

Chemical Principles

7. Liquids and Solids

Outline

Intermolecular forces

- Types
- Consequences

Liquid Properties

- Structures
- Properties

Solids Structures

- Types
- Unit Cells
- Properties

Intermolecular Forces

The Origin of Intermolecular interaction

Columbic interactions

$$E_p = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

E_p = potential energy

$q_1 q_2$ = charge of each atom

r = distance between $q_1 q_2$

The **strength** (E_p) **is determined** by both q and r.

The Types of Intermolecular Interaction

Type of interaction	Typical energy (kJ·mol ⁻¹)	distance dependence
Ion-Ion	250	1/r
ion-dipole	15	1/r ²
*dipole-dipole (stationary- solids/liquids)	2	1/r ³
dipole-dipole (rotating-gases)	0.3	1/r ⁶
dipole-induced-dipole	2	1/r ⁶
London or induced (or dispersion)	2	1/r ⁶

*A special case, **hydrogen bonding**, is a form of dipole-dipole, Typical energy 20 kJ·mol⁻¹.

The Origin of Intermolecular Forces: **radius**

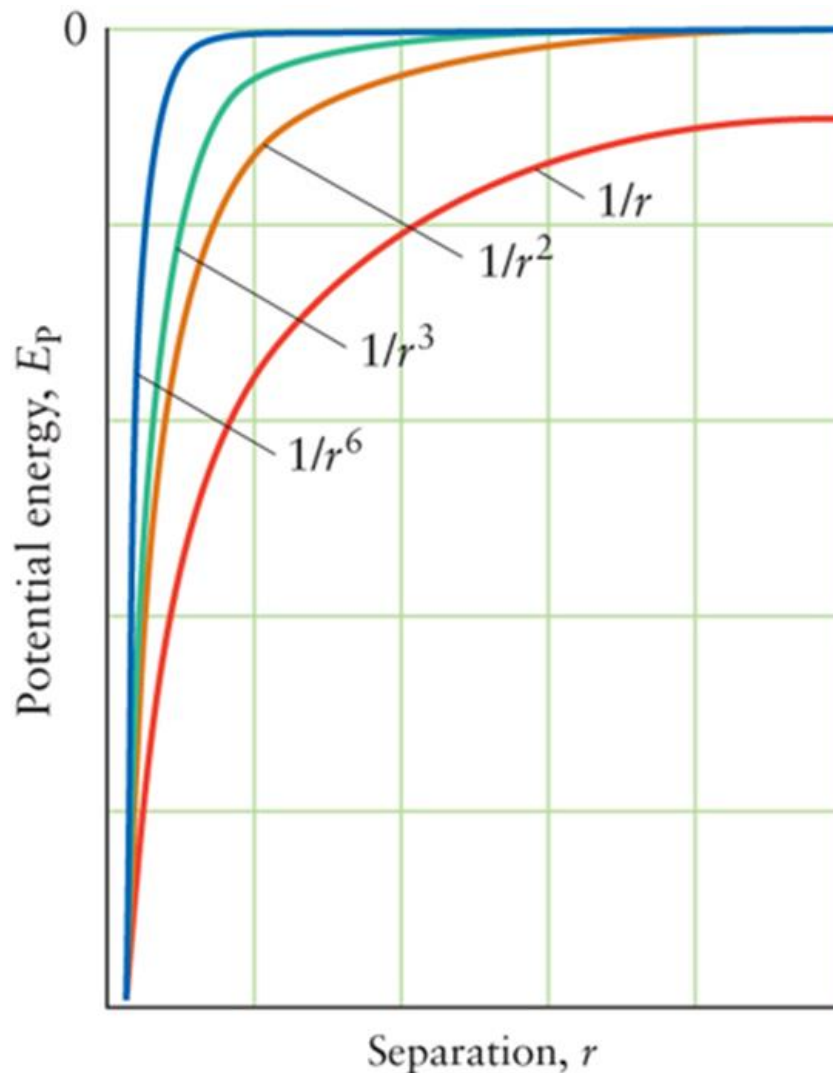
Ion-Ion	$1/r$
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ion-dipole	$1/r^2$
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*dipole-dipole (stationary)	$1/r^3$
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dipole-dipole (rotating)	$1/r^6$
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Dipole –induced dipole	
London	

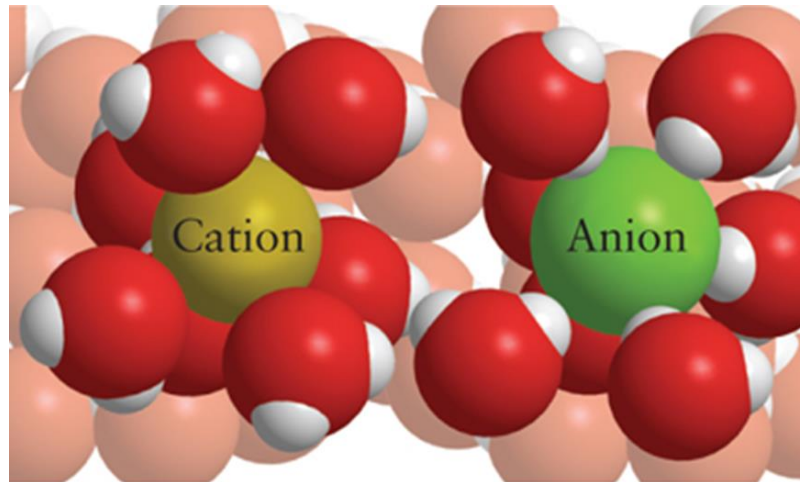


The significance of **Ion-dipole**

One example of ion-dipole is hydration, which is the attachment of water to solute particles is called **hydration**.

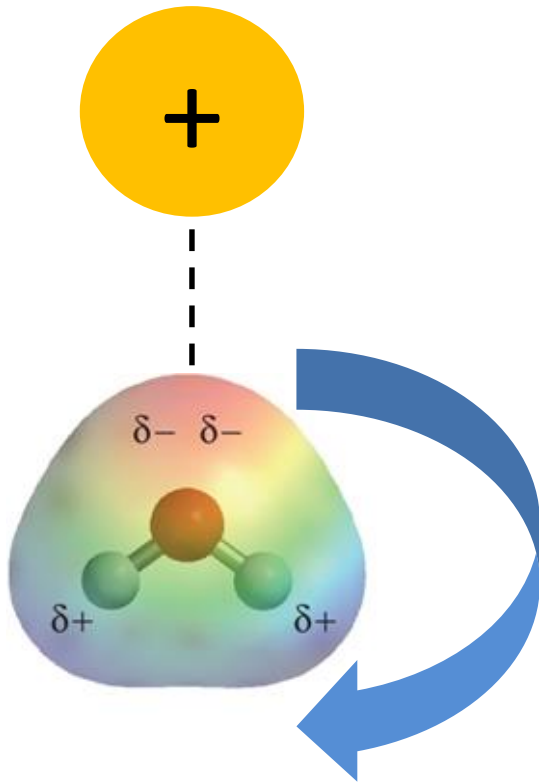
Water has **a permanent dipole**. Note the configuration weakens the interactions.

It is the origin of relative permittivity $\epsilon_p = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r r}$, for water, $\epsilon_r \approx 80$



The Ion-dipole interaction

Z is the charge number of the ion and μ is the electric dipole moment on the polar atom (here H_2O).



At static configuration $E_p \propto \frac{|z|\mu}{r^2}$

Considering Boltzmann weighted rotation $E_p \propto \frac{|z|\mu}{r^4}$

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.

$$E_p \propto \frac{|z|\mu}{r^2}$$

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.

Compare, 136 pm for Ba^{2+} and 138 pm for K^{+}

K^{+} salts are *not* hydrated versus Ba^{2+} salts which hydrate.

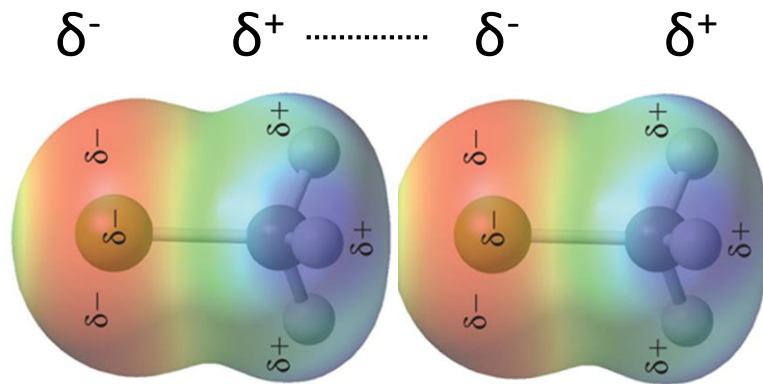
Barium chloride is found as $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$;

Potassium chloride is anhydrous, KCl only

Lanthanum is both smaller (122 pm) and highly charged (La^{3+}) and therefore, has a strong ion-dipole interactions.

Its salts include $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

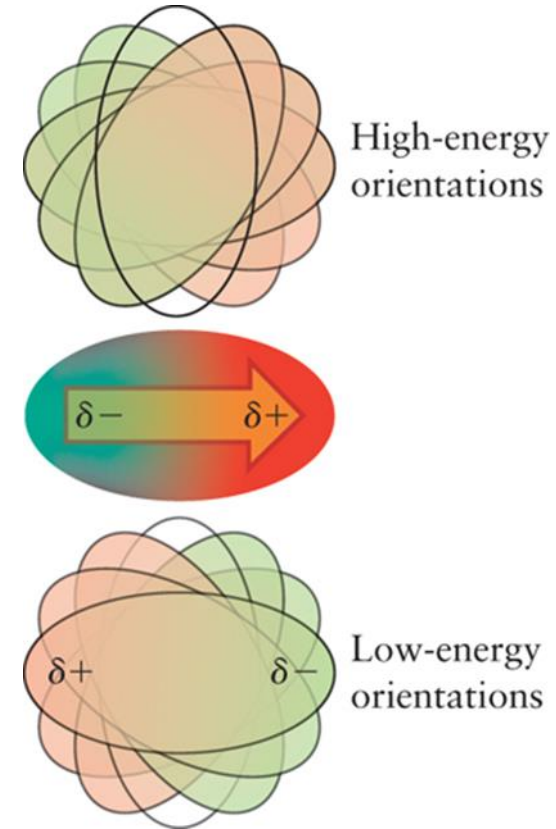
Dipole-Dipole Interaction



Stationary: $E_p \propto \frac{\mu_1 \mu_2}{r^3}$

The most plausible configuration

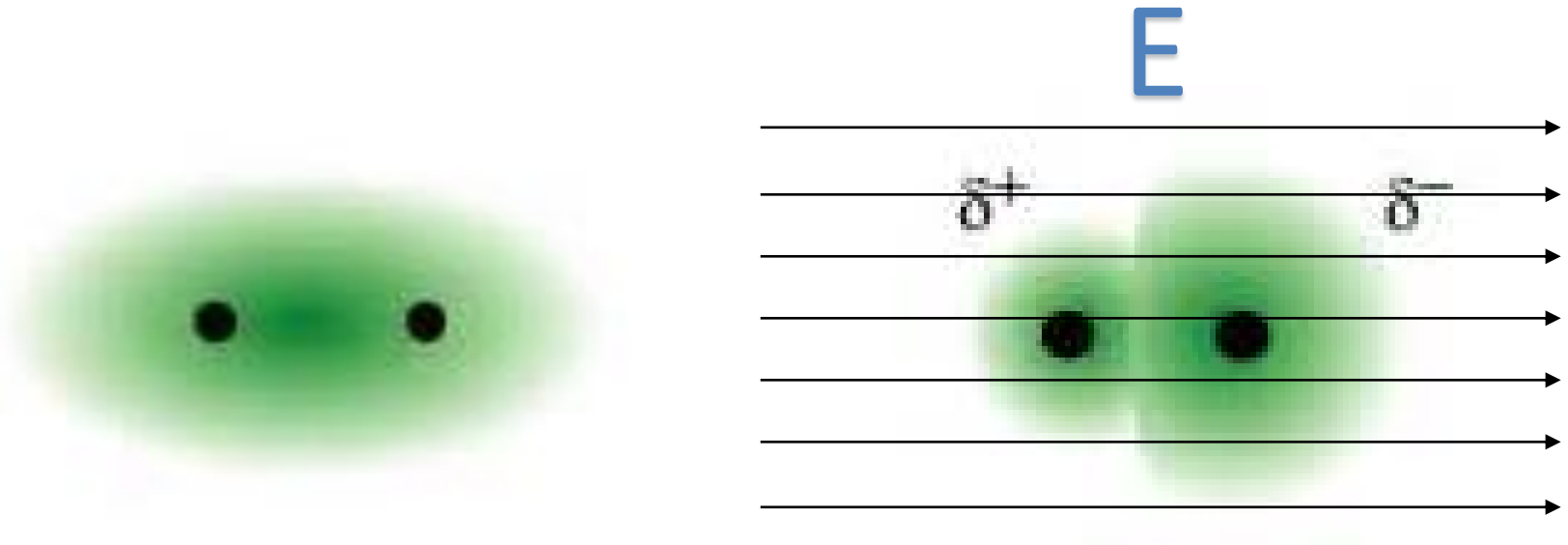
Rotating: Molecules are distributed in various energy configurations.



Considering Boltzmann weighted configurations, $E_p \propto \frac{\mu_1 \mu_2}{r^6}$

Polarizability

Under external field, the electron cloud distort, causing an induced dipole moment

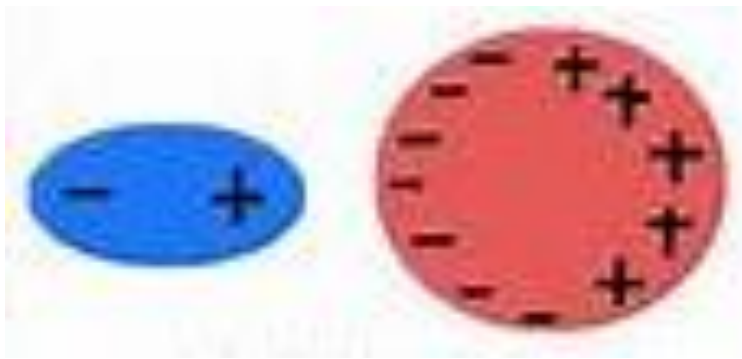


The induced dipole moment is proportional to the strength of external field, the coefficient is called polarizability

$$\mu^* = \alpha E$$

Dipole – induced dipole interaction

A permanent dipole causes an induced dipole, the interaction between the two molecules



$$E_p \propto \frac{\mu_1^2 \alpha_2}{r^6}$$

It does not have a rotation effect.

Induced dipole – Induced dipole, the London dispersion energy

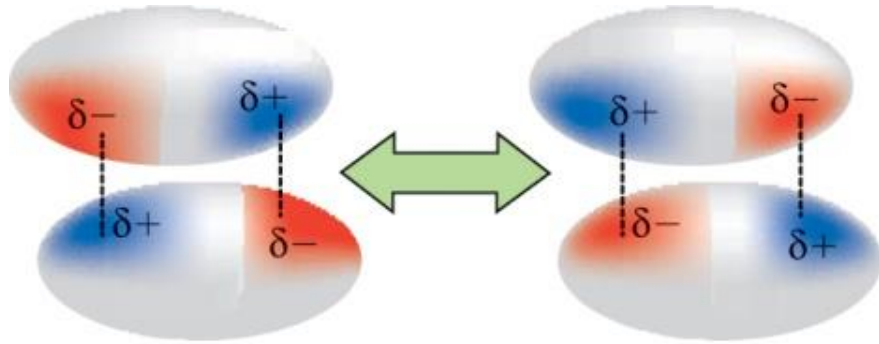


FIGURE 6.6 The rapid fluctuations in the electron distribution in two neighboring molecules result in two instantaneous electric dipole moments that attract each other. The fluctuations flicker into different positions, but each new arrangement in one molecule induces an arrangement in the other that results in mutual attraction.

In a moment, electrons *pile-up*, in one region of the molecule.

A temporary dipole is created and a weak intermolecular interaction takes place.

London interaction:

$$E_p \propto \frac{\alpha_1 \alpha_2}{r^6}$$

London dispersion and molecular size

- The phase transition point is an indication of strength of inter-molecular interactions.
- London interaction depends on polarizability: $E_p \propto \frac{\alpha_1 \alpha_2}{r^6}$
- The larger molecule, the higher polarizability

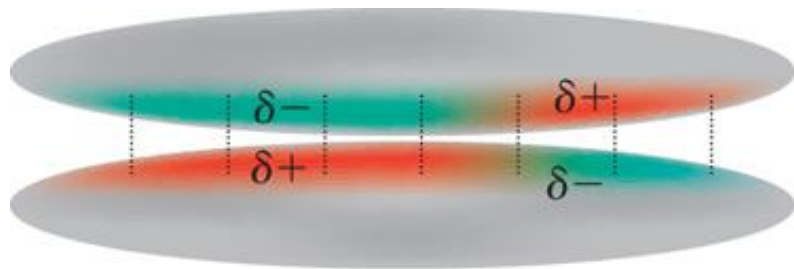
TABLE 6.2 Melting and Boiling Points of Substances*

Substance	Melting point (°C)	Boiling point (°C)	Substance	Melting point (°C)	Boiling point (°C)
Noble gases			Inorganic substances with small molecules		
He	-270 (3.5 K) [†]	-269 (4.2 K)	H ₂	-259	-253
Ne	-249	-246	N ₂	-210	-196
Ar	-189	-186	O ₂	-218	-183
Kr	-157	-153	H ₂ O	0	100
Xe	-112	-108	H ₂ S	-86	-60
Halogens			NH ₃	-78	-33
F ₂	-220	-188	CO ₂	—	-78s
Cl ₂	-101	-34	SO ₂	-76	-10
Br ₂	-7	59	Organic compounds		
I ₂	114	184	CH ₄	-182	-162
Hydrogen halides			CF ₄	-150	-129
HF	-93	20	CCl ₄	-23	77
HCl	-114	-85	C ₆ H ₆	6	80
HBr	-89	-67	CH ₃ OH	-94	65
HI	-51	-35	glucose	142	d
			sucrose	184d	—

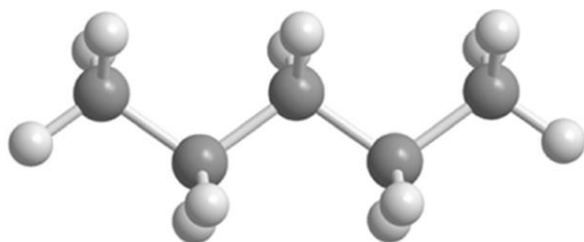
*Abbreviations: s, solid sublimes; d, solid decomposes.

[†]Under pressure.

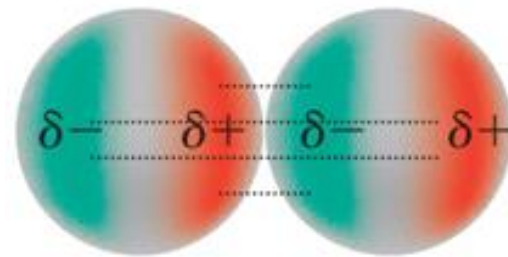
London dispersion energy and molecular shape



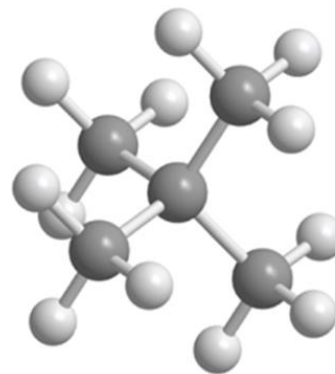
Rod-like molecules have a **greater interaction region**



8 Pentane, C_5H_{12}



Spherical shaped molecules have smaller **contact points**.



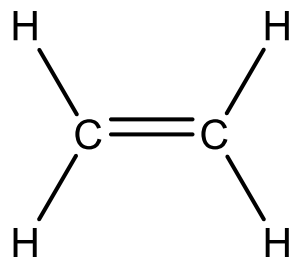
9 2,2-Dimethylpropane, $C(CH_3)_4$

Boiling Points: 36°C (isomers)

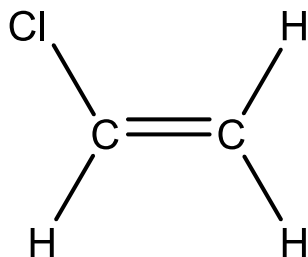
10°C

Which has the higher boiling point or strongest intermolecular forces?

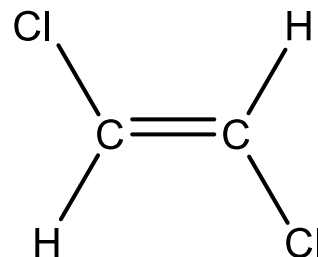
- A. 1
- B. 2
- C. 3
- D. 4



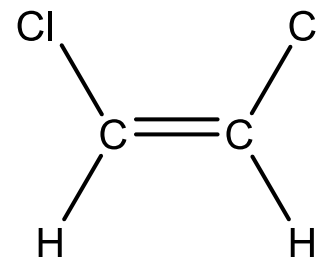
1



2



3



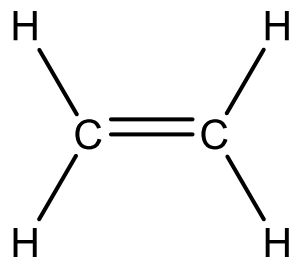
4

Which has the higher boiling point or strongest intermolecular forces?

- A. 1
- B. 2
- C. 3
- D. 4

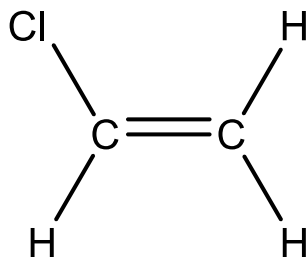
#3 is nonpolar because the two opposing Cl dipoles cancel.

#4 is more polarizable than #2.



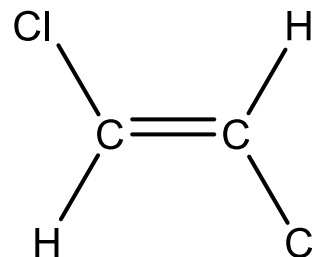
1

B.P. -104°C



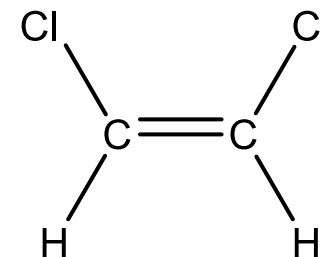
2

-13°C



3

48°C



4

60°C

London dispersion energy is important

Explain the trend in the boiling points of the hydrogen halides: HCl, -85°C ; HBr, -67°C ; HI, -35°C .

All have a permanent dipole, considering

	H-Cl	H-Br	H-I
Electronegativity	2.2-3.2	2.2-3.0	2.2-2.7
Dipole Moment	1.08	0.82	0.44

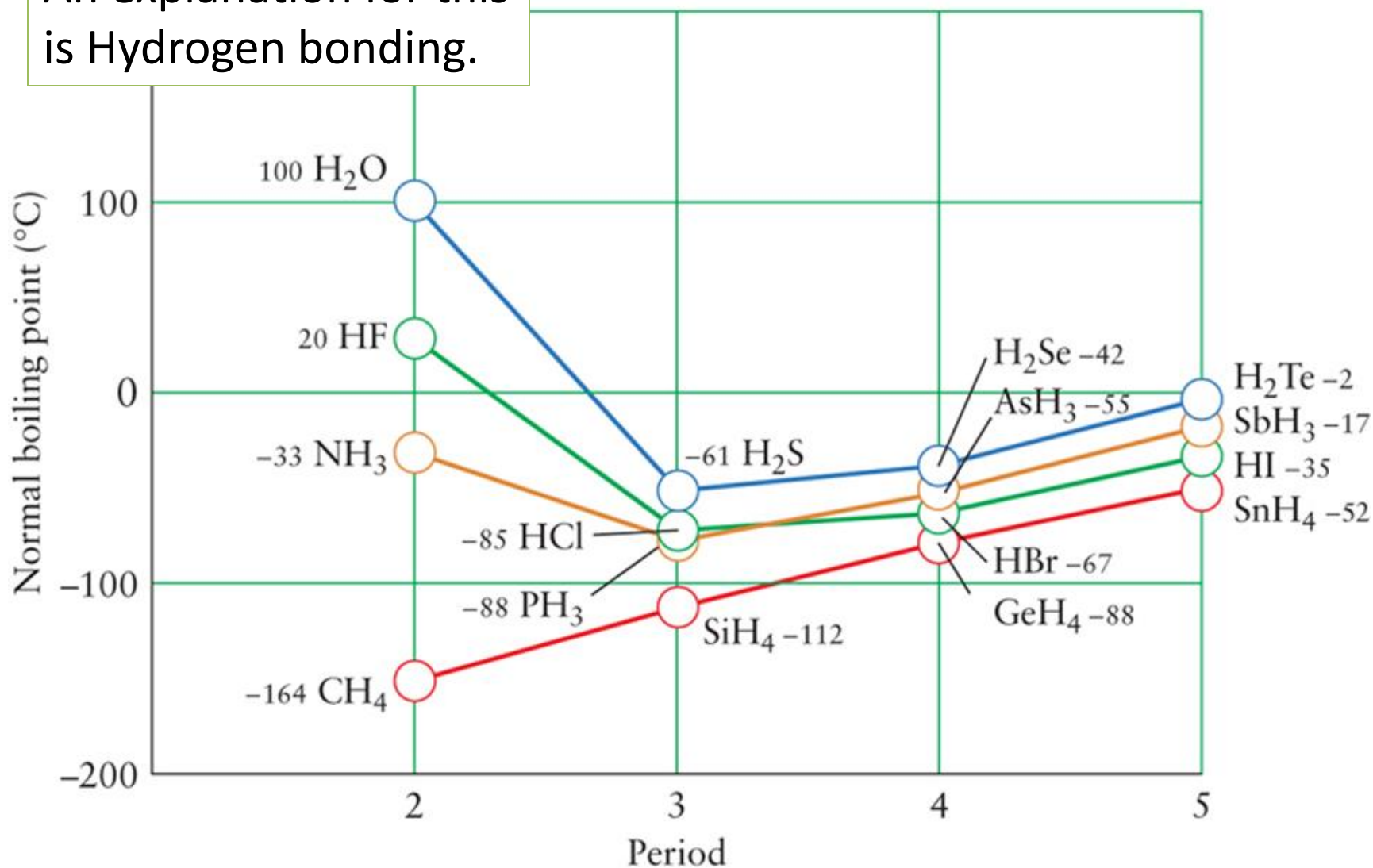
The data cannot explain the raising boiling points. The dipole-dipole interaction is not dominating.

The London dispersion energy dominates

Hydrogen Bonding

When plotting experimental values we find our approximations are off by as much as **200 degrees!**

An explanation for this is Hydrogen bonding.



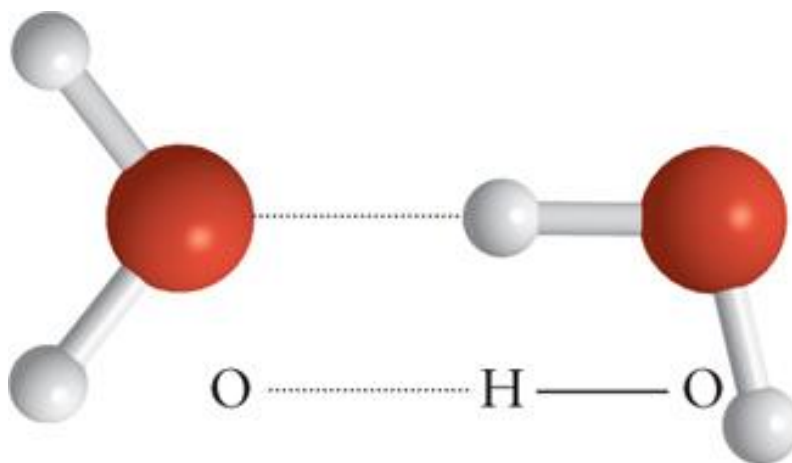
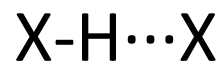
Hydrogen Bonding

Specific molecules with hydrogen attached to a strong electronegative atoms N, O, or F, form bridging hydrogen bonds to electron **lone pairs** on N, O, or F atoms.

H atom is almost completely unshielded by the electronegative atom its bound to.

The electron lone pair donates electron to hydrogen

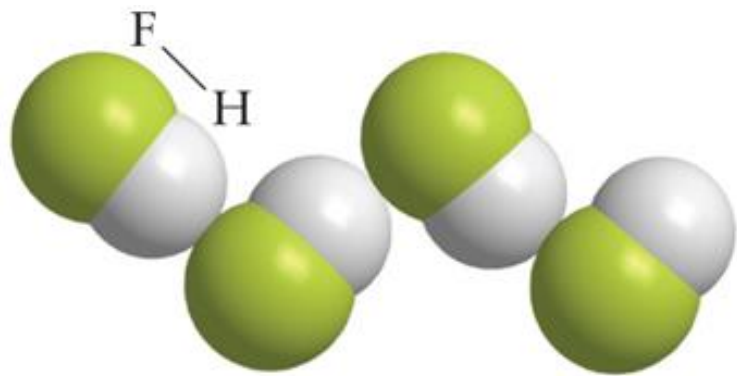
Hydrogen Bonds



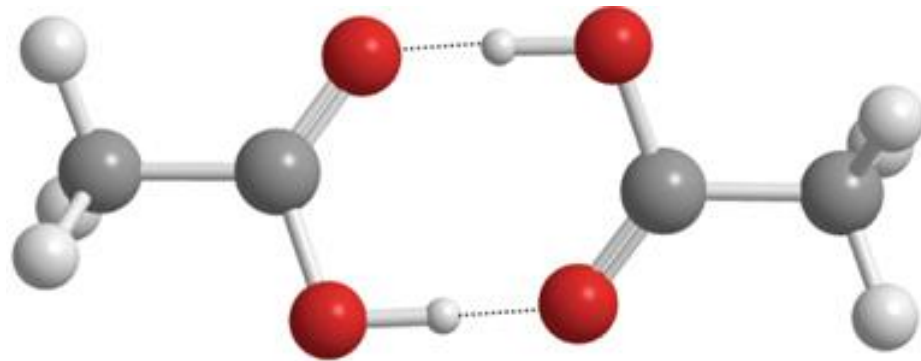
Hydrogen Bonding

Hydrogen bonding is strong enough to survive even in the vapor phase.

Liquid hydrogen fluoride, forms **zigzag chains** of HF molecules. The vapor of acetic acid, CH_3COOH , contains **dimers**, pairs of molecules, linked by two hydrogen bonds.



Hydrogen fluoride, $(\text{HF})_n$



Acetic acid dimer

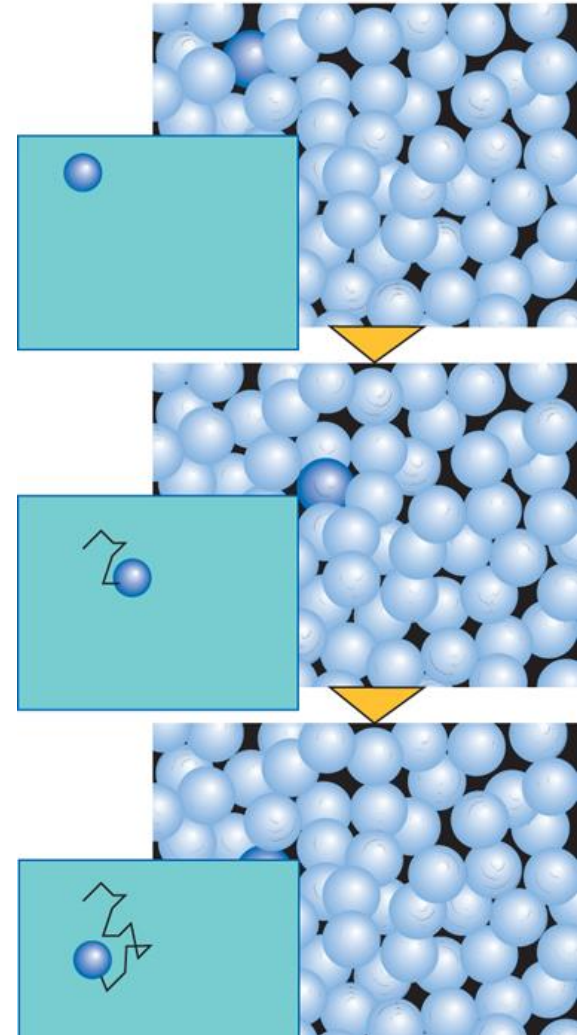
Liquid Structures

Liquid Structure

Liquids molecules are randomly distributed and constantly tumbling each other.

Short-range order - the immediate vicinity of an atom is like in the solid

Long range disorder – completely randomness.



Order in phases of matter

Gas-phase molecules have complete freedom to move, and movement is highly disordered.

Liquid-phase molecules are randomly distributed with short-range order. There is mobility, yet not enough to escape each other.

Amorphous solids molecules are randomly distributed but locked in place without mobility, only oscillation.

Crystalline solids have long-range order, orderly arrangements repeat regularly, no mobility, oscillation only.

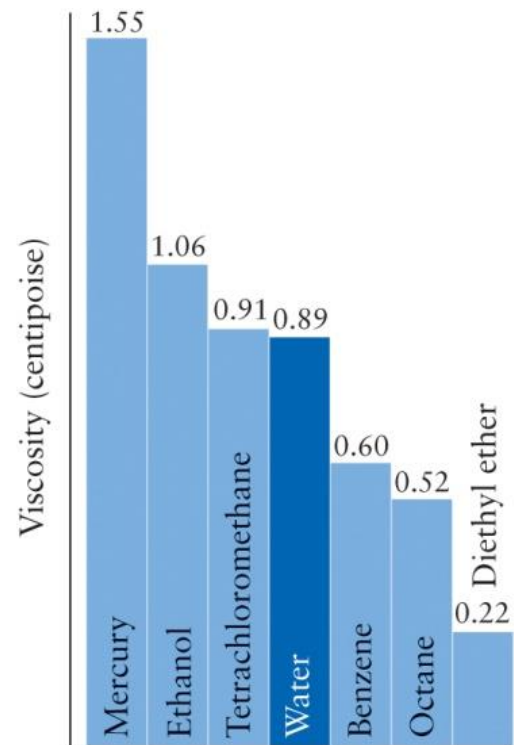
Intermolecular interactions in Liquid

- Molecules are in close contact in liquid, so the intermolecular interactions are strong, cannot be ignored.
- Because molecules are in close contact, liquid cannot be compressed easily.
- To evaporate liquid, the intermolecular interaction must be overcome by raising kinetic energy (temperature).
- The most common (general) interaction is dispersion energy. The electrostatic interactions may become important for polar molecules.
- The interactions are very complicated. To predict liquid properties from intermolecular interactions is not trivial.

Viscosity

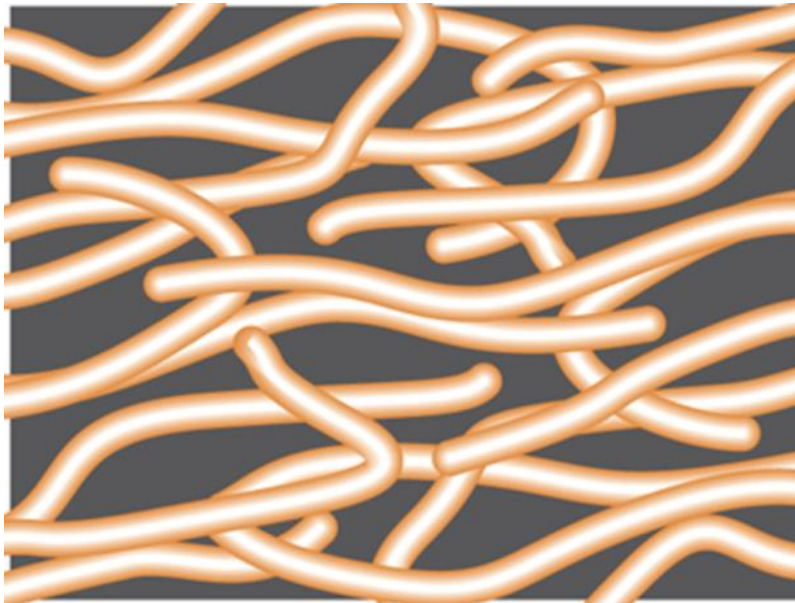
- Viscosity reflects intermolecular interaction.
- It measures liquid resistance to flow: the higher the viscosity of the liquid, the more sluggish the flow.
- Viscosity reflects the strength of intermolecular strength.

FIGURE 6.12 The viscosities of several liquids. Liquids composed of molecules that cannot form hydrogen bonds are generally less viscous than those that can form hydrogen bonds. Mercury is an exception: its atoms stick together by a kind of metallic bonding, and its viscosity is very high. The centipoise (cP) is the unit commonly used to report viscosity ($1 \text{ cP} = 10^{-3} \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$).



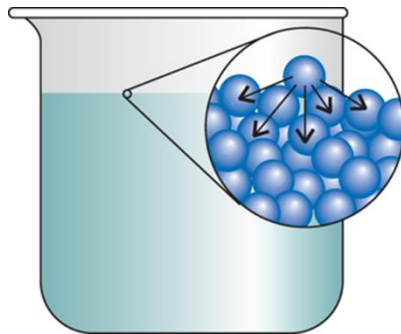
Viscosity

- Viscosity also depends on how molecules interact with each other
- Hydrocarbon chains with 19 or more carbons that form spaghetti-like structures, the viscosity increases dramatically



Surface Tension

- Surface tension is another indication of intermolecular interaction in liquid.
- At surface, the molecules interactions are reduced, the net force pulls the molecules inward.
- It causes energy to increase the surface area because more molecules need to be brought to the surface.
- The stronger intermolecular energy is, the larger surface tension is.
- Surface tension is defined as the **free energy** increase per area, it **decreases** with rising temperatures.



Liquid	Surface tension, γ (mN·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

Adhesion and Cohesion

Adhesion is the interaction between the liquid and surface of a (solid) substance.

e.g. Water spreads out over clean glass due to adhesion between the silica groups in glass and water.

Cohesion is a bulk forces binding a material. It is the total intermolecular interaction (negative value with respect to vapor)

e.g. Water stay as liquid or form a drop due to cohesion.

Hydrophobicity of surface

The contact angle measures the hydrophobicity of surface.

It is determined by three factors – the liquid surface tension, the liquid-surface adhesion and gas-surface adhesion.

- Surface tension pulls the liquid into sphere
- The adhesion with liquid increase the coverage
- The adhesion with gas reduce the coverage.



Capillary action is how liquids flow up narrow tubes.

The **upward** curved meniscus of water forms because both water and glass have comparable forces:
 $\text{Adhesion} \approx \text{Cohesion}$

The **downward** meniscus of mercury forms because the cohesive forces in mercury is strong than between mercury atoms and the glass:
 $\text{Cohesion} > \text{Adhesion}$

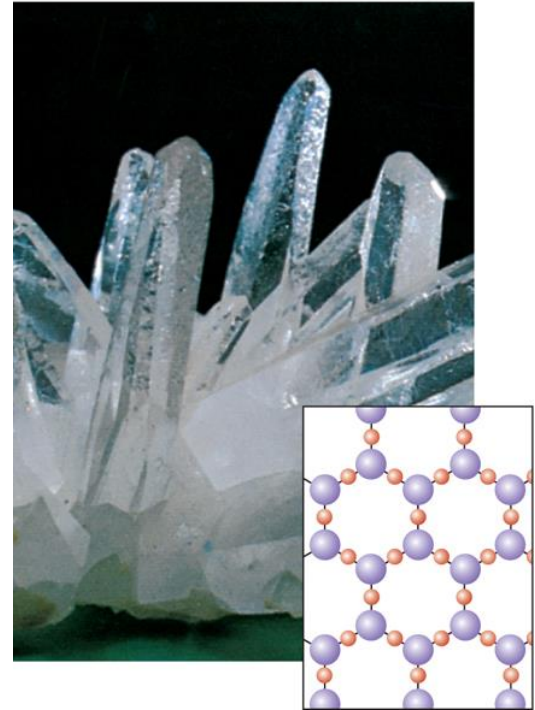


Solid Structures

Crystalline solids

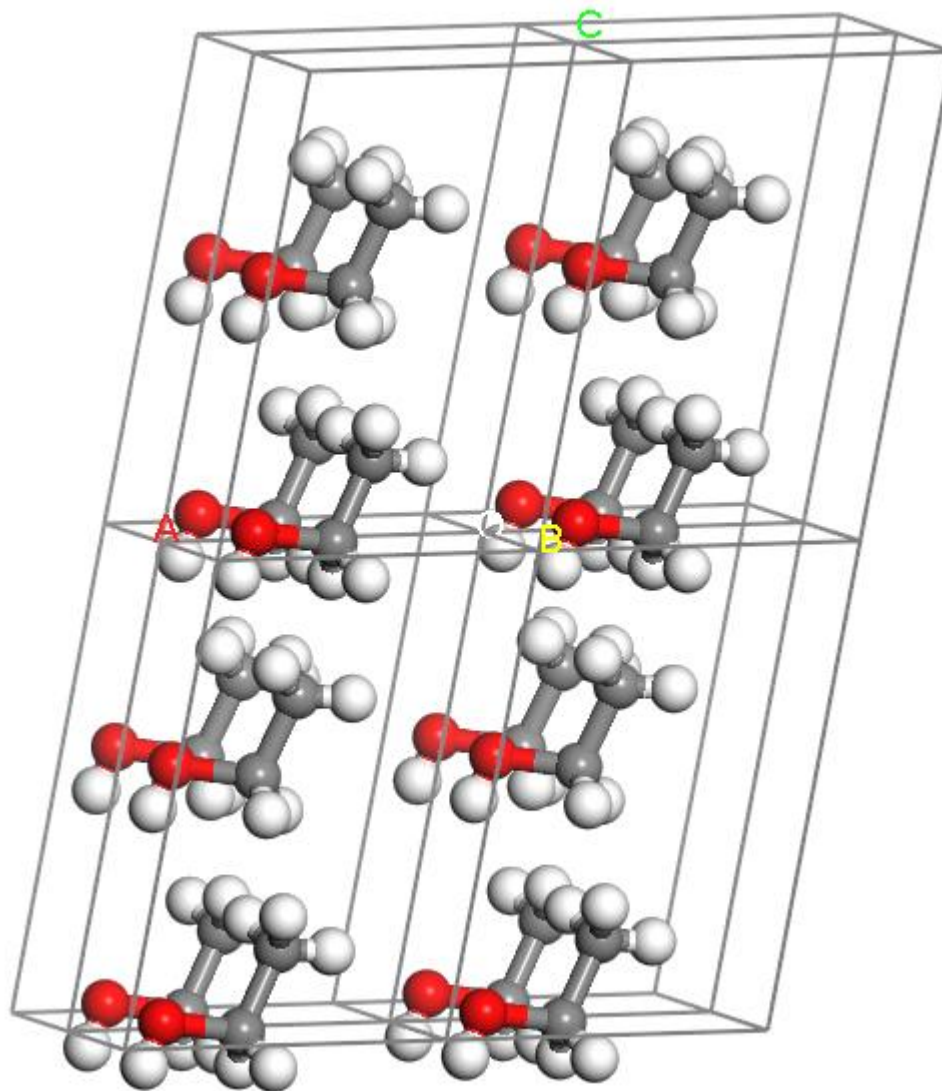
Crystalline solids are classified :

- Molecular solids: discrete molecules with strong intermolecular forces.
- Network solids: atoms covalently bonded.
- Metallic solids: cations held together by electron sea.
- Ionic solids: mutual attractions of cations and anions.



Molecular Solids

Ethanol crystal

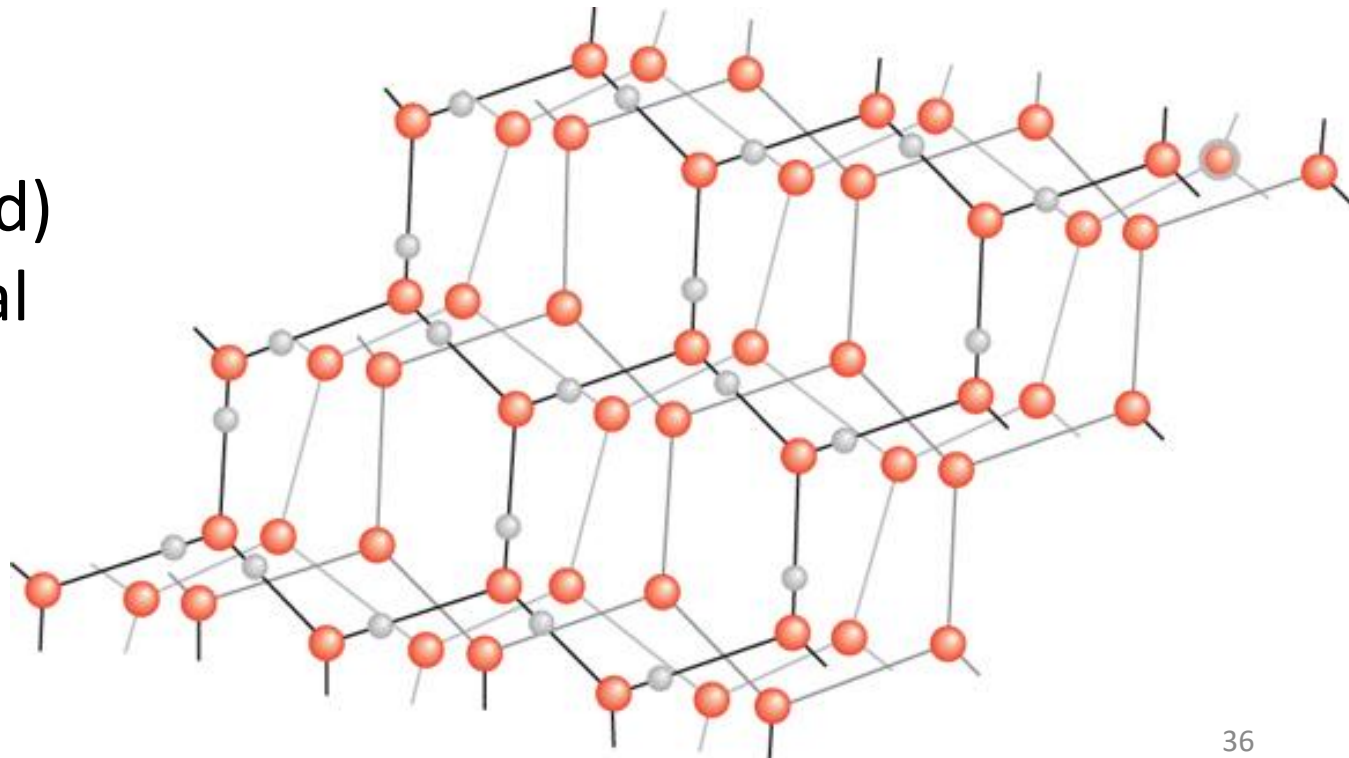


Molecular Solids

Molecular solids are held together by intermolecular forces.

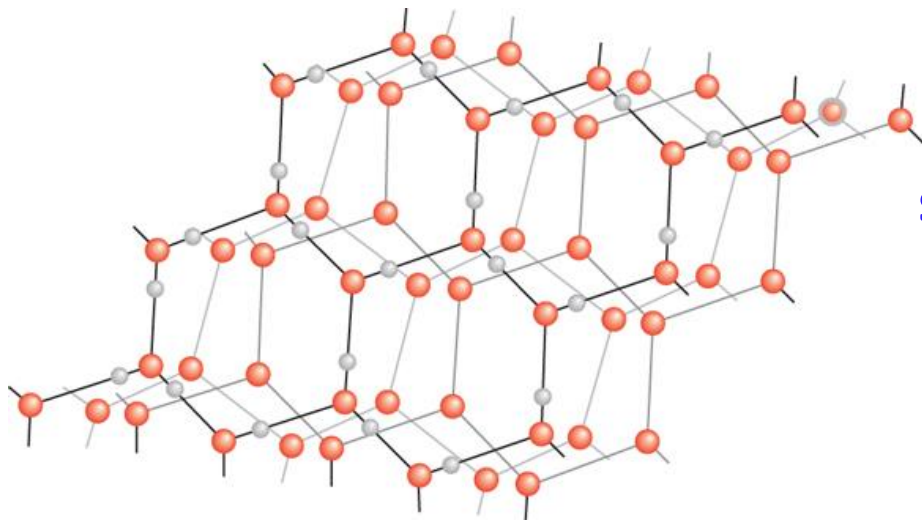
Ice is made up of water molecules that are held together by hydrogen bonds.

Each oxygen (red) has a tetrahedral geometry.

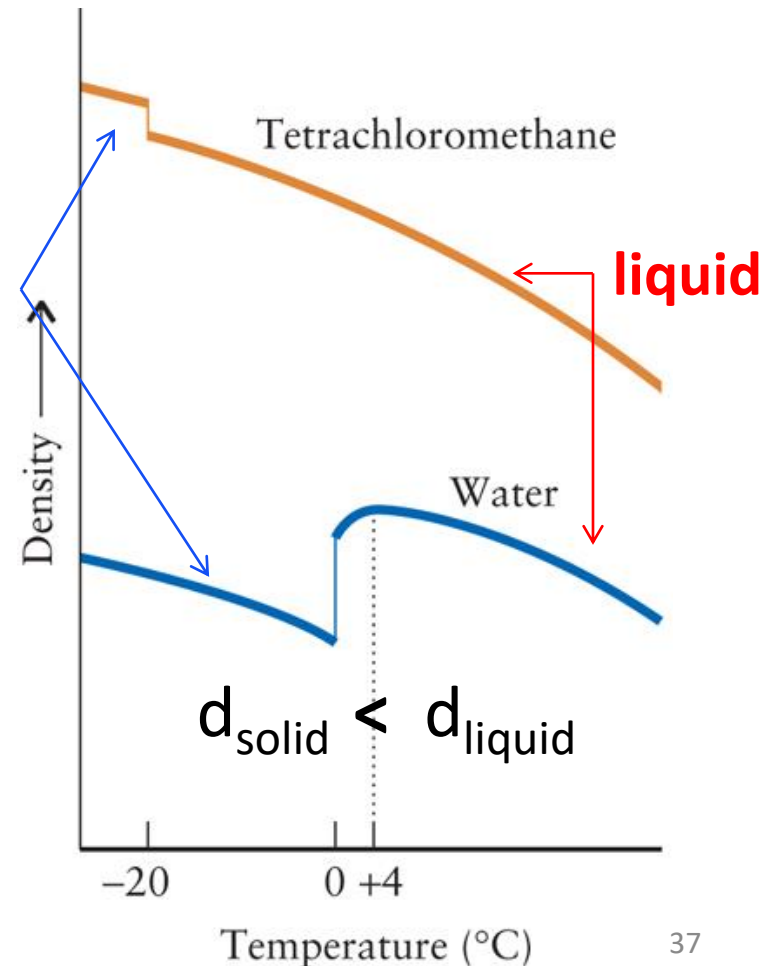


Molecular Solids

The openness of ice's network explains its lower density than liquid water ($0.92 \text{ g}\cdot\text{cm}^{-3}$ and $1.00 \text{ g}\cdot\text{cm}^{-3}$, at 0°C).



solid



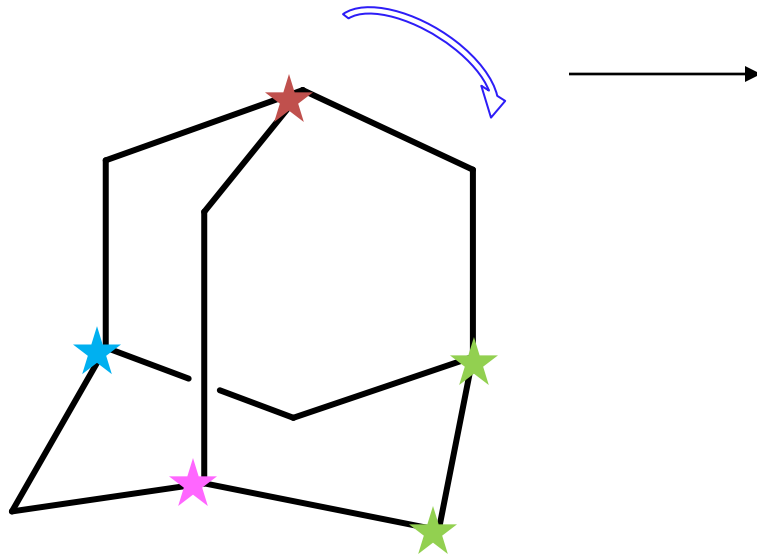
Network Solids

Atoms in network solids are joined to their neighbors by **strong covalent bonds**.

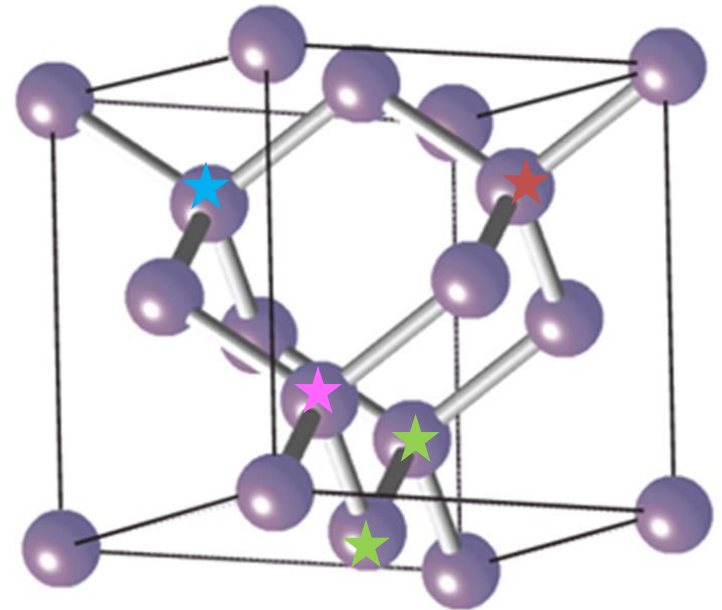
Therefore, network solids are very hard, rigid materials with high melting and boiling points.

Classification of Solids: **Network Solids**

Diamond and graphite, allotrope of carbon, are network solids.



Adamantane, composed of 3 six-membered rings, is the simplest nonrepeating set of atoms in diamond.

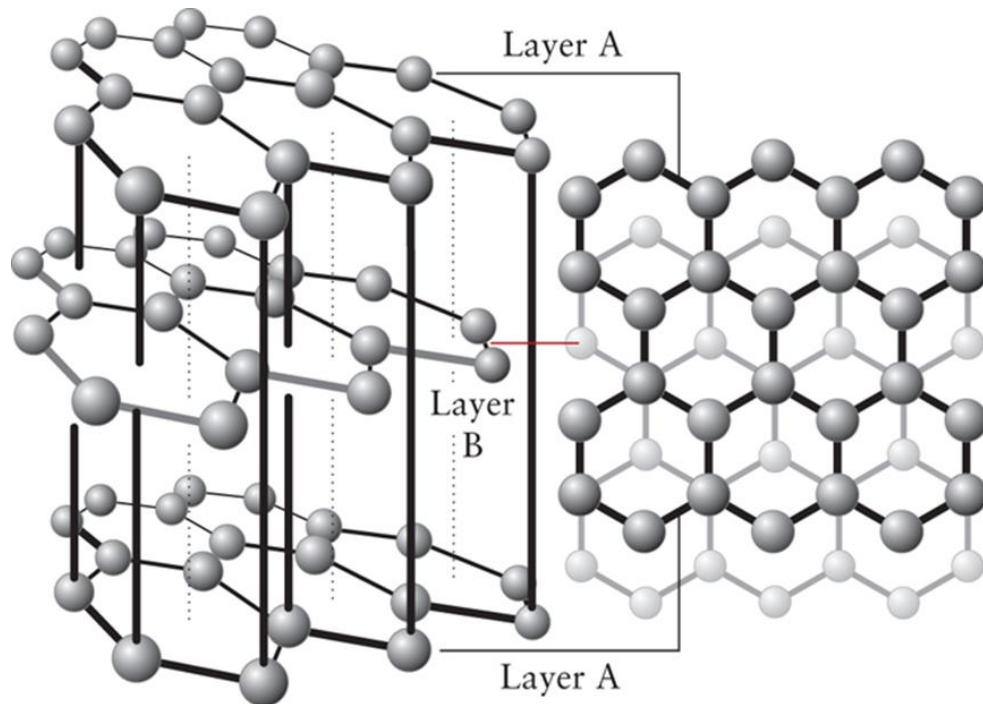


In diamond each carbon is covalently bonded to four neighbors.

Network Solids

Graphite, the "lead" in pencils, is black, lustrous, and an electrically conducting solid that vaporizes at 3700°C.

Flat sheets are sp^2 hybridized carbon atoms σ and π -bonded covalently into hexagons like chicken wire.

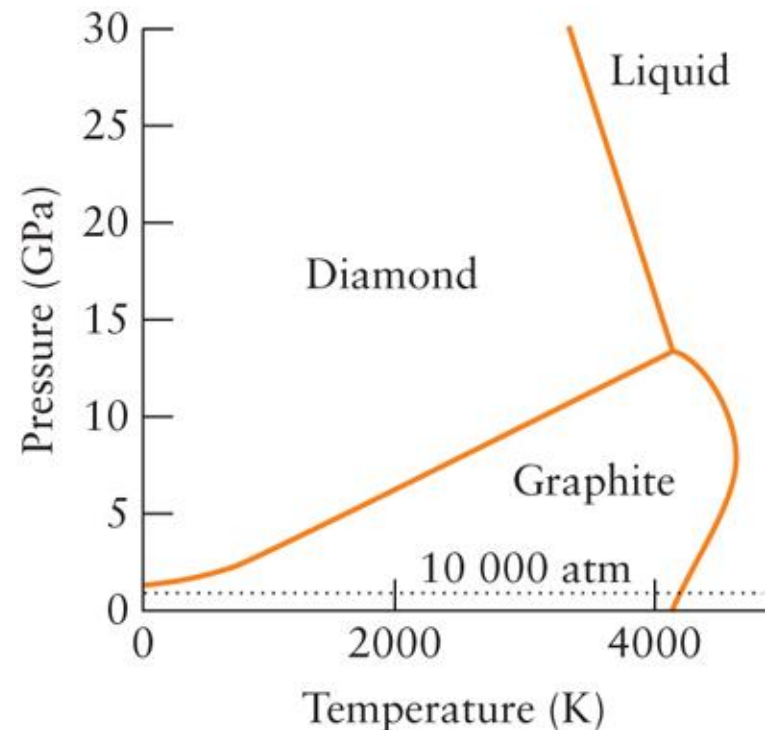


The pencil mark on paper are sheets or layers of graphite.

Diamond and Graphite

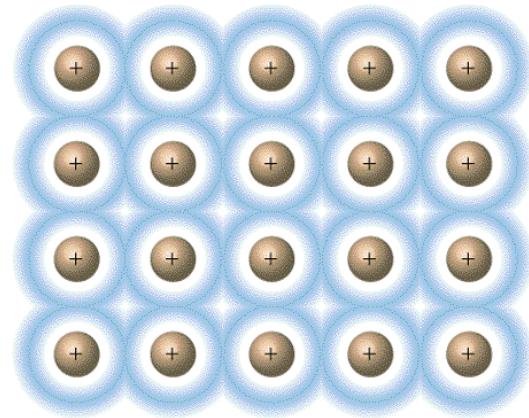
Diamonds are found deep within the Earth in rock known as kimberlite. Diamonds are formed in the lab by subjecting graphite to high pressure, 80 kbar at 1500°C, often chromium (III) is added.

Phase diagram – conditions of stable diamond and graphite.



Metallic Solids

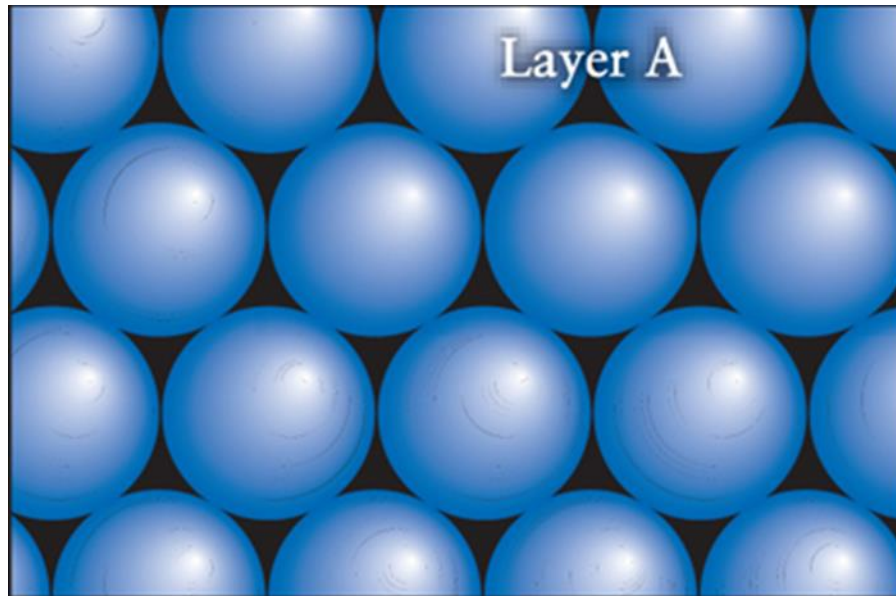
- The bonding is too strong for London dispersion and there are not enough electrons for covalent bonds.
- The metal nuclei float in a sea of electrons.
- Metals conduct because the electrons are delocalized and are mobile.
- Metals are often closely packed



Closed-packed Structures

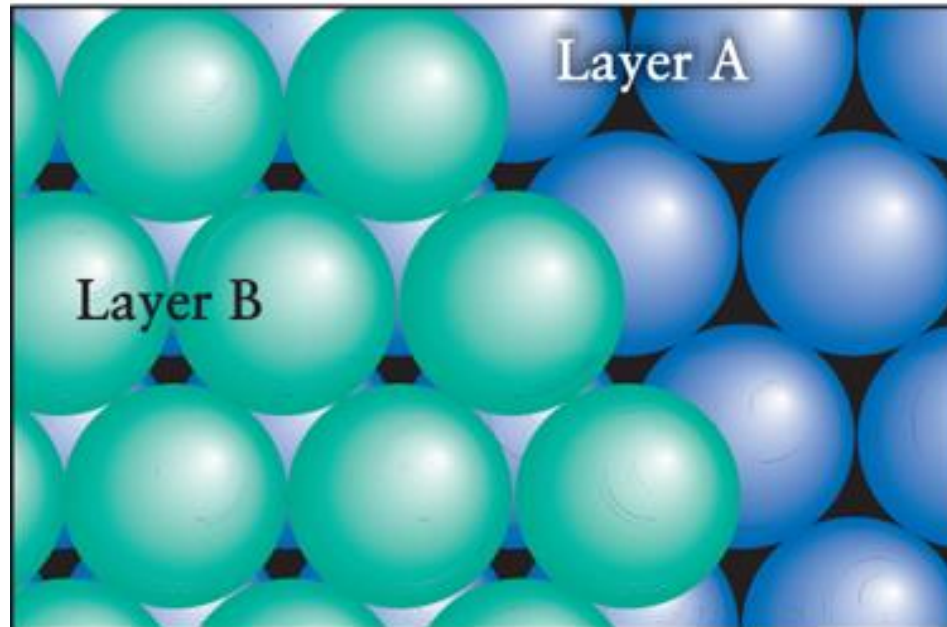
Closed-packed stacking starts by laying layer upon layer, in a highly efficient manor, of atoms on top of each other.

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



Closed-packed Structures

The **second layer** is added on top of the Layer A by resting particles in the small cavity created between each sphere in Layer A.

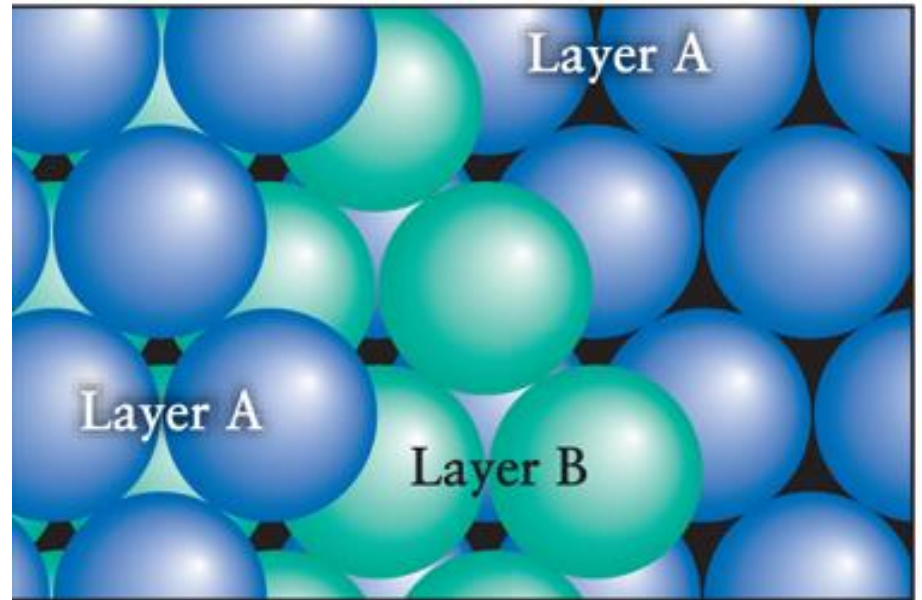


Closed-packed Structures

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

If the third layer is identical to Layer A, referred to as a ABABAB pattern, a **Hexagonal closed-pack** (hcp) structure is formed.

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

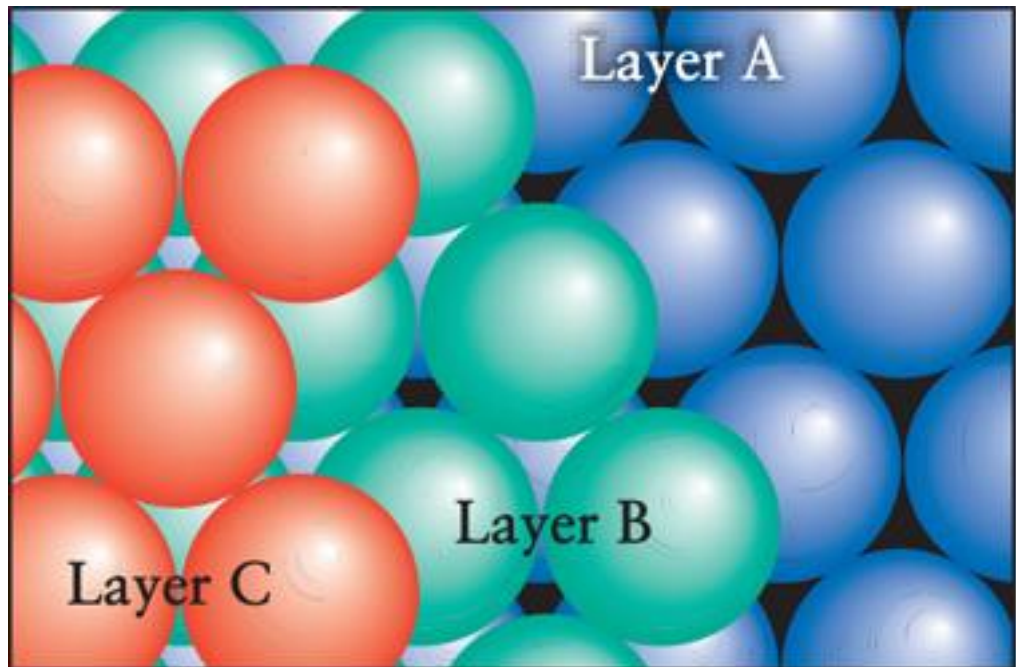


Closed-packed Structures

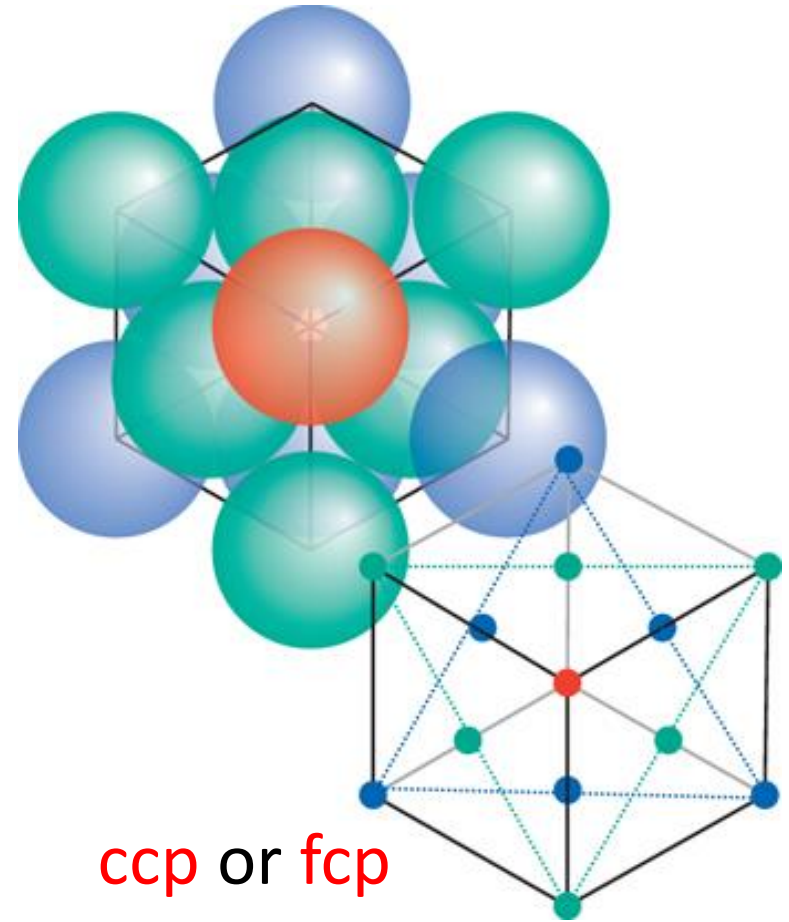
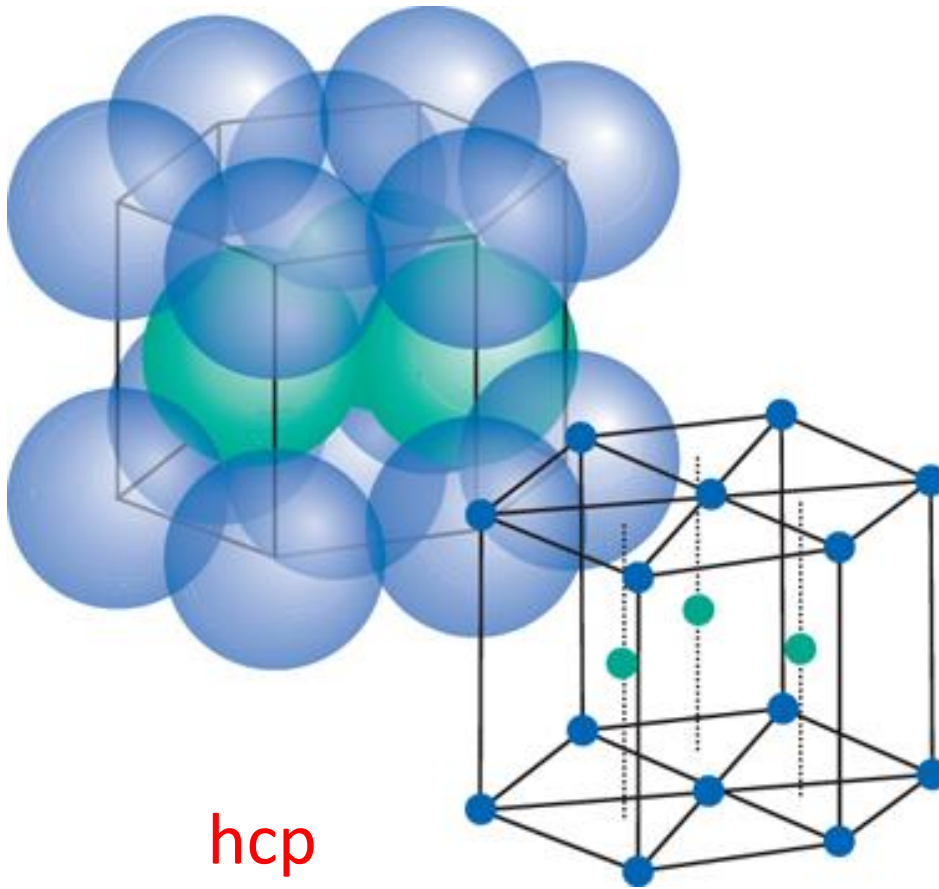
The second options differs slightly by placing a layer offset to Layer A, and is called **Layer C** or an ABCABC pattern.

A more common name is **Cubic closed-pack** (ccp).

Notice the hole disappears.



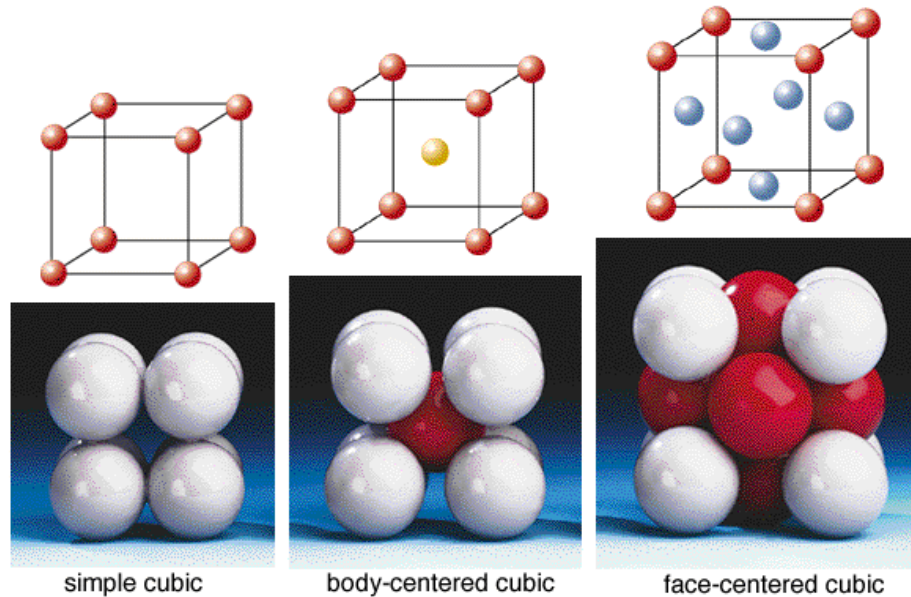
Two Closed-packed Structures



Both are close packed, have a **coordination number of 12**, which is the **maximum number** of atoms another atom can be bound to.

Unit Cells

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

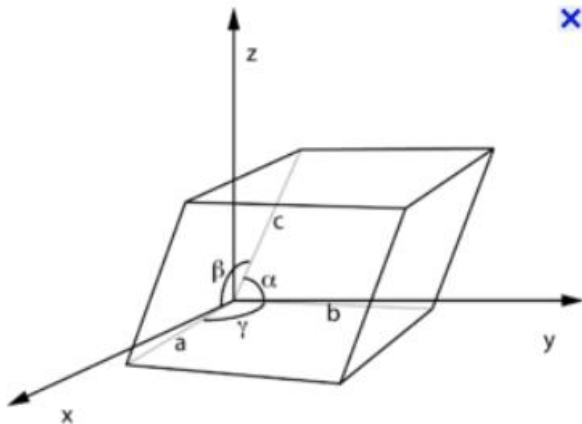
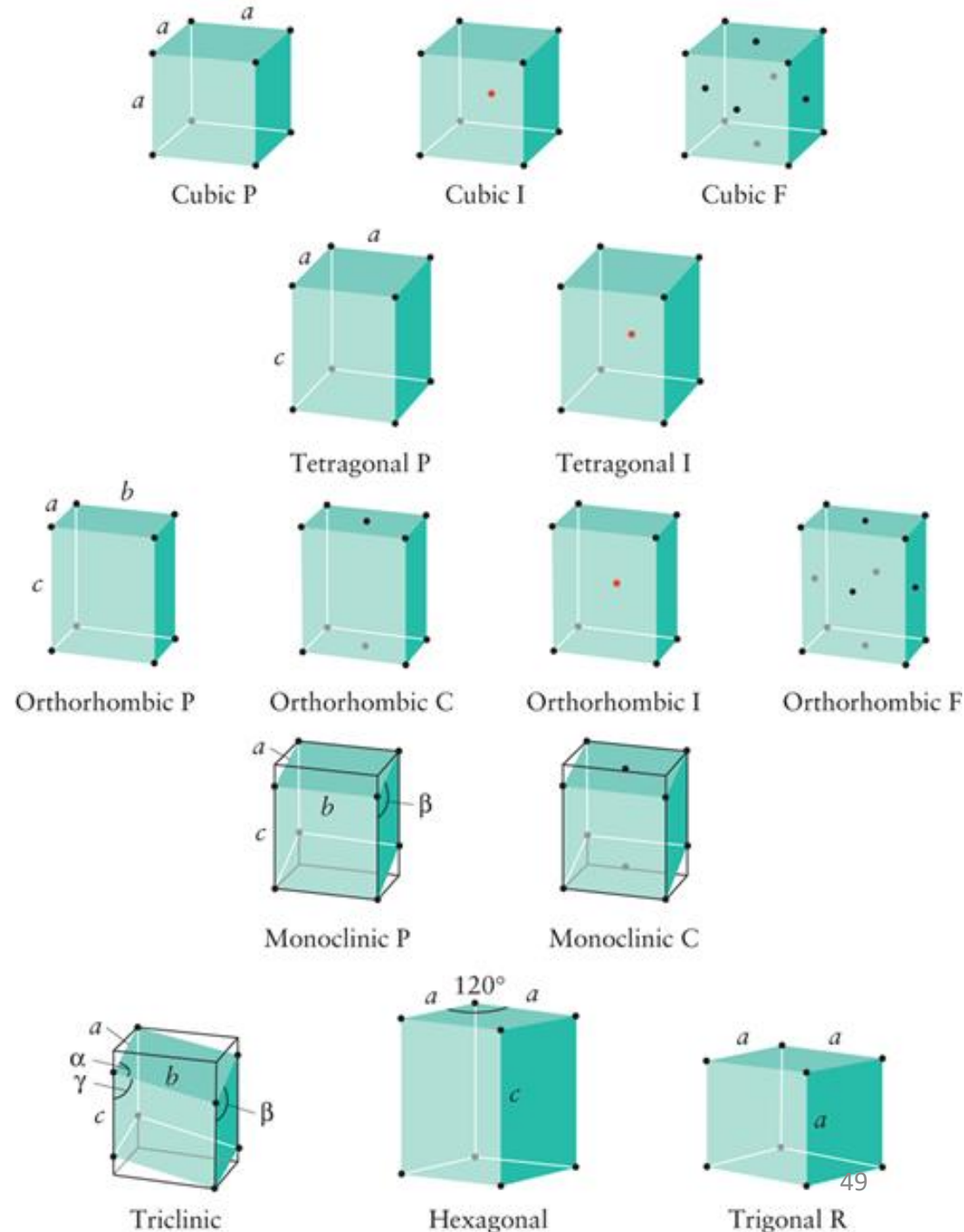


A crystal structure is constructed from a single type of unit cell stacking together without any gaps.

14 Unit Cells

All crystal structures can be expressed in only 14 **Bravais lattices**.

Differ by lengths of a , b , and c , as well as angles between a , b , and c .



Unit Cells: **Number of atoms** per unit cell

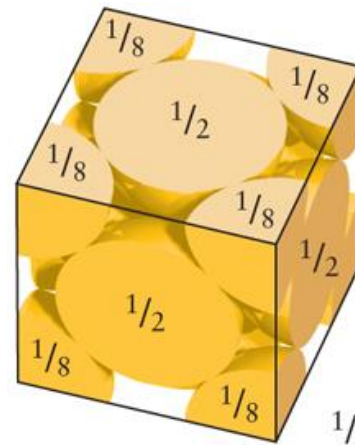
corner atom counts as $1/8$

face atom contributes $1/2$

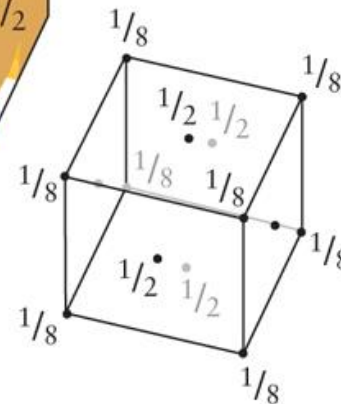
body atom counts as 1

The total number of atoms in an ccp unit cell is: $1/8 * 8 + 1/2 * 6 = 4$.

The mass of the unit cell is four times the mass of one atom.



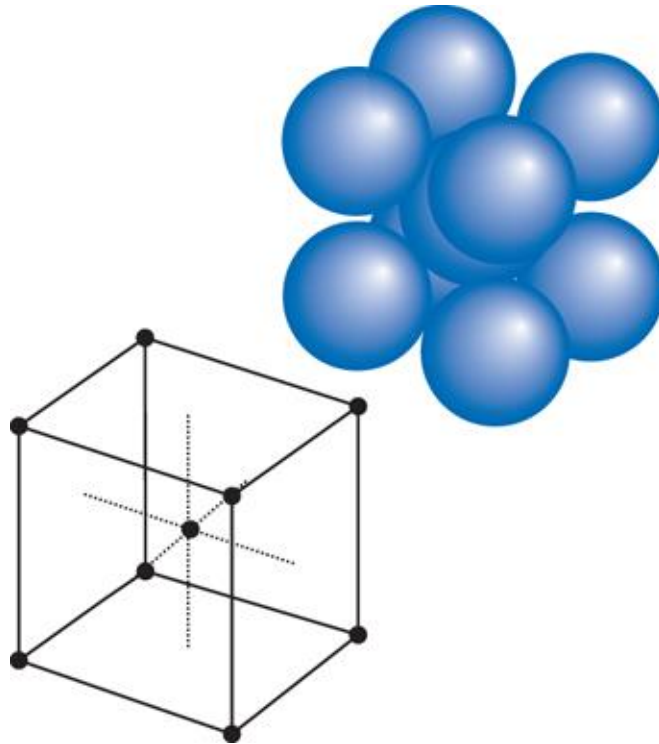
fcc/ccp



How many atoms are in a **body centered cubic**?

1 center atom and 8 corner atoms:

$$1 + (8 \times 1/8) = 2 \text{ overall.}$$



What percentage of space is occupied by atoms with a coordination number of 12?

Volume of sphere: $\frac{4}{3} \pi r^3$.

For 4 atoms $4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$

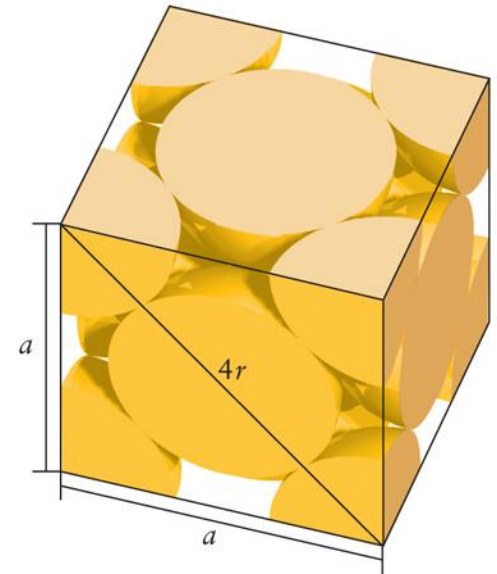
Total volume of the unit cell

since $a^2 + a^2 = (4r)^2$ so $a = 8^{1/2}r$.

volume $a^3 = (8^{1/2}r)^3$

Ratio:

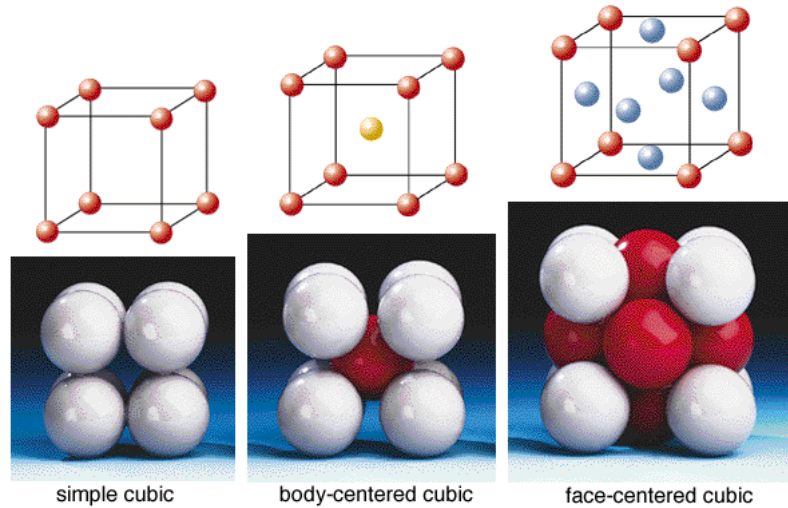
$$\frac{\frac{16}{3} \pi r^3}{8^{3/2} r^3} = \frac{16/3 \pi}{8^{3/2}} = 0.74$$



74% of the crystal's space is occupied by atoms and 26% is considered to be empty.

Three Cubic Unit Cells

face-centered cubic structure (fcc).
body-centered cubic structure (bcc)
A primitive cubic



Type	CN	Occ%
close packed (fcc)	12	74%
bcc	8	68%
primitive cubic	6	52%

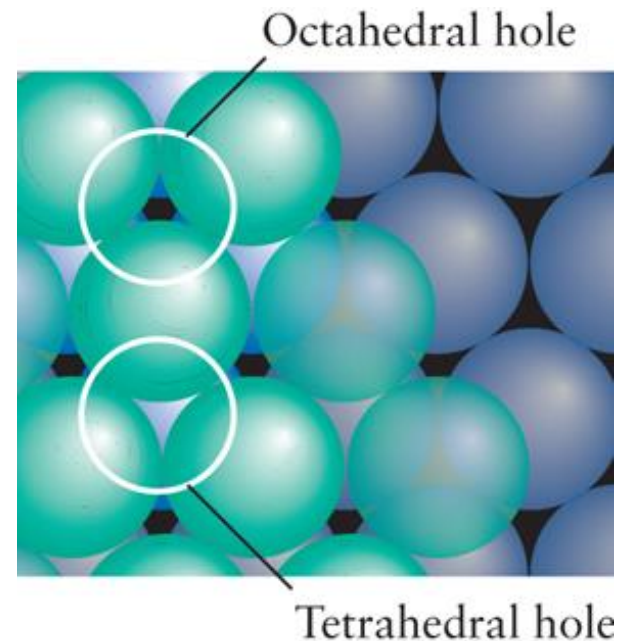
Ionic Structures

Ionic compounds pack spheres with different sized radii and charge.

Consider one type of ions packed with expanded holes for different type of ions, to reduce the repulsion

A tetrahedral hole allows smaller ion

An octahedral hole allows larger ion



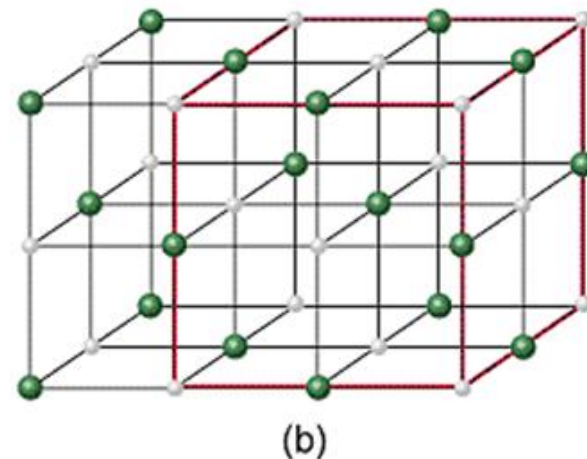
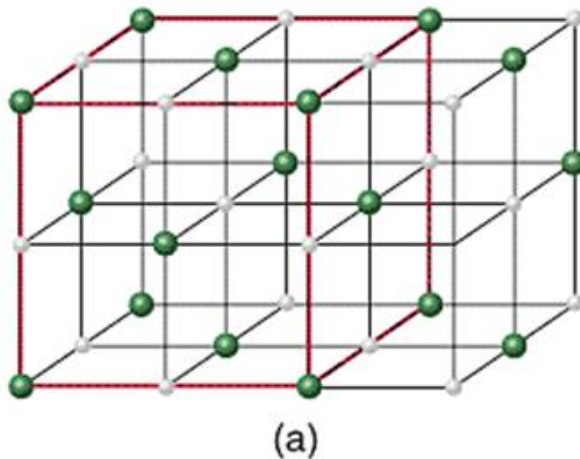
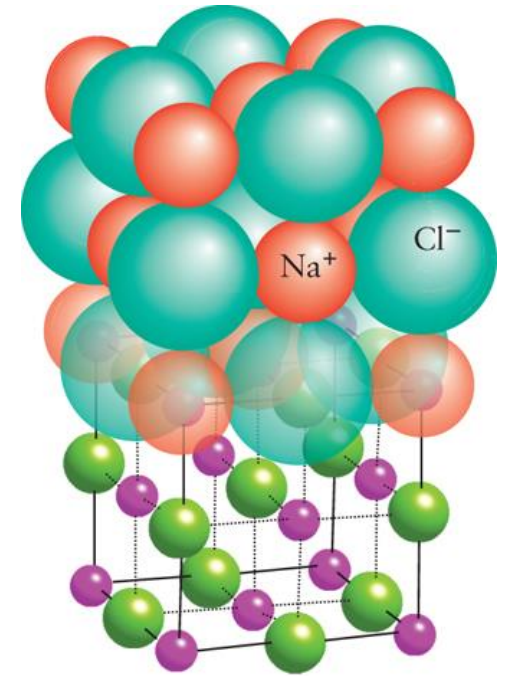
Ionic Structures

Rock-salt, a common name for the mineral NaCl, same for KBr, RbI, MgO, CaO, and AgCl.

Cl^- takes ccp arrangement

Na^+ fit into the **octahedral holes**

(6,6)-coordination



Ionic Structures – which way to pack?

The radius ratio = $\frac{\text{Radius of the smaller ion}}{\text{radius of the larger ion}}$

or $\rho = \frac{r_{\text{smaller}}}{r_{\text{larger}}}$

For a fcc structure like rock-salt the range is 0.4 to 0.7.

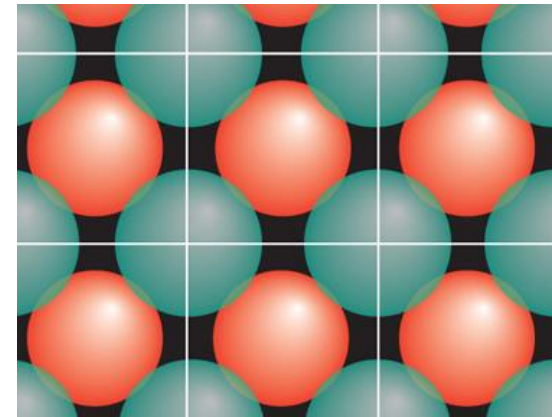
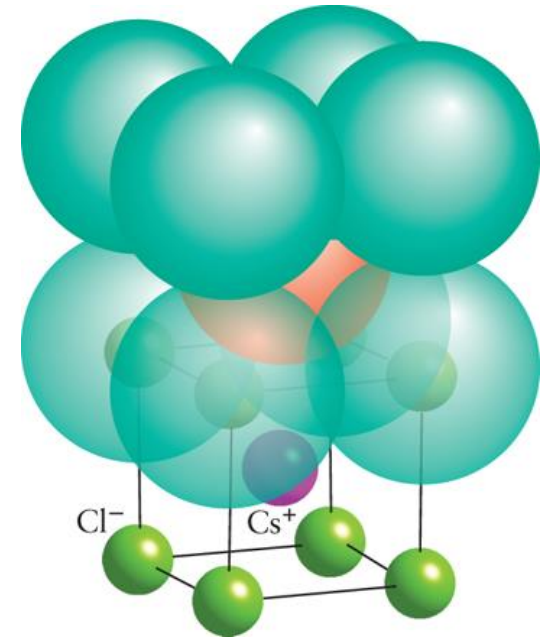
Ionic Structures – which pack

When $\rho > 0.7$ the cation and anion are about **the same size**, so more anions fit around each cation.

ρ for CsCl is 0.923, a body centered Cs^+ and primitive Cl^- .

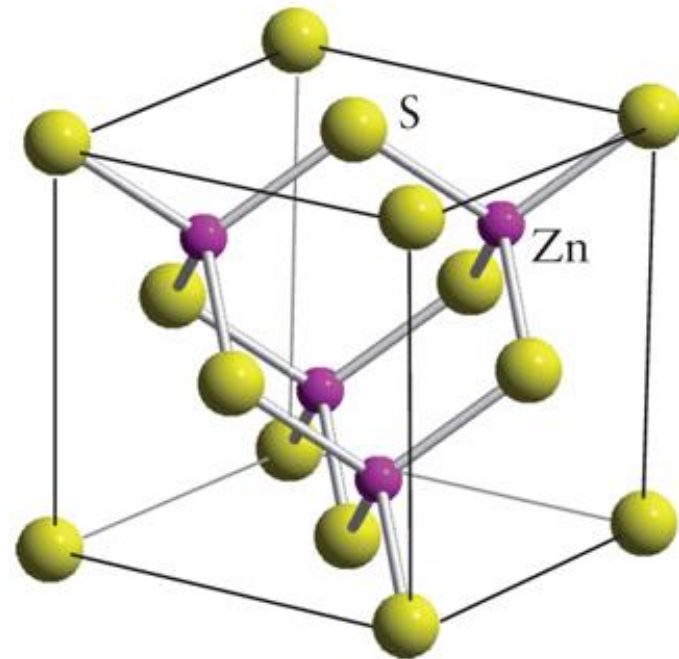
The structure has a $(8,8)$ -*coordination*.

Similar structures include CsBr, TlCl, and TlBr.



Ionic Structures – which pack

When p is less than 0.4 the ratio of cation to anion is smaller, then smaller tetrahedral holes open up for the cation.



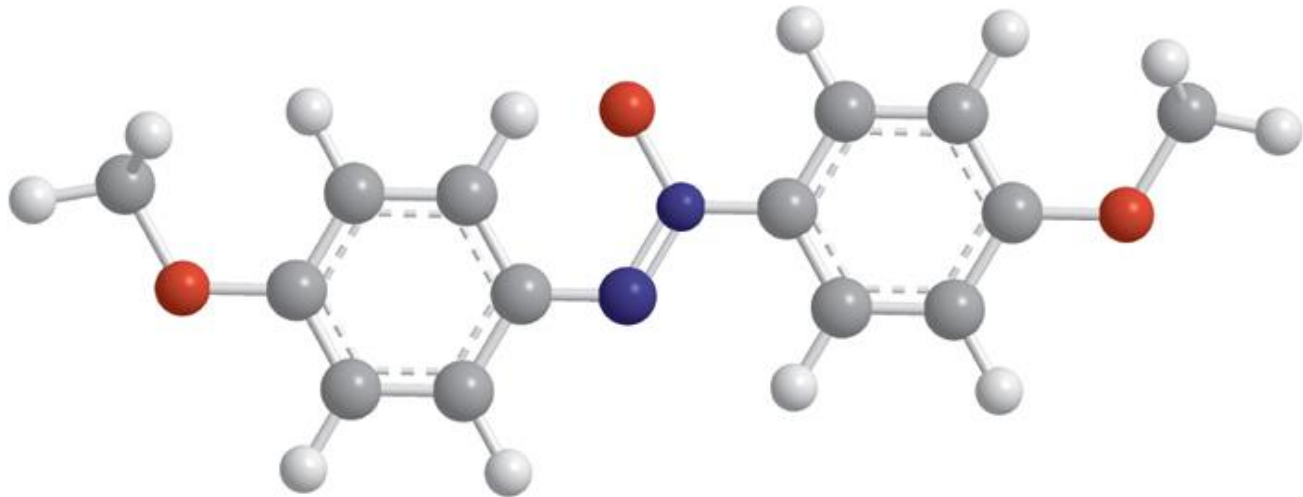
ZnS structure is fcc close-packed lattice of the big S²⁻ anions, with the small Zn²⁺ cations occupying the tetrahedral holes.

Each Zn²⁺ ion is surrounded by 4 S²⁻ ions, and each S²⁻ ion is surrounded by 4 Zn²⁺ ions. The zinc-blende structure has (4,4) coordination.

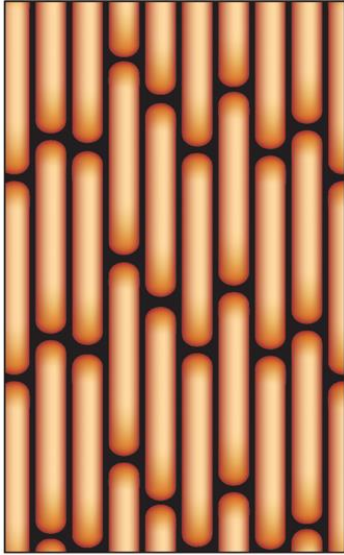
Liquid Crystals

Liquid crystals

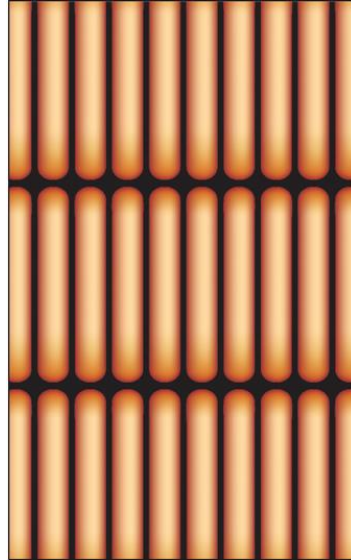
- **Liquid crystals** are neither a solid nor a liquid, but intermediate called a **mesophase**.
- Here molecules have fluidity of a liquid and some order of a molecular solid.
- They are **responsive** to changes in temperature and electric fields.
- p-azoxyanisole (below), is long and rod like, enabling stacking like dry, uncooked spaghetti.



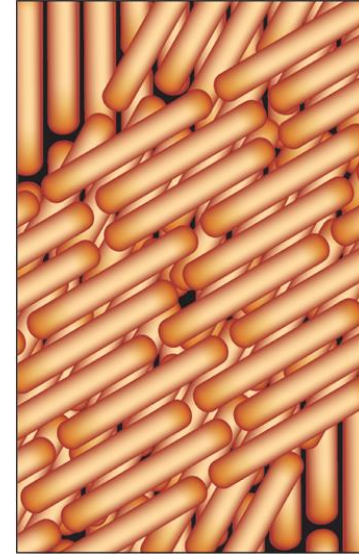
Liquid crystals



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.

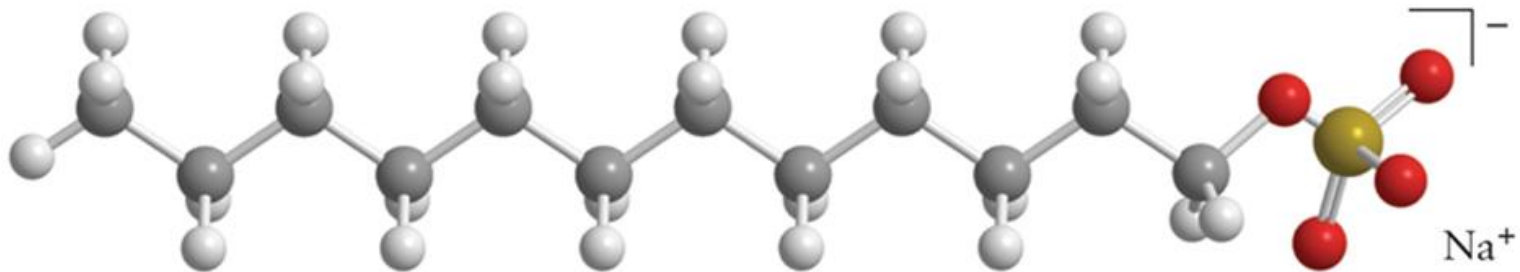
Thermotropic liquid crystals are made by melting the solid phase, usually have a short temperature range between the solid and the liquid states.

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

Lyotropic liquid crystals

Lyotropic liquid crystals are layered structures that result from the action of a solvent on a solid or liquid. Examples are cell membranes and aqueous solutions of detergents and lipids (fats).

Detergent surfactant, sodium lauryl sulfate, a long, nonpolar hydrocarbon chains attached to polar heads.



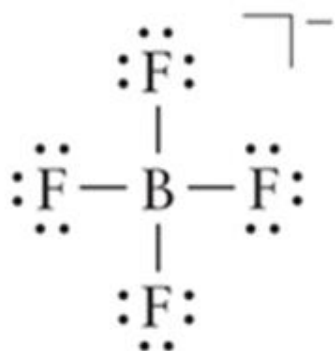
15 Sodium lauryl sulfate

Ionic Liquids

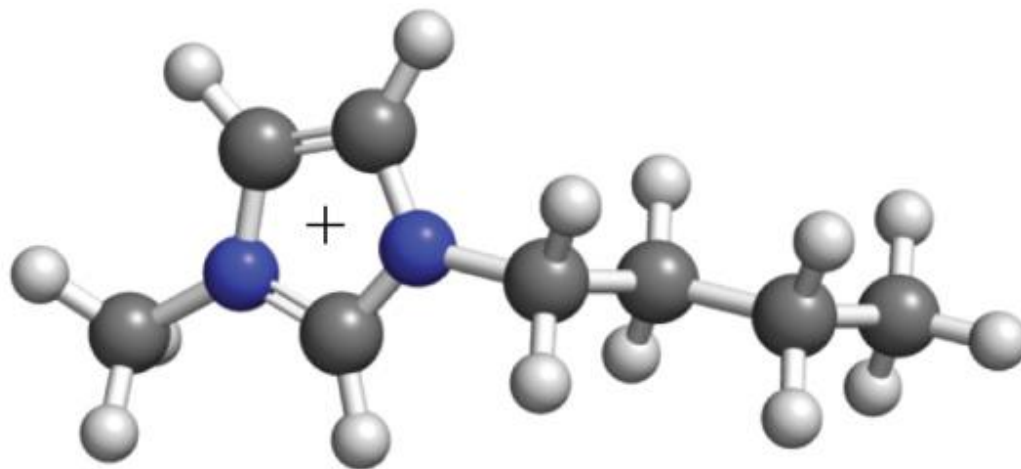
Ionic liquids are relatively small anion, such as BF_4^- , and a relatively large organic cation, such as 1-butyl-3-methylimidazolium.

Ions reduce vapor pressure so reduces air pollution.

Electrolytes



Tetrafluoroborate, BF_4^-



16 1-Butyl-3-methylimidazolium ion