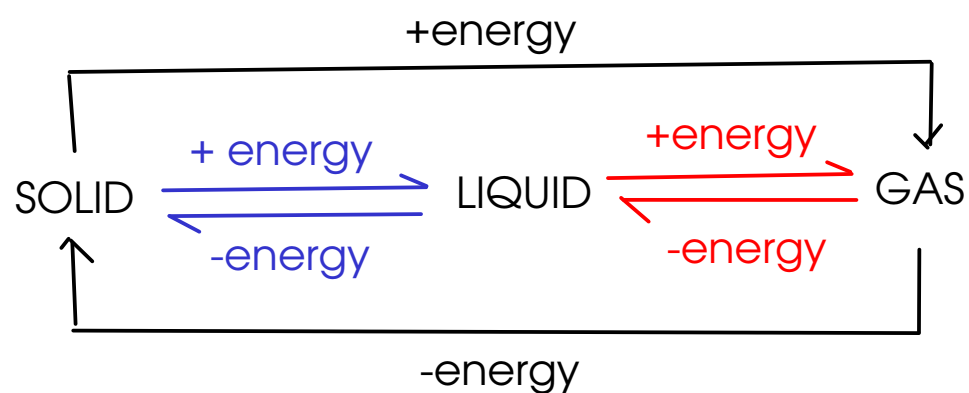


PHASE CHANGES

- To understand solids and liquids at the molecular level, it will help to examine PHASE CHANGES in a little more detail.

A quick review of the phase changes...

Phase change	Description	Energy change
Melting	Solid to liquid	Endothermic
Sublimation	Solid to gas	Endothermic
Vaporization	Liquid to gas	Endothermic
Deposition	Gas to solid	Exothermic
Freezing	Liquid to solid	Exothermic
Condensation	Gas to liquid	Exothermic

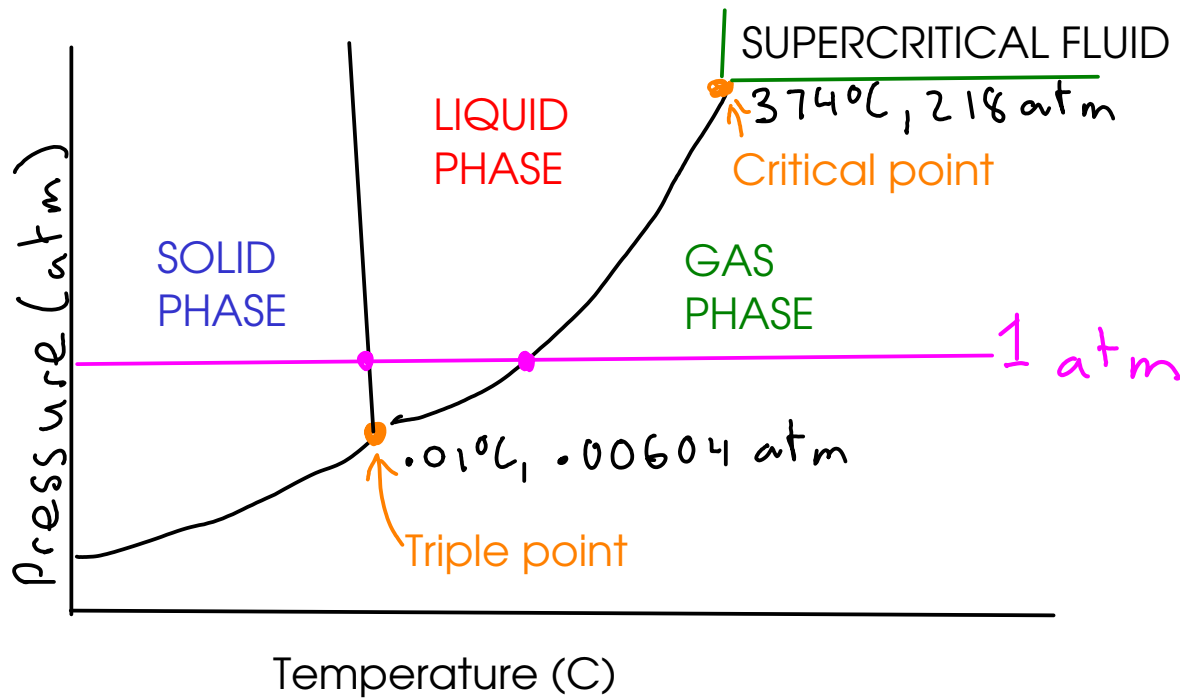


ΔH_{fus} : enthalpy change
to melt 1 mol of solid

ΔH_{vap} : enthalpy change
to vaporize 1 mol
of liquid

PHASE DIAGRAMS

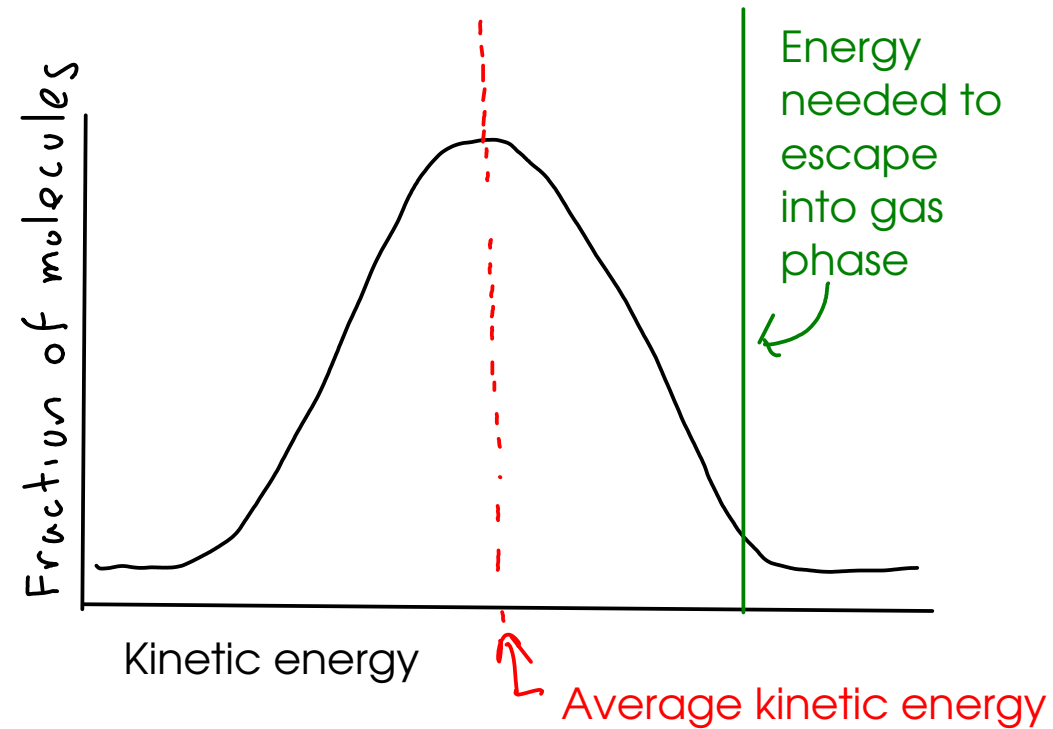
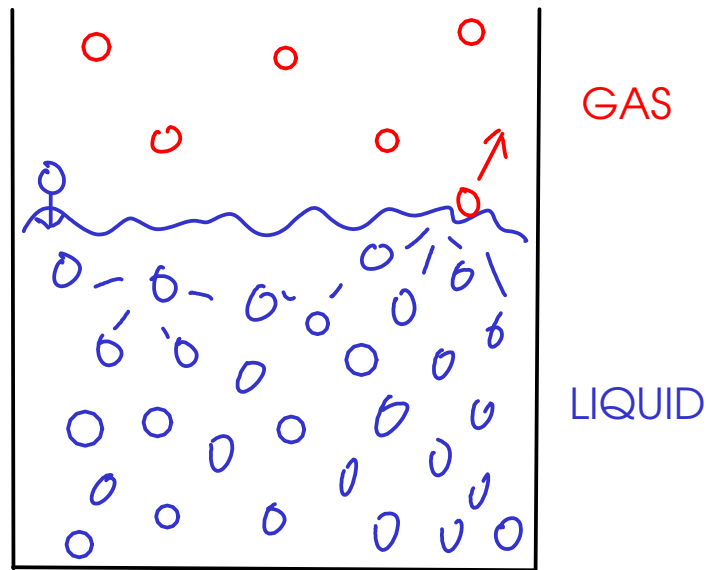
- are a convenient way to show experimental data on when bulk phase changes occur.



SAMPLE PHASE
DIAGRAM FOR
WATER

- The curves on the phase diagram represent bulk phase changes.
- The TRIPLE POINT is a set of conditions where all six phase changes occur at the same time; in other words all three phases coexist
- The CRITICAL POINT occurs where there stops being a distinction between the gas and liquid states. This occurs at high pressure and high temperature, where the substance has the density of a liquid but the fluidity of a gas. This is called a SUPERCRITICAL FLUID. Supercritical fluids - like supercritical carbon dioxide - are often used as environmentally friendly SOLVENTS.
- The normal boiling point and freezing points are on the curves. The normal melting point is the point on the solid/liquid curve at 1 atm , while the normal boiling point is on the liquid/gas curve at 1 atm !

VAPORIZATION IN MORE DETAIL



- For a molecule to move from the liquid phase to the gas phase, it must acquire enough KINETIC ENERGY (which depends on molecular SPEED) to break away from the INTERMOLECULAR FORCES holding the molecule in the liquid.

- The AVERAGE KINETIC ENERGY of molecules is proportional to the TEMPERATURE. On average, molecules in both the liquid and the solid state move faster at higher temperatures.

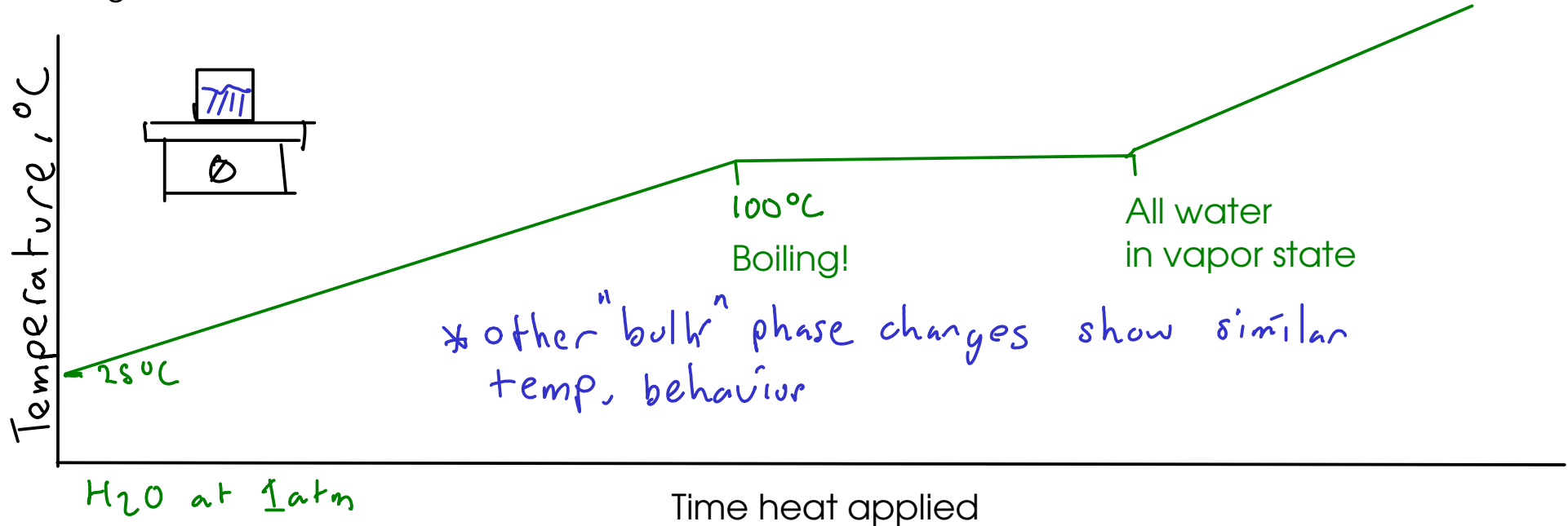
- Even at room temperature, some of the molecules have enough kinetic energy to escape into the gas phase. This accounts for the tendency of volatile liquids to evaporate from open containers even well away from the boiling point.

- As we increase temperature, the gaussian curve above shifts to the right, and a higher fraction of molecules have enough energy to vaporize.

TEMPERATURE PROFILE OF VAPORIZATION

- To increase the rate of vaporization, we can increase the temperature. At the BOILING POINT, the pressure of the vaporizing water is enough to push back against the liquid water and bubbles of vapor form in the liquid: BOILING

- If we look at the temperature changes up to and through the boiling point, we see something interesting...



DURING THE BOILING PROCESS, as long as you have some liquid water remaining, the temperature will remain constant - EVEN AS YOU CONTINUE TO APPLY HEAT!

How do we explain this behavior?



- The VAPORIZATION itself requires an energy input. What's that energy doing? Breaking water molecules away from one another (breaking apart the water's intermolecular forces).

LIQUIDS

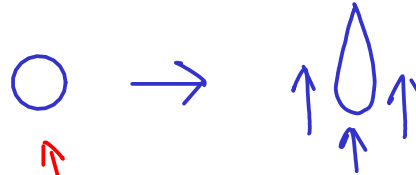
- FLUID, DENSE, INCOMPRESSIBLE

- Possess a few unique properties

① SURFACE TENSION

- a measure of the tendency of a liquid to minimize its surface area, or the resistance to the breaking of a liquid surface.

Liquid droplets tend to be spherical...



... but friction causes falling droplets to take on the traditional "drop" shape.

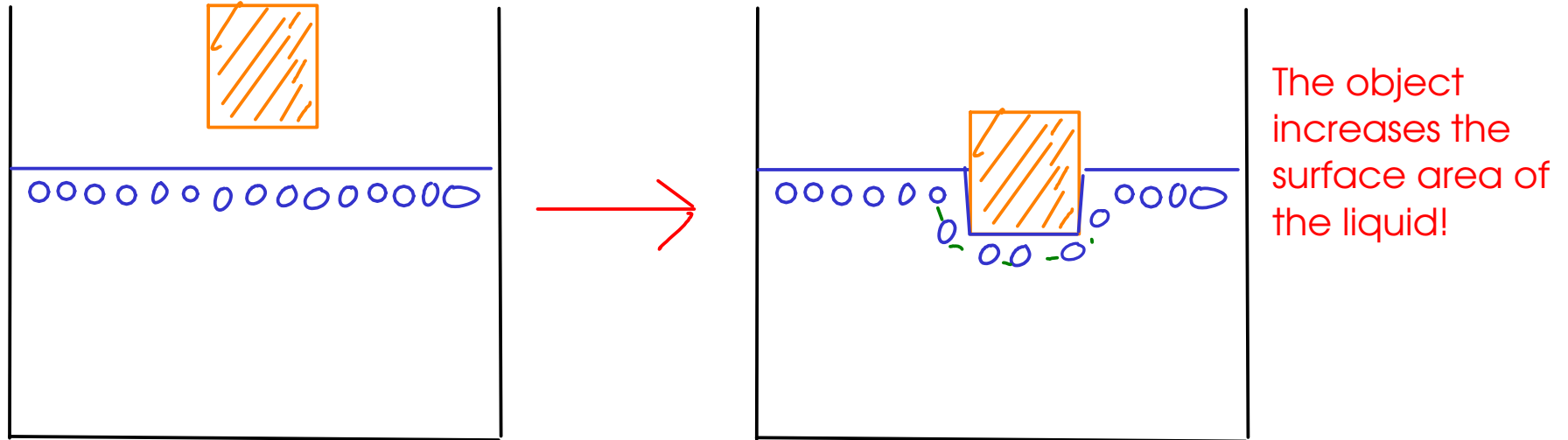
A sphere has the smallest surface area for a given volume.

② VISCOSITY (also for gases)

- a measure of a liquid's resistance to flow, or "thickness"

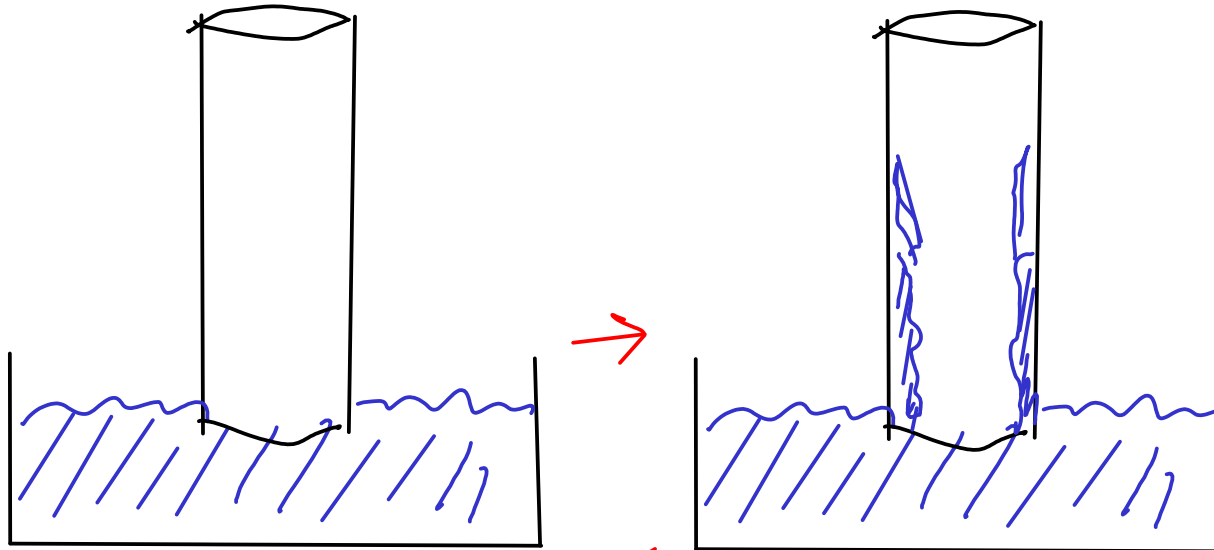
SURFACE TENSION

- Surface tension can be explained by looking at liquid molecules as being attracted to each other by INTERMOLECULAR FORCES.

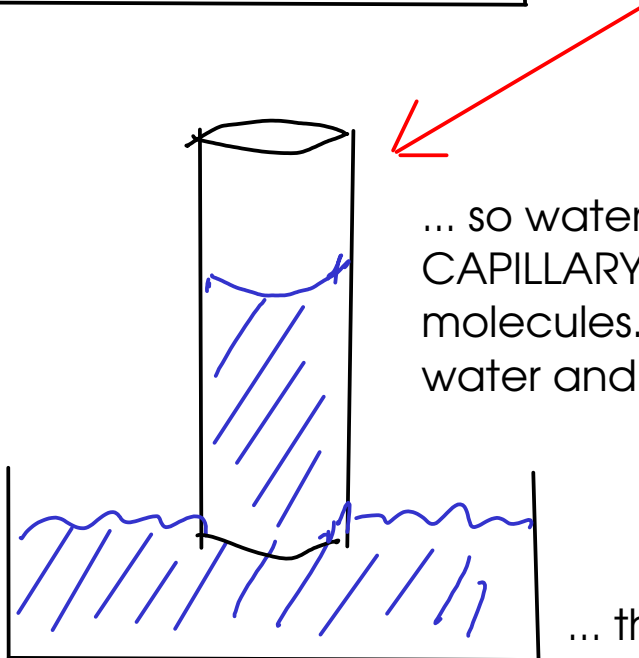


For the object to penetrate the liquid surface, it must push water molecules at the surface apart. Since these water molecules ARE ATTRACTED TO ONE ANOTHER, the liquid will resist!

- Surface tension also explains CAPILLARY ACTION, the drawing up of WATER into a glass tube. Water is attracted to glass, and will climb up the surface of a glass tube.



... but this greatly increases the SURFACE AREA of the water, and pulls the water molecules farther from each other.

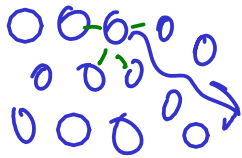


... so water is PULLED UP THE MIDDLE OF THE CAPILLARY by the attractive force between water molecules. This minimizes the surface area of the water and gets water molecules closer to one another.

... the water is pulled up AGAINST GRAVITY!

VISCOSITY

- viscosity can also be explained (at least partially) by looking at INTERMOLECULAR FORCES!
- For a liquid to FLOW, its molecules must move past one another. This means that some of the molecules must move farther away from other molecules. Since the molecules in the liquid state are ATTRACTED TO ONE ANOTHER, that means the flowing will be slowed.
- Viscosity is also determined by STRUCTURE. Liquids with large chains (like oils) which can rotate and tangle in one another will also be viscous.



Molecules have to move past one another to flow, and stronger attractions between molecules make that more difficult!

INTERMOLECULAR FORCES IN LIQUIDS

- "Intermolecular forces" is a generic term. It refers to any number of forces that exist between molecules!

- In liquids, there are three main types of intermolecular force

① **DIPOLE-DIPOLE INTERACTIONS**
- only for polar molecules

② **LONDON DISPERSION FORCES**
- exist in all liquids

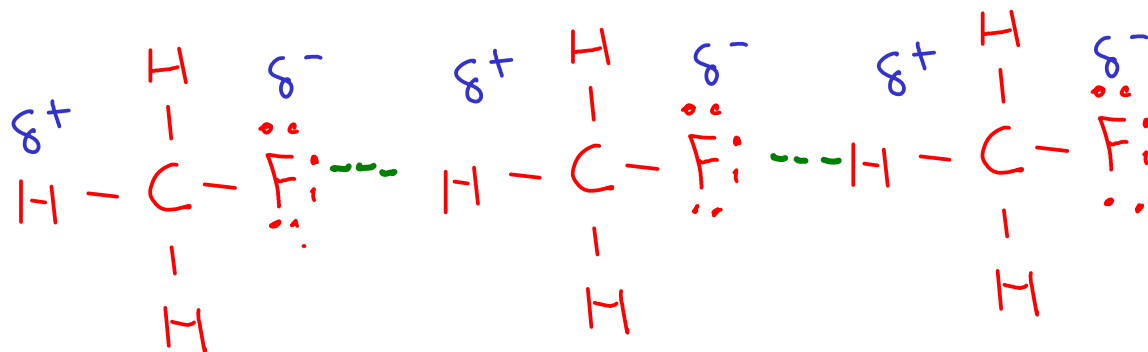
③ **HYDROGEN BONDS**
- exist only when hydrogen is directly bonded to a highly electronegative atom.



van der Waals forces...

DIPOLE-DIPOLE INTERACTIONS

- attractions between the positive pole of one polar molecule and the negative pole of another
-

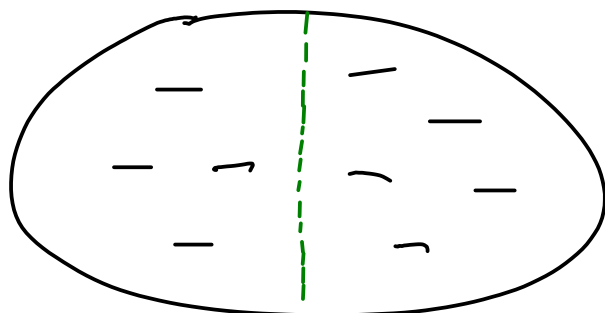


Attractions between the oppositely-charged poles of polar molecules

- Dipole-dipole interactions occur only between POLAR molecules
- Dipole-dipole interactions are weak relative to the other two kinds of intermolecular forces in liquids
- The more polar a molecule is (the larger the dipole moment), the stronger its dipole-dipole interactions.

LONDON DISPERSION FORCES

- often called "London forces" for short.
 - occurs because electron density is - at any given point in time - likely to be uneven across a molecule due to the simple fact that electrons are MOVING!
-



Let's say that at one point in time, the electrons around a molecule are here. At this moment, there is a TEMPORARY (INSTANTANEOUS) DIPOLE.

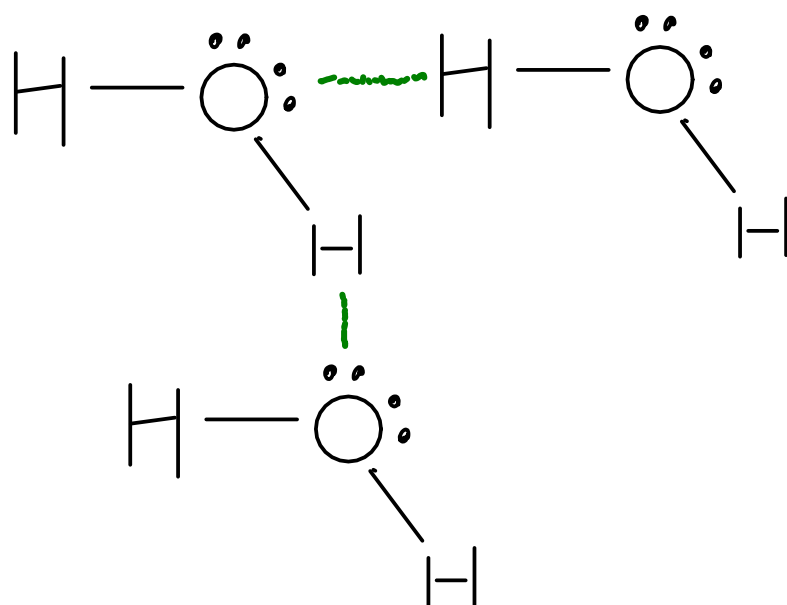
This dipole can interact (and even induce) dipoles on other, nearby molecules.

What happens when the electrons move around some more? The dipole may flip, and the surrounding INDUCED DIPOLES flip along with it. This results in a net ATTRACTIVE FORCE between molecules.

- London forces occur in all molecules, polar or nonpolar.
- London forces increase in strength as molecules get larger. The larger a molecule is, the more easily instantaneous dipoles form and the more easily dipoles can be induced.
- London forces are often the most important interaction between molecules in the liquid state, unless the molecules are capable of HYDROGEN BONDING.

HYDROGEN BONDING

- can happen when there is a HYDROGEN ATOM bonded DIRECTLY to either O, N, or F and that O, N, or F atom has at least one lone pair.



When hydrogen bonds to a very electronegative atom, electron density is pulled away from hydrogen.

Since hydrogen has no core electrons, this effectively exposes the hydrogen nucleus.

The exposed hydrogen nucleus is strongly attracted to any nearby electron density, such as the lone pairs on an adjacent molecule.

- Hydrogen bonds are the strongest type of intermolecular force in the liquid state. They are ALMOST as strong as a covalent bond.

- Hydrogen bonds form in several important molecules: water, ethanol, nucleic acids (they hold the DNA helix together)

FORCES AND OBSERVABLE PROPERTIES

- These intermolecular forces affect observable liquid properties!

① MELTING AND BOILING POINTS

- Stronger forces mean higher melting and boiling points.

② SURFACE TENSION

- Stronger forces mean greater surface tension.

③ VISCOSITY

- Stronger forces mean a more viscous (thick) substance.

... but viscosity is also affected by molecular structure!

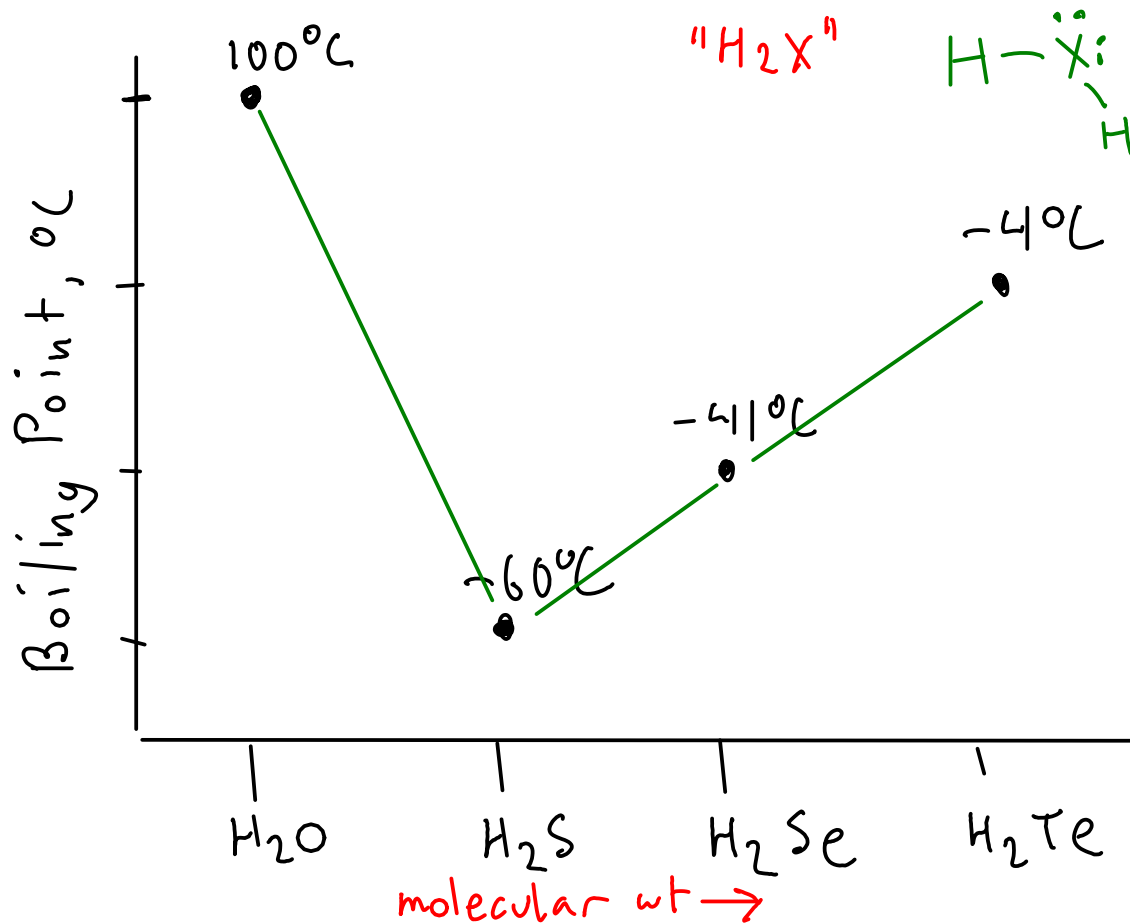
④ VAPOR PRESSURE

... is the PARTIAL PRESSURE of vapor over a liquid's surface. The liquid boils when its vapor pressure equals atmospheric pressure.

- Stronger forces mean a LOWER vapor pressure.

COMPARING MOLECULES

- In general, heavier molecules have stronger intermolecular forces than lighter molecules. (London forces depend on size!)
- For molecules OF SIMILAR SIZE, a polar molecule will have stronger intermolecular forces than a nonpolar one.
- Molecules that hydrogen bond will have much stronger intermolecular forces than you would otherwise expect.



These molecules are similar in structure.

The boiling points of the sulfide, selenide, and telluride increase with molecular weight, as we expect.

Water is capable of HYDROGEN BONDS, so its boiling point is much greater than the others in the series, even though it has a much smaller molecular weight!

SOLIDS

- RIGID, DENSE, and INCOMPRESSIBLE

- Properties of interest:

① MELTING POINT

- Temperature at which the bulk phase change from solid to liquid occurs

② HARDNESS and BRITTLENESS

- hardness: resistance of a solid to deformation (shape change) caused by the application of a force

- brittleness: tendency of a material to fracture or break rather than to deform.

③ CONDUCTIVITY

- ability of a material to conduct an electric current

... these properties will be influenced by the KINDS OF FORCES holding the solid together!

CLASSIFICATION OF SOLIDS: By attractive forces

- Solids may be classified either by the type of forces holding the solid together or by structure. We'll discuss forces first.
- Some solids are held together by the same sorts of forces found in liquids. But there are more options for solids!
- There are four kinds of solids when classified by forces.

① MOLECULAR SOLIDS

- held together by the same kinds of forces that hold liquids together:

- Ⓐ van der Waals forces: London dispersion forces and dipole-dipole interactions
- Ⓑ hydrogen bonds

... generally, these forces are the weakest.

Examples: candle wax, water ice

Generally, molecular solids:

- have LOW MELTING POINTS
- are SOFT
- are NONCONDUCTORS

② METALLIC SOLIDS

- held together by METALLIC BONDS, which involve electron sharing throughout the body of the metal..

... strength of these metallic bonds is variable.

Examples: iron, gold, copper, zinc, other metals

Generally, metallic solids:

- have a wide range of MELTING POINTS, though almost all melt above room temperature.
- range from SOFT to HARD. Many are MALLEABLE, meaning they deform before breaking.
- are good CONDUCTORS of both heat and electricity

③ IONIC SOLIDS

- held together by IONIC BONDS:

... generally, these forces are much stronger than the ones in molecular solids.

Examples: sodium chloride, any ionic compound

Generally, ionic solids:

- have HIGH MELTING POINTS, well over room temperature
- are HARD
- are NONCONDUCTORS of electricity in the solid phase, but CONDUCT when melted or dissolved into a liquid solution.

④ COVALENT NETWORK SOLIDS

- held together by COVALENT BONDS.
- are, in essence, giant molecules where the entire solid (not simply individual molecules WITHIN the solid) are held together by covalent bonds.

... these are the strongest kind of forces holding solids together.

Example: diamond

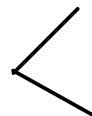
Generally, covalent network solids:

- have EXTREMELY HIGH MELTING POINTS. Most don't melt at all - they decompose before melting.
- are EXTREMELY HARD. The hardest materials known are covalent network solids.
- are NONCONDUCTORS

Relative strengths of the forces holding solids together:

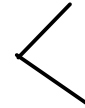
INTERMOLECULAR
FORCES

molecular solids



IONIC
BONDS

ionic solids



COVALENT
BONDS

covalent network solids

... the stronger the forces, the:

- HARDER a material
- HIGHER the melting point of the material

Metallic bonds vary considerably, so they have been left out of the comparison!