CHEM2100J
Chemistry
Autumn 2024

Chapter 06
Liquids and Solids

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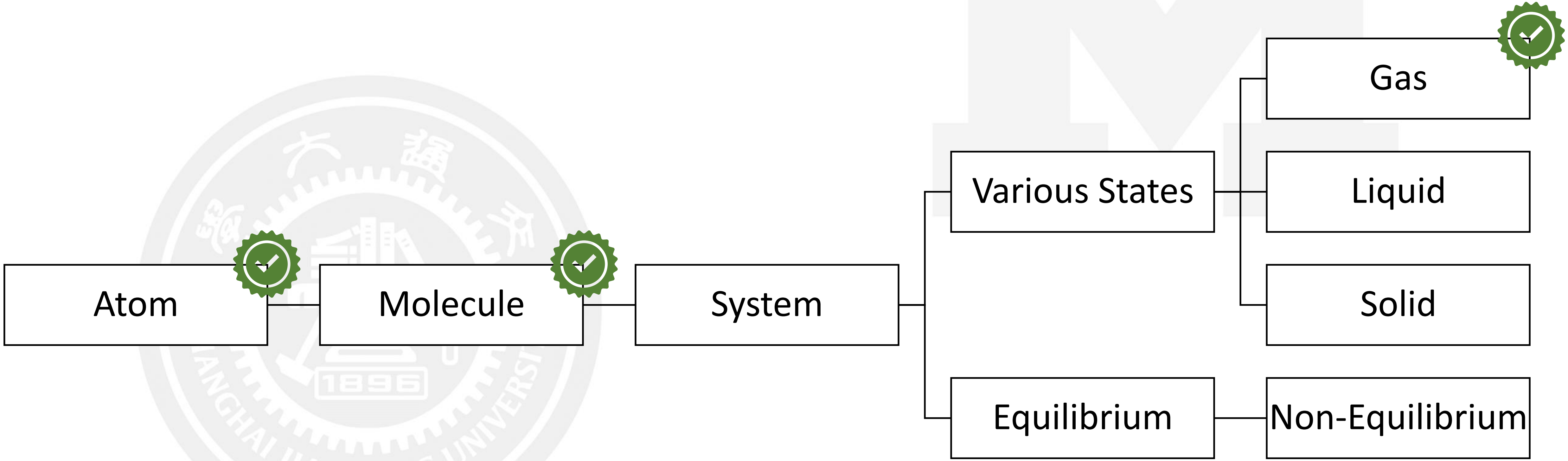
The Journey So Far



Intermolecular Forces

Why are some matters gaseous, while others are liquid or solid? How to think about this in terms of intermolecular forces?

How do I think about the melting point and boiling point of matters?

The Origin of Intermolecular Forces

Attractive force arise from Coulombic interaction

$$E_p = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

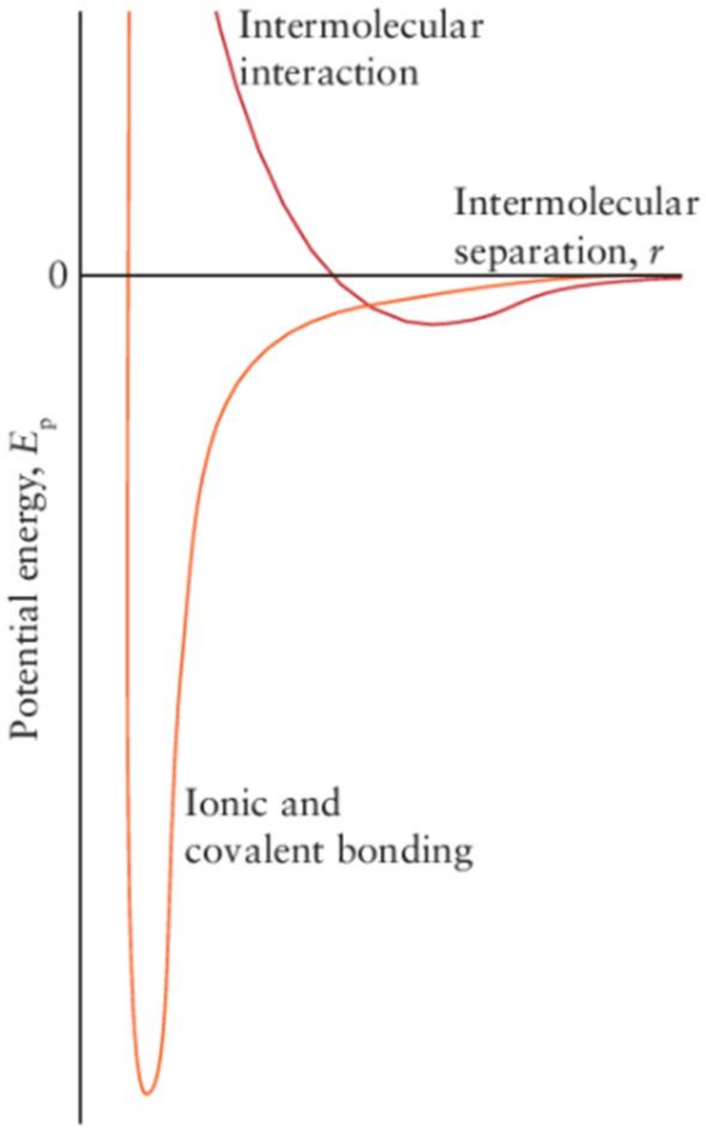
E_p: potential energy

$q_1 q_2$: charge of each atom

r: distance between $q_1 q_2$

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

Different Types of Intermolecular Forces



Interaction Type	E_p dependence	Typical E_p / kJ·mol^{-1}	Interacting species
Ion-ion	$\frac{-\lvert z\rvert^2}{r}$	250	Ions
Ion-dipole	$\frac{-\lvert z\rvert\mu}{r^2}$	15	Ions and polar molecules
Dipole-dipole	$\frac{-\mu_1\mu_2}{r^3}$	2	Stationary polar molecules
	$\frac{-\mu_1\mu_2}{r^6}$	0.3	Rotating polar molecules
Dipole-induced dipole	$\frac{-\mu_1{}^2\alpha_2}{r^6}$	2	Molecules, at least one must be polar
London (dispersion)	$\frac{-\alpha_1\alpha_2}{r^6}$	2	All types of molecules and ions
Hydrogen bonding*		20	Molecules containing an N-H, O-H, or F-H bond

*Hydrogen bonding is a special case of dipole-dipole interaction.

The Origin of Intermolecular Forces: Radius

As the power increases, the interaction becomes increasingly sensitive to distance.

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

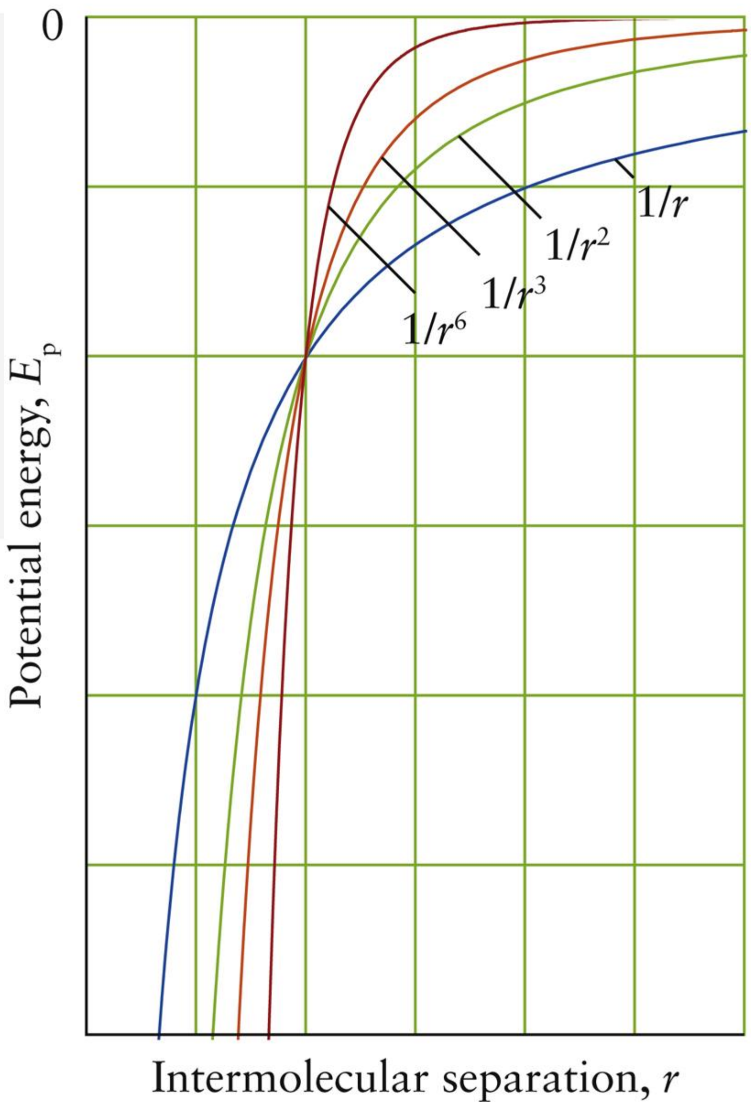


Figure 3F.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e

Ion-Ion Interaction

Ion-ion interactions are some of the strongest forces between molecules.

Oppositely charged ions attract each other.

The effect is dependent on 1/*r*.

Calculated as crystal lattice energy where the ions form extended repeating units.

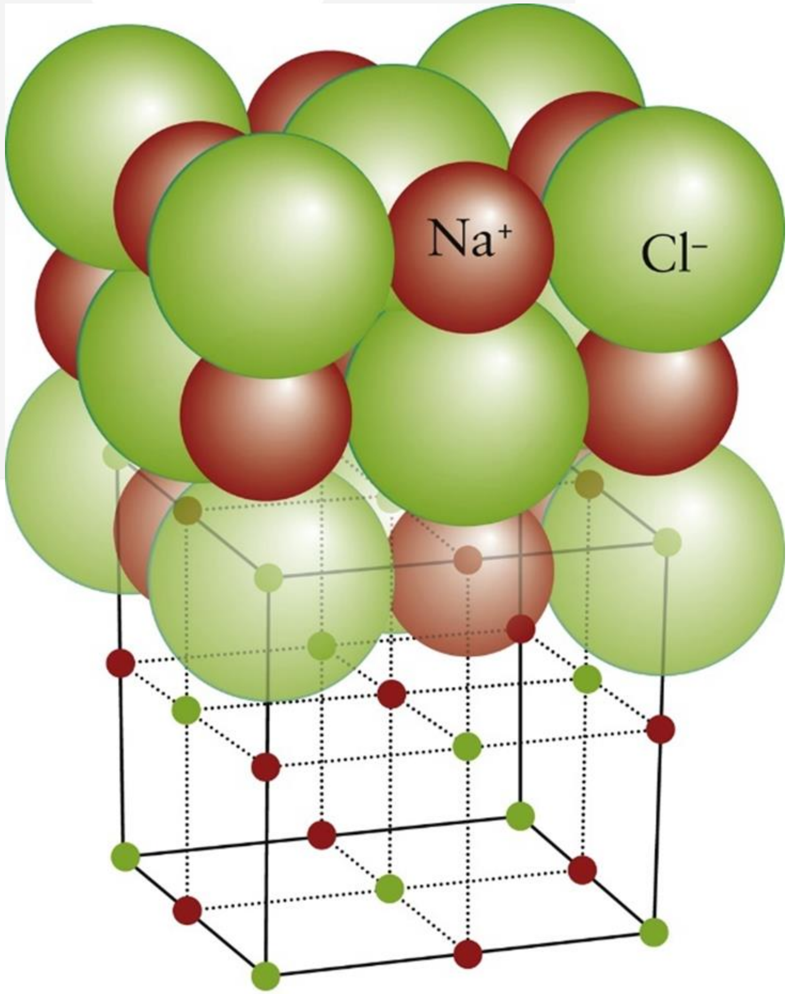


Figure 3H.28
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Ion-Dipole Interactions

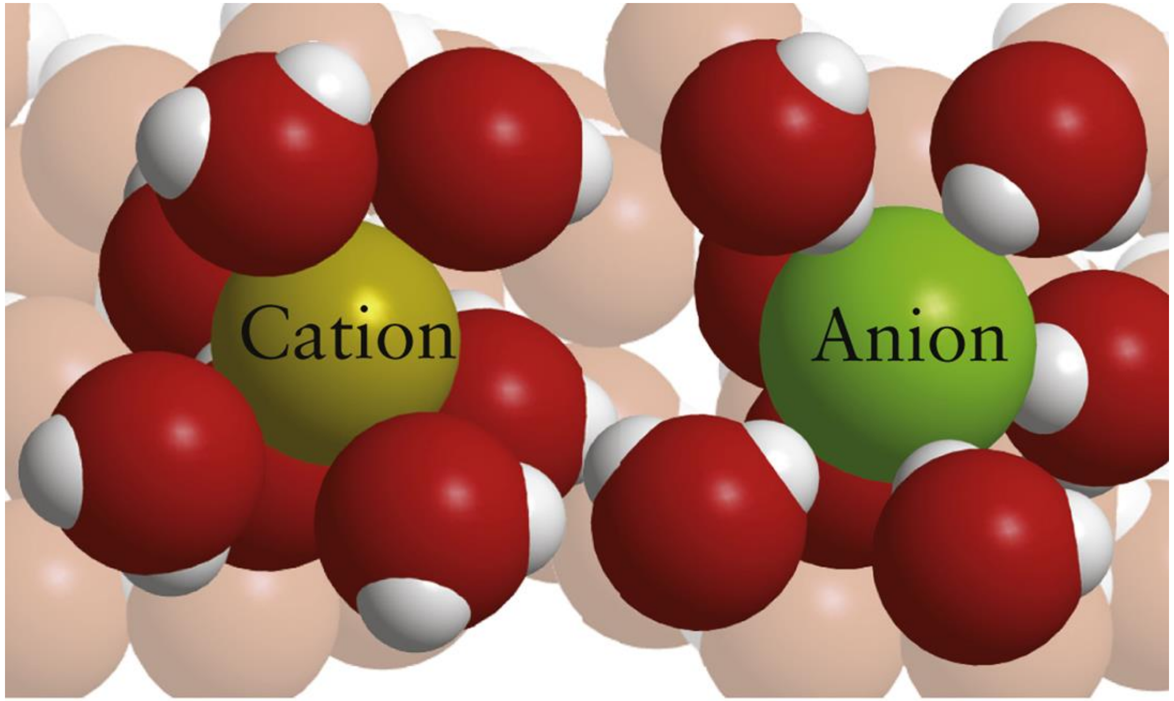

Figure 3F.2
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The attachment of water to solute particles is called **hydration**. Hydration of ions is due to the polar character of the H_2O molecule.

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

Dipole-Dipole Interactions: Arrangement

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

Here, μ_1 and μ_2 are the dipole moments.

Molecules arrange themselves into the **lowest energy, least repulsive** configuration.

Molecules with permanent dipoles form a **dipole-dipole** interaction.

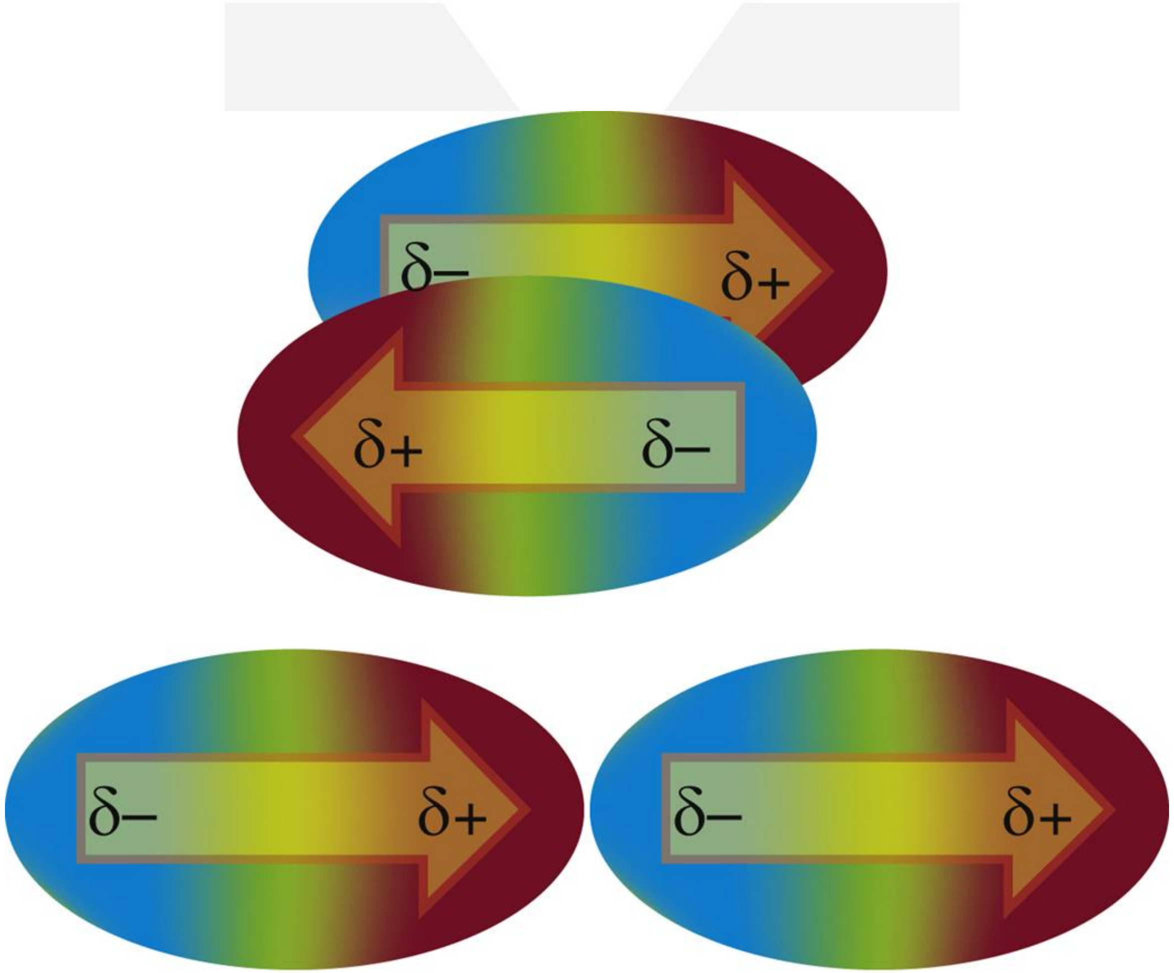

Figure 3F.4
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Dipole-Dipole Interactions: Alignment and Radius

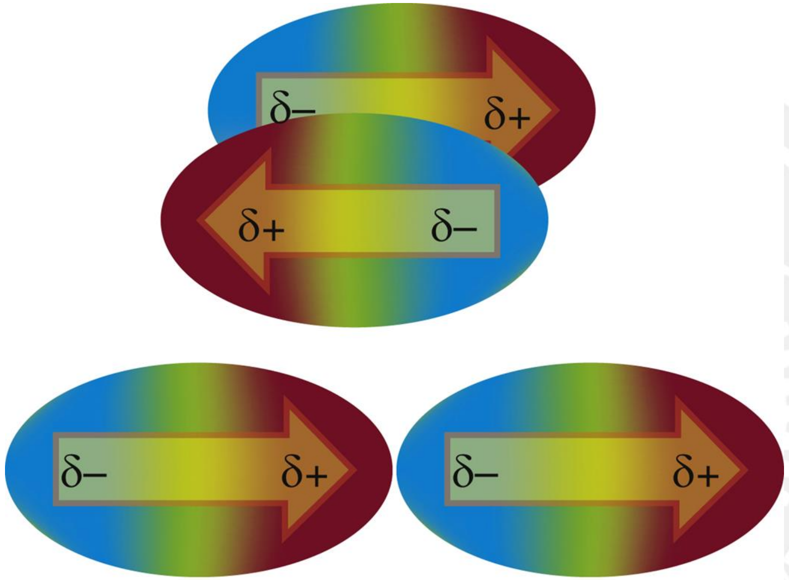

Figure 3F.4
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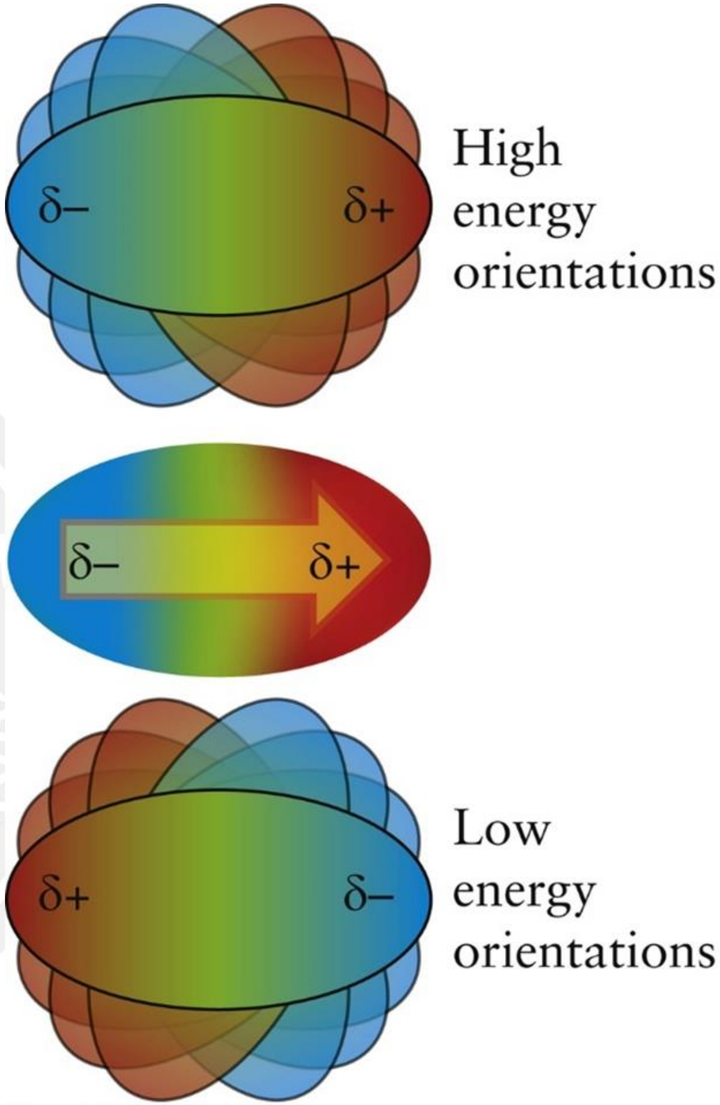

Figure 3F.5
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Stationary:

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

Rotating, gas phase:

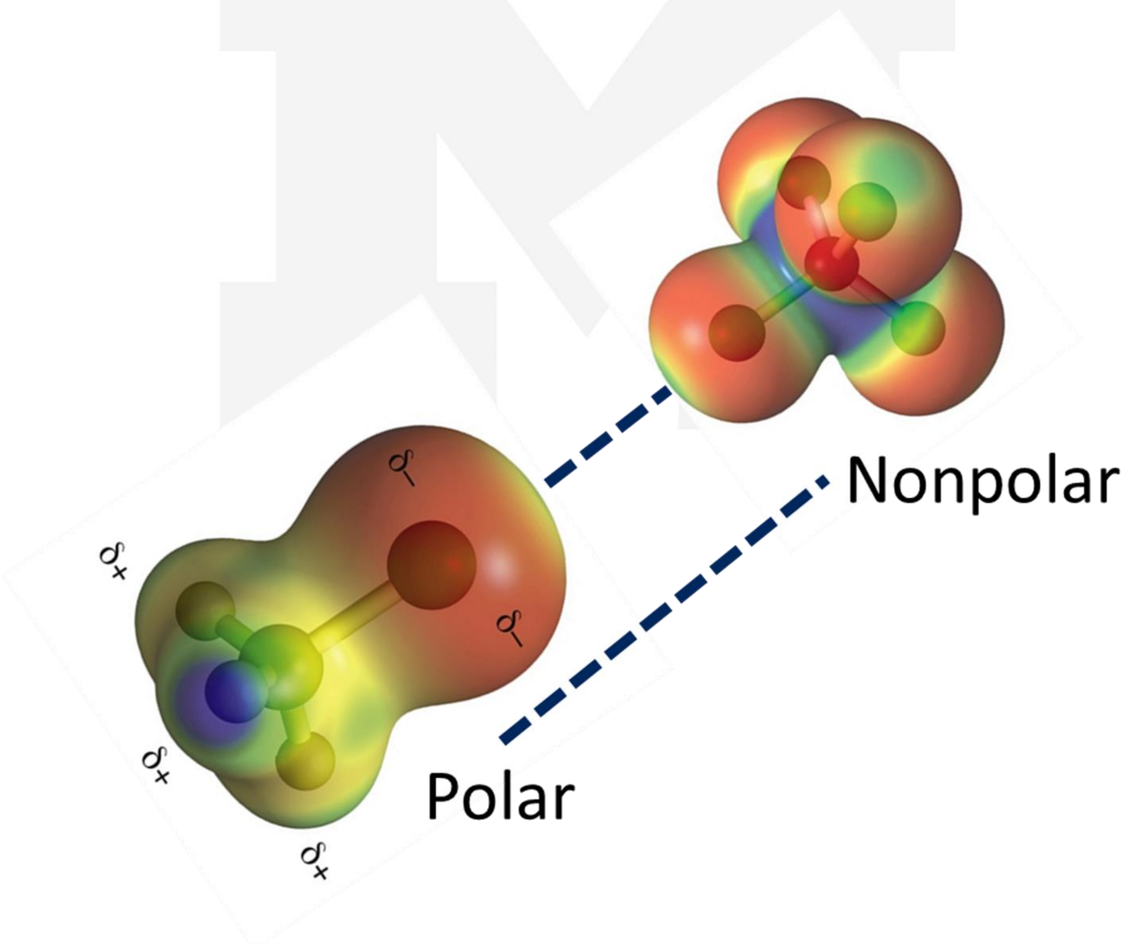
$$E_p \propto \frac{\mu_1 \mu_2}{r^6}$$

So, **doubling** the **radius** **decreases** the strength by $2^6 = 64$.

Dipole-Induced-Dipole Interactions

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

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

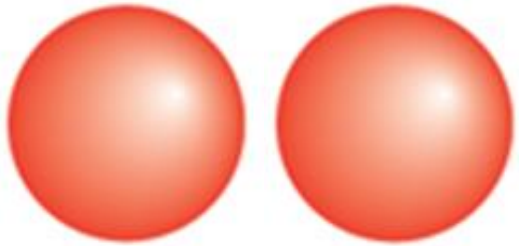


London Dispersion Forces

Attractive forces between **nonpolar molecules** are London forces.

Even nonpolar noble gases can be liquefied, as well as many nonpolar compounds, such as pentane (next slide) and hydrocarbons that make up gasoline.

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



Nonpolar molecules have symmetrical electron clouds.

London Forces (Induced Dipole)

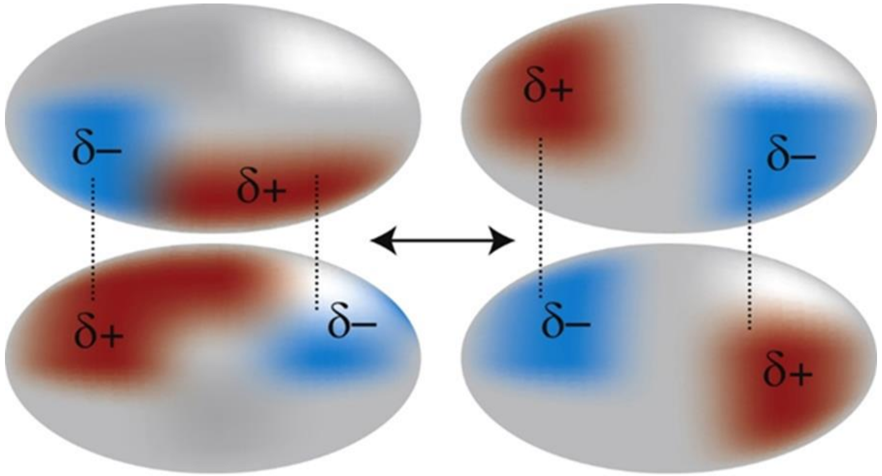


Figure 3F.7
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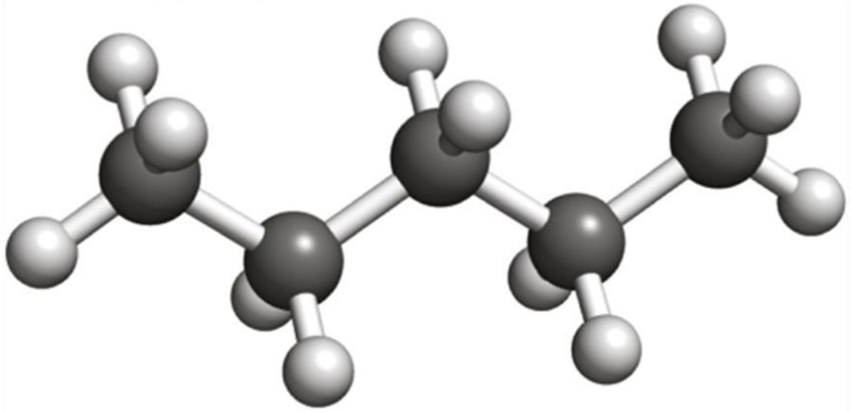

8 Pentane, C_5H_{12}

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

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

London Forces (Induced Dipole)

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Instantaneous dipole moments create distortions in the electron cloud, which become partially positively (δ^+) and partially negatively (δ^-) charged.

These **fleeting partial negative charge** can attract a **fleeting partial positive charge**, in neighboring molecules, and the entire process can reverse itself every 10^{-16} s.

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

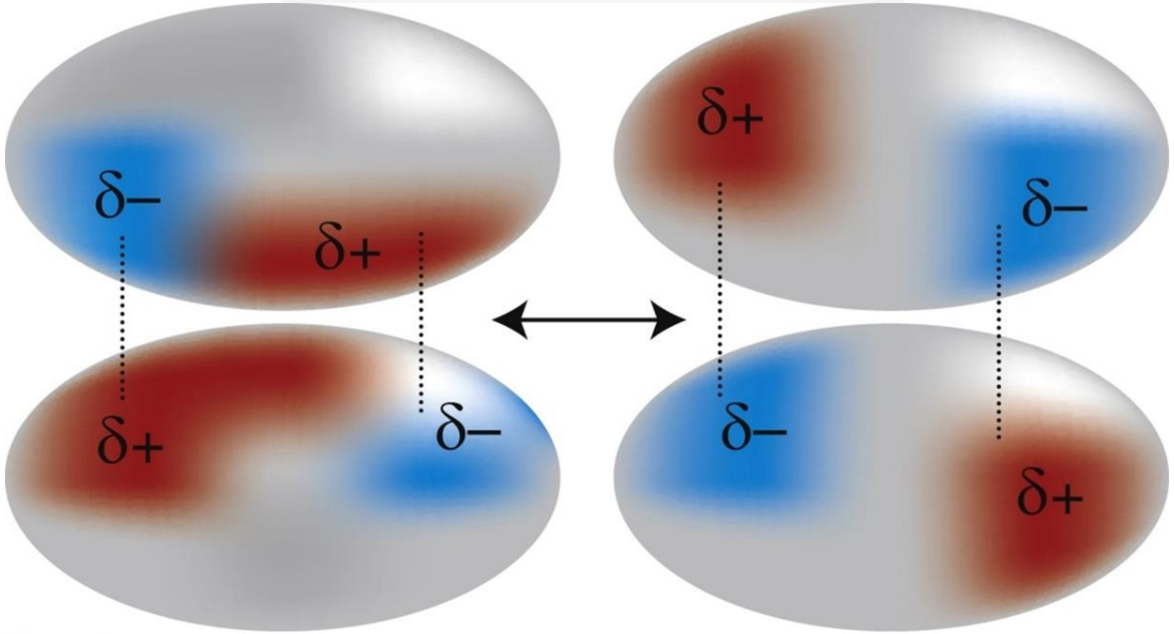

Figure 3F.7
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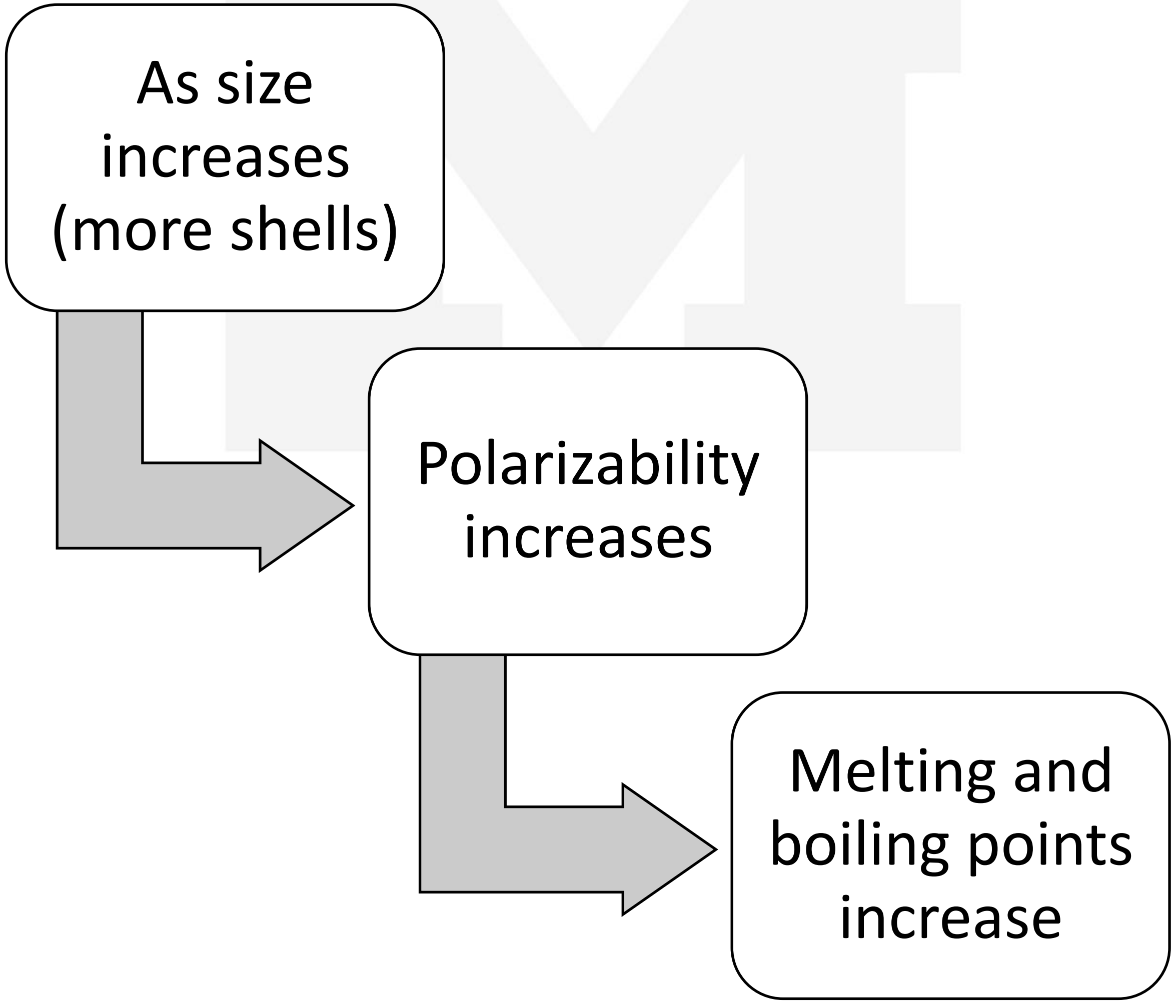
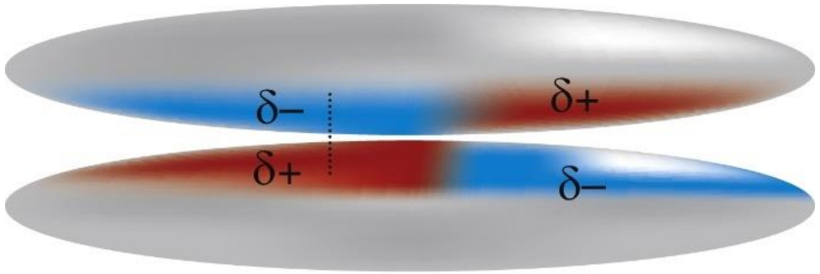
London Forces: Size

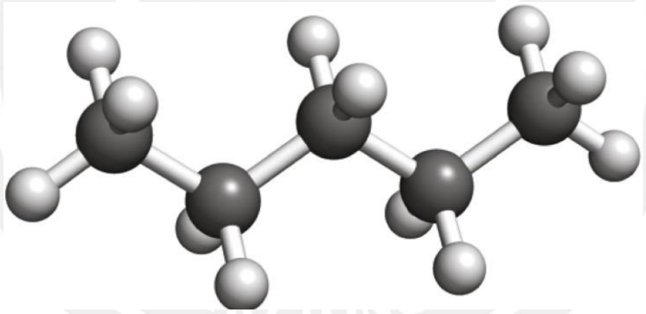
Gas	T_m / K	T_b / K
He	(3.5) under higher pressure	4.4
Ne	24.7	27.3
Ar	83.6	87.4
Kr	115.8	121.5
Xe	161.7	166.6
F_2	53.5	85.0
Cl_2	171.6	239.1
Br_2	265.8	332.0
I_2	386.9	457.4



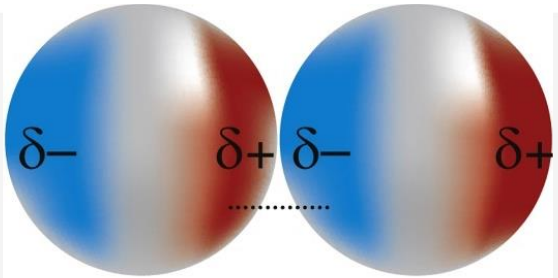
London Forces: Shape



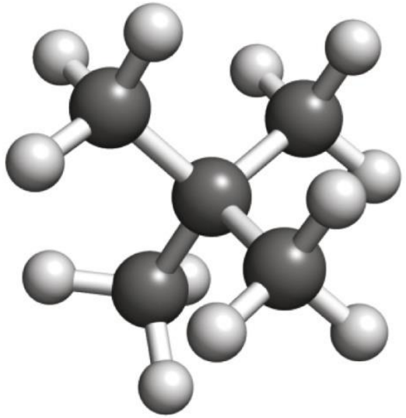
Rod-like molecules have a greater surface area, more contact points for molecules to join together.



$$T_{b,Pentane(C_5H_{12})} = 36\ °C$$



Ball-shaped or spherical molecules have fewer contact points for molecules to join together.



$$T_{b,2,2-Dimethylpropane(C(CH_3)_4)} = 10\ °C$$

Hydrogen Bonding

London interactions are "universal" in the sense that they apply to all molecules regardless of their chemical identity.

Similarly, the dipole-dipole interaction depends only on the polarity of the molecule, regardless of its chemical identity.

However, there is another **very strong interaction** between molecules that is **specific to molecules** with certain types of atoms.

A special case of dipole-dipole interaction is **hydrogen bonding**. The typical bond energy is 20 $kJ \cdot mol^{-1}$.

Hydrogen Bonding

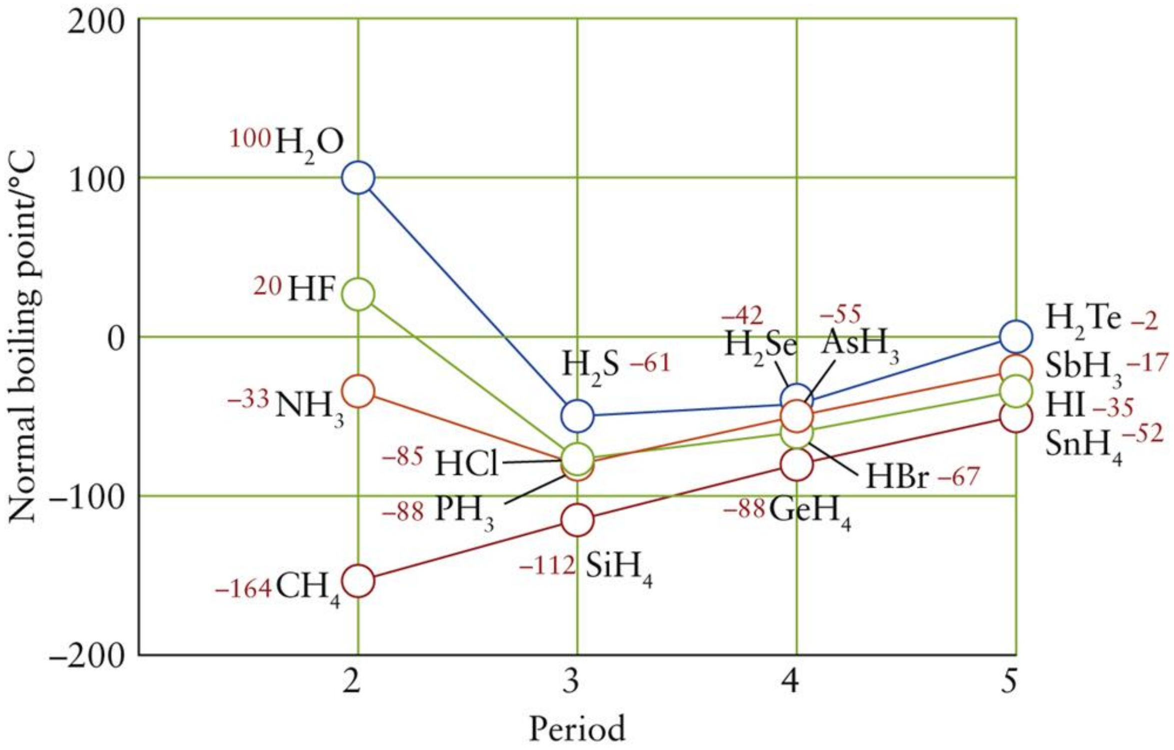


Figure 3F.10
Atkins, *Chemical Principles: The Quest for Insight*, 7e

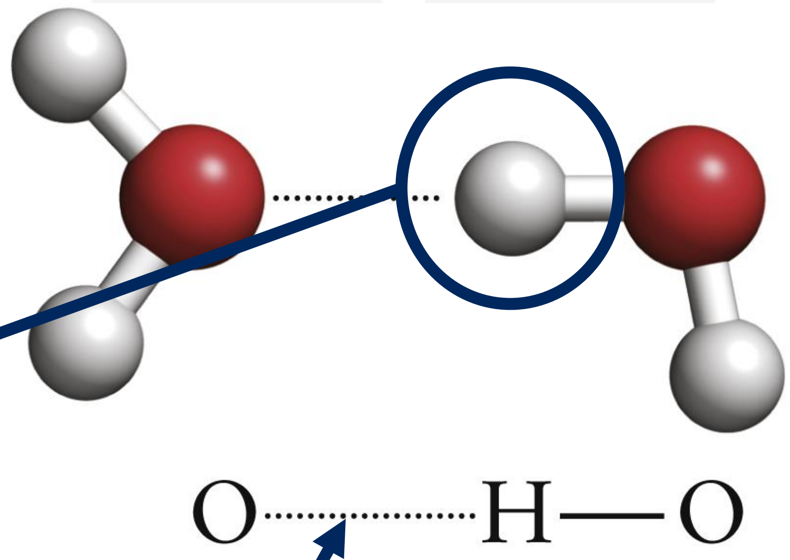
If you were asked to estimate the boiling point of NH_3, H_2O, or HF you would perhaps extrapolate backward (notice Group 14’s nice linear slope).

Off by as much as 200 °C**!**

Bridging Hydrogen Bonds

Specific molecules with strong electronegative atoms N, O, or F form **bridging hydrogen bonds**.

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



10 Hydrogen bond (in water)

Atkins, *Chemical Principles: The Quest for Insight*, 7e

Bridging Hydrogen Bonds

Hydrogen bonding is much stronger than London interactions, it is the second strongest!

Interaction Type	E_p dependence	Typical E_p / kJ·mol^{-1}	Interacting species
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Hydrogen bonding		20	Molecules containing an N-H, O-H, or F-H bond

Hydrogen Bonding

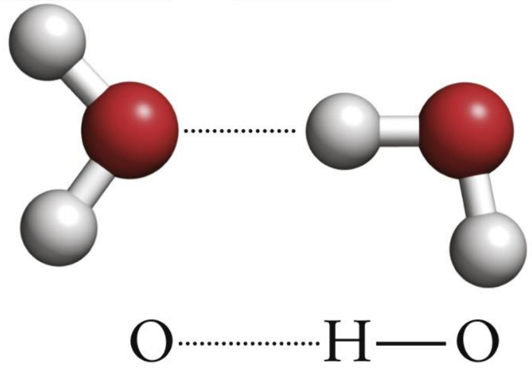
A **hydrogen bond is denoted by a dotted line**, so the hydrogen bond between two O atoms is denoted O-H···O.

The O-H bond length is 101 pm and the H···O distance is a bit longer; in ice it is 175 pm.

Hydrogen Bonds

X-H···X

X = N, O, F



10 Hydrogen bond (in water)

Liquids

Liquid Structure: An Atomic View

Liquid molecules are randomly and constantly tumbling each other.

We imagine a liquid as a group of jostling molecules.

Flowing liquids are like a crowd of people leaving a stadium.

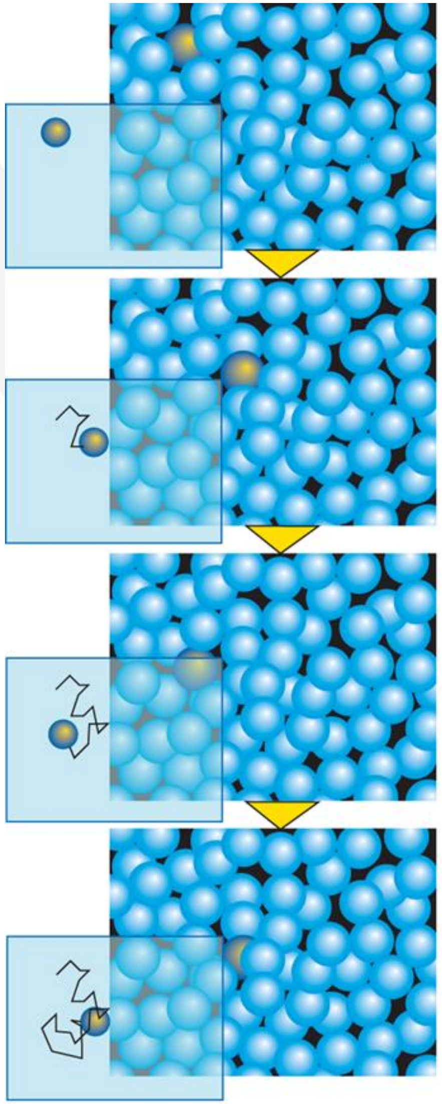


Figure 3G.1
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Intermolecular Forces: Viscosity

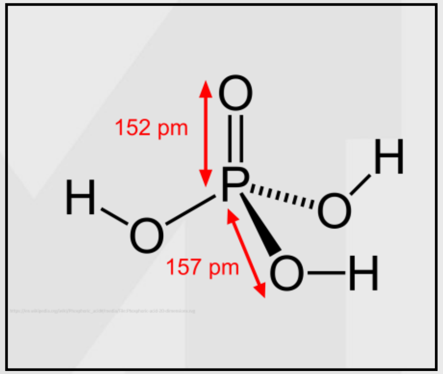
Viscosity is a liquid's resistance to flow:
The higher the viscosity of the liquid, the more sluggish the flow.

Water is easy to pour; it has low viscosity.

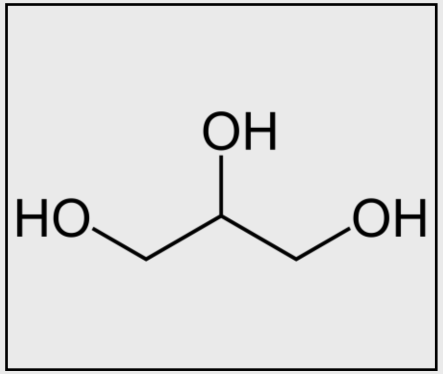
Compared to water, molasses has a high viscosity at room temperature, so it is "viscous".

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.



Phosphoric acid



Glycerol

https://en.wikipedia.org/wiki/Glycerol#/media/File:Glycerin_Skelett.svg
https://en.wikipedia.org/wiki/Phosphoric_acid#/media/File:Phosphoric-acid-2D-dimensions.svg

Intermolecular Forces: Surface Tension

Surface tension is the reason that 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.

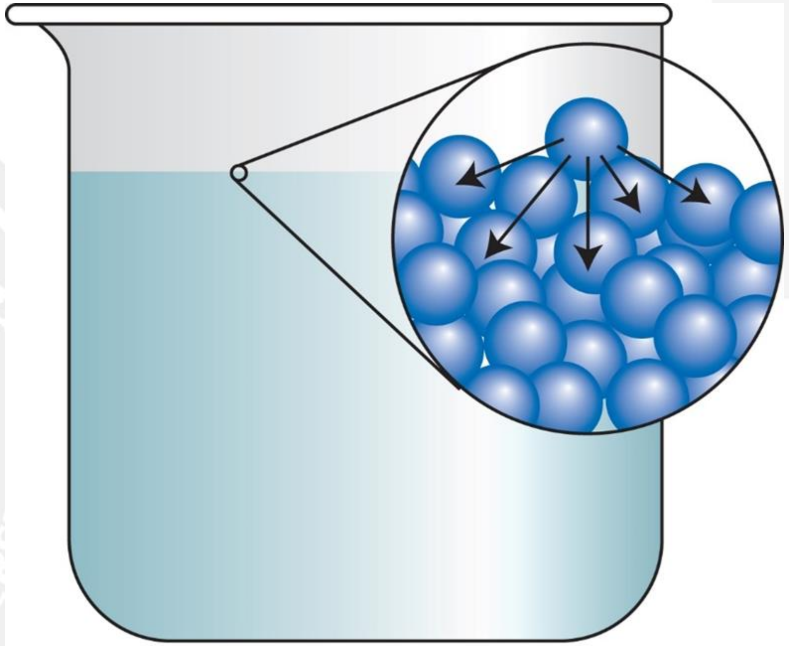


Figure 3G.4
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Liquid	Surface Tension γ / $mN \cdot m^{-1}$ @25 °C
Benzene	28.88
Carbon tetrachloride	27
Ethanol	22.8
Hexane	18.4
Mercury	472
Methanol	22.6
Water	72.75 58.0 @100 °C

Intermolecular Forces: Surface Tension

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

Adhesion ≈ Cohesion

The **downward** meniscus (convex) of mercury forms because the cohesive forces in mercury is stronger than between mercury atoms and the glass:

Cohesion > Adhesion

Figure 3G.6
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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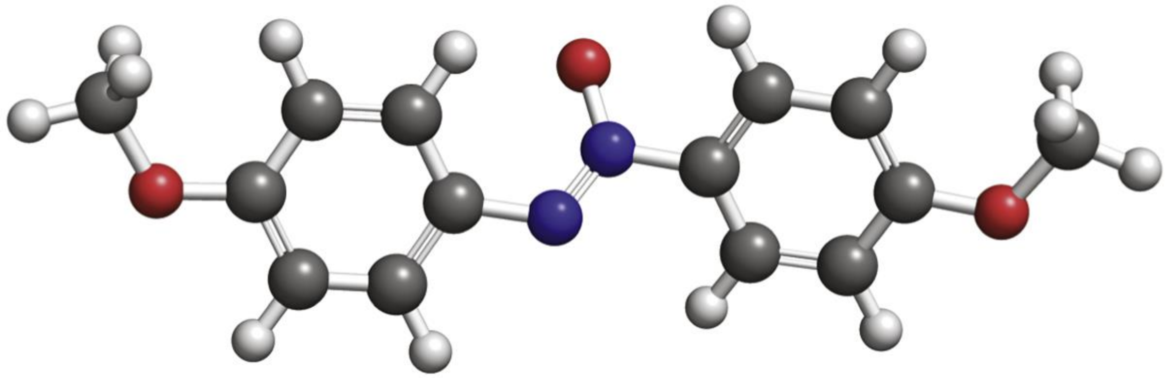
Liquid Crystals

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

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



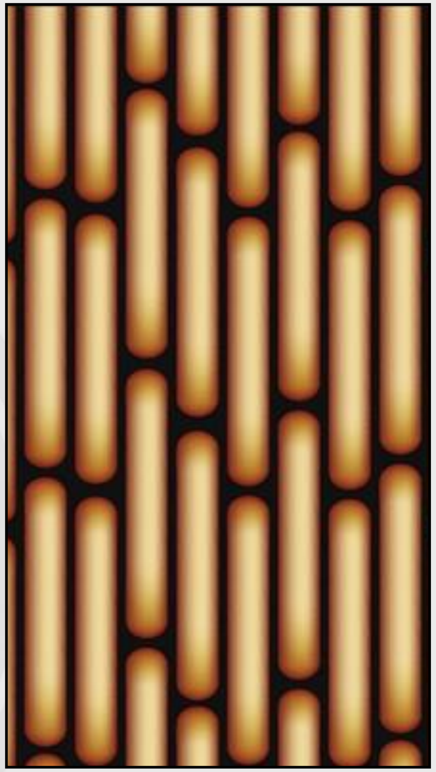
2 *p*-Azoxyanisole

p-azoxyanisole is long and rod-like, like dry, uncooked spaghetti, enabling stacking.

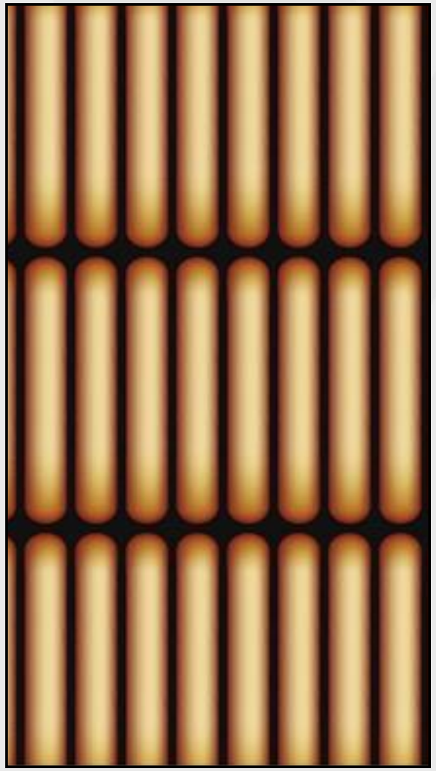
Liquid Crystals

Anisotropic materials [depend on the direction]() of measurement.

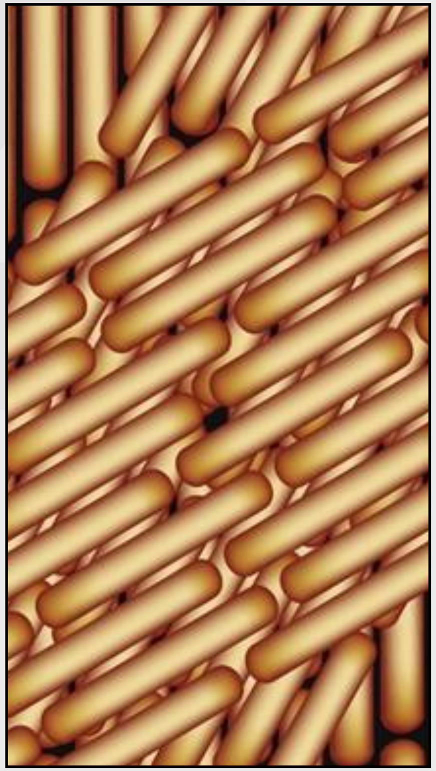
Isotropic materials do not depend on orientation: water's viscosity is the same in all directions.



Nematic phase
parallel molecules, staggered along their long axes.



Smectic phase
molecules are parallel and line up to form sheets



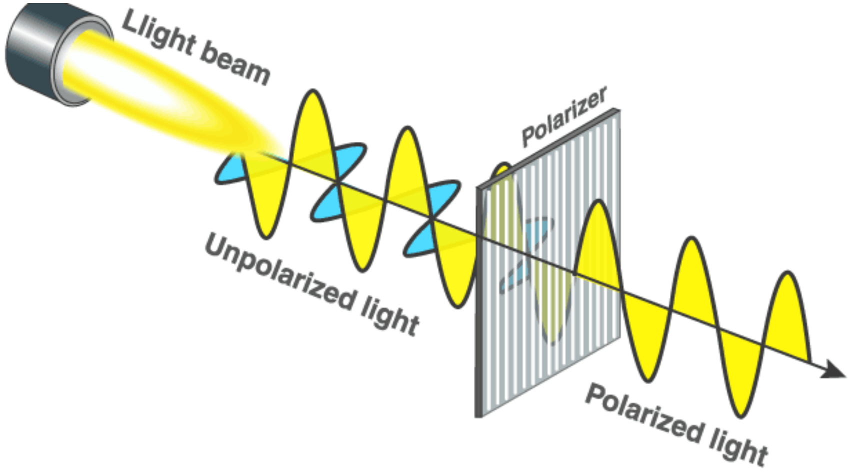
Cholesteric phase
sheets of parallel molecules are rotated relative to their neighbors and form a helical structure

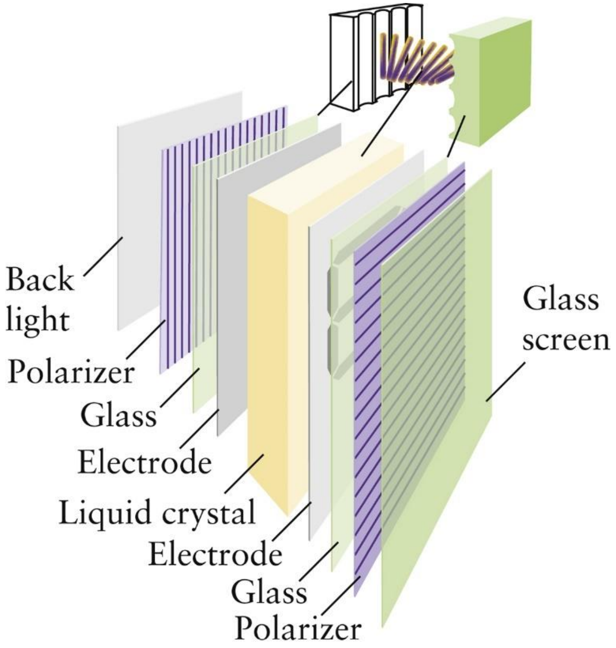
Side Quest: Liquid Crystal Display

In an LCD (**liquid-crystal display**) television or computer monitor, layers of nematic phase liquid crystal lie between glass or plastic plates.

Light is polarized when a potential difference is applied. The molecules rotate until they are oriented with the electric field and become **opaque,** forming dark spots on a screen.

The electrode twist is lost when a potential difference is applied.





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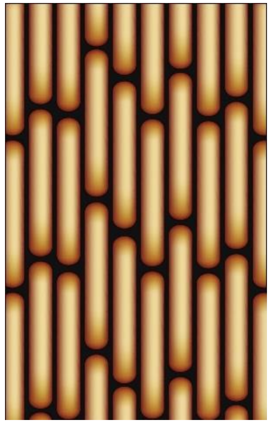


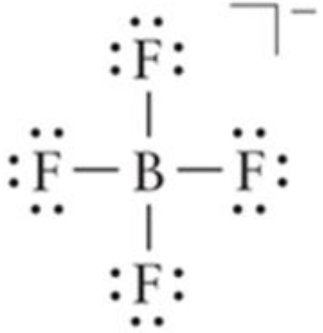
nematic phase

Ionic Liquids

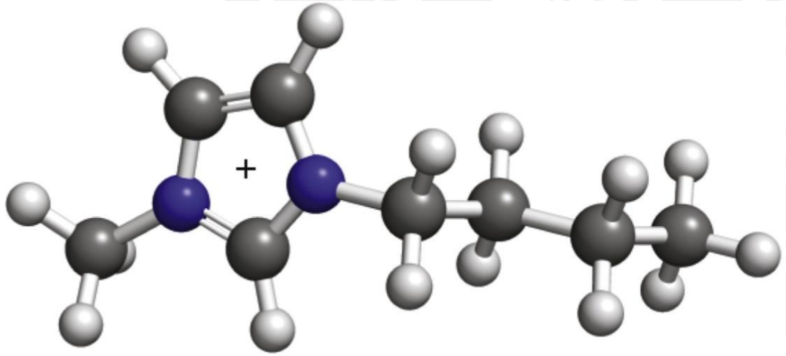
Liquid solvents are heavily used in industry to extract substances from natural products and to promote the synthesis of desired compounds.

The hazardous nature of many of these solvents has led to the use of a new class of solvents called **ionic liquids**.

Ionic Liquids



Tetrafluoroborate, BF_4^-



4 1-Butyl-3-methylimidazolium ion

Ionic liquids are typically made by combining relatively small anion, such as BF_4^- with a relatively large organic cation, such as 1-butyl-3-methylimidazolium.

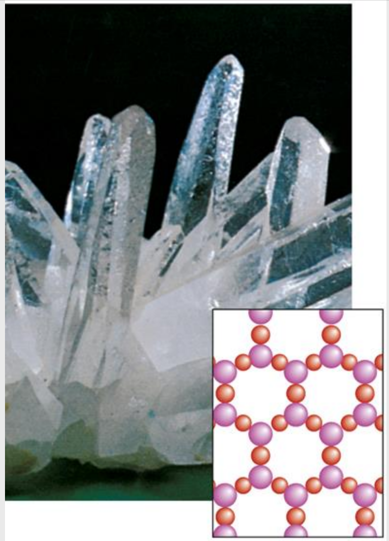
When making rubber tires for instance, ionic liquids help reduce the rubber vapour pressure and so reduce air pollution. Ionic liquids can be recycled and extracted from groundwater.

Solids

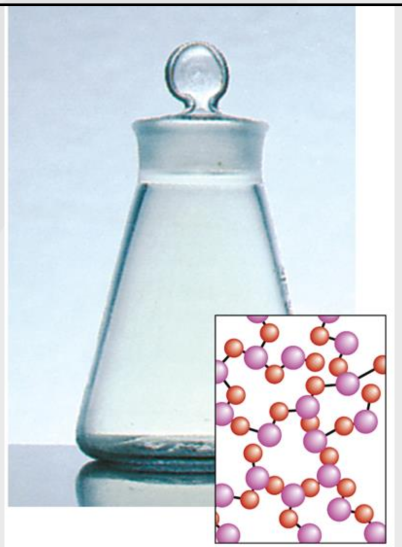
Crystalline and Amorphous Solids

Crystalline solids have long-range order.

Amorphous solids have short-range order.



Quartz
Long-range order



Glass
Short-range oder

Molecular Solids

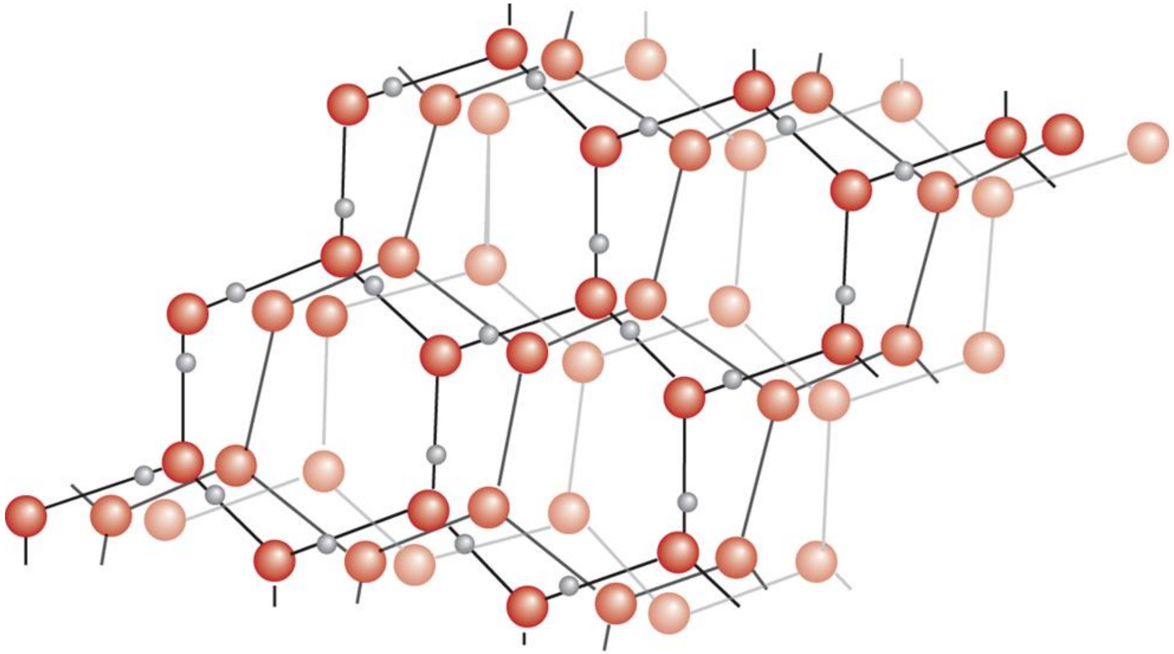


Figure 3H.3
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Molecular solids are held together by intermolecular forces.

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

Each oxygen (red) has a tetrahedral geometry.

Molecular Solids

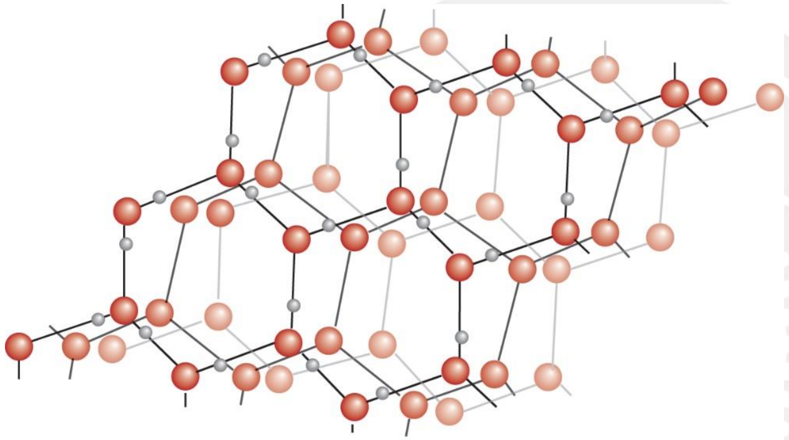

Figure 3H.3
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The openness of ice's network explains its lower density than liquid water (0.92 g·cm^{-3} vs. 1.00 g·cm^{-3} at 0 °C).

Ice is a unique example of a solid that floats in its own liquid.

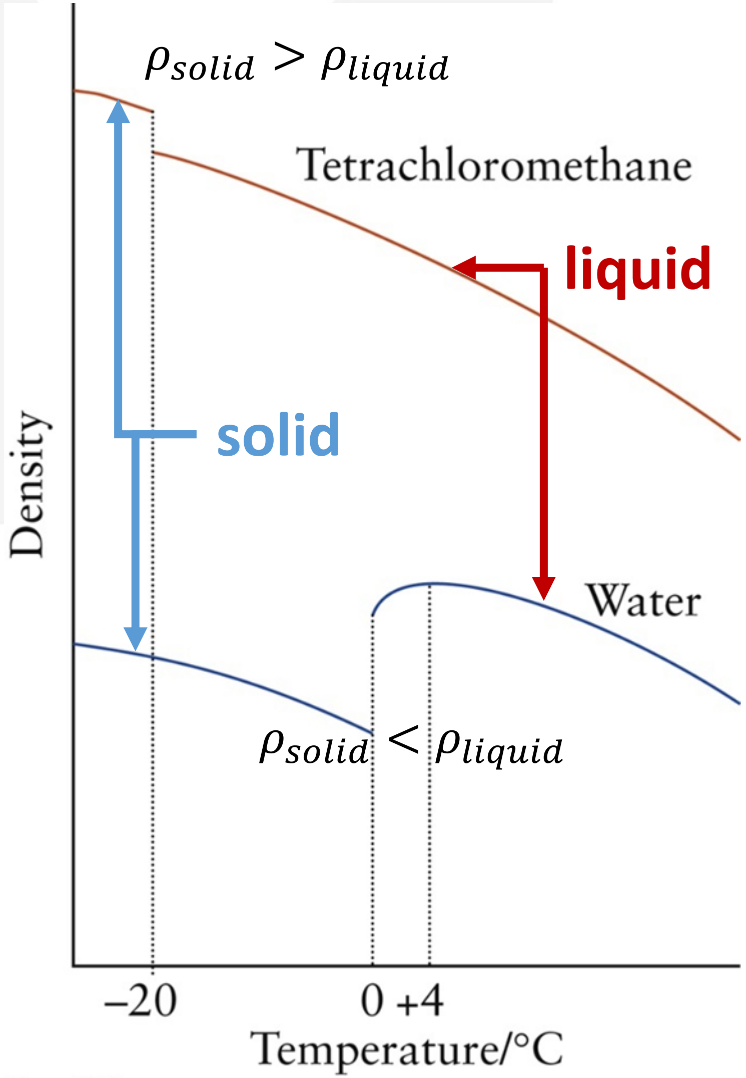

Figure 3H.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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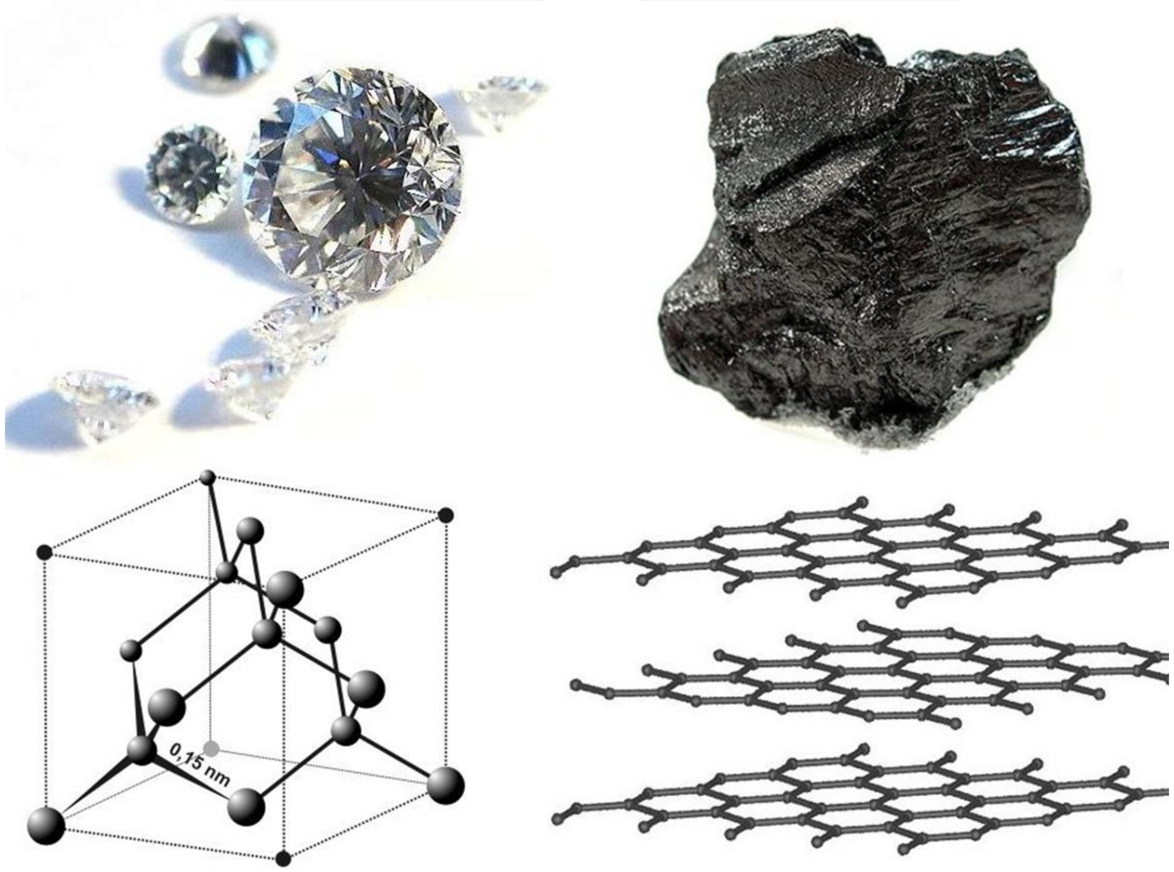
Network Solids

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.

Network Solids

Diamond and graphite, allotropes of carbon, are network solids. (Covalent bonds)



https://commons.wikimedia.org/w/index.php?curid=7223557

Metallic Solids

Metals are cations bound tightly together by a sea of swirling electrons that the metals have lost.

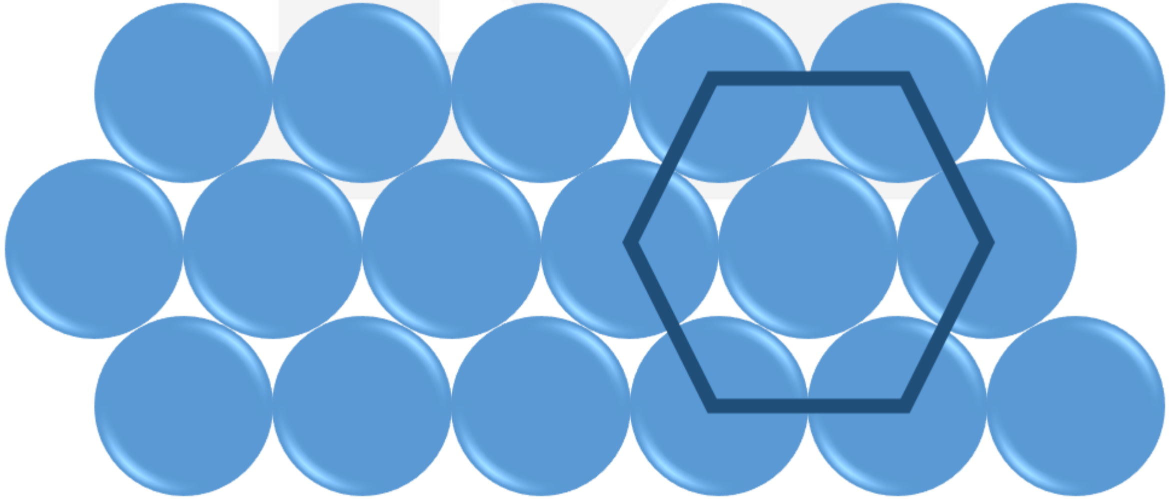
Many metallic structures are close-packed.

Close-packed Structures

Close-packed structures are layer upon layer, in a highly efficient manner, of atoms on top of each other.

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

This layer is often referred to as Layer A.

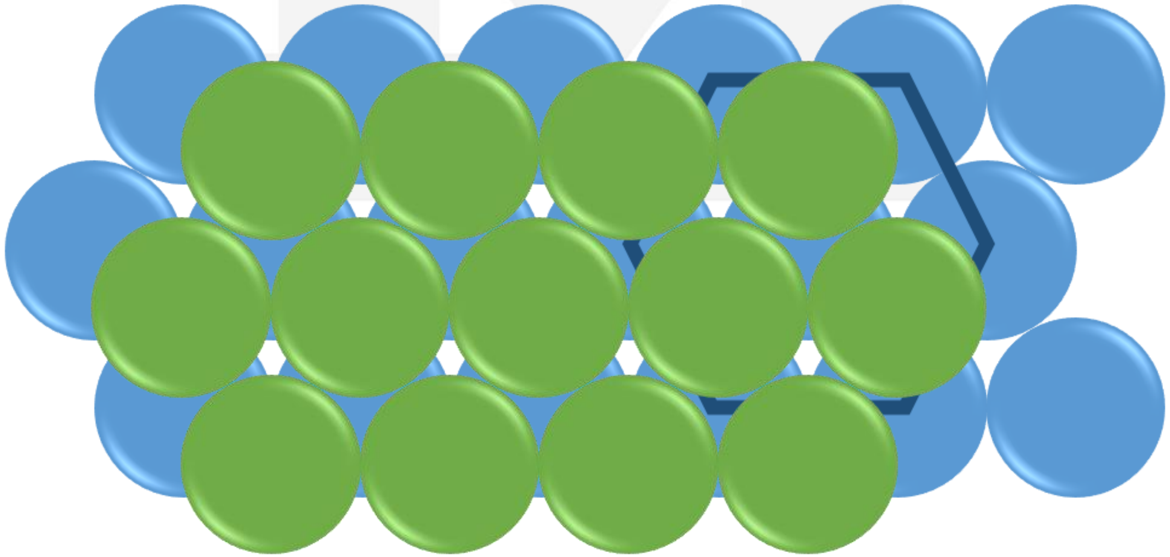


Close-packed Structures

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

This layer is called **Layer B**.

Notice how the spheres rest in the small cavities created between the spheres in Layer A.



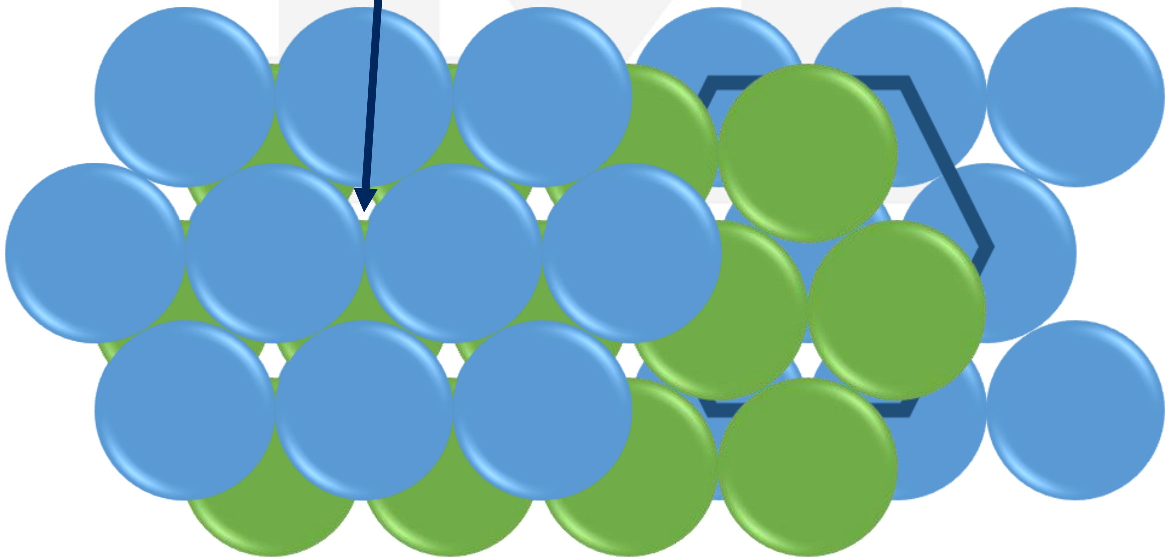
Close-packed Structures

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

In the first option a third layer, now referred to as an ABABAB pattern, positions the top Layer A directly over A Layer on the bottom.

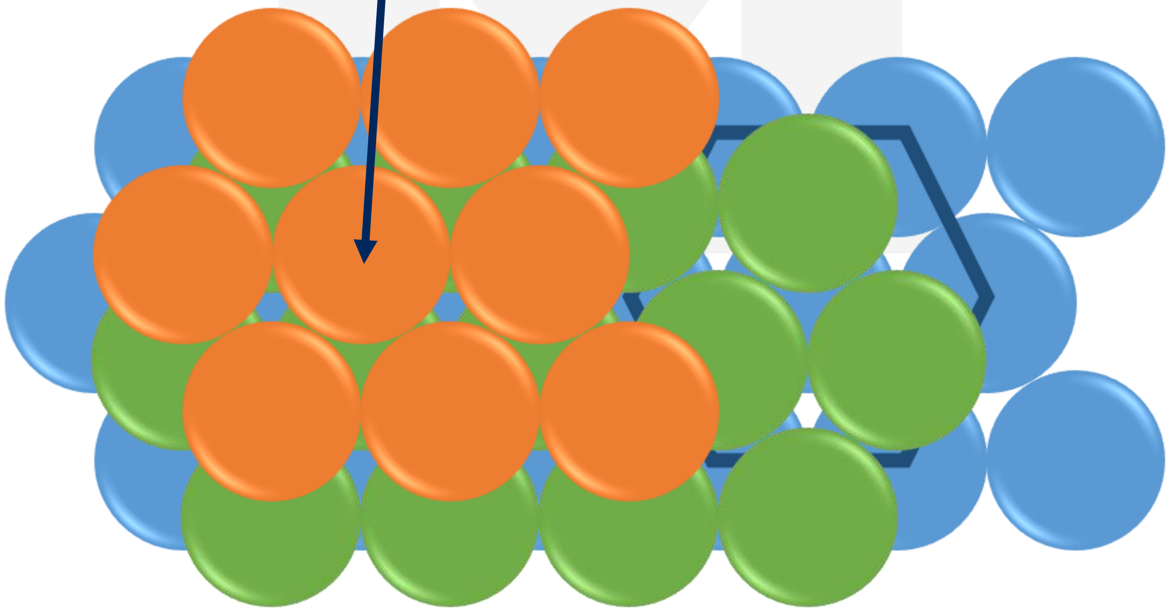
A more common name for this is **Hexagonal close-pack** (hcp).

Notice the **hole** visible all the way through.



Close-packed Structures

Notice the **hole** disappears.



In the second option the third layer, now referred to as an ABCABC pattern, places the top layer, Layer C, offset to Layer A.

A more common name is **cubic close-pack** (ccp).

HCP vs. 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 at any one time.

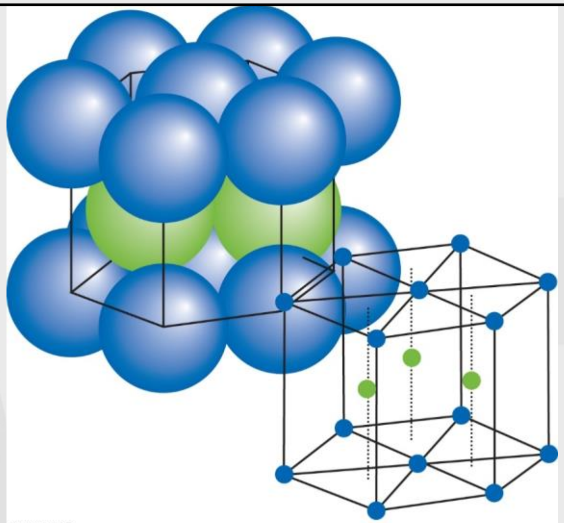


Figure 3H.15
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hcp

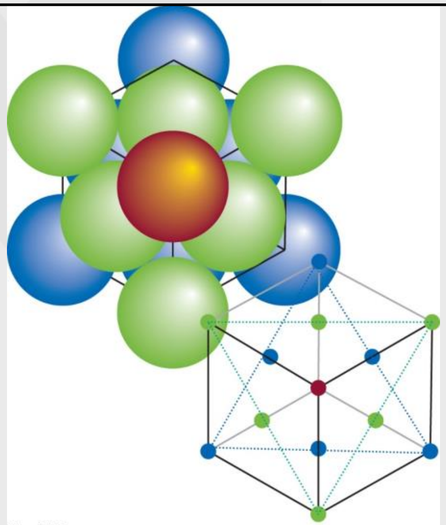

Figure 3H.17
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ccp

Describing 3D Solid Structures

Simple description of 3D solid structures

Repeating of unit cells

Unit Cells

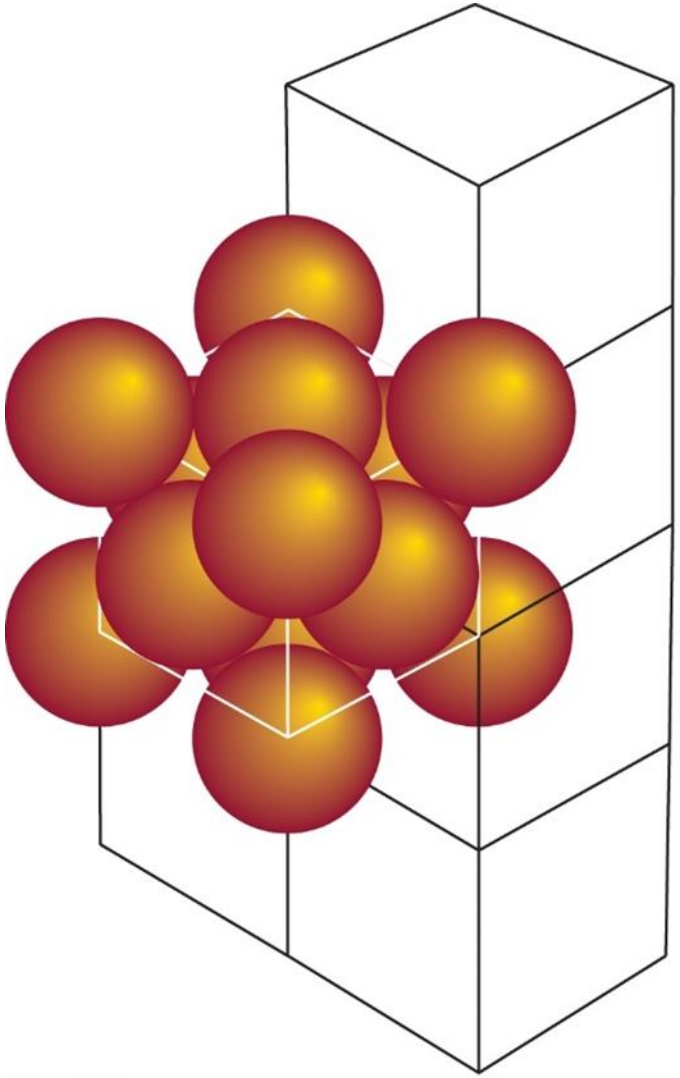

Figure 3H.20
Atkins, *Chemical Principles: The Quest for Insight*, 7e

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

The atoms in a unit cell can stack, or arrange themselves, into one of **three types of cubic structures**:

1. Primitive cubic
2. Body-centered cubic
3. Face-centered cubic (cubic close packed)

A crystal structure is constructed from unit cells of a single type that stack together without any gaps.

Unit Cells

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.

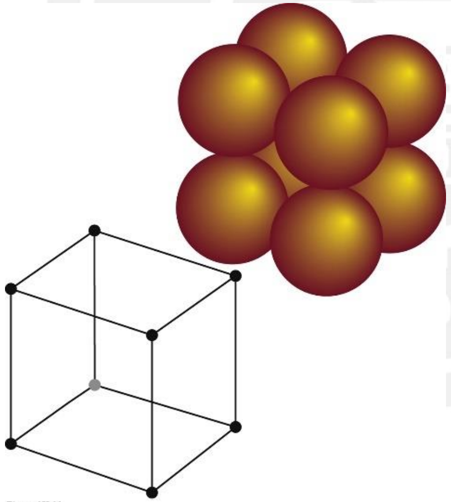

Figure 3H.22
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In a body-centered cubic structure (bcc), a single atom lies at the center of a cube formed by eight other atoms. This structure is **not close packed**.

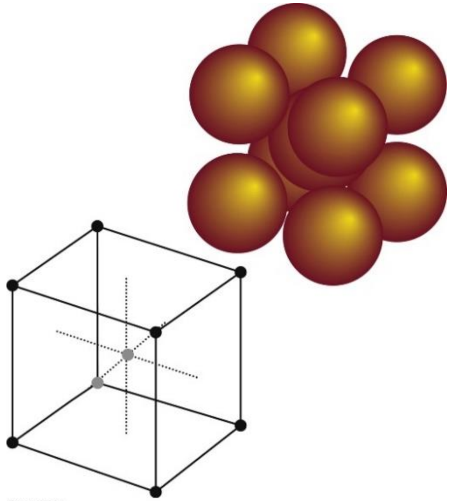

Figure 3H.21
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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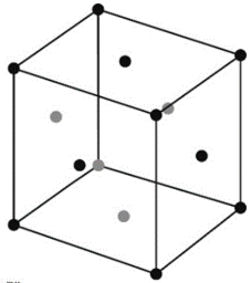
A face-centered cubic (fcc, cubic close packed) unit cell has an atom at the center of each face of the unit cell; this structure is identical to the cubic close packed structure.



Crystal Lattices

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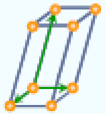
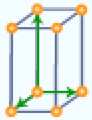
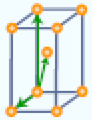
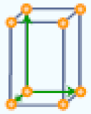
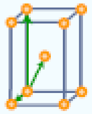
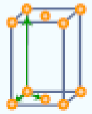
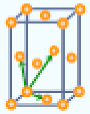
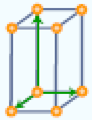
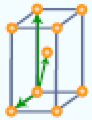
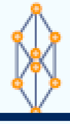
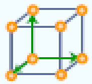
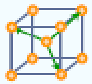
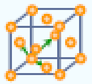
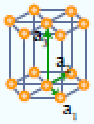
4 Lattice Types

7 Crystal Classes

Bravais Lattice	Parameters	Simple (P)	Volume Centered (I)	Base Centered (C)	Face Centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

7 crystal systems + 4 lattice types

14 Bravais lattices

Number of Atoms per Unit Cell

The number of atoms in a fcc structure is:

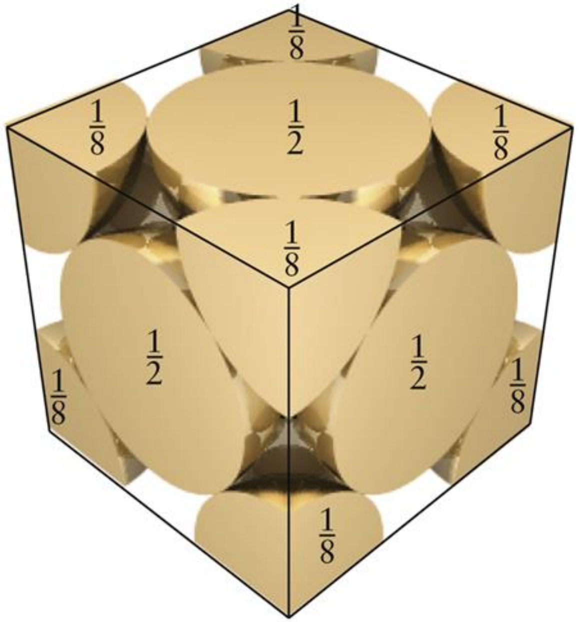
8 **corner** atoms contribute $8 \times \frac{1}{8} = 1 \text{ atom}$

6 **face** atoms contribute $6 \times \frac{1}{2} = 3 \text{ atoms}$

The total number of atoms in a fcc unit cell is:

$$1 + 3 = 4$$

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



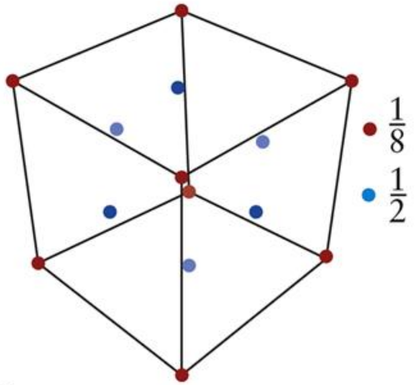


Figure 3H.26
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Short Quiz

How many atoms are in a **body-centered cubic** unit cell?

1 centre atom and 8 corner atoms:

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

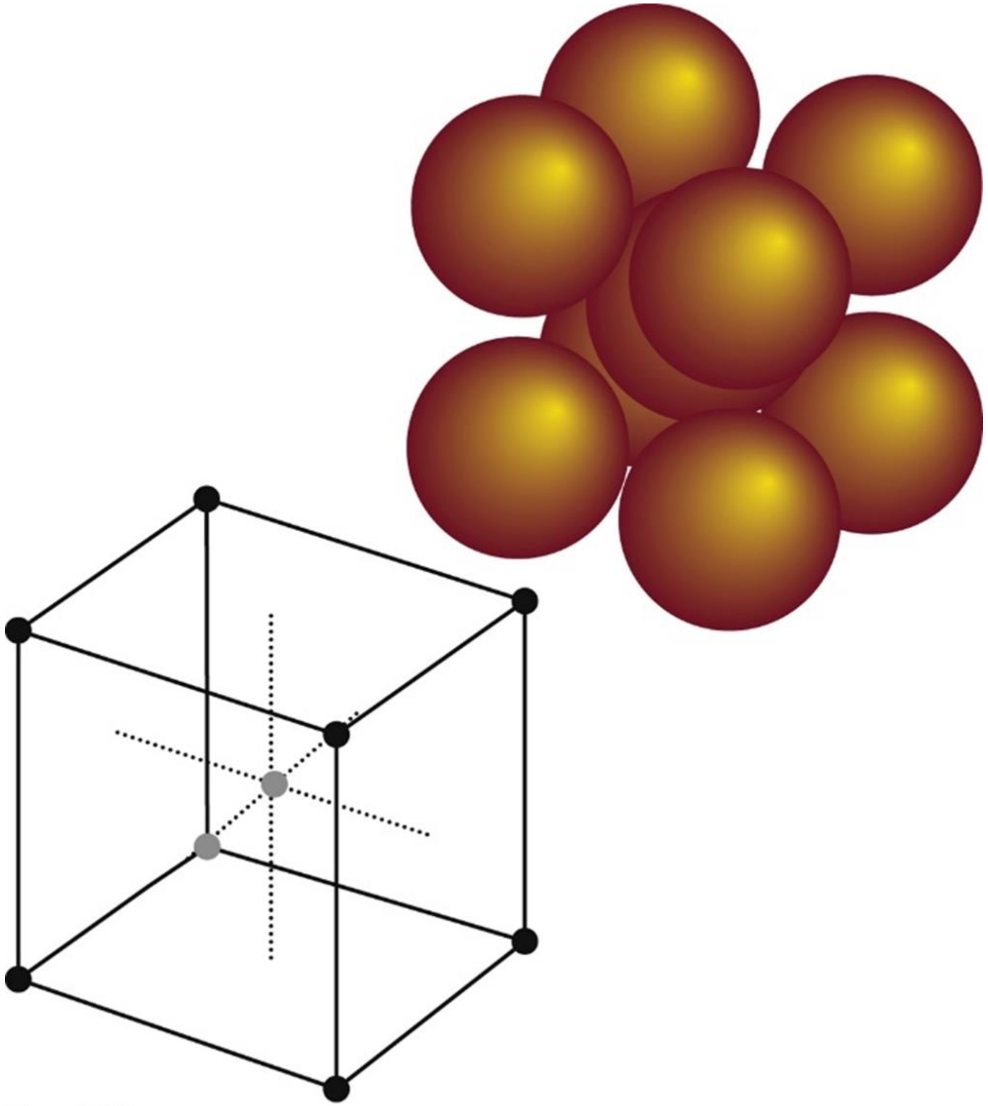

Figure 3H.21
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Ionic Structures

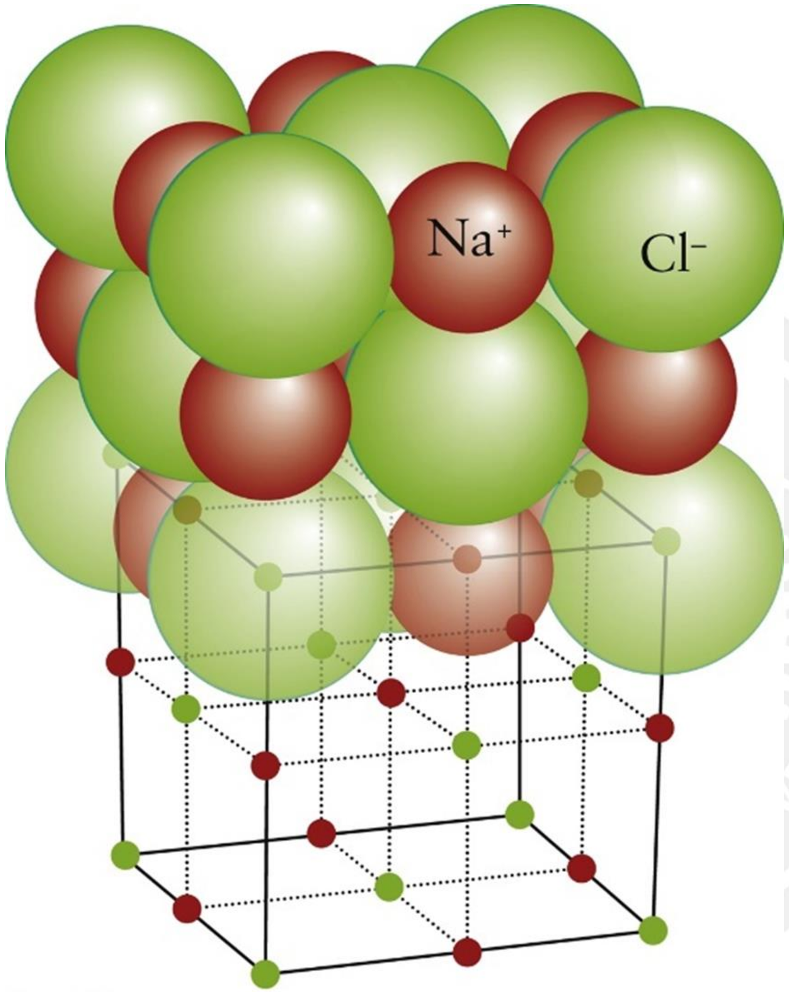

Figure 3H.28
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Whereas metals have similar atomic radii, ionic radii vary greatly in size due to their ionic charges.

Rock salt, a common name for the mineral NaCl, has an **fcc Cl^- arrangement.** However, **Na^+** is small enough to fit into the gaps; these gaps in fcc structures are called **octahedral holes**.

In this arrangement the Na^+ ions are large enough to prevent the Cl^- ions from touching, thereby reduce the Cl^- repulsions.

Ionic Structures

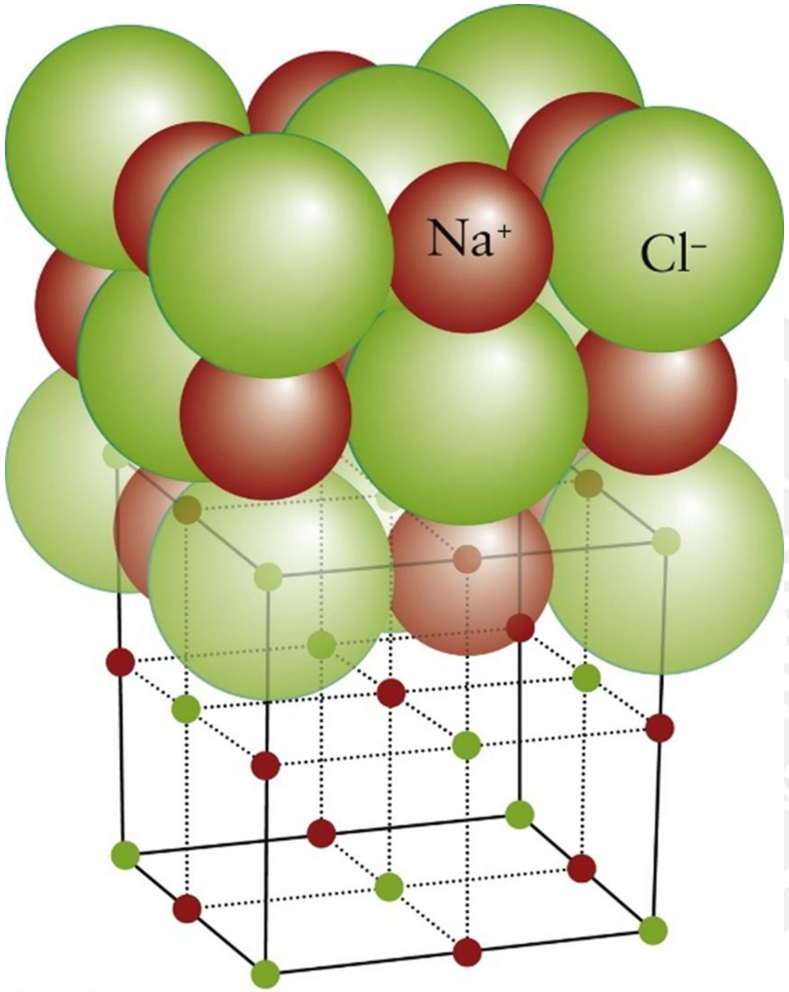

Figure 3H.28
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Both the cation and anion are each bound to 6 other ions.

Other fcc anions with cations in octahedral holes include KBr, RbI, MgO, CaO, and AgCl.

Billions of unit cells stack together to recreate the smooth faces of the crystal of sodium chloride.

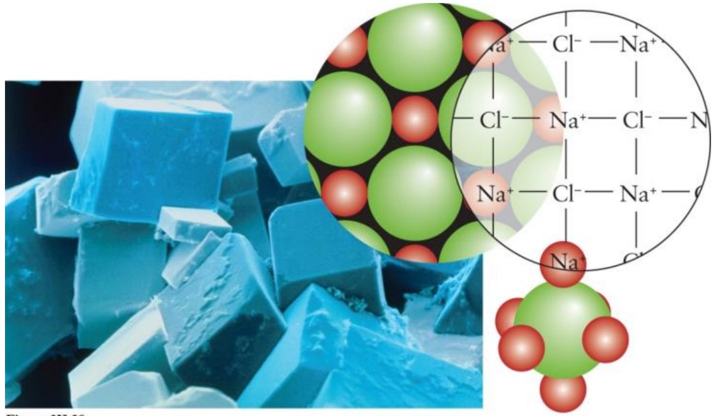

Figure 3H.29
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(Photo: Andrew Syred/Science Source.)

Search for New Materials

Civilizations depend on the development of new materials.

Concrete led to advances in architecture and construction.

Silicon-based semiconductors transformed calculators and communications.

Batteries built from new battery materials are powering all mobile electronics and are penetrating into electric vehicles and even stationary storage.