

# **CHEM103**

# **General Chemistry**

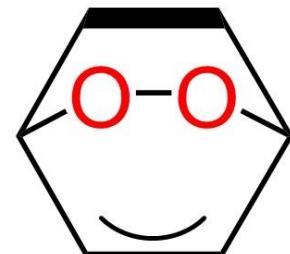
## **Chapter 11: Liquids and Intermolecular Forces**



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# **Review on Chapter 9**

**Valence-Shell Electron-Pair Repulsion Theory (VSEPR):** (Non)Bonding Electron Pairs, Electron Domains, Molecular Geometry

**Valence Bond (VB) Theory:** Orbital Overlap, Hybrid Orbital, Hybridization

**Molecular Orbital (MO) Theory:** Bonding Molecular Orbital, Anti-bonding Molecular Orbital, Bond Order, Energy-Level Diagram

( $\sigma$ ) Sigma-Bond, ( $\pi$ ) Pi-Bond, Paramagnetism & Diamagnetism

# Outline of Chapter 11

van der Waals Interactions, London Dispersion forces,  
Dipole-Dipole Interactions, Ion-Dipole Interactions &  
Hydrogen Bond

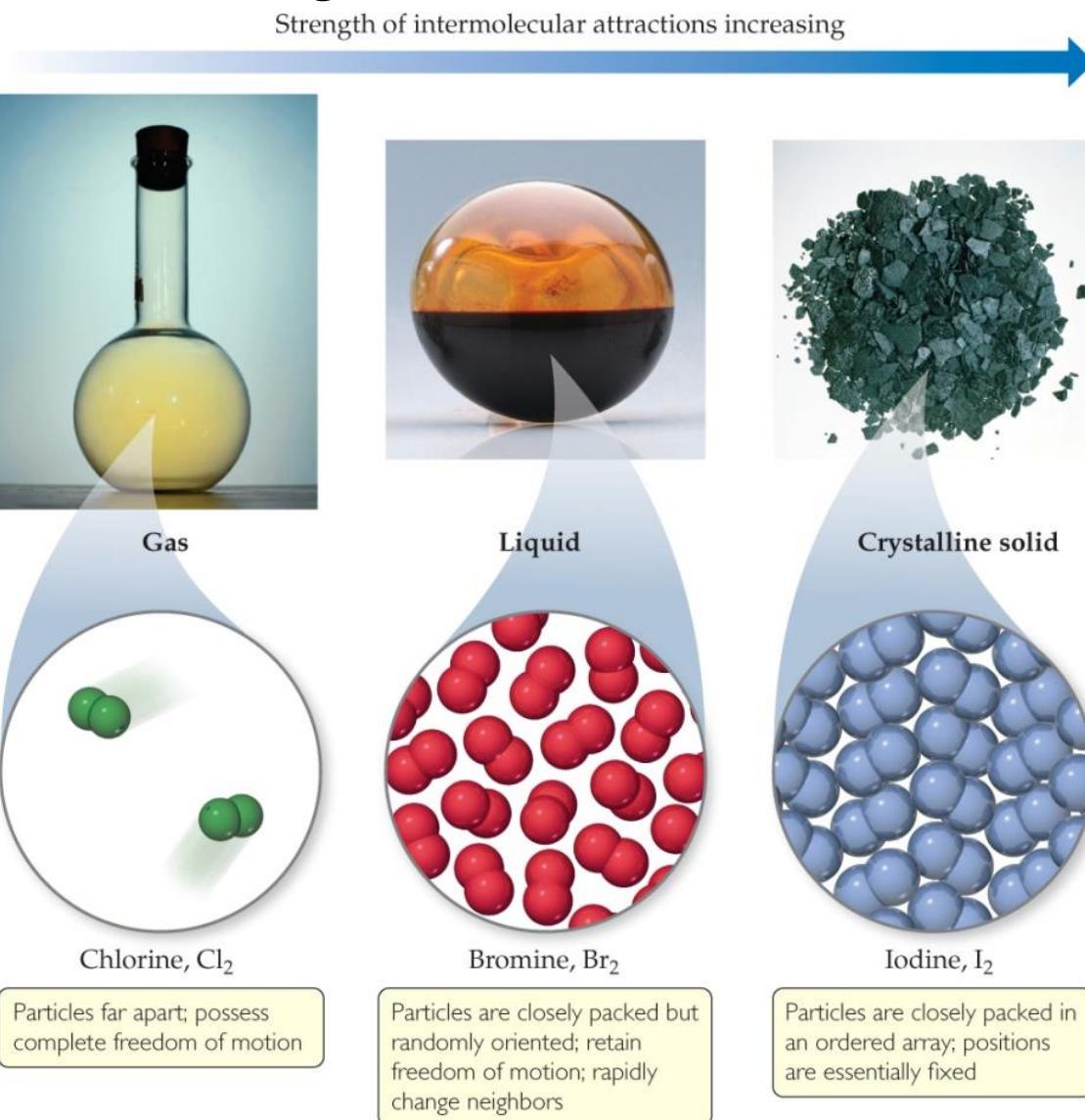
Polarizability, Boiling Point, Melting Point, Vapor Pressure, Viscosity, Surface Tension, Cohesion and Adhesion, Capillary Action

Phase Diagram, Heat of Fusion/Vaporization/Sublimation, Heating Curves, Critical Temperature and Pressure, Supercritical Fluids

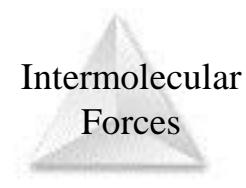
Liquid Crystals

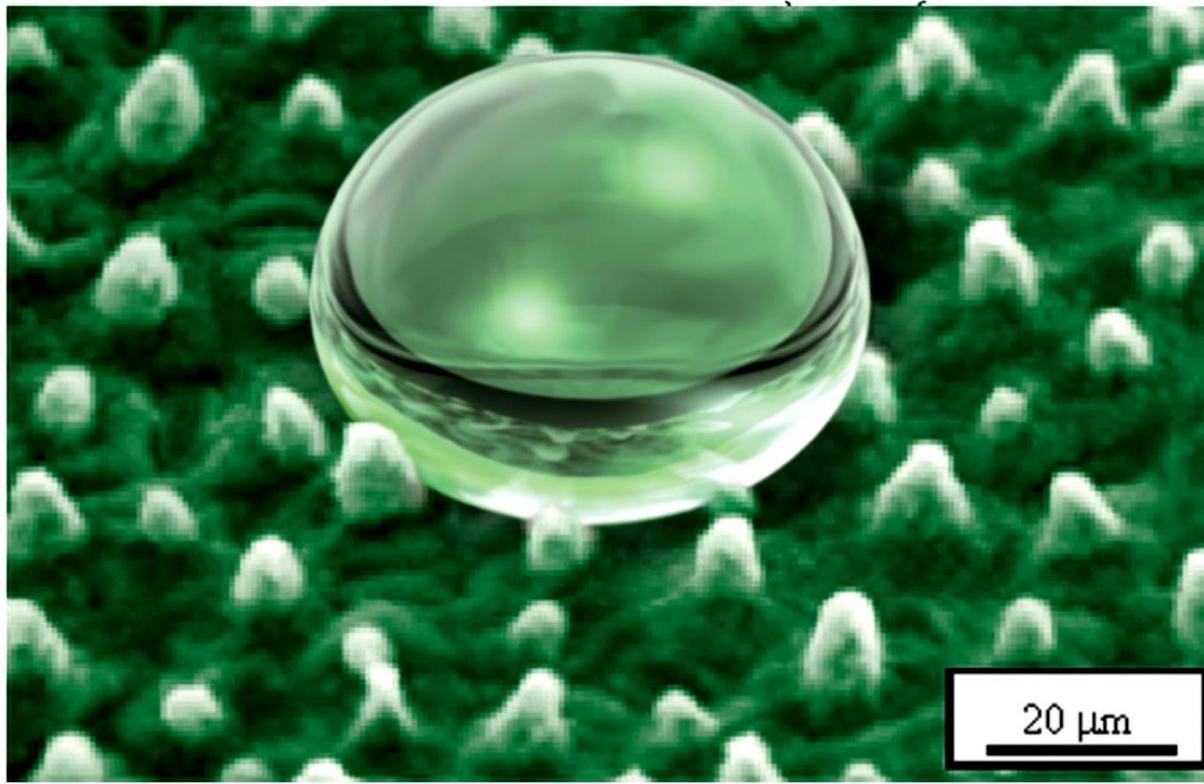
# States of Matter

- The fundamental difference between **states** of matter: the strength of the **intermolecular forces** of attraction.



- Stronger forces bring molecules closer together.



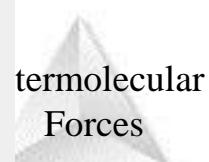


Rough surface minimizes contact between water & leaf;

- Because in the solid and liquid states particles are closer together, we refer to them as *condensed phases*.

**Table 11.1 Some Characteristic Properties of the States of Matter**

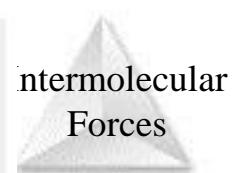
Gas	Assumes both volume and shape of its container Expands to fill its container Is compressible Flows readily Diffusion within a gas occurs rapidly
Liquid	Assumes shape of portion of container it occupies Does not expand to fill its container Is virtually incompressible Flows readily Diffusion within a liquid occurs slowly
Solid	Retains own shape and volume Does not expand to fill its container Is virtually incompressible Does not flow Diffusion within a solid occurs extremely slowly



- The **state** of a substance at a particular temperature & pressure depends on two factors:
  1. **kinetic energy** of the particles.
  2. **strength/energy of the attractions (& repulsion)** between the particles.

**Table 11.2 Comparing Kinetic Energies and Energies of Attractions for States of Matter**

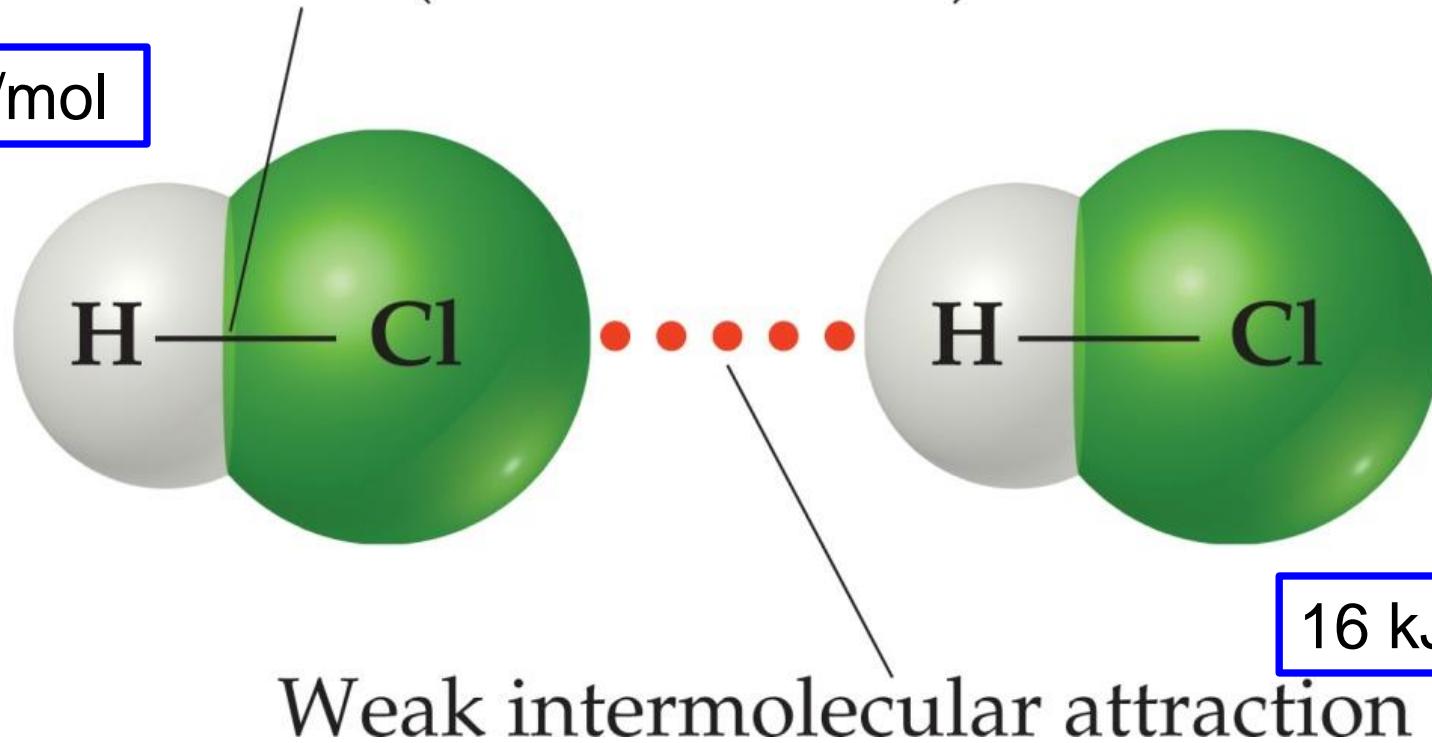
Gas	Kinetic energies >> energies of attraction
Liquid	Comparable kinetic energies and energies of attraction
Solid	Energies of attraction >> kinetic energies



# Intermolecular Forces

Strong intramolecular  
attraction (covalent bond)

431 kJ/mol



- The attractions between molecules are **NOT** as **strong** as the intramolecular attractions (bonds) that hold compounds together.

- Many **physical properties** reflect (and are determined by) **intermolecular forces**: E.g. boiling points (B.P.), melting points (M.P.) & vapor pressure.

**Table 11.3 Melting and Boiling Points of Representative Substances**

Force Holding Particles Together	Substance	Melting Point (K)	Boiling Point (K)
<b><i>Chemical bonds</i></b>			
Ionic bonds	Lithium fluoride (LiF)	1118	1949
Metallic bonds	Beryllium (Be)	1560	2742
Covalent bonds	Diamond (C)	3800	4300
<b><i>Intermolecular forces</i></b>			
Dispersion force	Nitrogen (N <sub>2</sub> )	63	77
Dipole–dipole force	Hydrogen chloride (HCl)	158	188
Hydrogen-bonding force	Hydrogen fluoride (HF)	190	293

# Types of Intermolecular Force

From the weakest one to the strongest forces:

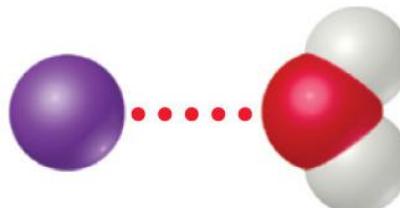
- **van der Waals forces**: London dispersion forces (色散力) & Dipole–dipole forces



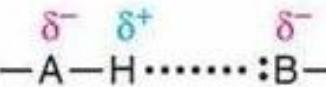
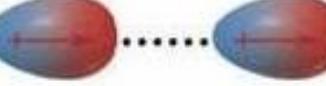
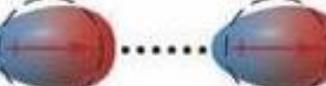
- **Hydrogen bonding**



- **Ion–dipole forces**



●	H
●	F
●	Na <sup>+</sup>
●	O

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
<b>Nonbonding (Intermolecular)</b>				
Ion-dipole		Ion charge–dipole charge	40–600	$\text{Na}^+ \cdots \text{O}-\text{H}$
H bond		Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$\begin{matrix} \ddot{\text{O}} & -\text{H} \\   & \cdots &   \\ \text{H} & & \text{H} \end{matrix}$
Dipole-dipole		Dipole charges	5–25	$\text{I}-\text{Cl} \cdots \text{I}-\text{Cl}$
Ion-induced dipole		Ion charge–polarizable e⁻ cloud	3–15	$\text{Fe}^{2+} \cdots \text{O}_2$
Dipole-induced dipole		Dipole charge–polarizable e⁻ cloud	2–10	$\text{H}-\text{Cl} \cdots \text{Cl}-\text{Cl}$
Dispersion (London)		Polarizable e⁻ clouds	0.05–40	$\text{F}-\text{F} \cdots \text{F}-\text{F}$

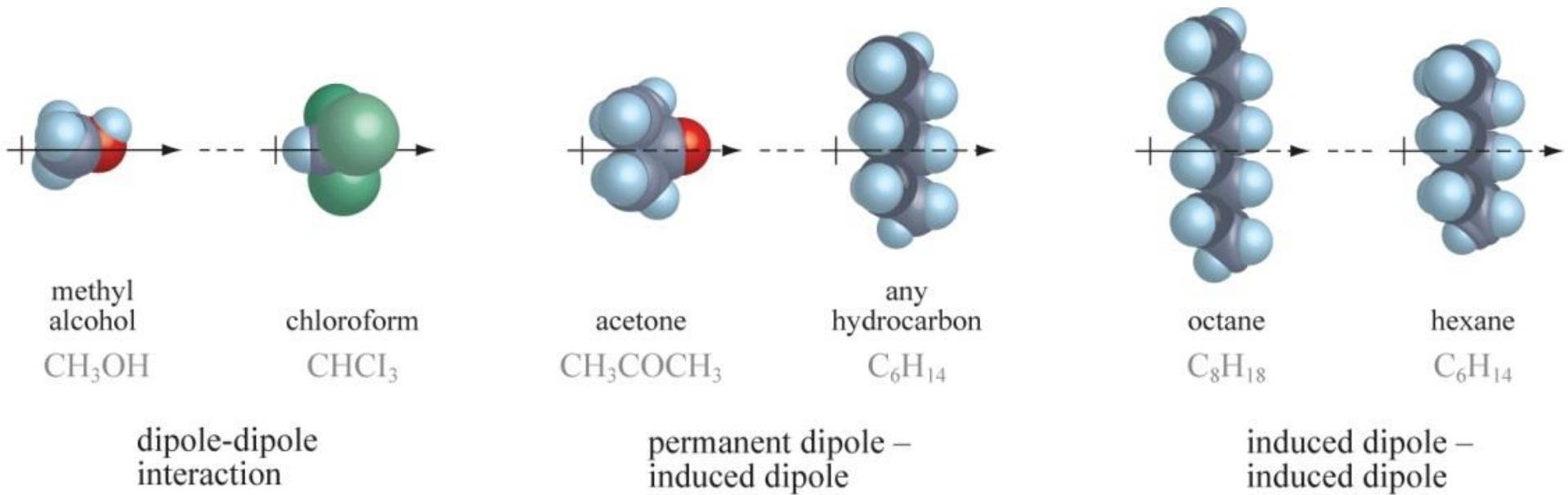
**(Extra Info.)**

Figure 2.2 Noncovalent interactions

## (Extra Info.)

Type of Interaction	Model	Example	Dependence of Energy on Distance
(a) Charge–charge Longest-range force; nondirectional			$1/r$
(b) Charge–dipole Depends on orientation of dipole			$1/r^2$
(c) Dipole–dipole Depends on mutual orientation of dipoles			$1/r^3$
(d) Charge–induced dipole Depends on polarizability of molecule in which dipole is induced			$1/r^4$
(e) Dipole–induced dipole Depends on polarizability of molecule in which dipole is induced			$1/r^5$
(f) Dispersion Involves mutual synchronization of fluctuating charges			$1/r^6$
(g) van der Waals repulsion Occurs when outer electron orbitals overlap			$1/r^{12}$
(h) Hydrogen bond Charge attraction + partial covalent bond			Length of bond fixed

# van der Waals Interactions



Strongest (left) to weakest (right):

Dipole–dipole interaction

Dipole–induced dipole interaction

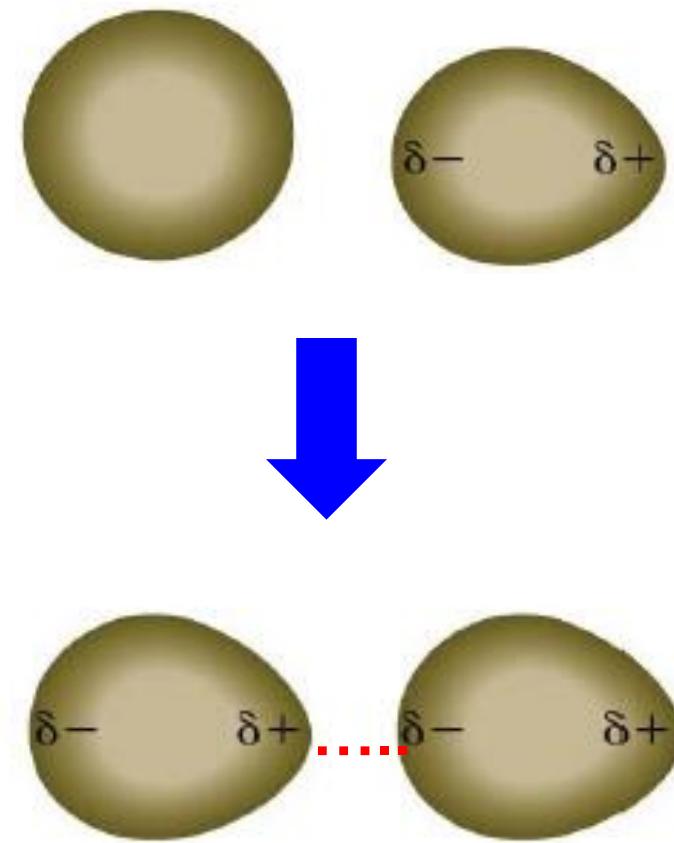
Induced dipole–induced dipole interaction

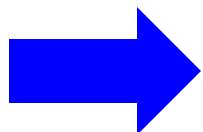
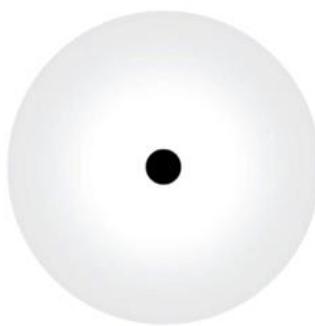
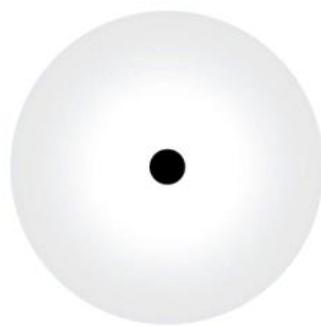
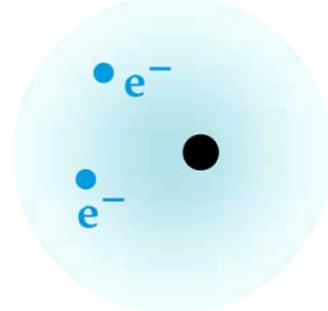
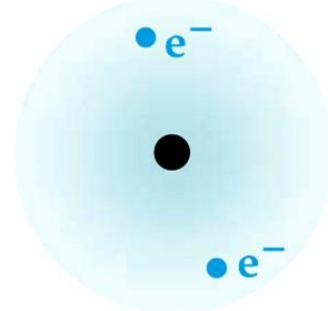
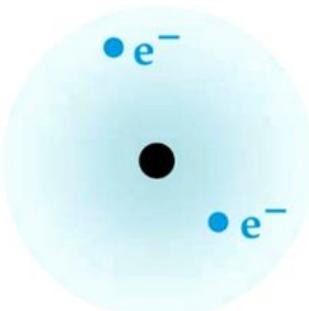
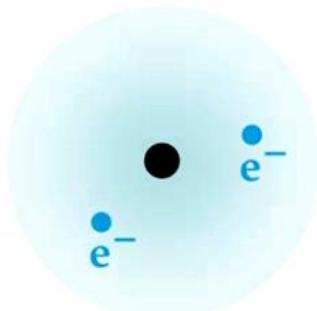


Johannes Diderik van der Waals

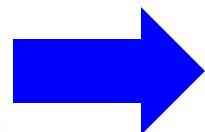
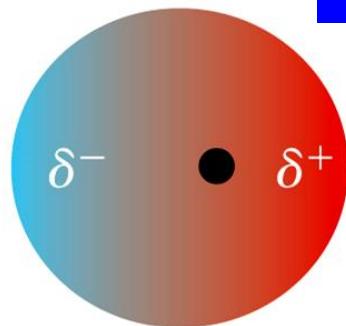
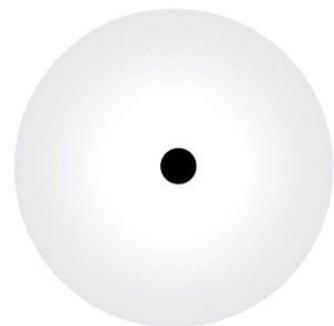
# London Dispersion Forces

- These forces are **present in all molecules**, whether they are polar or nonpolar.
- The tendency of an electron cloud to distort is called **polarizability**.
- Instantaneous induced-dipole induced-dipole interactions.
- Generally, the **greater** the **polarizability**, the **larger** dispersion forces.





### Polarization view



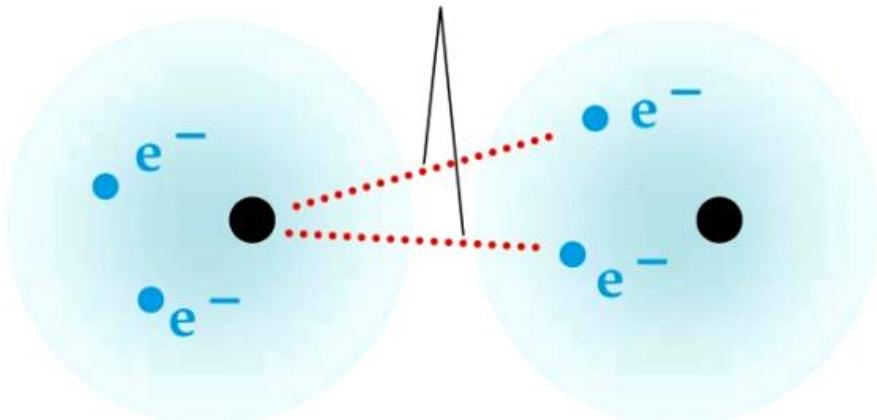
(a) Two helium atoms, no polarization

The 2 electrons in the 1s orbital of two He atoms repel each other.

(b) Instantaneous dipole on atom B

At **this instant**, then, the He atom B is polar.

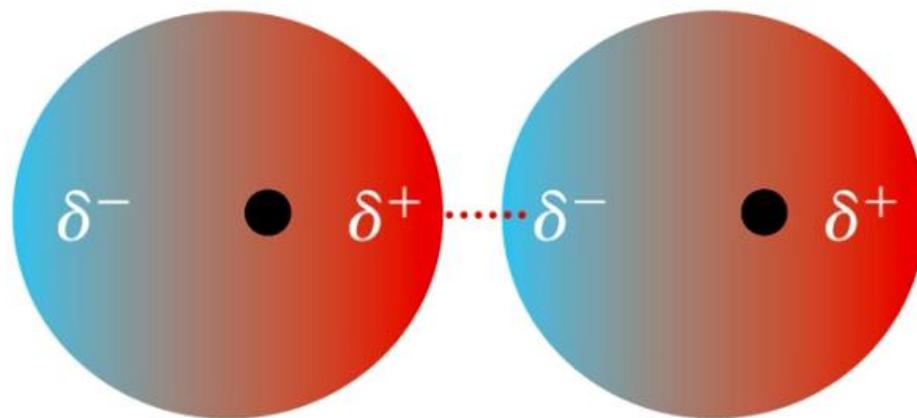
## Electrostatic attraction



Atom A

Atom B

Then, the **instantaneous induced dipole** on the He atom B **induce** a **dipole** on the He atom A, to avoid e-e repulsion.



Atom A

Atom B

London dispersion forces (or dispersion forces) are **attractions between an instantaneous induced dipole & an induced dipole.**

(c) Induced dipole on atom A



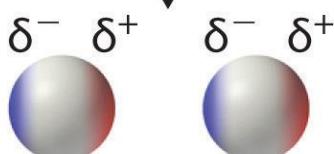
He(A)      He(B)

No polarization



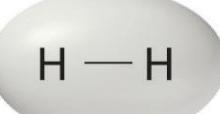
He(A)      He(B)

Instantaneous dipole on atom A

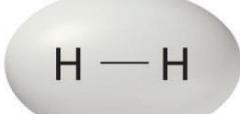


He(A)      He(B)

Induced dipole  
on atom B

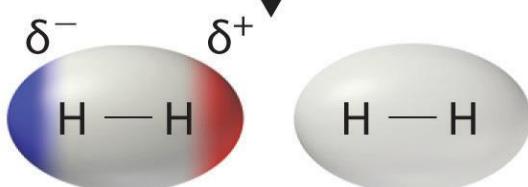


H<sub>2</sub>(A)



H<sub>2</sub>(B)

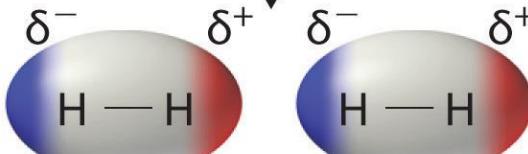
No polarization



H<sub>2</sub>(A)

H<sub>2</sub>(B)

Instantaneous dipole on molecule A



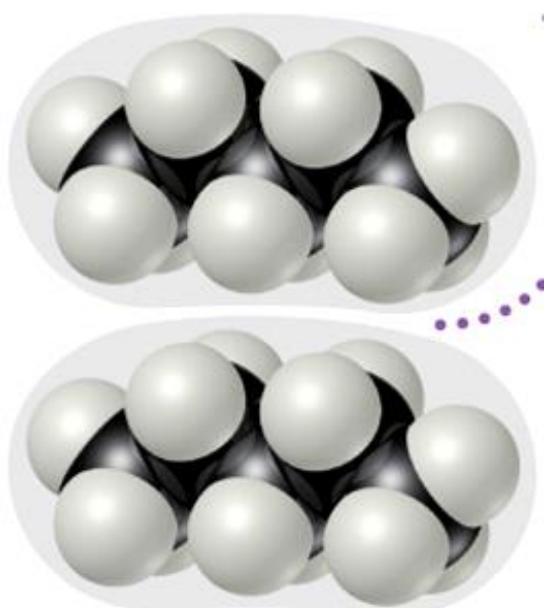
H<sub>2</sub>(B)

Induced dipole on  
molecule B

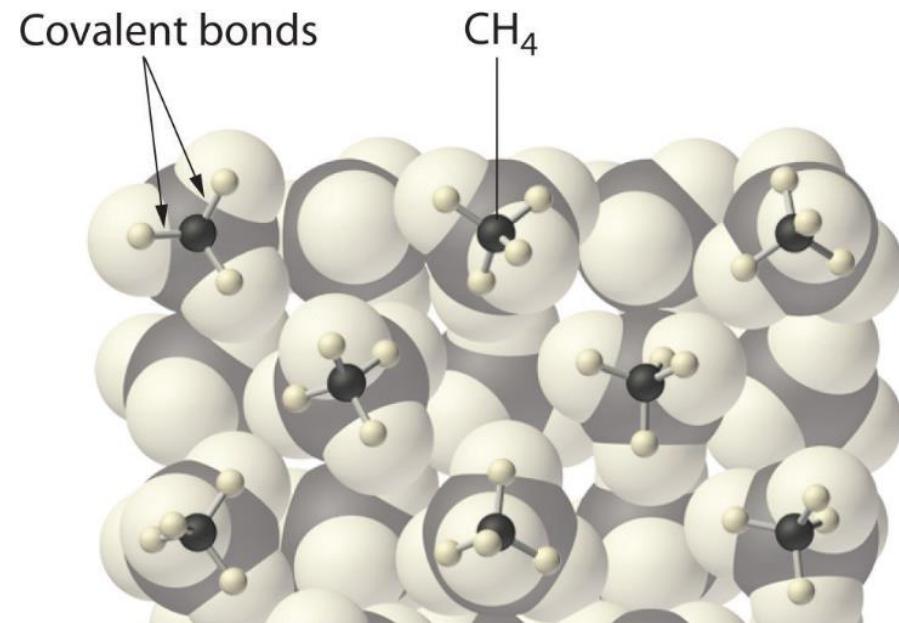
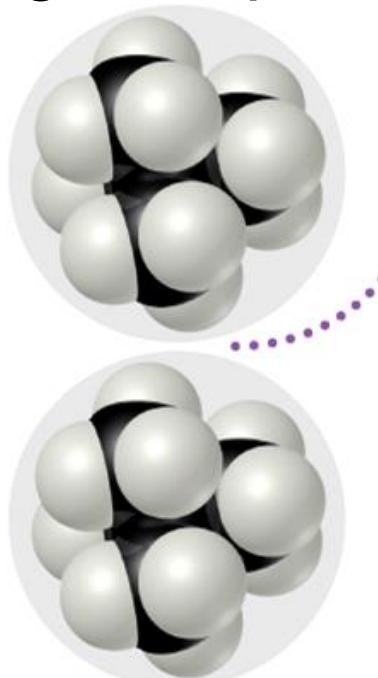
London dispersion forces  
for He atoms (left) and  
H<sub>2</sub> molecules (right)

# Factors Affecting Amount of Dispersion Force

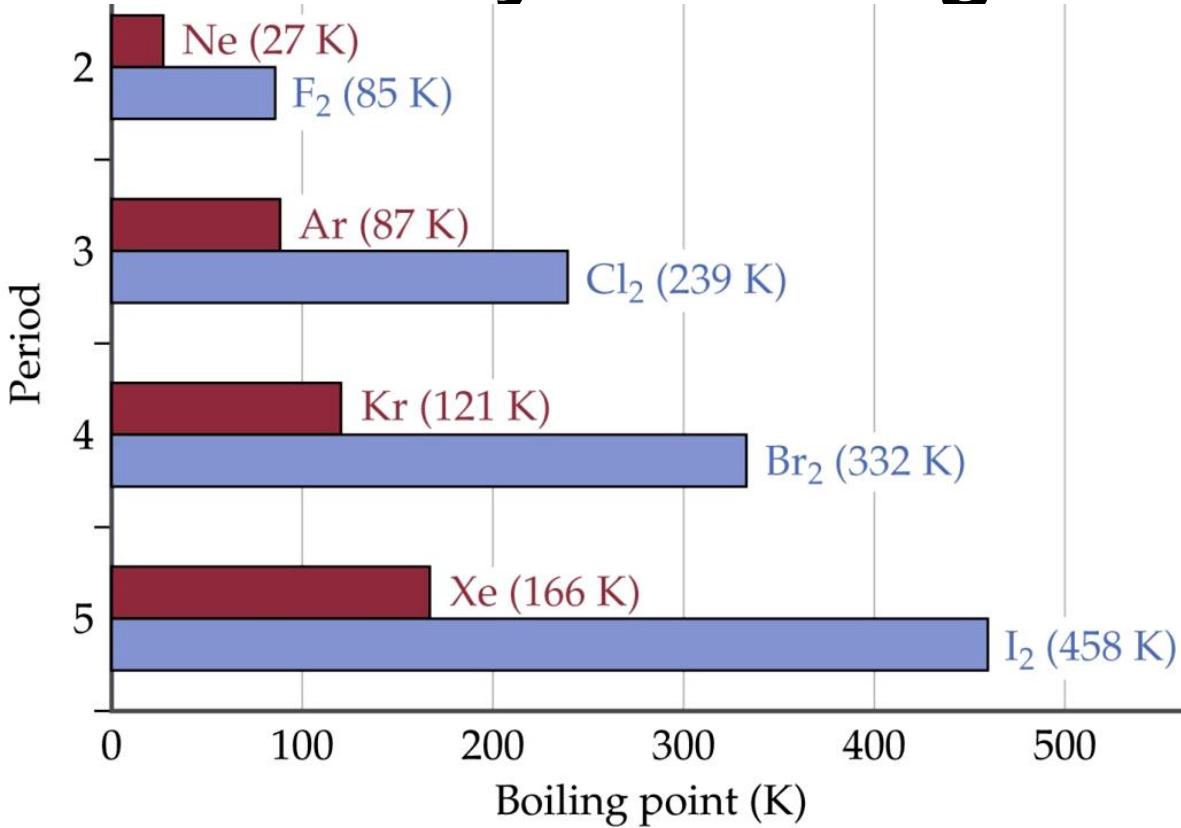
- Number of electrons in an atom (**more electrons, more dispersion force**).
- **Larger size** of atom or molecule/**molecular weight**.
- Shape of molecules with similar masses (more compact, less dispersion force (like neopentane); long, tend to have stronger dispersion (like *n*-pentane)).



$bp = 309.4\text{ K}$   
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# Polarizability & Boiling Point

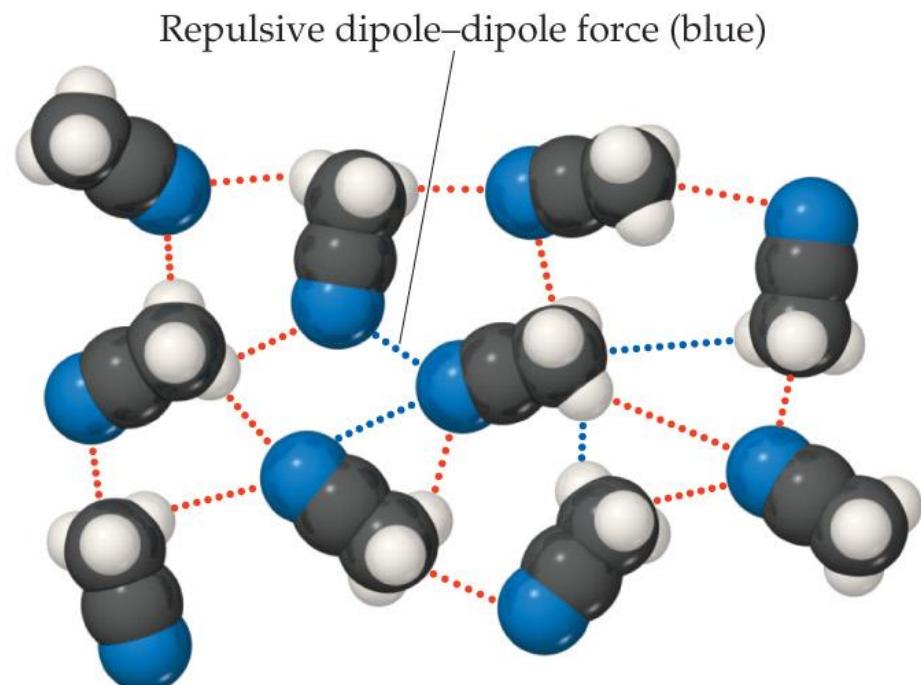
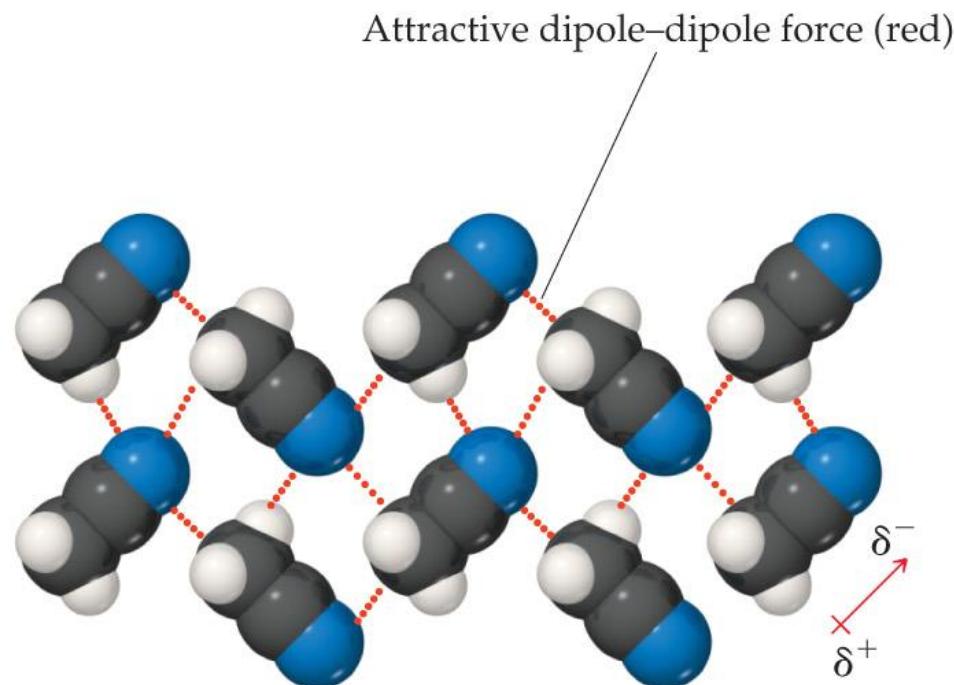


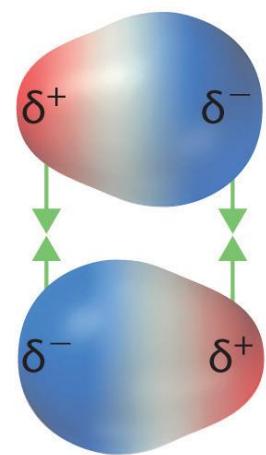
- **Larger atoms** have larger electron clouds that are easier to polarize (greater **polarizability**), due to **weaker attraction** between the valence electrons & nucleus.
- Thus, the strength of dispersion forces generally increase with **increased molecular weight**

→ **larger B.P.**

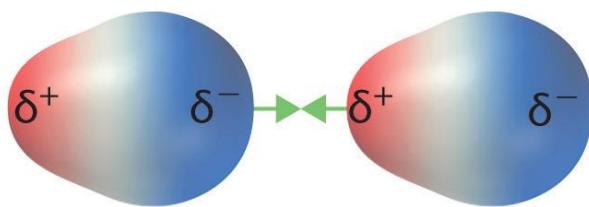
# Dipole–Dipole Interactions

- Polar molecules have a permanent dipole (a more positive and a more negative end: two poles,  $\delta^+$  and  $\delta^-$ ) and are attracted to each other.
- The oppositely charged ends attract each other.

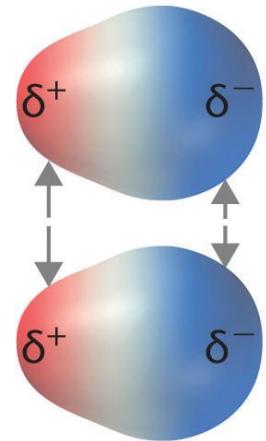




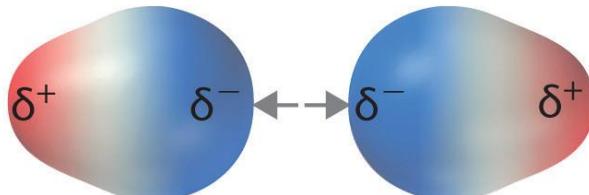
**(a) Attraction**



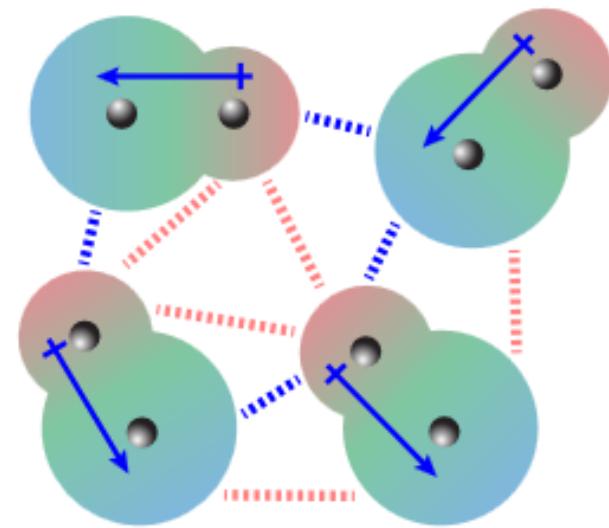
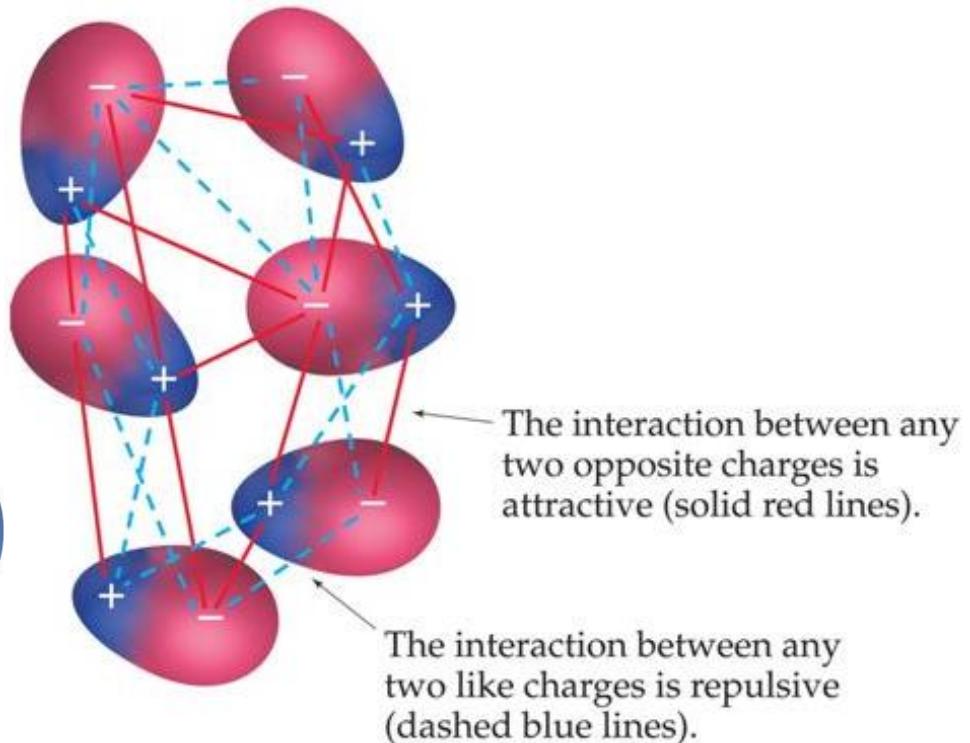
**(b) Attraction**



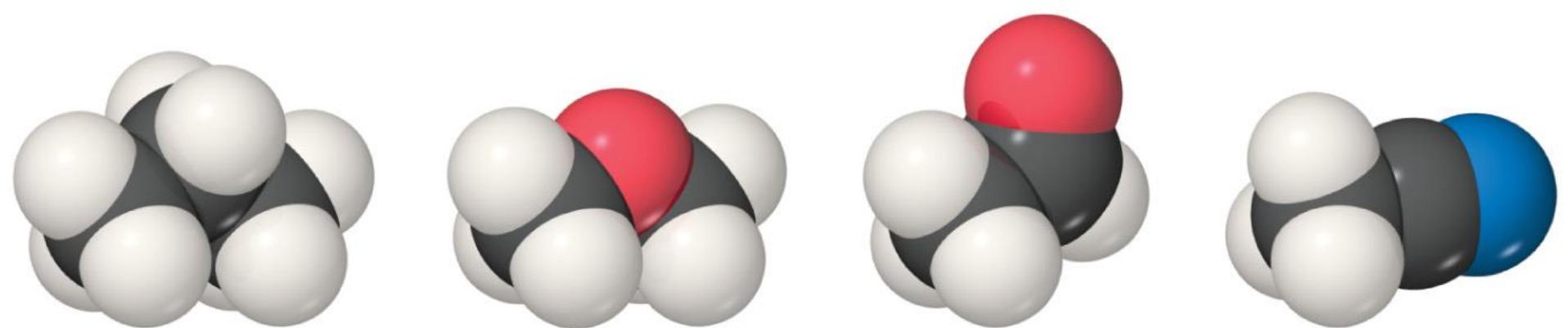
**(c) Repulsion**



**(d) Repulsion**



attraction  
repulsion



Propane  
 $\text{CH}_3\text{CH}_2\text{CH}_3$   
 MW = 44 amu  
 $\mu = 0.1 \text{ D}$   
 bp = 231 K

Dimethyl ether  
 $\text{CH}_3\text{OCH}_3$   
 MW = 46 amu  
 $\mu = 1.3 \text{ D}$   
 bp = 248 K

Acetaldehyde  
 $\text{CH}_3\text{CHO}$   
 MW = 44 amu  
 $\mu = 2.7 \text{ D}$   
 bp = 294 K

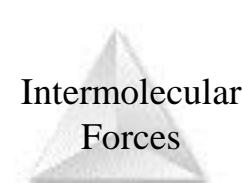
Acetonitrile  
 $\text{CH}_3\text{CN}$   
 MW = 41 amu  
 $\mu = 3.9 \text{ D}$   
 bp = 355 K

Increasing polarity  
 Increasing strength of dipole–dipole forces

- For molecules of **approximately equal mass & size**,
- the strength of intermolecular **attraction increases with increasing polarity**.
  - the **more polar** the molecule, the **higher its boiling point**.

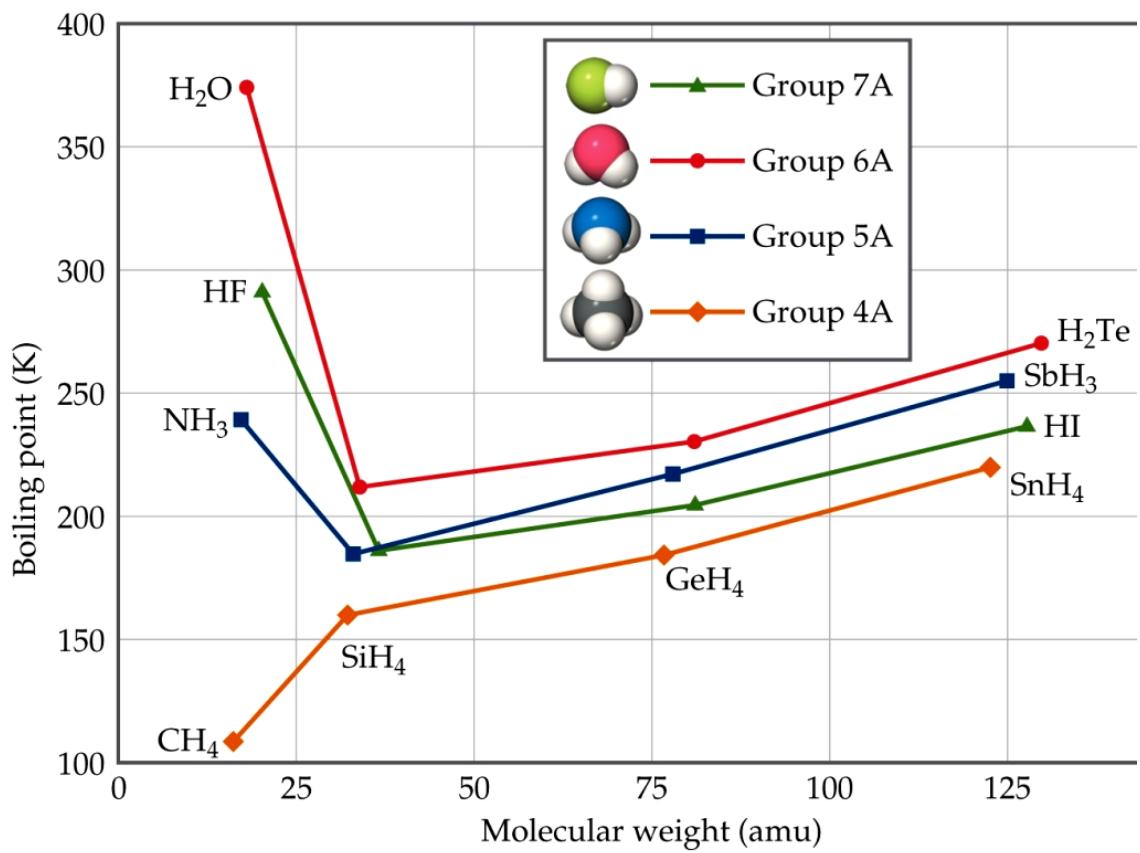
# Which Have a Greater Effect

- If two molecules are of **comparable size and shape**, **dipole–dipole** interactions will likely be the dominating force.
- If one molecule is **much larger** than another, **dispersion forces will possibly** determine its physical properties.



Intermolecular  
Forces

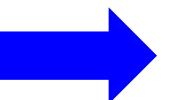
# How Do We Explain This?



- The **nonpolar series** follow the expected trend: **higher B.P.** as the group member gets **larger**.

- The **polar series** **follow** the trend **except** for the **smallest** molecules in each group.

**H<sub>2</sub>O:** a high melting point, specific heat & heat of vaporization.

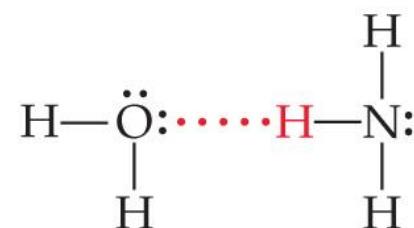
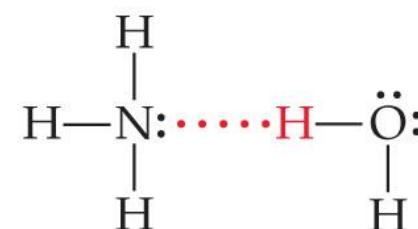
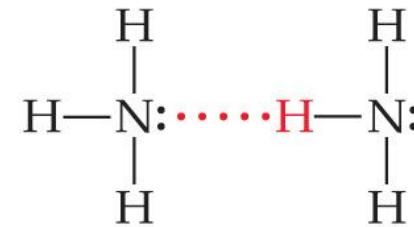


Intermolecular forces between H<sub>2</sub>O are very strong. (**Hydrogen bonding**)

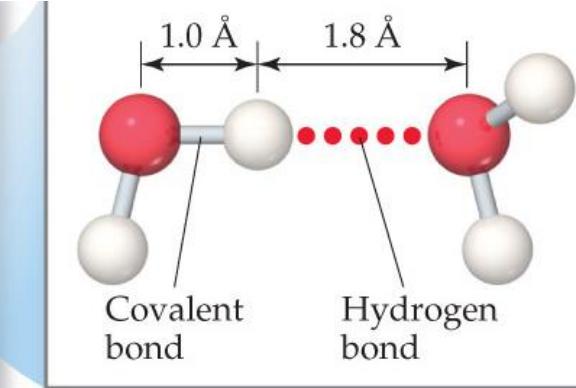
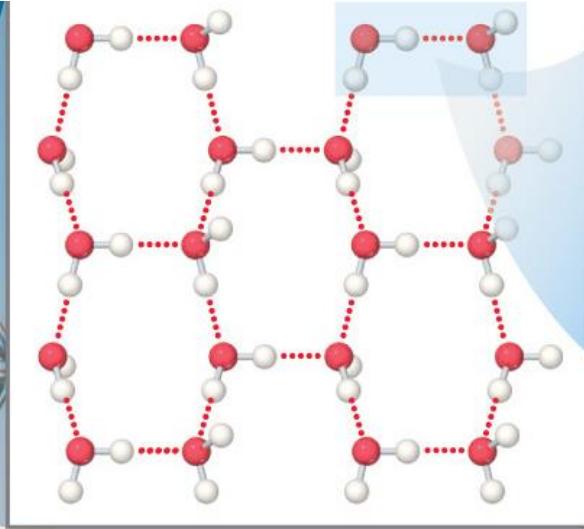
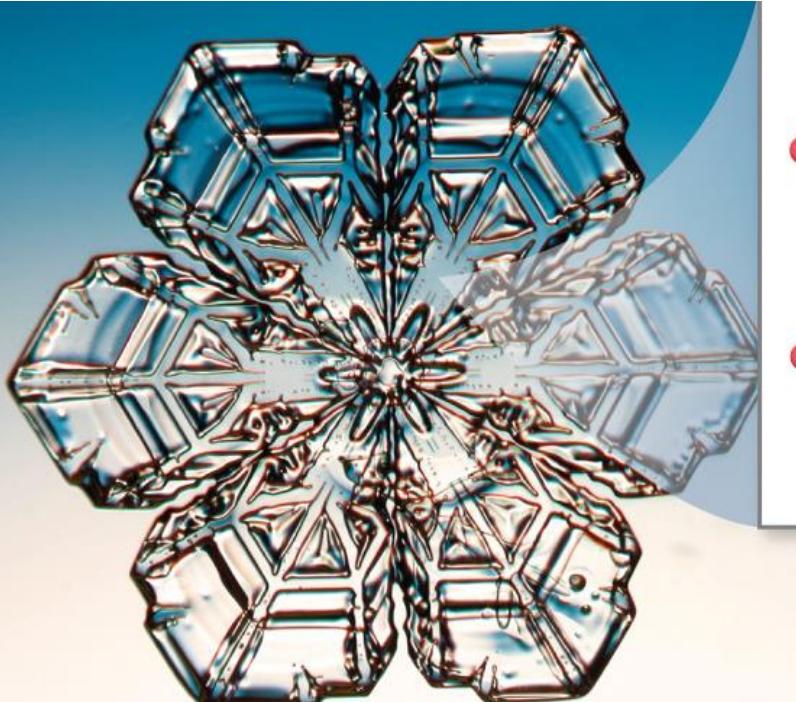
# Hydrogen Bonding

- The **dipole–dipole interactions** experienced are unusually strong, when H is bonded to **N, O, or F**.
- A hydrogen bond is an **attraction between a hydrogen atom attached to a highly electronegative atom (X) & a nearby large electronegative atom (Y)** in another molecule or chemical group. X or Y: **N, O, or F**

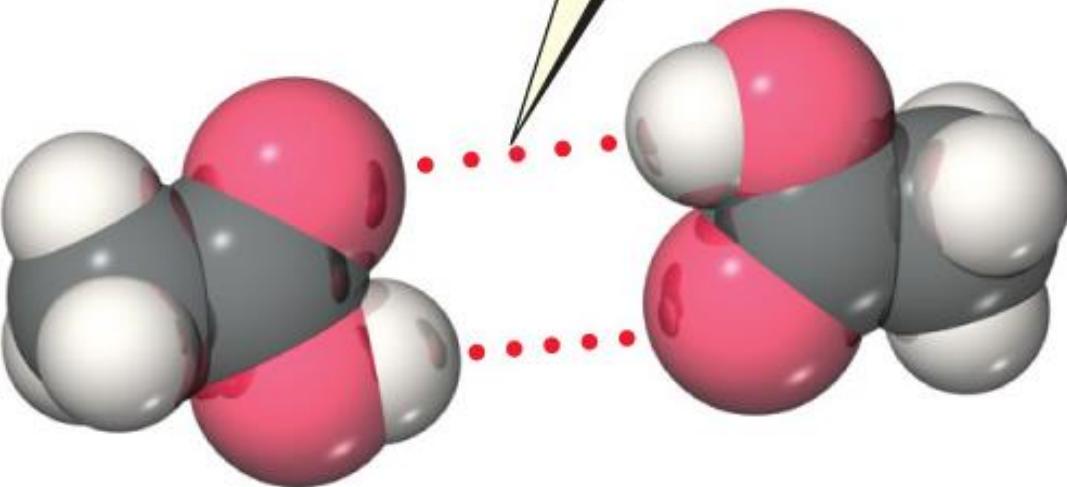
Covalent bond,  
*intramolecular*      Hydrogen bond,  
*intermolecular*



- The high electronegativity of N, O, and F interact with a nearly bare nucleus (H, which contains one proton).



Each molecule can form two hydrogen bonds with a neighbor

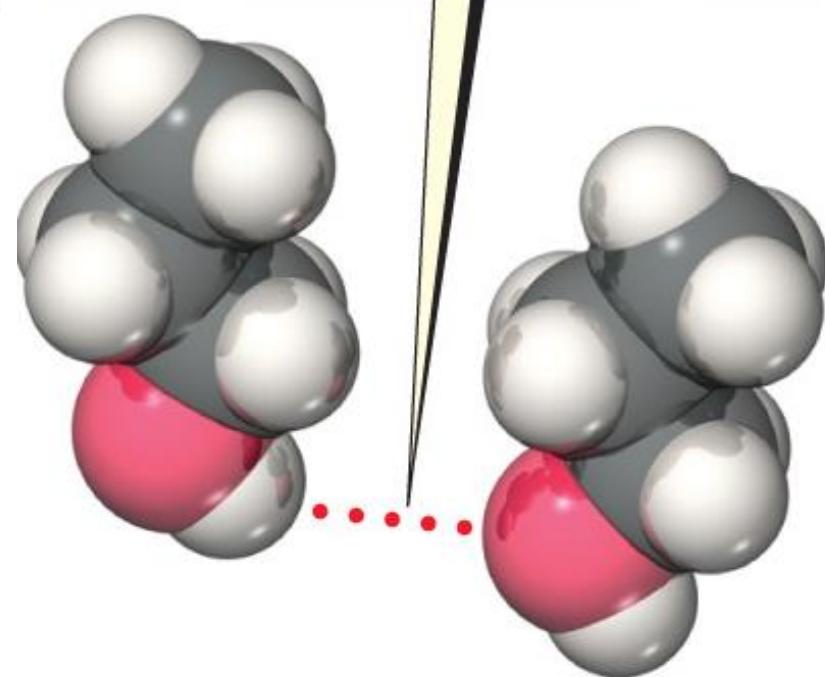


Acetic acid,  $\text{CH}_3\text{COOH}$

MW = 60 amu

bp = 391 K

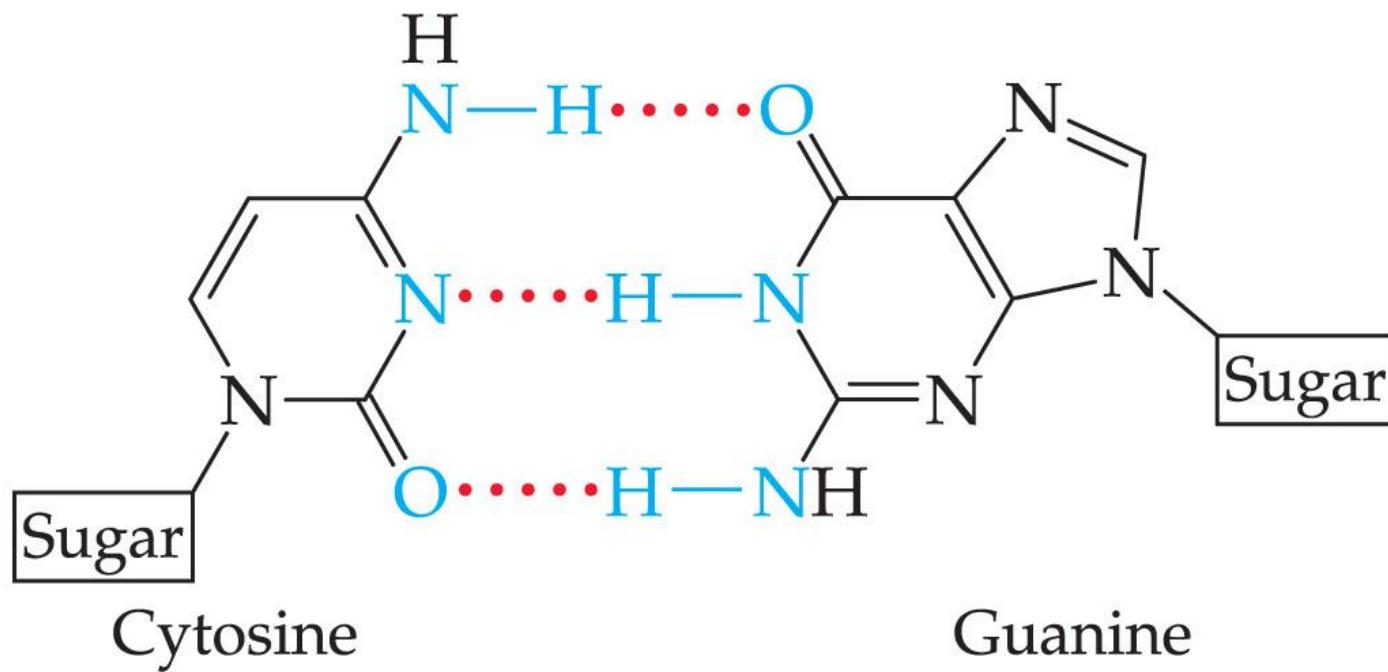
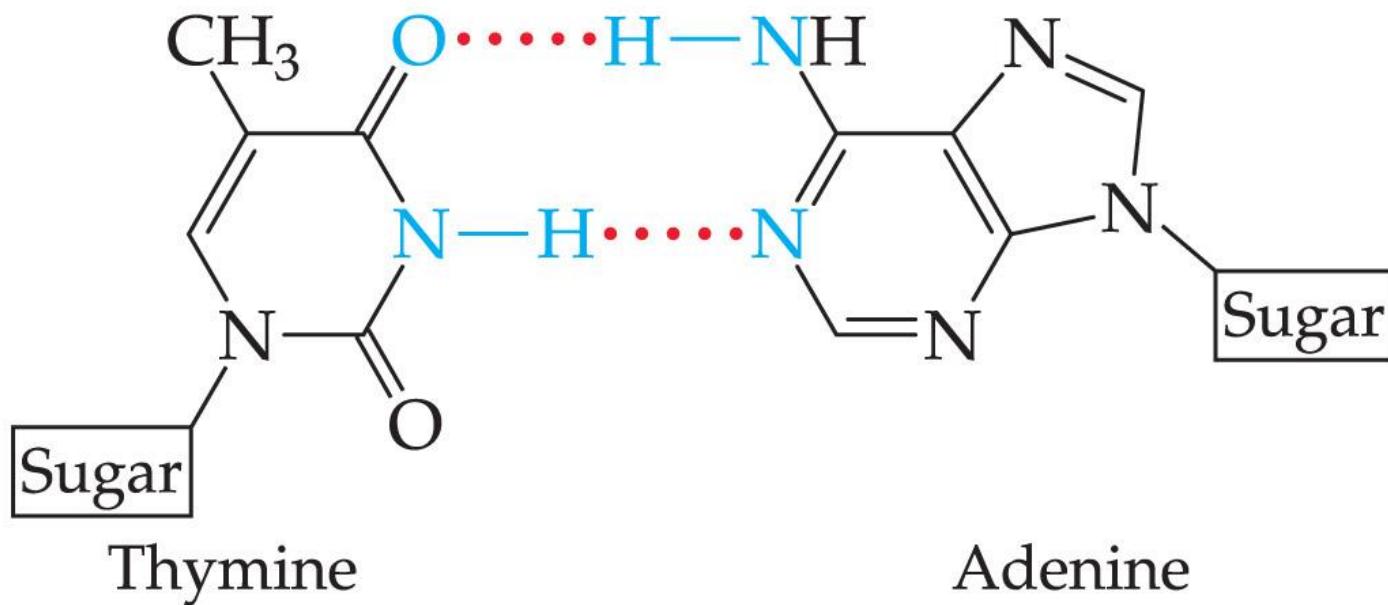
Each molecule can form one hydrogen bond with a neighbor



1-Propanol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

MW = 60 amu

bp = 370 K



# (Extra Info.)

Table 2. Strong, moderate, and weak hydrogen bonds following the classification of Jeffrey.<sup>[6]</sup> The numerical data are guiding values only.

	Strong	Moderate	Weak
interaction type	strongly covalent	mostly electrostatic	electrostat./ dispers.
bond lengths [Å]			
H ··· A	1.2–1.5	1.5–2.2	> 2.2
lengthening of X–H [Å]	0.08–0.25	0.02–0.08	< 0.02
X–H versus H ··· A	X–H ≈ H ··· A	X–H < H ··· A	X–H ≪ H ··· A
X ··· A [Å]	2.2–2.5	2.5–3.2	> 3.2
directionality	strong	moderate	weak
bond angles [°]	170–180	> 130	> 90
bond energy [kcal mol <sup>-1</sup> ]	15–40	4–15	< 4
relat. IR shift $\Delta\tilde{\nu}_{\text{XH}}$ [cm <sup>-1</sup> ]	25 %	10–25 %	< 10 %
<sup>1</sup> H downfield shift	14–22	< 14	

Dimer	Energy
[F–H–F] <sup>-</sup>	39
[H <sub>2</sub> O–H–OH <sub>2</sub> ] <sup>+</sup>	33
[H <sub>3</sub> N–H–NH <sub>3</sub> ] <sup>+</sup>	24
[HO–H–OH] <sup>-</sup>	23
NH <sub>4</sub> <sup>+</sup> … OH <sub>2</sub>	19
NH <sub>4</sub> <sup>+</sup> … Bz	17
HOH … Cl <sup>-</sup>	13.5
O=C–OH … O=C–OH	7.4
HOH … OH <sub>2</sub>	4.7; 5.0
N≡C–H … OH <sub>2</sub>	3.8
HOH … Bz	3.2
F <sub>3</sub> C–H … OH <sub>2</sub>	3.1
Me–OH … Bz	2.8
F <sub>2</sub> HC–H … OH <sub>2</sub>	2.1; 2.5
NH <sub>3</sub> … Bz	2.2
HC≡CH … OH <sub>2</sub>	2.2
CH <sub>4</sub> … Bz	1.4
FH <sub>2</sub> C–H … OH <sub>2</sub>	1.3
HC≡CH … C≡CH <sup>-</sup>	1.2
HSH … SH <sub>2</sub>	1.1
H <sub>2</sub> C=CH <sub>2</sub> … OH <sub>2</sub>	1.0
CH <sub>4</sub> … OH <sub>2</sub>	0.3; 0.5; 0.6; 0.8
C≡CH <sub>2</sub> … C≡C	0.5
CH <sub>4</sub> … F–CH <sub>3</sub>	0.2

(Extra Info.)

Calculated hydrogen  
bond energies  
(kcal/mol) in  
some gas phase  
dimers.

Angew. Chem. Int.  
Ed. 2002, 41, 48

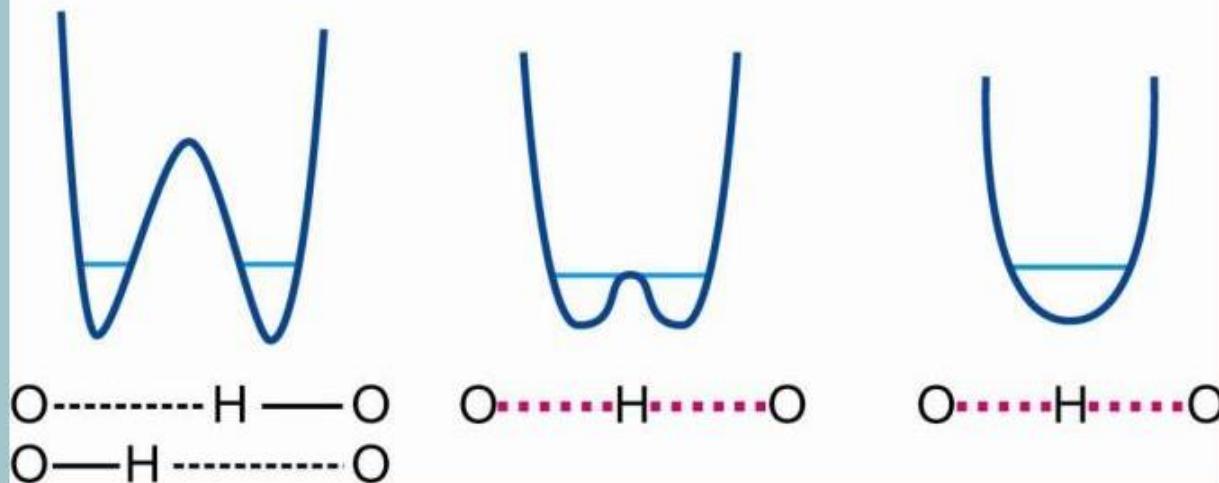
Intermolecular  
Forces



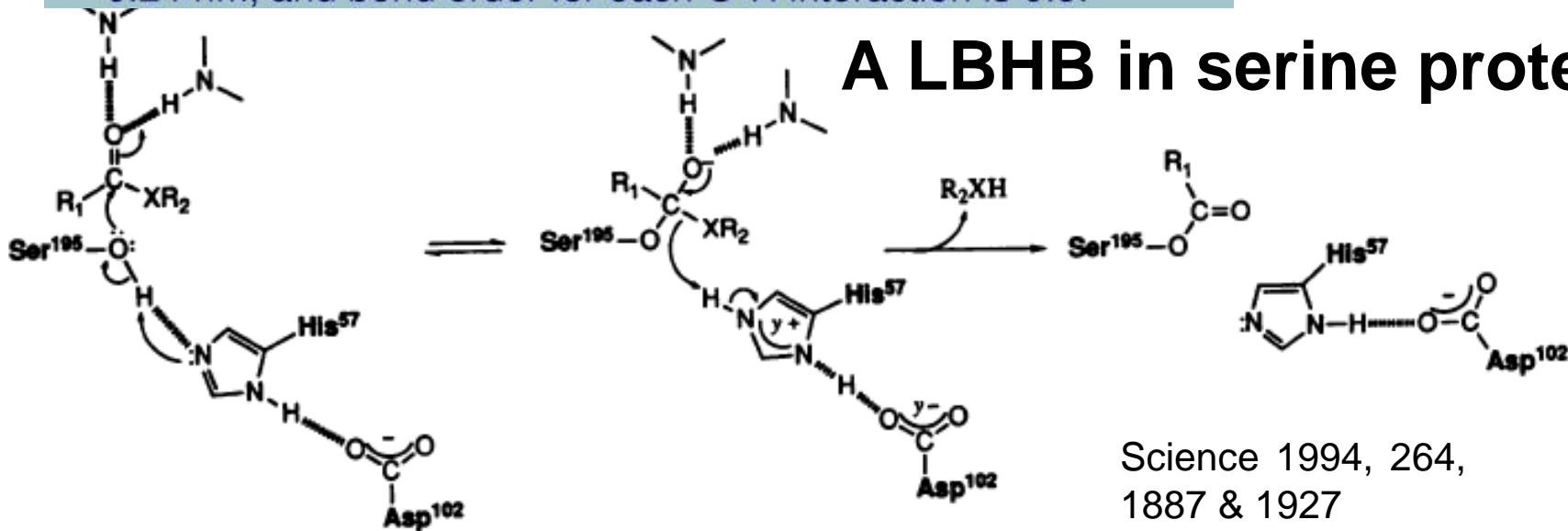
(a)

(b)

(c)

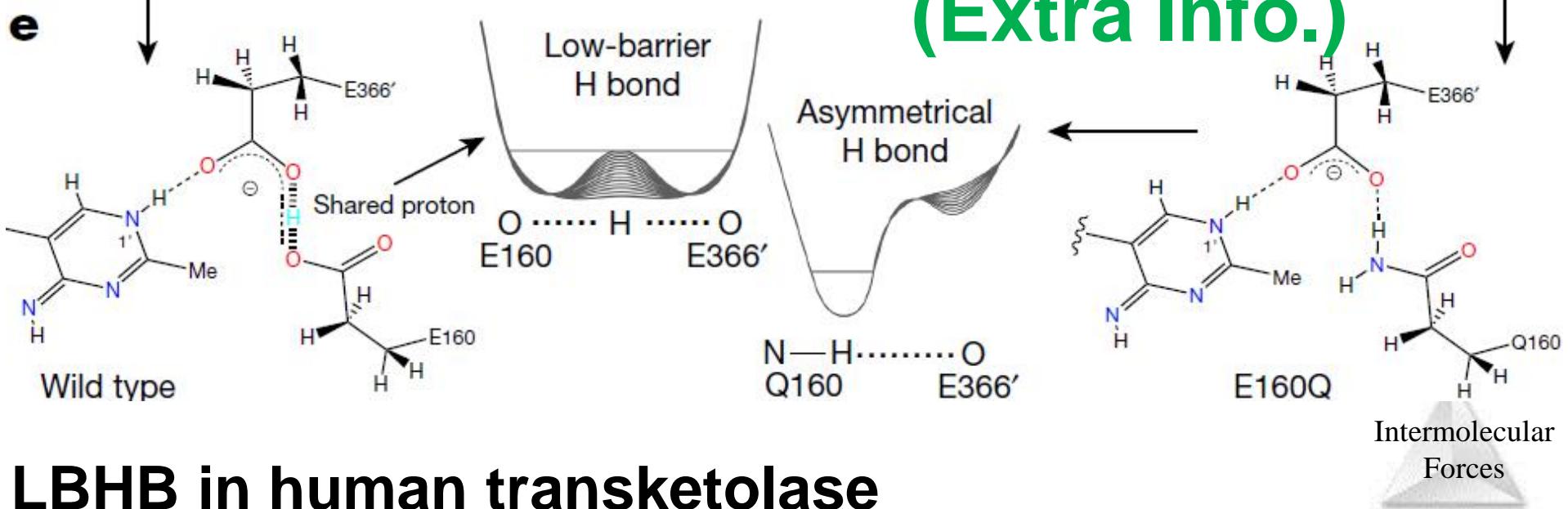
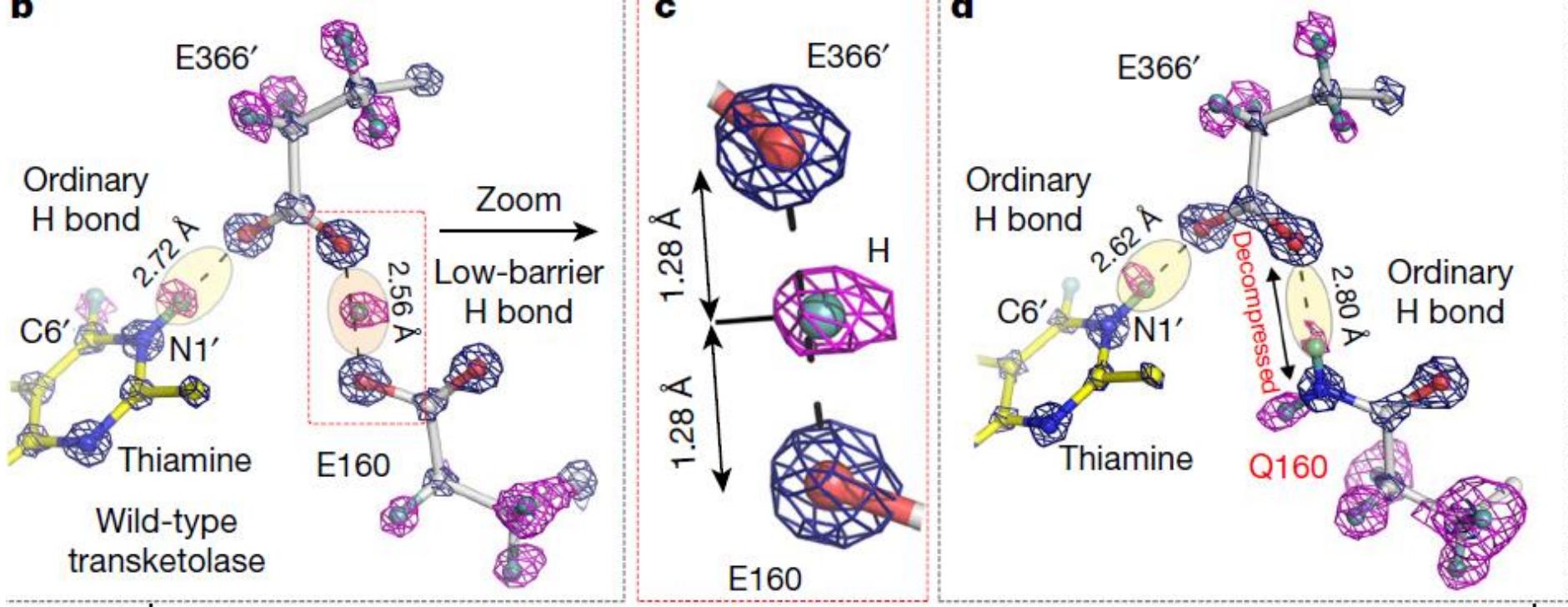


Energy diagrams for conventional H bonds (a), and low-barrier hydrogen bonds (b and c). In (c), the O-O distance is 0.23 to 0.24 nm, and bond order for each O-H interaction is 0.5.



Science 1994, 264,  
1887 & 1927

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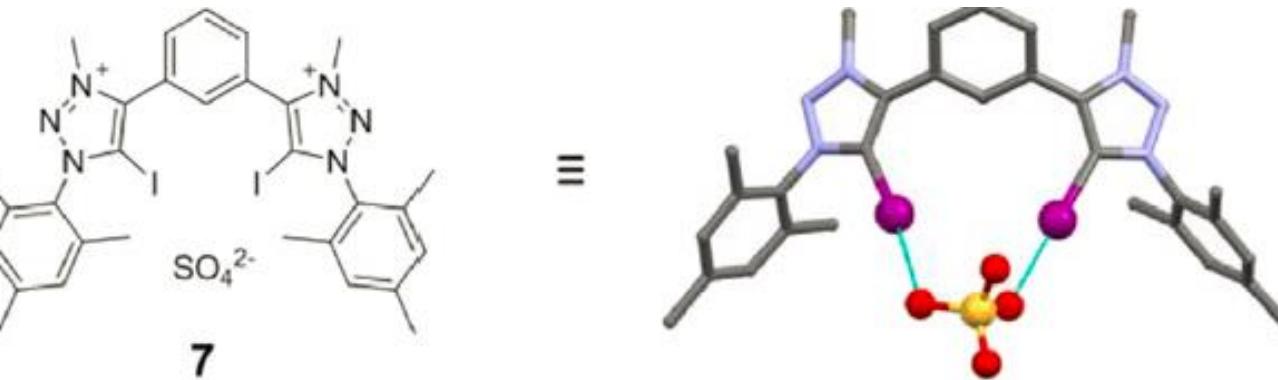
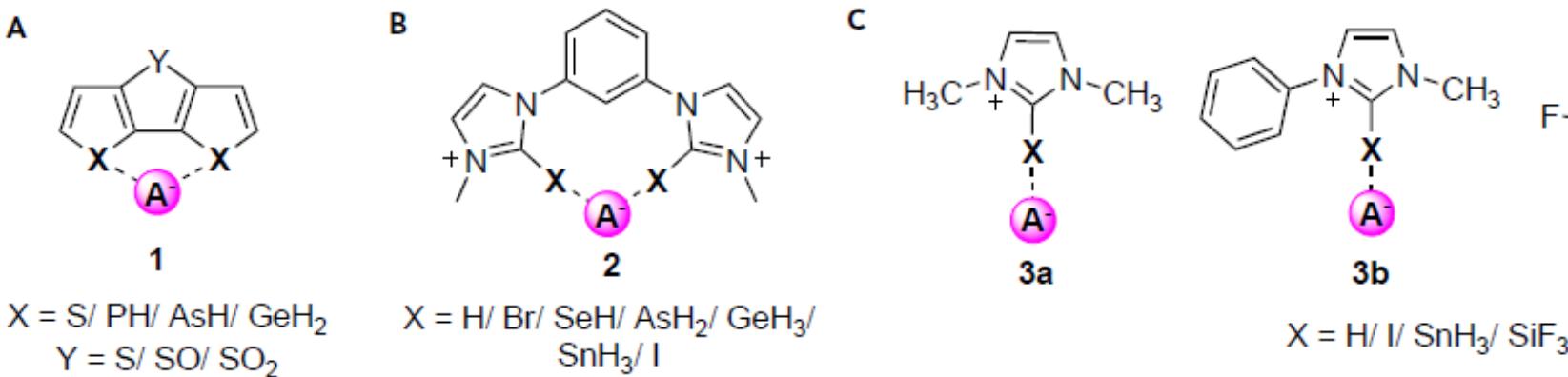
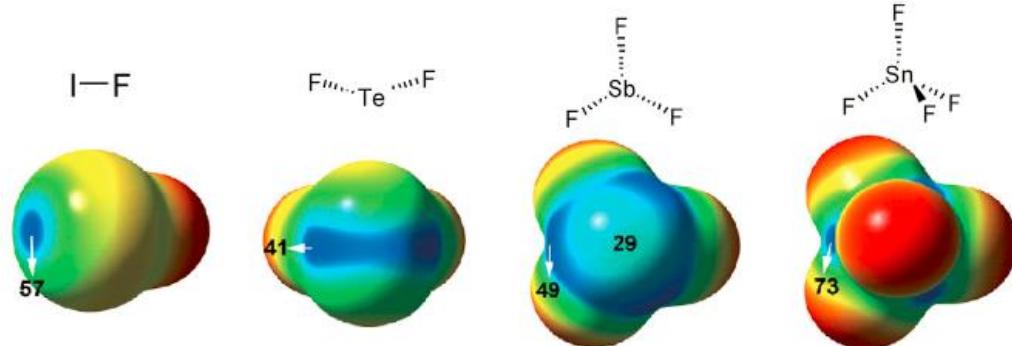
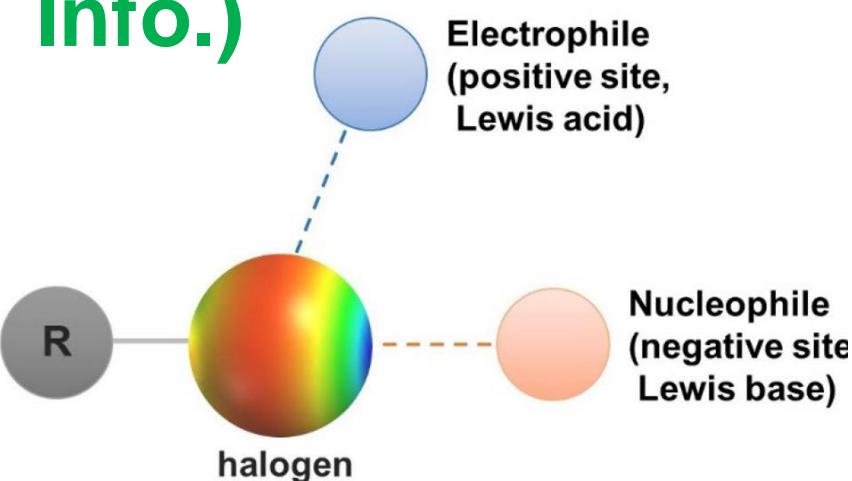


# LBHB in human transketolase

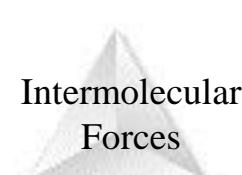
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Nature 2019, 573, 609

# $\sigma$ -Hole Interactions, Halogen Bond (Extra Info.)

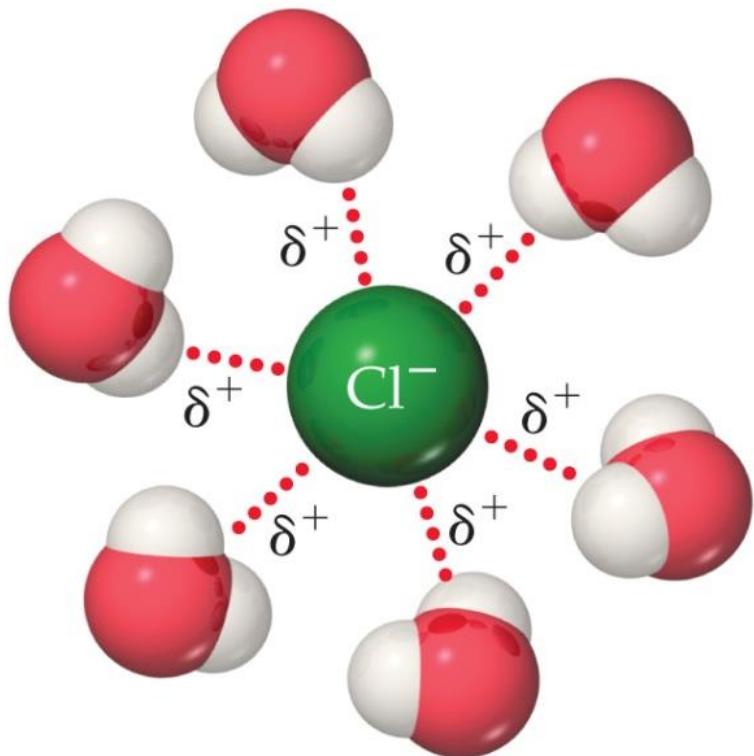


$A^-$  = halide ion

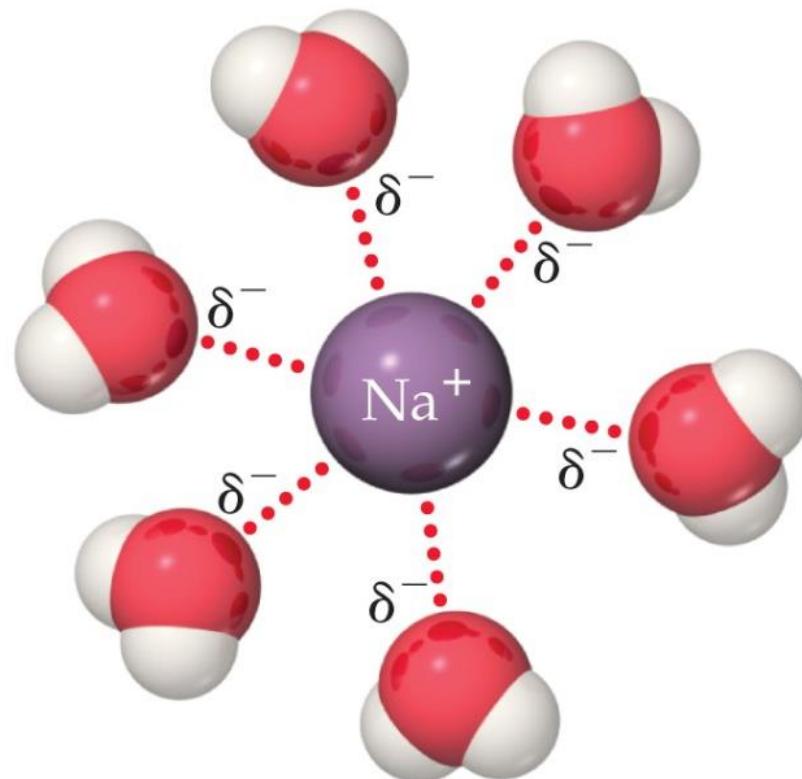


# Ion–Dipole Interactions

- Ion–dipole interactions are found in **solutions of ions**.
- The strength of these forces is what makes it possible for **ionic substances to dissolve** in **polar solvents**.

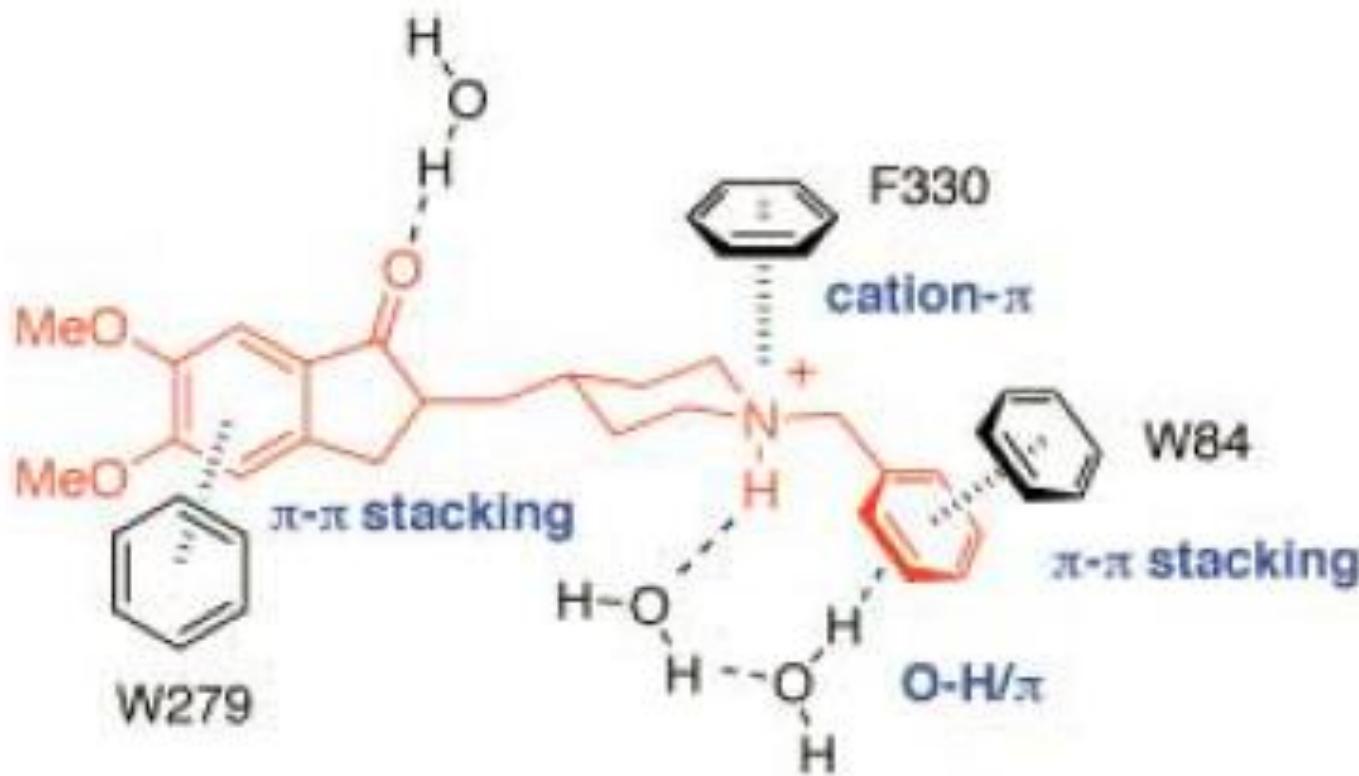


Positive ends of polar molecules are oriented toward negatively charged anion



Negative ends of polar molecules are oriented toward positively charged cation

# (extra info.) Interactions with $\pi$ -systems



**Figure 1.** Binding mode of the anti-Alzheimer drug E2020 within the active site of acetylcholinesterase from *Torpedo californica* (PDB code: 1EVE).<sup>[1]</sup>

# (extra info.) Interactions with $\pi$ -systems

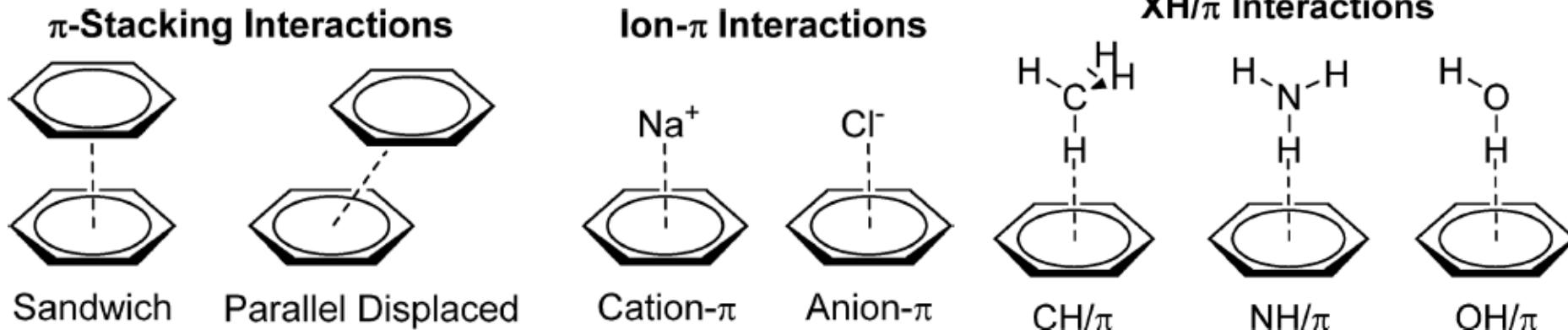
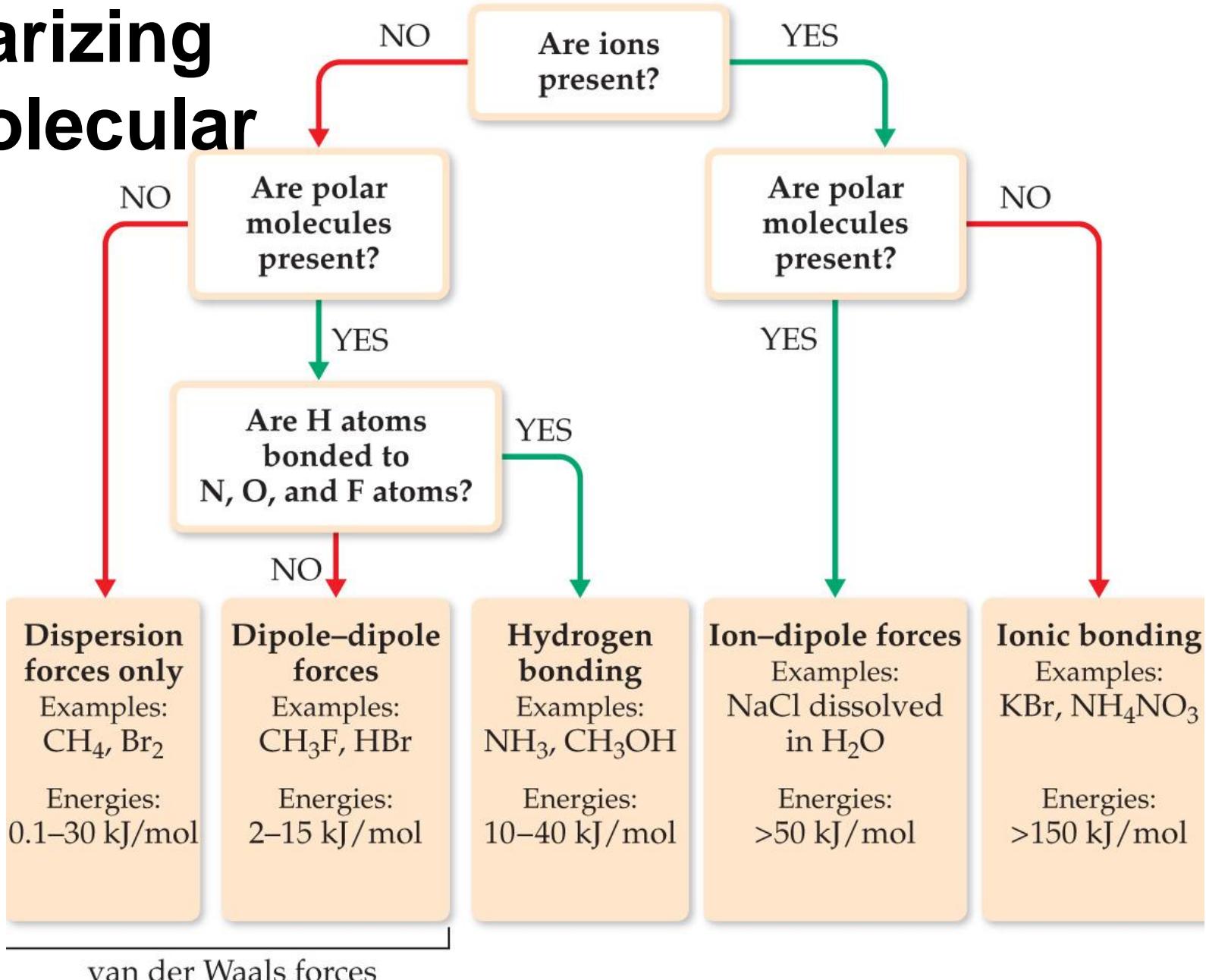


Table 1. Gas-Phase Ion Molecule Binding Energies<sup>a</sup> (kcal/mol)

A. Experimental Measurements

ion	molecule	binding energy <sup>b</sup>	ref	ion	molecule	binding energy <sup>b</sup>
Li <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	38.3 <sup>c</sup>	11	NH <sub>4</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> F	(14.4) <sup>f</sup>
Na <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	28.0	8	NH <sub>4</sub> <sup>+</sup>	1,4-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	(13.0) <sup>f</sup>
K <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	19.2	2	NH <sub>4</sub> <sup>+</sup>	C <sub>2</sub> H <sub>4</sub>	10.0
K <sup>+</sup> •C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>	18.8	2	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	18.8
K <sup>+</sup> •(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	14.5	2	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	cyclohexene	11.6
K <sup>+</sup> •(C <sub>6</sub> H <sub>6</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	12.6	2	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	pyrrole	(18.6) <sup>f</sup>
K <sup>+</sup>	H <sub>2</sub> O	17.9	2	(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	15.9
Al <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	35.2	26	NMe <sub>4</sub> <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	9.4
NH <sub>4</sub> <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	19.3	13	NMe <sub>4</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	9.5
NH <sub>4</sub> <sup>+</sup>	1,3,5-C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub>	21.8	13	C <sub>2</sub> H <sub>5</sub> OH <sub>2</sub> <sup>+</sup>	C <sub>6</sub> H <sub>6</sub>	21.0

# Summarizing Intermolecular Forces

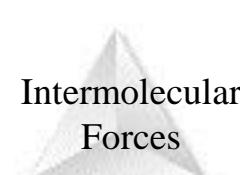
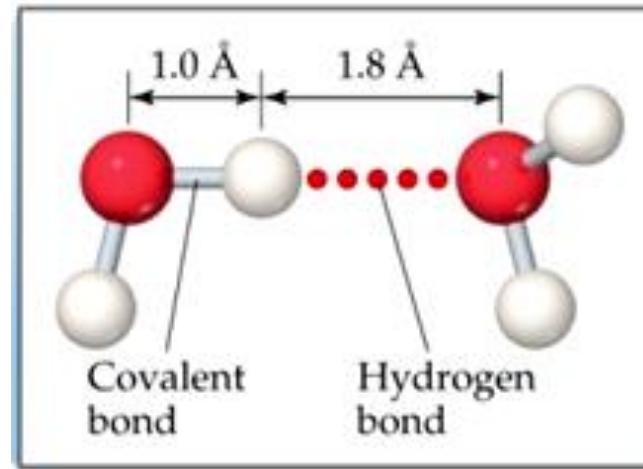


List the substances  $\text{CCl}_4$ ,  $\text{CBr}_4$ , and  $\text{CH}_4$  in order of increasing boiling point.

- A.  $\text{CH}_4 < \text{CBr}_4 < \text{CCl}_4$
- B.  $\text{CCl}_4 < \text{CH}_4 < \text{CBr}_4$
- C.  $\text{CH}_4 < \text{CCl}_4 < \text{CBr}_4$
- D.  $\text{CBr}_4 < \text{CCl}_4 < \text{CH}_4$

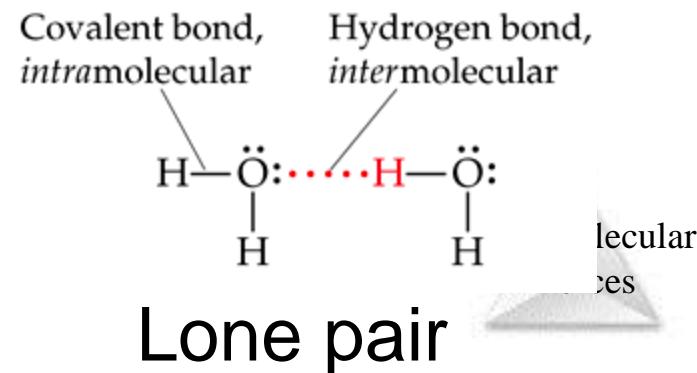
What is the approximate H—O $\cdots\cdots$ H bond angle in ice, where H—O is the covalent bond and O $\cdots\cdots$ H is the hydrogen bond?

- A. Approximately  $90^\circ$
- B. Approximately  $109^\circ$
- C. Approximately  $120^\circ$
- D. Approximately  $180^\circ$



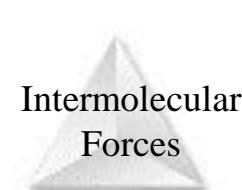
To form a hydrogen bond what must the non-hydrogen atom (N, O, or F) involved in the bond possess?

- A. The non-hydrogen atom must have a nonbonding electron pair.
- B. The non-hydrogen atom must have low electronegativity.
- C. The non-hydrogen atom must have a large atomic size.
- D. The non-hydrogen atom must have a small electron affinity.



In which mixture do you expect to find ion–dipole forces: CH<sub>3</sub>OH in water or Ca(NO<sub>3</sub>)<sub>2</sub> in water?

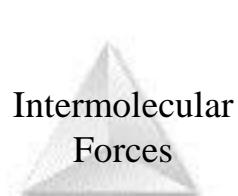
- A. CH<sub>3</sub>OH in water, because CH<sub>3</sub>OH is a strong electrolyte and forms ions.
- B. Ca(NO<sub>3</sub>)<sub>2</sub> in water, because Ca(NO<sub>3</sub>)<sub>2</sub> is a strong electrolyte and forms ions.
- C. CH<sub>3</sub>OH in water, because CH<sub>3</sub>OH is a weak electrolyte and forms ions.
- D. Ca(NO<sub>3</sub>)<sub>2</sub> in water, because Ca(NO<sub>3</sub>)<sub>2</sub> is a weak electrolyte and forms ions.



Intermolecular  
Forces

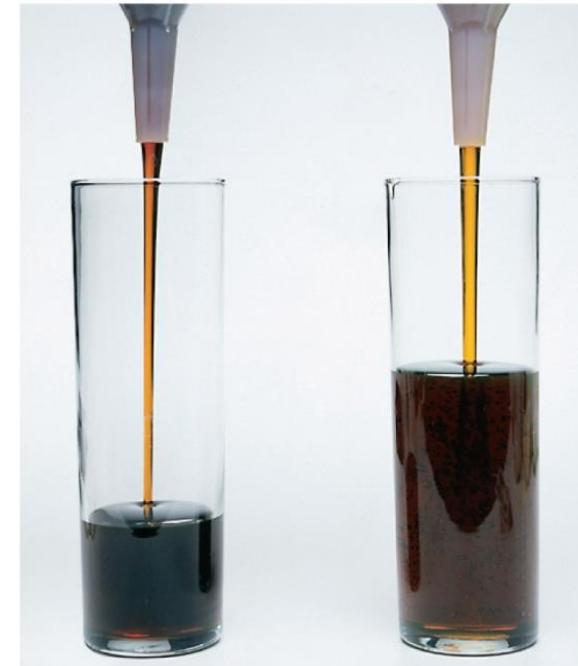
# Liquid Properties Affected by Intermolecular Forces

- Boiling point & melting point
- Viscosity (粘度)
- Surface tension
- Capillary action (毛细管作用)



# Viscosity

- **Resistance** of a liquid to flow.
- Related to the **ease** with which molecules can **move past each other**.
- Increases with stronger **intermolecular forces** and decreases with higher **temperature**.



SAE 40  
higher number  
higher viscosity  
slower pouring

SAE 10  
lower number  
lower viscosity  
faster pouring

Substance	Formula	Viscosity (kg/m·s)
Hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$3.26 \times 10^{-4}$
Heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$4.09 \times 10^{-4}$
Octane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$5.42 \times 10^{-4}$
Nonane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$7.11 \times 10^{-4}$
Decane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$1.42 \times 10^{-3}$

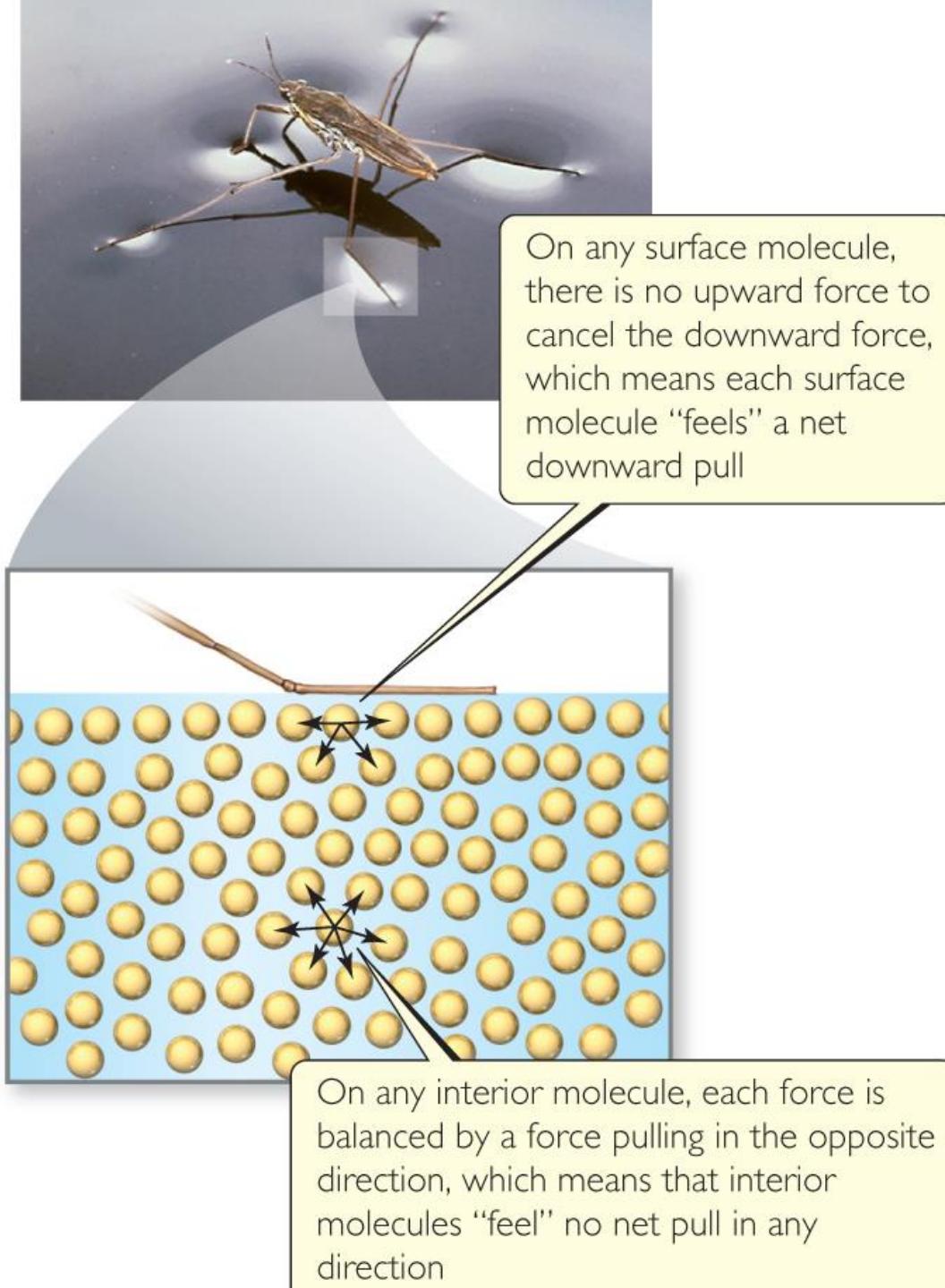
# Viscosity



Intermolecular  
Forces

# Surface Tension

- Water acts as if it has a “skin” on it due to extra **inward forces on its surface**. Those forces are called the **surface tension**.



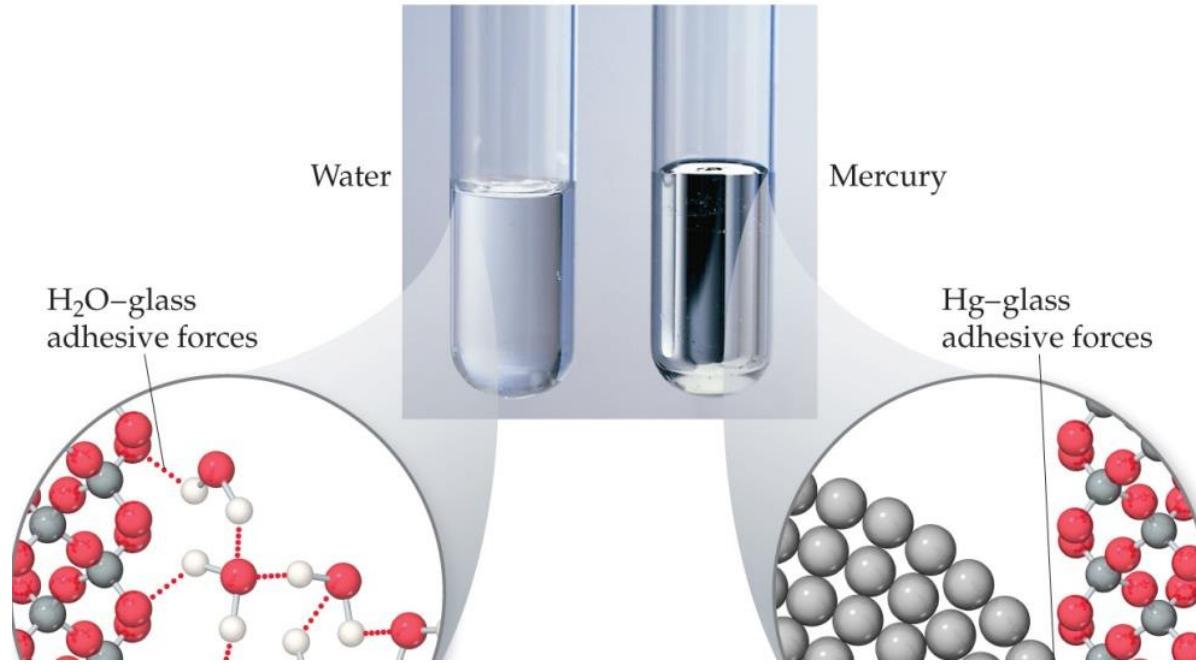
- It results from the net inward force experienced by the molecules on the surface of a liquid.

# Cohesion (内聚力) & Adhesion (黏附力)

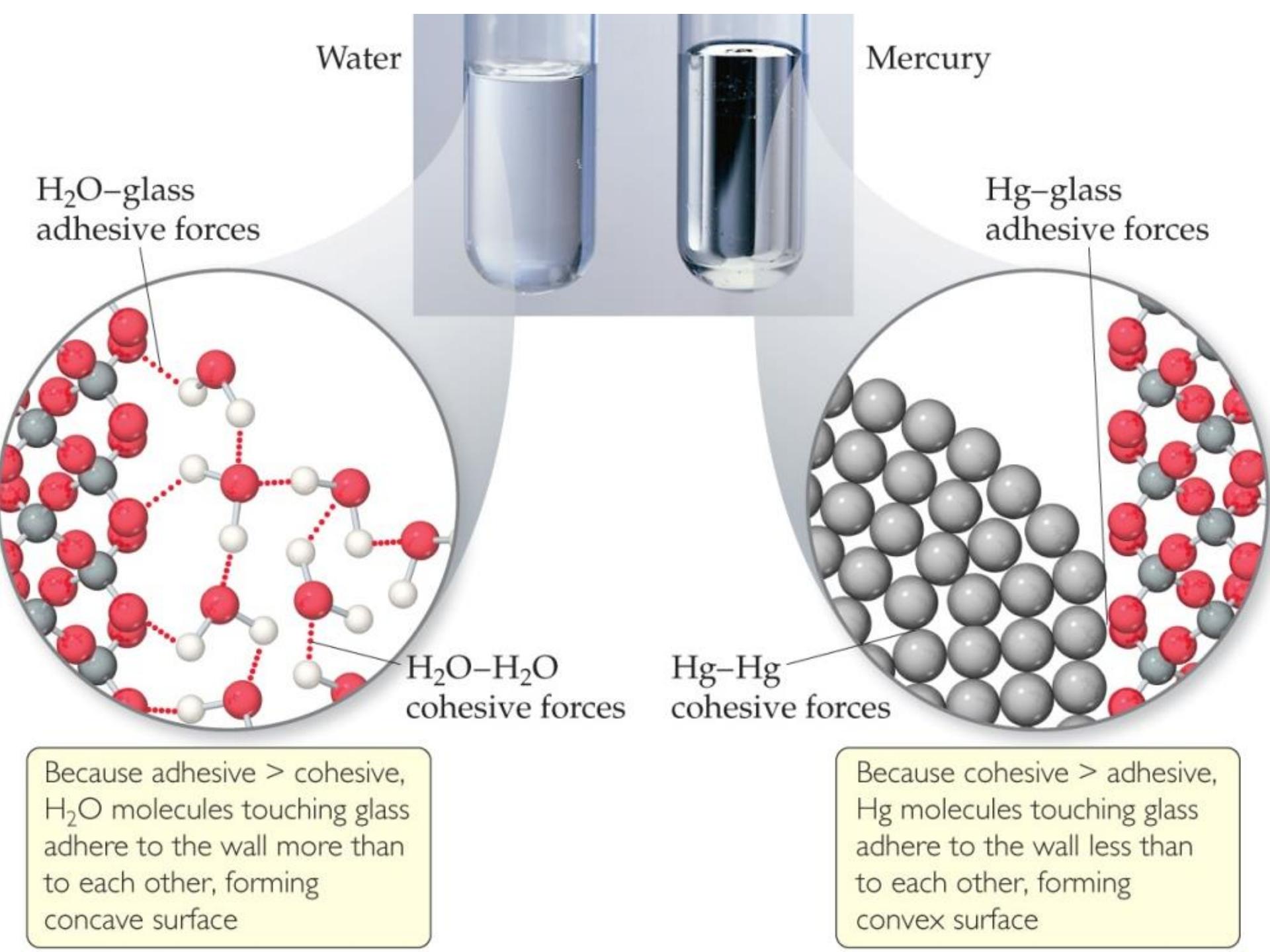
- Intermolecular forces that bind **similar molecules** to one another are called *cohesive forces*.
- Intermolecular forces that bind a substance to a **surface** are called *adhesive forces*.
- These forces are important in capillary action.



# Capillary Action



- The rise of liquids up **narrow** tubes.
- **Adhesive forces** attract the **liquid** to the **wall** of the tube.
- **Cohesive forces** attract the **liquid to itself**.
- Water has stronger adhesive forces with glass; mercury has stronger cohesive forces with itself.

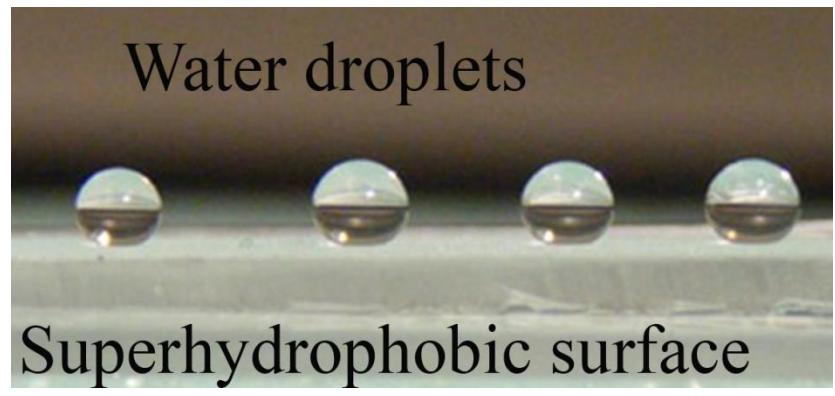




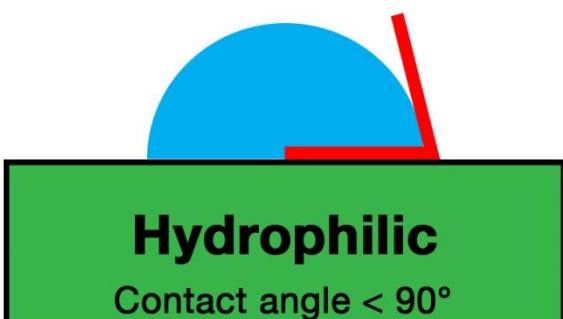
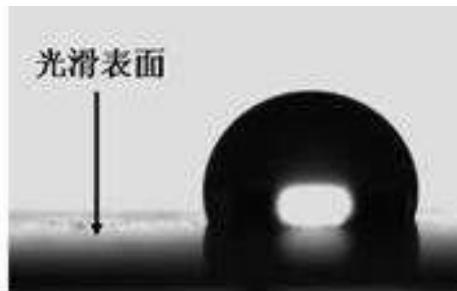
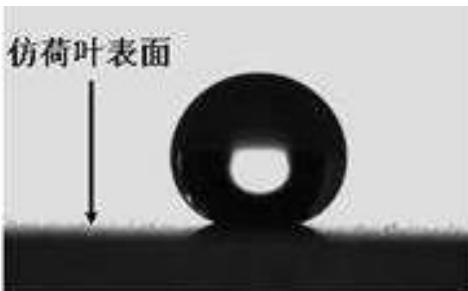
superhydrophobic



hydrophilic hydrophobic

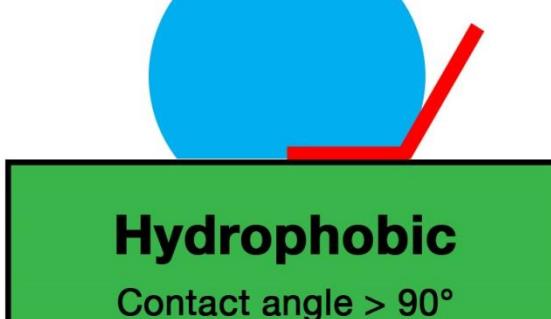


Water droplets  
Superhydrophobic surface  
(extra info.)



Hydrophilic

Contact angle < 90°



Hydrophobic

Contact angle > 90°



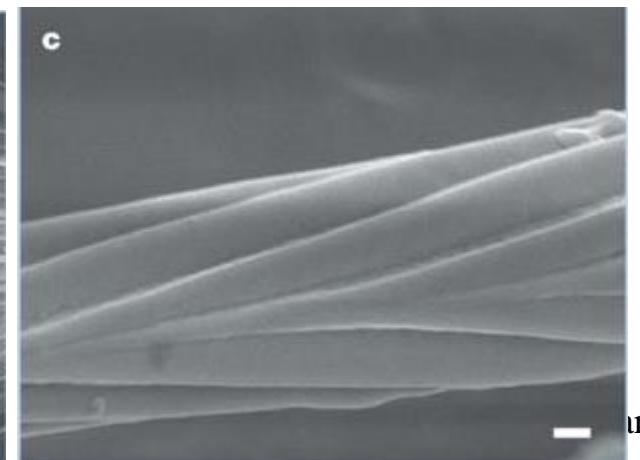
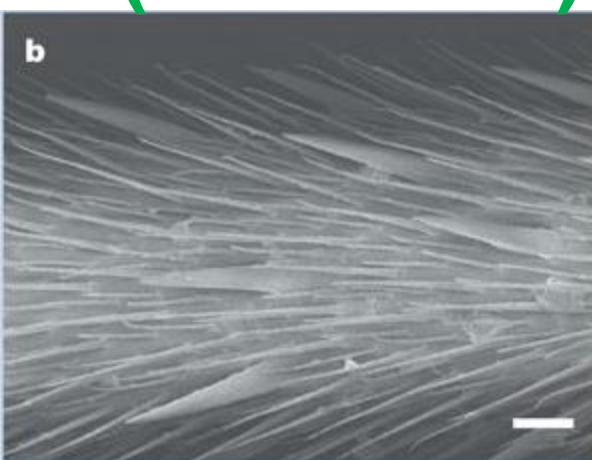
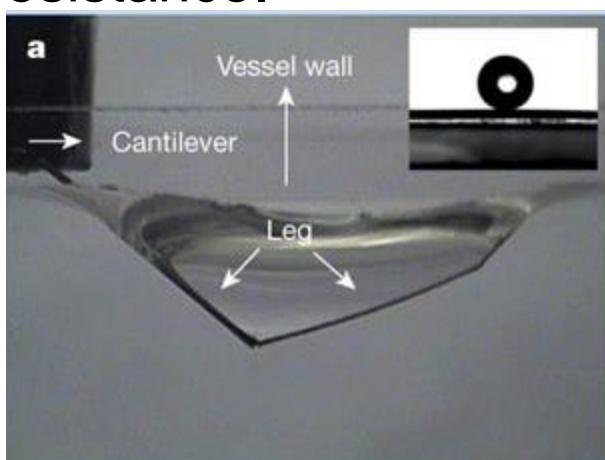
Superhydrophobic

Contact angle > 150°

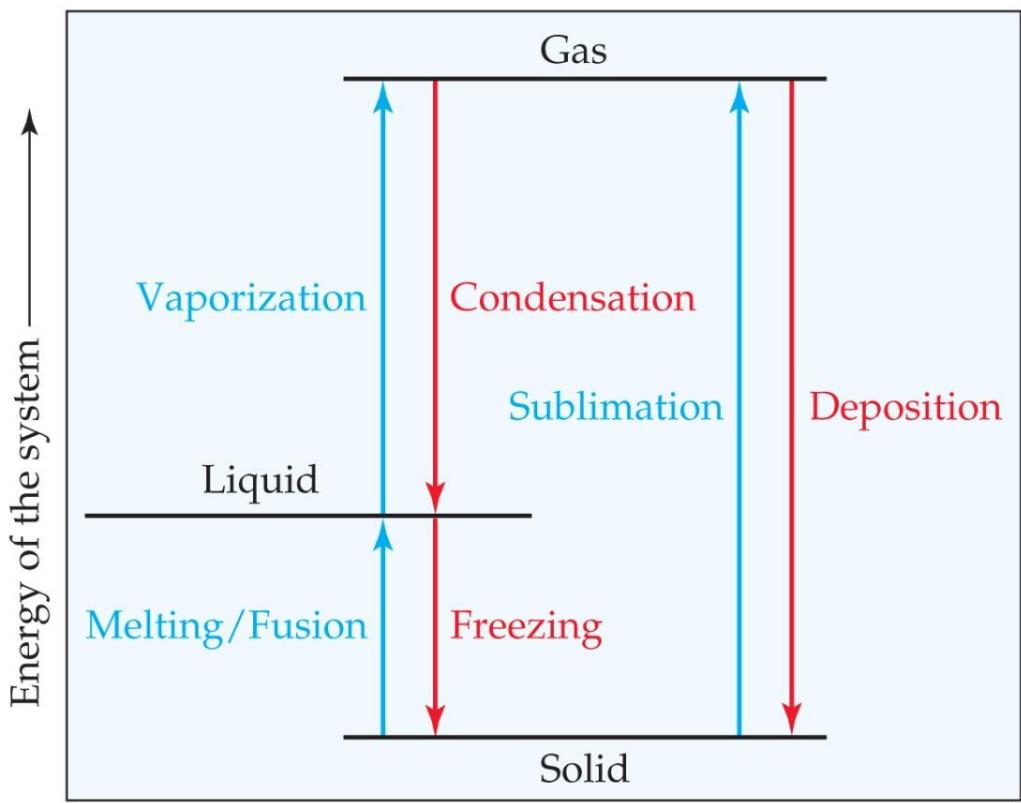
# Water-Repellent Legs of Water Striders

- Water striders (*Gerris remigis*) have remarkable non-wetting legs that enable them to stand effortlessly and move quickly on water, a feature believed to be due to a surface-tension effect caused by secreted wax.
- Jiang L and *et al.* show that it is the special hierarchical structure of the legs, which are covered by large numbers of oriented tiny hairs (microsetae) with fine nanogrooves, that is more important in inducing this water resistance.

(extra info.)



# Phase Changes



— Endothermic process (energy added to substance)  
— Exothermic process (energy released from substance)

- Conversion from one **state** of matter to another is called a **phase change**. Accompanied by a **change in the energy** of the system.

- Energy is either **added or released** in a phase change.
- Phase changes: **melting & freezing, vaporizing & condensing (蒸发/冷凝), subliming & depositing (升华/沉淀)**.

# Phase Change of Chlorine from Gas to Liquid



Forces

# Phase Change of Bromine from Liquid to Gas to Solid



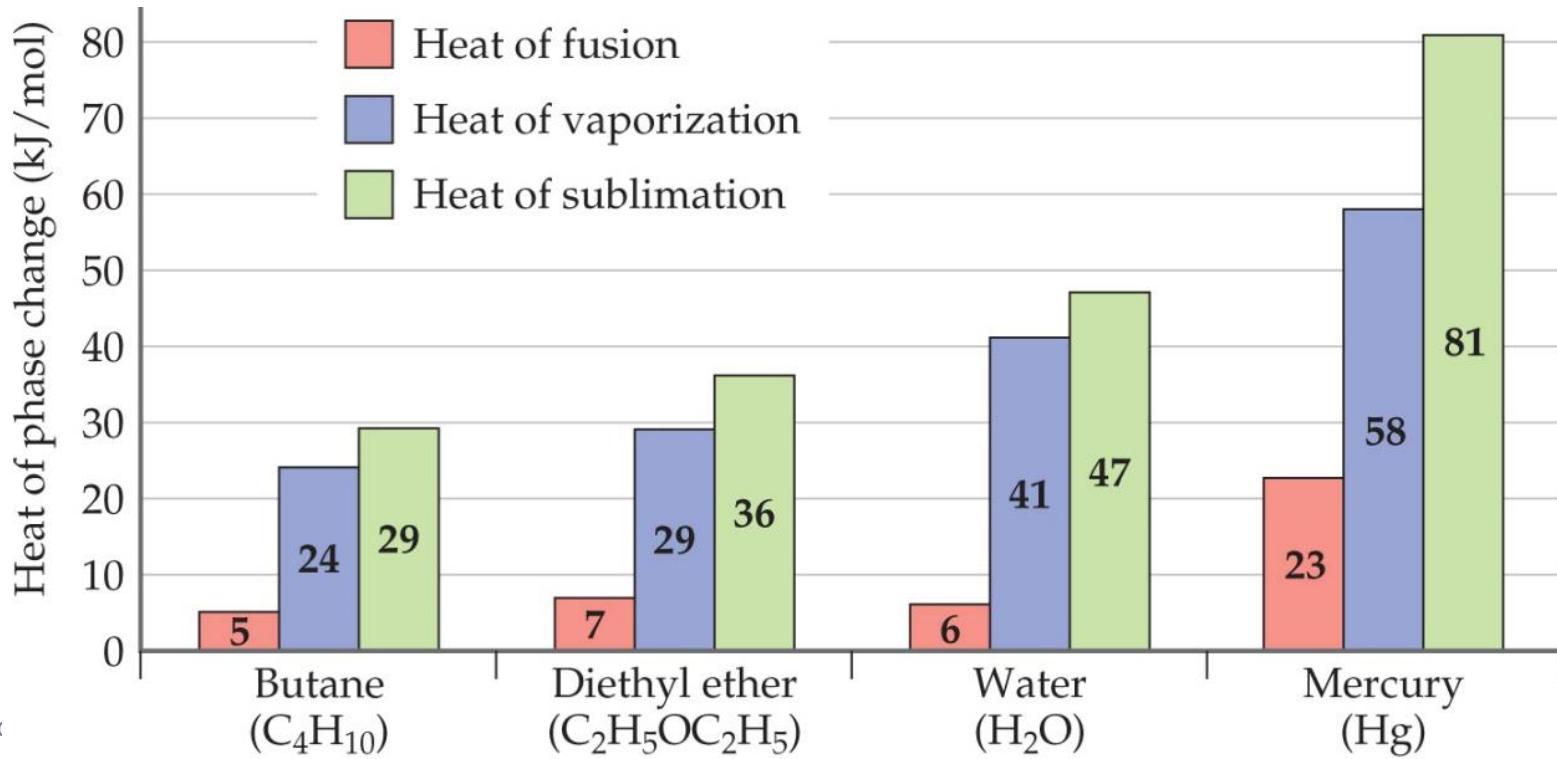
Forces

# Phase Change of Iodine from Solid to Gas to Solid

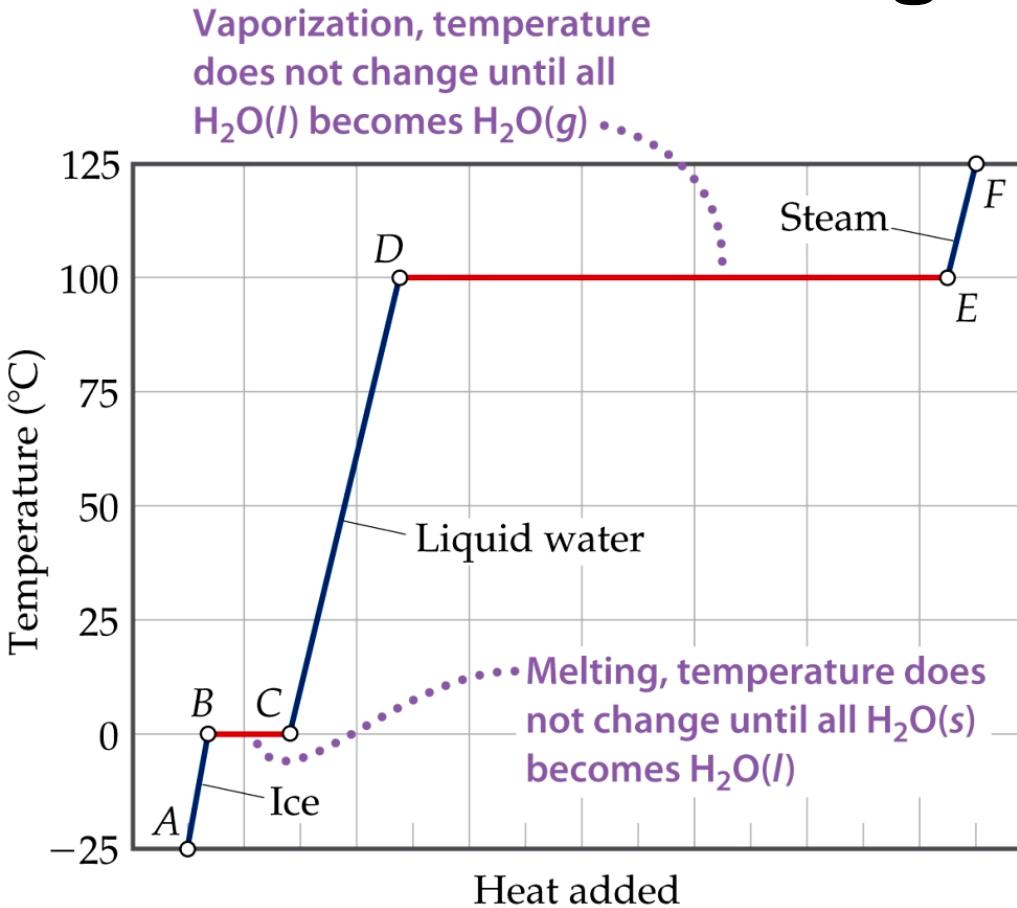


# Energy Change & Change of State

- Heat of **fusion** (溶化): the energy required to change a **solid** to a **liquid** at its **melting point**.
- Heat of **vaporization**: the energy required to change a **liquid** to a **gas** at its **boiling point**.
- Heat of **sublimation**: the energy required to change a **solid** directly to a **gas**.



# Heating Curves



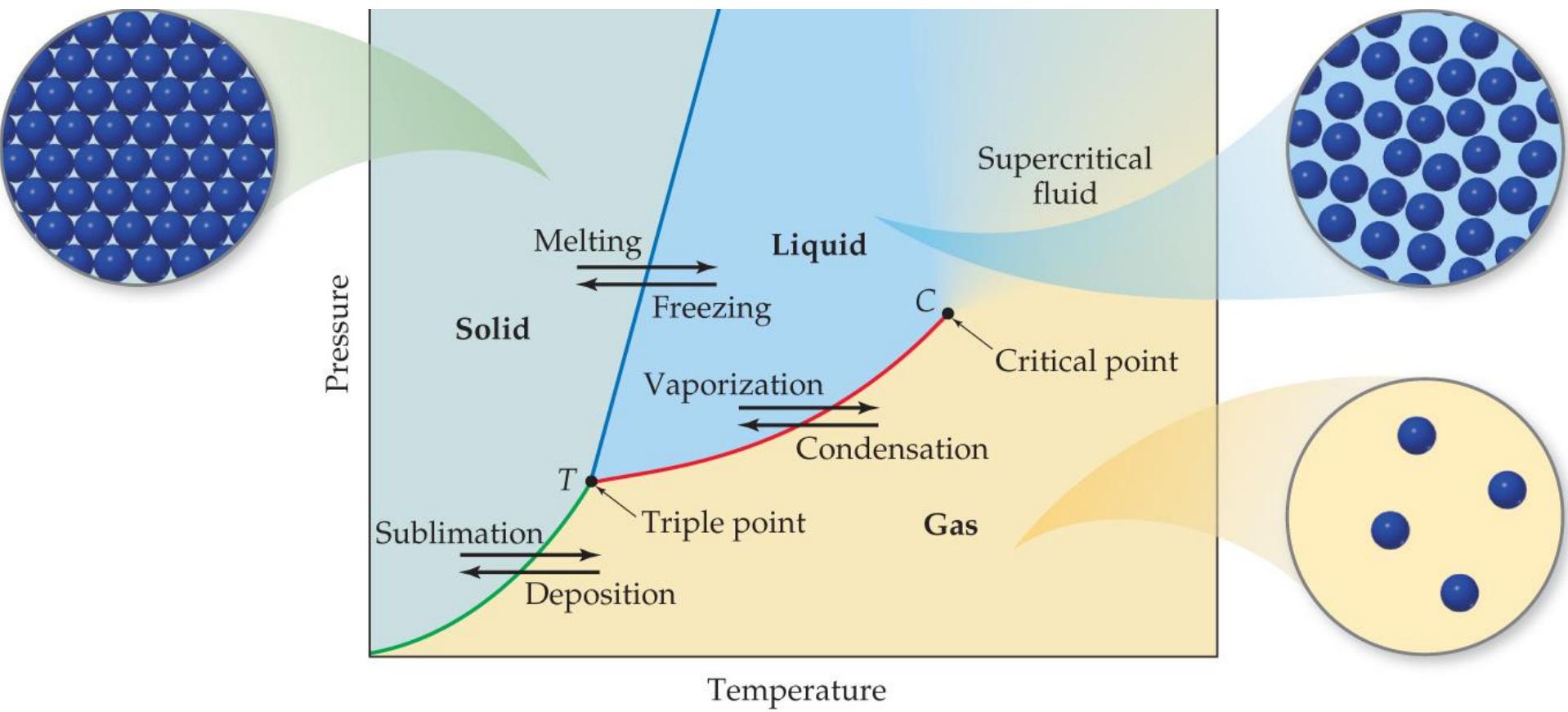
- Within a phase, heat ( $q$ ) is the product of specific heat, sample mass, & temperature change ( $C_s * M * \Delta T$ ).
- The **temperature** of the substance does **not rise during a phase change**.

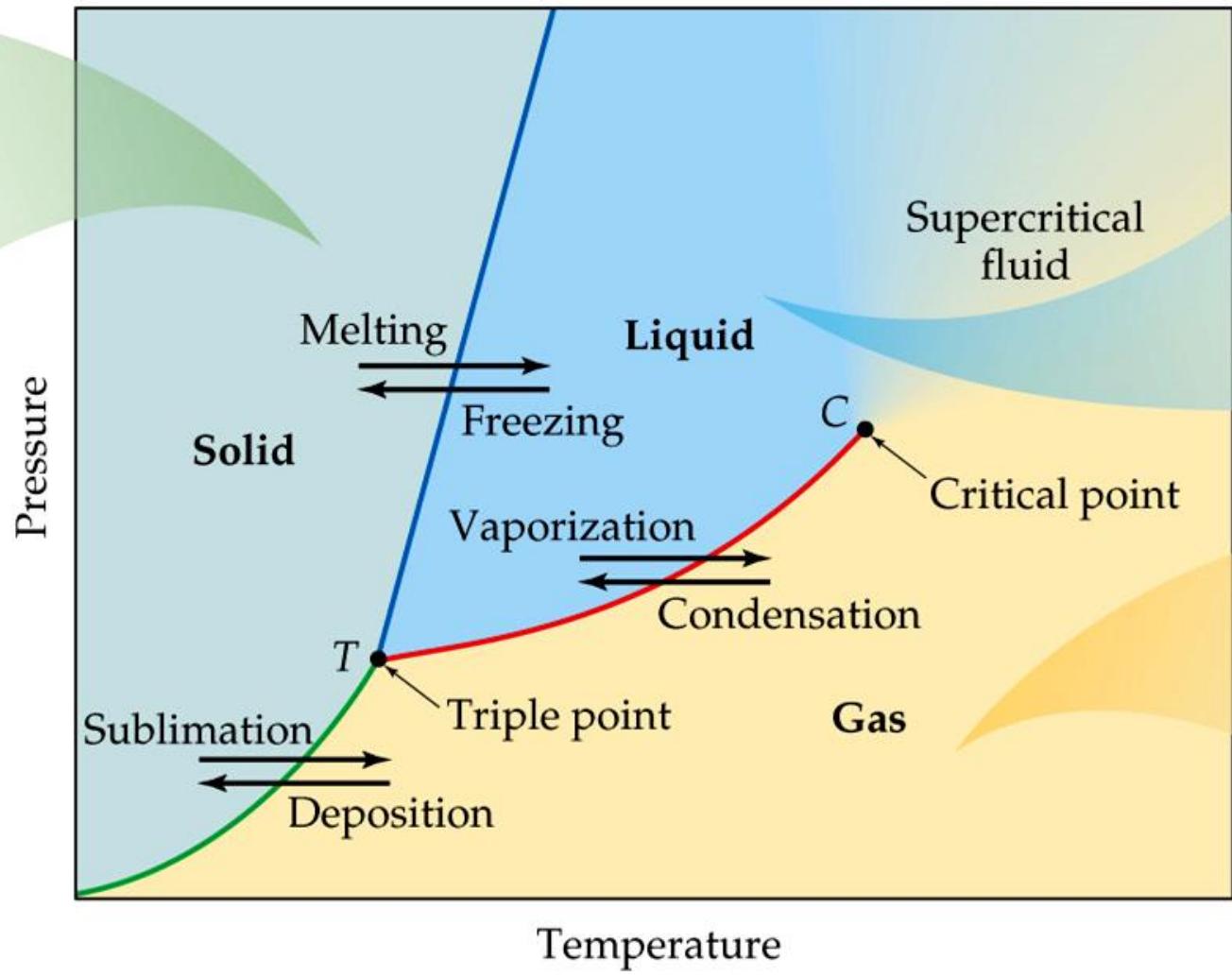
- For the phase changes, the **product of mass & heat of fusion of vaporization is heat**. The heat added to the system at the melting & boiling points goes into **pulling the molecules farther apart from each other**.

Intermolecular  
Forces

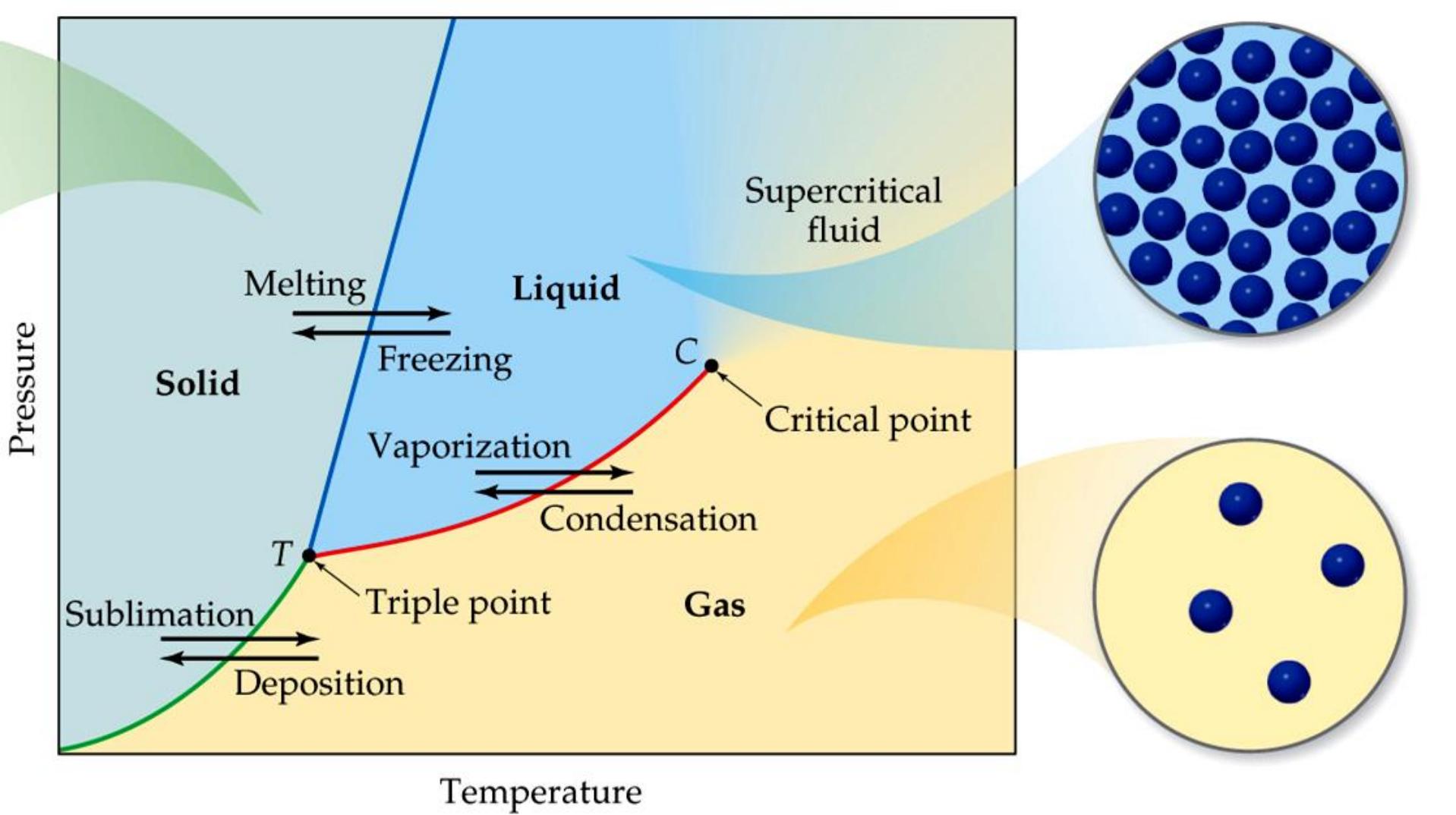
# Phase Diagram

- A graph of pressure vs. temperature for a substance & the places where **equilibrium exist between phases**.
- It shows (i) melting, boiling, & sublimation points at different pressures; (ii) the triple point and critical point.

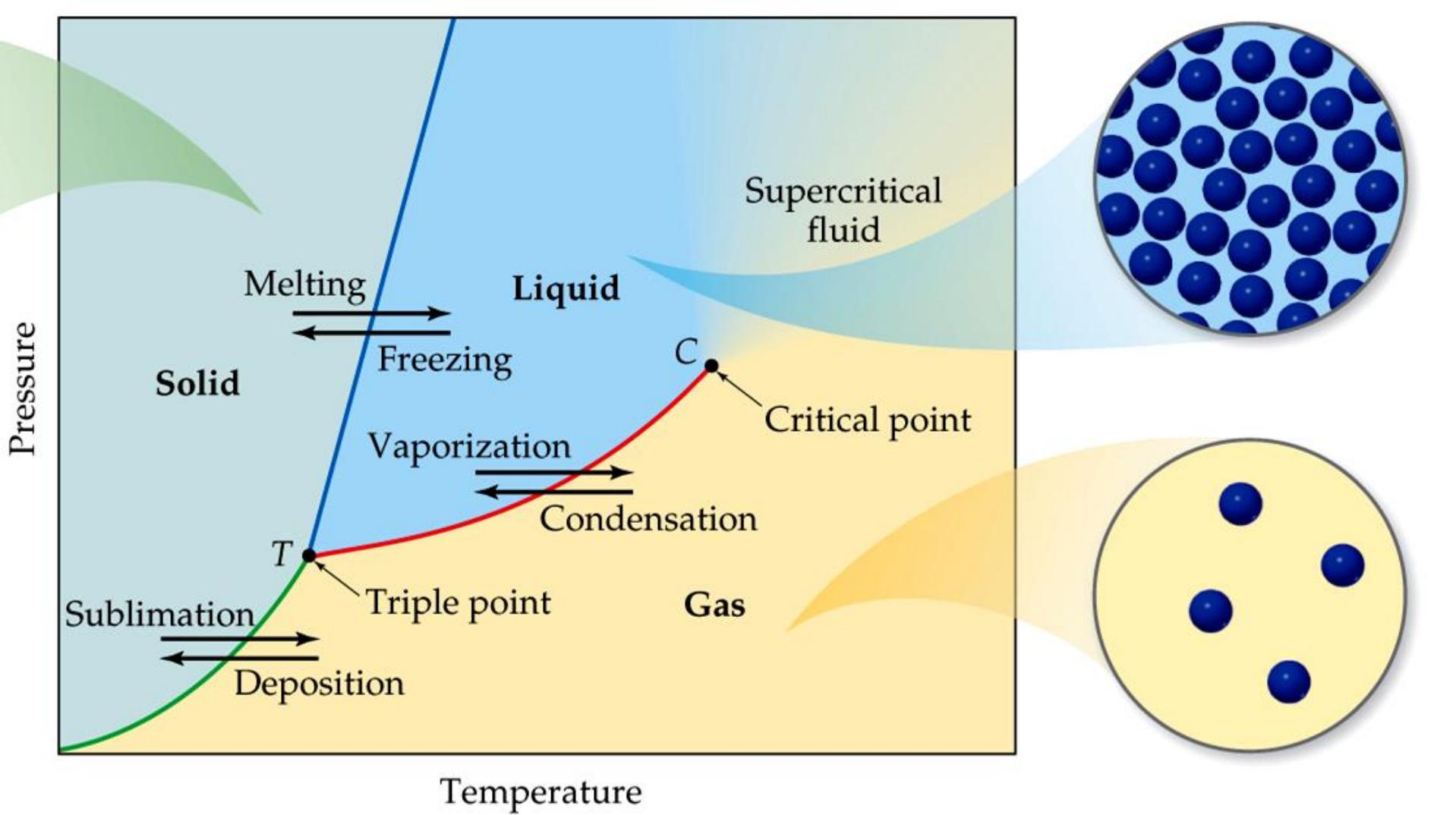




**Green Curve:** sublimation curve, **separates the solid phase from the gas phase** and represents the **change in the vapor pressure** of solid as it sublimes at different temperature. the sublimation point at each pressure.

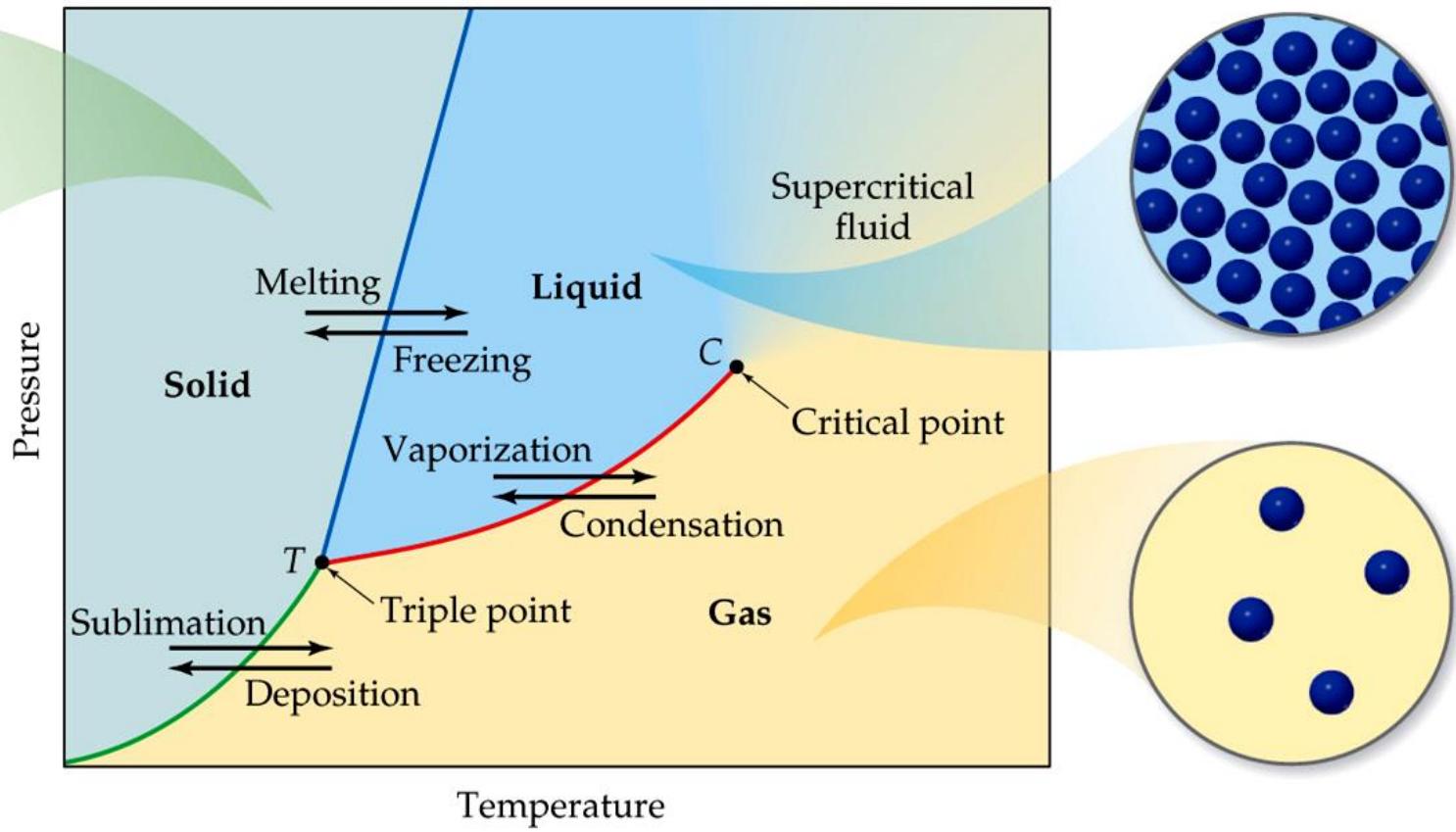


**Red Curve:** vapor-pressure curve of the liquid, representing equilibrium between the **liquid** and **gas** ends at **critical point** & the **change in boiling point** with increasing pressure.



**Blue Curve:** melting curve, separates the **solid** phase from the **liquid** phase and represents the **change in melting point** of the solid with increasing pressure.

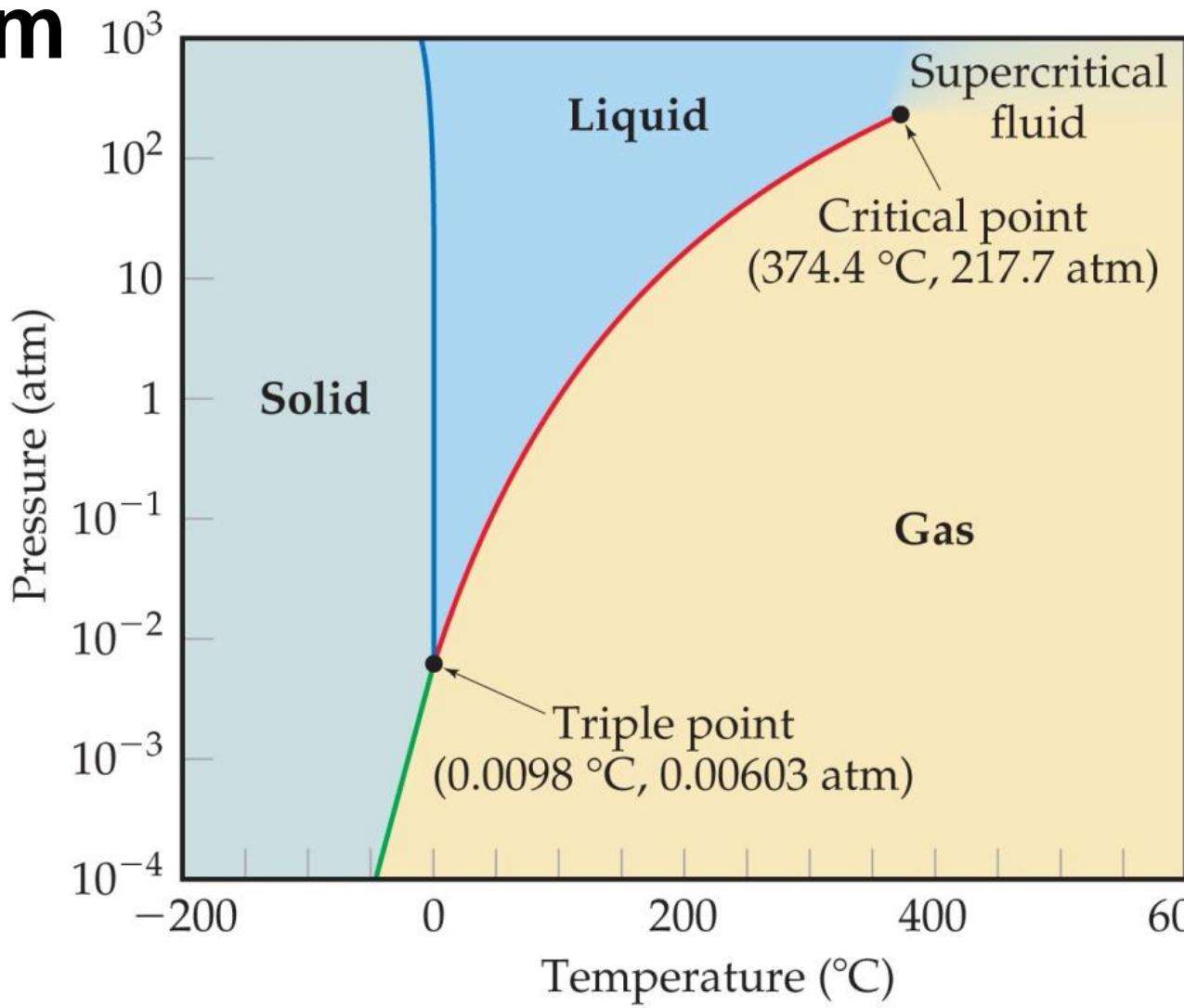
Intermolecular Forces



- The liquid–vapor interface starts at the **triple point (T)**, at which **all three states are in equilibrium**, and ends at the **critical point (C)**, above which the **liquid & vapor** are **indistinguishable** from each other.

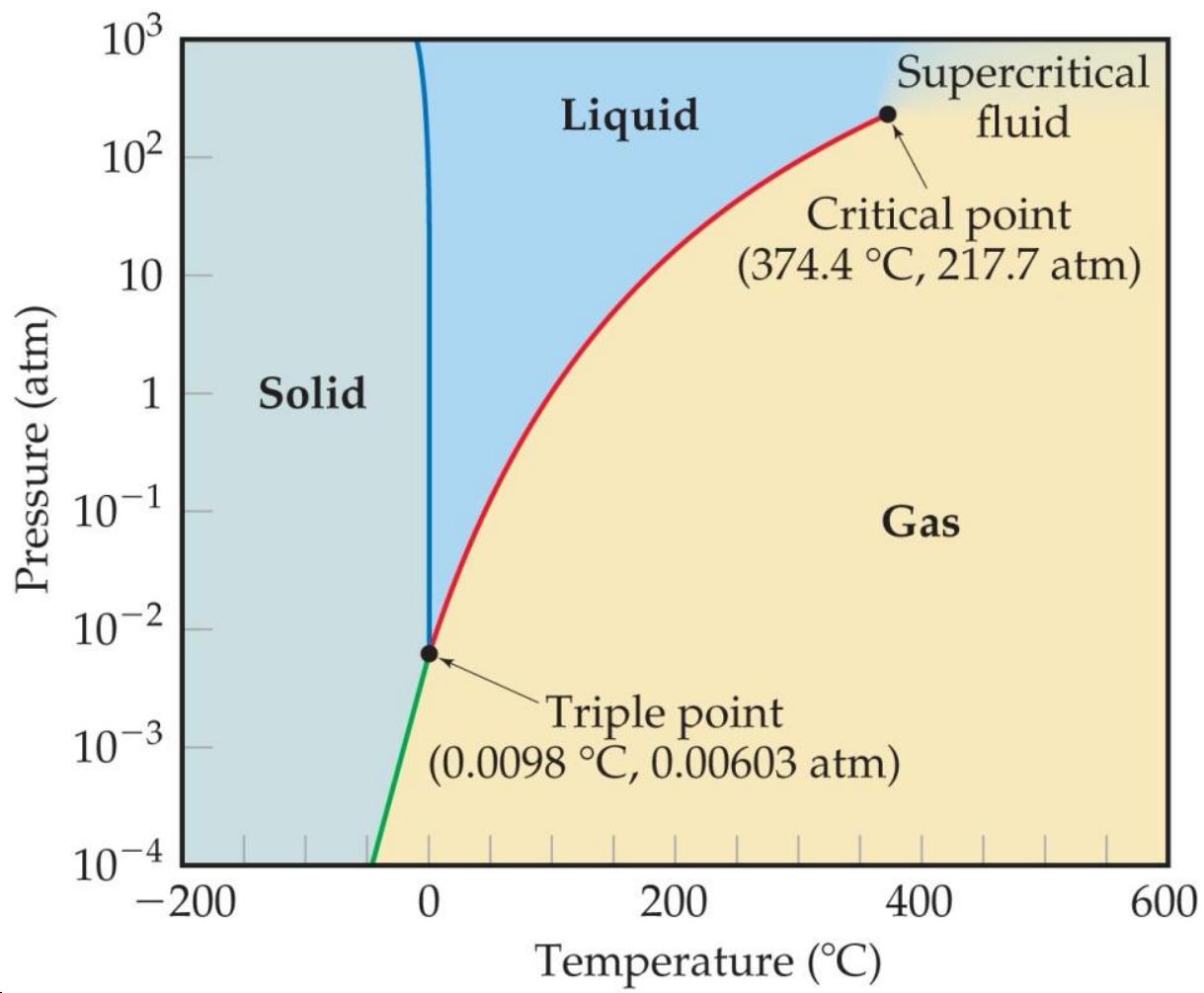
Intermolecular  
Forces

# Phase Diagram of Water



- The high critical temperature & critical pressure, due to the strong intermolecular forces between water molecules: **Hydrogen bond**.

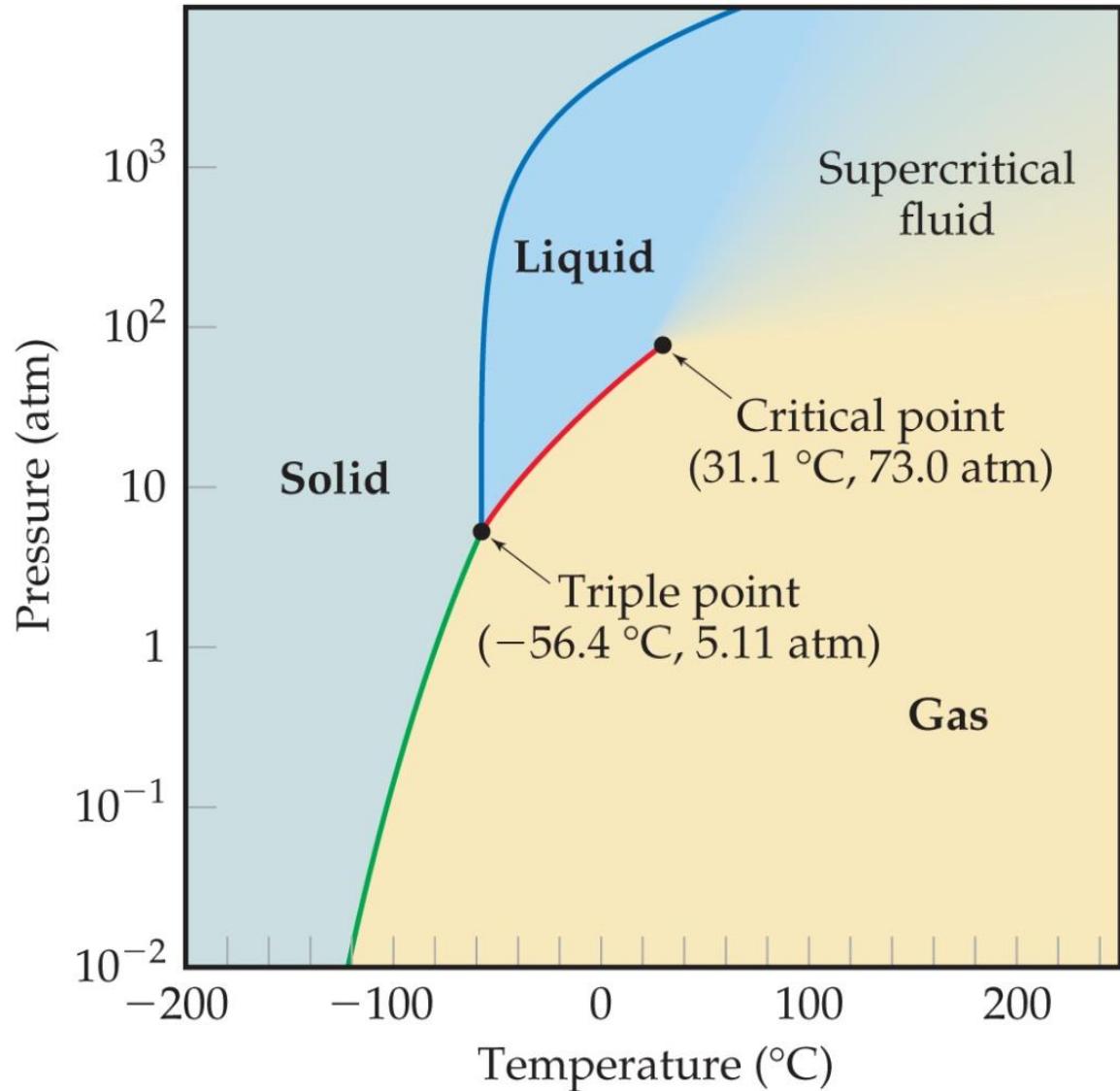




- **Unusual features:**

- The slope of the solid-liquid line is **negative**.
- the pressure is **increased**, just below the melting point, water goes from a solid to a liquid
- the melting point **decreases**.

# Phase Diagram of Carbon Dioxide



- Unusual features:
  - cannot exist in the liquid state at pressures  $< 5.11\text{ atm}$  (triple point).
  - $\text{CO}_2$  sublimes at normal pressures.

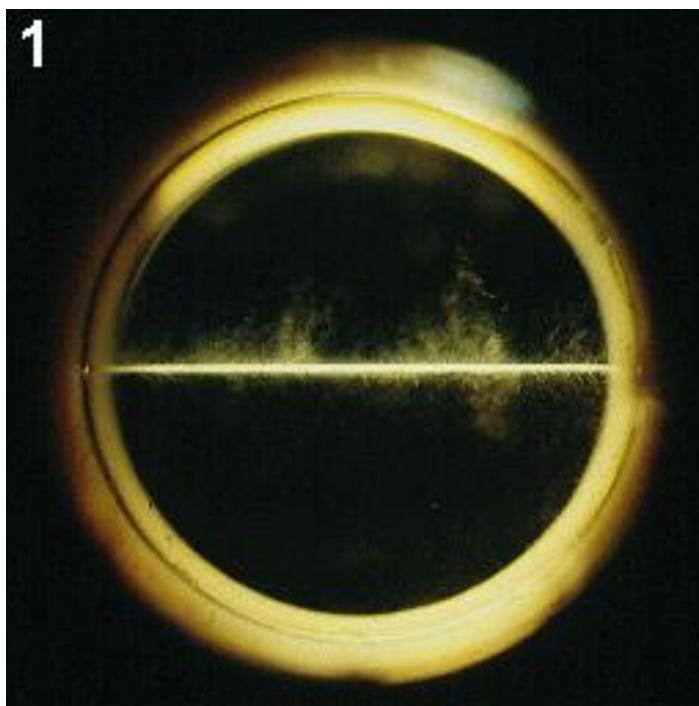
# Critical Temperature and Pressure

- The highest temperature at which a distinct liquid phase can form: **critical temperature**.
- Critical pressure:** The pressure needed to compress the liquid at this critical temperature.

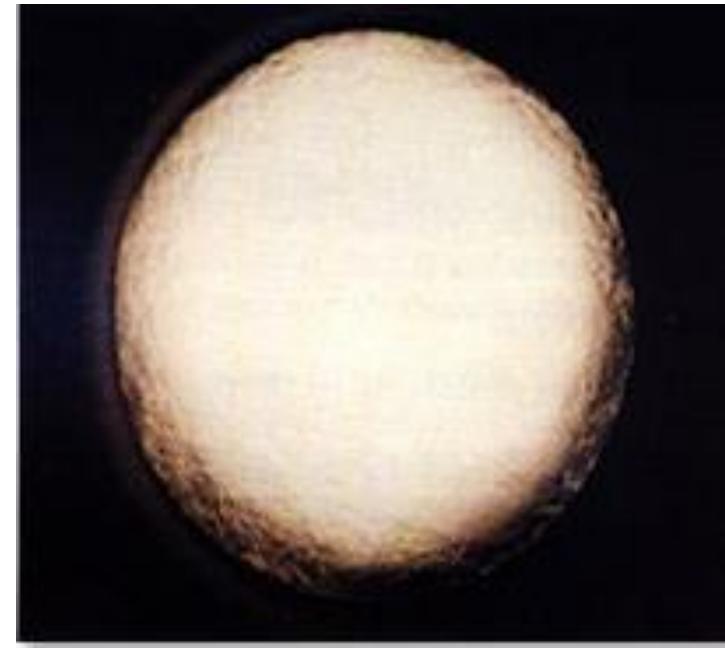
Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen, N <sub>2</sub>	126.1	33.5
Argon, Ar	150.9	48.0
Oxygen, O <sub>2</sub>	154.4	49.7
Methane, CH <sub>4</sub>	190.0	45.4
Carbon dioxide, CO <sub>2</sub>	304.3	73.0
Phosphine, PH <sub>3</sub>	324.4	64.5
Propane, CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	370.0	42.0
Hydrogen sulfide, H <sub>2</sub> S	373.5	88.9
Ammonia, NH <sub>3</sub>	405.6	111.5
Water, H <sub>2</sub> O	647.6	217.7

# Supercritical Fluids

- The state beyond this **critical temperature** is called a **supercritical fluid**.
- The **liquid & gas phase** become **indistinguishable** from each other.



Below the critical parameters,  
two distinct phases exist



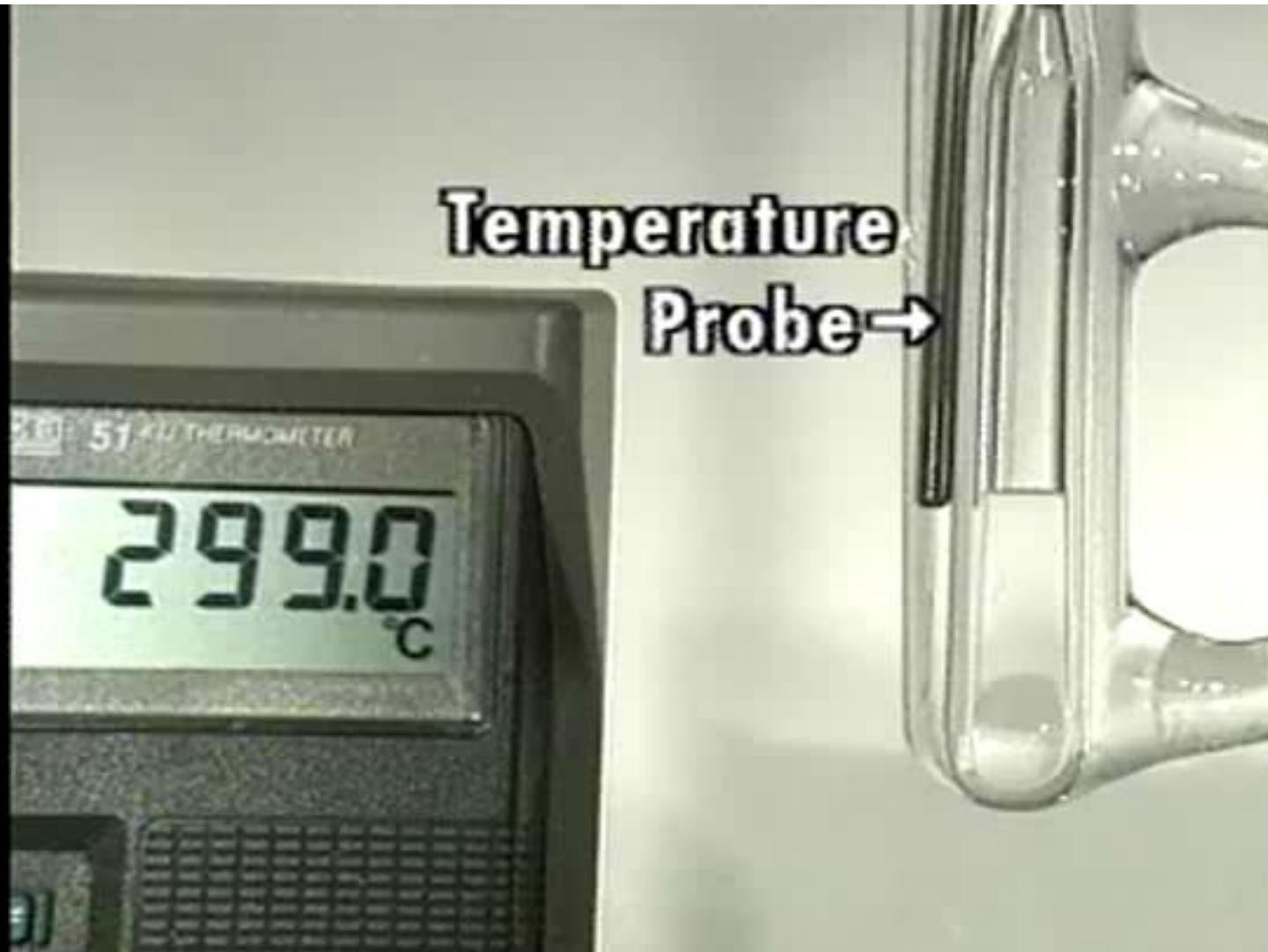
Supercritical

# Critical Point of Benzene



Forces

# Critical Point of Benzene

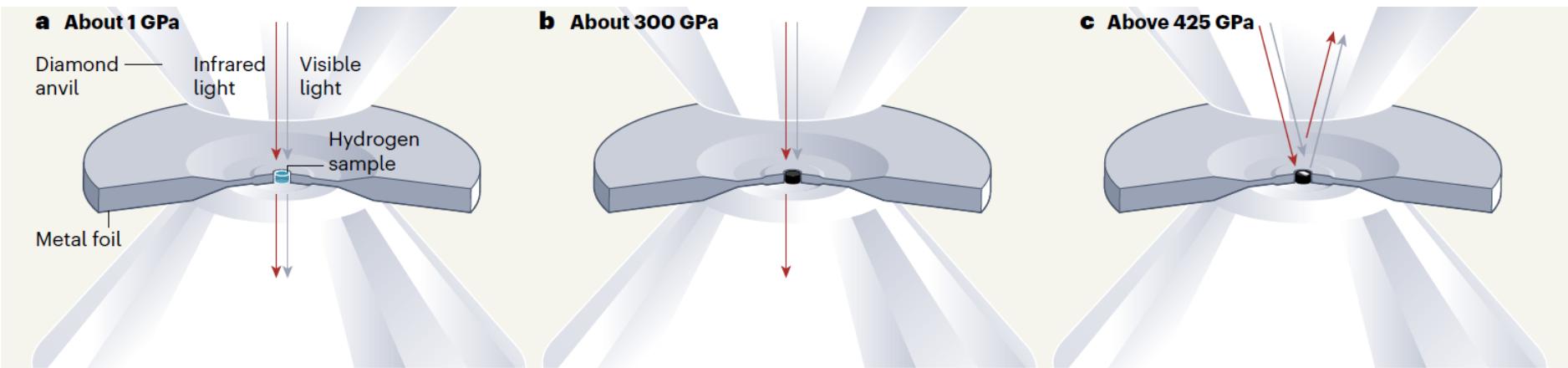


Intermolecular  
Forces

# Critical Point of Benzene



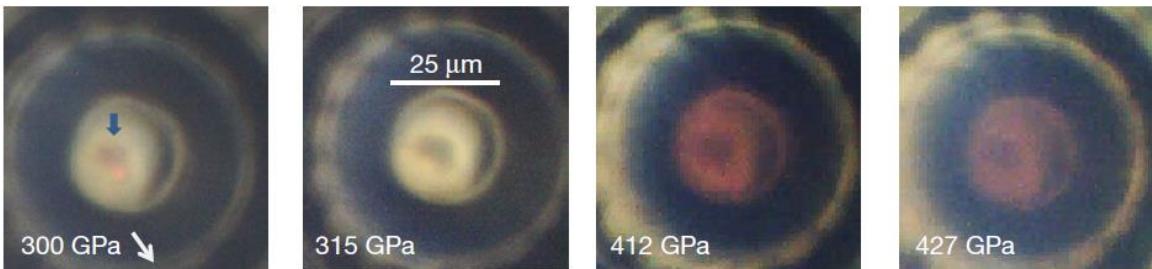
Forces



**Figure 1 | Effect of increasing pressure on cold solid hydrogen.** **a**, Loubeyre *et al.*<sup>5</sup> have studied solid hydrogen at extreme pressure and low temperature using a device known as a diamond anvil cell. This device compresses a sample of the material, which is confined to a microscopic chamber in a thin metal foil, between two diamond anvils. At first when the pressure is applied, the sample

is transparent to both infrared and visible light (GPa, gigapascals). **b**, When the pressure is raised to roughly 300 GPa, the dense hydrogen loses its transparency to visible light. **c**, Finally, when the pressure is above 425 GPa, the sample becomes reflective to both infrared and visible light, indicating a shift into the long-sought metallic state of hydrogen.

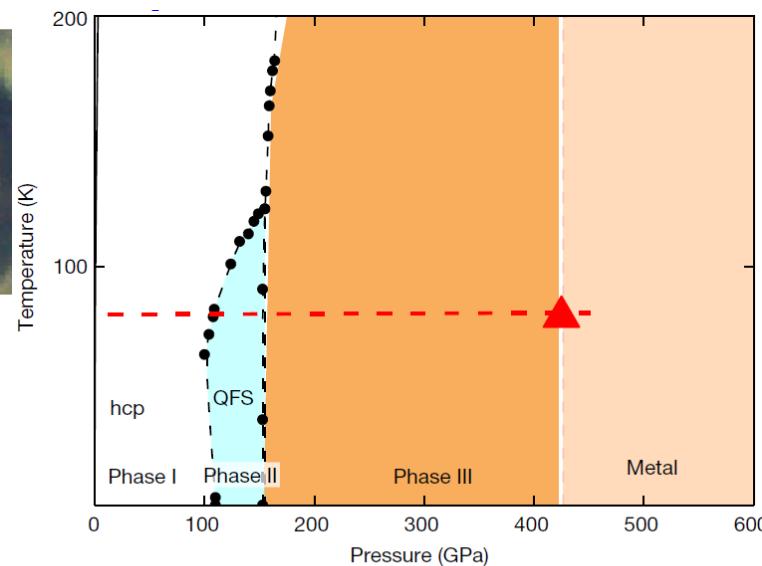
## Extra Info.



626 | Nature | Vol 577 | 30 January 2020

Nature | Vol 577 | 30 January 2020 | 631

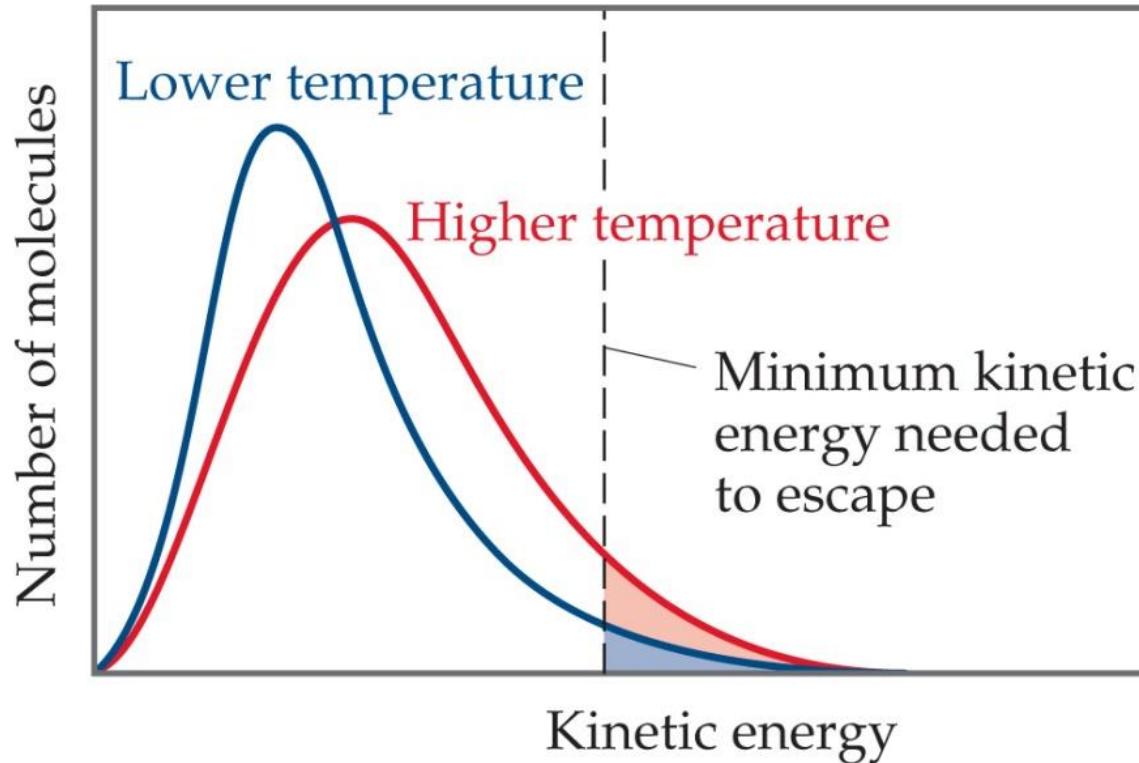
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**Fig. 4 | Low-temperature phase diagram of solid hydrogen.** The red dashed

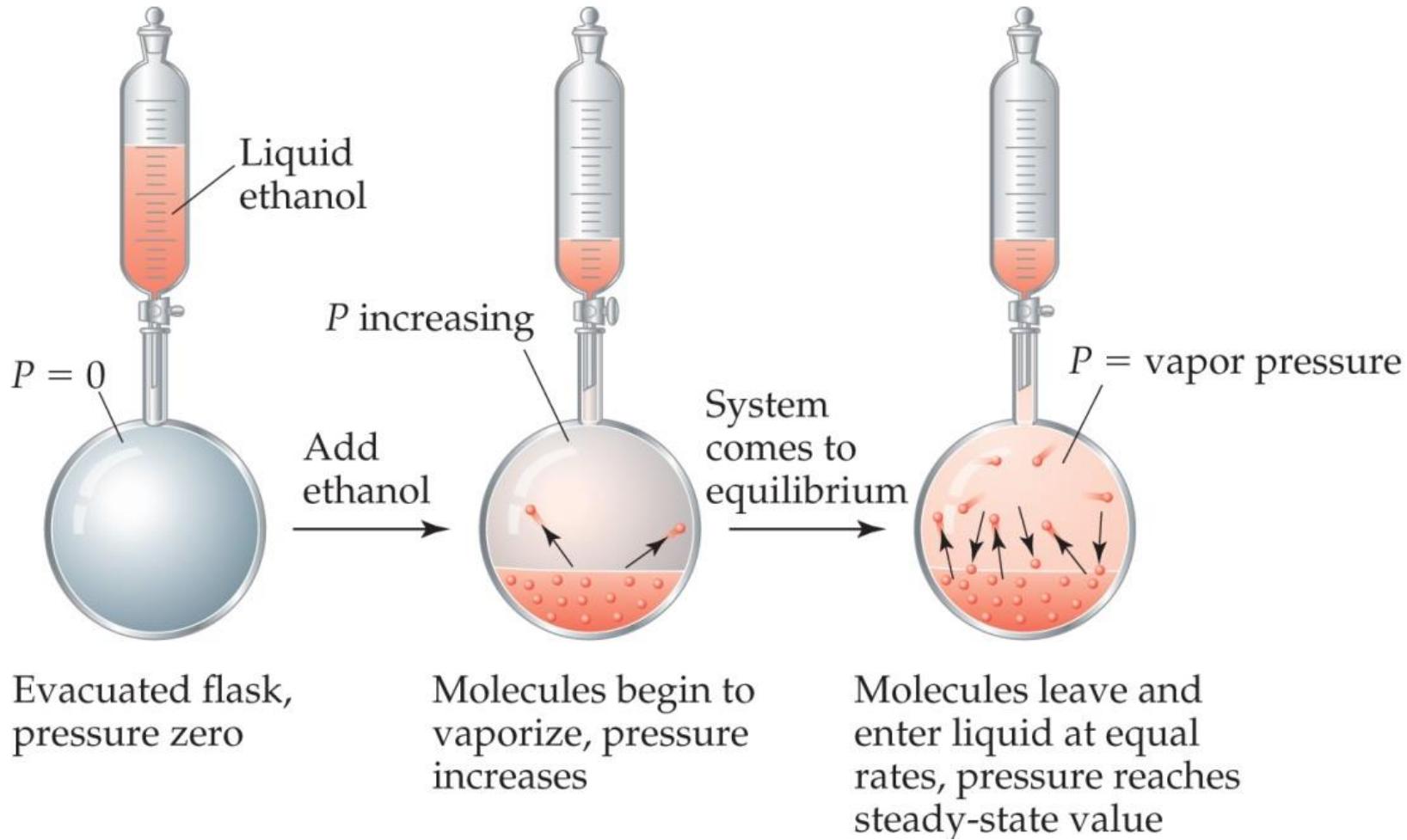
# Vapor Pressure

- At *any temperature*, some molecules have enough energy to escape the surface and become a gas.
- When the pressure of the vapor becomes constant, we call vapor pressure.



Blue area = number of molecules having enough energy to evaporate at lower temperature

Red + blue areas = number of molecules having enough energy to evaporate at higher temperature

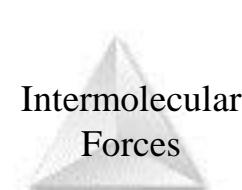


- As more molecules escape from the liquid, the pressure they exert increases.
- The liquid & vapor reach a state of dynamic equilibrium: liquid molecules evaporate & vapor molecules condense *at the same rate*.

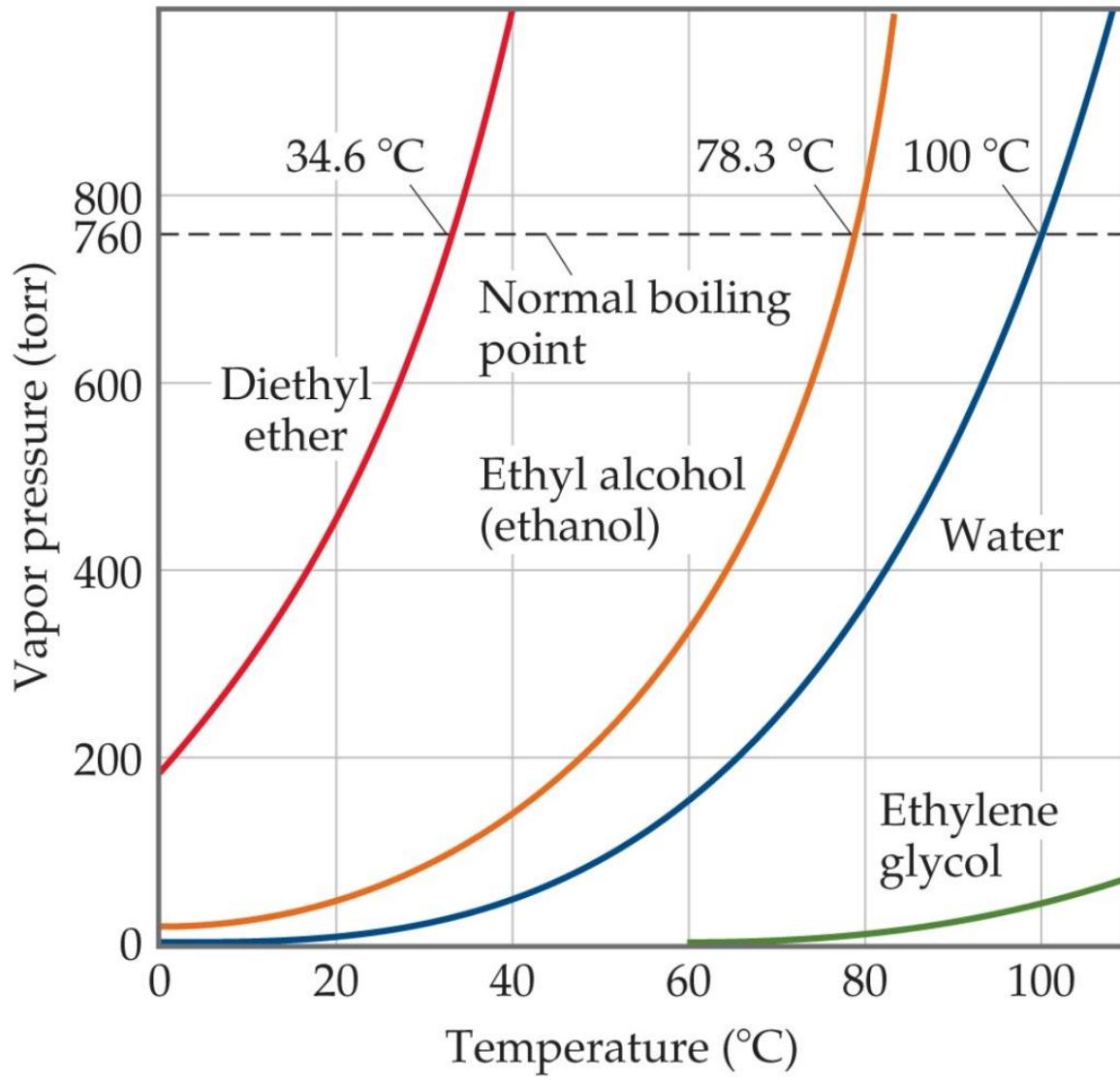
# Vapor Pressure

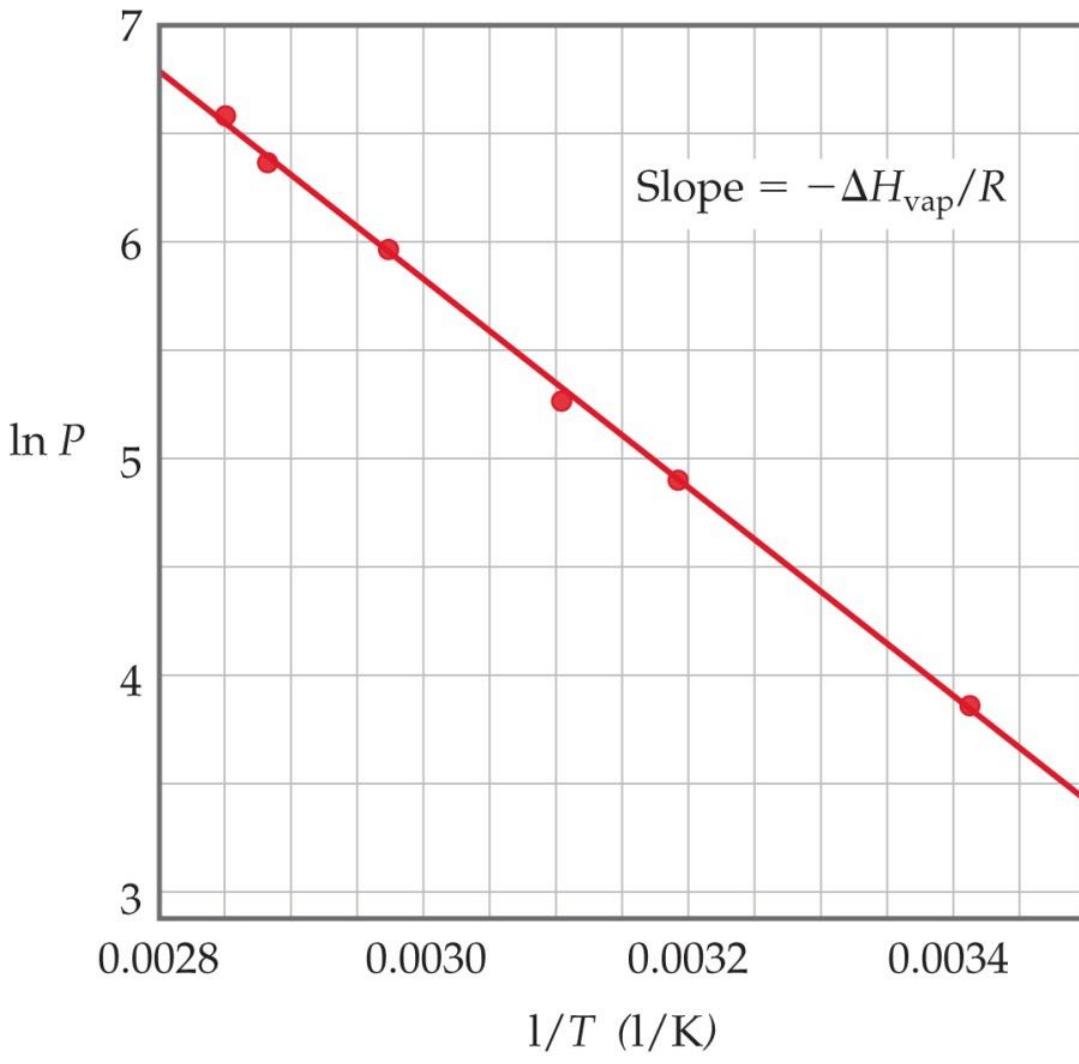
Vapor Pressure (torr)	10.0	40.0	100.0	400.0
$T$ for $\text{CH}_2\text{Cl}_2$ ( $^{\circ}\text{C}$ )	-43.3	-22.3	-6.3	24.1
$T$ for $\text{CH}_3\text{I}$ ( $^{\circ}\text{C}$ )	-45.8	-24.2	-7.0	25.3

- As the temperature rises, the fraction of molecules that have enough energy to break free increases and thus, vapor pressure increases.



- The **boiling point** of a liquid is the temperature at which its **vapor pressure equals atmospheric pressure**.
- The **normal boiling point** : the temperature at which its vapor pressure is 760 torr (1 atm).





- The natural log of the vapor pressure of a liquid is inversely proportional to its temperature.

- Clausius–Clapeyron equation:

$$\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + C$$

$C$  is a constant;  $T$  is the absolute temperature;  
 $R$  is the gas constant (8.314 J/mol-K);  
 $\Delta H_{\text{vap}}$  is the molar enthalpy of vaporization

# Liquid Crystals



$145\text{ }^{\circ}\text{C} < T < 179\text{ }^{\circ}\text{C}$   
Liquid crystalline phase

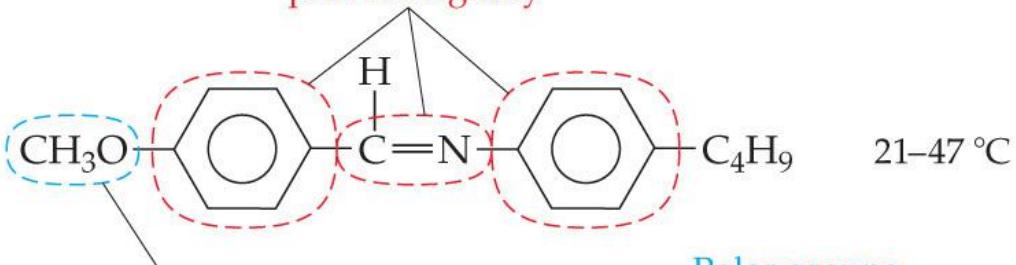


$T > 179\text{ }^{\circ}\text{C}$   
Liquid phase

- Some substances do not go directly from the solid state to the liquid state.
- In this **intermediate state**, liquid crystals **have some traits of solids and some of liquids**.

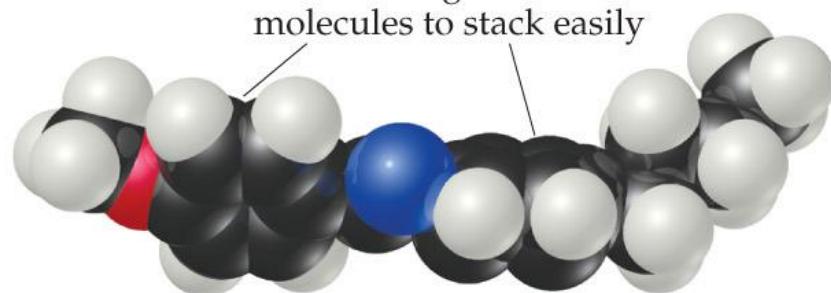
Intermolecular  
Forces

Double bonds provide rigidity

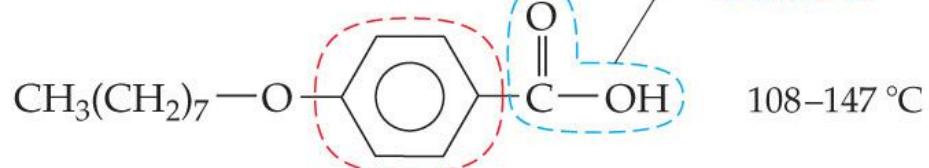


21–47 °C

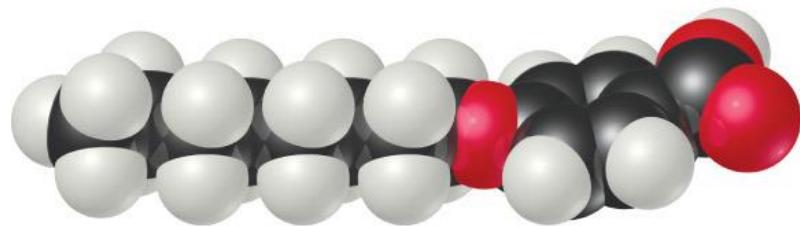
Benzene rings allow molecules to stack easily



Polar groups create dipole moments

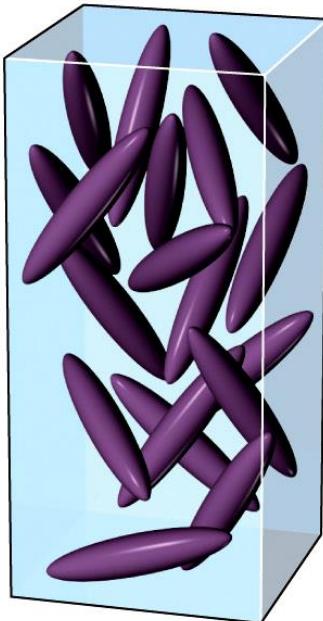


108–147 °C



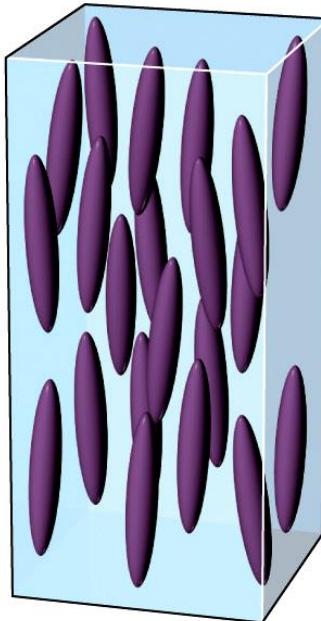
- Molecules in liquid crystals have some degree of order.
- Length are much **greater than width**, **rigid**, **flat**, **dipole-dipole interaction**, **easily align**.

# Liquid Crystals



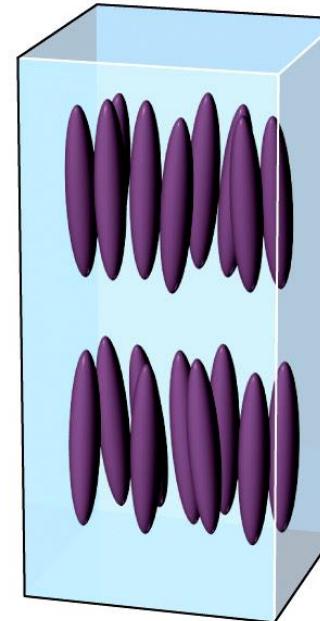
**Liquid phase**

Molecules arranged randomly



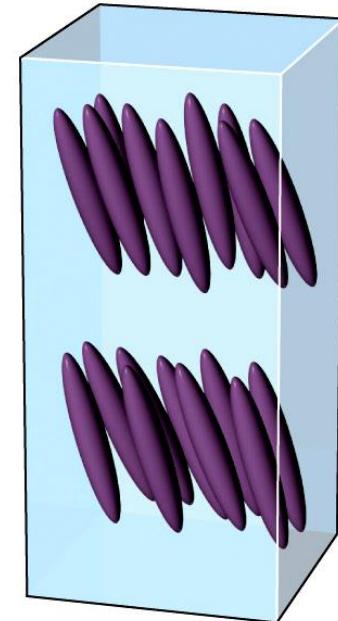
**Nematic liquid crystalline phase**

Long axes of molecules aligned, but ends are not aligned



**Smectic A liquid crystalline phase**

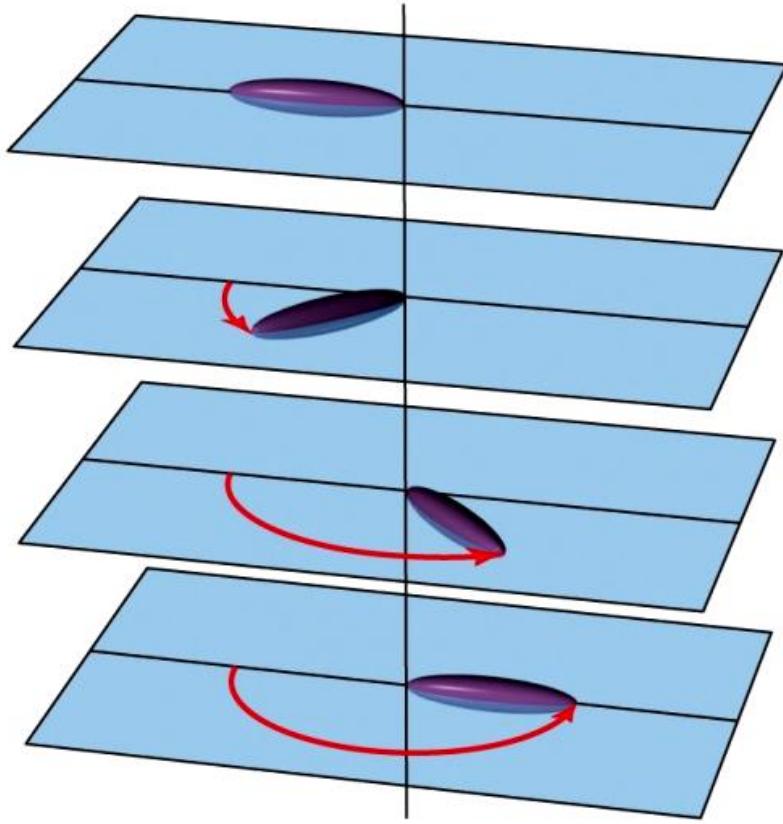
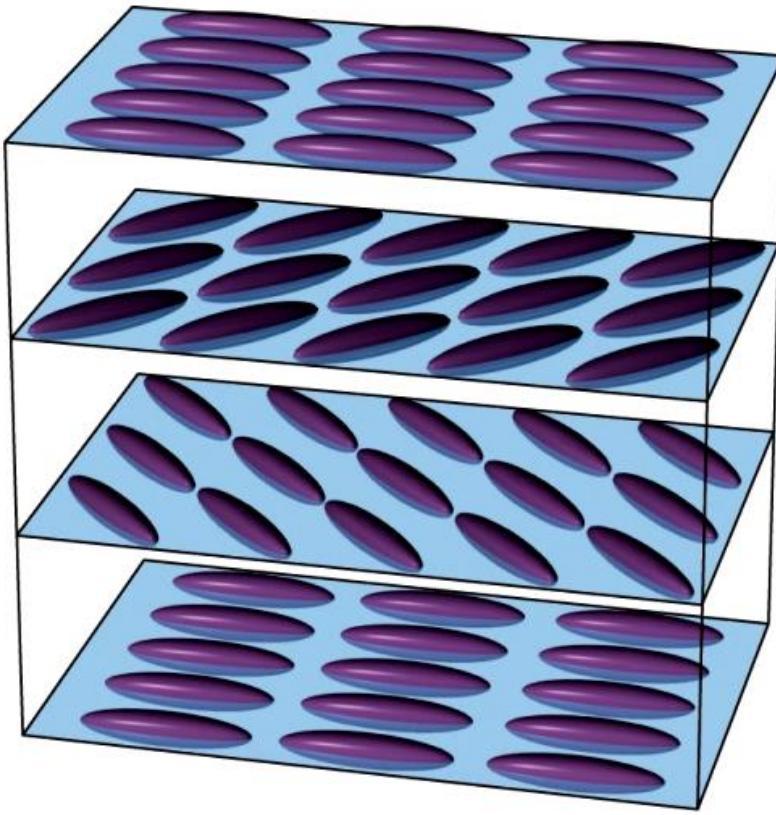
Molecules aligned in layers, long axes of molecules perpendicular to layer planes



**Smectic C liquid crystalline phase**

Molecules aligned in layers, long axes of molecules inclined with respect to layer planes

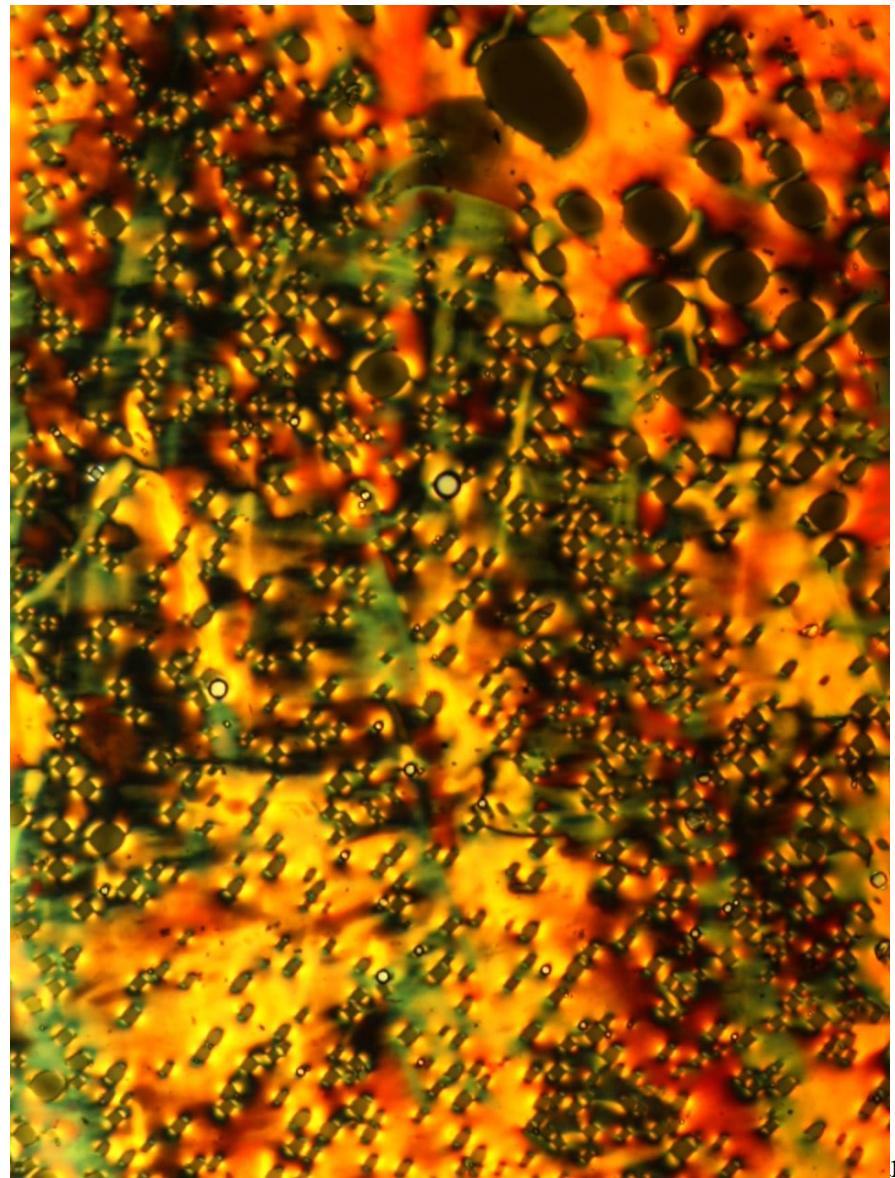
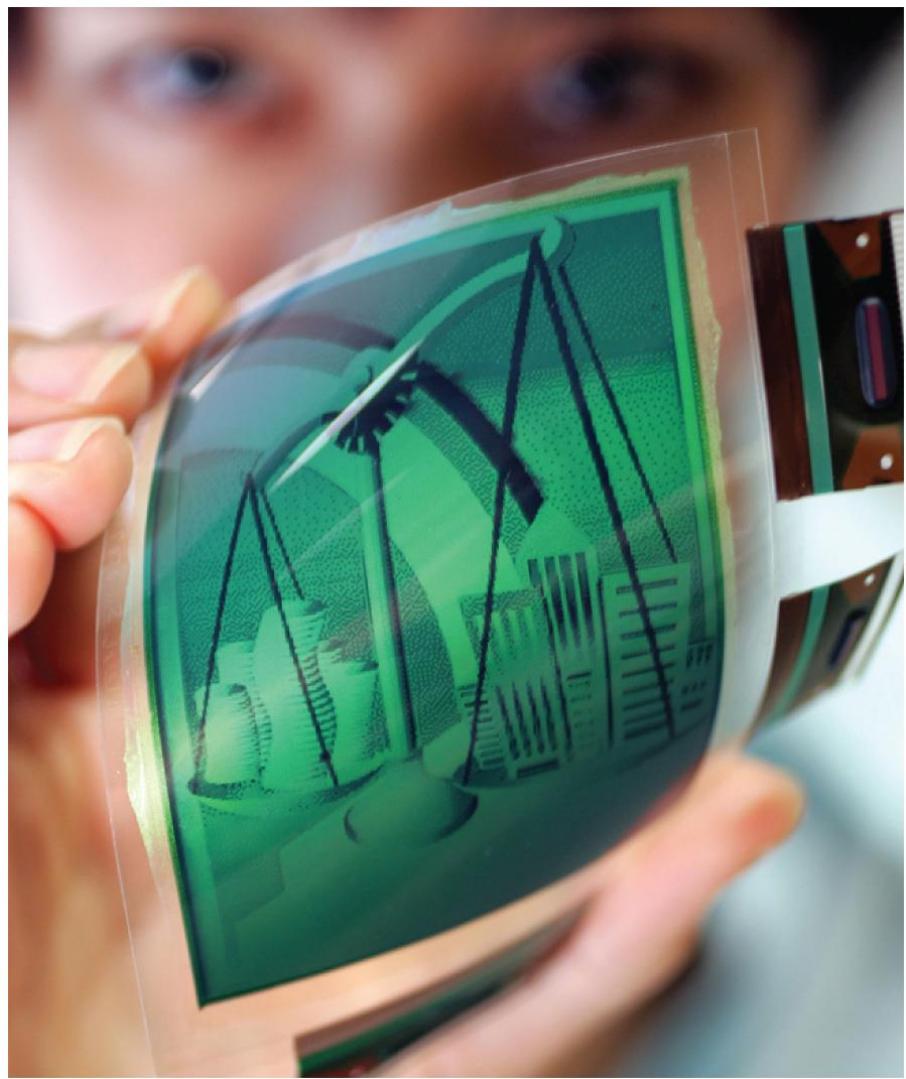
- In **nematic liquid crystals**, molecules **ordered in 1D**, along the long axis.
- In **smectic liquid crystals**, molecules are **ordered in 2Ds**, along the long axis & in layers.



In a cholesteric liquid crystal the molecules pack into layers; the long axis of each molecule is oriented parallel to its neighbors within the same layer

The direction along which the molecules point rotates from one layer to the next, resulting in a spiraling pattern resembling the threads of a screw

**In cholesteryl liquid crystals, nematic-like crystals are layered at angles to each other.**  
(<https://newshub.sustech.edu.cn/zh/html/201908/25235.html>)



Forces

## How do viscosity and surface tension change

- a. as temperature increases,
  - b. as intermolecular forces of attraction become stronger?
- A. Viscosity increases as intermolecular forces increase while surface tension decreases. Both viscosity and surface tension increase with increasing temperature.
- B. Viscosity decreases as intermolecular forces increase while surface tension increases. Both viscosity and surface tension increase with decreasing temperature.
- C. Both viscosity and surface tension increase as intermolecular forces increase and temperature decreases.
- D. Both viscosity and surface tension decrease as intermolecular forces increase and temperature increases.

If the inside surface of each tube were coated with wax, would the general shape of the water meniscus change? Would the general shape of the mercury meniscus change?

Shape of Water Meniscus

- A. Yes, Inverted U
- B. No change
- C. No change
- D. Yes, Inverted U

Shape of Hg Meniscus

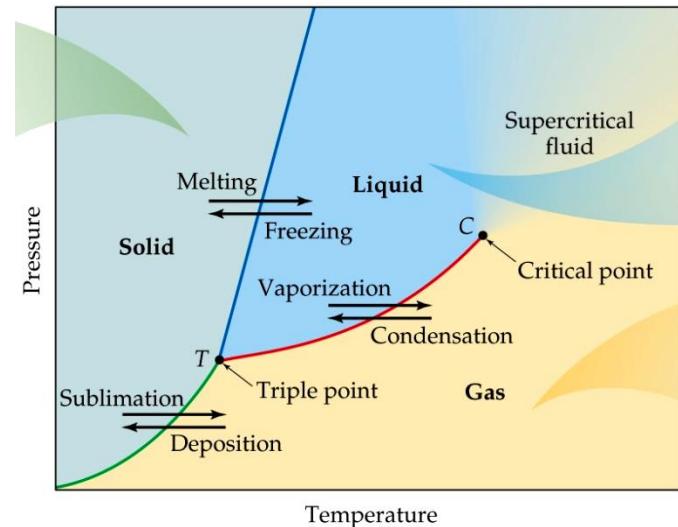
- Yes, downward U
- Yes, downward U
- No change
- No change

Is it possible to calculate the heat of sublimation for a substance given its heats of vaporization and fusion? If so, what is the relationship?

- A. No, because we are not dealing with state functions.
- B. No, because we need heat of melting.
- C. Yes,  $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$
- D. Yes,  $\Delta H_{sub} = \Delta H_{fus} - \Delta H_{vap}$

If the pressure exerted on a liquid is increased, while the temperature is held constant, what type of phase transition will eventually occur?

- A. Freezing
- B. Melting
- C. Vaporization
- D. Condensation



Which force below is the strongest intermolecular attractive force?

- a. Hydrogen bonding
- b. Ion-dipole forces
- c. Dipole-dipole forces
- d. London dispersion forces

Which force below increases in strength as the molecular weight of the compound increases?

- a. Hydrogen bonding
- b. Ion-dipole forces
- c. Dipole-dipole forces
- d. London dispersion forces

Which compound below is not capable of forming hydrogen bonds?

- a.  $\text{CH}_4$
- b.  $\text{NH}_3$
- c.  $\text{H}_2\text{O}$
- d. HF

Which compound below has the highest boiling point?

- a.  $\text{H}_2\text{O}$
- b.  $\text{H}_2\text{S}$
- c.  $\text{H}_2\text{Se}$
- d.  $\text{H}_2\text{Te}$

Which element below has the highest boiling point?

- a. Kr
- b. F<sub>2</sub>
- c. Cl<sub>2</sub>
- d. Br<sub>2</sub>

Which substance below has a greater density in its liquid state than in its solid state?

- a. Iron
- b. Glass
- c. Water
- d. Carbon dioxide

The energy required to cause a liquid to boil is called the \_\_\_\_\_ of the liquid.

- a. boiling point
- b. freezing point
- c. heat of vaporization
- d. heat of fusion

The highest temperature at which a substance can exist in its liquid state is called its \_\_\_\_\_ point.

- a. boiling
- b. freezing
- c. triple
- d. critical

The temperature and pressure at which all three phases exist simultaneously is called the \_\_\_\_\_ point of a substance.

- a. boiling
- b. freezing
- c. triple
- d. critical

At high altitudes, the boiling point of water is

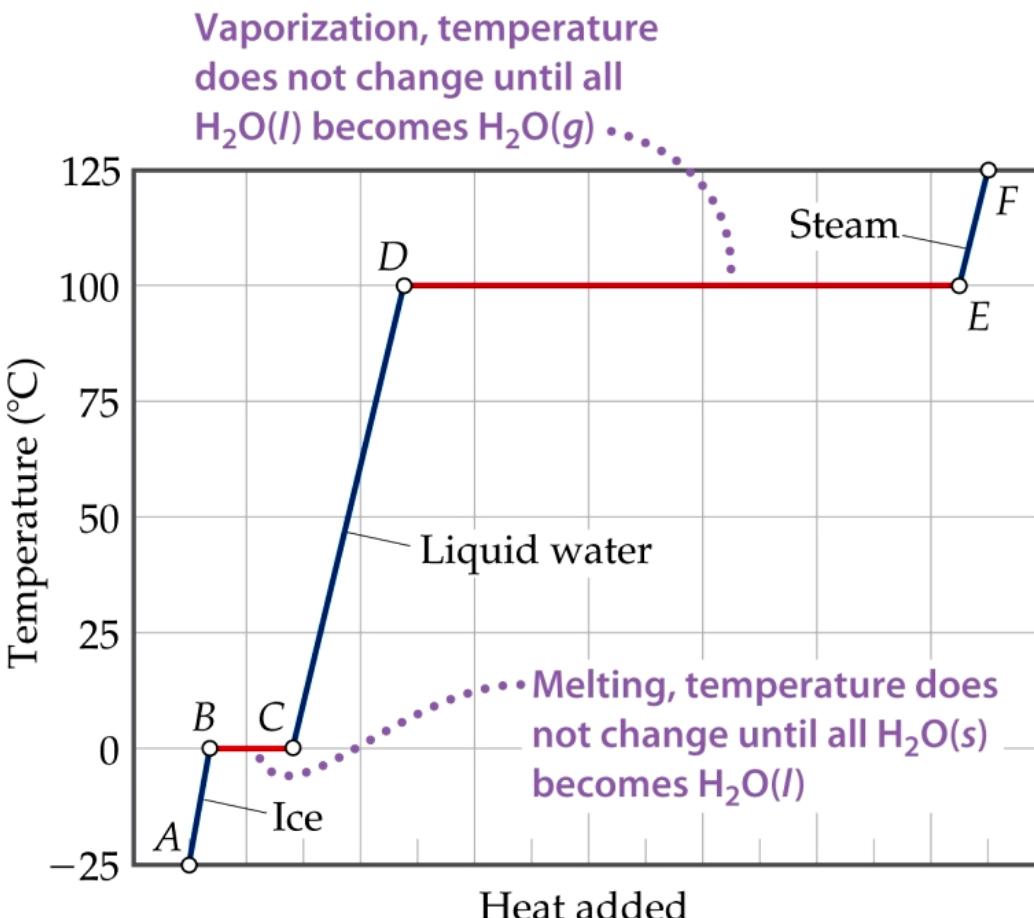
- a. 100 degrees Celsius.
- b. greater than 100 degrees Celsius.
- c. less than 100 degrees Celsius.
- d. equal to its freezing point.

Isopropyl alcohol feels cool to the touch because it has an (X) heat of (Y).

- a. X = exothermic, Y = vaporization
- b. X = endothermic, Y = vaporization
- c. X = exothermic, Y = fusion
- d. X = endothermic, Y = fusion

Predicting Types and Relative Strengths of Intermolecular Attraction: List the substances  $\text{BaCl}_2$ ,  $\text{H}_2$ , CO, HF, and Ne in order of increasing boiling point.

Calculate the enthalpy change upon converting 1.00 mol of ice at  $-25\text{ }^{\circ}\text{C}$  to steam at  $125\text{ }^{\circ}\text{C}$  under a constant pressure of 1 atm. The specific heats of ice, liquid water, and steam are 2.03 J/g-K, 4.18 J/g-K, and 1.84 J/g-K, respectively. For  $\text{H}_2\text{O}$ ,  $\Delta H_{\text{fus}} = 6.01\text{ kJ/mol}$  and  $\Delta H_{\text{vap}} = 40.67\text{ kJ/mol}$



# **Summary of Chapter 11**

van der Waals Interactions, London Dispersion forces,  
Dipole-Dipole Interactions, Ion-Dipole Interactions &  
Hydrogen Bond

Polarizability, Boiling Point, Melting Point, Vapor Pressure, Viscosity, Surface Tension, Cohesion And Adhesion, Capillary Action

Phase Diagram, Heat of Fusion/Vaporization/Sublimation, Heating Curves, Critical Temperature and Pressure, Supercritical Fluids

Liquid Crystals

**Thank You for Your  
Attention!  
Any Questions?**

