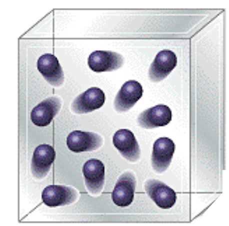
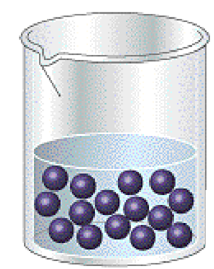
Liquids & Solids

States

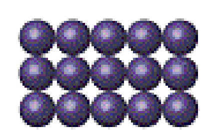
Gas → High kinetic energy (move fast) → Low attractive forces



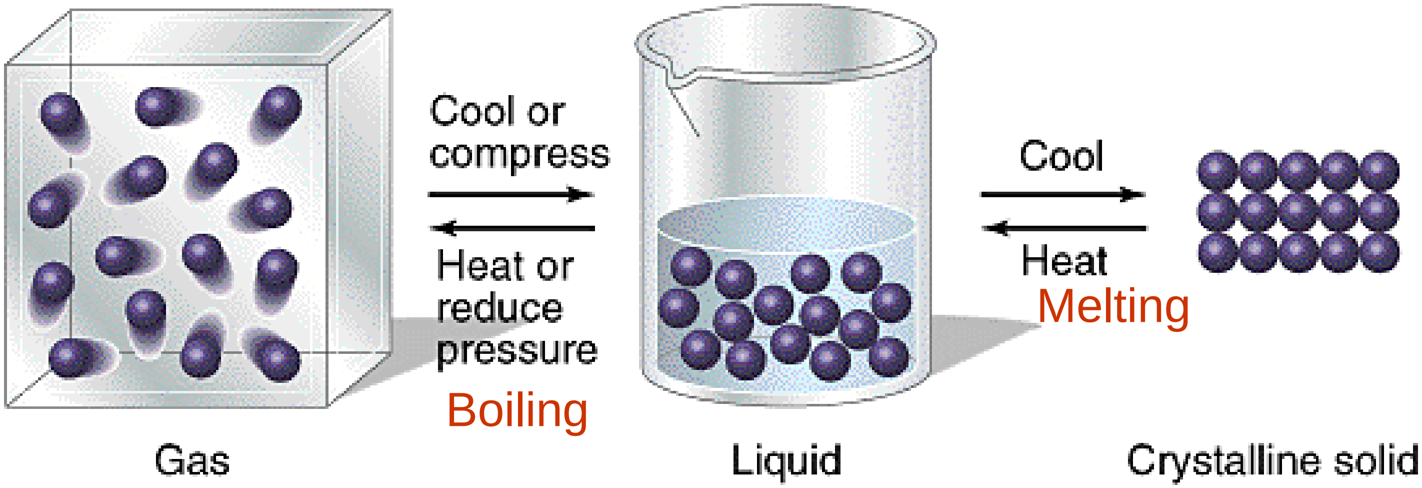
Liquid → Medium kinetic energy (move slow) → medium attractive forces



Solid → Low kinetic energy (move slower) → High attractive forces



Physical Changes



Change of states

Intermolecular forces

- London dispersion forces
- Dipole-dipole interaction
- Dipole-induced-dipole interaction
- Ion-dipole interaction
- Hydrogen bonding

< **ionic bond**
covalent bond

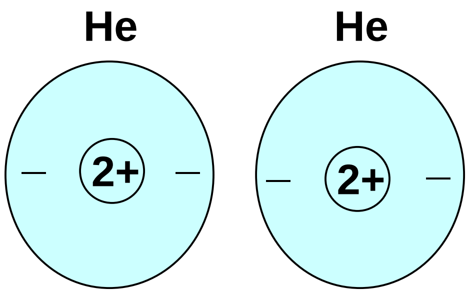
↓

Intramolecular forces

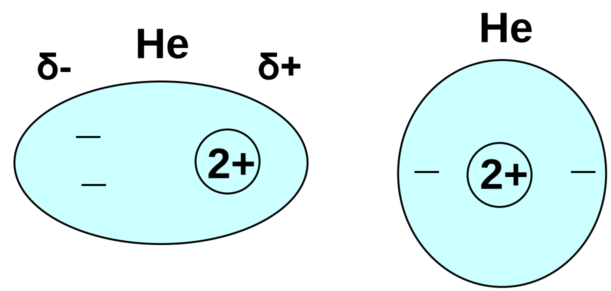
London dispersion forces

Attractive forces between all molecules

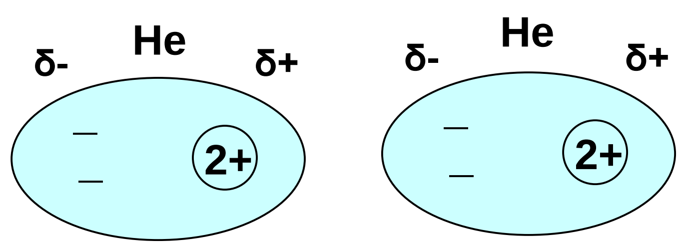
Only forces between nonpolar covalent molecules



No Polarity



Original Temporary
Dipole



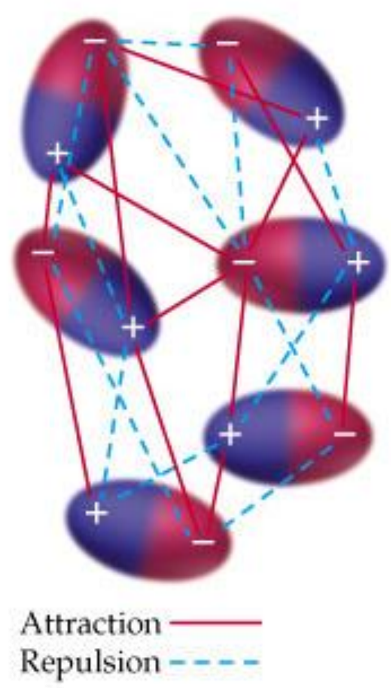
Original Temporary
Dipole

Induced Temporary
Dipole

London dispersion forces

He: T = -240°C (1 atm) → liquid

T ↓ ⇨ Kinetic energy ↓ Move slower ⇨ Attractive forces become more important ⇨ liquid



London Dispersion Forces: Size

	Melting Pt. (°C)	Boiling Pt. (°C)
He	-270 (3.5 K)	-269 (4.2 K)
Ne	-249	-246
Ar	-189	-186
Kr	-157	-153
Xe	-112	-108
F_2	-220	-188
Cl_2	-101	-34
Br_2	-7	59
I_2	114	184

As size increases (more shells)

↓

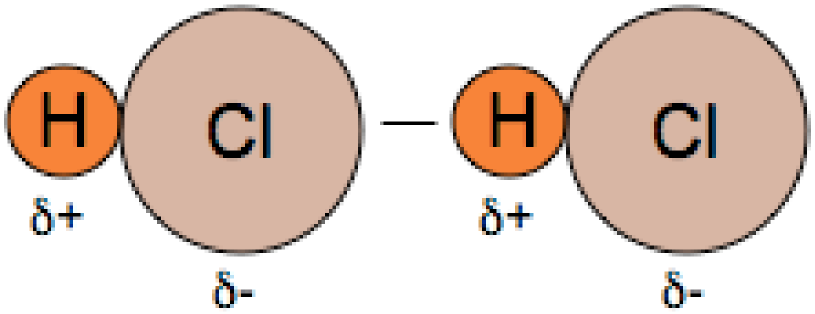
polarizability increases

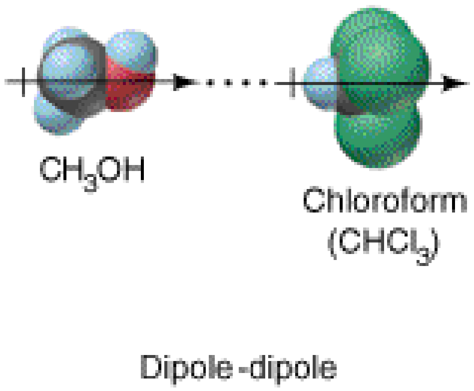
↓

melting and boiling points increase

Dipole-Dipole Interactions

Attractive force between two polar molecules.





stronger than London dispersion forces

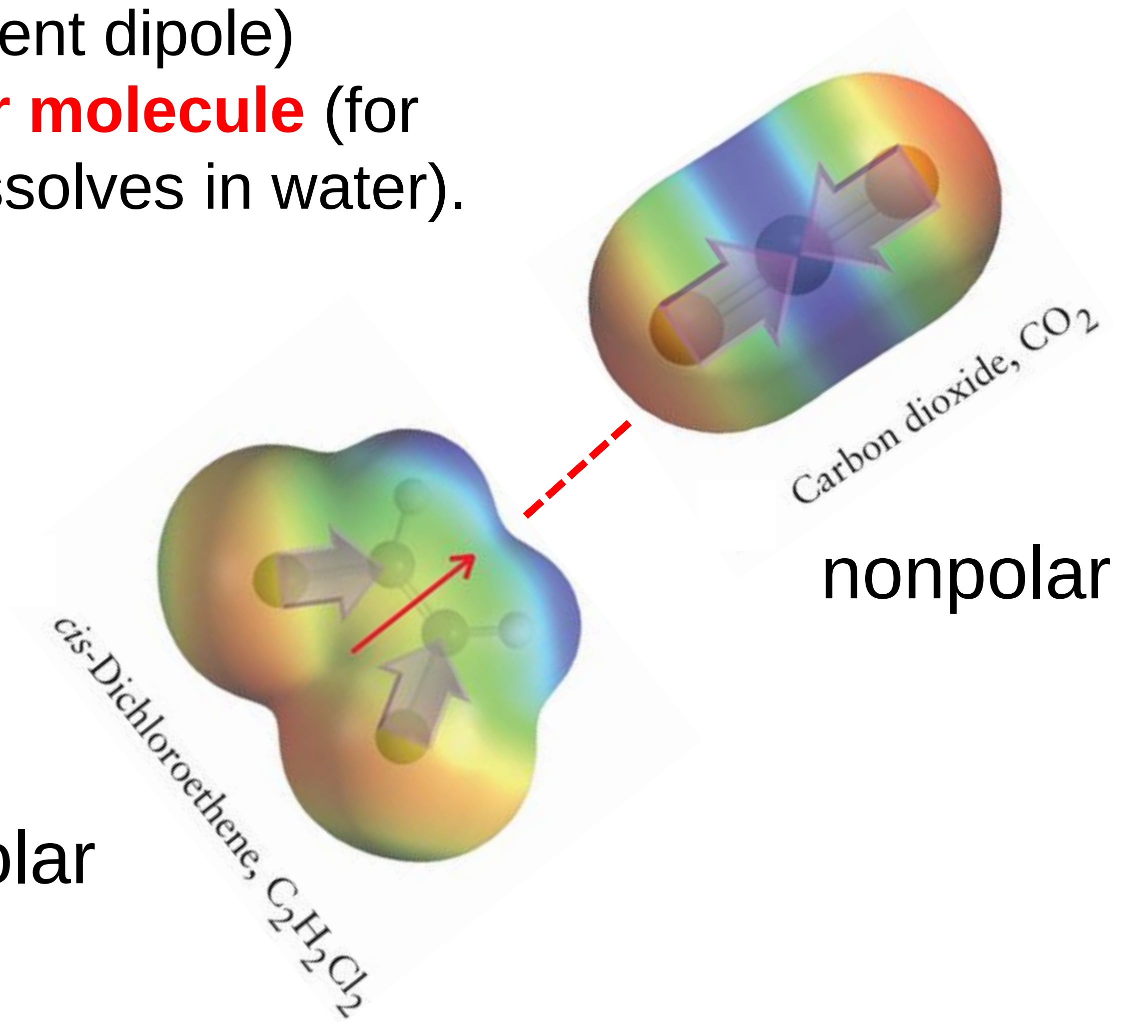
↓

↑ intermolecular forces → ↑ boiling point

Dipole-induced-dipole Interactions

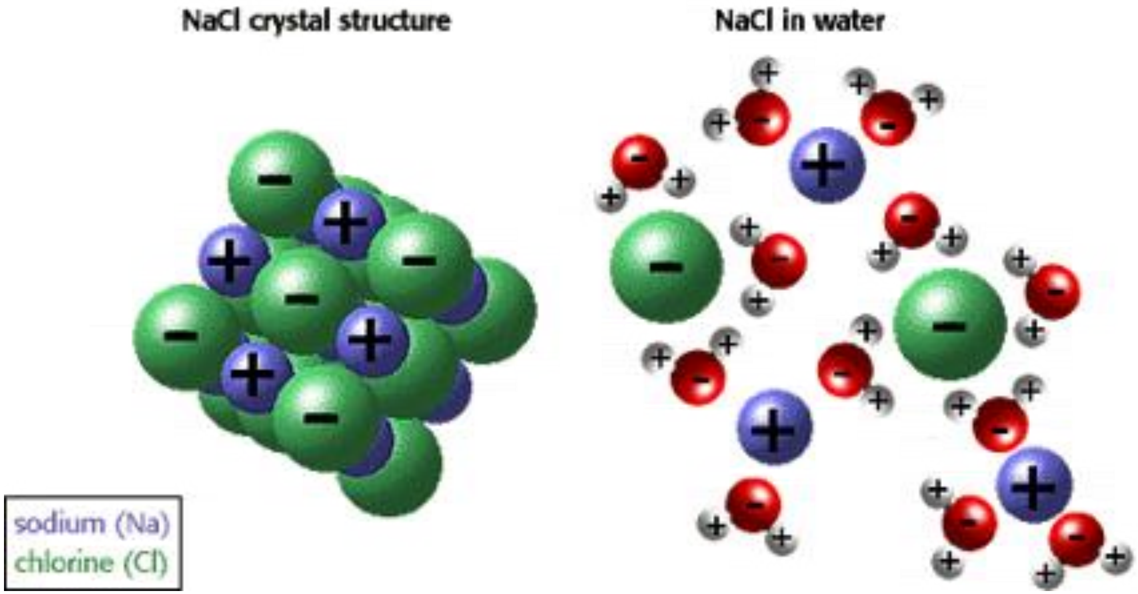
Closely related to the London interaction.

Polar molecules (permanent dipole) **interacts** with a **nonpolar molecule** (for example, when oxygen dissolves in water).



Ion-Dipole Interactions

Attractive force between ionic compounds and polar molecules.

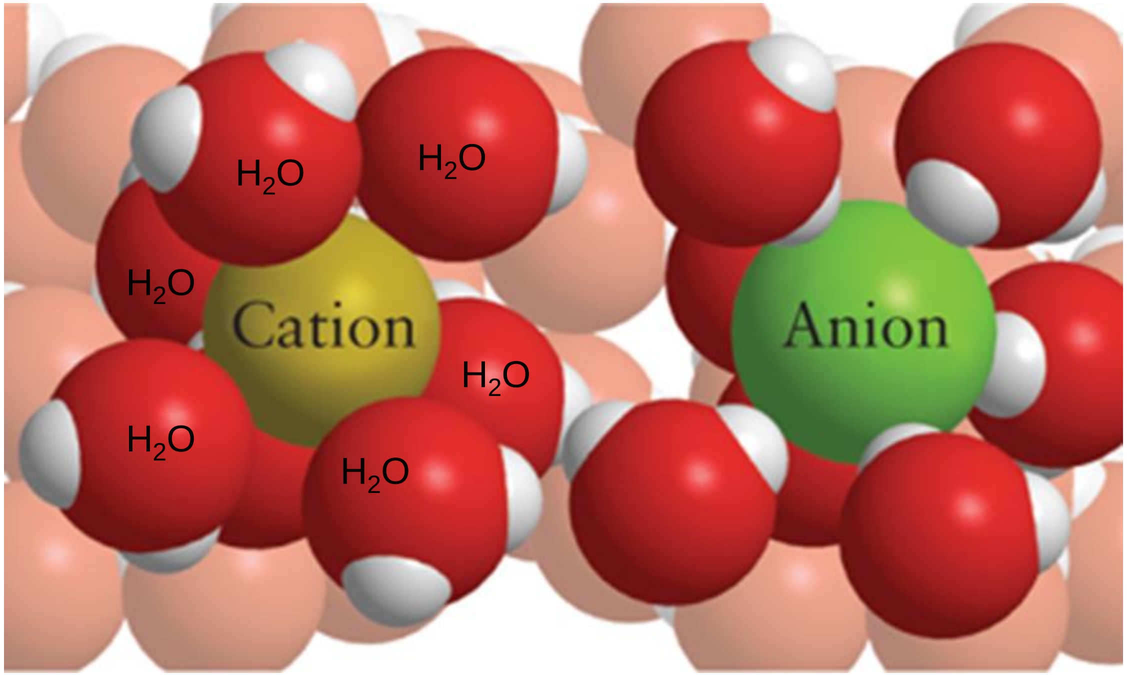


Very strong attraction.

Ion-Dipole Interactions

The attachment of water to solute particles is called **hydration**. Hydration of ions is due to the polar character of the H_2O molecule.

Note which end of the water is attracted to either a anion or cation. Remember water has **a permanent dipole**.



Ion-Dipole Interactions

Ion-Dipole: **Smaller radius**, r, means greater hydration

Smaller cations have a stronger ion-dipole interactions verses Large cations.

This allows **Small cations to extensively hydrated** while **Large cations** do not hydrate.

Li^+ and Na^+ commonly form hydrated salts,

Heavier, bigger Group 1 ions (K^+, Rb^+, and Cs^+) do not.

Ammonium salts are usually **anhydrous**, or water free, for a similar reason: an NH_4^+ ion has about the same radius (143 pm) as an Rb^+ ion (149 pm) .

Ion-Dipole: **Higher charge**, z, means greater hydration

We expect ions of the **same size** to hydrate the same.

Ba^{2+} and K^+ have the same size.

K^+ salts are *not* hydrated verses Ba^{2+} salts are hydrated.
Barium chloride is found as $BaCl_2 \cdot 2H_2O$;
Potassium chloride is anhydrous.

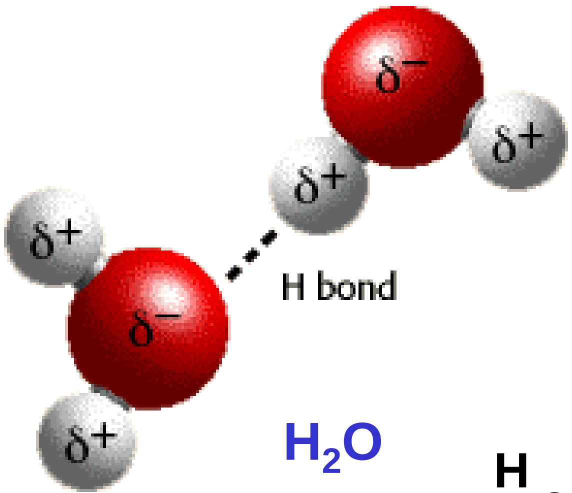
Why: **Barium has a higher ionic charge Ba^{2+}**.

Lanthanum is both smaller and highly charged (La^{3+}) and therefore, has a strong ion-dipole interactions. Its salts include $La(NO_3)_3 \cdot 6H_2O$ and $La_2(SO_4)_3 \cdot 9H_2O$.

Hydrogen Bonds

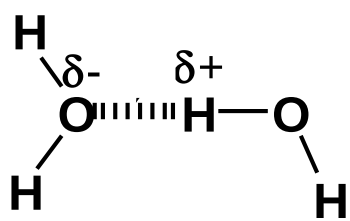
A special case of dipole-dipole

Between H bonded to O, N, or F (high electronegativity) → δ+
and a nearby O, N, or F → δ-

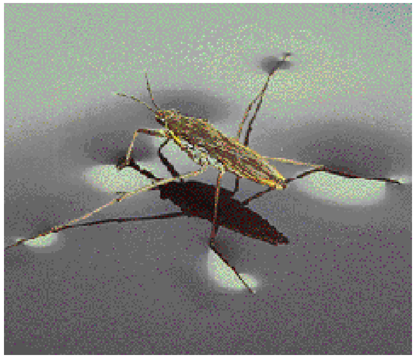


H_2O

Stronger than dipole-dipole interactions
& London dispersion forces



High boiling point

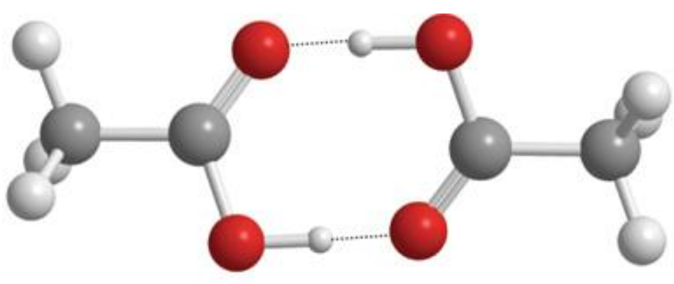


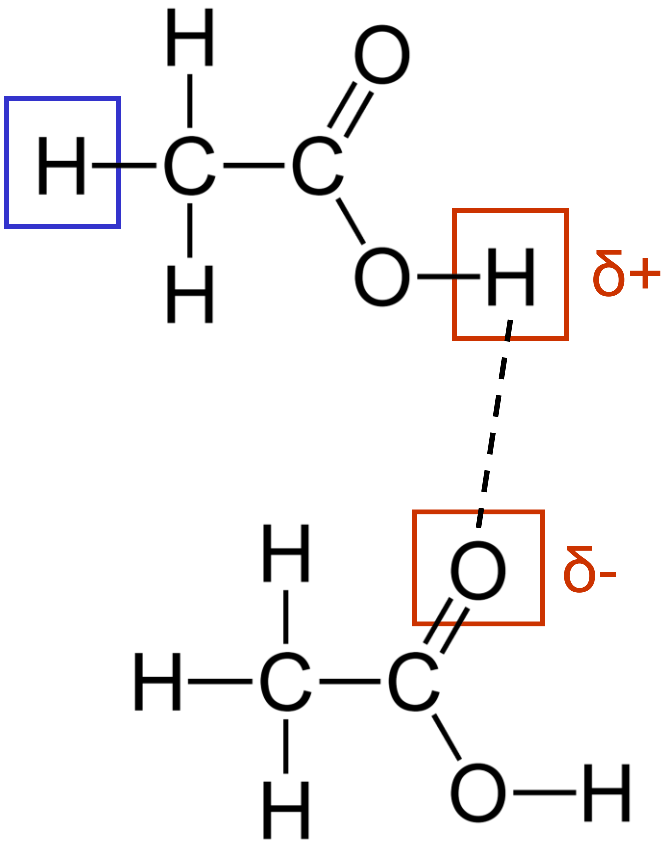
surface tension

Hydrogen bonding

CH_3COOH

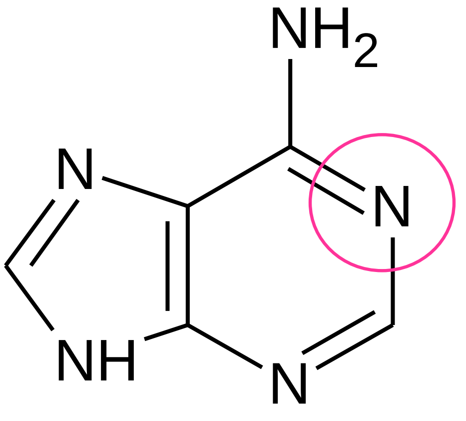
Acetic acid



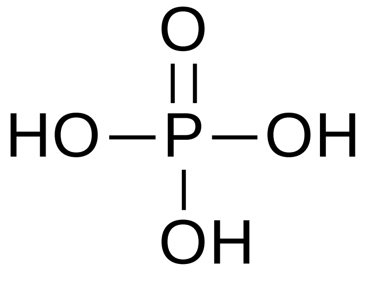


dimers: pairs of molecules, linked by two hydrogen bonds.

What possible hydrogen bonds between the “N” on adenine, circled, could occur with phosphoric acid?

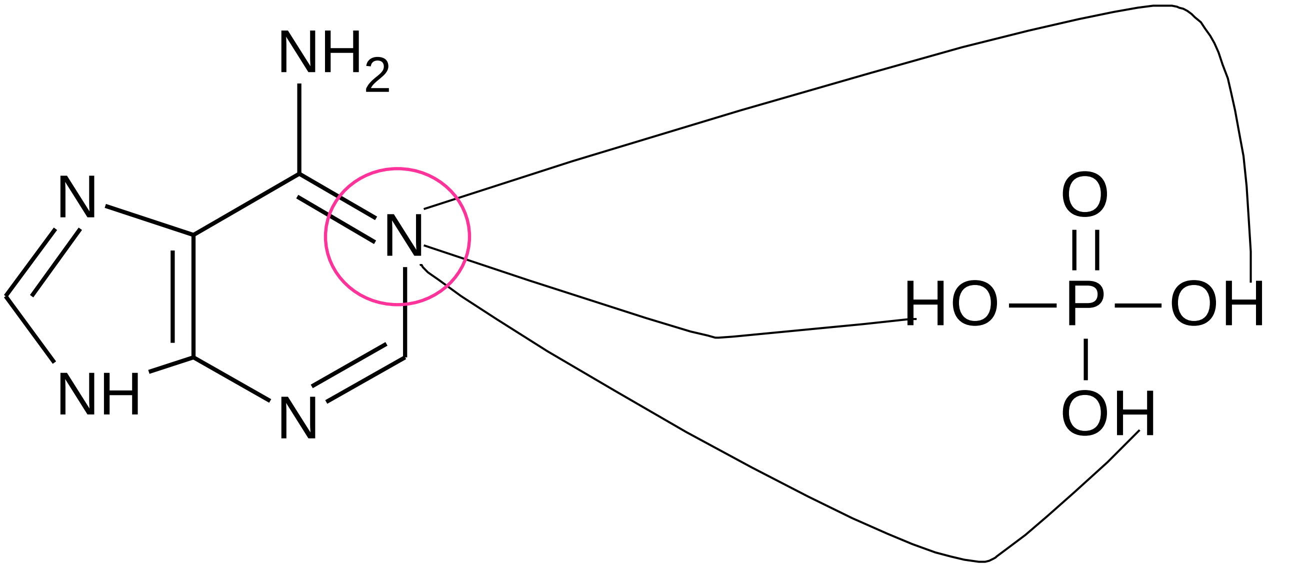


Adenine



Phosphate

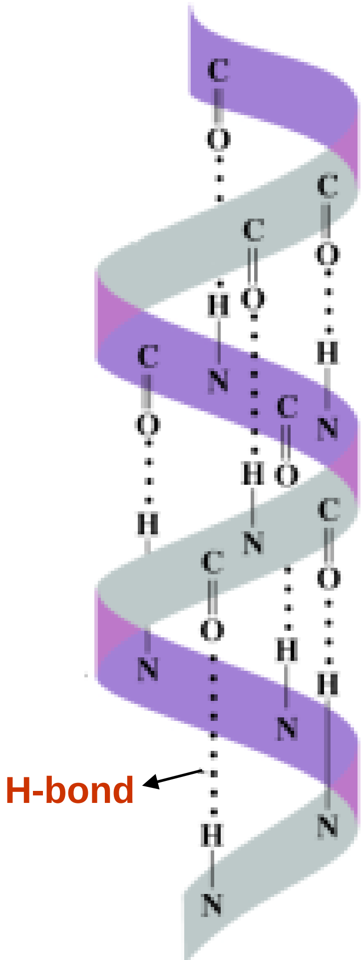
What possible hydrogen bonds between the “N” on adenine, circled, could occur with phosphoric acid?



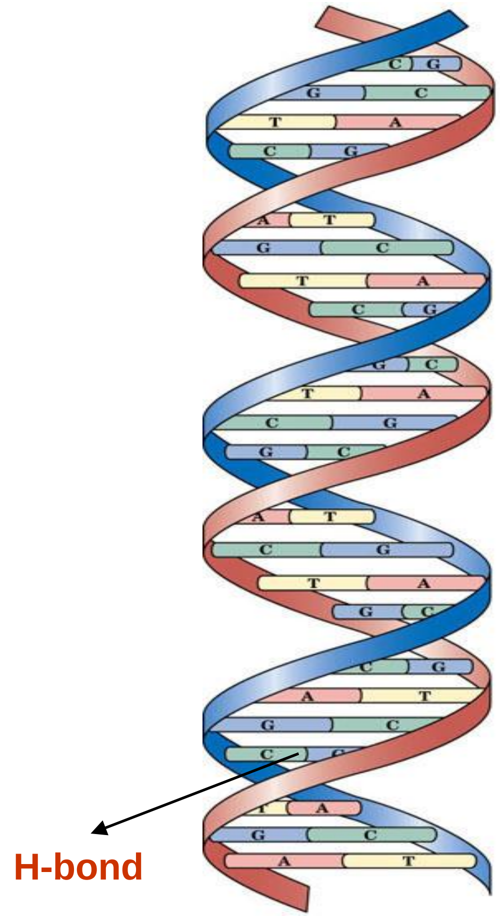
Adenine

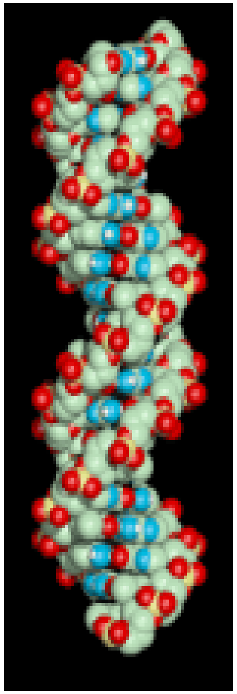
Phosphate

H-bonding in our body



Protein (α-helix)





DNA

Viscosity & Surface Tension

Viscosity is liquids resistance to flow: the higher the viscosity of the liquid, the more sluggish the flow.

Compared to water, honey has high viscosities at room temperature, so it is "viscous ."

Water is easy to pour, it has low viscosity.

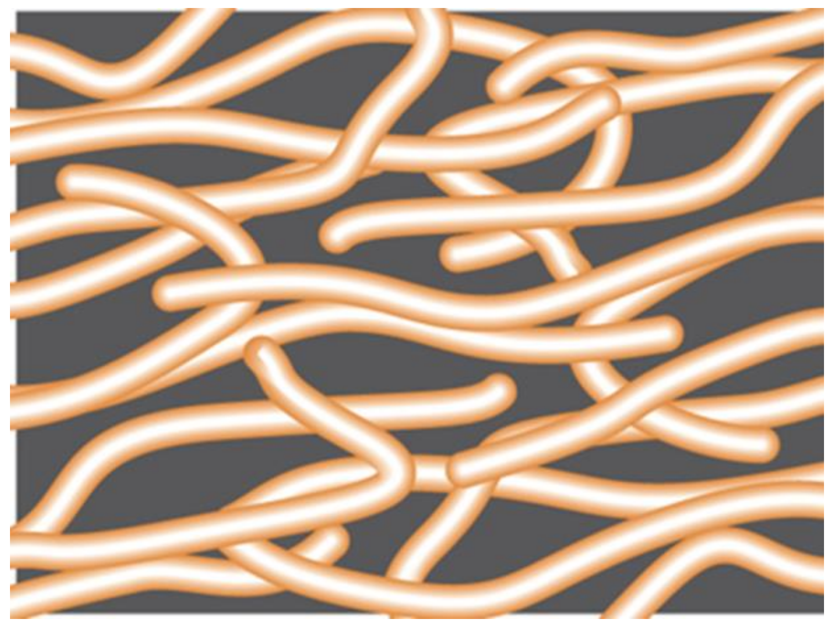
Phosphoric acid, H_3PO_4, and glycerol, $HOCH_2CH(OH)CH_2OH$, are very viscous because of the *numerous hydrogen bonds* between the molecules.

↑ Viscosity indicates ↑intermolecular strength.

Viscosity & Surface Tension

London forces dominate **Nonpolar hydrocarbons.**

Instead viscosity is due to hydrocarbon chains with 19 or more carbons, that form spaghetti-like structures.

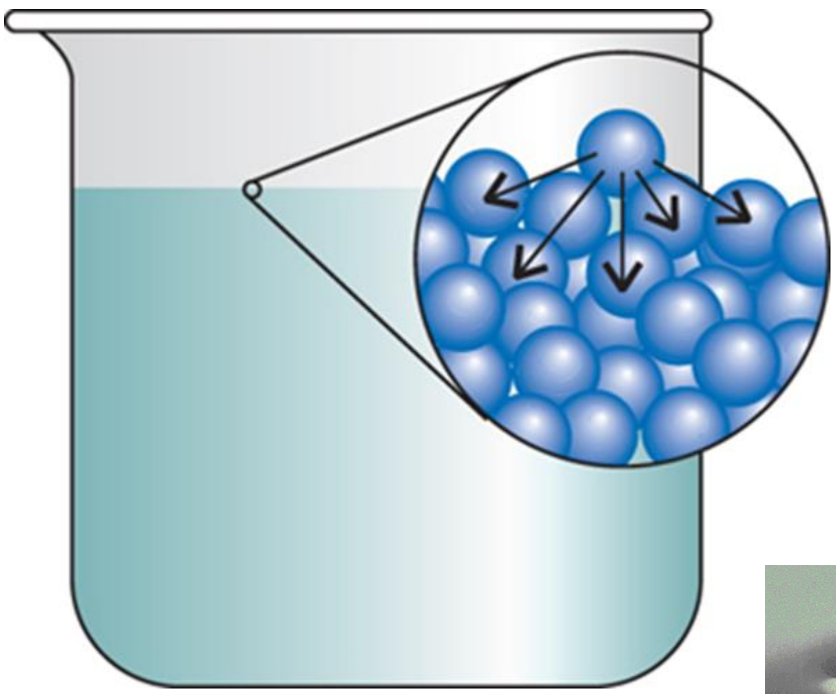


Viscosity & Surface Tension

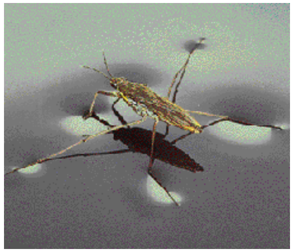
Surface tension is why the surface of a liquid is smooth.

Strong forces pull the molecules together, with a net inward pull.

Water has a surface tension about 3 times greater than most other liquids.



Liquid	Surface tension, γ ($mN \cdot m^{-1}$)
benzene	28.88
carbon tetrachloride	27.0
ethanol	22.8
hexane	18.4
mercury	472
methanol	22.6
water	72.75
	58.0 at 100°C



Viscosity & Surface Tension

Surface tension **pulls** the molecules into the most compact shape, a sphere.

Attractive forces between water are greater than between water and the waxy hydrocarbon leave surface (London) cause droplets.

Surface tension **decreases** with rising temperatures.

Viscosity & Surface Tension

Adhesion two surfaces or materials sticking together.

Water spreads out over a paper towel due to adhesion between –OH groups in paper and water.

Cohesion two surfaces or materials not attracted to each other.

Water beads-up on a waxy surface due to lack of cohesion.

Viscosity & Surface Tension

Capillary action is how liquids flow up narrow tubes.

The **upward** curved meniscus of water forms because both water and glass have comparable forces:

Adhesion ≈ Cohesion

The **downward** meniscus of mercury forms because the cohesive forces in mercury is strong than between mercury atoms and the glass:

Cohesion ≠ Adhesion

Boiling & Melting points

Factors that affect boiling point:

1. Intermolecular forces:

London dispersion forces < Dipole-Dipole interactions < Hydrogen bonds

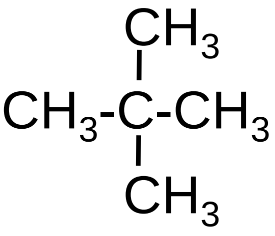
2. Number of sites for intermolecular interactions (surface area):

Larger surface (more electrons) $\rightarrow$ more sites for London $\rightarrow \uparrow$ b.p.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ > $CH_3\text{-}CH_2\text{-}CH_3$

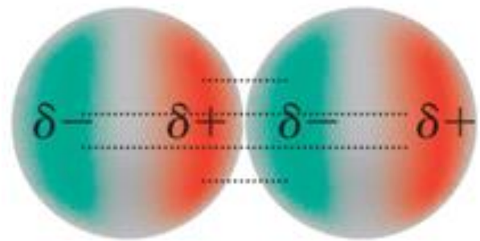
3. Molecular shape: With the same molecular weight.

linear $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ > spherical

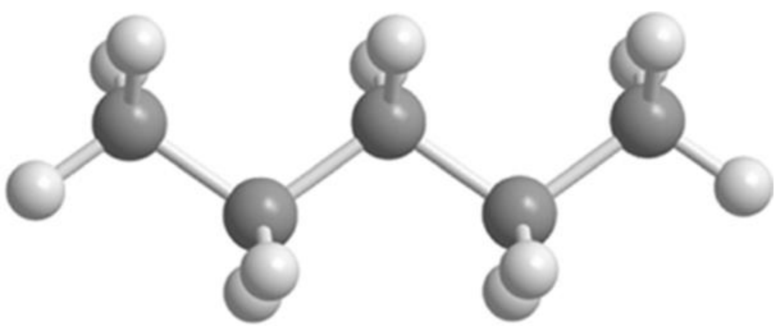


London Forces: Shape

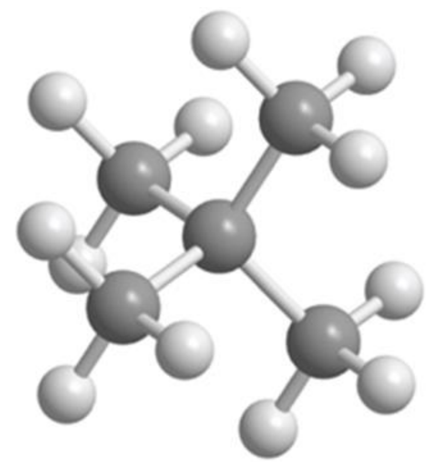
Rod-like molecules have a **greater surface area**, **<u>more</u> contact points** for molecules to join together.



Ball or spherical shaped molecules have **<u>fewer</u> contact points** for molecules to join together.



Pentane, C_5H_{12}



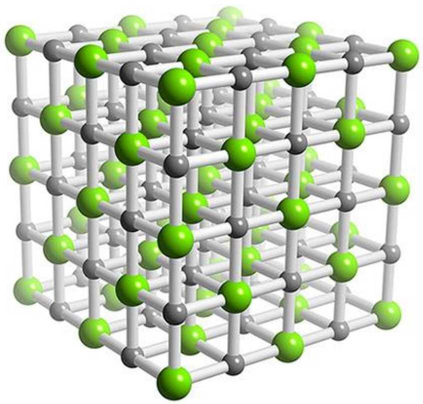
2,2-Dimethylpropane, $C(CH_3)_4$

Boiling Points: 36°C (isomers) 10°C

Solid

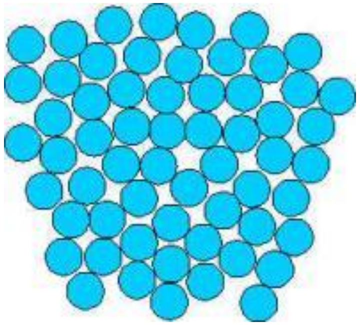
Crystalline solid (Network solids)

long-range order



Amorphous solid

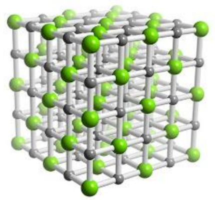
short-range order



Crystalline solids (Network solids)

Crystalline solid

Ionic solids: Consist of ions (metal-nonmetal) NaCl



Stable - High melting points

Molecular solids: Consist of molecules. Sugar, Ice

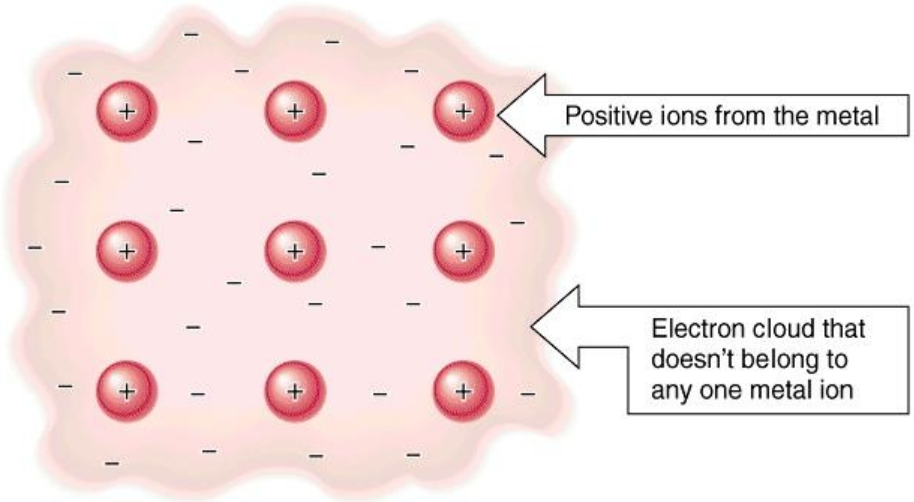
Lower melting points

Hold together by intermolecular forces:
London dispersion forces, Dipole-Dipole interaction, H-Bond

Atomic solids: Consist of atoms. Diamond, Graphite, Metals

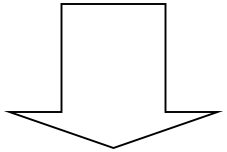
Different melting points (because of forces between atoms).

Metallic solids



Electron Sea Model

Valance electrons are shared among the atoms in a nondirectional way.



Metals conduct heat and electricity.

They are malleable and ductile.

We can make alloys.

Metallic solids

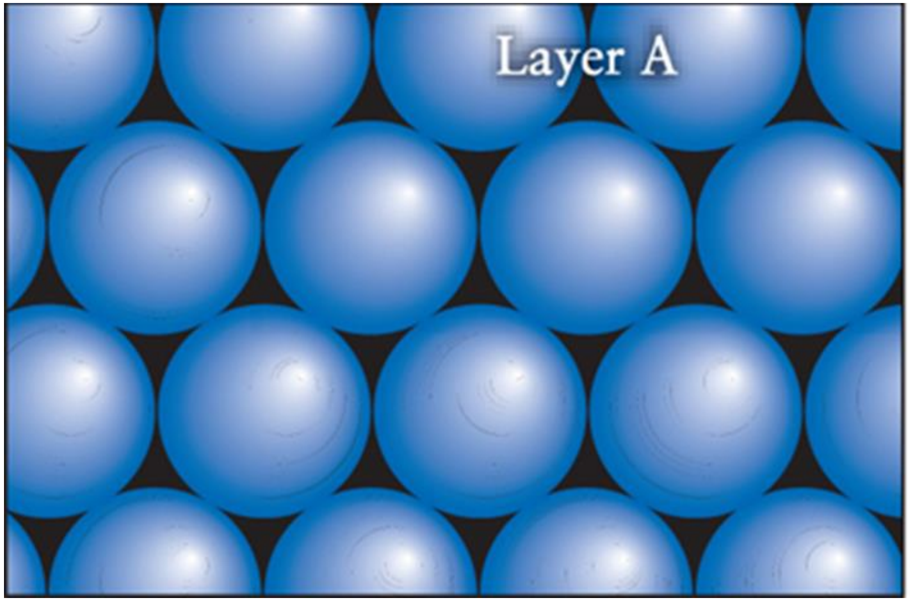
Metals are thought of as spheres adopting a **close-packed structure**, in which the hard spheres stack, wasting as little space as possible, like this fruit on display.

Metallic solids

Closed-packed stacking starts by laying layer upon layer, in a highly efficient manor, of atoms on top of each other.

The **first layer** is a hexagon with spheres (atoms) packed as tightly as possible.

This is often referred to as **Layer A**.

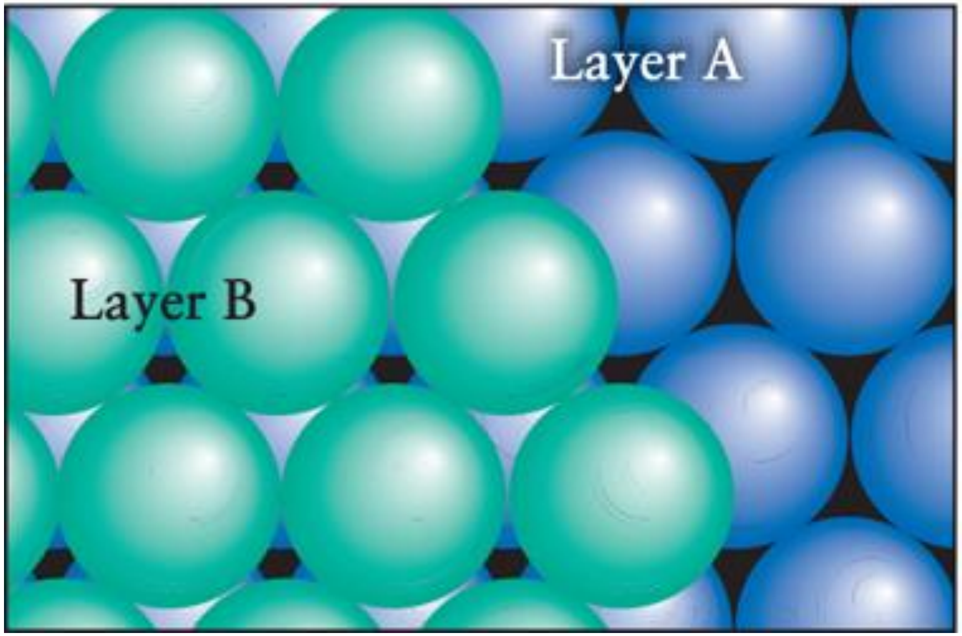


Metallic solids

Next a **second layer** is added on top of the Layer A.

This is called **Layer B**.

Notice how the spheres rest in the small cavity created between each sphere in Layer A.



Metallic solids

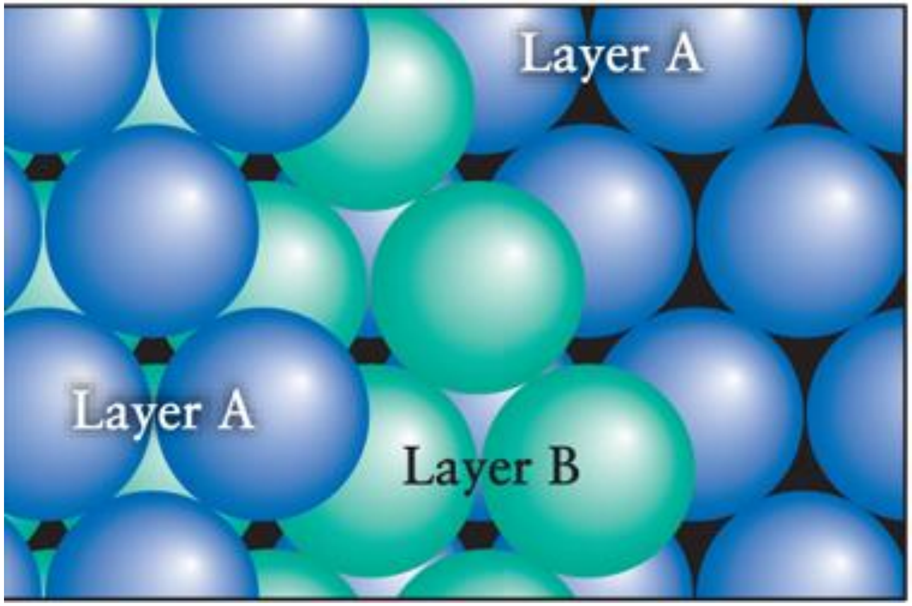
For the **third layer**, there are two options:

Option 1:

Shown is a third layer identical to Layer A, referred to as a ABABAB pattern. Each atoms is over the atom in Layer A.

A more common name for this is **Hexagonal Closed-Pack** (hcp).

Notice the hole visible all the way to the first layer.



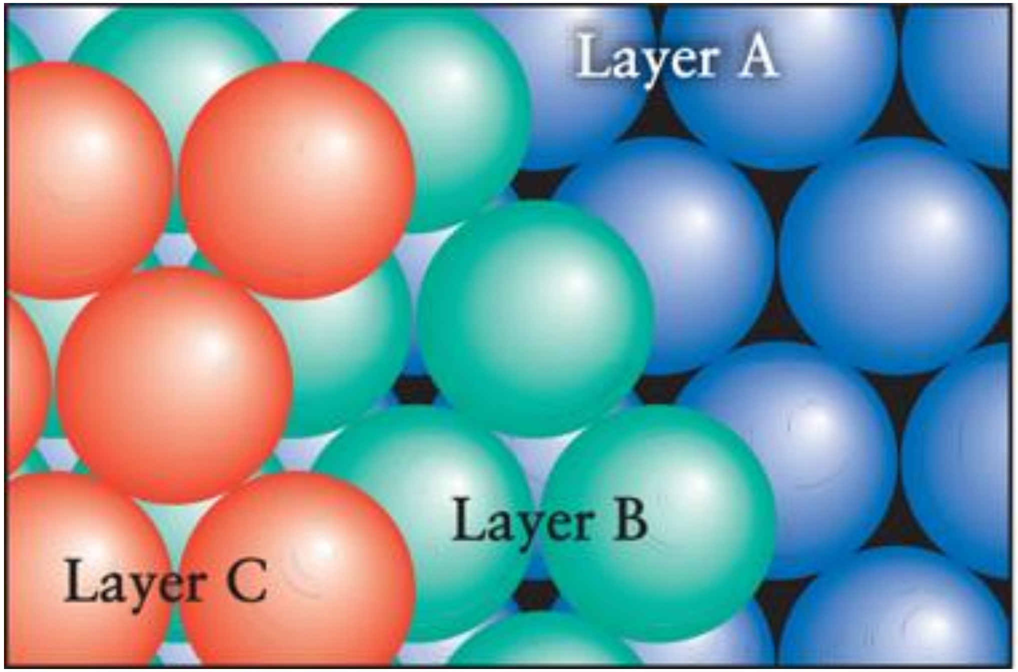
Metallic solids

Option 2:

The second options differs slightly by placing a layer offset to Layer A, and is called **Layer C** or an ABCABC pattern.

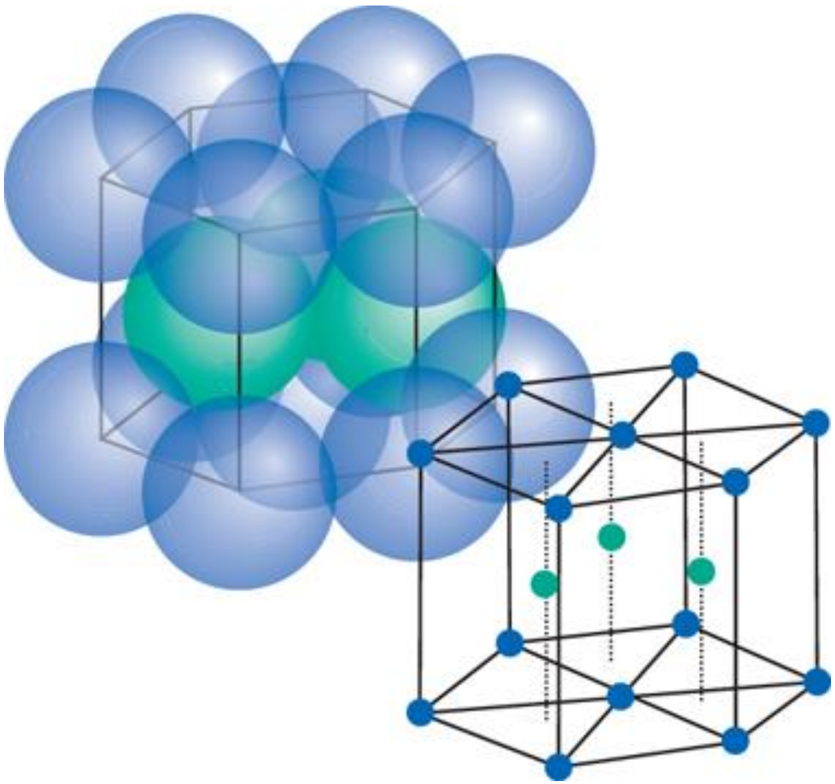
A more common name is **Cubic Closed-Pack** (ccp).

Notice the hole disappears.

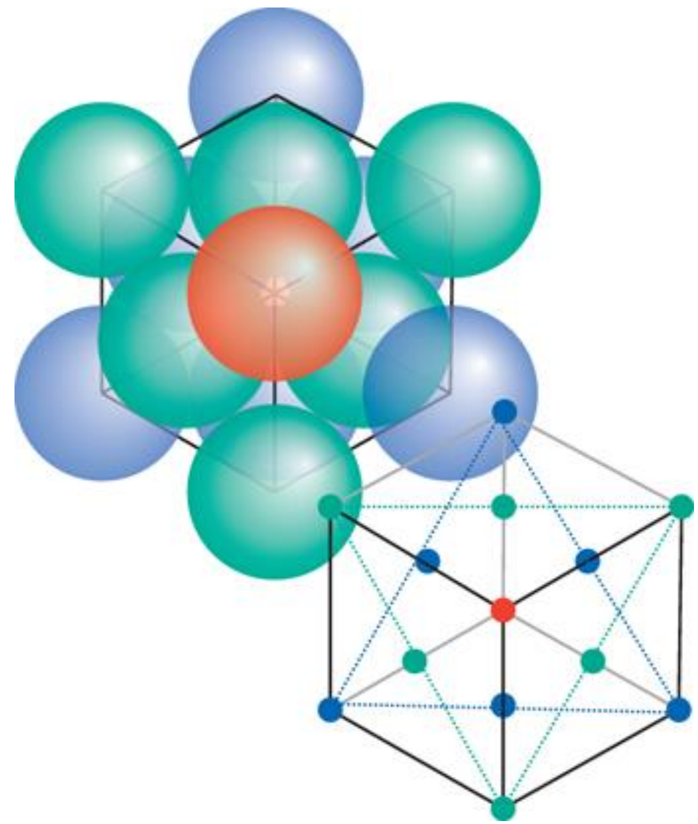


Metallic solids

hcp



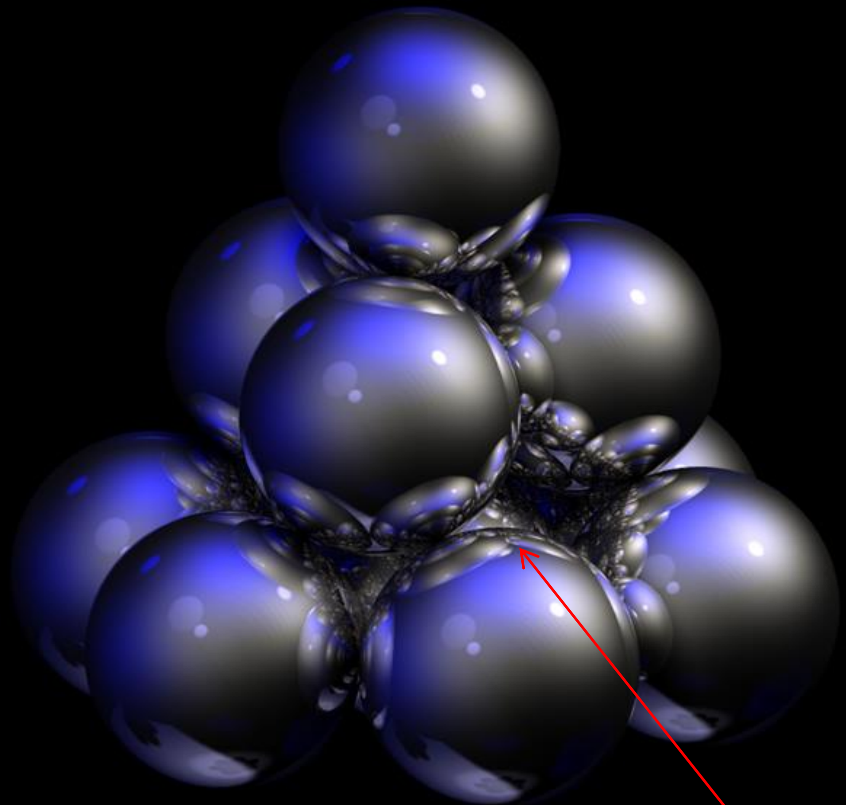
ccp

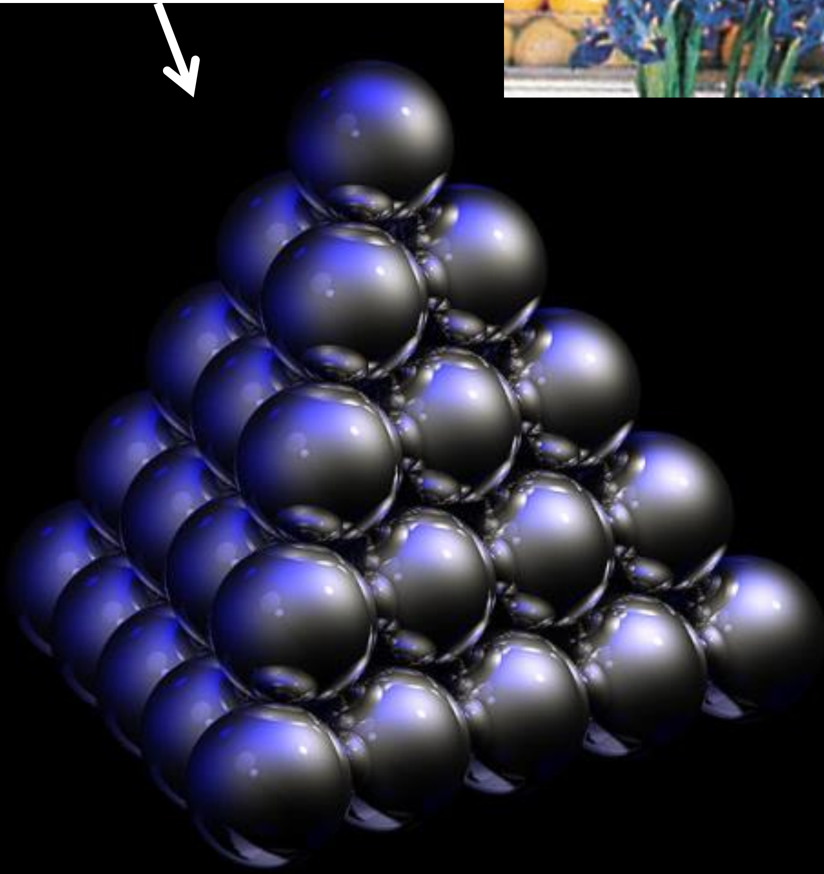


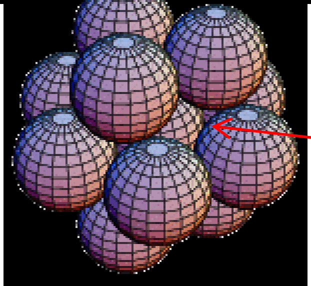
In each structure each atom has a coordination number of 12, which is the **maximum number** of atoms another atom can be bound to a any one time.

hcp

ccp (sometimes called face centered cubic, fcc).







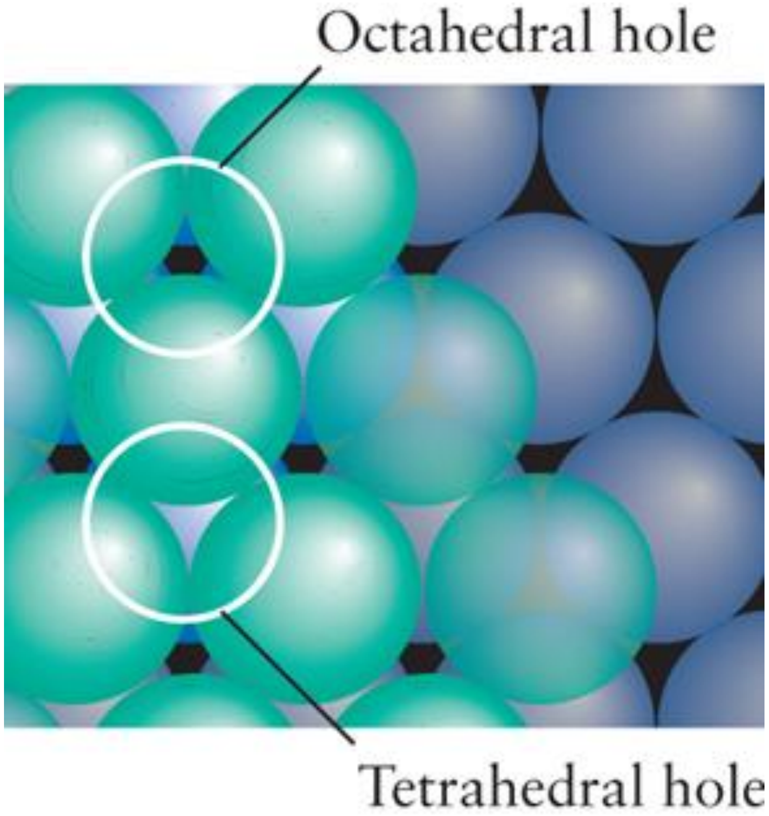
You can see another sphere

Alloys

Holes in a close-packed structure can be filled with smaller atoms to form alloys.

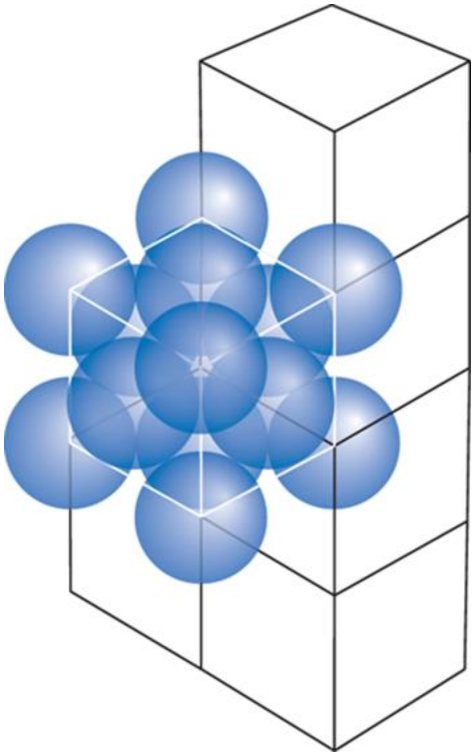
If a dip **between three atoms** is directly covered by another atom, we obtain a tetrahedral hole, or hcp.

When a dip in a layer coincides with a dip in the **next layer**, we obtain an octahedral hole, or fcp.



Unit Cells

The smallest region of the crystal lattice that repeats itself, this is referred to as the **unit cell**.

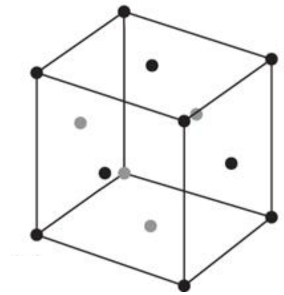


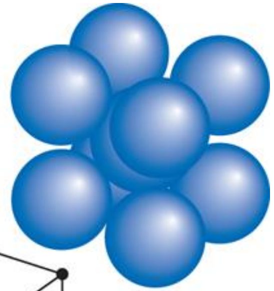
From the cubic arrangement exist three types of cubic structures:

1. Primitive cubic
2. Body centered cubic
3. Cubic closed-packed

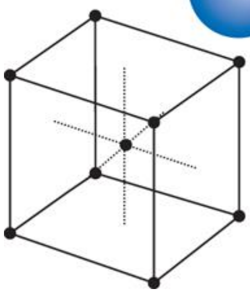
Unit Cells

A cubic close-packed unit cell has an atom at the center of each face of the unit cell; for this reason, it is also called a face-centered cubic structure (ccp either fcp or hcp).

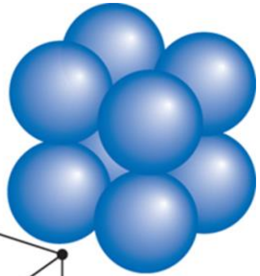


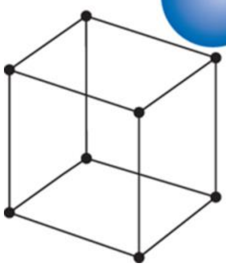


A body-centered cubic structure (bcc), single atom lies at the center of a cube formed by eight other atoms. This structure is not close packed.



A primitive cubic structure has an atom at each corner of a cube. The atoms touch along the edges. This structure is known for only one element, polonium.





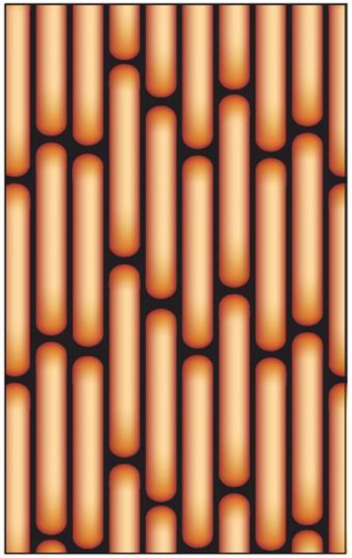
Liquid Crystals

Liquid crystals are neither a solid nor a liquid, but intermediate called a **mesophase**. Here molecules have fluidity of a liquid and some order of a molecular solid.

They are **responsive** to changes in temperature and electric fields.

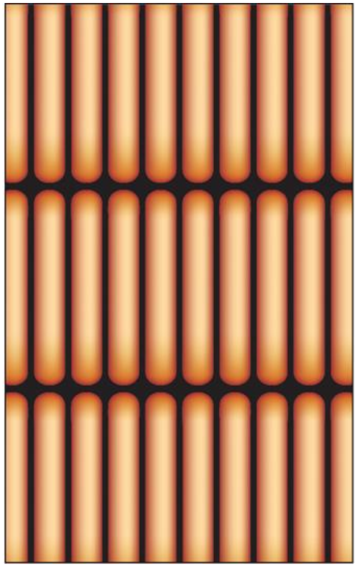
Liquid Crystals

Anisotropic materials **depend on the direction** of measurement. **Isotropic** materials do not depend on orientation, water's viscosity is the same in all directions.



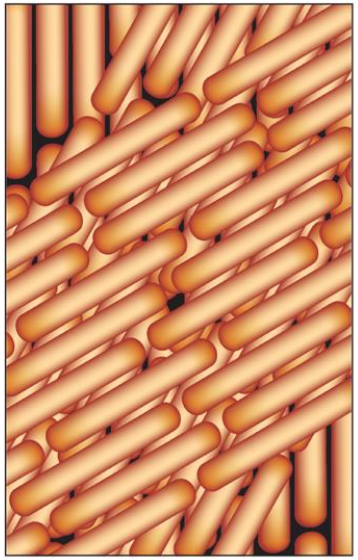
Nematic phase

parallel molecules, and staggered along their long axes.



Smectic phase

molecules are parallel and they line up next to form sheets.



Cholesteric phase

sheets of parallel molecules are rotated relative to their neighbors and form a helical structure.

Liquid Crystals

Thermotropic liquid crystals are made by melting the solid phase, usually have a short temperature range between the solid and the liquid states.

Thermotropic liquid crystals become isotropic liquids when heated above a characteristic temperature.

These are used in applications such as watches, computer screens, and thermometers.