Gases

"The particles of the air are in contact with each other, yet they do not fit closely in every part, but void spaces are left between them, as in the sand on the sea shore: the grains of sand must be imagined to correspond to the particles of air, and the air between the grains of sand to the void spaces between the particles of air. Hence, when any force is applied to it, the air is compressed, and, contrary to its nature, falls into the vacant spaces from the pressure exerted on its particles: but when the force is withdrawn, the air returns again to its former position from the elasticity of its particles, as is the ease with horn shavings and sponge, which, when compressed and set free again, return to the same position and exhibit the same bulk."　　**Hero of Alexandria, ~ AD 60**

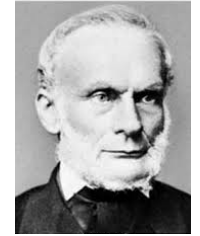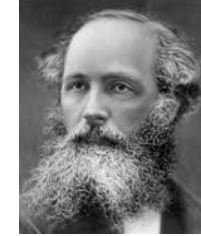5.6　Kinetic Molecular Theory of Gases

5.7　Effusion and Diffusion

5.8　Collisions of Gas Particles with Container Walls

5.9　Intermolecular Collisions

5.10　Real Gases

homework due
Monday, Tuesday

Kinetic Molecular Theory of Gases

postulates of kinetic theory:

molecular volume is negligible compared to distance between molecules

large number of molecules, ceaseless random motion

no forces of attraction/repulsion between molecules

all collisions are elastic (no energy lost)

**ON A MOLECULAR LEVEL WHAT IS THE
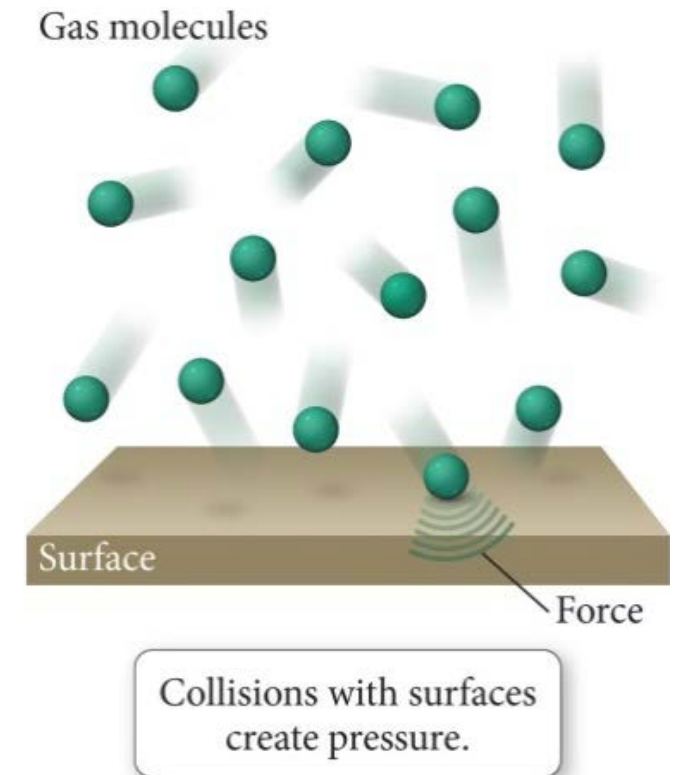PRESSURE OF AN IDEAL GAS DUE TO?**

P = force/area

force = ma

$\quad$ = $m\Delta u/\Delta t$

$\quad$ = $\Delta(mu)/\Delta t$ (mu is momentum)

$P \sim$ (# collisions) × (change in momentum per collision)

Gas molecules

Surface

Force

Collisions with surfaces
create pressure.

Kinetic Molecular Theory of Gases

$P \sim$ (# collisions) × (change in momentum per collision)

conclusions

1. $PV = nRT = \frac{1}{3} Nm\langle u^2\rangle$
2. $\frac{1}{2} N_o m\langle u^2\rangle = \frac{3}{2} RT$ average kinetic energy (T)
3. $\langle u^2\rangle = 3RT / M$

root-mean-square (rms) speed $= \sqrt{\langle u^2\rangle}$ $u_{rms} = \sqrt{3RT / M}$

most probable $= \sqrt{(2RT / M)}$

average $= \sqrt{(8RT / \pi M)}$

Boltzmann's constant, $k_B = R/N_0$ --> $PV = nRT = Nk_B T$

$2 \times m \Rightarrow$
$2 \times$ momentum
$P \sim m$

$2 \times N / V \Rightarrow$
$2 \times$ # collisions
$P \sim N / V$

$2 \times u \Rightarrow$
$2 \times$ # collisions
$+ 2 \times$ momentum
$P \sim u^2$
$P \sim Nmu^2 / V$

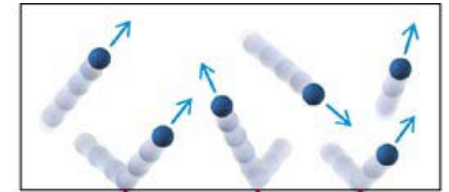**EX 10.** What is u_{rms} for helium at -73°C? $M = 4.006$ g/mol

$u_{rms} =$

$\sqrt{[3 (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (273.15 - 73) \text{ K} / 4.0026 \times 10^{-3}}$ **kg**/mol]

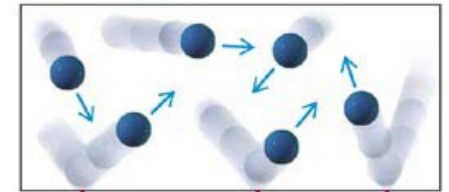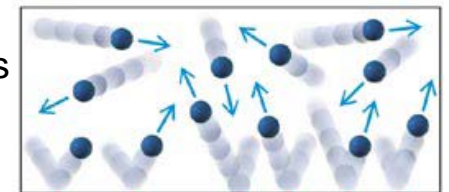$= 1120 \text{ m s}^{-1}$ [**1 J** (kinetic energy $\sim mu^2$) = **1 kg m^2 s^{-2}**]

(a)

(b)

(c)
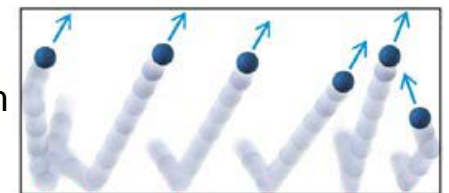
(d)

Maxwell-Boltzmann Distribution Law

distribution of velocities of the particles in an ideal gas

$$f(u) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} u^2 e^{-mu^2/2kT}$$
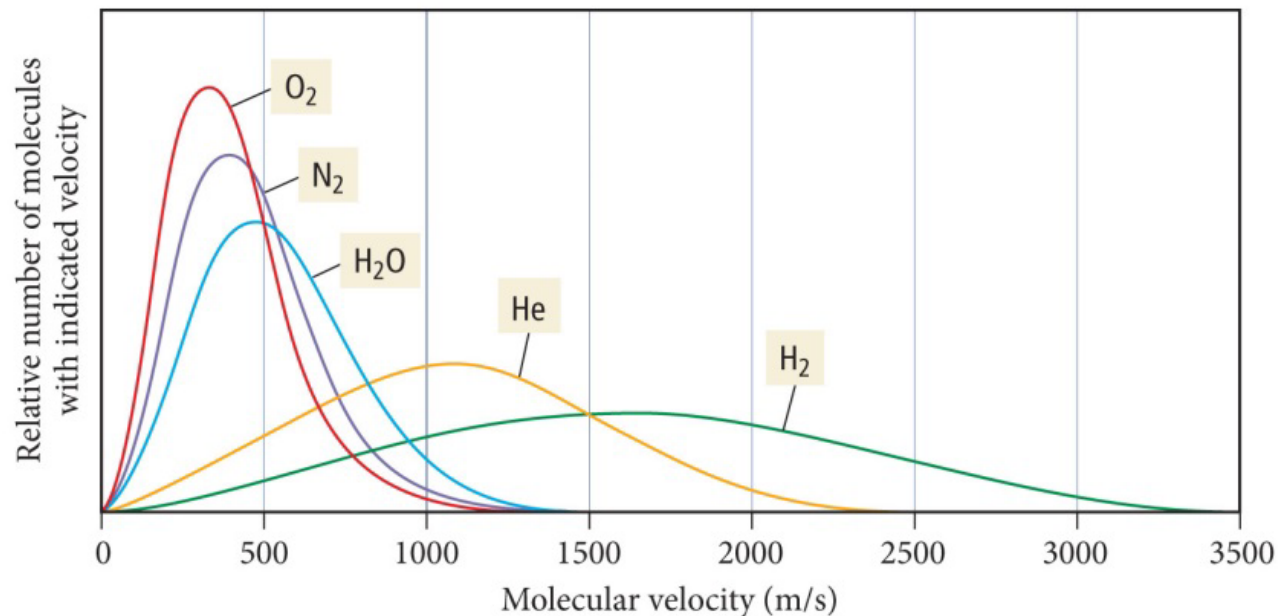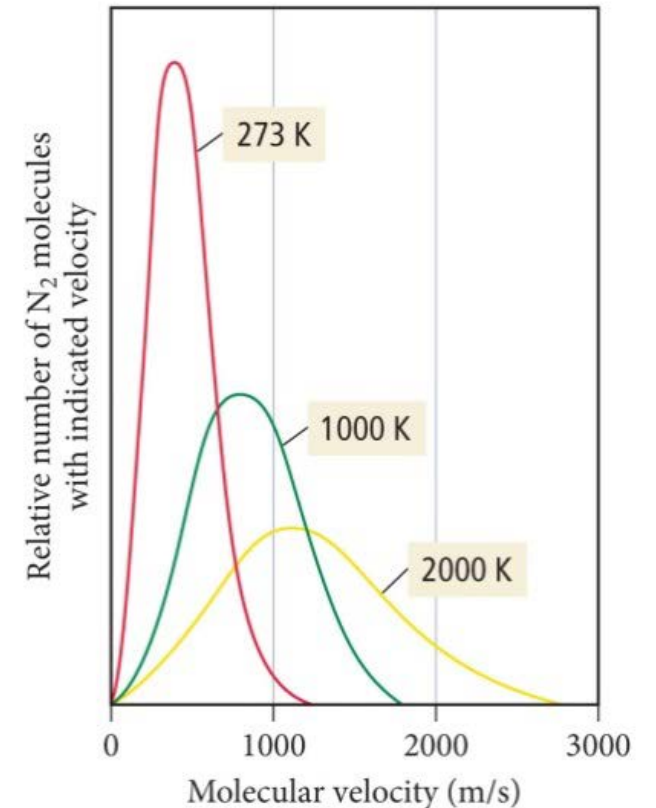
Variation of Velocity Distribution with Molar Mass

Variation of Velocity Distribution with Temperature

Graham's Law of Effusion

OBSERVATION: effusion rate for escape
of a gas through a tiny hole into a
vacuum

$$\propto 1 / \sqrt{M}$$

KINETIC THEORY
INTERPRETATION: two gases at
same T, P, V contain
equal numbers of molecules (Avogadro)
so

Before effusion

During effusion

Vacuum

Porous barrier

N_2

H_2

Lighter molecules (H_2) with
higher average speeds strike
the barrier more often and
pass more often through it
than heavier, slower molecules
(N_2) at the same temperature.

$$\frac{\text{effusion rate of A}}{\text{effusion rate of B}} = \frac{\text{urms(A)}}{\text{urms(B)}} = \sqrt{\frac{M_B}{M_A}}$$

Collisions of Gaseous Molecules with a Wall

Problem: Consider an area **A** of wall **W** in contact with a volume **V** of gas containing **N** molecules. We want to calculate the frequency of molecular collisions with the wall, the number of molecules that strike the wall per unit time.

Let ΔN_W be the number of molecules that strike the wall W in the time interval Δt. Then the collision rate (Z_W) is $\Delta N_W / \Delta t$. What effects this rate? We might expect that $\Delta N_W / \Delta t$ is proportional to

1. the area of the wall, A
2. number of molecules per unit volume, N/V
3. the average speed (moving towards the wall)

Area = A

Volume
$= A u_x \Delta t$

$u_x \Delta t$
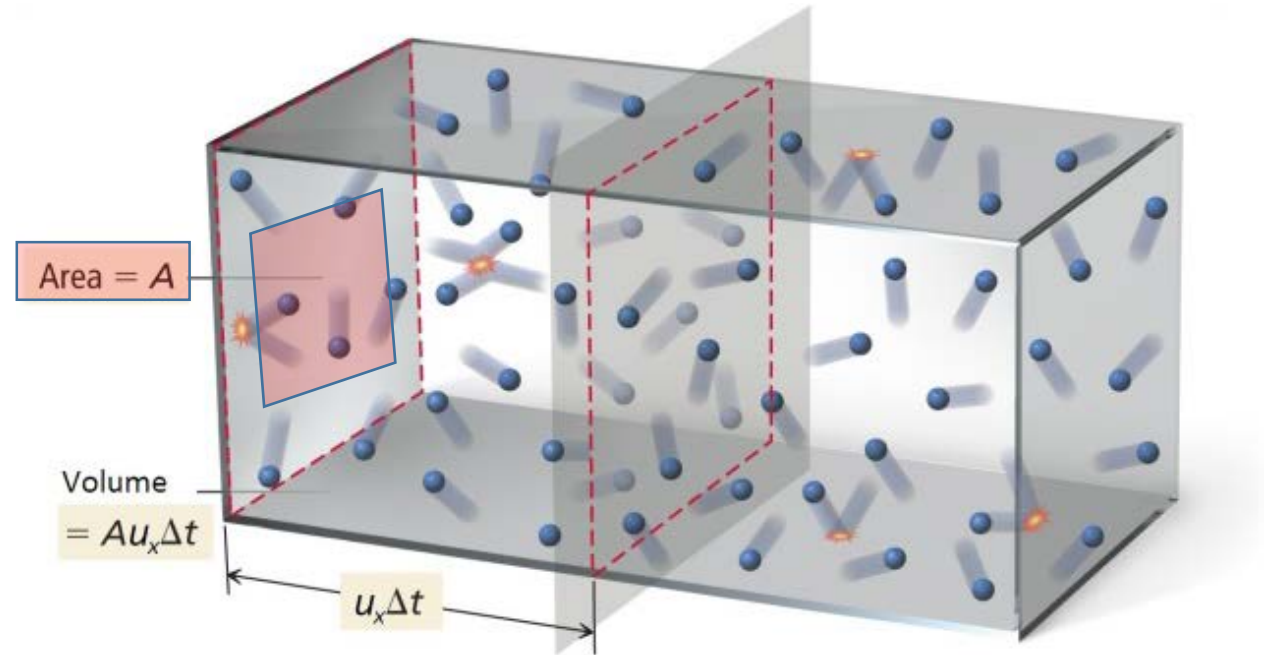
$$Z_W = \Delta N_W / \Delta t$$
$$= (\,N/V\,)(\,A\,)(\tfrac{1}{2}\,\langle u \rangle_{1D})$$
$$= (\,N/V\,)(\,A\,)(\tfrac{1}{4}\,\langle u \rangle_{3D})$$

$$\mathbf{Z_W = (\,N/V\,)\,A\,(\tfrac{1}{4}\,\langle u \rangle)}$$

$$\langle u \rangle = \sqrt{(8RT/\pi M)}$$

Collisions Between Gaseous Molecules (Intermolecular)

cross sectional area is really
perpendicular to direction of motion

Collisions of molecules with container walls give us pressure; collisions with light photons, spectroscopy; collisions with one another, chemical reactions.
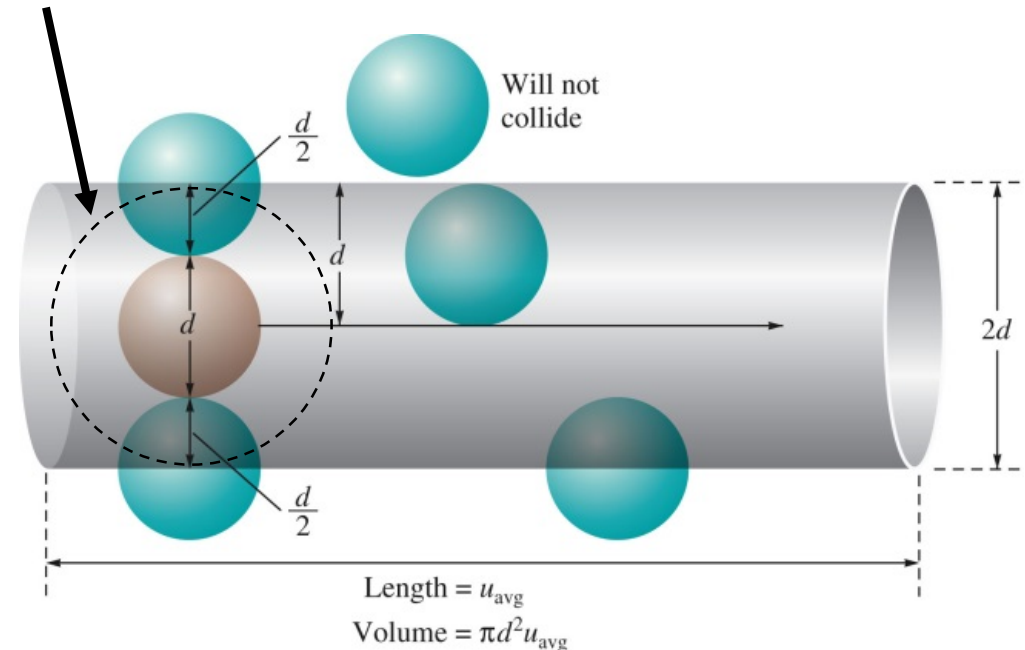
Problem: Calculate the frequency of collisions of a molecule with the other molecules of the gas (brown molecule has a cross sectional area centered about it perpendicular to its motion)

Let Z be the collision rate. What effects this rate? We might expect that Z is proportional to

1. the cross sectional area, πd^2
2. number of molecules per unit volume, N/V
3. the relative velocity of the molecule with respect to the other molecules

$$\mathbf{Z = \sqrt{2}\,(N/V)\,\pi d^2\,\langle u\rangle}$$

$\dfrac{d}{2}$ d $2d$

Will not collide

d $\dfrac{d}{2}$

Length $= u_{avg}$
Volume $= \pi d^2 u_{avg}$

since distance = velocity × time

mean free path (average distance a molecule travels between successive collisions is

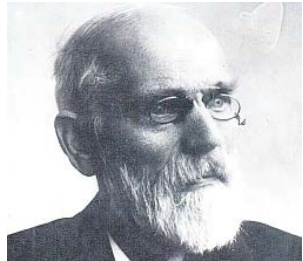$$\lambda \;=\; \langle u\rangle / Z \;\mathbf{=\; 1\,/\,\sqrt{2}\,(N/V)\,\pi d^2}$$

Real Gases

"The particles of the air are in contact with each other, yet they do not fit closely in every part, but void spaces are left between them, as in the sand on the sea shore: the grains of sand must be imagined to correspond to the particles of air, and the air between the grains of sand to the void spaces between the particles of air. Hence, when any force is applied to it, the air is compressed, and, contrary to its nature, falls into the vacant spaces from the pressure exerted on its particles: but when the force is withdrawn, the air returns again to its former position from the elasticity of its particles, as is the ease with horn shavings and sponge, which, when compressed and set free again, return to the same position and exhibit the same bulk."   **Hero of Alexandria, ~ AD 60**

"Thus far we have always considered molecules to be material points, and thus have introduced a simplification in the model which is at once in contradiction with the actual phenomena. Even a molecule in the simplest form, consisting of a single atom, must have a certain extension; the various forces exerted upon it by the other molecules can thus not be considered to act upon a single point."   **Johannes Diderik van der Waals, 1873**

(Nobel Prize in Physics in 1910 "for his work on the equation of state for gases and liquids".)

5.10 – Real Gases
   interactions (attractions and repulsions)
   compressibility, Z
   van der Waals equation of state (simplest to account for intermolecular forces
   existence of liquid and solid phases
   real, ideal, and van der Waals

Characteristics of a Real Gas

Real gases – interact and have molecular volume

Compare energy to realistic potential – $V(r)$

molecules very close, repel, non-zero volumes over-lap; separate further attract, van der Waals forces

$V(r)$ has a minimum (distance for maximum attraction)

large separations, approach ideal ($P \sim 0$), big V - molecular size becomes negligible; large distance, electrons don't "feel" one another
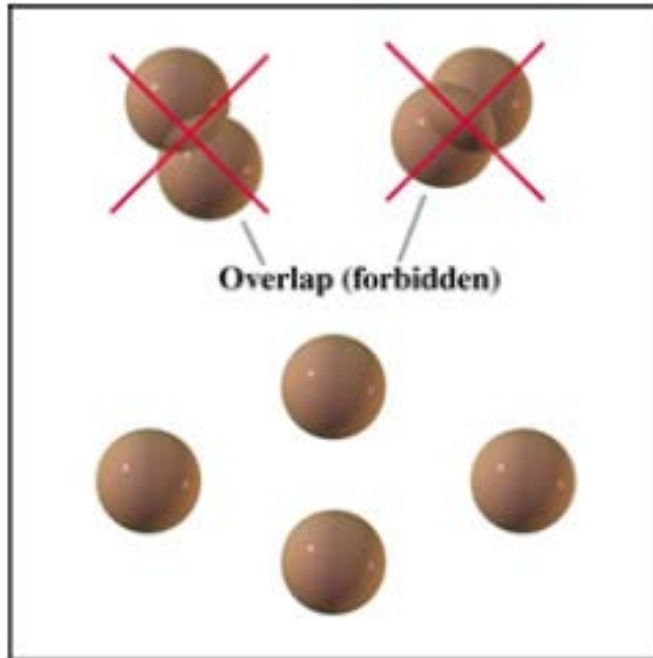
transition to ideal at $|V(r_{trans})| \sim kT$

Attraction due to electron response to electrons in other molecules, fluctuating dipole moments – Polarizability, varies depending upon molecule
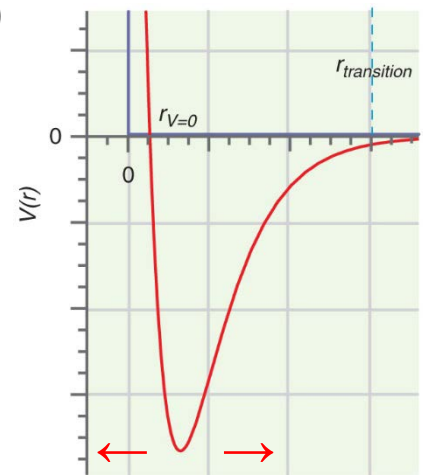

Real gas   Ideal gas

$r_{transition}$

$r_{V=0}$

0

$V(r)$

r

0

repulsion | attraction
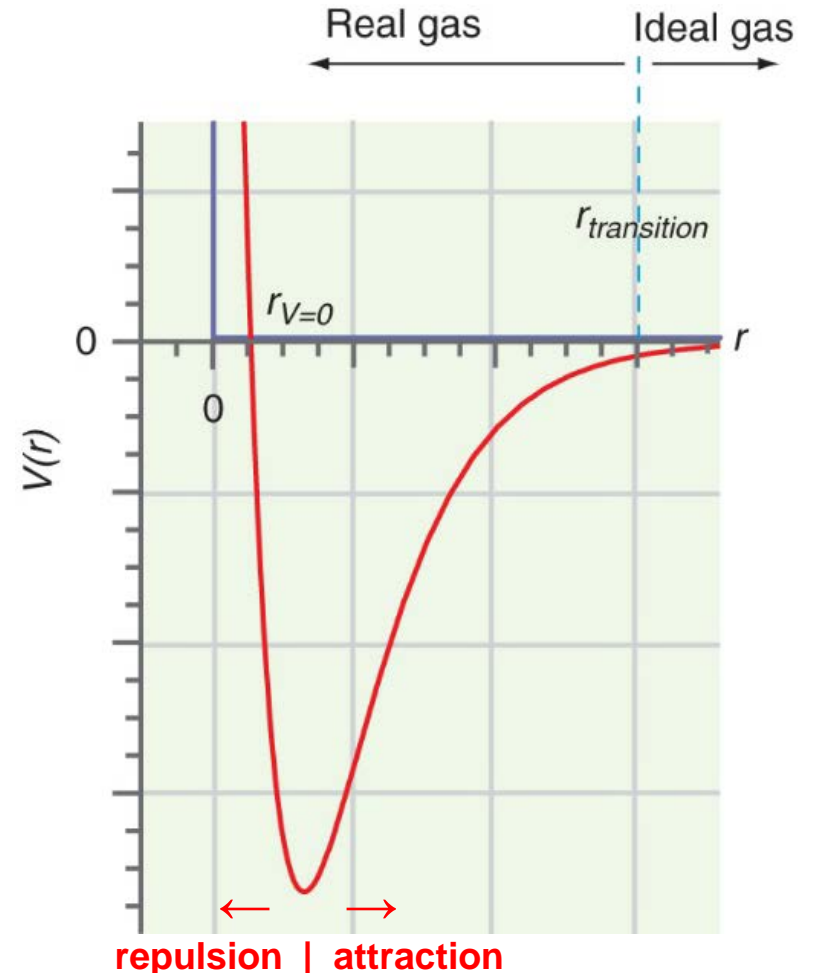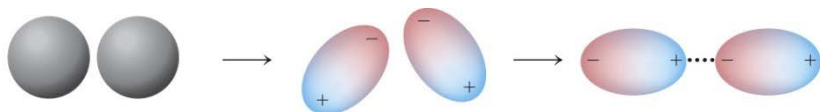
Potential energy for two atoms or molecules

Characteristics of a Real Gas
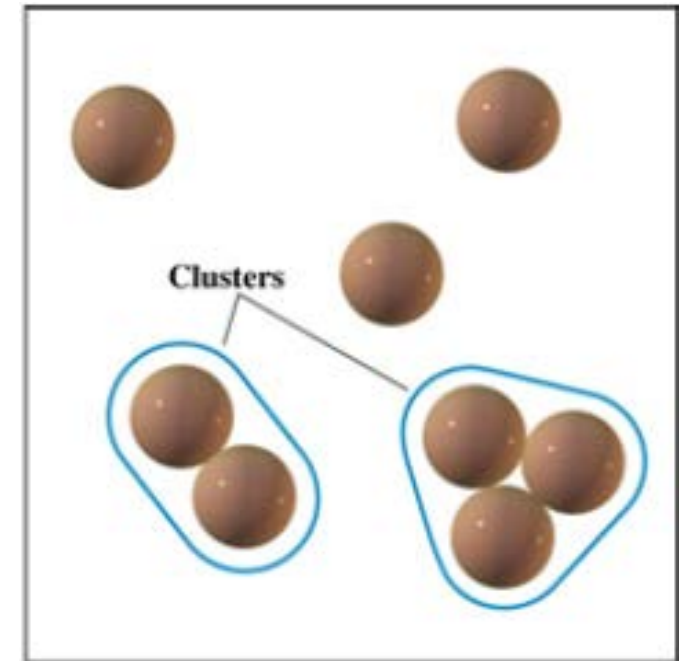

Overlap (forbidden)

Repulsive forces

Pressure is lowered at attractive distances and raised at very short repulsive distances result: low T, high P, get high density -> gives a minimum V for a liquid or solid phase (liquids and solids could not exist were it not for attractive forces)

repulsion | attraction


Clusters

Attractive forces

Compressibility

The effect of **attractive** and **repulsive** forces can be seen in the compressibility, Z where

$$Z = PV / nRT = PV_m / RT$$

$Z=1$ for an ideal gas and deviations from unity are due to **attractive** and **repulsive** forces between the atoms or molecules.

Pressure is lowered at **attractive** distances (easier to compress) and raised at short (**repulsive**) distances (harder to compress)

PV_m / RT versus P for several real gases at 25°C
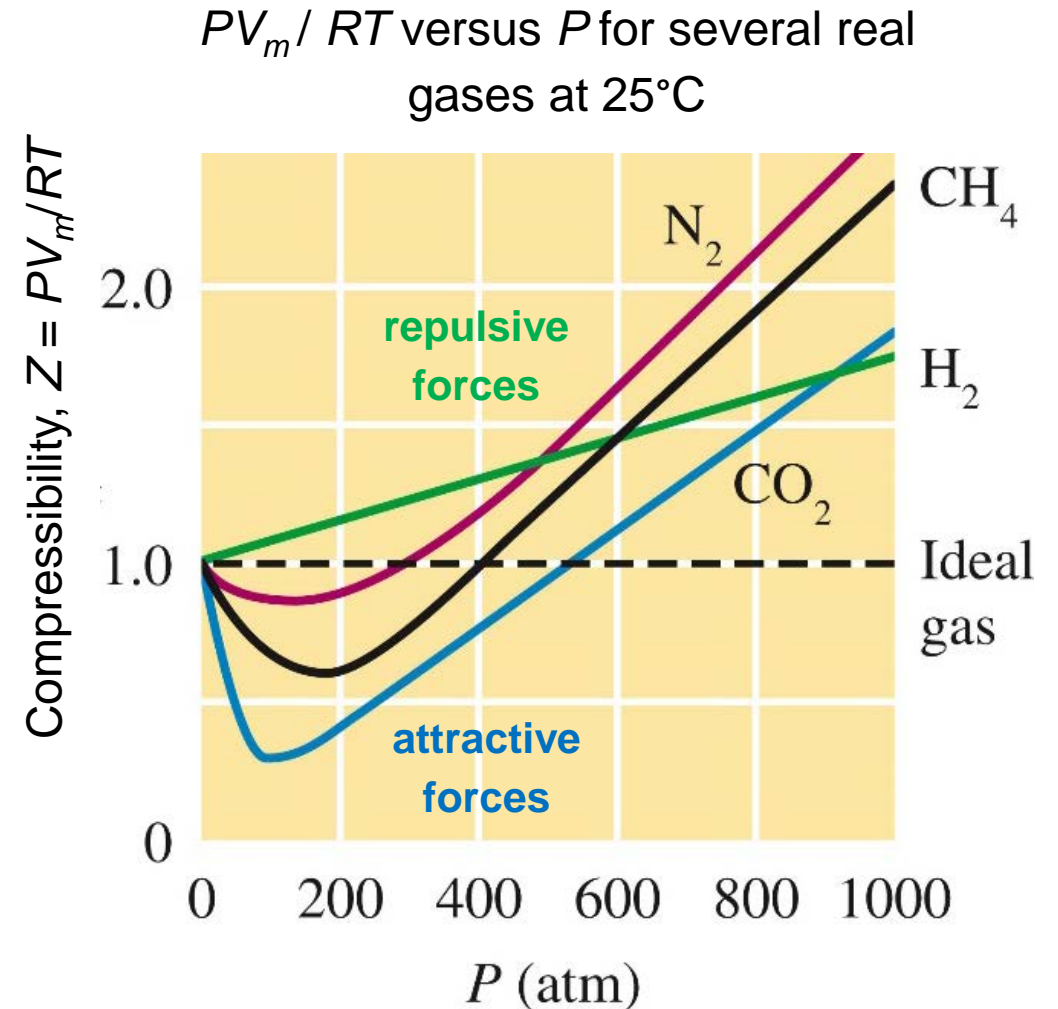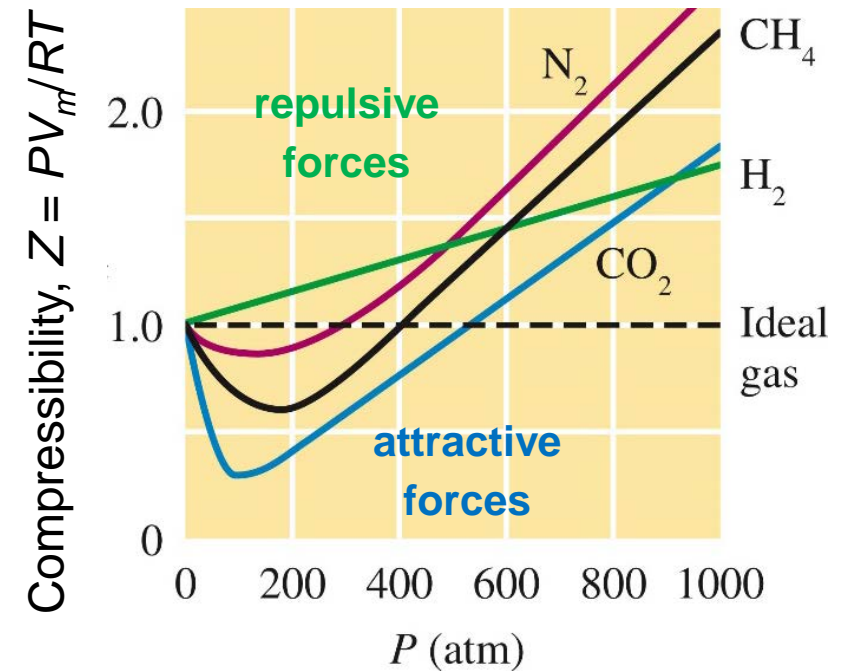
Van der Waals Equation of State (EOS)

First eos accounting for attractive and repulsive forces given by van der Waals:

$$P = nRT / (V - bn) - a (n^2 / V^2)$$

rearranging:

$$PV / nRT = 1 / (1 - bn/V) - an / RTV$$

shows how compressibility is effected by these forces: **attractive** forces (through **a**) decrease Z ratio < 1, **repulsive** forces (through **b**) increase Z ratio > 1 where repulsive forces account for finite molecular size; **a,b** vary with molecular properties, fit to experimental observables.

Van der Waals Equation of State (EOS)

$P = nRT / (V - bn) - a(n^2 / V^2)$

$PV = nRT$

$(P + a\, n^2 / V^2)(V - bn) = nRT$

$$\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT$$

Van der Waals Constants of Several Gases			
Name	Formula	a (atm L^2 mol^{-2})	b (L mol^{-1})
Ammonia	NH_3	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO_2	3.592	0.04267
Hydrogen	H_2	0.2444	0.02661
Hydrogen chloride	HCl	3.667	0.04081
Methane	CH_4	2.253	0.04278
Nitrogen	N_2	1.390	0.03913
Nitrogen dioxide	NO_2	5.284	0.04424
Oxygen	O_2	1.360	0.03183
Sulfur dioxide	SO_2	6.714	0.05636
Water	H_2O	5.464	0.03049