Chapter 19: The Kinetic Theory of Gases

Avogadro's number

$$N_A = 6.02 \times 10^{23} \text{ /mole}$$

Number of moles in a sample:

$$n = N/N_A \quad ; N = \text{number of atoms or molecules}$$

Universal Gas Constant

$$R = 8.31 \text{ J/mol} \cdot \text{K}$$

Boltzmann constant

$$k = R/N_A = 1.38 \times 10^{-23} \text{ J/K}$$

Ideal Gases

At *low* gas densities, *all* gases can be treated as ideal gases. Ideal gases obey the relation:

$$pV = nRT \quad \text{(ideal gas law)}$$

IF n is constant, then $\dfrac{p_i V_i}{T_i} = \dfrac{p_f V_f}{T_f} = nR$

p: **absolute** (not gauge) **pressure**.

V: **volume** of the gas

n: number of **moles** of gas present.

T: the **temperature** in **Kelvin**. It ***MUST*** be in Kelvin!

R: **gas constant** (same for all gases) $R = 8.31\ \text{J/mol} \cdot \text{K}$

Ideal Gases

$$pV = nRT$$

Three variables in the ideal gas law (4 if you count n -- but let n be constant for now).

Consider special cases

Pressure:

Isobaric -- constant pressure

Volume:

Isochoric (or isovolumic) -- constant volume

Temperature:

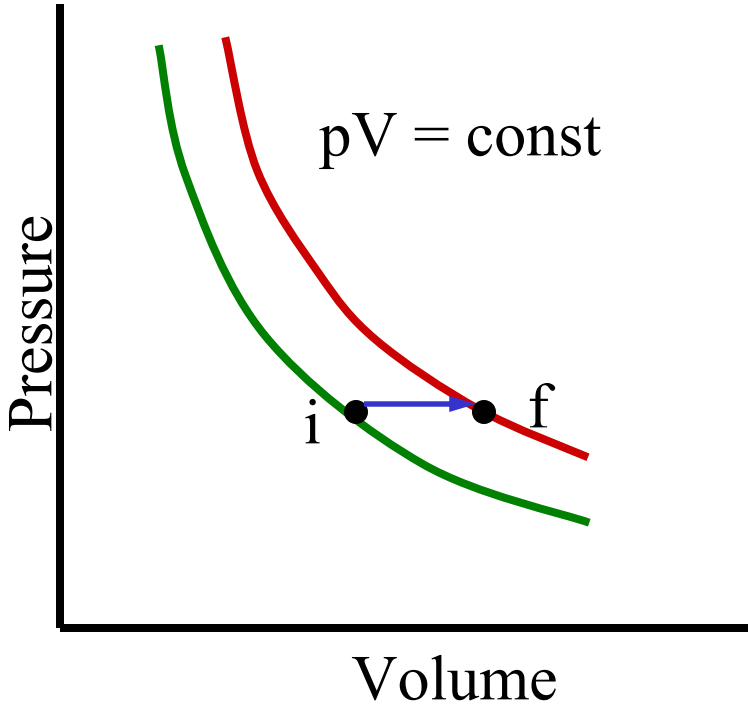
Isothermal -- constant temperature

Ideal Gases

$$pV = nRT$$

Three variables in the ideal gas law (with n being constant).

Consider special cases



Pressure:

Isobaric -- constant pressure

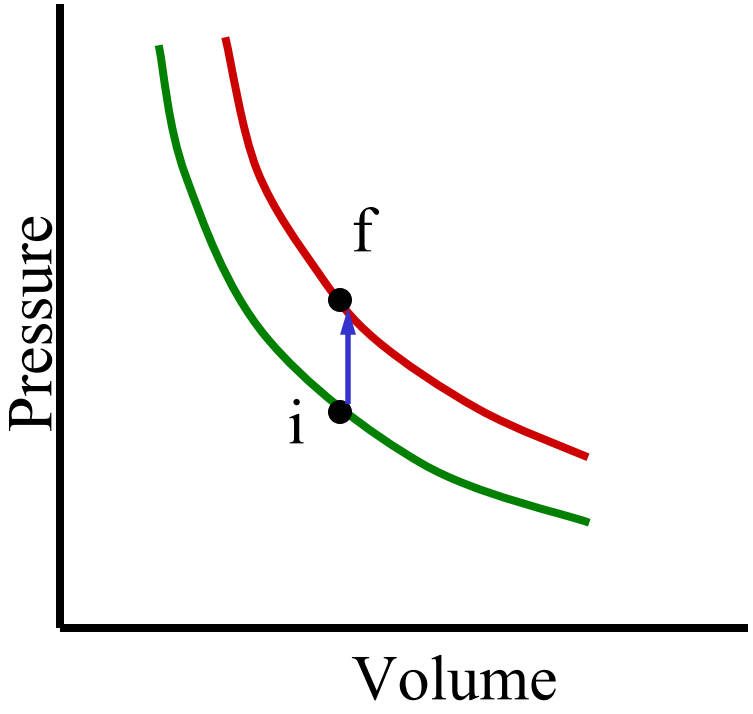
$$W = \int_{V_i}^{V_f} p\,dV = p\int_{V_i}^{V_f} dV = p\left(V_f - V_i\right) = p\Delta V$$

Ideal Gases

$$pV = nRT$$

Three variables in the ideal gas law (with n being constant).

Consider special cases



Volume:

Isochoric -- constant volume

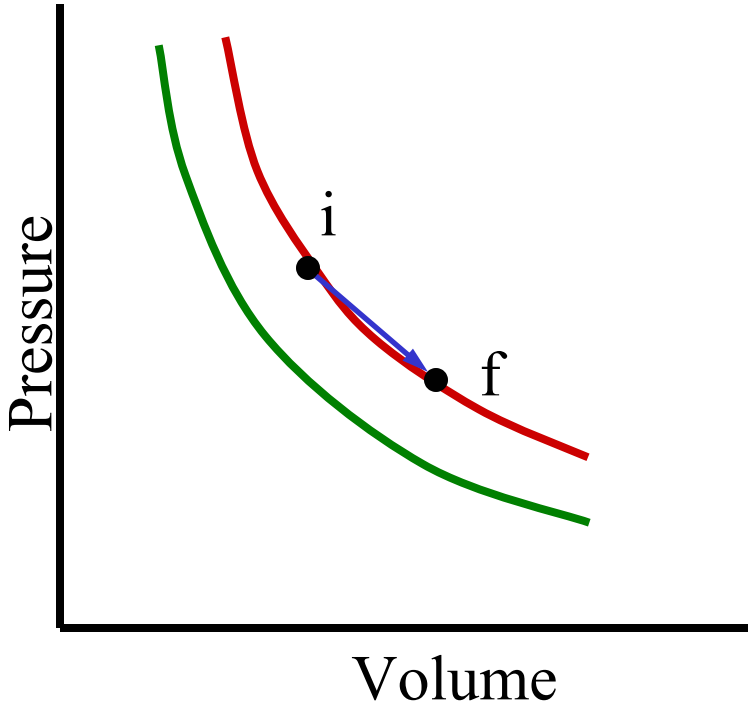
$$W = \int_{V_i}^{V_f} p\,dV = \int_{V_i}^{V_i} p\,dV = 0$$ since the integral limts are equal

Ideal Gases

$$pV = nRT$$

Three variables in the ideal gas law (with n being constant).

Consider special cases



Temperature:

Isothermal -- constant temperature

Gas expands from V_i to V_f, $p = nRT/V$

$$W = \int_{V_i}^{V_f} p\,dV = \int_{V_i}^{V_f} \frac{nRT}{V}\,dV$$

$$= nRT\int_{V_i}^{V_f} \frac{dV}{V} = nRT[\ln V]_{V_i}^{V_f} = nRT \ln \frac{V_f}{V_i}$$

Summary of Work $W = \int p dV$

Work done at **constant pressure**

p is constant, $W = p\,(V_f - V_i) = p\,\Delta V$

Work done at **constant volume**

$dV = 0$, so $W = 0$

Work done by ideal gas at **constant temperature**

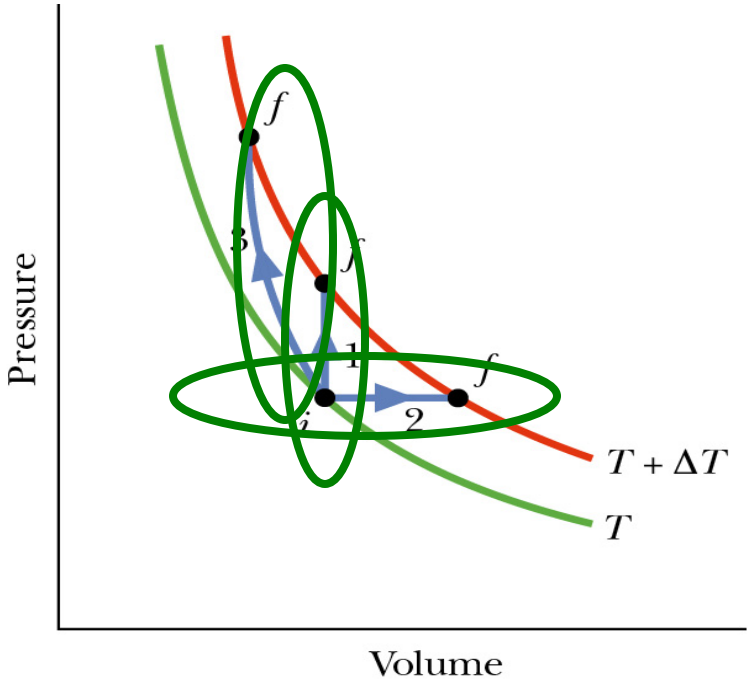
$$W = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT[\ln V]_{V_i}^{V_f} = nRT \ln \frac{V_f}{V_i}$$

Molar specific heat of an ideal gas

Molar specific heat:

$$Q = c\,n\,(T_f - T_i)$$

The specific heat *c* is a value that depends on the ability of a substance to **absorb energy**. As such, c depends on both the type of material and whether the process is a constant volume process or a constant pressure process.



1) Constant-volume process

2) Constant-pressure process

3) Arbitrary process

Molar specific heat of an ideal gas

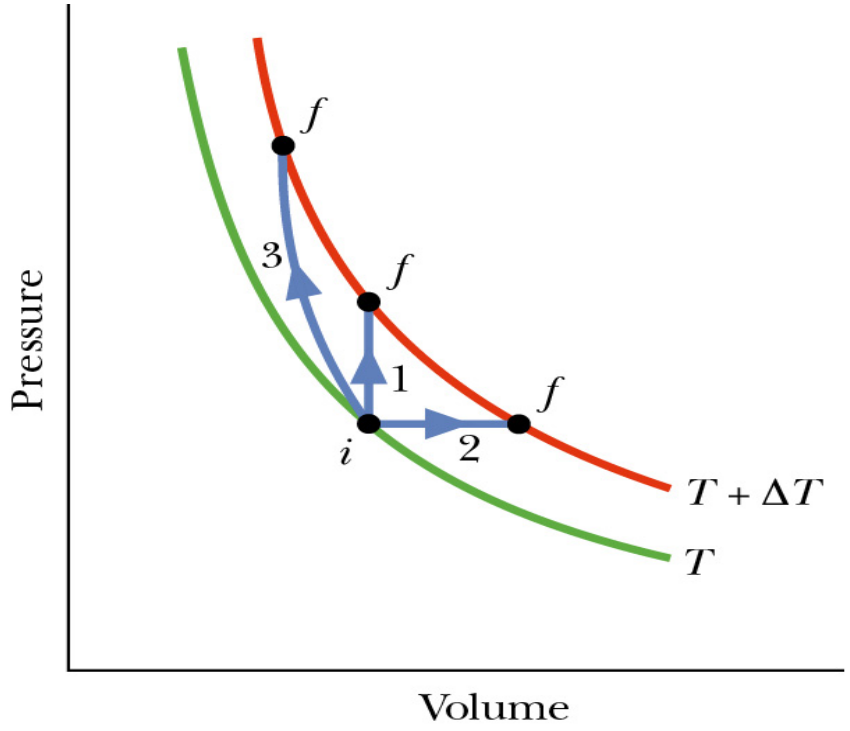
Molar specific heat at constant volume: C_V

$Q = n C_V \Delta T$(constant V process)

since V = constant, W = 0,

thus $\Delta E_{int} = Q - W = n C_V \Delta T$ or $E_{int} = n C_V T$

For ideal gas, the change in internal energy depends only on the change in gas temperature.



Molar specific heat at constant pressure: C_p

$Q = n C_p \Delta T$ (constant Pressure process)

$\Delta E_{int} = Q - W,$

since p = constant, $W = p\Delta V = nR\Delta T$

$$\Delta E_{int} = n C_V \Delta T = n C_p \Delta T - nR\Delta T = n(C_p - R)\Delta T$$

Therefore $\boxed{C_V = C_p - R}$

or $\boxed{C_P = C_V - R}$

Degrees of Freedom

Particles can absorb energy depending on their structure. A degree of freedom is the way the particle can move.

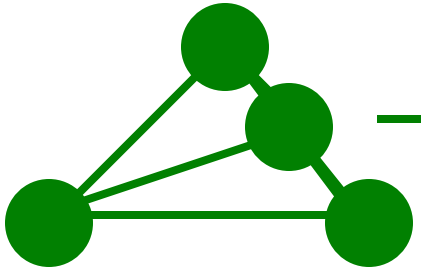
All particles can move in x-, y-, and z-directions.

→ 3 degrees of freedom

diatomic molecules (N_2, O_2, etc.) have two rotational axes.

→ 2 more degrees of freedom

polyatomic molecules (CH_4, H_2O, etc) have three rotational axes.



→ 3 more degrees of freedom

Degrees of Freedom

Particles can absorb energy depending on their structure.
A degree of freedom is the way the particle can move.

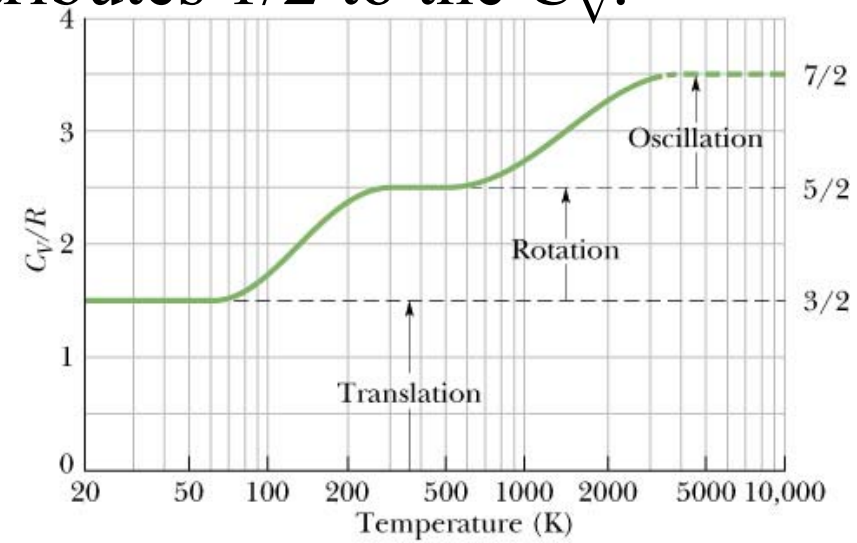
Molecule	Translational	Rotational	Total	C_V
monotomic	3	0	3	3/2
diatomic	3	2	5	5/2
polyatomic	3	3	6	6/2 = 3

Each degree of freedom contributes 1/2 to the C_V.

monatomic $\Delta E_{int} = \frac{3}{2} nR\Delta T$

diatomic $\Delta E_{int} = \frac{5}{2} nR\Delta T$

polyatomic $\Delta E_{int} = 3nR\Delta T$



Degrees of Freedom

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monotomic $\Delta E_{int} = \frac{3}{2} nR\Delta T$

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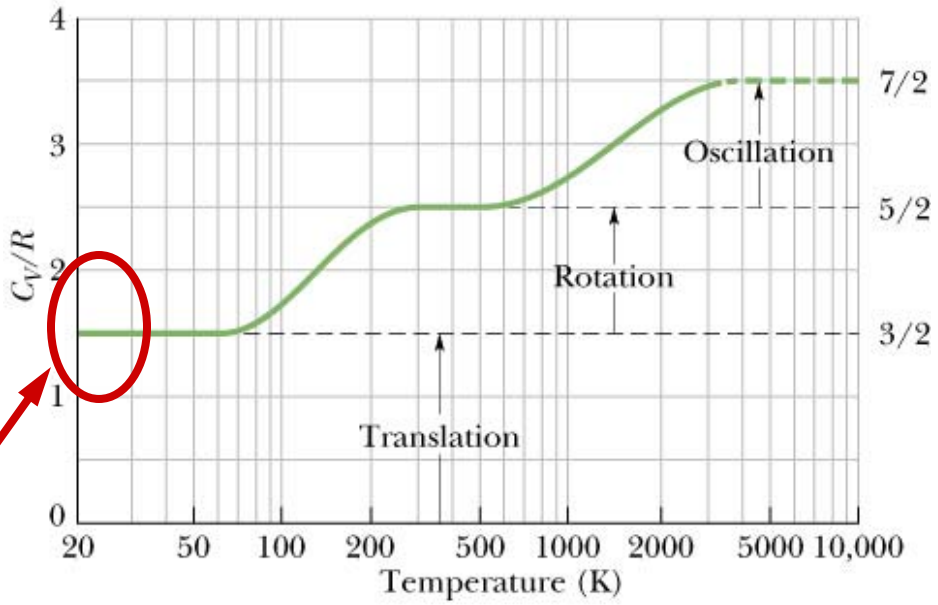


Remember Quantum physics corrects this for low temperatures!

Adiabatic expansion of an ideal gas.

For an adiabatic process, $Q = 0$.

$pV^{\gamma} = $ a constant

$\gamma = C_p/C_V$ treat γ as a constant that depends on the type of the gas molecules.

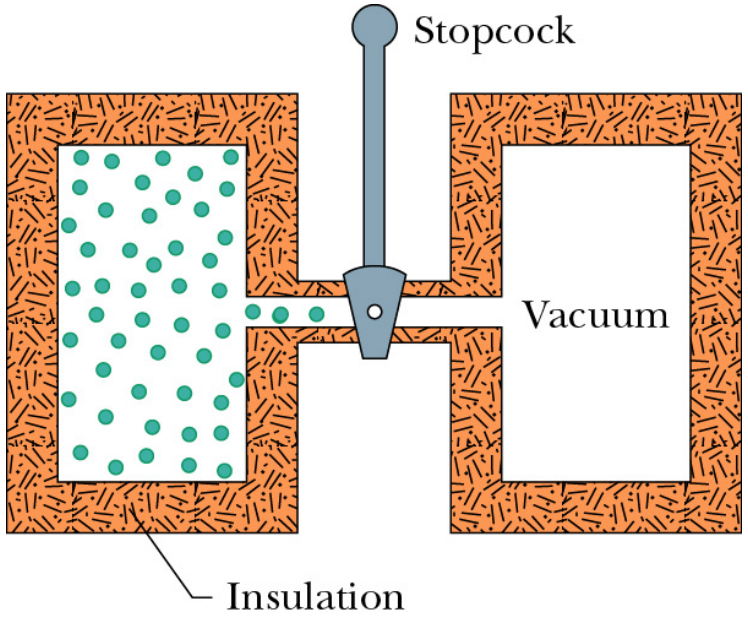
Free expansions

$Q = W = 0,$

So $\Delta E_{int} = 0,$

Therefore $T_i = T_f$

or $P_iV_i = P_fV_f$



Isobaric --- constant pressure process

$$Q = n C_p \Delta T, \qquad W = p \Delta V$$

Isothermal --- constant temperature process

$$\Delta E_{int} = 0, \qquad Q = W = nRT \ln(V_f/V_i)$$

Isochoric process --- constant volume process

$$Q = \Delta E_{int} = n C_V \Delta T, \qquad W = 0$$

Adiabatic expansion of an ideal gas

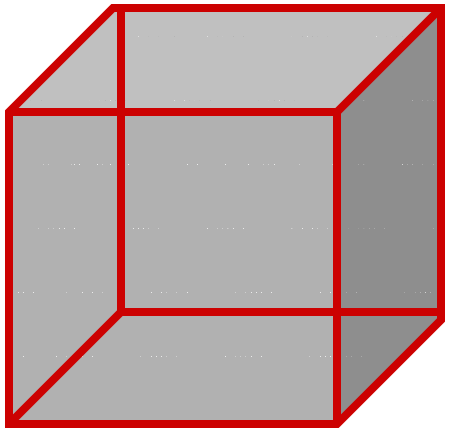
$$Q = 0, \quad pV^{\gamma} = \text{a constant}$$

$\Delta E_{int} = Q - W$ for all processes.

Free expansion

$$Q = W = 0 \Rightarrow \Delta E_{int} = 0, \Rightarrow T_i = T_f \Rightarrow p_i V_i = p_f V_f$$

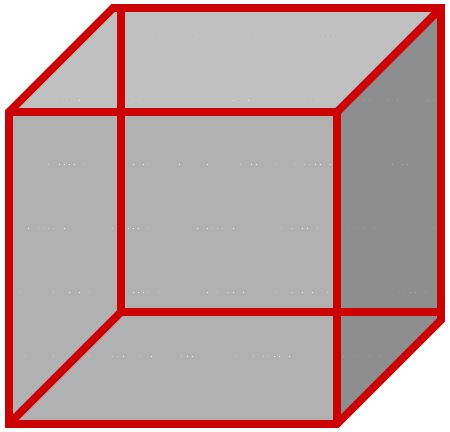
A Quiz



Can one mole of an ideal gas at a temperature of 300K occupy a fixed volume of $10^{-2}m^3$ (ten liters) at one atmosphere ($1.01x10^5 N/m^2$) of pressure?
Remember: $R = 8.31\ J/mol \cdot K$

1) yes.
2) No. The gas needs to be heated up to occupy that volume with that pressure.
3) No. The gas needs to be cooled down to occupy that volume with that pressure.
4) Depends on the type of ideal gas molecules.

A Quiz



$$pV = nRT$$

$$pV = (1.01 \times 10^5 N/m^2)(10^{-2} m^3)$$
$$= 1010\ Nm = 1{,}010\ J$$

$$nRT = (1.0 mol)(8.31\ J/mol \cdot K)(300K)$$
$$= 2{,}493\ J$$

Can one mole of an ideal gas at a temperature of 300K occupy a fixed volume of $10^{-2} m^3$ (ten liters) at one atmosphere ($1.01 \times 10^5 N/m^2$) of pressure? Remember: $R = 8.31\ J/mol \cdot K$

1) yes.
2) No. The gas needs to be heated up to occupy that volume with that pressure.
3) No. The gas needs to be cooled down to occupy that volume with that pressure.
4) Depends on the type of

$$T = pV/nR$$
$$= 1010J/(1.0)(8.31) = 122\ K$$

The Microscopic World

What causes pressure?

Chapter 19: the Microscopic World

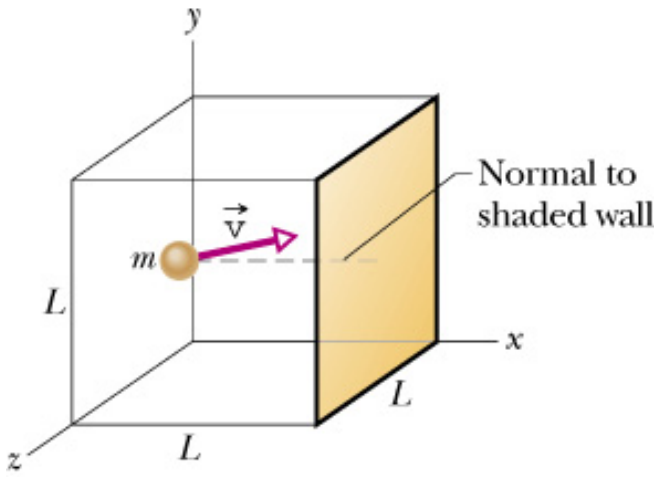
All macroscopic (i.e., human scale) quantities must ultimately be explained on the **microscopic** scale.

Pressure

Definition of pressure:

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

But now what is force?



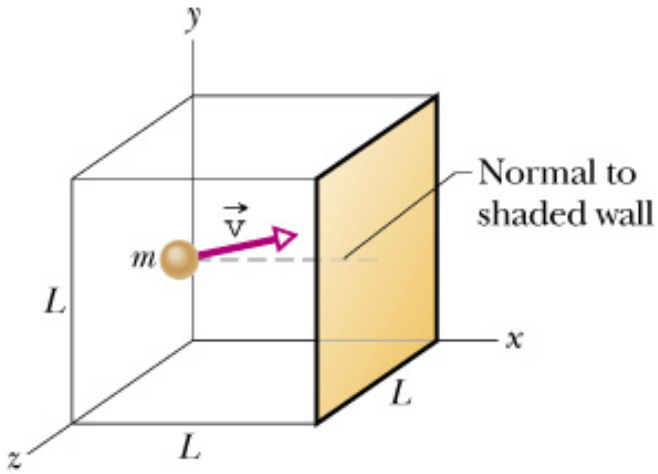
Relate force to impulse and change in momentum.

$$\vec{F} \equiv \frac{d\vec{p}}{dt} \quad \Rightarrow \quad d\vec{p} = \vec{F}dt$$

$$\Delta p_x = p_f - p_i = (-mv_x) - (mv_x) = -2mv_x$$

Take Δt to be the time that molecule takes in hitting the wall, bouncing off and then hitting it again. It will have traveled 2L in that time with speed v_x.

$$\frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$



Area of wall: L^2

Thus the pressure will be:

$$p = \frac{F_x}{L^2} = \frac{mv_{x1}^2/L + mv_{x2}^2/L + \ldots + mv_{xN}^2/L}{L^2}$$

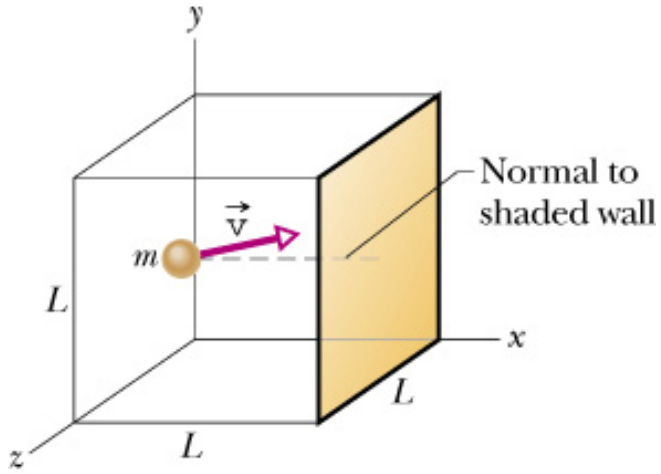
$$= \left(\frac{m}{L^3}\right)\left(v_{x1}^2 + v_{x2}^2 + \ldots + v_{xN}^2\right)$$

Since there are N molecules in the box, $N = nN_A$ and N is usually a *very* big number, we can use the average speed instead of the actual speeds.

$$p = \frac{F_x}{L^2} = \frac{mv_{x1}^2/L + mv_{x2}^2/L + \ldots + mv_{xN}^2/L}{L^2}$$

$$= \left(\frac{m}{L^3}\right)\left(v_{x1}^2 + v_{x2}^2 + \ldots + v_{xN}^2\right)$$

$$= \left(\frac{m}{L^3}\right)\left(v_x^2\right)_{avg}$$



The volume of the box is L^3, so

$$p = \frac{mnN_A}{V}\left(v_x^2\right)_{avg}$$

v_{rms}

Since there are 3 dimensions, $v_x^2 + v_y^2 + v_z^2 = v^2$ and each dimension is the same, $v_x^2 = v_y^2 = v_z^2 \Rightarrow v^2 = 3v_x^2$

$$p = \frac{mnN_A}{V}\left(v_x^2\right)_{avg} = \frac{mnN_A}{V}\left(\frac{1}{3}v^2\right)_{avg} = \frac{mnN_A}{3V}\left(v^2\right)_{avg}$$

$(v^2)_{avg}$ is the average of the squared speed -- which makes the speed the (square) **root** of the **mean** (average) **squared** speed -- i.e., root-mean-squared speed, v_{rms}.

$$\sqrt{(v^2)_{avg}} = v_{rms}$$

Rearrange $p = \frac{mnN_A}{3V}\left(v_{rms}^2\right) \Rightarrow v_{rms} = \sqrt{\frac{3pV}{nmN_A}}$

gas temperature

mN_A is the molar mass M of the gas and using the ideal gas law pV = nRT :

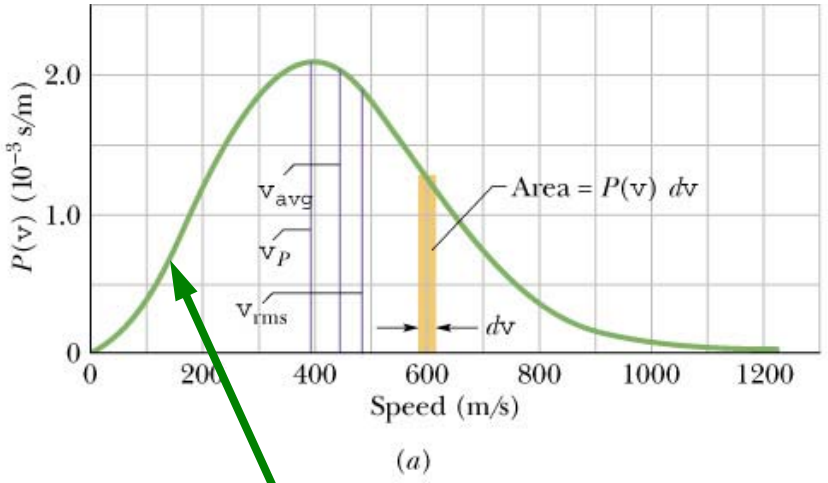
$$v_{rms} = \sqrt{\frac{3pV}{n\,mN_A}} = \sqrt{\frac{3nRT}{n\,M}} = \sqrt{\frac{3RT}{M}}$$

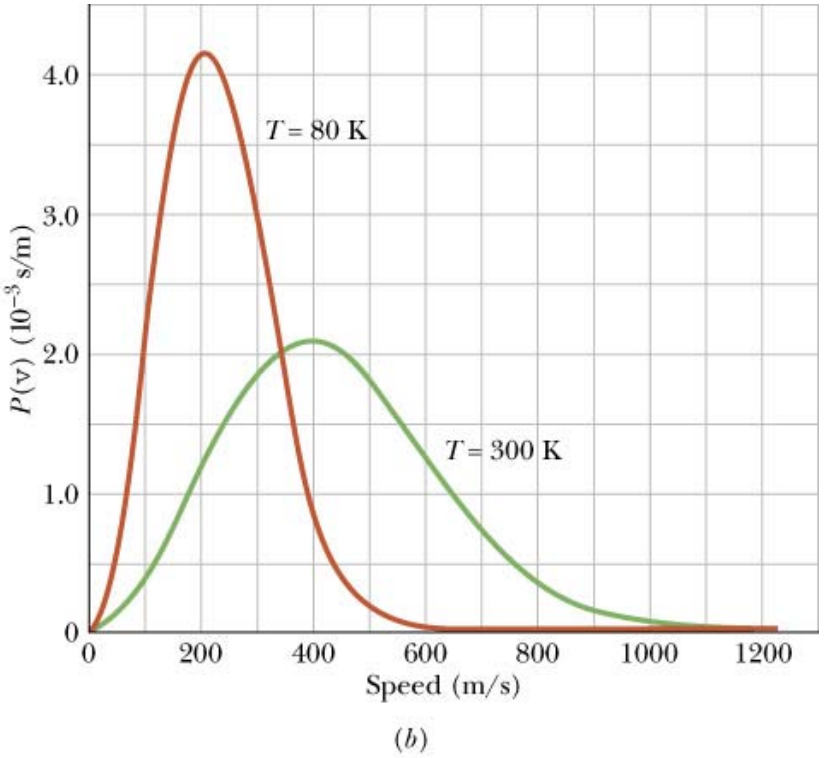
Thus, the characteristic speed of the gas molecules is related to the temperature of the gas!

Gas	v_{rms} (m/s)
Hydrogen	1920
Helium	1370
N_2	517
escape $\text{speed}_{\text{Earth}}$	1120

Maxwell-Boltzmann Distribution

Define a function P(v) whose area (integral) equals 1.

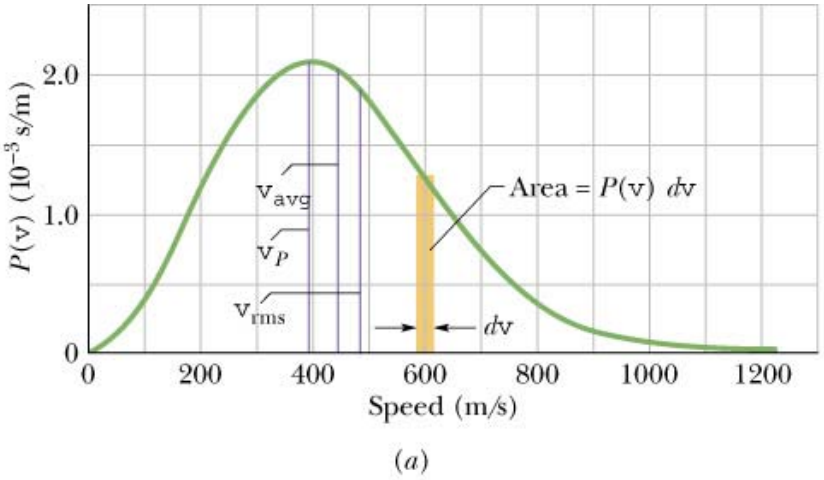




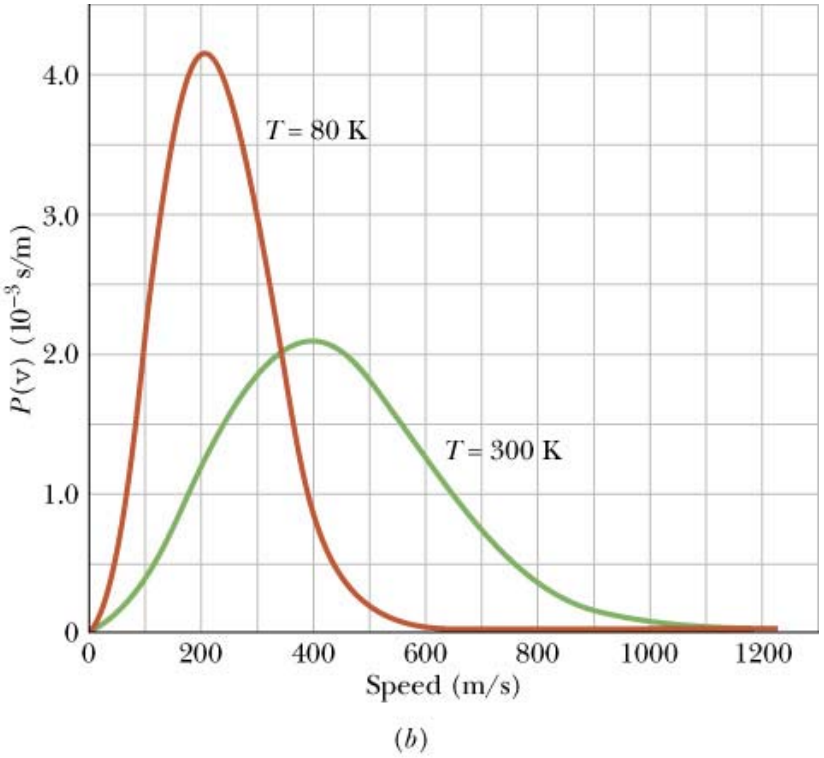
$$P(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

P(v) is the Maxwell-Boltzmann Probability function

Maxwell-Boltzmann Distribution



(a)

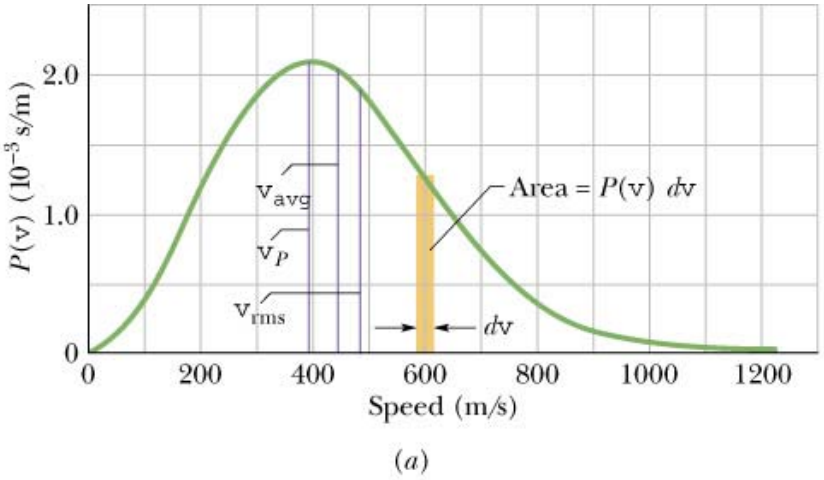


(b)

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

Math: $$x_{avg} = \int_{allspace} x\, f(x)\, dx$$

Maxwell-Boltzmann Distribution



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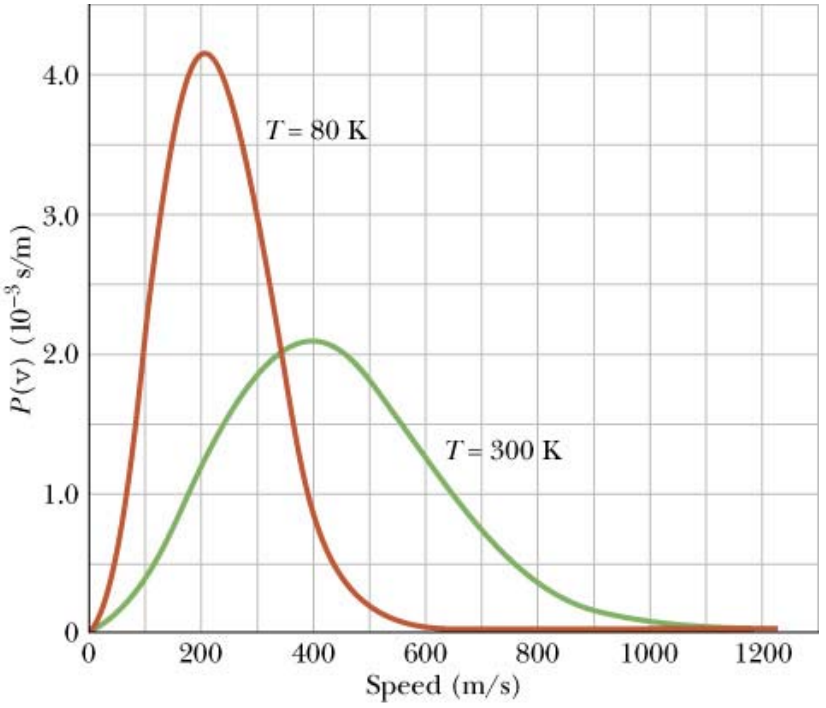


(b)

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

Thus, $$v_{avg} = \int_0^\infty v\,P(v)\,dv = \sqrt{\frac{8RT}{\pi M}}$$

and $$v_{avg}^2\ (\equiv v_{rms}^2) = \int_0^\infty v^2\,P(v)\,dv = \frac{3RT}{M}$$

Kinetic Energies

Average kinetic energy:

$$K_{avg} = \tfrac{1}{2} m\left(v^2\right)_{avg} = \tfrac{1}{2} m v_{rms}^2$$

$$= \left(\tfrac{1}{2} m\right)\frac{3RT}{M} = \left(\tfrac{1}{2}\right)\frac{3RT}{M/m} = \frac{3RT}{2N_A} = \left(\frac{3}{2}\right)\left(\frac{R}{N_A}\right)T = \tfrac{3}{2} kT$$

Kinetic energy only depends on the gas's temperature!

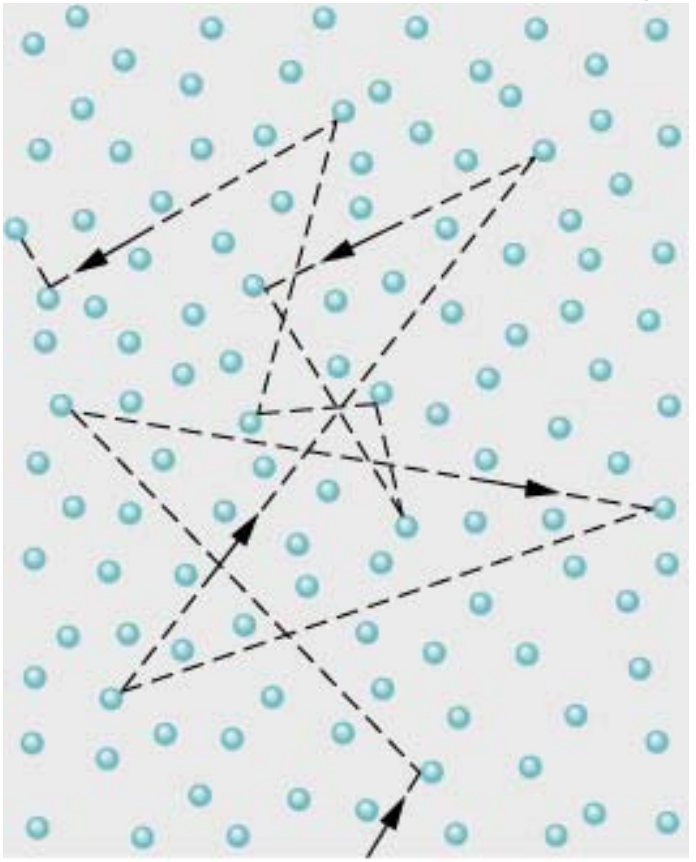
$$K_{avg} = \tfrac{1}{2} m\, v_{rms}^2 = \tfrac{3}{2} kT$$

The "3" comes from the three dimensions: x, y, and z!

Brownian Motion

But.... not all the molecules are going at that speed.
Some are going *faster* and some sloooower than v_{rms}.

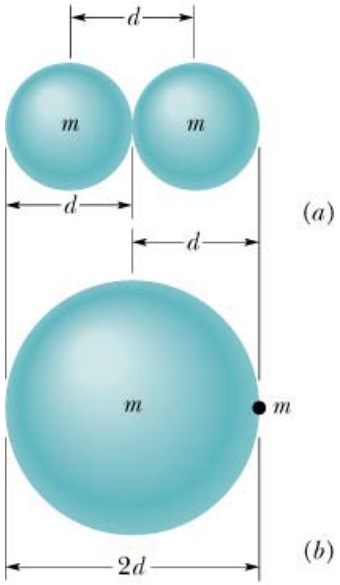
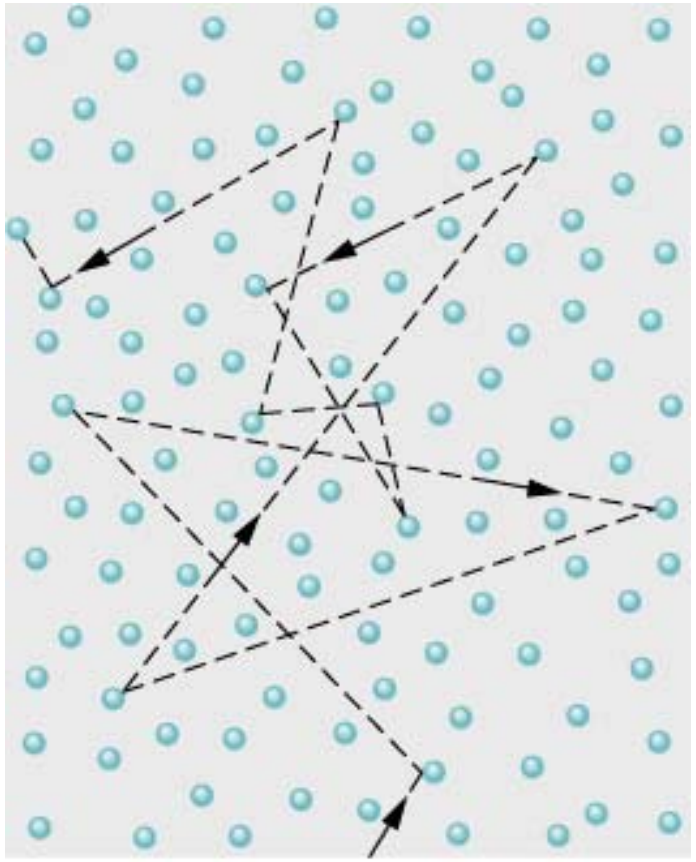
A gas molecule interacting with neighboring molecules is like you trying to get to the concession stand during a rock concert!



p.s.: Einstein, 1905

Mean Free path

Define the mean-free-path λ as the distance between collisions.

$$\lambda = \frac{1}{\sqrt{2}\,\pi d^2\, N/V}$$

Molecular sizes