**Lots and lots of theoretical equations** for molecular velocities and speeds. Another academic exercise. Another *Zzzzzz* ...

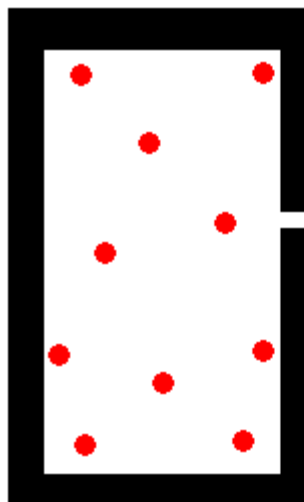
**No!**

**Lots and lots of practical applications too!** Predict:

- rates of molecular collisions (important for reaction rates – reactant molecules need to collide to react)
- rates of molecular collision with surfaces (important for gas/solid reactions, catalysis, crystallization, etc.)
- leak rates
- isotope separation (*e.g.*,  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$ )
- transport properties, such as viscosity, diffusion and heat conduction (*next Chapter*)

## Section 16.5 Molecular Collisions with Surfaces and Gas Effusion

- How many gas molecules hit the wall of a container per unit area per second?
- What does the collision rate depend on?
- If there is a hole in the wall of a container, how rapidly do the gas molecules leak out (effusion)?



use rates of effusion to  
measure vapor pressures?



Calculating wall collision rates illustrates a useful application of velocity distribution functions. Analysis:

Consider molecules hitting a wall of **area A** perpendicular to the  $x$  axis.

In time interval  $dt$ , a molecule moves distance  $v_x dt$  in the  $x$ -direction

A molecule hits the wall in the time interval  $dt$  if the molecule is moving toward the wall ( $v_x > 0$ ) and within distance  $v_x dt$  of the wall.

The number of molecules in volume  $Av_x dt$  with velocities from  $v_x$  to  $v_x + dv_x$  is

$$\frac{N}{V} (Av_x dt) f(v_x) dv_x$$

Collision rate per unit surface area per unit time is calculated from

$$\frac{N}{V} (Av_x dt) f(v_x) dv_x$$

by: dividing by wall area  $A$

dividing by time interval  $dt$

integrating over all molecules moving toward the wall

$$Z_c = \frac{N}{V} \int_0^{\infty} v_x f(v_x) dv_x = \frac{p}{kT} \int_0^{\infty} v_x \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT} dv_x$$

Molecular collision rate with a wall per unit area per unit time.

$$Z_c = \frac{p}{\sqrt{2\pi mkT}} = \frac{N}{V} \sqrt{\frac{kT}{2\pi m}} = \frac{N}{V} \frac{\langle v \rangle}{4}$$

$Z_c$  is proportional to the number of molecules per unit volume,  $T^{1/2}$  and  $m^{-1/2}$ .

**Example 1** A container holds argon at 1 atm and 298 K. How many argon atoms hit the container wall per square centimeter per second?

Collision rate per unit area per unit time:

$$\begin{aligned}Z_c &= \frac{p}{\sqrt{2\pi mkT}} \\&= \frac{101325 \text{ Pa}}{\sqrt{2\pi (0.0400 \text{ kg mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1}) (1.381 \times 10^{23} \text{ J K}^{-1}) (298 \text{ K})}} \\&= 2.44 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}\end{aligned}$$

Collision rate per unit time for area  $A = 1.00 \text{ cm}^2 = (0.0100 \text{ m})^2$ :

$$\begin{aligned}&= AZ_c = (0.000100 \text{ m}^2) (2.44 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}) \\&= 2.44 \times 10^{23} \text{ s}^{-1}\end{aligned}$$

**Wow!** About Avogadro's number per second per square centimeter!

**Example 2** A container is filled with an equimolar mixture of argon at 0.500 bar and helium at 0.500 bar at 298 K. Calculate the leak rate of argon and helium into a vacuum through a circular pinhole of area  $0.0100 \mu\text{m}^2$ . Also calculate the composition of the leaked gas.

Collision rate per unit area per unit time:

$$Z_c = \frac{p}{\sqrt{2\pi mkT}}$$

**$Z_c$  for argon:**

$$\begin{aligned} &= \frac{50,000 \text{ Pa}}{\sqrt{2\pi (0.0400 \text{ kg mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1}) (1.381 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})}} \\ &= 1.20 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1} \end{aligned}$$

**Leak rate for argon through hole of area  $A = 0.0100 \mu\text{m}^2$ :**

$$\begin{aligned} &= AZ_c = (0.0100 \times 10^{-12} \text{ m}^2) (1.20 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}) \\ &= 1.20 \times 10^{13} \text{ argon atoms per second} \end{aligned}$$

## Example 2 *cont.*

Collision rate per unit area per unit time for helium:

$$Z_c = \frac{50,000 \text{ Pa}}{\sqrt{2\pi} (0.00400 \text{ kg mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1}) (1.381 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})}$$
$$= 3.79 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}$$

**Leak rate for helium through hole of area  $A = 0.0100 \mu\text{m}^2$ :**

$$= AZ_c = (0.0100 \times 10^{-12} \text{ m}^2) (3.79 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1})$$
$$= 3.79 \times 10^{13} \text{ helium atoms per second}$$

Application:  
isotope  
separation

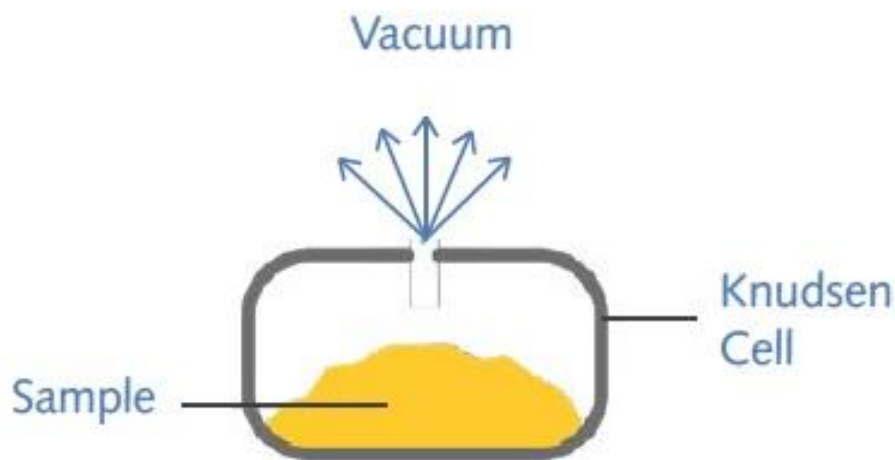
**Mole fraction of He in the leaked gas mixture:**

$$= \frac{Z_c(\text{He})}{Z_c(\text{He}) + Z_c(\text{Ar})} = \frac{3.79 \times 10^{13}}{3.79 \times 10^{13} + 1.20 \times 10^{13}} = 0.760$$

(compared to He mole fraction 0.500 in the container)

**Example 3** *Invert the procedure:* use measured leak rates to calculate the vapor pressure of solids and liquids.

An organic compound (molar mass  $M = 256 \text{ g mol}^{-1}$ ) leaks out of a small hole (area  $A = 1.235 \times 10^{-10} \text{ m}^2$ ) in the wall of a Knudsen cell into a vacuum chamber. A leak rate of 0.123 mg in 6 minutes is measured at 500 K. Calculate the vapor pressure of the compound.



### **Knudsen Vapor Pressure Cell**

The weight of the cell is measured before and after gas effusion for a timed interval.

### Example 3 (cont.)

Measured leak rate in units of molecules per square meter per second:

$$Z_c = \frac{\Delta N}{A\Delta t} = \frac{(0.000123 \text{ g} / 254 \text{ g mol}^{-1}) (6.022 \times 10^{23} \text{ mol}^{-1})}{(1.23 \times 10^{-10} \text{ m}^2) (6 \text{ min} \times 60 \text{ s min}^{-1})} = 6.56 \times 10^{24} \text{ m}^{-2} \text{ s}^{-1}$$

Solve  $Z_c = \frac{p}{\sqrt{2\pi mkT}}$  for the vapor pressure  $p$ .

$$6.58 \times 10^{24} \text{ m}^{-2} \text{ s}^{-1} = \frac{p}{\sqrt{2\pi \left( \frac{0.256 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \right) (1.381 \times 10^{-23} \text{ J K}^{-1}) (500 \text{ K})}}$$

**vapor pressure  $p = 894 \text{ Pa} = 0.00894 \text{ bar}$**

# Applications of Effusion

- vapor pressure measurements
- molecular weight determination: **leak rate**  $\propto M^{-1/2}$   
**Graham's Law**
- isotope separation ( *e.g.*,  $^{235}\text{UF}_6$  /  $^{238}\text{UF}_6$  )
- leak detection  
(Why is helium frequently used?)





**Example** Gas molecules at initial pressure  $p(t = 0)$  leak out of a container (volume  $V$ ) through a hole of area  $A$  into a vacuum. Derive an expression for the **gas pressure  $p(t)$  as a function of time**.

---

leak rate:  
(molecules per second)

$$\frac{dN}{dt} = -Z_c A = -\frac{p}{\sqrt{2\pi mkT}} A$$

substitute  $N = pV/kT$ :

$$\frac{d(pV/kT)}{dt} = -\frac{p}{\sqrt{2\pi mkT}} A$$

rearrange:

$$\frac{1}{p} \frac{dp}{dt} = \frac{d \ln p}{dt} = -\frac{A}{\sqrt{2\pi mkT}}$$

integrate from  $t = 0$  to  $t$ :

$$\ln p(t) - \ln p(0) = -\frac{A}{\sqrt{2\pi mkT}} (t - 0)$$

$$p(t) = p(0) e^{-At / \sqrt{2\pi mkT}}$$

## Section 16.6 Molecular Collisions

- Kinetic theory treating gas molecules as **point masses** used in Sections 16.1 – 16.5 to analyze:
  - ◆ pressure exerted on a wall
  - ◆ translational kinetic energy
  - ◆ molecular velocities
  - ◆ molecular speeds
  - ◆ rates of molecular collisions with a wall
  - ◆ rates of molecular effusion through a hole
- Molecular collisions analyzed in this Section are different: depend on **molecular sizes and cross-sectional areas**
- Rates of molecular collisions are important for understanding rates of chemical reactions, mean free paths, viscosity, thermal conductivity, and mixing by molecular diffusion

# Collisions of Gas Molecules

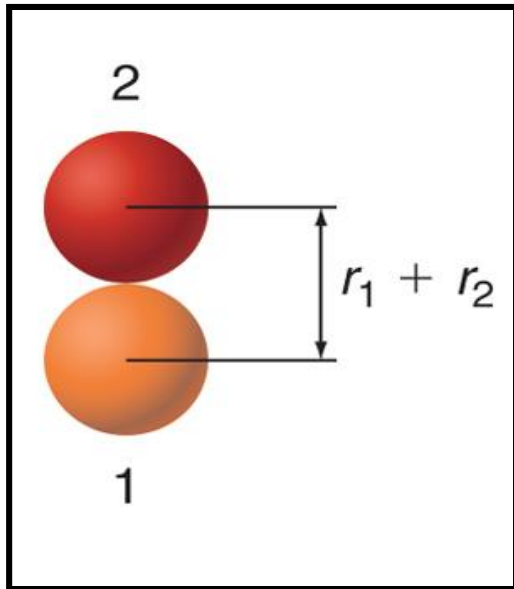
Analyzing molecular collisions is *tricky!*

Depends on:

- molecular masses, sizes and shapes
- intermolecular potential energies
- **relative** velocities
- direction of approach

# Collisions of Gas Molecules

Approximation used here: molecules are treated as **hard spheres**



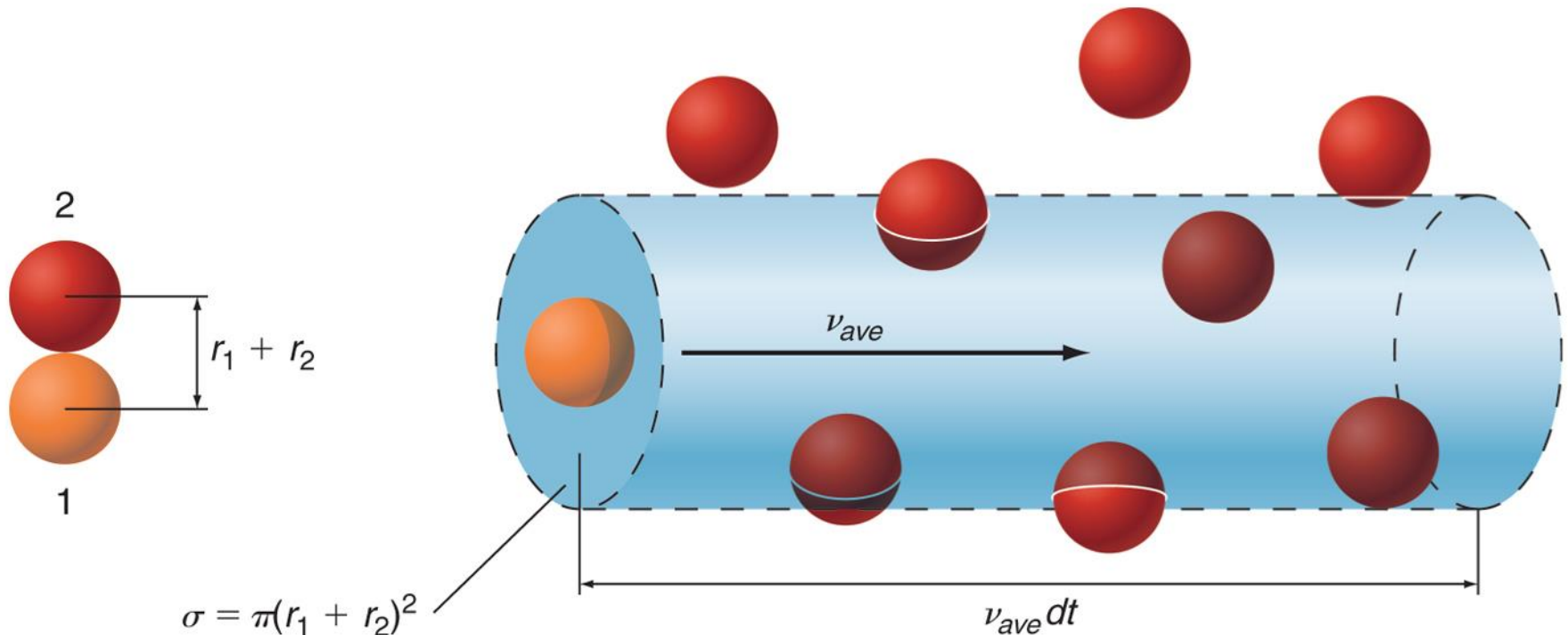
- intermolecular potential energy is zero at distances between centers beyond  $r_1 + r_2$
- potential energy is infinite at shorter distances
- molecules do not interact unless the distance between their centers is  $r_1 + r_2$
- **collisions are elastic** (no change in total kinetic translational kinetic energy)

# Collisions of Gas Molecules

If molecules of type 2 are stationary:  
molecules of type 1 collide in time  $dt$   
with all molecules of type 2 in the cylinder  
of volume  $\pi (r_1 + r_2)^2 v_{ave} dt = \pi \sigma^2 v_{ave} dt$

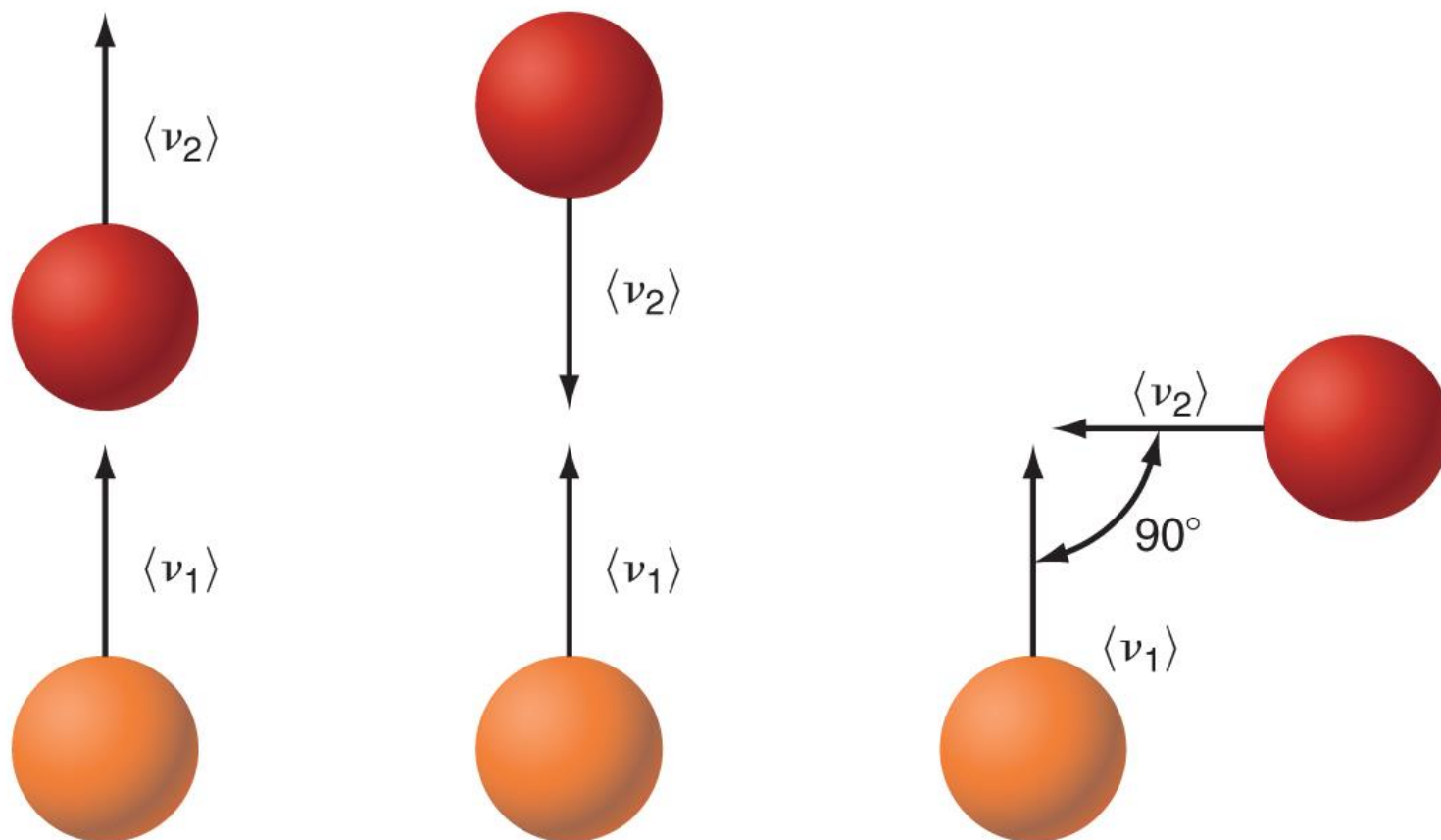
**collision cross  
sectional area**

$$\sigma = \pi (r_1 + r_2)^2$$

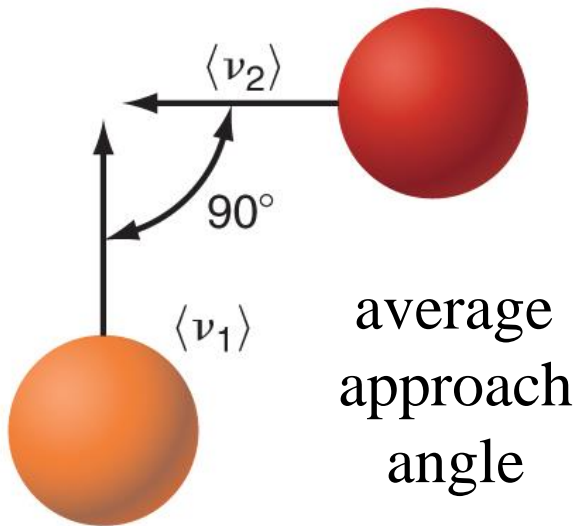


***But wait !*** All molecules are moving! Use **average relative speeds** to calculate collision rates.

Angles of approach range from  $0^\circ$  to  $180^\circ$ .  $90^\circ$  is the average angle.



# Mean Relative Speed $\langle v_{12} \rangle$ of Molecules 1 and 2



**reduced mass:**

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

using the Pythagorean theorem:

$$\langle v_{12} \rangle = \sqrt{\langle v_1 \rangle^2 + \langle v_2 \rangle^2}$$

$$= \sqrt{\frac{8kT}{\pi m_1} + \frac{8kT}{\pi m_2}}$$

$$\langle v_{12} \rangle = \sqrt{\frac{8kT}{\pi \mu}}$$

**Example** Calculate the average relative speed  $\langle v_{12} \rangle$  of H<sub>2</sub> (1) and O<sub>2</sub> (2) molecules at 298 K.

molecular  
masses

$$m_1 = \frac{2.016 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 3.348 \times 10^{-26} \text{ kg}$$

$$m_2 = \frac{32.00 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 5.314 \times 10^{-26} \text{ kg}$$

reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = 3.150 \times 10^{-26} \text{ kg}$$

$$\langle v_{12} \rangle = \sqrt{\frac{8kT}{\pi \mu}} = \sqrt{\frac{8 (1.381 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})}{\pi (3.150 \times 10^{-26} \text{ kg})}} = 1824 \text{ m s}^{-1}$$

**Note:** The mean relative speed of H<sub>2</sub> and O<sub>2</sub> is closer to the mean speed of H<sub>2</sub> (1920 m s<sup>-1</sup>) than to the mean speed of O<sub>2</sub> (482 m s<sup>-1</sup>). *Why?*



## Collisions of Molecule 1 with Molecule 2

In time  $dt$  molecule 1 sweeps out collision volume  $\sigma \langle v_{12} \rangle dt$ .

Number of collisions per second for a **single molecule of type 1** with molecules of type 2:

$$z_{12} = \frac{N_2}{V} \frac{\sigma \langle v_{12} \rangle dt}{dt} = \frac{p_2}{kT} \sigma \sqrt{\frac{8kT}{\pi\mu}} \quad (\text{units: s}^{-1})$$

Total number of collisions of molecules 1 and molecules 2 per unit volume per second (called the **collision density**):

$$Z_{12} = \frac{N_1}{V} z_{12} = \frac{p_1}{kT} \frac{p_2}{kT} \sigma \sqrt{\frac{8kT}{\pi\mu}} \quad (\text{units: m}^{-3} \text{ s}^{-1})$$

Collision cross sectional area  $\sigma = \pi (r_1 + r_2)^2$ . Reduced mass  $\mu = m_1 m_2 / (m_1 + m_2)$ .

# Collisions of Molecule 1 with Molecule 1

Number of collisions per second for a **single molecule of type 1** with other molecules of type 1:

$$z_{11} = \frac{N_1}{V} \frac{\sigma \langle v_{11} \rangle dt}{dt} = \frac{p_1}{kT} \sigma \sqrt{2} \sqrt{\frac{8kT}{\pi m_1}}$$

Total number of collisions of molecules 1 and molecules 1 per unit volume per second (**note:** a factor of 1/2 is included so each collision is only counted once):

$$Z_{11} = \frac{1}{2} \frac{N_1}{V} z_{11} = \frac{1}{2} \frac{p_1}{kT} z_{11} = \left( \frac{p_1}{kT} \right)^2 \frac{\sigma}{\sqrt{2}} \sqrt{\frac{8kT}{\pi m_1}}$$

Collision cross sectional area  $\sigma = \pi (r_1 + r_1)^2$ . Reduced mass  $\mu = m_1 m_1 / (m_1 + m_1) = m_1 / 2$ .

**TABLE 33.1** Collisional Parameters for Various Gases

Species	$r$ (nm)	$\sigma$ (nm <sup>2</sup> )
He	0.13	0.21
Ne	0.14	0.24
Ar	0.17	0.36
Kr	0.20	0.52
N <sub>2</sub>	0.19	0.43
O <sub>2</sub>	0.18	0.40
CO <sub>2</sub>	0.20	0.52

**Example** Calculate the collision frequency  $z_{11}$  and the collision density  $Z_{11}$  for  $O_2$  gas at 298 K and 1 bar.

$$z_{11} = \frac{p_1}{kT} \sigma \sqrt{2} \sqrt{\frac{8kT}{\pi m_1}} = \frac{p_1}{kT} \sigma \sqrt{2} \sqrt{\frac{8RT}{\pi M}}$$

$$= \frac{101325 \text{ Pa}}{(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} (0.40 \times 10^{-18} \text{ m}^2) \sqrt{2} \sqrt{\frac{8 (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})}{\pi (0.03200 \text{ kg mol}^{-1})}}$$

$$z_{11} = 6.18 \times 10^9 \text{ s}^{-1}$$

(collisions per second for one  $O_2$  molecule)

$$Z_{11} = \frac{1}{2} \frac{p_1}{kT} z_{11} = \frac{1}{2} \frac{101325 \text{ Pa}}{(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} (6.18 \times 10^9 \text{ s}^{-1})$$

$$Z_{11} = 7.61 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}$$

collisions per cubic meter per second

$$Z_{11} = 1.26 \times 10^8 \text{ mol L}^{-1} \text{ s}^{-1}$$

moles of collisions per liter per second

## Section 16.7 Mean Free Path

**mean free path  $\lambda$**  the average distance a molecule travels between collisions with other molecules

Useful for analyzing transport of heat, momentum, and mass.

Calculated by dividing the average distance travelled per unit time by the number of collisions per unit time.

For a gas consisting of one type of molecules:

$$\lambda = \frac{\langle v \rangle}{z_{11}} = \frac{\langle v \rangle}{\frac{N}{V} \sigma \sqrt{2} \langle v \rangle}$$

$$\lambda = \frac{V}{N \sqrt{2} \sigma} = \frac{kT}{p \sqrt{2} \sigma}$$

$\lambda$  is proportional to  $T$ ,  $p^{-1}$  and  $\sigma^{-1}$

**Example** Calculate the mean free path for argon at 1 atm and 298 K. Is  $\lambda$  large compared to the size of an Ar atom?

Data:  $\sigma = 0.36 \times 10^{-18} \text{ m}^2$

Ar atom diameter =  $0.29 \times 10^{-9} \text{ m}$

$$\lambda = \frac{kT}{p\sqrt{2}\sigma} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{(101325 \text{ Pa})\sqrt{2}(0.36 \times 10^{-18} \text{ m}^2)}$$

mean free path  $\lambda = 79.8 \times 10^{-9} \text{ m} = 79.8 \text{ nm}$

An Ar atom travels on average  $79.8 \text{ nm}/0.29 \text{ nm} = 275$  diameters between collisions.

## ! Warnings !

- 1) The flow properties of a gas change significantly at pressures so low the mean free path is comparable to the dimensions of the container holding the gas → “ballistic” flow.
- 2) The hard-sphere “billiard ball” model used in this Chapter for molecular collisions is an approximation.
- 3) More realistic (and more complicated!) models exist, such as the Lennard-Jones intermolecular potential energy

$$V(r) = \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

# Collision Trajectories for Lennard-Jones Interaction Potentials

