Lecture 6 CH131 Summer 1

Thursday, May 30, 2019

The will be lab on Friday, May 31

- Molecular speeds
- Distribution of molecular speeds, CDF https://goo.gl/gzgjQE
- How intermolecular attraction affects gas behavior
- How molecular size affects gas behavior
- Gas law for real gases: van der Waals equation

Ch10: Solids, liquids and phase transitions

- Intermolecular forces

Next lecture: Continue ch 10

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Root mean square speed

The root mean square speed of a gas is the square root of the mean (average) squared speed u^2_{avg},

$$u_{rms} = \sqrt{u^2{}_{avg}} = \sqrt{3RT/M}$$

$$R = 8.314 \frac{\text{J}}{\text{K mol}} = 8.314 \frac{\text{kg m}^2/\text{s}^2}{\text{K mol}}$$

$$\sqrt{\frac{\text{kg m}^2\ \text{K}}{\text{K mol}\ 32\text{g/mol} * \text{kg}/1000\text{g}}} = \sqrt{\text{m}^2/\text{s}^2} = \text{m/s}$$

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[TP] The rms speed, u_{rms}, of O_2 at 25 °C is about ...
($R = 8.314 \frac{\text{J}}{\text{K mol}} = 8.314 \frac{\text{kg m}^2/\text{s}^2}{\text{K mol}}$)

0%	1. 250 m/s
100%	2. 500 m/s
0%	3. 750 m/s
0%	4. 1000 m/s

$$\sqrt{\frac{3 * 8.314\ \text{kg m}^2/\text{s}^2\ 298\text{K}}{\text{K mol} \cdot 32\text{g/mol} * 10^{-3}\text{kg/g}}}$$

$$= \frac{\text{m}}{\text{s}}\sqrt{\frac{25 * 300 * 10^3}{32}}$$

$$= \frac{\text{m}}{\text{s}}\sqrt{250 * 10^3}$$

$$\frac{\text{m}}{\text{s}}\sqrt{25} * 10^2 = 500\text{m/s}$$

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Calculate rms speed of O_2 at 25 °C

$$u^2{}_{avg} = \frac{3RT}{M}$$

$$u_{rms} = \sqrt{u^2_{avg}} = u\sqrt{\frac{3RT}{M}}$$

$$R = 8.314 \frac{\text{J}}{\text{K mol}} = 8.314 \frac{\text{kg m}^2/\text{s}^2}{\text{K mol}}$$

Answer: 482 m/s ≈ 500 m/s

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[TP] The rms speed of O_2 at 25 °C is about 500 m/s. Without using a calculator, use the rms speed of O_2 to estimate that the rms speed of H_2 at the same temperature is about …

6%	1.	4000 m/s
94%	2.	2000 m/s
0%	3.	1000 m/s
0%	4.	500 m/s
0%	5.	250 m/s

$$\frac{u_{H_2}}{u_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

$$u_{H_2} = 4 * u_{O_2} = 2000 \text{ m/s}$$

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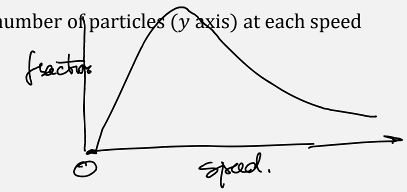
Distribution of molecular speeds

Distribution of speeds is a plot of the number of particles (y axis) at each speed (x axis).



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Distribution of molecular speeds

Say we 20,000 particles, all with the same speed $u = 500$ m/s.

Make a sketch of the corresponding distribution of speeds.

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Distribution of molecular speeds

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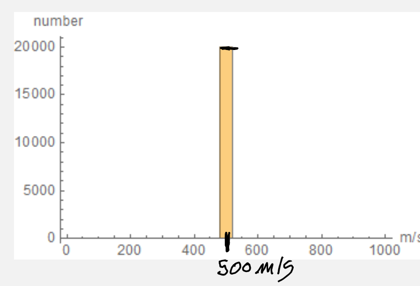
Make a sketch of the corresponding distribution of speeds.



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Distribution of molecular speeds

We have said that collisions between gas particles results in the particles having different speeds.

Make a sketch of a possible distribution of just three speeds, 300, 500, and 700 m/s, of the 20,000 particles.

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Distribution of molecular speeds

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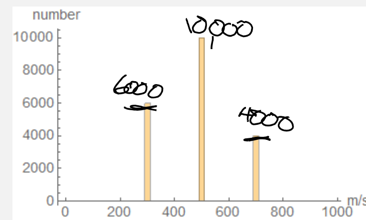
Make a sketch of a possible distribution of just three speeds, 300, 500, and 700 m/s, of the 20,000 particles.



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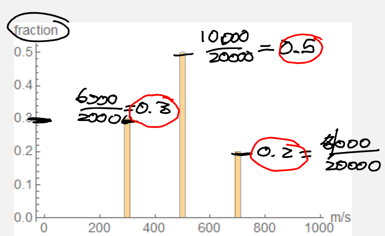
Distribution of molecular speeds

We have said that collisions between gas particles results in the particles having different speeds.

It is convenient to express the distribution in terms of fractional number of particles rather than number of particles.



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Distribution of molecular speeds

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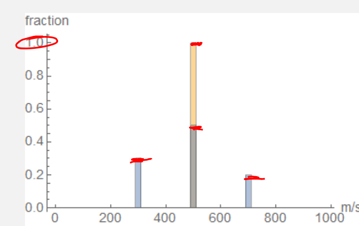

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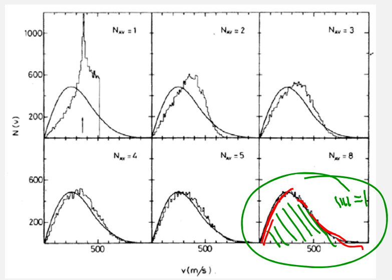
Distribution of molecular speeds

Here is what happens to the speeds of 20,000 particles, all initially at the same speed, after they each have undergone successive numbers of collisions.

Bonomo & Riggi,
Am. J. Phys. ,Vol 52, p 54 (1984)
http://dx.doi.org/10.1119/1.13809



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Distribution of molecular speeds

At 300 K, the rms speed of O_2 is $u_{rms} = 500$ m/s.

Sketch the Maxwell-Boltzmann distribution of speeds of O_2 at 300 K, from 0 m/s to 4000 m/s, marking the position of u_{rms} on the x axis.

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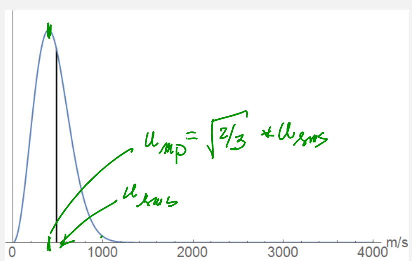
Distribution of molecular speeds

At 300 K, the rms speed of O_2 is $u_{rms} = 500$ m/s.

Sketch the Maxwell-Boltzmann distribution of speeds of O_2 at 300 K, from 0 m/s to 4000 m/s, marking the position of u_{rms} on the x axis,



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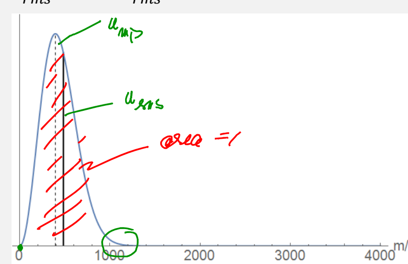
Distribution of molecular speeds

The rms speed, u_{rms}, is slightly higher than the most probable speed, u_{mp}, because of the exponential tail extending to very high speeds.

$$u_{\text{mp}} = \sqrt{2/3}\; u_{rms} \approx 0.82\; u_{rms}$$



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u_{rms} versus temperature

The rms speed of O_2 at 300 K is 500 m/s and the rms speed of O_2 at 1200 K is 1000 m/s. Sketch the distribution of speeds for O_2 at these two temperatures on the same axes, marking the position of the two rms speeds on the x axis.

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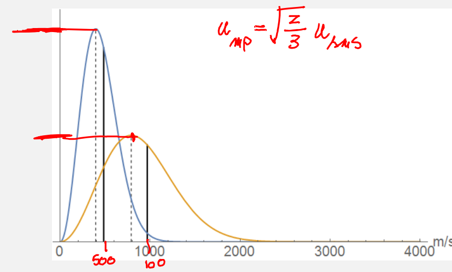
u_{rms} versus temperature

The rms speed of O_2 at 300 K is 500 m/s and the rms speed of O_2 at 1200 K is 1000 m/s. Sketch the distribution of speeds for O_2 at these two temperatures on the same axes, marking the position of the two rms speeds on the x axis.

$u_{mp} = \sqrt{\frac{2}{3}}\, u_{rms}$



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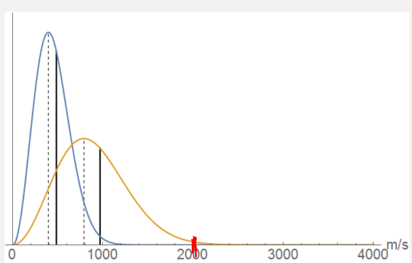
u_{rms} versus temperature

Add to your sketch the distribution of speeds of H_2 at 300 K.



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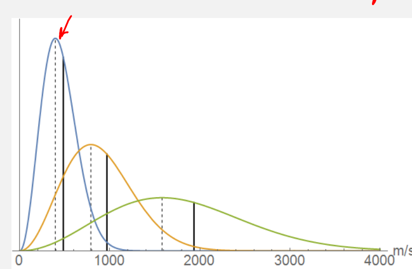
u_{rms} versus temperature

Add to your sketch the distribution of speeds of H_2 at 300 K.

$u_{rms} = \sqrt{\frac{3RT}{M}}$



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Effect of intermolecular attraction

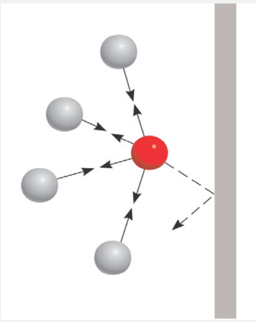
Gas particles attract one another: van der Waals a

hitting wall $\propto \frac{n}{V}$

pulling back $\propto \frac{n}{V}$

combined effect $\propto \left(\frac{n}{V}\right)^2$

$p_{\text{observed}} = p_{\text{ideal}} - a\left(\frac{n}{V}\right)^2$



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Energy density and molecular attractions

We have seen that we can interpret pressure as $\frac{\text{energy}}{\text{volume}}$, $1\ \text{Pa} = 1\ \text{J/m}^3$

Let's apply this interpretation to

$p_{\text{observed}} = p_{\text{ideal}} - a\left(\frac{n}{V}\right)^2$

$p_{\text{ideal}} = nRT/V$ is just the kinetic energy density (kinetic energy per unit volume) of the ideal gas.

Similarly, $-a\left(\frac{n}{V}\right)^2$ is the corresponding potential energy density of the gas due to the interpartical interactions.

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[TP] Predict the effect of intermolecular attraction on the pressure exerted by a gaseous molecule in a collision with the wall of its container. The stronger the attraction, the ...

18% 1. greater the pressure
82% 2. smaller the pressure
0% 3. The pressure will not be affected
0% 4. Cannot answer without knowing the temperature
0% 5. Cannot answer without knowing the polarity of the molecule

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[TP] Equal amounts of gases A and C are in a single container. The molar masses of the gases are identical, but gas C has stronger intermolecular forces. The container is pierced with a hole 0.003 mm in diameter. After 5 minutes, the container will contain ...

6% 1. more A than C
0% 2. the same amount of A and C
94% 3. more C than A

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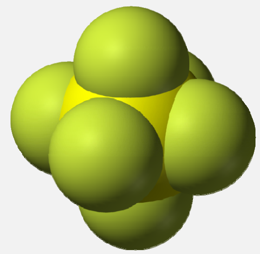
Effect of molecular size

While gas particles are tiny compared to the volume of their container, they do take up some space.

The graphic illustrates the electron cloud of SF_6.



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[TP] A gas in a rigid 2.5 L container has a pressure of 1.3 bar = 130 kPa. If 1.2 grams of small glass beads are added to the container (without changing the temperature), the pressure of the gas will …

33% 1. increase
33% 2. be unaffected
33% 3. decrease

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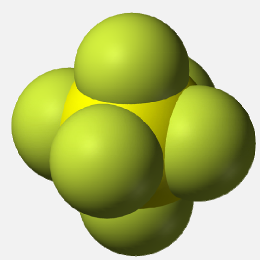
Effect of molecular size

Gas particles have a volume: van der Waals b

$$V_{\text{container}} = V_{\text{empty}} + bn$$



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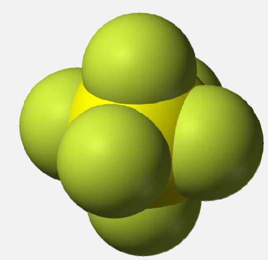
[TP] Gas particles have a volume measured by van der Waals b. For SF_6, $b = 88$ mL/mol. The percent of gas container volume taken up by the SF_6 molecules themselves is …

12% 1. 0.01%
24% 2. 0.05%
12% 3. 0.1%
35% 4. 0.5%
18% 5. 1%
0% 6. 5%



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Effect of molecular size

Gas particles have a volume: van der Waals b

$V = V_{\text{container}} = V_{\text{empty}} + bn$

For SF_6, $b = 88$ mL/mol

% of molar gas volume …

$\approx (0.088 / 22) \times 100\% = 0.40\%$

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A gas law for "real" gases: van der Waals equation

We know the ideal gas law $pV = nRT$ where p does not account for inter-particle attractions …

$$p = p_{\text{ideal}} = p_{\text{observed}} + a\left(\frac{n}{V_{\text{container}}}\right)^2$$

and V does not account for particle volume …

$$V = V_{\text{empty}} = V_{\text{container}} - bn$$

Combine these two expressions into an equation relating p_{observed}, $V_{\text{container}}$, and T.

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A gas law for "real" gases: van der Waals equation

We know the ideal gas law $pV = nRT$ where p does not account for inter-particle attractions and V does not account for particle volume …

$$p = p_{\text{ideal}} = p_{\text{observed}} + a\left(\frac{n}{V_{\text{container}}}\right)^2$$

$$V = V_{\text{empty}} = V_{\text{container}} - bn$$

$$p_{\text{ideal}}V_{\text{empty}} = \left\{p_{\text{observed}} + a\left(\frac{n}{V_{\text{container}}}\right)^2\right\}(V_{\text{container}} - bn) = nRT$$

This is known as the van der Waals equation

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Working with the van der Waals equation

In terms of $p = p_{\text{observed}}$ and $V = V_{\text{container}}$, the van der Waals equation is

$$\left\{p + a\left(\frac{n}{V}\right)^2\right\}(V - bn) = nRT$$

For calculations, rearrange this to express the observed p in terms of n, V, T, a, and b.

$$p = \frac{nRT}{V - bn} - a\left(\frac{n}{V}\right)^2$$

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Working with the van der Waals equation

$$p = \frac{nRT}{V - bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

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Working with the van der Waals equation

$$p = \frac{nRT}{V - bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

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$$p_{ideal} = \frac{nRT}{V} = 31.3 \text{ bar (confirm yourself)}$$

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Working with the van der Waals equation

$$p = \frac{nRT}{V - bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

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$$p_{ideal} = \frac{nRT}{V} = 31.3 \text{ bar (confirm yourself)}$$

$$p = \frac{nRT}{V - bn} - a\left(\frac{n}{V}\right)^2 = 32.5 \text{ bar} - 3.7 \text{ bar} = 28.8 \text{ bar (confirm yourself)}$$

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Working with the van der Waals equation

$$p = \frac{nRT}{V - bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

$$p_{ideal} = \frac{nRT}{V} = 31.3 \text{ bar (confirm yourself)}$$

$$p = \frac{nRT}{V - bn} - a\left(\frac{n}{V}\right)^2 = 32.5 \text{ bar} - 3.7 \text{ bar} = 28.8 \text{ bar (confirm yourself)}$$

Since the observed pressure is smaller than the ideal pressure, the effect of a is more important than b at 500. K.

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Working with the van der Waals equation

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 3000. K?

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Working with the van der Waals equation

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What are the ideal and observed pressures of 3.00 mol of Cl_2 confined in 4.00 L at 3000. K?

$p_{ideal} = \frac{nRT}{V} = 187.1$ bar (confirm yourself) (31.3 at 500K)

$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 = 195.3 \text{ bar} - 3.7 \text{ bar} = 191.6 \text{ bar}$ (confirm yourself)

Since the observed pressure is larger than the ideal pressure, the effect of b is more important than a at 3000. K.

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Working with the van der Waals equation

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

In general, the effect of b is muted at low T and so the effect of a dominates there, while for high T the effect of b dominates.

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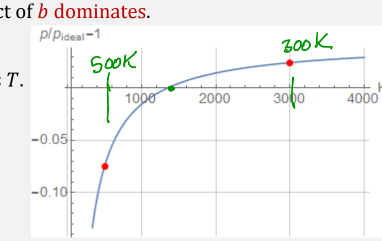
Working with the van der Waals equation

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

In general, the effect of b is muted at low T and so the effect of a dominates there, while for high T the effect of b dominates.

For 3.00 mol of Cl_2 confined in 4.00 L, here is $\frac{p}{p_{\text{ideal}}} - 1$ versus T.



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Working with the van der Waals equation

$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2$ and $R = 0.08314$ L bar/(L mol)

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What is the observed and ideal pressures of 8.00 mol of Cl_2 confined in 4.00 L at 27 °C? Use

$$p_{ideal} = \frac{nRT}{V} = 49.9 \text{ bar}$$

$$p = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 = 56.2 \text{ bar} - 26.3 \text{ bar} = 29.9 \text{ bar}$$

Since the observed pressure is smaller than the ideal pressure, the effect of a is more important than b at 27 °C

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Problem 7e:9.49 and 8e:9.51

$a = 3.640$ L^{2}bar/mol^2

$b = 0.04267$ L/mol

49. Using (a) the ideal gas law and (b) the van der Waals equation, calculate the pressure exerted by 50.0 g carbon dioxide in a 1.00-L vessel at 25°C. Do attractive or repulsive forces dominate?

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Intramolecular and intermolecular forces

Chemical changes are related to breaking and formation of covalent bonds due to intramolecular forces within molecules.

Intermolecular forces are forces of attraction between molecules

Physical changes are governed by intermolecular forces

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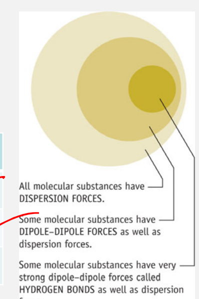
Intermolecular forces: stickiness!

- Stickiness: consequence of molecule•••molecule
- Coulombs law: opposite charges attract, like repel
- Three kinds of intermolecular electrical attraction …

Interaction	When	Strength
Dispersion	Always	Weak
Dipole-dipole	Polar molecules	Moderate
H-bonding	N-H•••, O-H•••, F-H•••	Strong



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