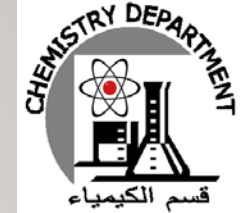




General Chemistry II

Chem 102



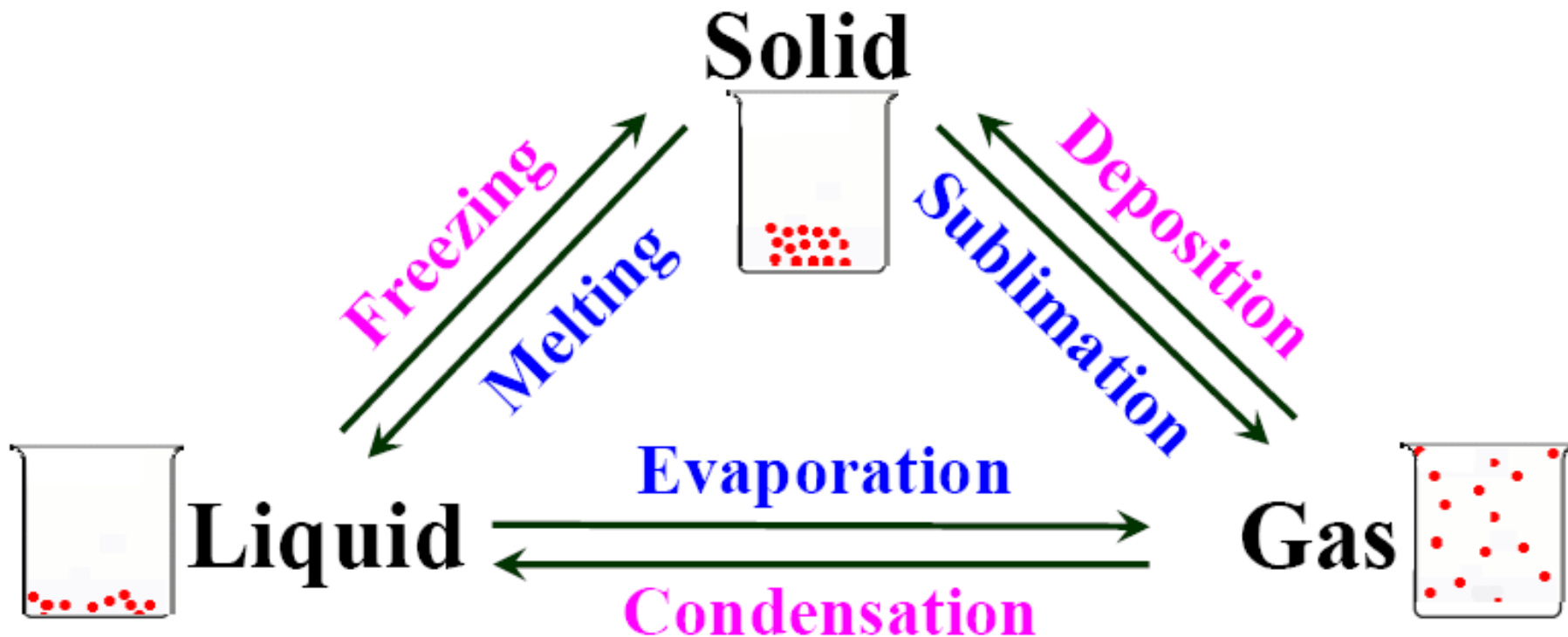
Lecture 3

Liquids and Solids

Ahmad Alakraa



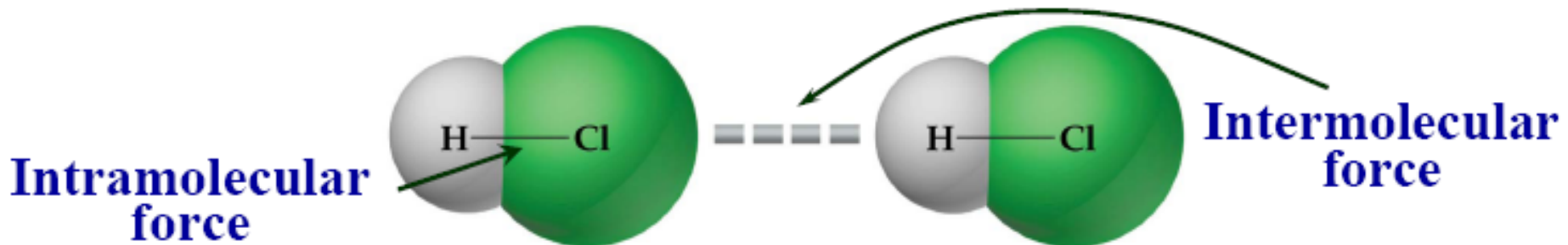
Recognize



Properties of liquids are intermediate between those of solids and gases

Intermolecular and intramolecular

- ✚ **Intermolecular forces:** are those forces between molecules in the condensed states (liquids or solids).
 - ✚ always physical in nature.
 - ✚ are responsible for bulk properties of materials (melting point, boiling point, etc.)
- ✚ **Intramolecular forces:** forces that hold atoms together within a molecule.
 - ✚ always chemical in nature.





Remember

✚ Intermolecular forces are much weaker than intramolecular forces.

It requires much less energy to **evaporate** a liquid than to **break** the bonds in the molecule.

Intramolecular Forces and Chemical Bonding

- ✚ Three major types of intramolecular chemical bonding are considered;
- ▶ electrostatic (ionic),
 - ▶ covalent, and
 - ▶ metallic bonding.

Electrostatic (ionic) bonding

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$

$$F = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 r^2}$$

- ▶ One atom gives one or more electrons to another atom or atoms (**Octet structure** and **Coulomb attraction** of opposite charges are deriving)
- ▶ The above equation represents the **Coulomb force** $F(r)$ between two static ions if an ion (a point-like body) of **charge** q_1 is at a center-to-center distance, r , away from another ion of charge, q_2 , in a vacuum.

ϵ_0 is the **vacuum permittivity** = $8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$

- ▶ The **ionic bonds** are **long-ranged**, **non-directional** and not so strong ($\approx 400 \text{ kJmol}^{-1}$)



Non directional

- ▶ because charge is uniform in all direction and each ion is surrounded by other ions from all directions.
- ▶ In **ionic solids** while stacking atoms, there are **no directional** requirements (bonding can be **at any angle**) but there are a size and charge requirements.
 - ▶ Each ion must have nearest neighbors of appropriate size and of opposite charge.



Long-ranged

- ▶ because they attract or repel other ions **beyond** the nearest and next-nearest neighbors.

Covalent bonding

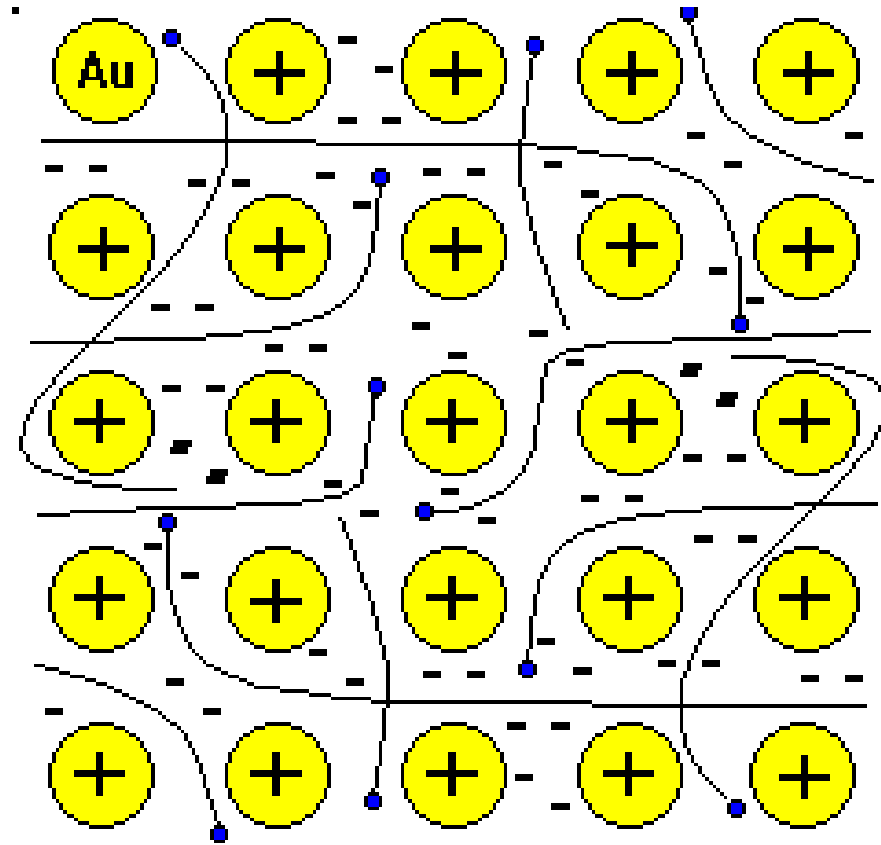
- ❑ Two atoms share one or more pairs of electrons between them to attain a more stable electronic grouping (**Octet electronic structure**). **Examples:** H_2 - N_2 - O_2 - Cl_2 - CH_4
- ❑ Covalent bonds are very **short-ranged** (**operate over very short interatomic separations** (**0.1–0.2 nm**)), highly **directional** and **strong**.
- ❑ **Directional means:** atoms prefer specific orientations (molecular geometry) in space relative to one another (**minimizing repulsion between bonding electrons is driving directionality**). As a result, molecules in which atoms are bonded covalently have definite shapes.

- ❑ **No charge requirements:** no need to have nearest neighbors of opposite charge.
- ❑ Typically covalent bond formation energies range from **200 to 1000 kJmol⁻¹** at room temperature.
- ❑ Covalent bonding can be **single** covalent, **double** covalent, or **triple** covalent depending on the number of pairs of electrons shared.
- ❑ When both shared electrons in a covalent bond come from the same atom, the bond is called a **coordinate covalent bond**

- ❑ Covalent bonds can be either **polar** or **nonpolar**. When the shared pair of electrons is not shared equally, one end of the bond is partially positive, and the other end is partially negative. This produces a bond with two poles called a **polar covalent bond**.
- ❑ Molecules having polar covalent bonds are called **dipolar or polar molecules**. Water is an example of a polar molecule.
- ❑ When two atoms of the same element share one or more pairs of electrons (such as H or N), the bond is called a nonpolar covalent bond. If all the bonds in a molecule are of this kind, the molecule is called a **nonpolar covalent molecule**.

Metallic bonding (Electron sea model)

□ The valence electrons are (**delocalized**) not closely associated with individual atoms, **but instead** move around atoms within the crystal.



□ The individual atoms can "**slip** تنزلق" over one another yet remain firmly held together by the electrostatic forces exerted by the electrons.

- ❑ This is why most metals can be **hammered** تطرق into thin sheets (**malleable** قابل للطرق) or drawn into thin wires (**ductile** قابل للسحب).
- ❑ When an electrical potential difference is applied, the electrons move freely between atoms, and current flows.
- ❑ **Metallic bonds** are sometimes as strong as ionic bonds.
- ❑ In **Metallic bonds** there are
 - ▶ no charge requirements,
 - ▶ no directional requirements, and
 - ▶ long range effects.


Intermolecular Forces and Physical Bonding



Major types

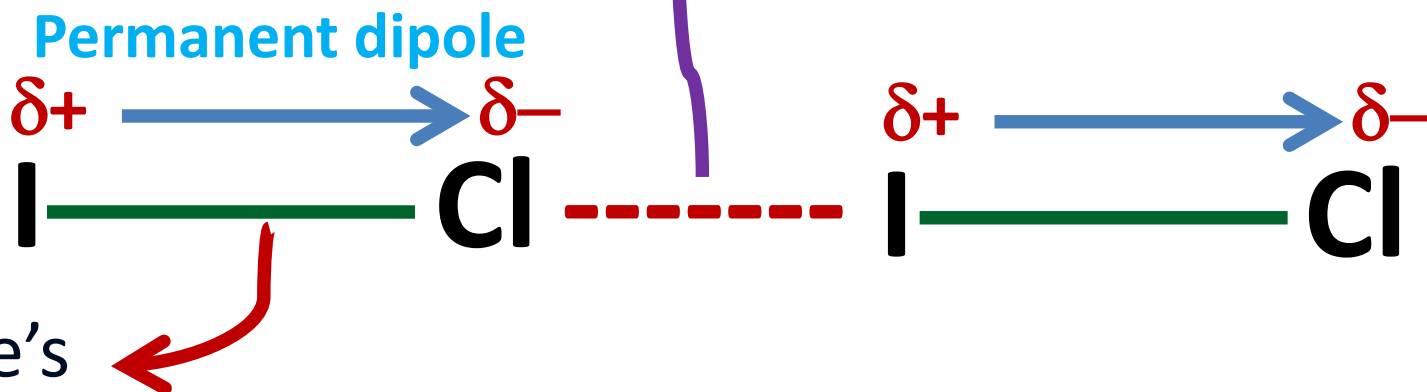
 **Dipole-Dipole forces.**

 **H-bonding**

 **Charge (ion)-Dipole forces.**

 **London Dispersion Forces.**

Dipole-dipole Forces



- ❑ Forces acting between polar molecules (molecules having **permanent** dipole moments)
- ❑ The origin of this force is **electrostatic**. As the **dipole moment** increases, the force increases.
- ❑ It is about **100 times** weaker than ionic interactions and falls off quickly with the distance, as a function of **$1/r^3$** .

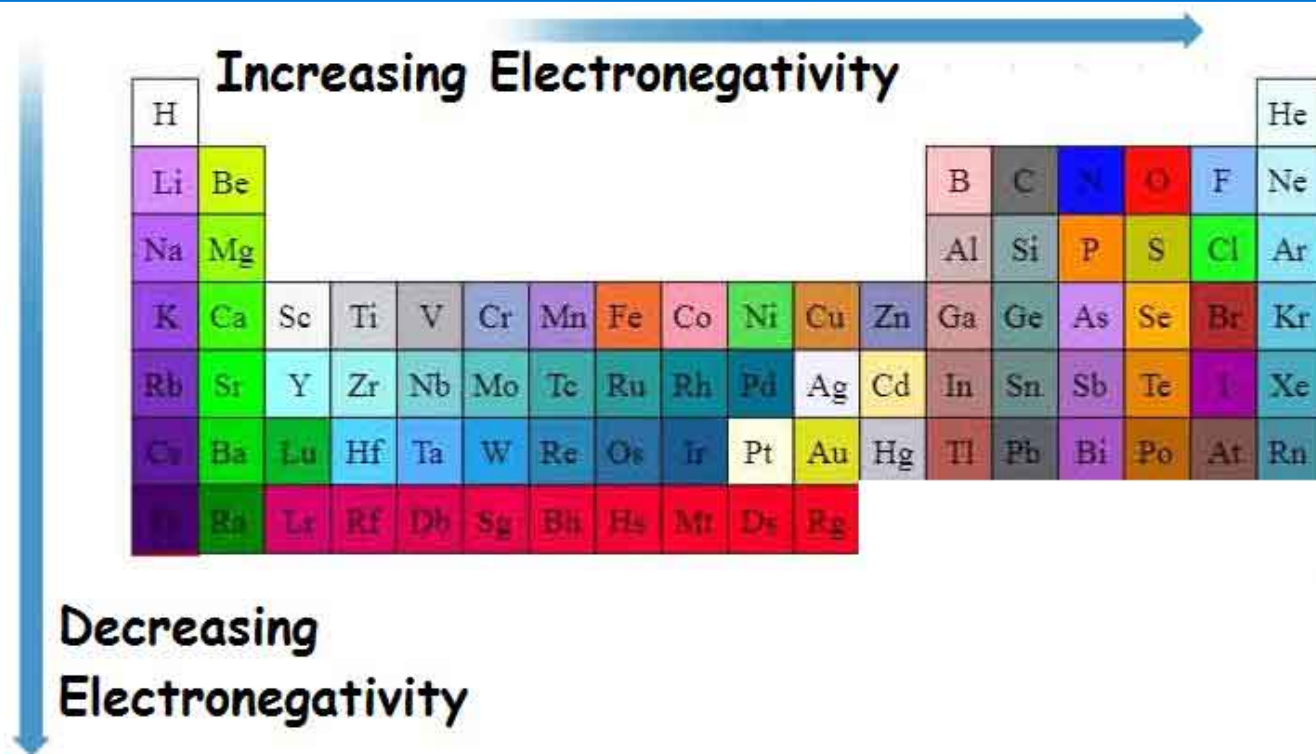
Factors affecting dipole-dipole forces

✚ Bond polarity

✚ The difference in **electronegativity** predicts this polarity

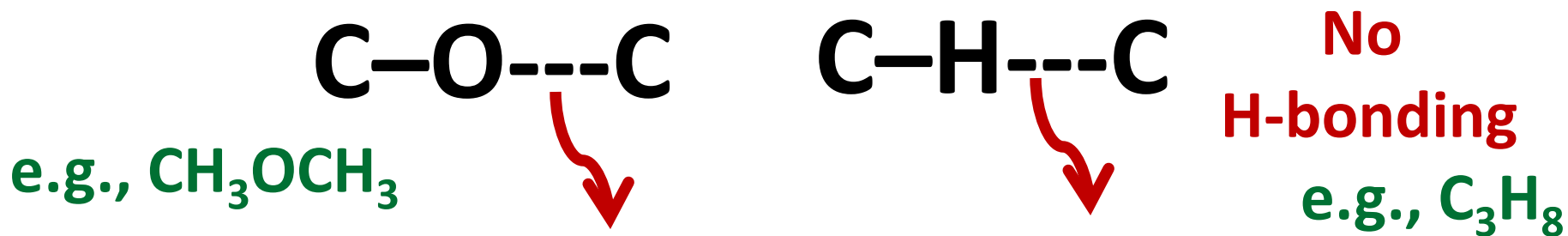
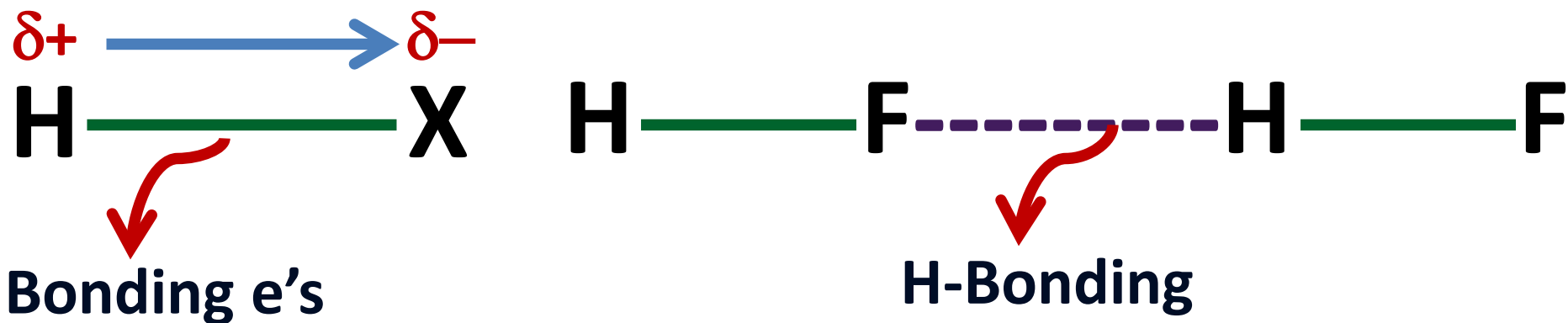
✚ Size of ions (how close they may approach each other) .

✚ The number of **H-bonds** per an atom and per a molecule.



Hydrogen bonding

a special case of **polar interactions** occurring when hydrogen is bonded to a **highly electronegative element** such as oxygen or fluorine, e.g., $\text{O}-\text{H}\cdots\text{O}$.



The slight difference in electronegativity does not permit **H-bonding**

Give reasons

The boiling points of hydrogen compounds of Gp. 5A, 6A and 7A decreases with the molar mass within a group? Or Why NH_3 , H_2O , and HF have the highest BPs?

Answer

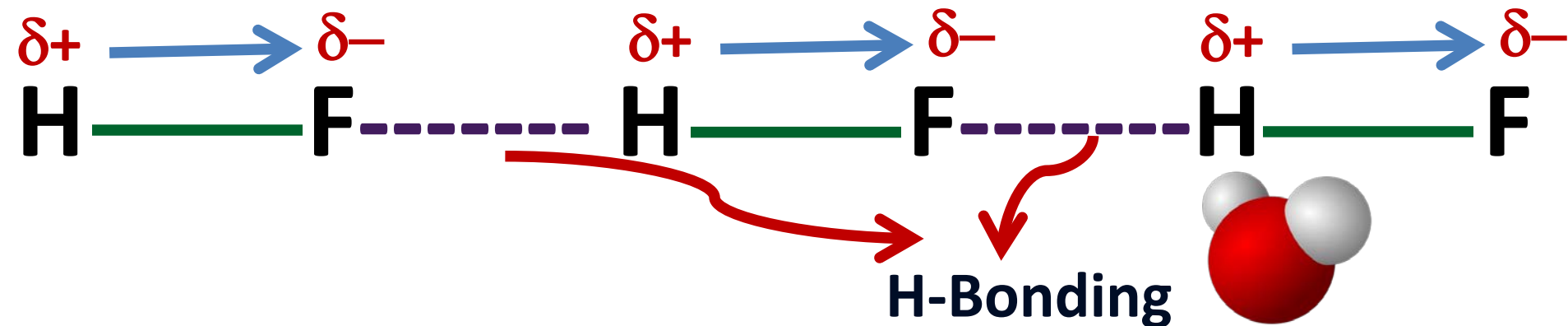
Because as we go down a group, the **electronegativity** of atoms decreases. Therefore, The **strength of H-bonding decreases** (lower energy is required for vaporization)

N 3.0	O 3.5	F 4.0
P 2.2	S 2.5	Cl 3.0
As 2.2	Se 2.6	Br 2.8

Give reasons

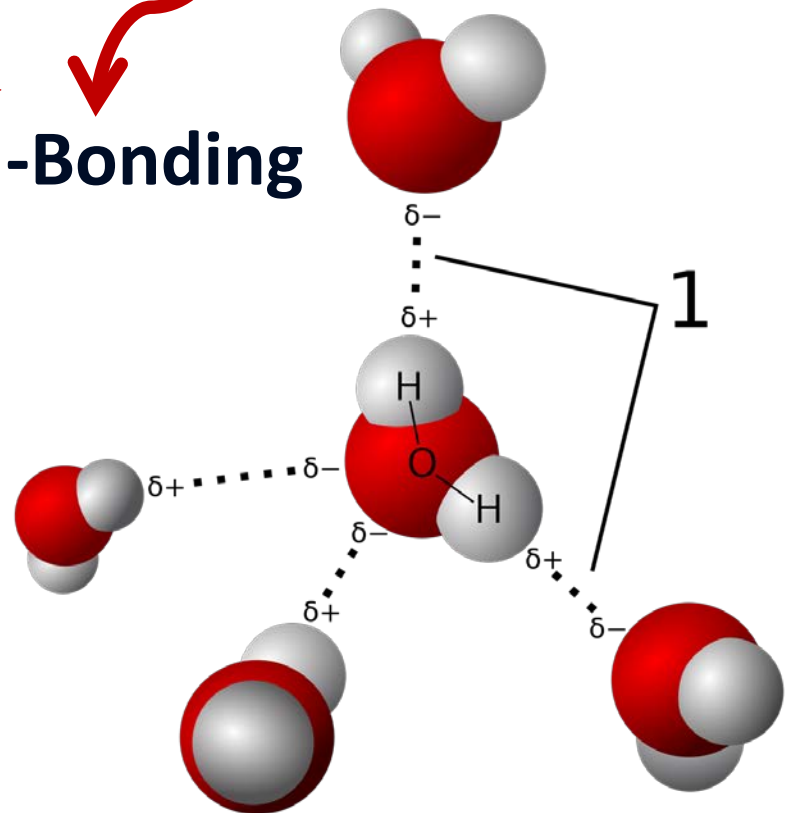
Although fluorine is more electronegative than oxygen, the BP of HF (19.5°C) is lower than that of H_2O (100°C). Why?

Answer



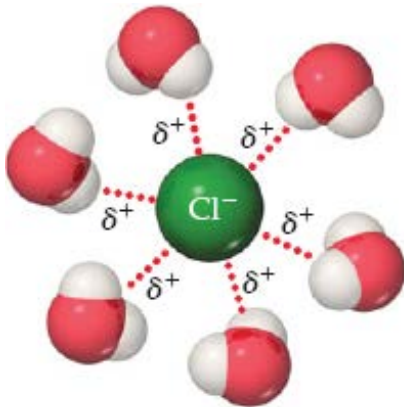
Because each water molecule participate in **4** intermolecular H-bonds but HF has only **2**.

H_2O molecules hold together more tightly.



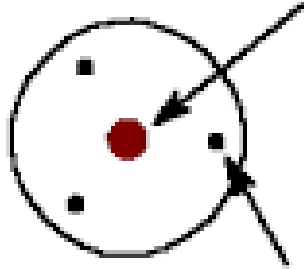
Charge (ion)-Dipole forces

- ❑ originated from interaction of a polar molecule to a charged ion (**cation** or **anion**)
- ❑ is about **10** to **20** times **weaker** than ion-ion interactions, and decreases with distance as **$1/r^2$** .



For **cations** ($^{19}\text{K} \rightarrow ^{18}\text{K}^+$) and **anions** ($^{17}\text{Cl} \rightarrow ^{18}\text{Cl}^-$) of equal charges, cations interact more strongly to dipoles than anions: **as** cations are usually **smaller** than anions in size, their **charge densities** will be higher and therefore interact more strongly.

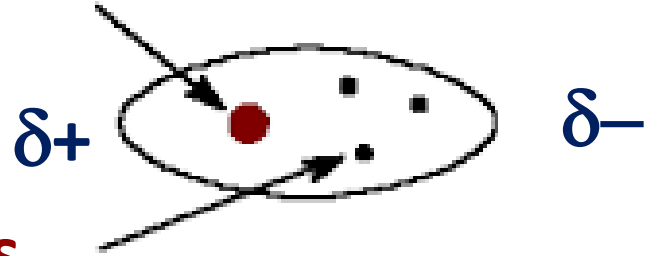
London Dispersion Forces (LDF)



Nucleus

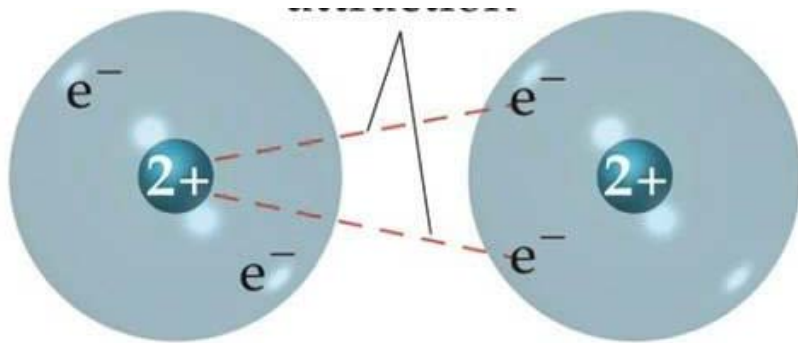
electrons

**Symmetric
distribution**



**Unsymmetrical
distribution**

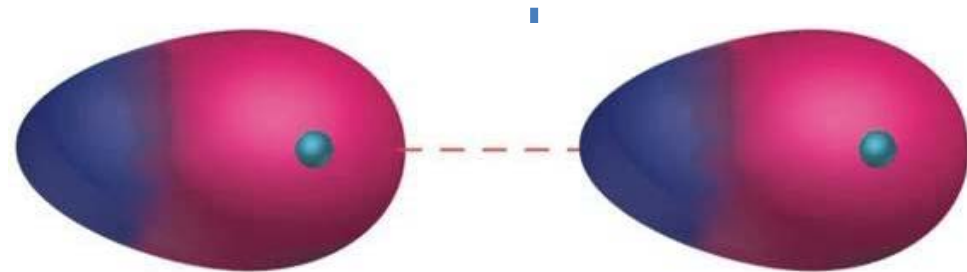
Electrostatic attractions



He atom 1

He atom 2

London Dispersion Forces



$\delta+$

$\delta-$

$\delta+$

$\delta-$

London Dispersion Forces

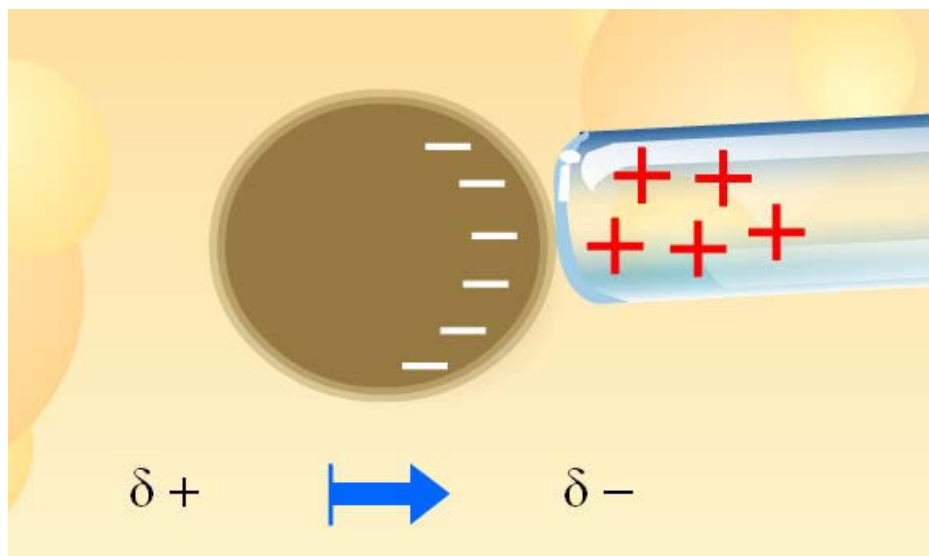
- is a subdivision of **van der Waals forces**
- is the major force in **noble gases** and non polar molecules.
- originates from **induction** الحث in non polar molecules.
 - ✓ The movement of the **valence e's** creates 'transient dipoles' "momentary non symmetrical electron distribution" and these in turn **induce** dipole moments in adjacent molecules.
 - ✓ **The transient dipole** in one molecule can be attracted to the transient dipole in a neighboring molecule, and the result is this **weak, short-ranged** attractive force.
- drop off rapidly with **distance**, decreasing as a function of **$1/r^6$**

Factors affecting LDF

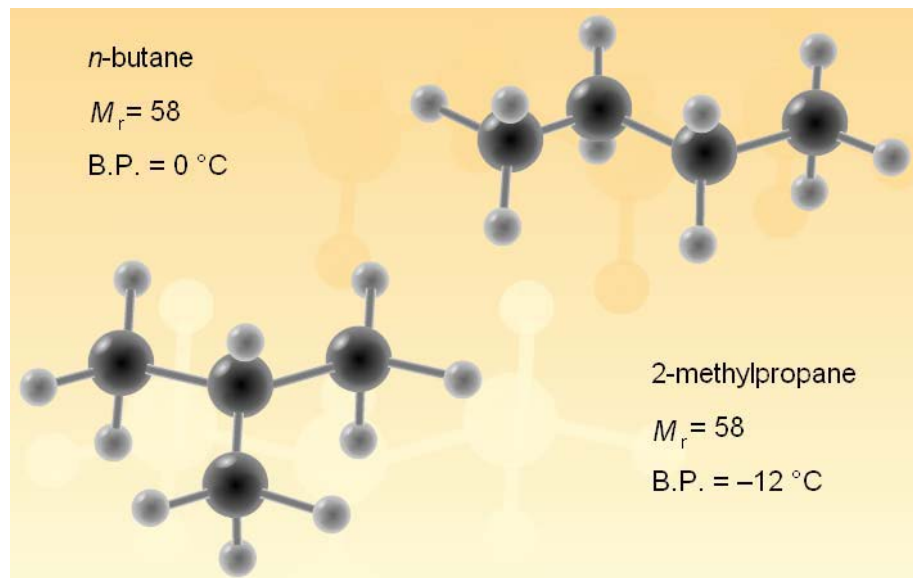
Molecular size

- The **strongest** LDF occur between **large molecules** of large electron clouds that are easily **distorted** or **polarized**.

Polarizability,



Molecular shape



n-Butane/2-methyl propane

Why do butane and 2-methylpropane have different boiling points?

- butane and 2-methylpropane have the **same molar masses**, but 2-methyl propane is **more branched** and thus the **available surface for interaction** with other molecules is smaller.
- This makes the **intermolecular forces** for 2-methylpropane weaker and thus the **boiling point lower**.

Q Why the noble gas elements have low freezing points?

Because for these **weak** interaction forces to be strong enough to produce a solid, the motions of the atoms must be greatly slowed down. This occurs at **low T**

°C
He -269.7
Ne -248.6
Ar -189.4
Kr -157.3
Xe -111.9
Rn -71

Q The freezing point increases as we go from He to Xe in 8A group elements. Explain why?

Because as we go from He to Xe, the atomic size increases and the **polarizability** (chance of occurring a **momentary dipole moment**) increases i.e., London Dispersion Force increases. Therefore, the temperature required for solids to form increases (no need to slow down too much for larger molecules).

°C

He

−269.7

Ne

−248.6

Ar

−189.4

Kr

−157.3

Xe

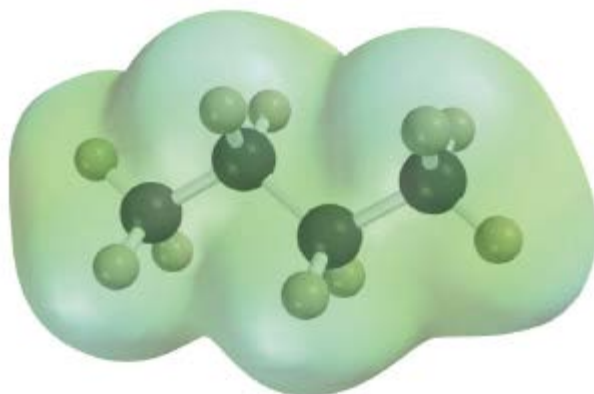
−111.9

Rn

−71

Structure affects properties

Why?

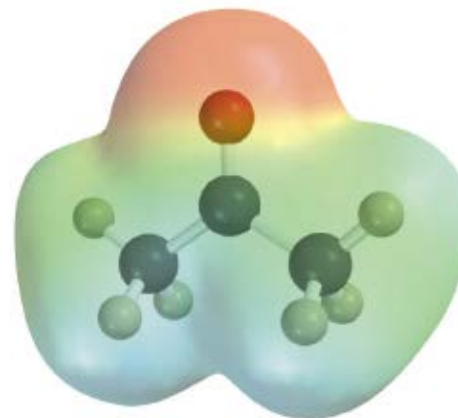
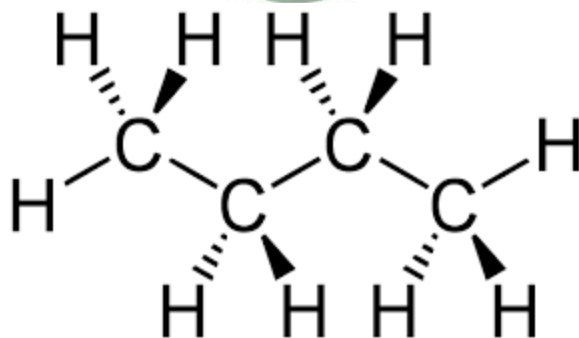


Butane

C_4H_{10}

58 g/mol

B.P. = -0.5°C

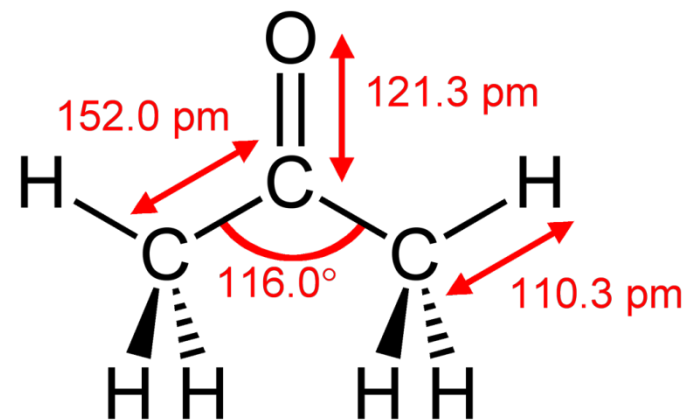


Acetone

C_3H_6O

58 g/mol

B.P. = 56.2°C



Polarizability

Relative Bond Strength

Increasing Bond Strength

London Dispersion, e.g., CH_4 , CCl_4 , Br_2 , F_2

Dipole-dipole, e.g., CH_3F , HBr







H-Bonding, e.g., NH_3 , CH_3OH , HCOOH

Ion-dipole, e.g., NaCl dissolved in H_2O

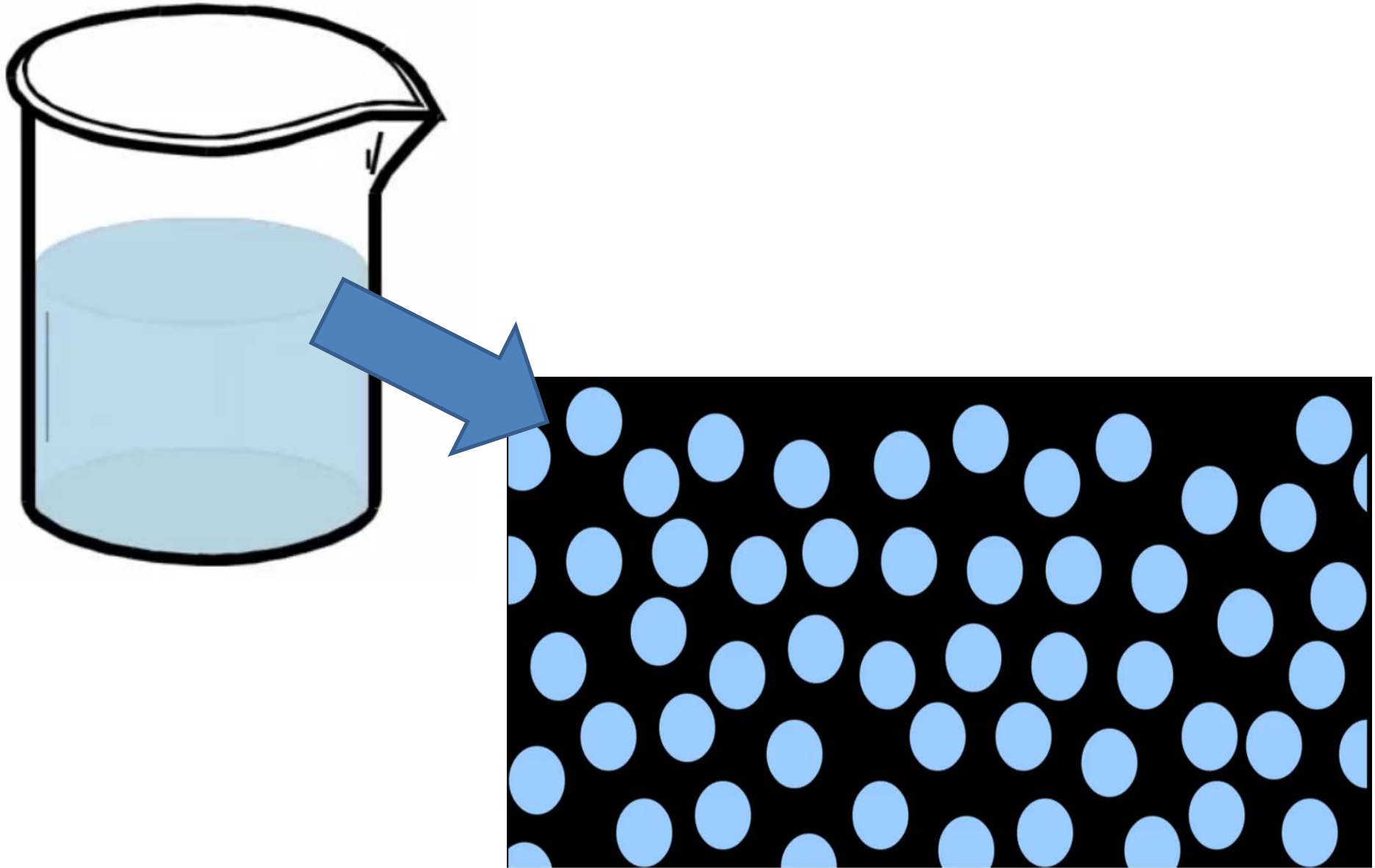
Ionic bonding, e.g., KBr , NH_4NO_3

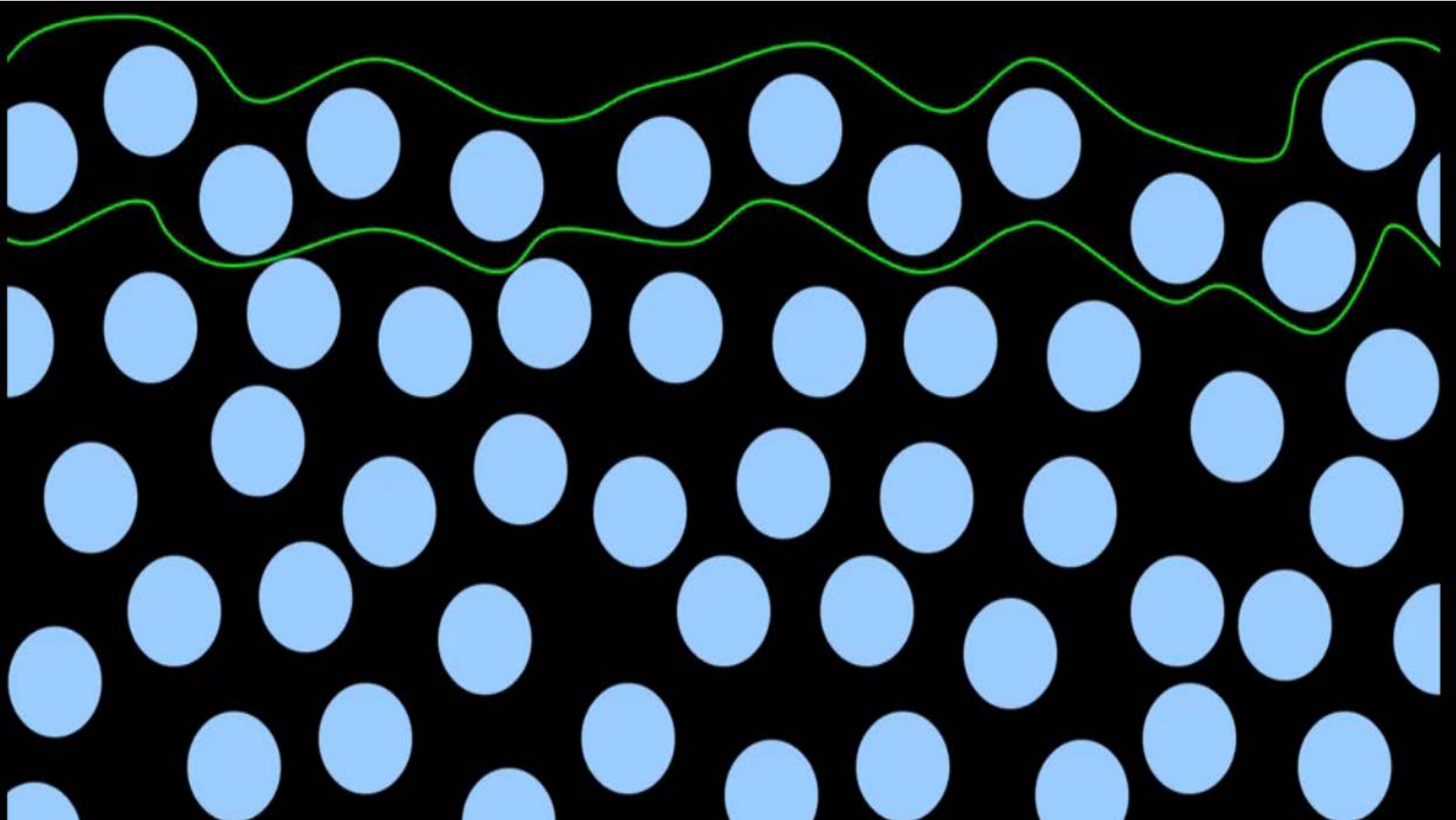
Why is I_2 a solid whereas Cl_2 is a gas? **Size effects**

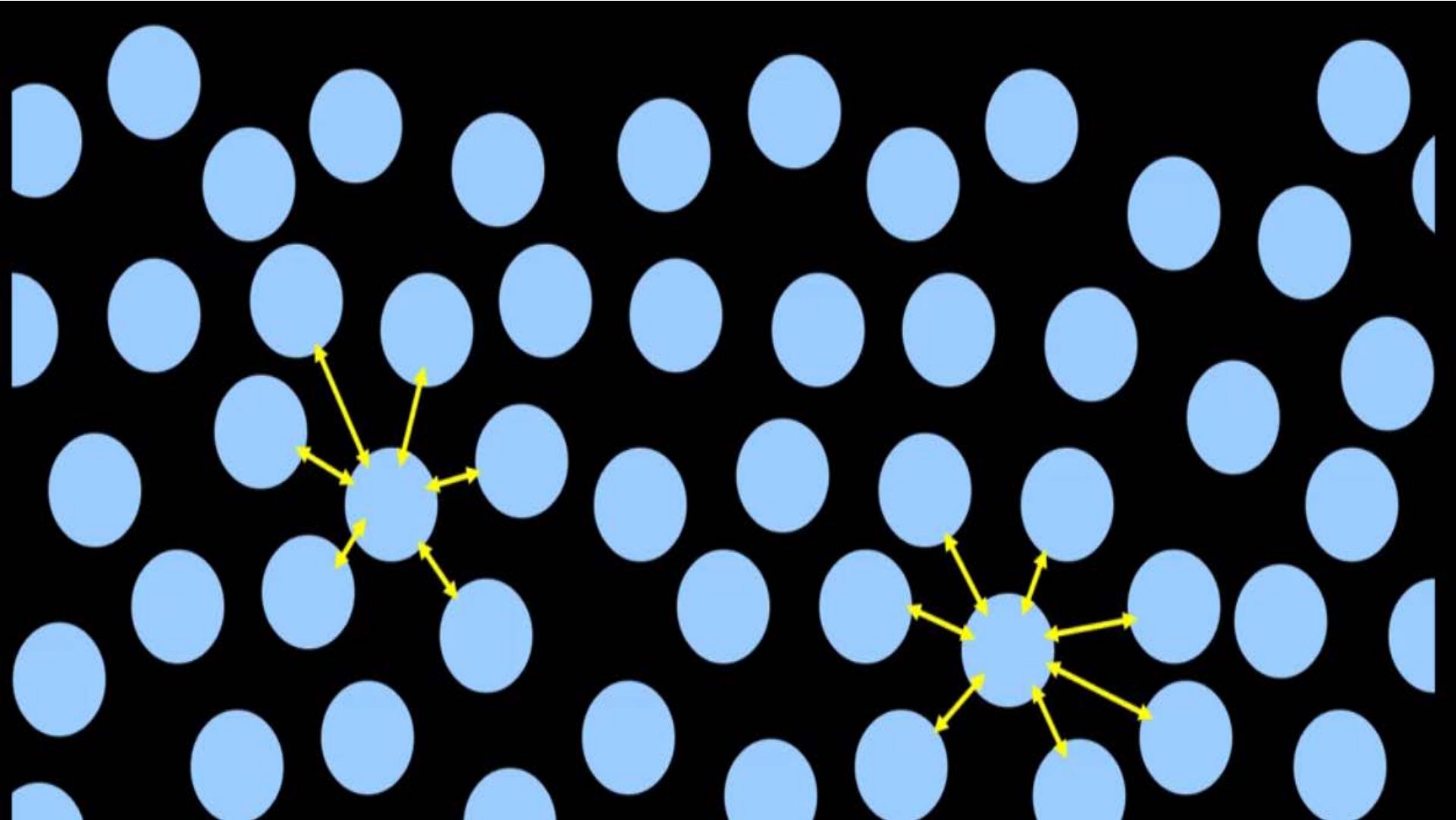
Compounds may involve several bonding

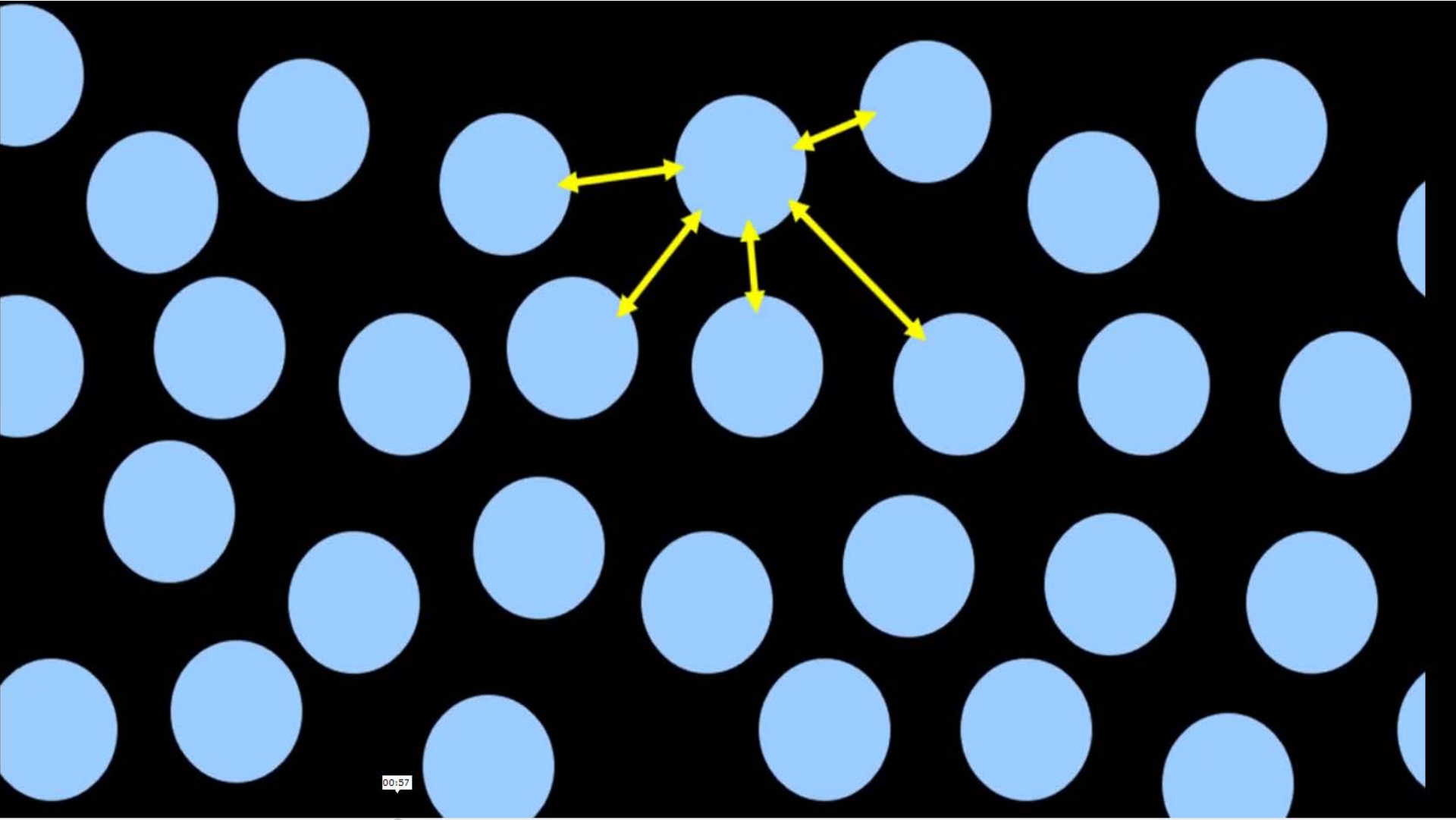
	Dispersion	Dipole-dipole	H-bonding
Non-polar Compounds			
Polar Compounds			
Compounds capable to form H-bonding			

Surface tension, γ Jm^{-2} or Nm^{-1}

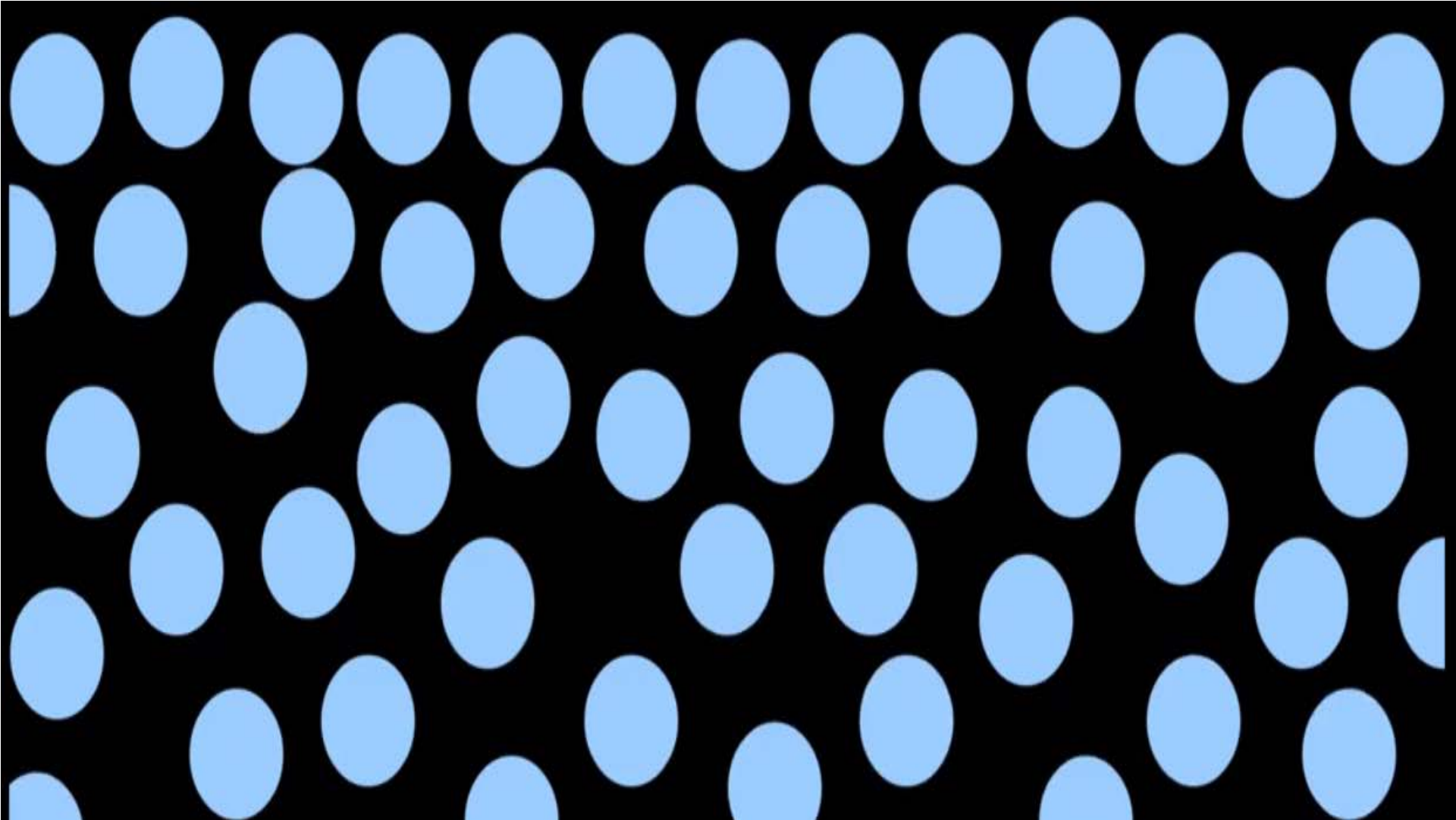


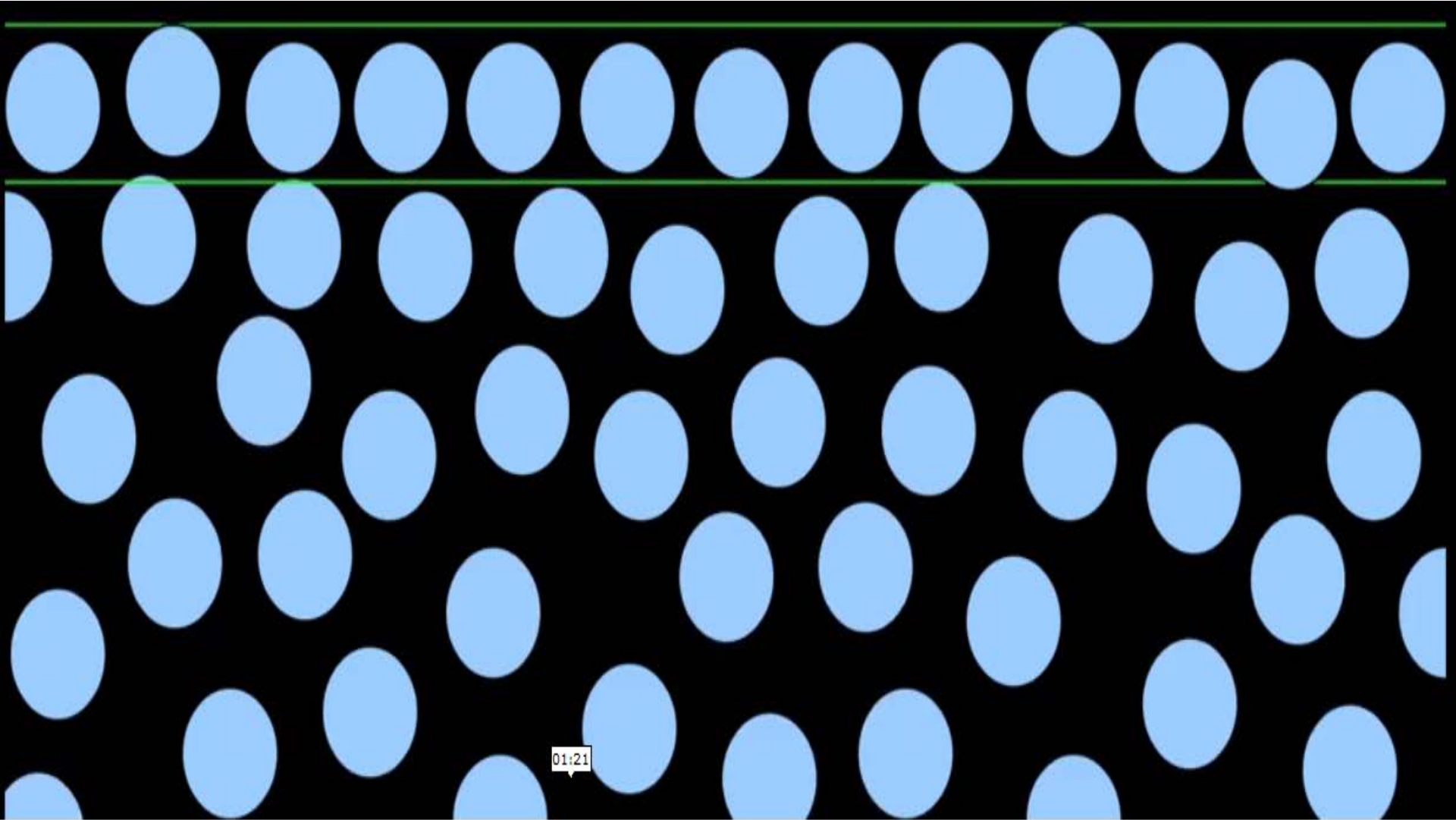




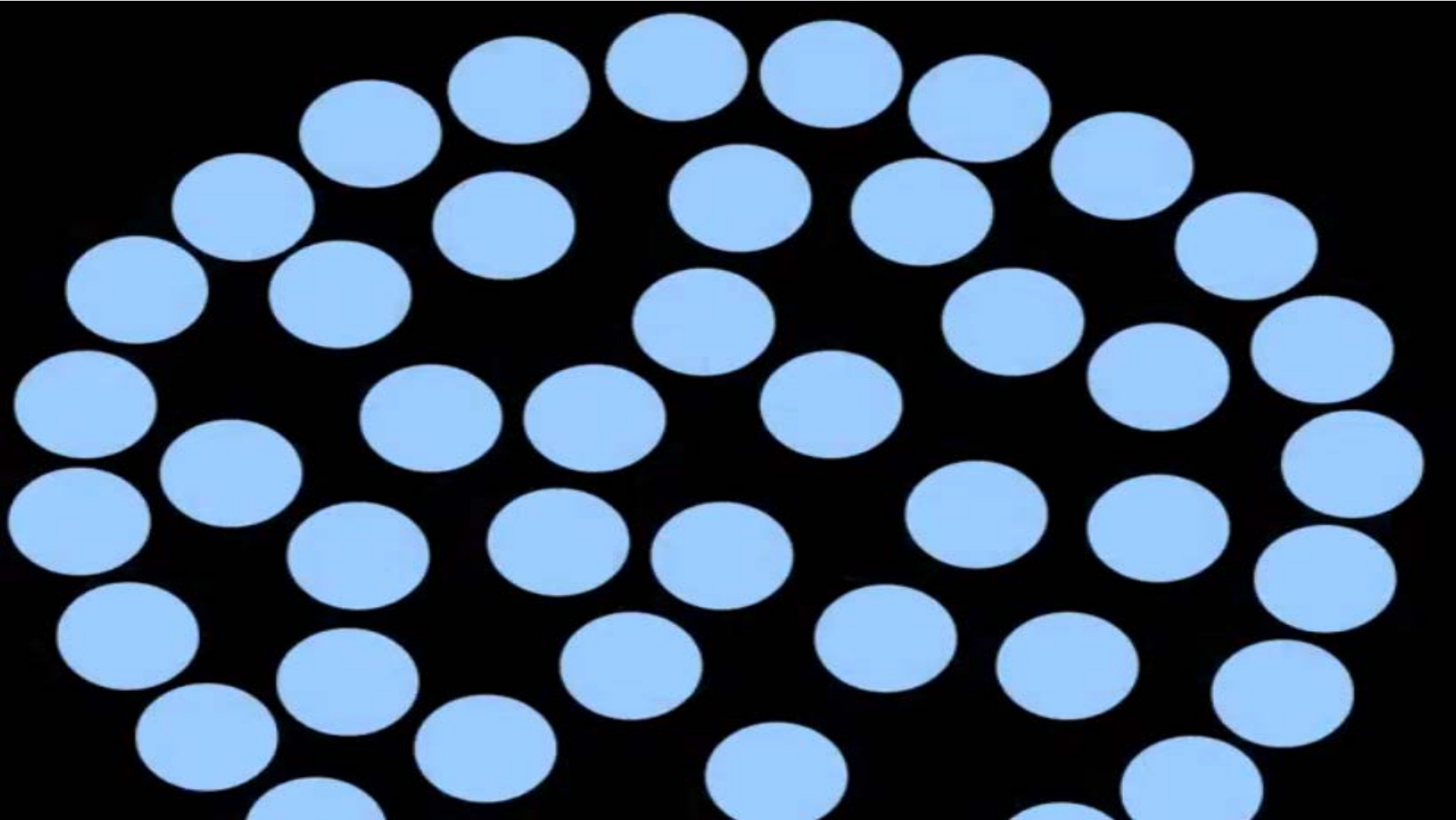


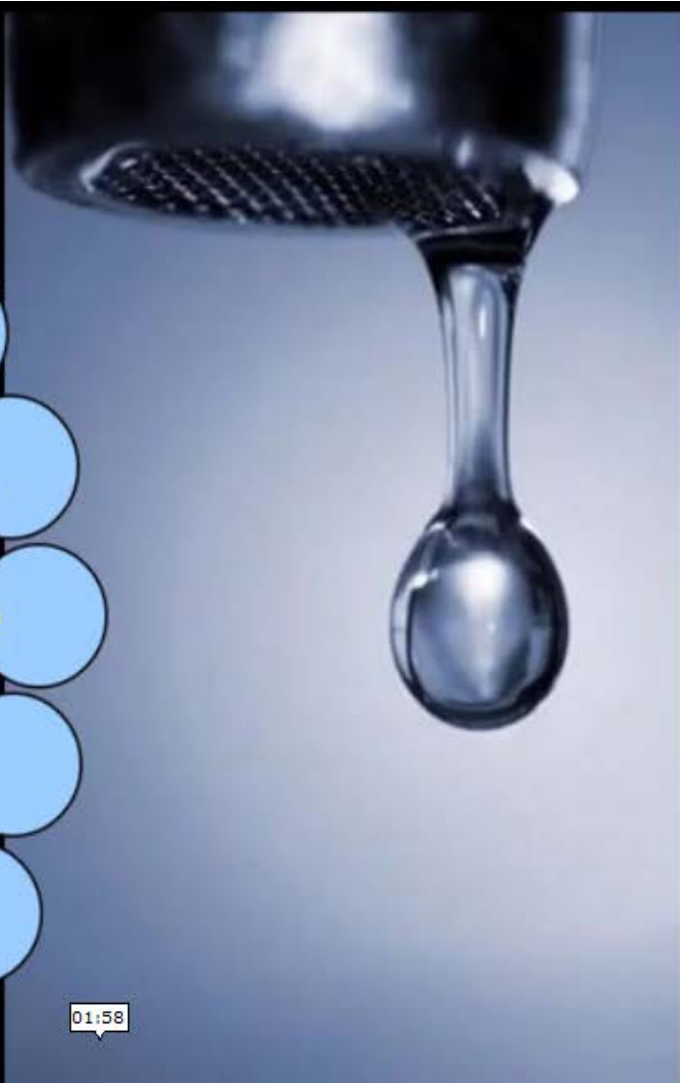
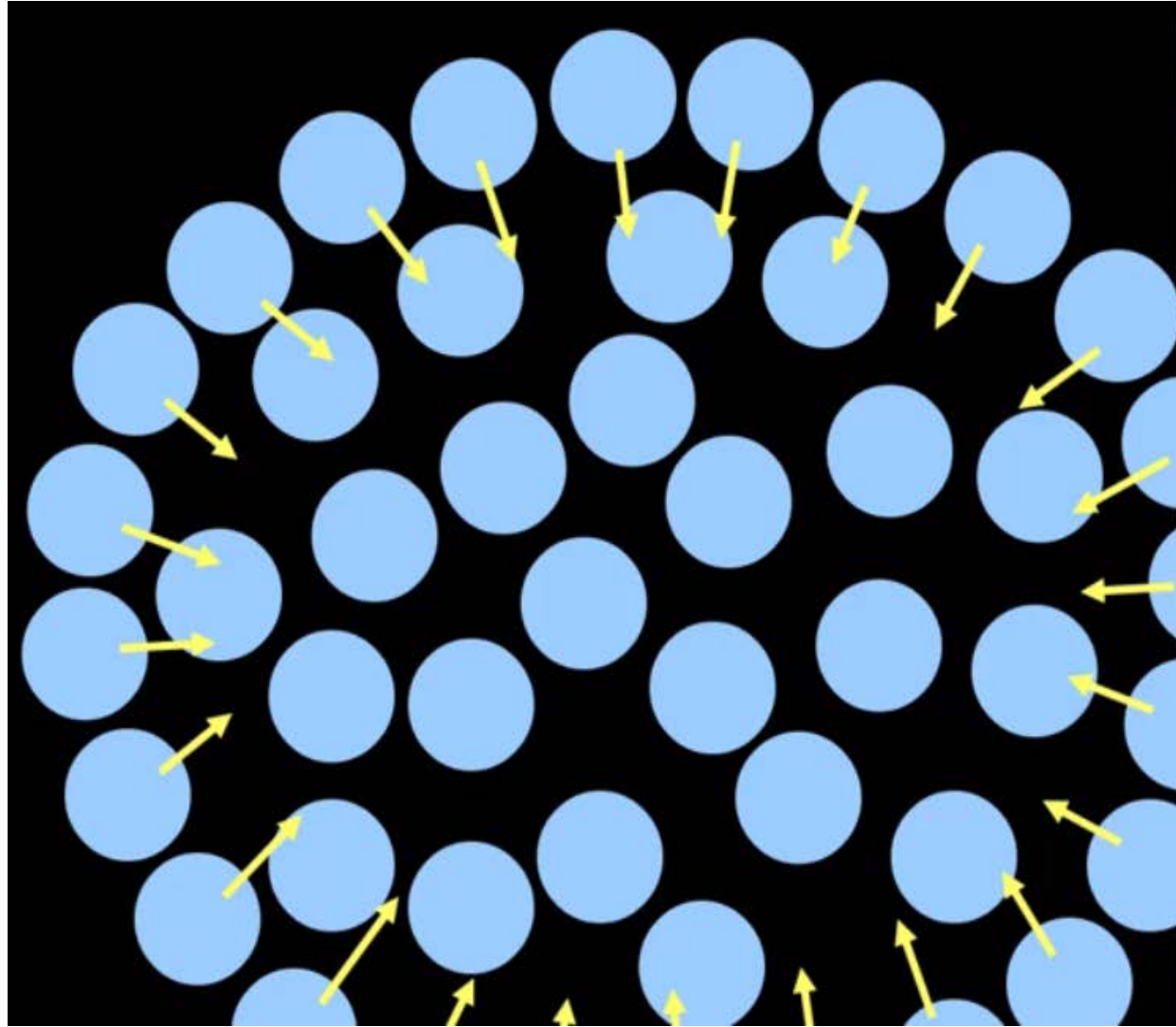
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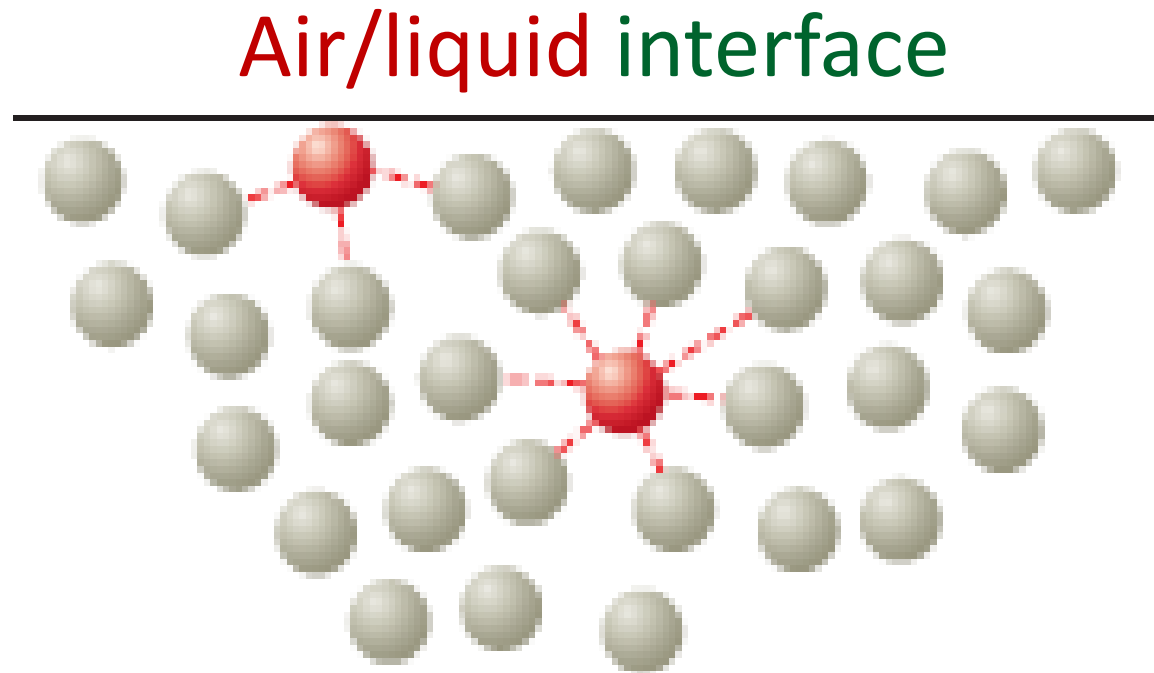


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Surface tension, γ Jm^{-2} or Nm^{-1}

- ▶ the **resistance** of a liquid to an **increase** in its **surface area**.
- ▶ is measured by the amount of **energy** required to stretch or **increase** the surface by **unit area**.

When a liquid is poured onto a solid surface, it tends to bead as droplets!!!!



✚ The effect of **unequal forces** on the surface molecules tends to **draw** them into the body of the liquid and causes a droplet of liquid to assume the shape that has the minimum surface area—a **sphere**.

✚ To **increase a liquid's surface area**, molecules must move from the interior of the liquid to the surface. **This requires energy**, since some intermolecular forces must be overcome.

✚ Liquids with relatively **large intermolecular forces**, such as those with **polar molecules**, tend to have relatively **high surface tensions**.

Capillary action

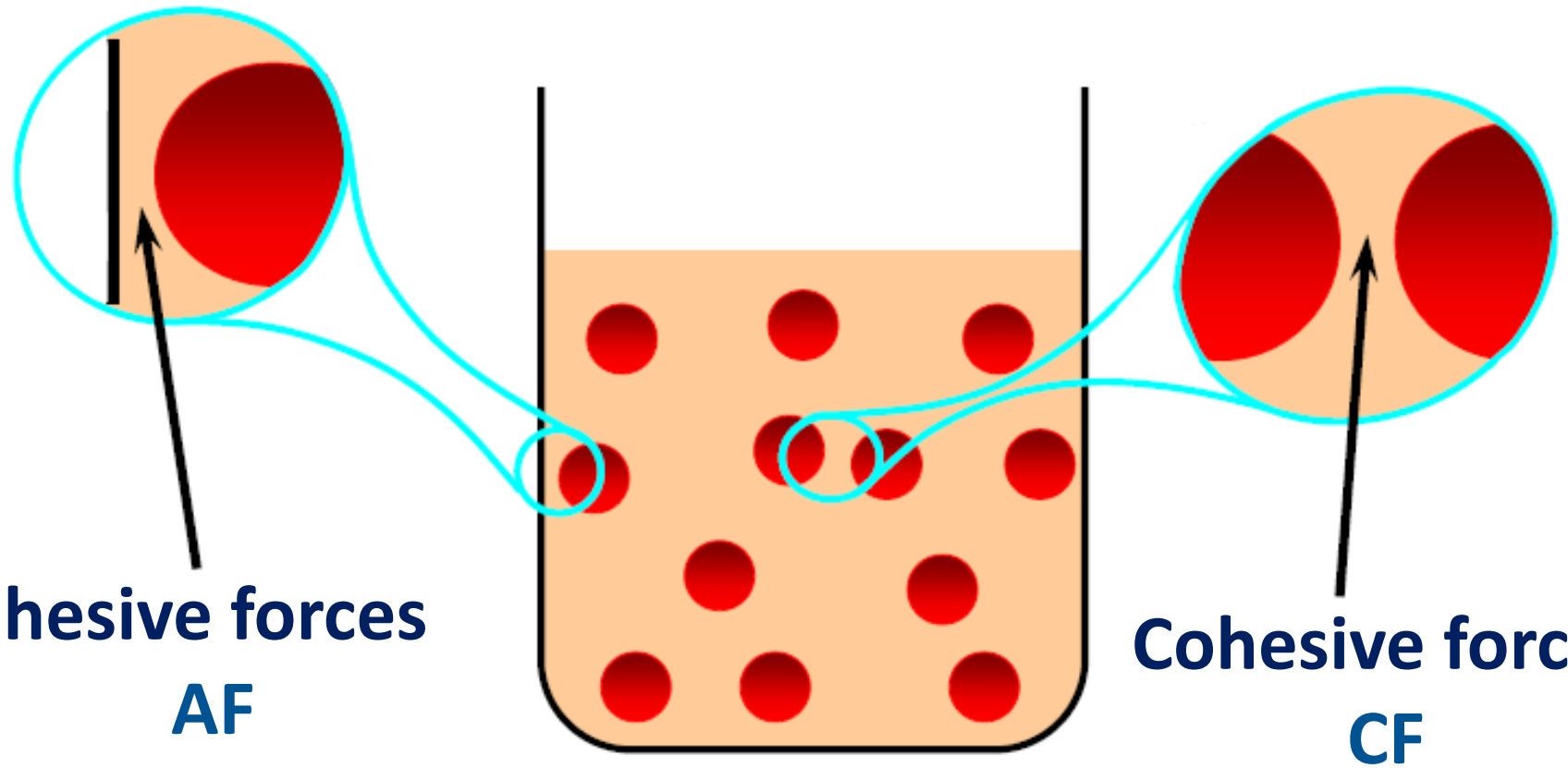
The phenomenon of **spontaneous rising** or **depression** of liquids in a **narrow capillary tube**

Cohesive forces intermolecular forces among the molecules of the liquid
CF

Adhesive forces forces between the liquid molecules and their container
AF

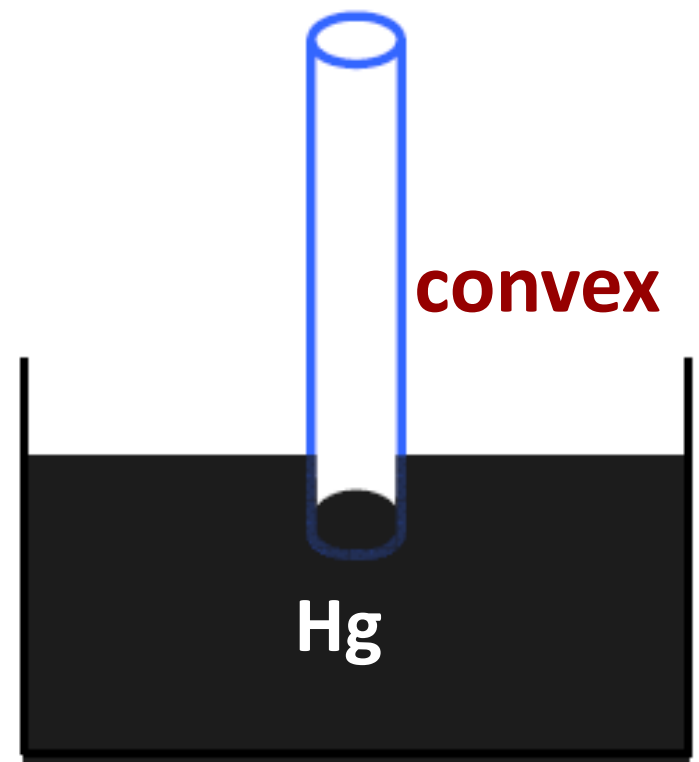
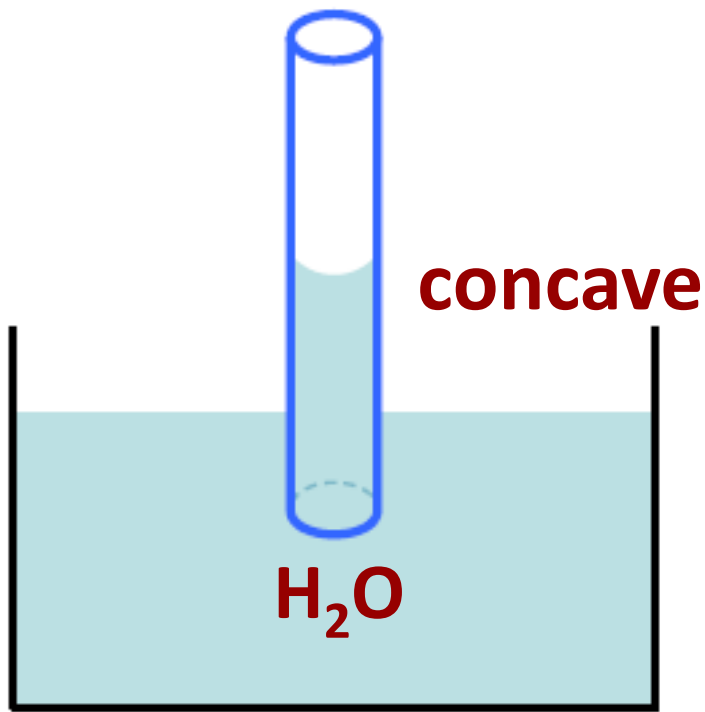
✚ A **glass** surface contains many oxygen atoms with partial **negative** charges that are attractive to the **positive** end of a polar molecule such as water.

Cohesive/Adhesion forces



Adhesive forces
AF

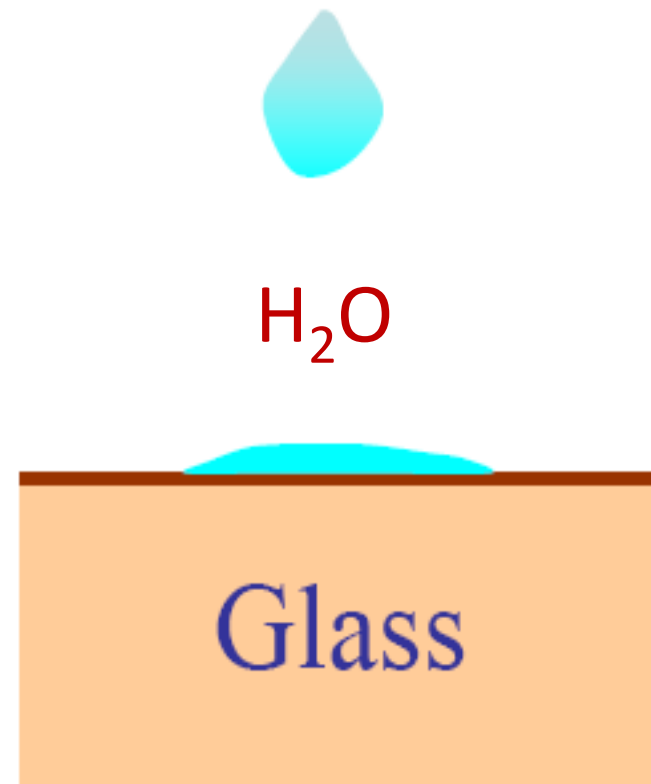
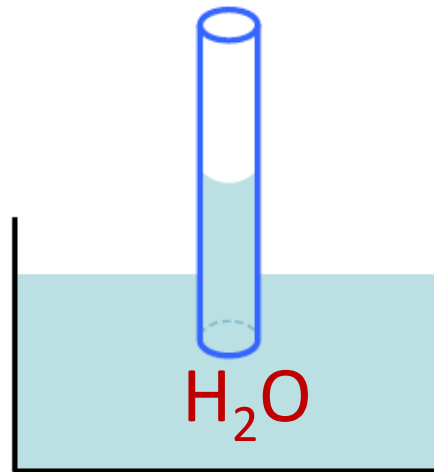
Cohesive forces
CF



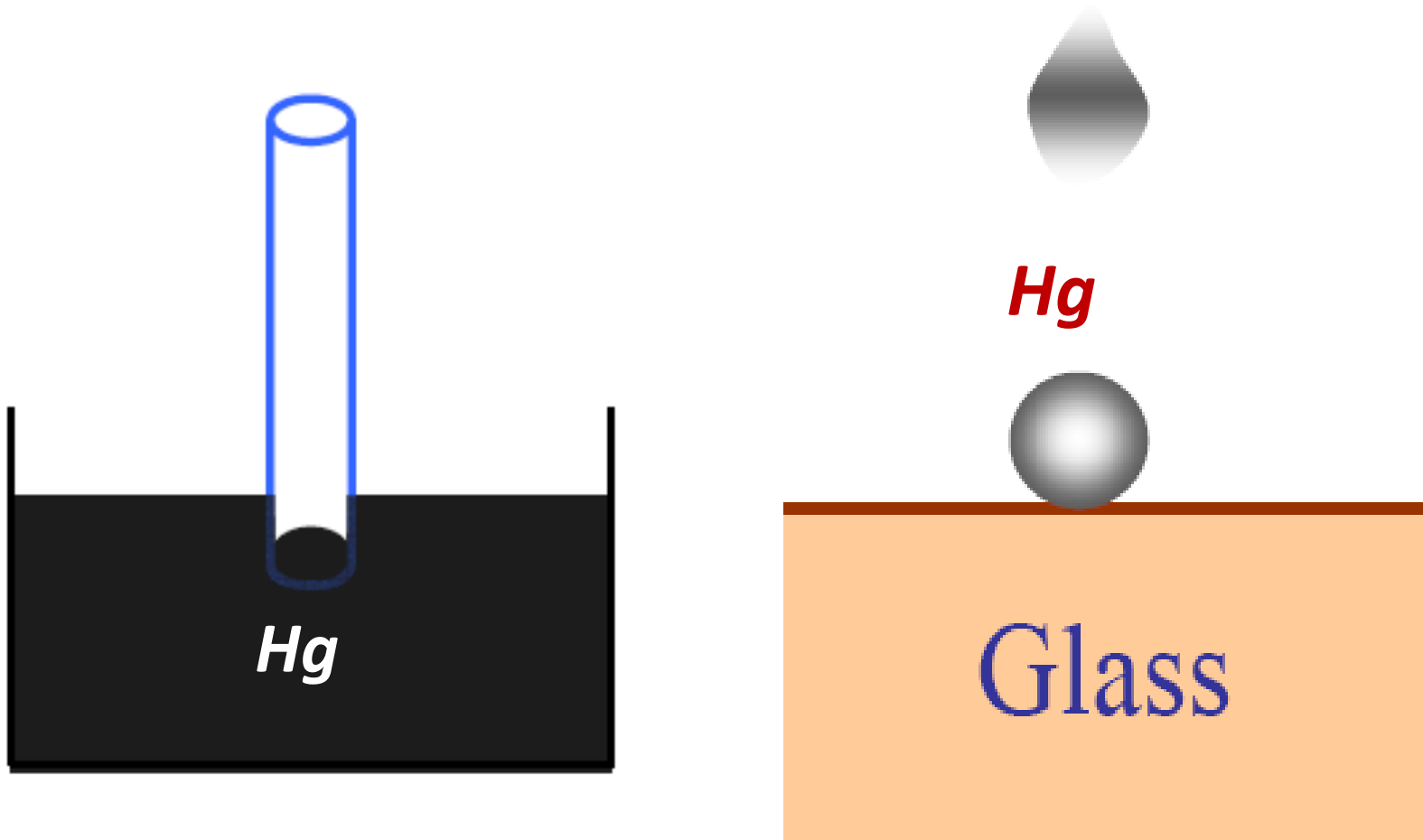
- ▶ This ability of water to “wet” glass makes it creep up يرتفع the walls of the tube where water surface touches the glass.
- ▶ This tends to increase the surface area of water, which is opposed by CF that try to minimize the surface.

- ▶ Because water has both **strong** (intermolecular) CF and **strong** AF to glass, it “pulls itself” up a glass capillary tube (a tube with a small diameter) to a height where the **weight of the column of water** just balances the water’s tendency to be attracted to the glass surface.

- The **concave** shape of the meniscus shows that **water’s AF** toward the glass are **stronger** than its CF.



- ▶ A non polar liquid such as mercury shows a **convex meniscus**. This behavior is characteristic of a liquid in which the **CF are stronger than the AF** toward glass.



Factors affecting γ

✚ **Nature of materials** and interfaces (intermolecular forces).

✚ **Temperature:** As $T \uparrow$, $\gamma \downarrow$

✚ **Additives**

✚ **inorganic salts** affect a little γ

✚ **organic additives** as soap, alcohol, acids, and esters lower γ of water

Viscosity, η

a measure of a liquid's resistance to flow. Unit of η is **poise (P)**

$$1\text{P} = 0.1 \text{ kg m}^{-1}\text{s}^{-1} = 1 \text{ g cm}^{-1}\text{s}^{-1} = 1 \text{ dyne s cm}^{-2}$$

$$10\text{P} = 1 \text{ kg m}^{-1}\text{s}^{-1} = 1 \text{ N s m}^{-2} = 1 \text{ Pa s (SI Unit)}$$

Factors affecting viscosity

1- Nature of the fluid: liquids with large intermolecular forces tend to be highly viscous.

- ▶ H_2O is highly viscous because of H-bonding.
- ▶ Glycerol (**has 3 – OH gps**) has an unusually high viscosity **due mainly to** its high capacity to form hydrogen bonds

2- Molecular mass and complexity:

leads to higher viscosity because very large molecules can become entangled with each other.

✚ Gasoline, **a non-viscous liquid**, contains hydrocarbon molecules of the type $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$, n varies from about 3 to 8.

✚ Grease, **which is very viscous**, contains much larger hydrocarbon molecules in which n varies from 20 to 25.

3- Temperature: Viscosity decreases ↓ rapidly with temperature ↑.

4- Additives: Addition of highly ionized salts decreases viscosity

Addition of suspended matters increases viscosity

Solids

Solids

Ionic

Molecular

Macromolecular

Metallic

Ionic

**Dipole-Dipole
London dispersion**

Giant

Covalent

**Delocalized
covalent**

**NaCl
MgO
CaCO₃**

**Sucrose
I₂
water**

**Diamond,
C
SiO₂**

**Cu
Na
Mg**

Ionic solids

- High mp, conductors in molten state or water solution.
- Usually **solids at 25°C** and soluble in water, insoluble in organic solvents
- Simple solids as **NaCl** and **MgO** melt without change in chemical composition.
- Polyatomic ionic solids as **CaCO₃** decompose before melting

Hydroxides  **Metal oxide** **H₂O gas**

Carbonates  **Metal oxide** **CO₂ gas**

Hydrated Salts  **Loss some water of crystallization**

Molecular solids

- They are **solids** at room temperature.
- Have **strong** intermolecular forces.
- They include **non-polar** substances of high molecular mass as:



M.wt. = 254

naphthalene

M.wt. = 128

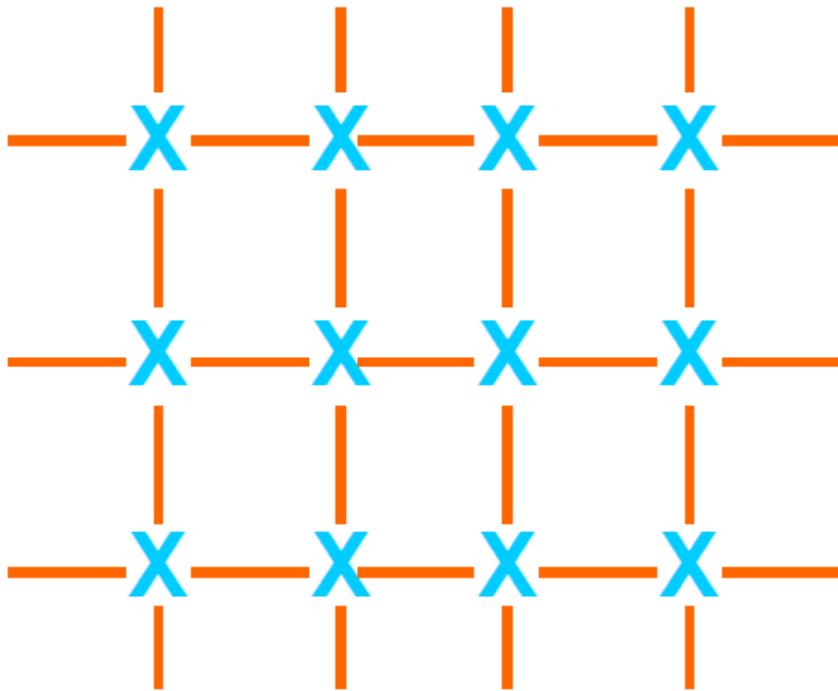
**Others contain hydrogen bonds
as:**

Ice

Urea

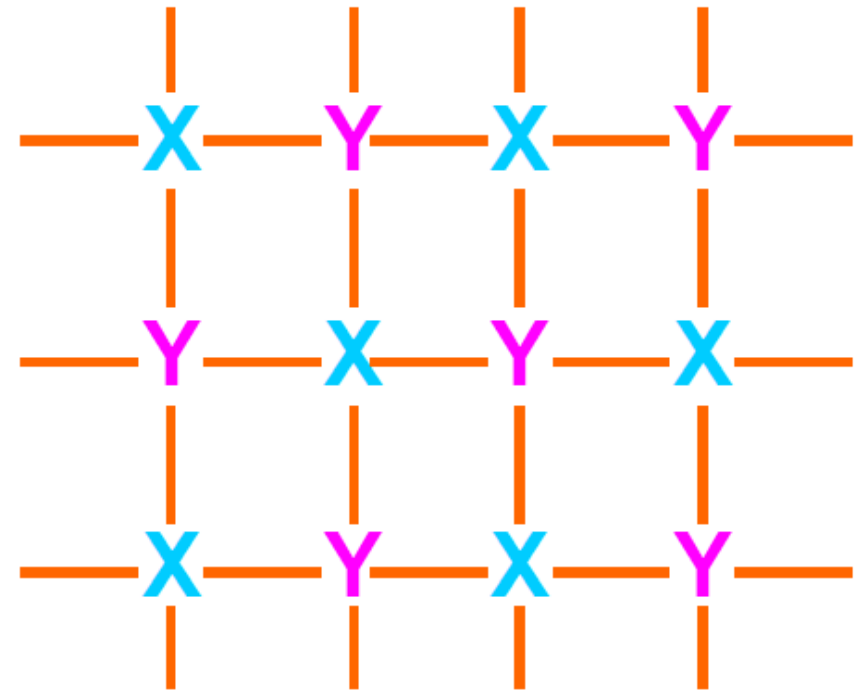
Macromolecular solids

- atoms are held together by a **two dimensional network** of **electron-pair bonds**, such as:



Element

Diamond, C

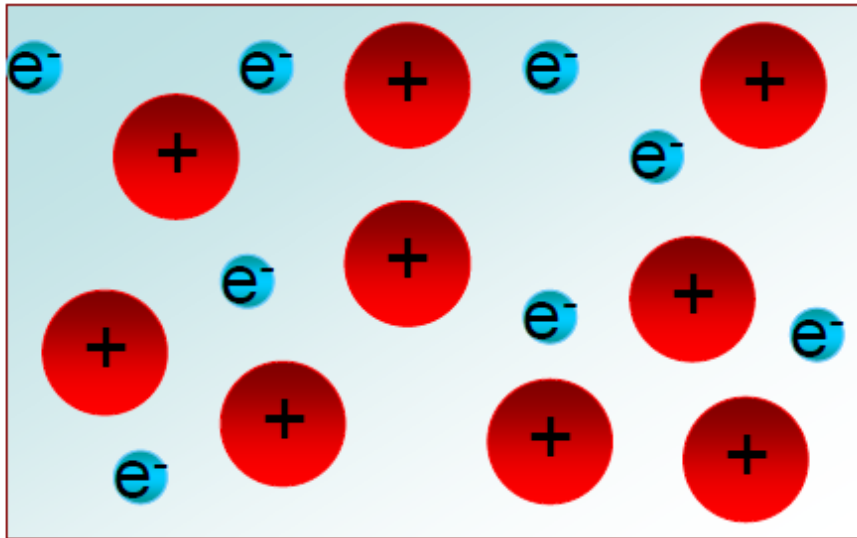


Compound

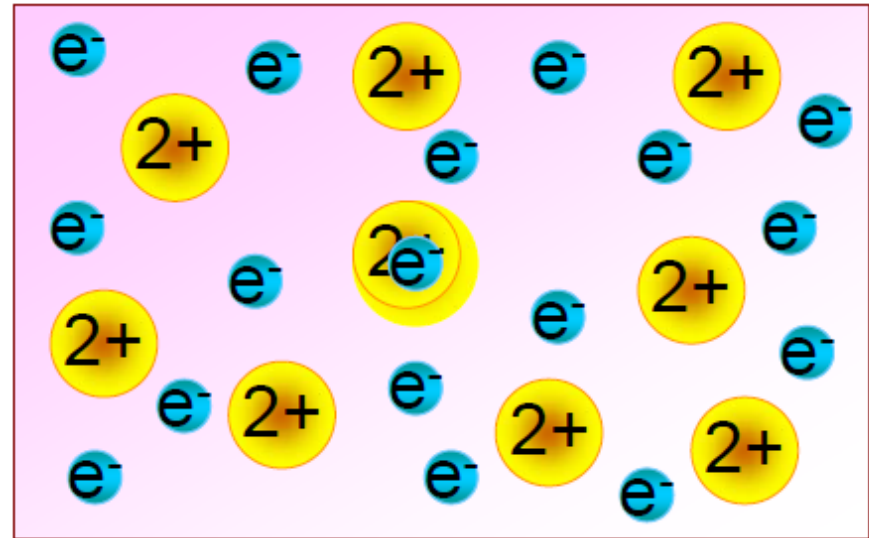
SiO₂

Metallic solids

- good conductors of electricity (**electron sea model**) and heat.
- ductile and malleable.
- their surfaces are good reflectors of light.



Na metal

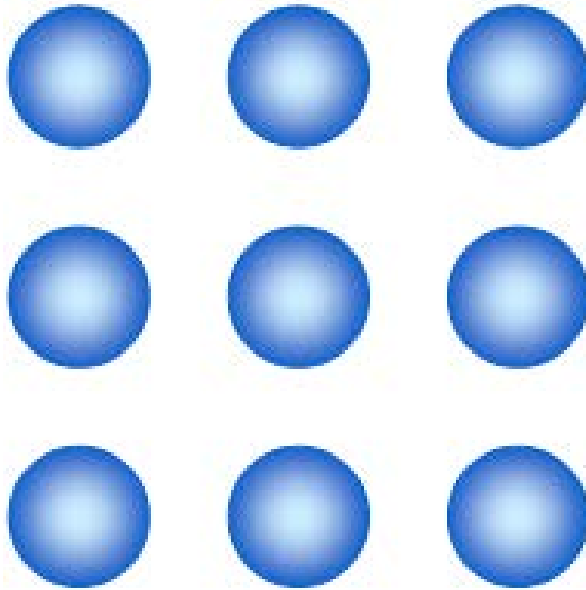


Mg metal

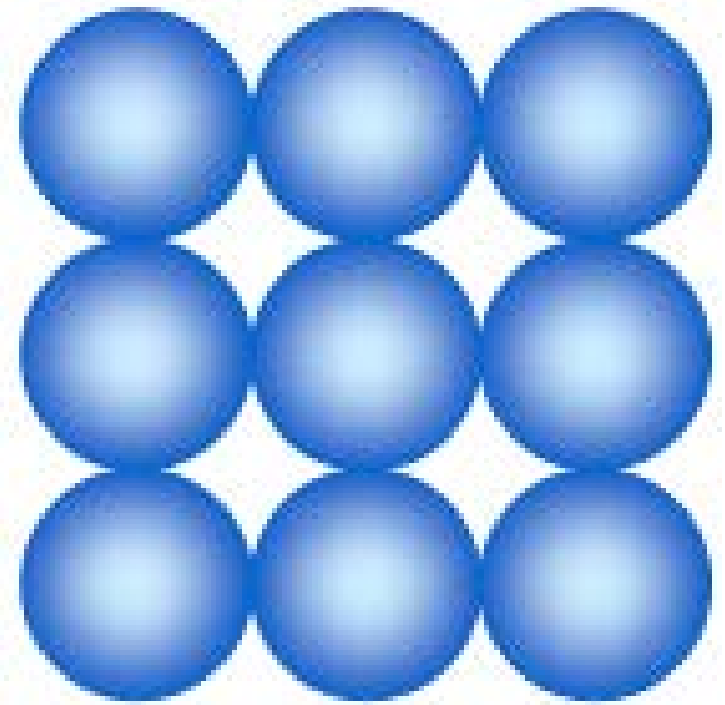
The **lattice energy** of Mg is greater than that of Na.

Structure and Bonding in Metals

- Metals are characterized by **high thermal and electrical conductivity**, **malleability** **قابلية الطرق** (hammered into thin sheets), and **ductility** **قابلية السحب** (drawn into thin wires) because of the non-directional covalent bonding in metallic crystals.
- A metallic crystal can be pictured as containing **spherical atoms** packed together **uniformly** and **most efficiently** using the **available space** and bonded to each other equally in all directions.
Closest Packing

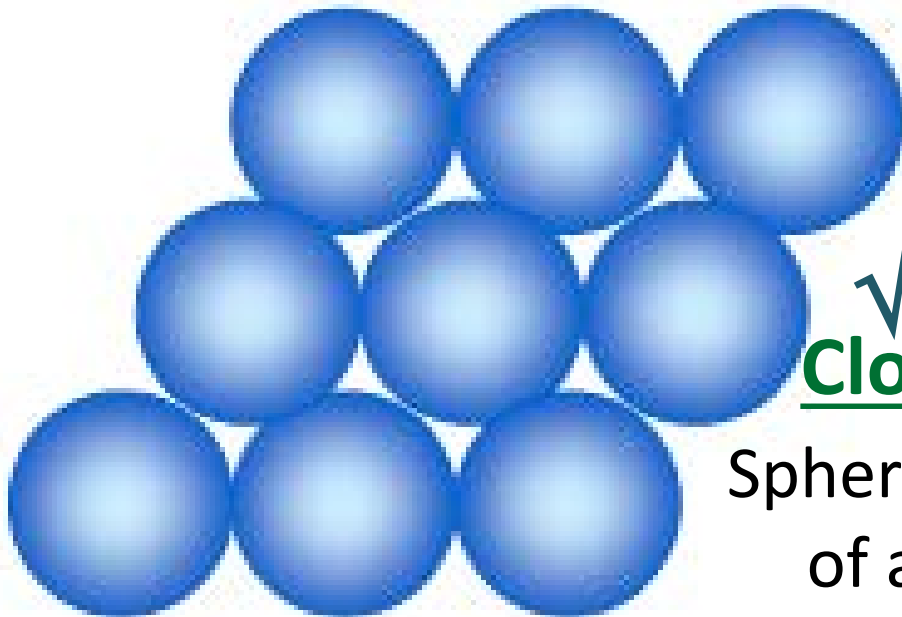


×



Square close Packing

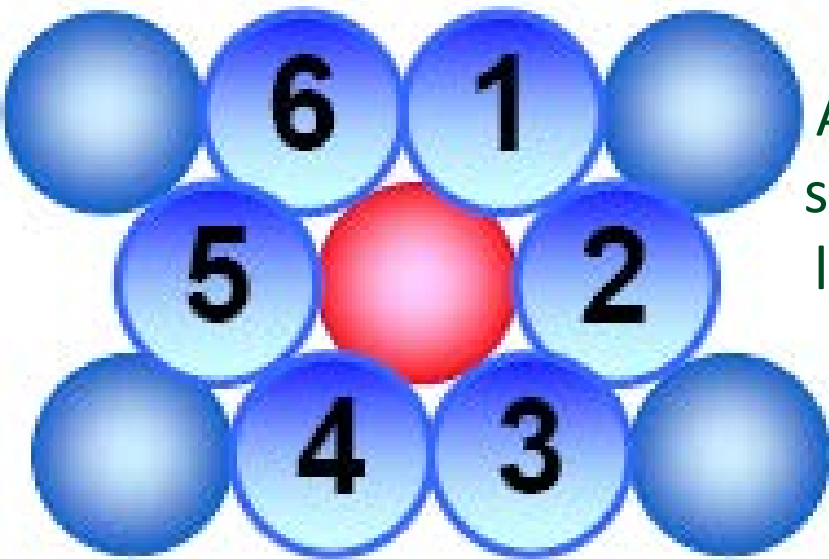
Spheres occupy 52.48 %
of available space



✓
Closest Packing

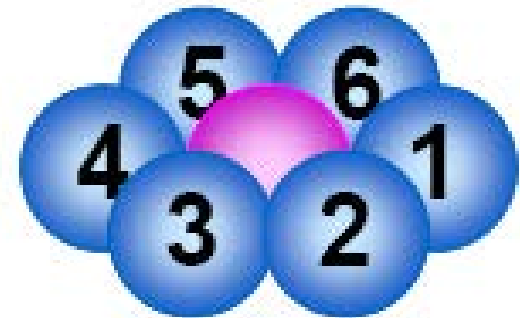
Spheres occupy 60.4 %
of available space

- The spheres are packed in layers, in which each sphere is surrounded by **six others**.
- In the second layer the spheres do not lie directly over those in the first layer. Instead, each one occupies an indentation (or **dimple**) formed by three spheres in the first layer.

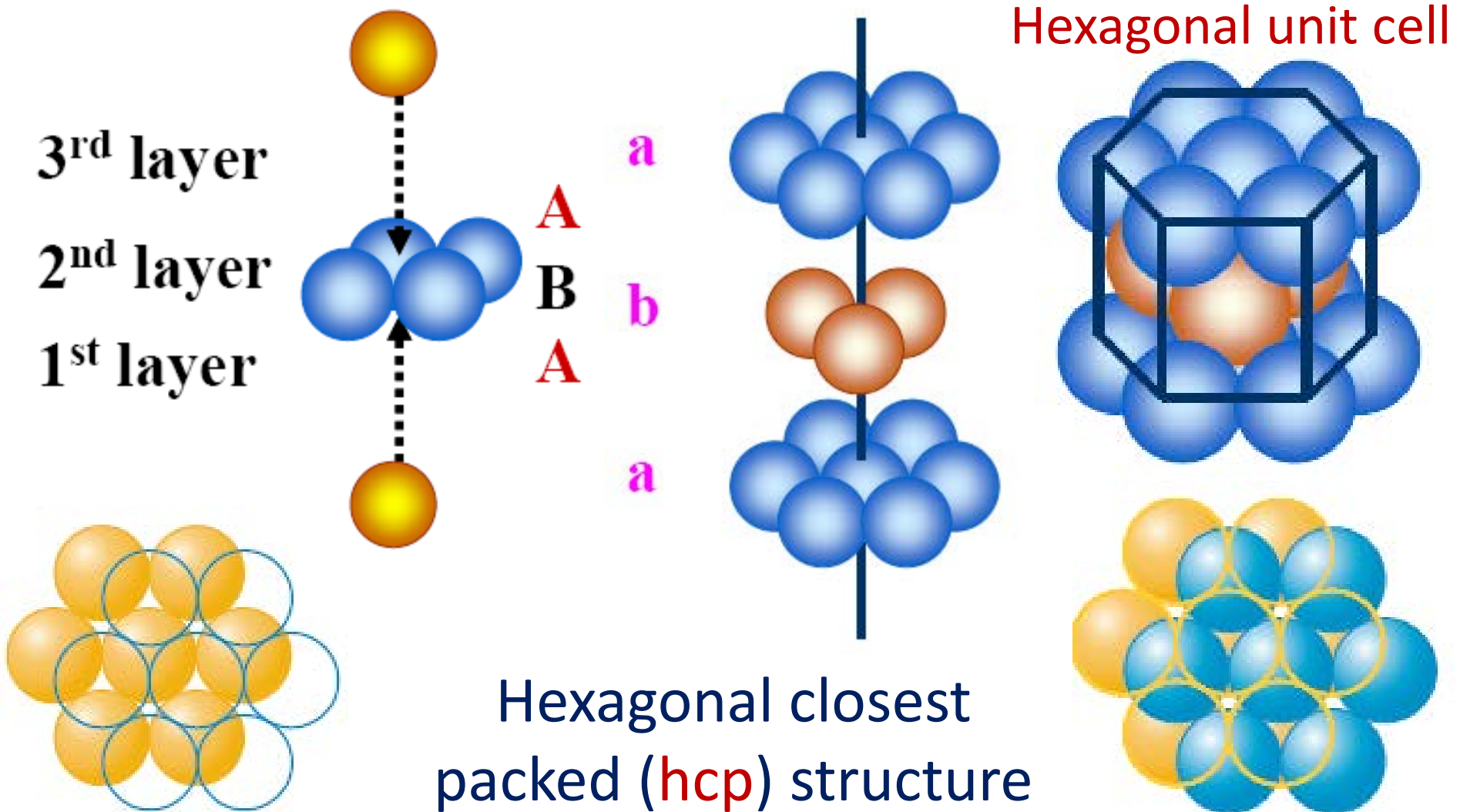


A sphere touches 6
spheres in the same
layer + 3 above + 3
below = 12

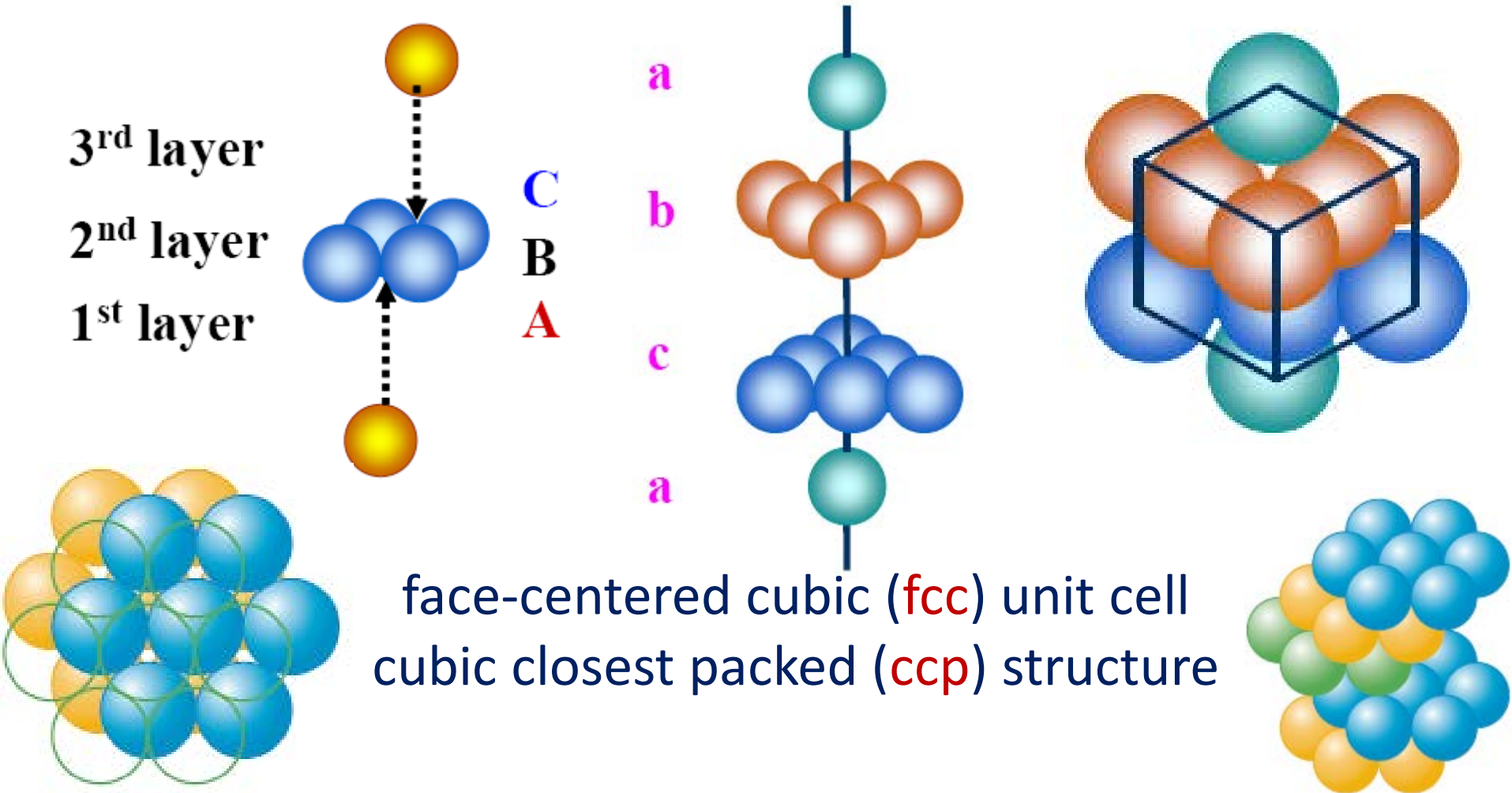
12 equivalent nearest neighbors



- In the third layer the spheres can occupy the dimples of the second layer in two possible ways:
 - Occupying positions so that each sphere in the third layer lies directly over a sphere in the first layer [the **aba** arrangement]

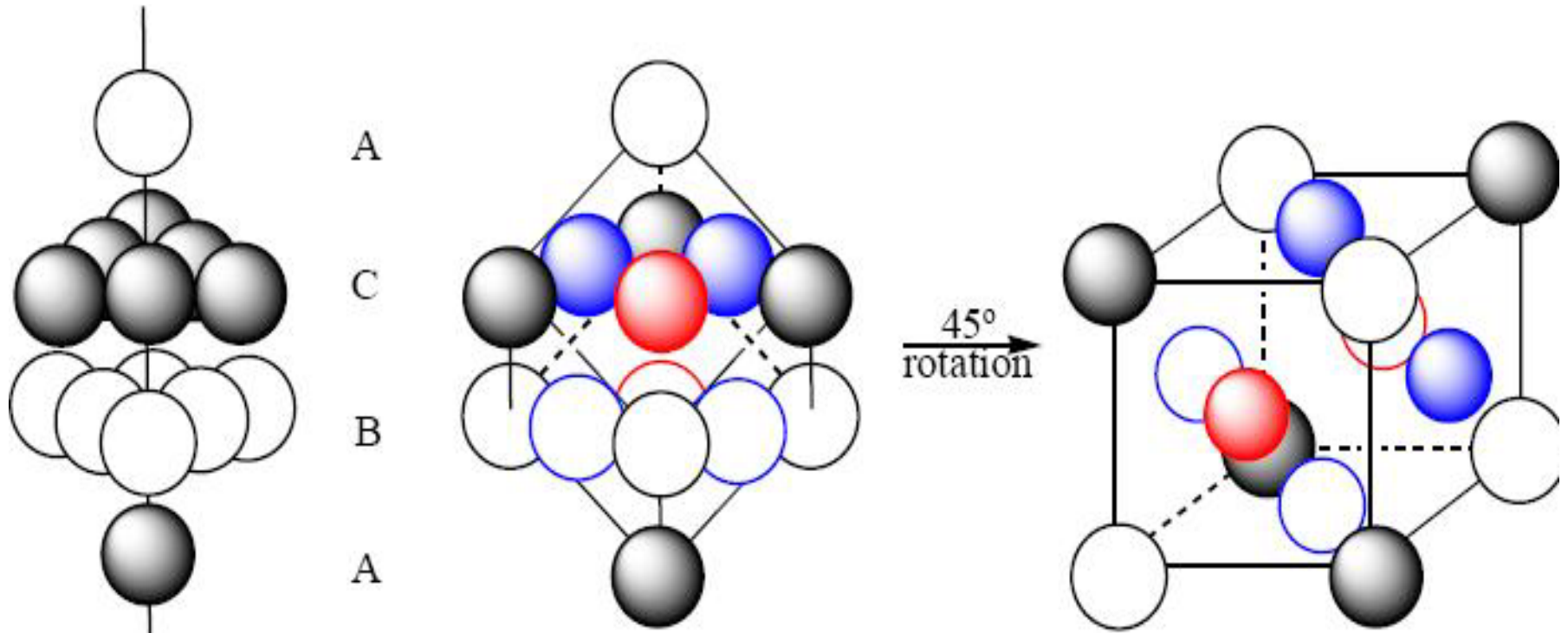


- Occupying positions so that no sphere in the third layer lies over one in the first layer [the **abc** arrangement].

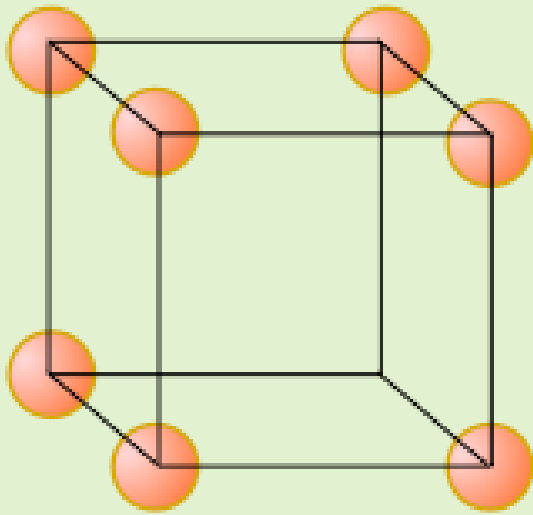


Unit Cell, UC

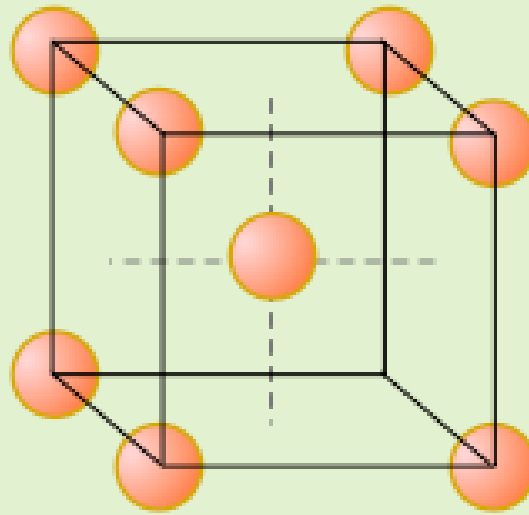
- the **smallest** group of atoms which has the overall symmetry of a crystal, and from which the entire lattice can be built up by repetition in three dimensions.
- If the cubic close packed structure is rotated by 45° the face centered cube (fcc) unit cell can be viewed



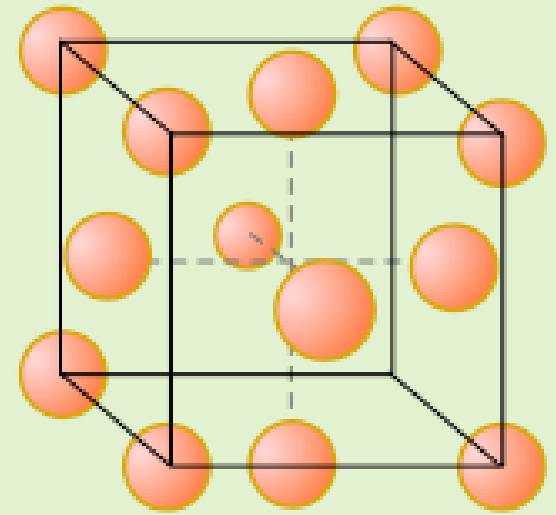
3 types of cubic lattices



simple cubic



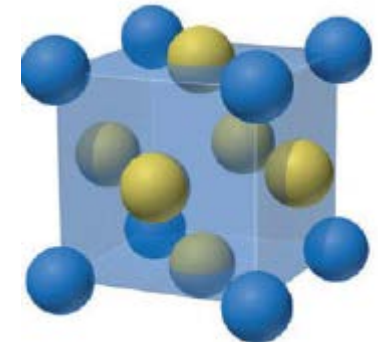
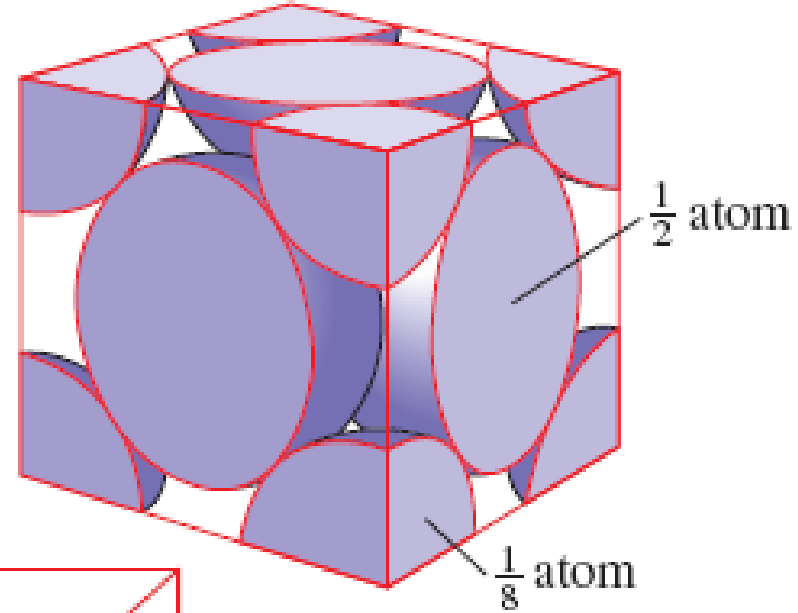
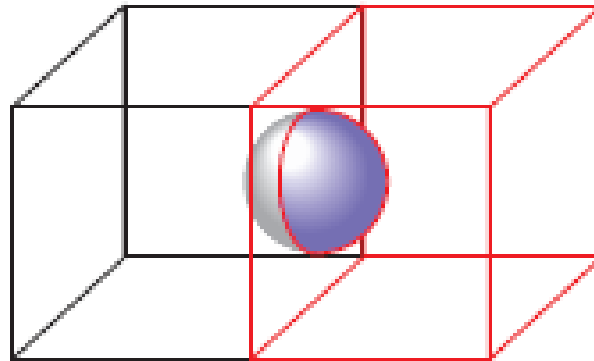
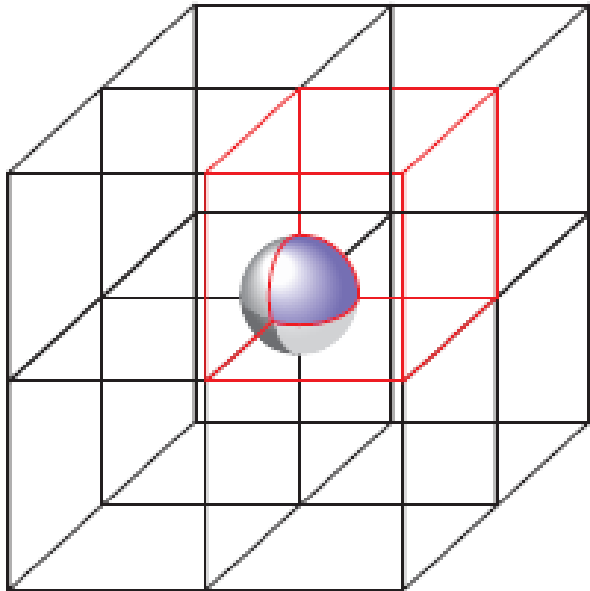
body-centered cubic



face-centered cubic
(cubic close-packing)

Net number of spheres (atoms) in fcc unit cells

- centers of the spheres on the cube's corners + spheres at the center of each face.



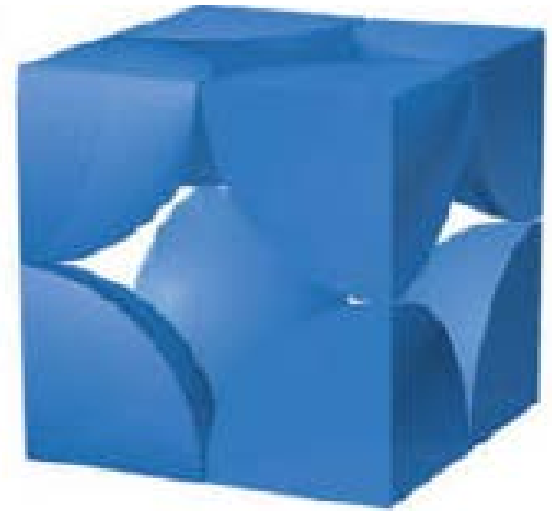
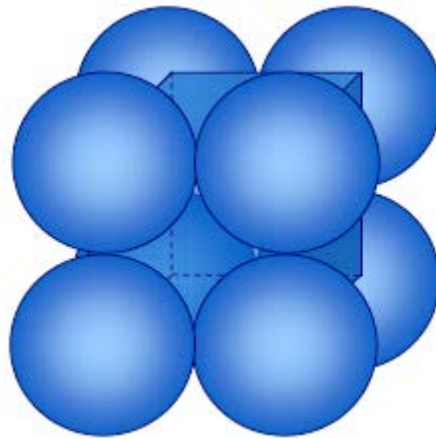
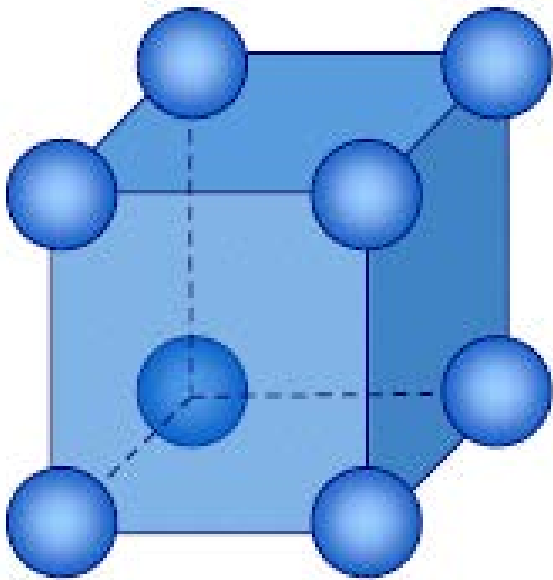
$$\text{Total spheres} = \left(8 \times \frac{1}{8} \right) + \left(6 \times \frac{1}{2} \right) = 4$$

Position of atoms and fraction in a single UC

Position of Atom in the Unit Cell	# of adjacent cells sharing atom	Fraction contained within a single unit cell
Cube Corner	8	1/8
Edge	4	1/4
Face	2	1/2
Internal (bulk)	1	1

Net number of spheres in simple cubic unit cell

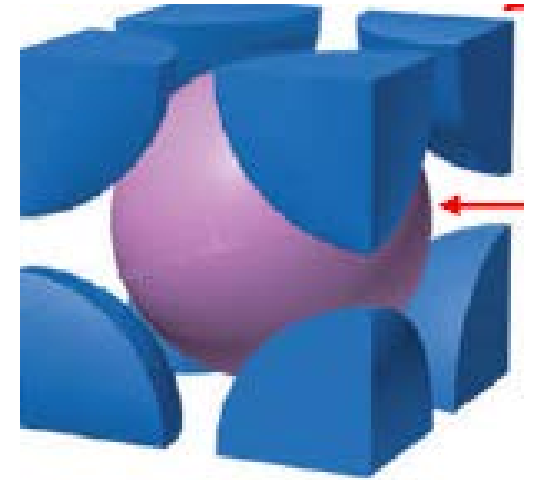
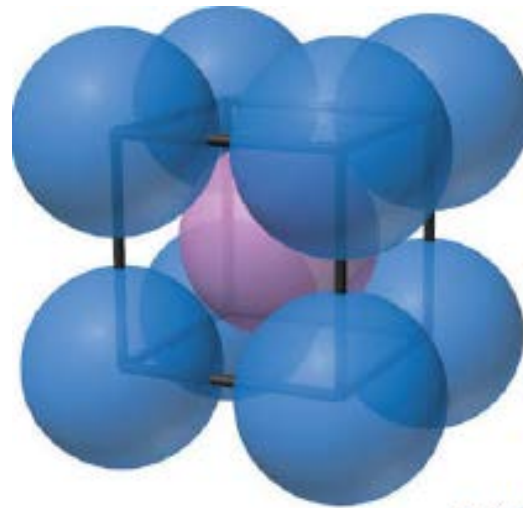
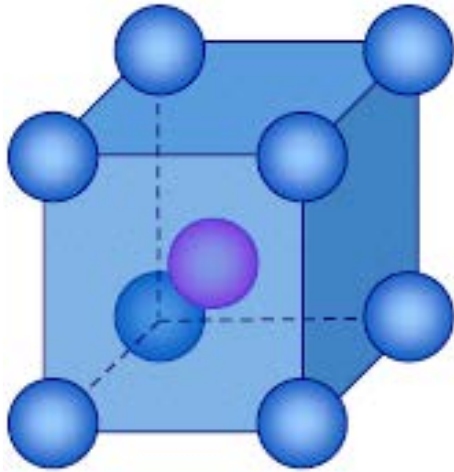
centers of the spheres on the **cube's corners**



$$\text{Total spheres} = \left(8 \times \frac{1}{8} \right) = 1$$

Net number of spheres in **bcc** unit cell

centers of the spheres on the cube's corners + 1 sphere in the center

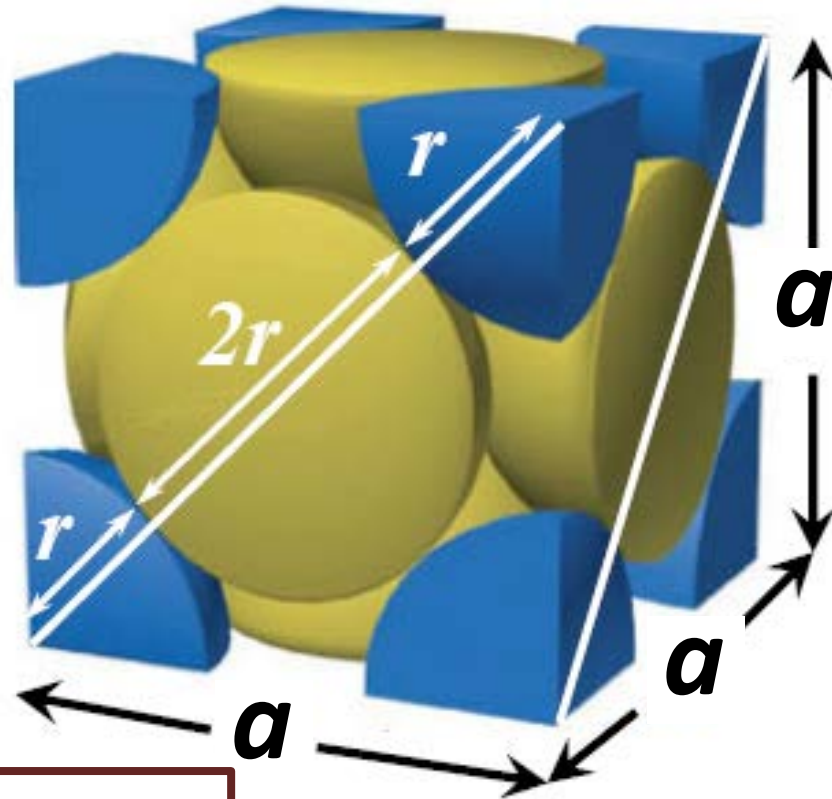


$$\text{Total spheres} = \left(8 \times \frac{1}{8} \right) + (1 \times 1) = 2$$

Density of a Closest Packed Solid

Silver crystallizes in a cubic closest packed structure. The radius of a silver atom is 1.44 \AA ($1 \text{ \AA} = 10^{-8} \text{ cm}$). Calculate the density of solid silver.

- The structure is ccp, which means the unit cell is **face-centered cubic**.
- Find the volume of this unit cell for silver and the net number of atoms it contains.
- Atoms touch along the diagonals for each face and not along the edges of the cube.



$$\text{Diagonal length} = r + 2r + r = 4r$$

□ Find the length of the edge of the cube by the Pythagorean theorem

$$(4r)^2 = a^2 + a^2 = 2a^2$$

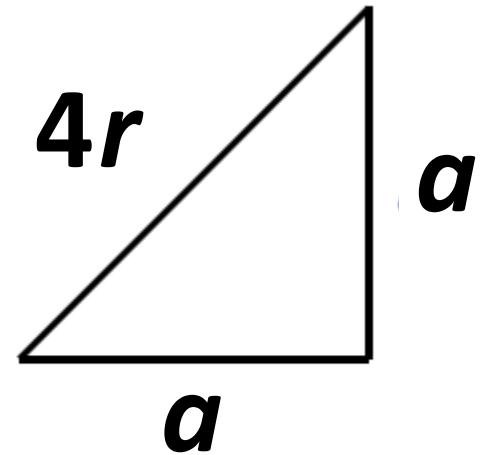
$$a^2 = 8r^2$$

$$a = r\sqrt{8}$$

radius of a silver atom is 1.44 \AA .

$$a = r\sqrt{8} = 1.44 \overset{\circ}{\text{A}} \sqrt{8} = 4.07 \overset{\circ}{\text{A}}$$

$$V (\text{unit cell}) = a^3 = 67.4 \left(\overset{\circ}{\text{A}} \right)^3 = 6.74 \times 10^{-23} \text{ cm}^3$$



4 Ag atoms occupy $6.74 \times 10^{-23} \text{ cm}^3$

$$\text{Atomic mass of Ag} = \frac{107.9 \text{ g}}{\text{mol}} = \frac{107.9 \text{ g}}{6.022 \times 10^{23} \text{ atoms}}$$

Calculate the mass of 4 atoms existing in the fcc unit cell

$$\text{mass of Ag unit cell} = \frac{107.9 \text{ g}}{6.022 \times 10^{23} \text{ atoms}} \times 4 \text{ atoms} = 71.7 \times 10^{-23} \text{ g}$$

$$\text{density of Ag} = \frac{\text{mass}}{\text{volume}} = \frac{71.7 \times 10^{-23} \text{ g}}{6.74 \times 10^{-23} \text{ cm}^3} = 10.6 \text{ g cm}^{-3}$$

Generally

$$\text{density (d)} = \frac{Z \times M}{a^3 \times N_A}$$

d = Density (g/cm³) **Z** = number of atoms per unit cell

M = Molar mass in g/mol **a** = Edge length in cm

N_A = Avogadro number = 6.022×10^{23} atoms/mol

Value of Z {
simple cubic = 1
bcc = 2
ccp or fcc = 4

Relationship between atomic radius and edge length

Simple cubic

$$r = \frac{a}{2}$$

BCC

$$r = \frac{a\sqrt{3}}{4}$$

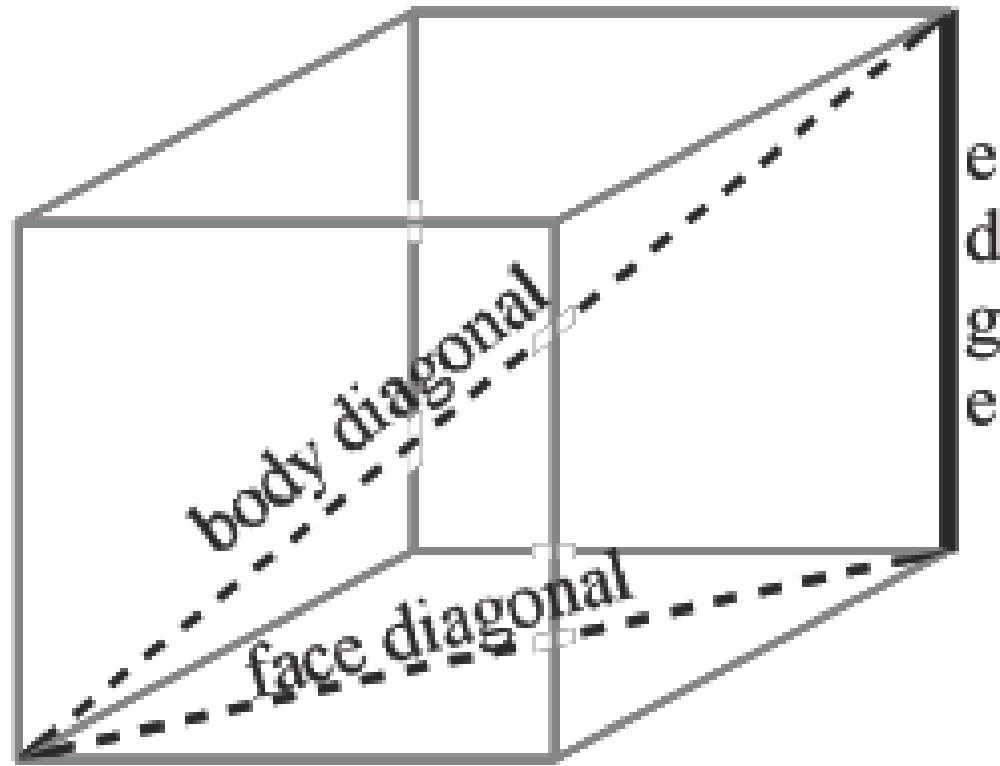
FCC

$$r = \frac{a\sqrt{2}}{4}$$

$$a = r\sqrt{8}$$

Usually

$$\begin{aligned} \text{fd}^2 &= a^2 + a^2 = 2 a^2 \\ \text{bd}^2 &= \text{fd}^2 + a^2 \\ &= a^2 + a^2 + a^2 = 3 a^2 \end{aligned}$$



- ✚ The length of the cell edge is represented by **a**.
- ✚ The direction from a corner of a cube to the farthest corner is called **body diagonal (bd)**.
- ✚ The **face diagonal (fd)** is a line drawn from one vertex to the opposite corner of the same face.
- ✚ If the edge is **a**, then we have

- If atoms touch each other along the **body diagonal** (bd), thus, the body diagonal has a length that is four times the radius of the atom, r , i.e., **$bd = 4r$**

$$(4r)^2 = 2a^2 + a^2 = 3a^2$$

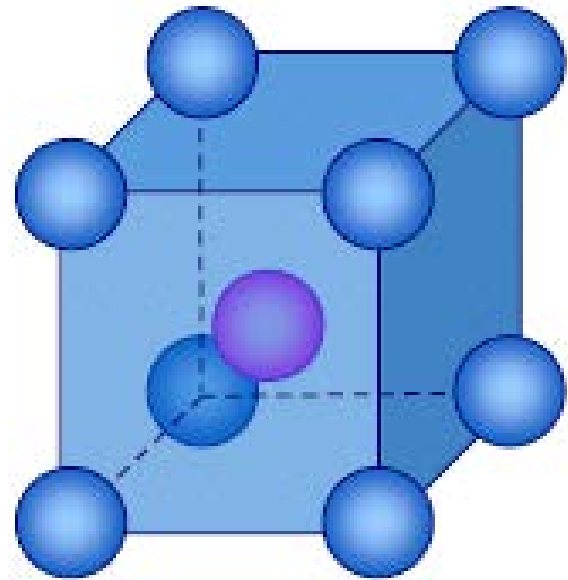
$$4r = a\sqrt{3}$$

$$a = \frac{4r}{\sqrt{3}}$$

$$r = \frac{a\sqrt{3}}{4}$$

Packing fraction for a bcc
packed structure

$$r = \frac{a\sqrt{3}}{4} \quad \Rightarrow \quad a = \frac{4r}{\sqrt{3}}$$



$$\text{Packing fraction} = \frac{V_{\text{sphere}}}{V_{\text{unit cell}}} = \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3} \pi}{8} = 0.6802$$

The packing fractions are

fcc and hcp

74.05 %

bcc

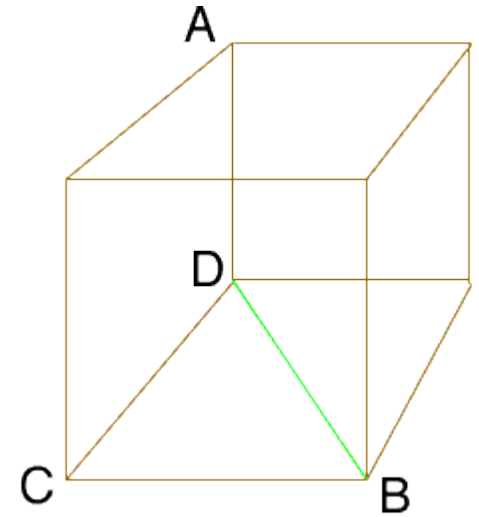
68.02 %

simple cubic

52%

Packing fraction of fcc lattice = 0.74

- Atoms are touched along the face diagonal (fd).
- For spheres of radius r , the diagonal of the cube face is equal to $4r$, and is also equal to $\sqrt{2} a$, where a is the dimension of the unit cell.



$$|DB|^2 = |DC|^2 + |CB|^2$$

As there are 6 atoms in the faces and half of each is in the unit cell:

$$r = \frac{a\sqrt{2}}{4}$$

$$6 \times \frac{1}{2} \times \frac{4}{3} \pi r^3 = 4\pi \left(\frac{a\sqrt{2}}{4} \right)^3 = 0.55536 a^3$$

There are also 8 atoms in the corners of the unit cell, and 1/8 of each is in the cell:

$$8 \times \frac{1}{8} \times \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{a\sqrt{2}}{4} \right)^3 = 0.18512 a^3$$

The volume of the unit cell is a^3 and the total volume of the spheres in the unit cell is

$$V(\text{spheres}) = (0.5536 + 0.18512) = 0.74048 a^3$$

$$\text{Packing fraction} = \frac{0.74048 a^3}{a^3} = 0.74048$$