CHEM103
General Chemistry

Chapter 11: Liquids and Intermolecular Forces

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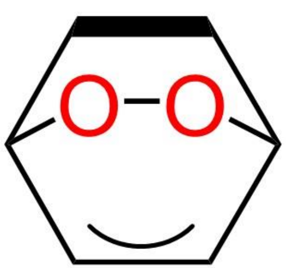


Review on Chapter 9

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

(σ) Sigma-Bond, (π) Pi-Bond, Paramagnetism & Diamagnetism

Outline of Chapter 11

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

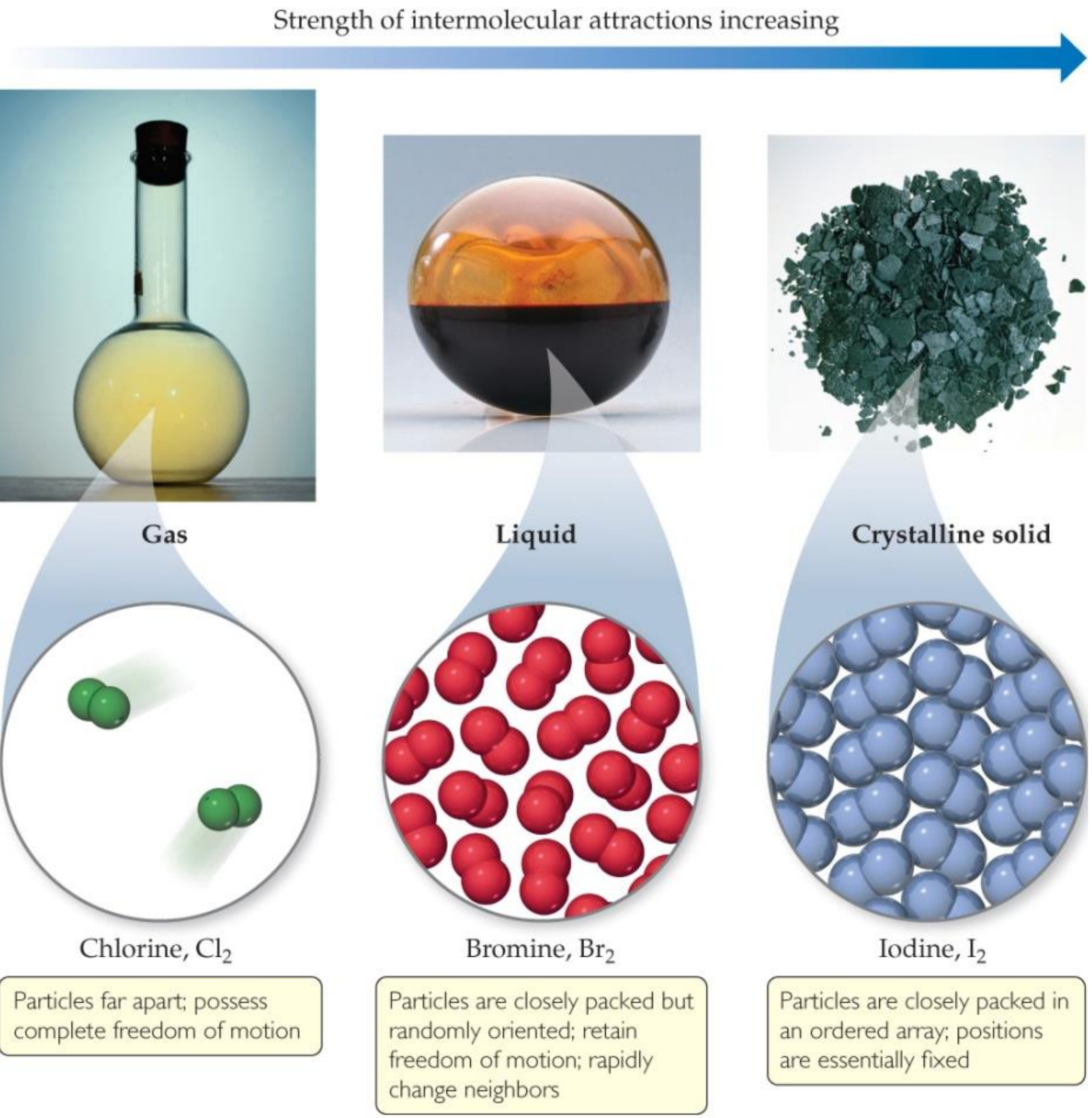
Polarizability, Boiling Point, Melting Point, Vapor Pressure, Viscosity, Surface Tension, Cohesion and Adhesion, Capillary Action

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

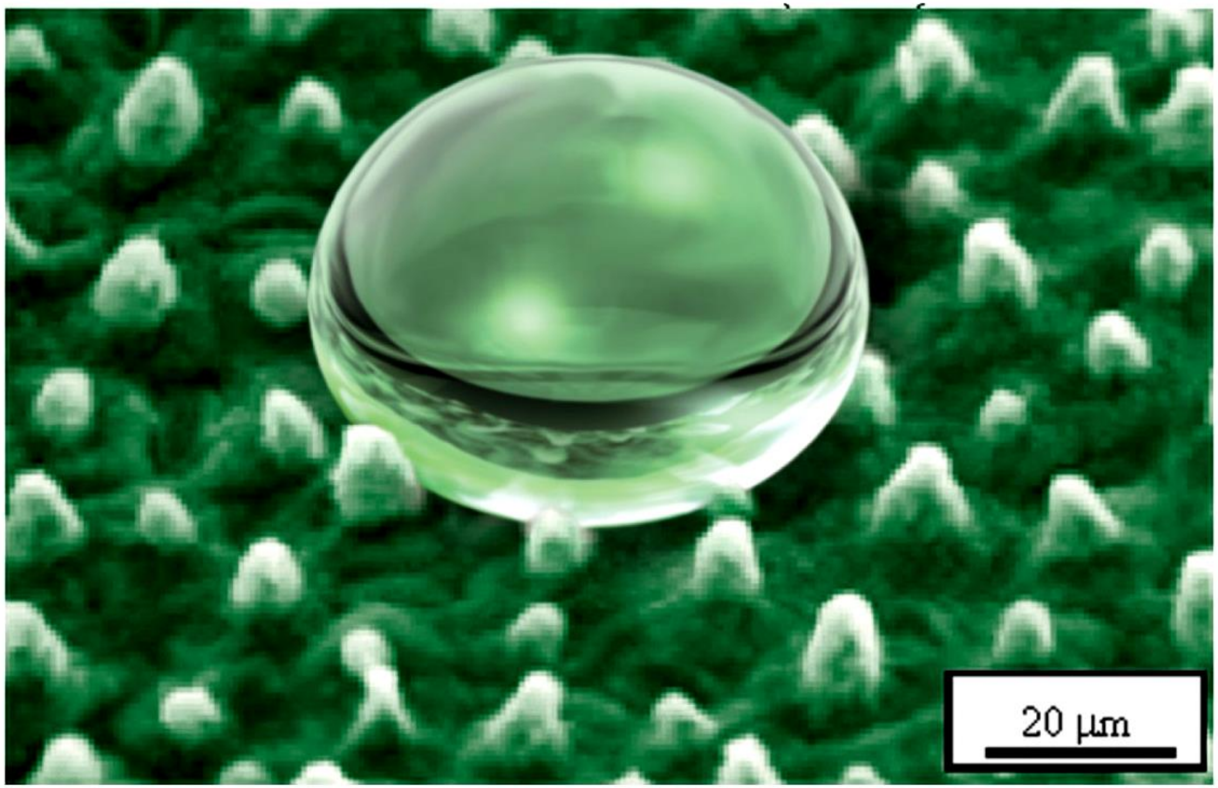
Liquid Crystals

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

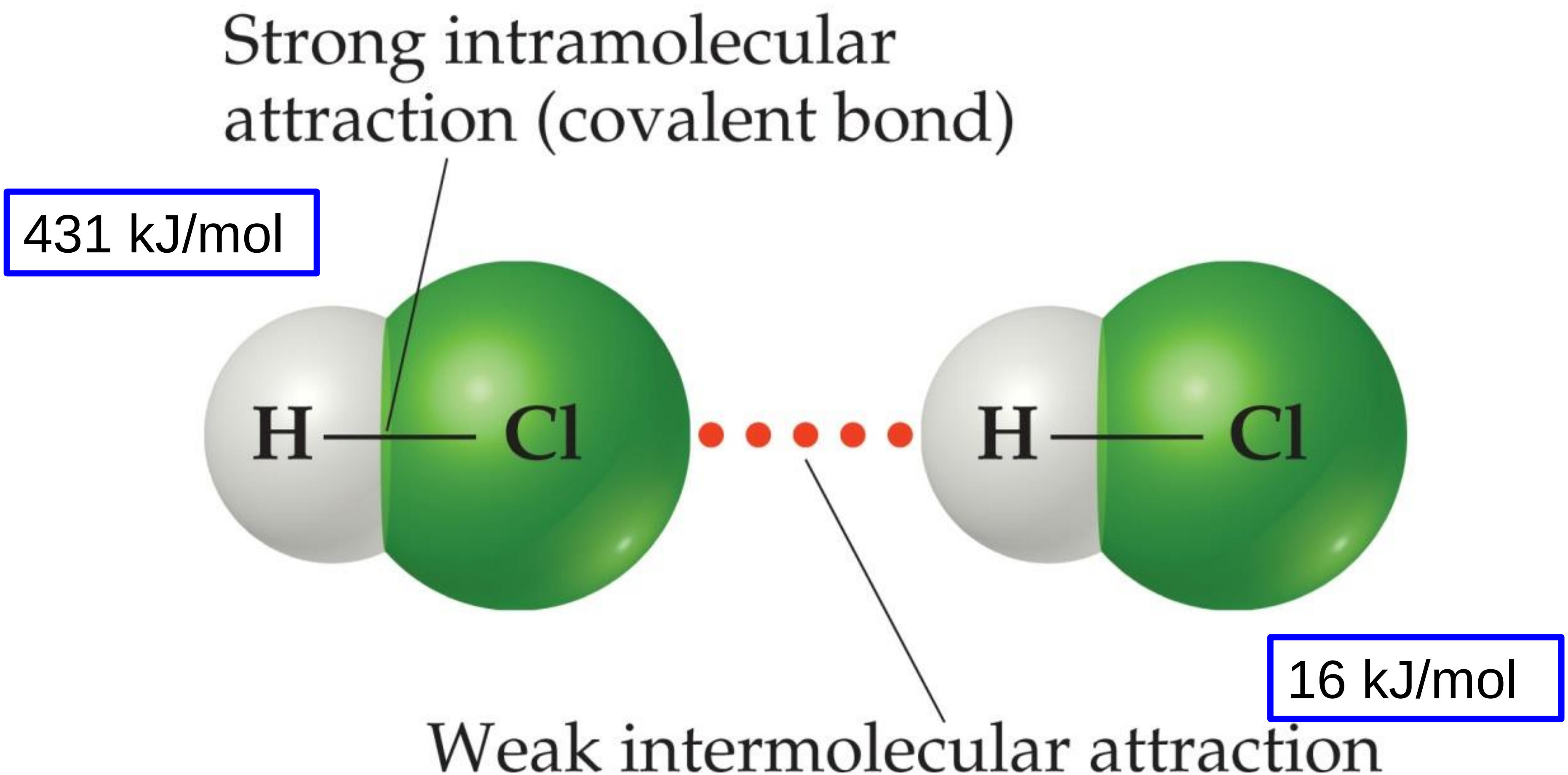
Gas	Assumes both volume and shape of its container
	Expands to fill its container
	Is compressible
	Flows readily
	Diffusion within a gas occurs rapidly
Liquid	Assumes shape of portion of container it occupies
	Does not expand to fill its container
	Is virtually incompressible
	Flows readily
	Diffusion 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



- 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)
Chemical bonds			
Ionic bonds	Lithium fluoride (LiF)	1118	1949
Metallic bonds	Beryllium (Be)	1560	2742
Covalent bonds	Diamond (C)	3800	4300
Intermolecular forces			
Dispersion force	Nitrogen (N_2)	63	77
Dipole–dipole force	Hydrogen chloride (HCl)	158	188
Hydrogen-bonding force	Hydrogen fluoride (HF)	190	293

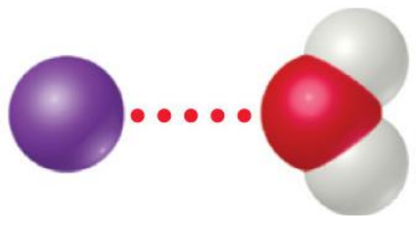
Types of Intermolecular Force

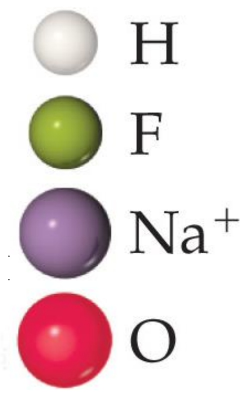
From the weakest one to the strongest forces:

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

- **Hydrogen bonding**

- **Ion–dipole forces**





Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge–dipole charge	40–600	$Na^+ \cdots O(H)_2$
H bond	δ^- δ^+ δ^- —A—H·······:B—	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$:\ddot{O}(H)—H\cdots:\ddot{O}(H)—H$
Dipole-dipole		Dipole charges	5–25	I—Cl····I—Cl
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	$Fe^{2+}\cdots O_2$
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	H—Cl····Cl—Cl
Dispersion (London)		Polarizable e^- clouds	0.05–40	F—F····F—F

(Extra Info.)

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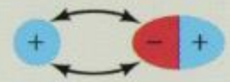
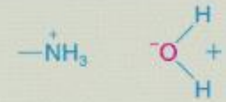
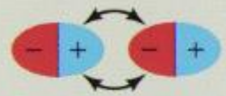
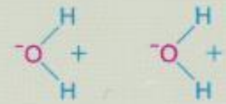
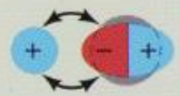
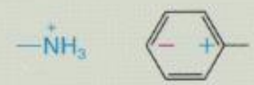
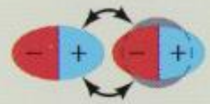
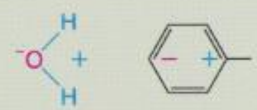
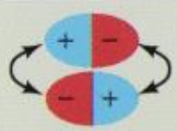
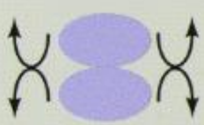
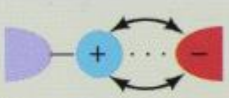
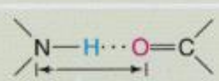
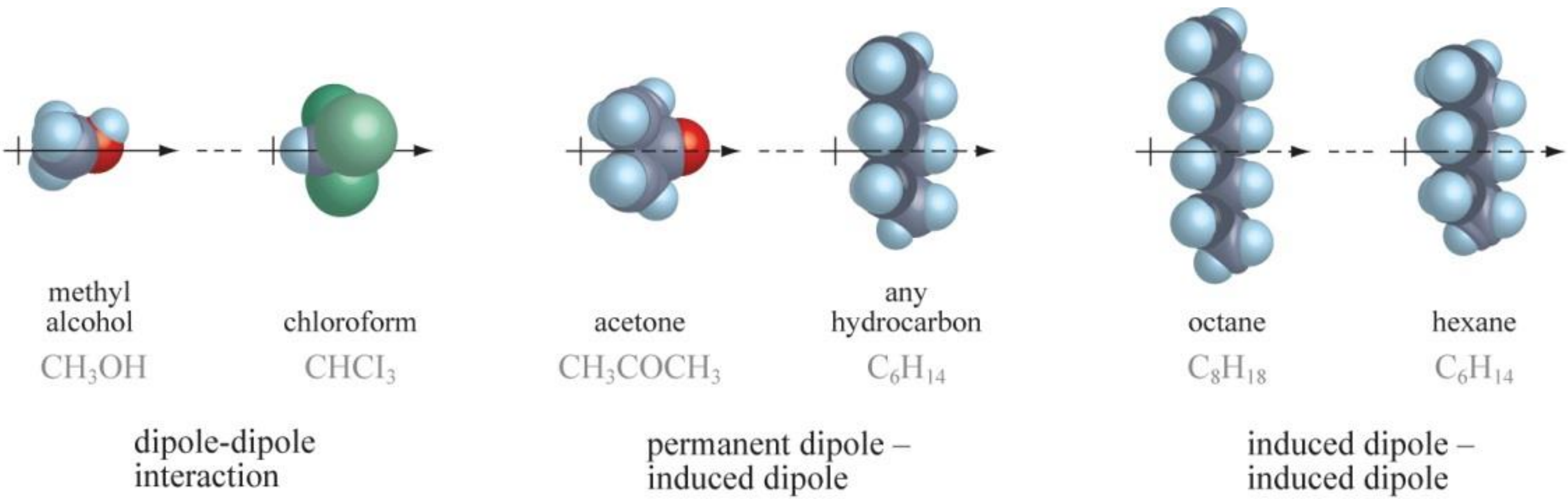
http://www.chem.ufl.edu/~itl/4411/lectures/lec_g.html

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	 Donor Acceptor	 Hydrogen bond length	Length of bond fixed

van der Waals Interactions



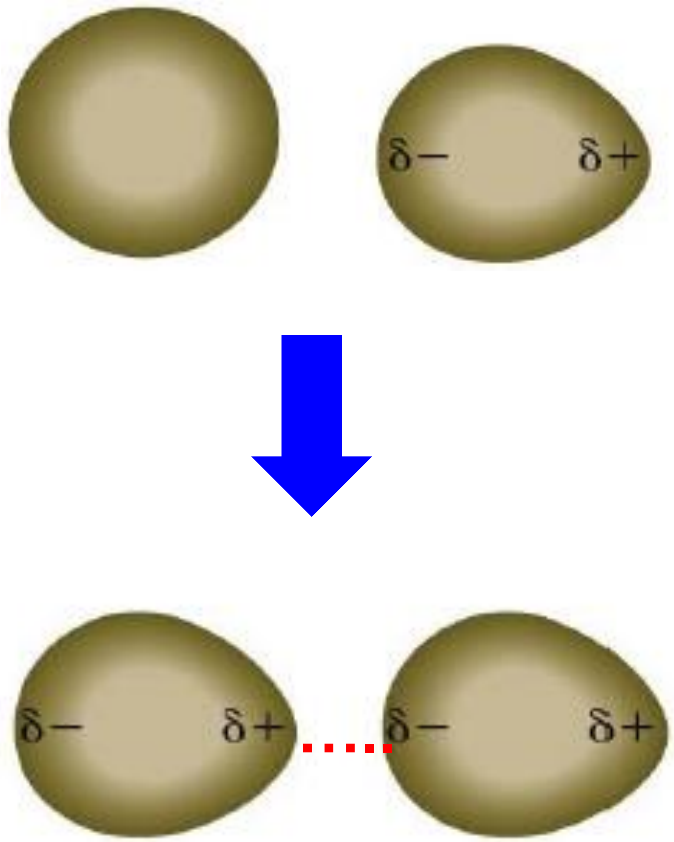
Strongest (left) to weakest (right):

Dipole–dipole interaction
Dipole–induced dipole interaction
Induced dipole–induced dipole interaction

Johannes Diderik van der Waals

London Dispersion Forces

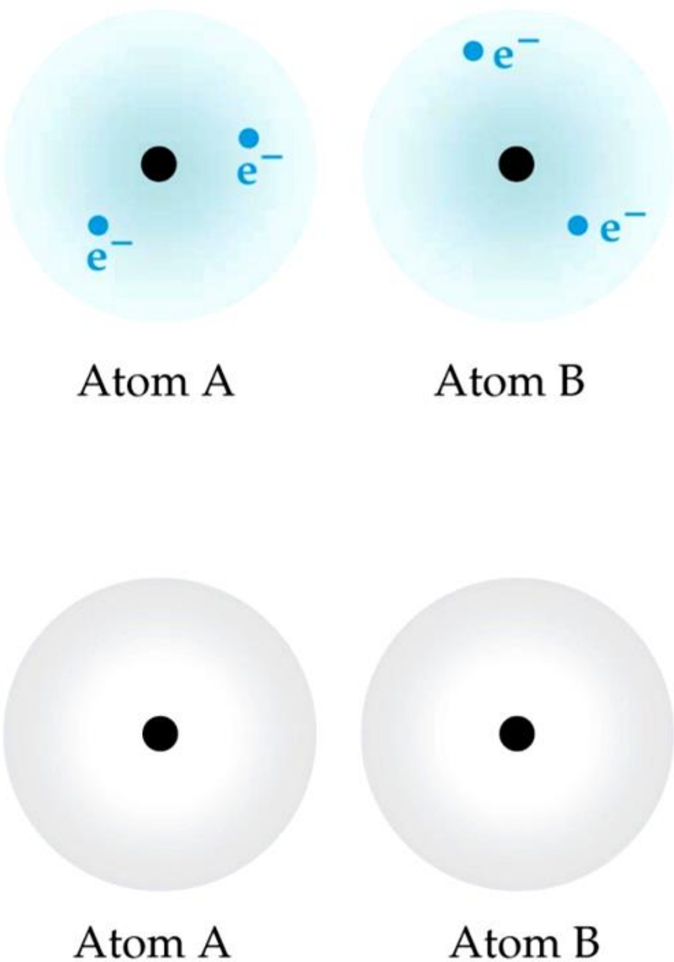
- These forces are **present in all molecules**, whether they are polar or nonpolar.



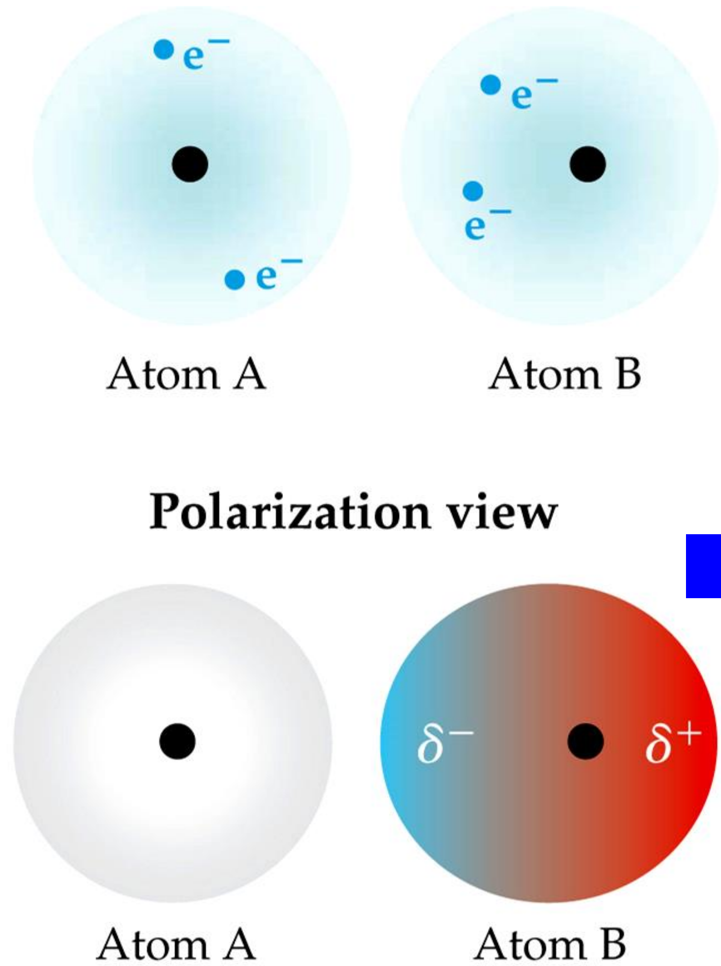
- The tendency of an electron cloud to distort is called polarizability.

- Instantaneous induced-dipole induced-dipole interactions.

- Generally, the **greater polarizability**, the **larger dispersion forces**.



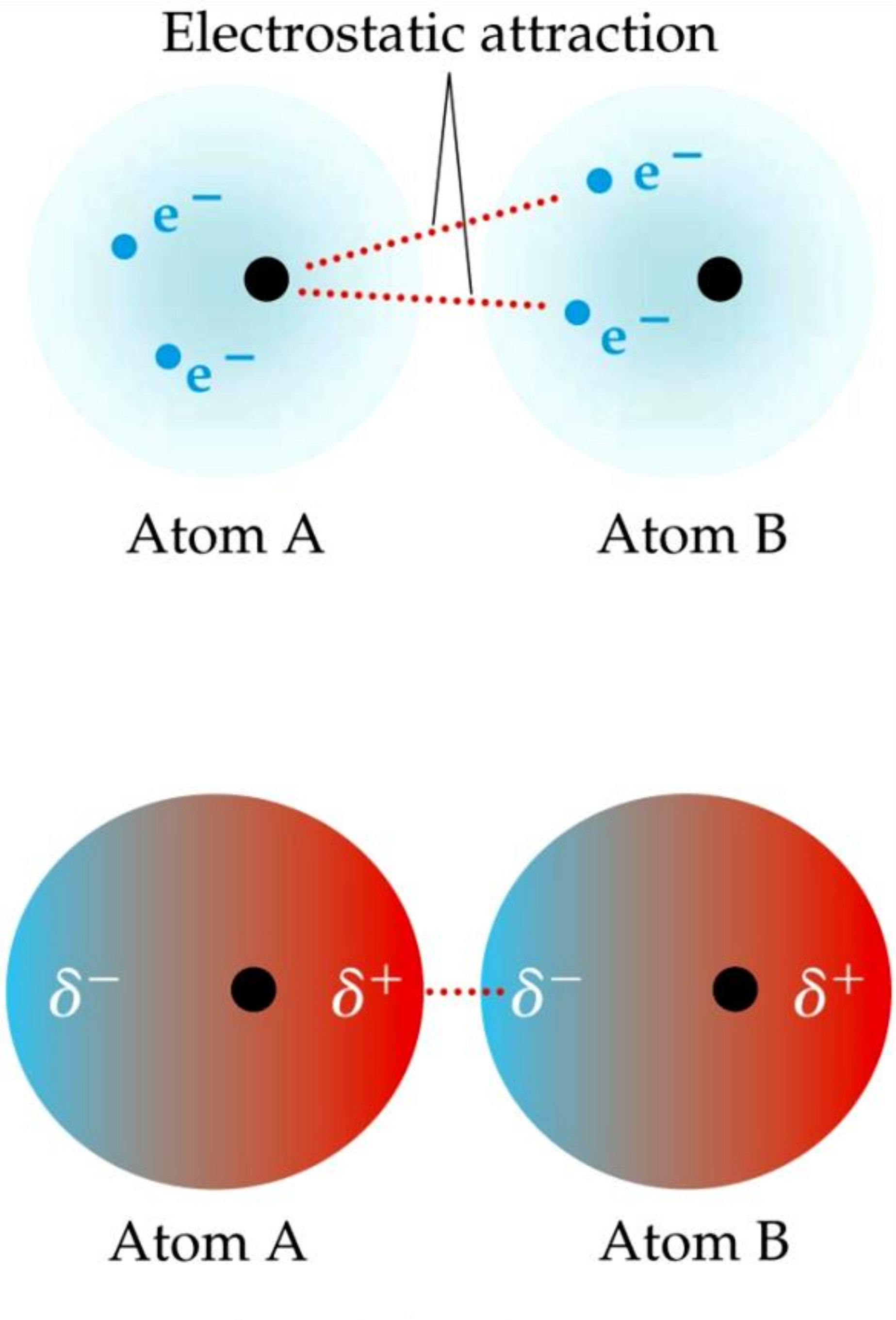
(a) Two helium atoms, no polarization



(b) Instantaneous dipole on atom B

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

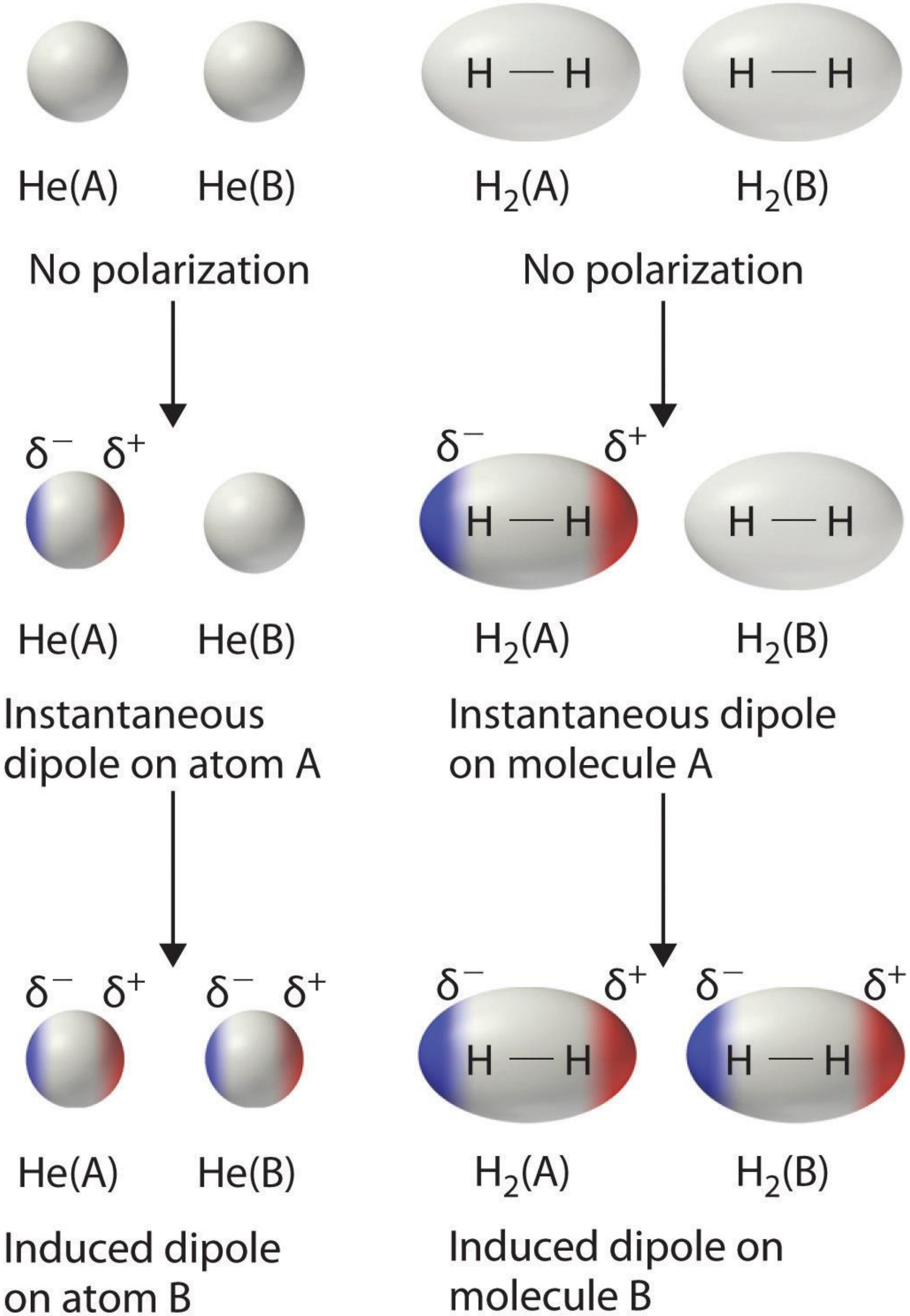
At **this instant**, then, the He atom B is **polar**.



(c) Induced dipole on atom A

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

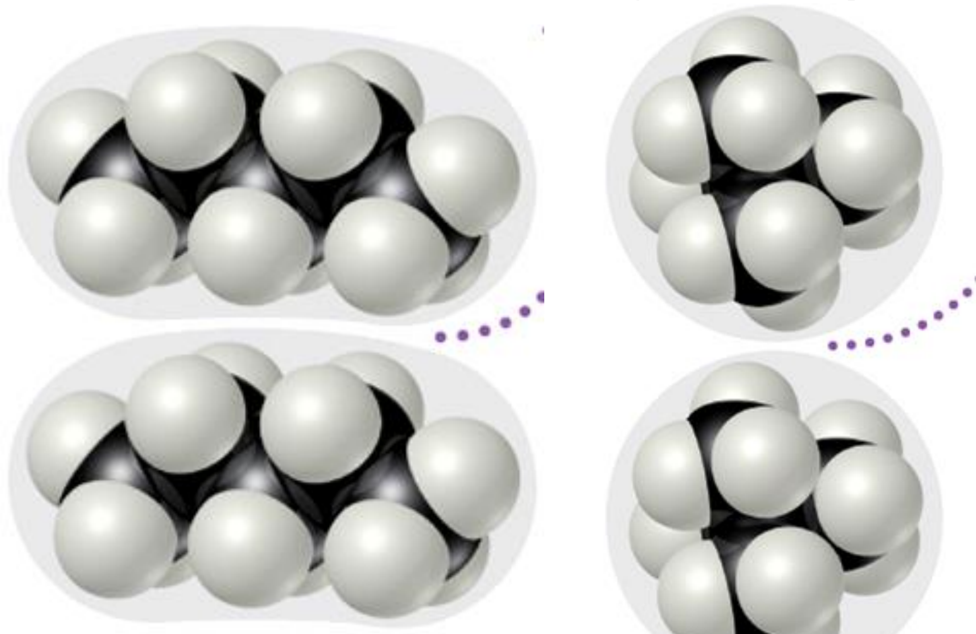
London dispersion forces (or dispersion forces) are **attractions between an instantaneous induced dipole & an induced dipole**.



London dispersion forces for He atoms (left) and H_2 molecules (right)

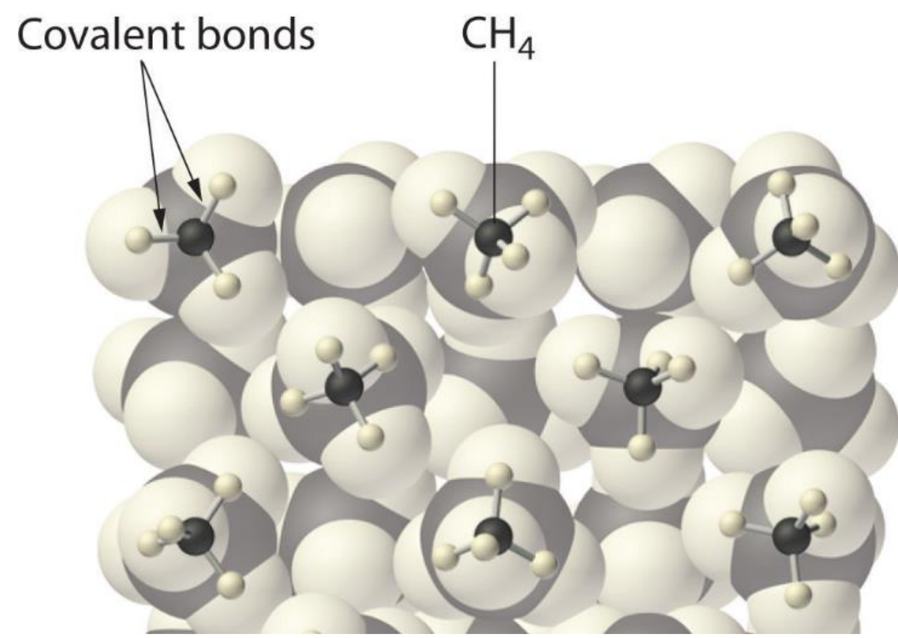
Factors Affecting Amount of Dispersion Force

- 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)).

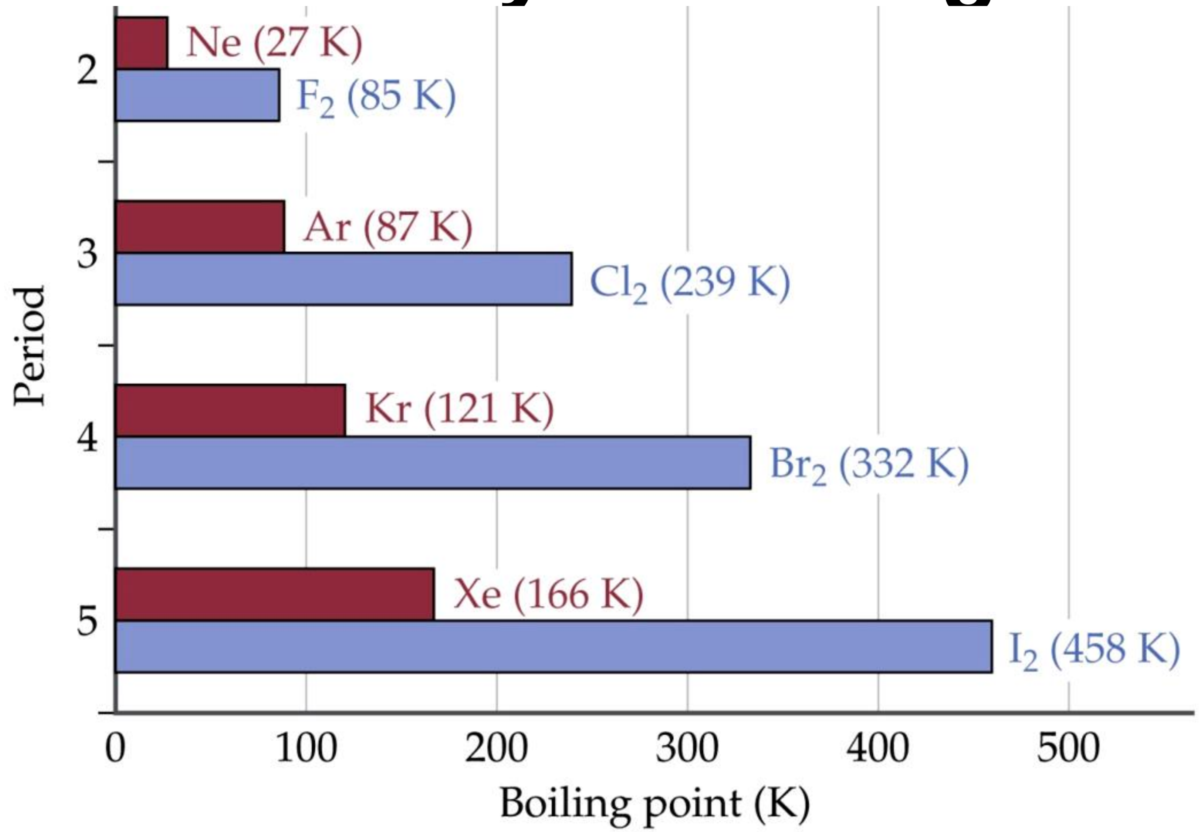


n-Pentane (C_5H_{12})
bp = 309.4 K

Neopentane (C_5H_{12})
bp = 282.7 K



Polarizability & Boiling Point

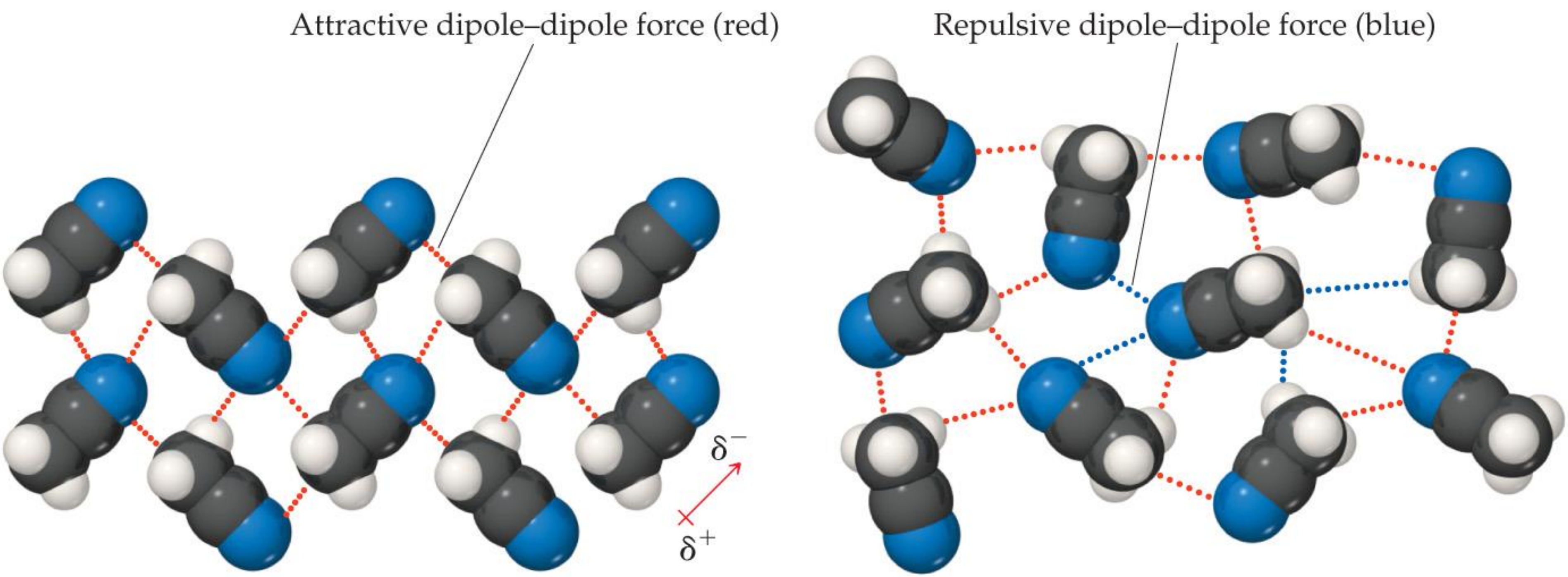


- **Larger atoms** have larger electron clouds that are easier to polarize (greater **polarizability**), due to **weaker attraction** between the valence electrons & nucleus.
- Thus, the strength of dispersion forces generally increase with **increased molecular weight** → **larger B.P.**

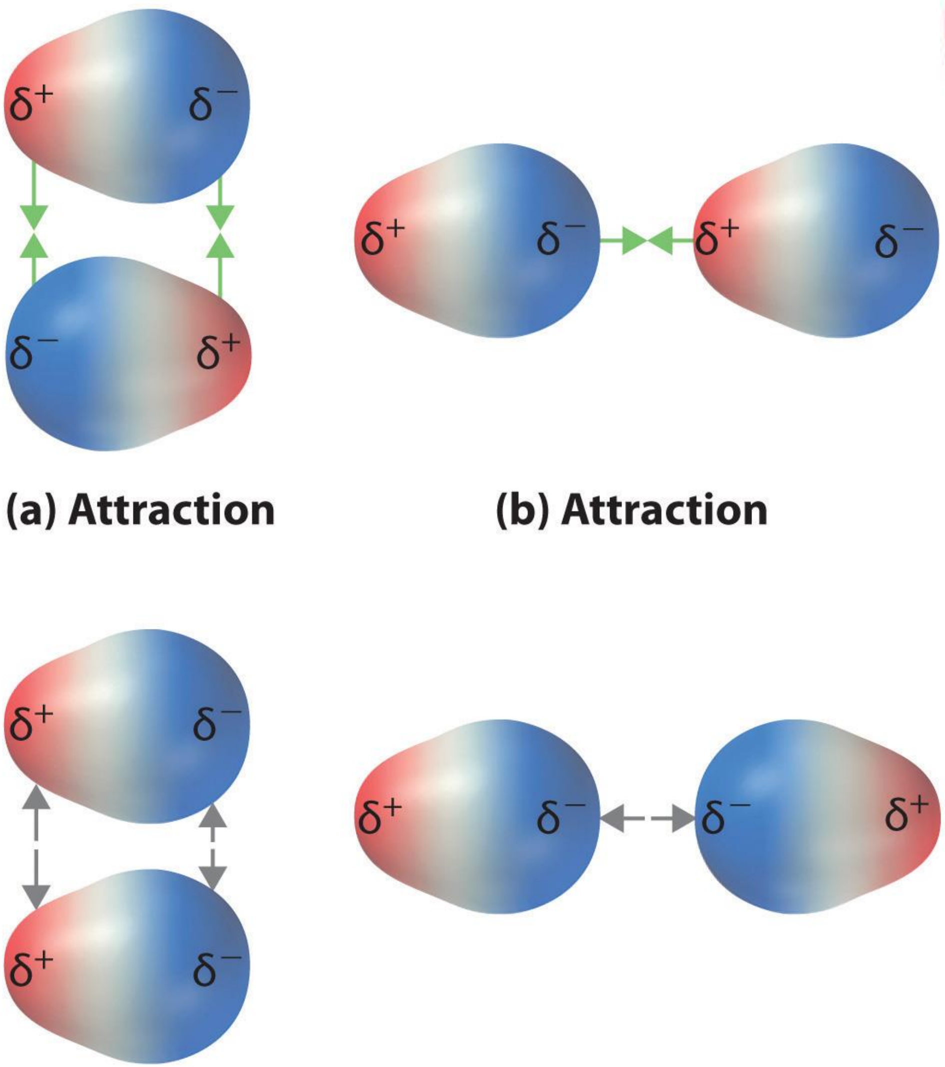
Dipole–Dipole Interactions

- **Polar molecules** have a **permanent dipole** (a more positive and a more negative end: two poles, δ^+ and δ^-) and are **attracted to each other**.

- The **oppositely charged ends attract** each other.



(a) Solid CH_3CN **(b)** Liquid CH_3CN

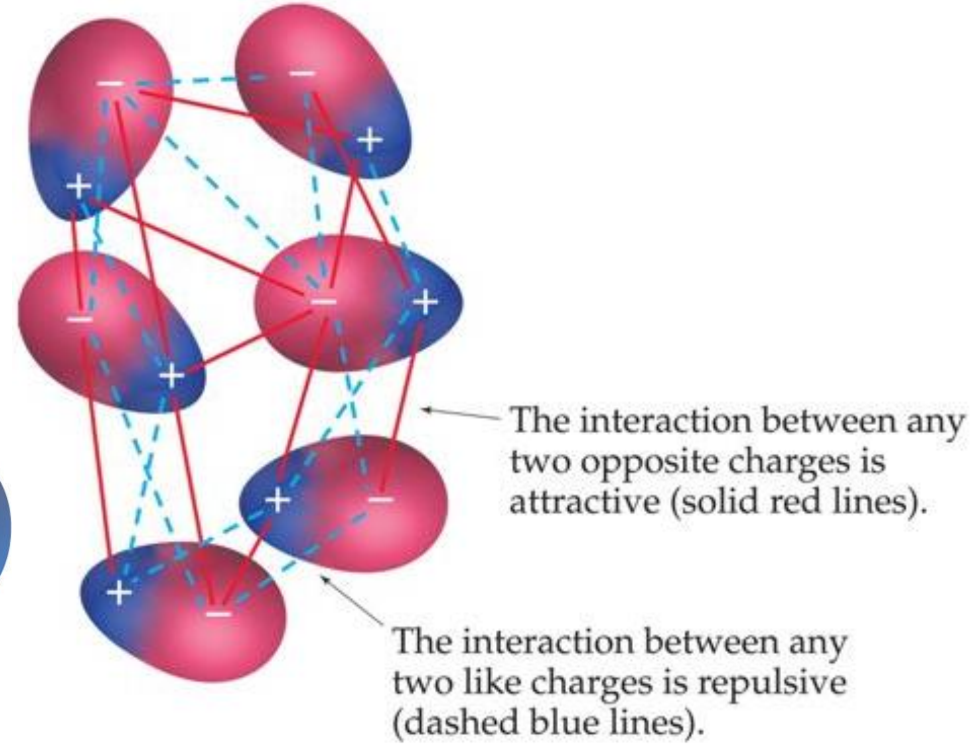


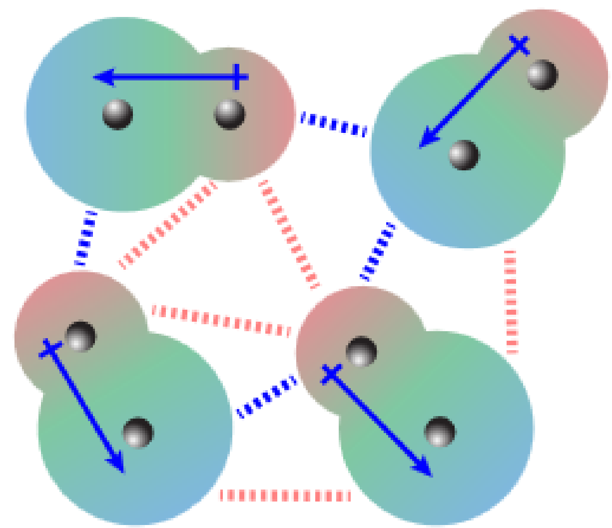
(a) Attraction

(b) Attraction

(c) Repulsion

(d) Repulsion





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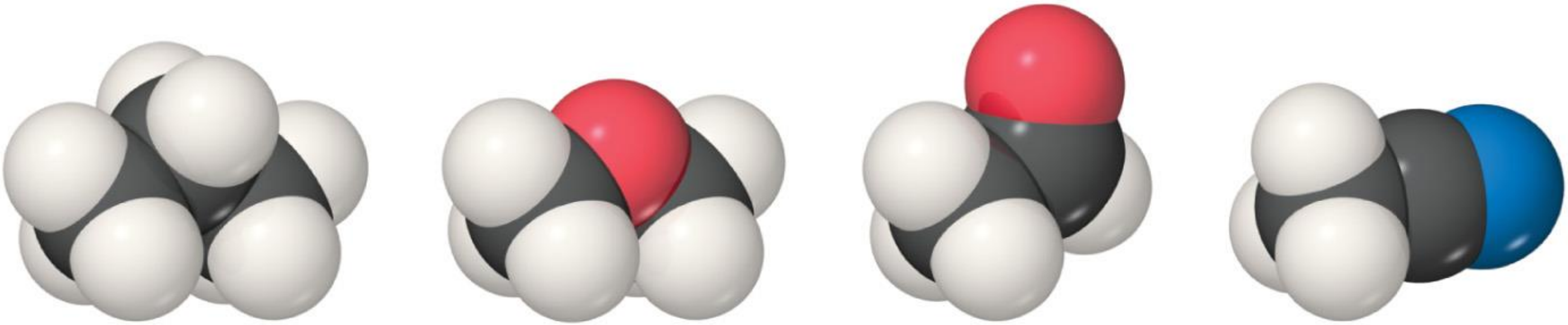


Propane	Dimethyl ether	Acetaldehyde	Acetonitrile
$CH_3CH_2CH_3$	CH_3OCH_3	CH_3CHO	CH_3CN
MW = 44 amu	MW = 46 amu	MW = 44 amu	MW = 41 amu
μ = 0.1 D	μ = 1.3 D	μ = 2.7 D	μ = 3.9 D
bp = 231 K	bp = 248 K	bp = 294 K	bp = 355 K

Increasing polarity
Increasing strength of dipole–dipole forces

For molecules of **approximately equal mass & size**,

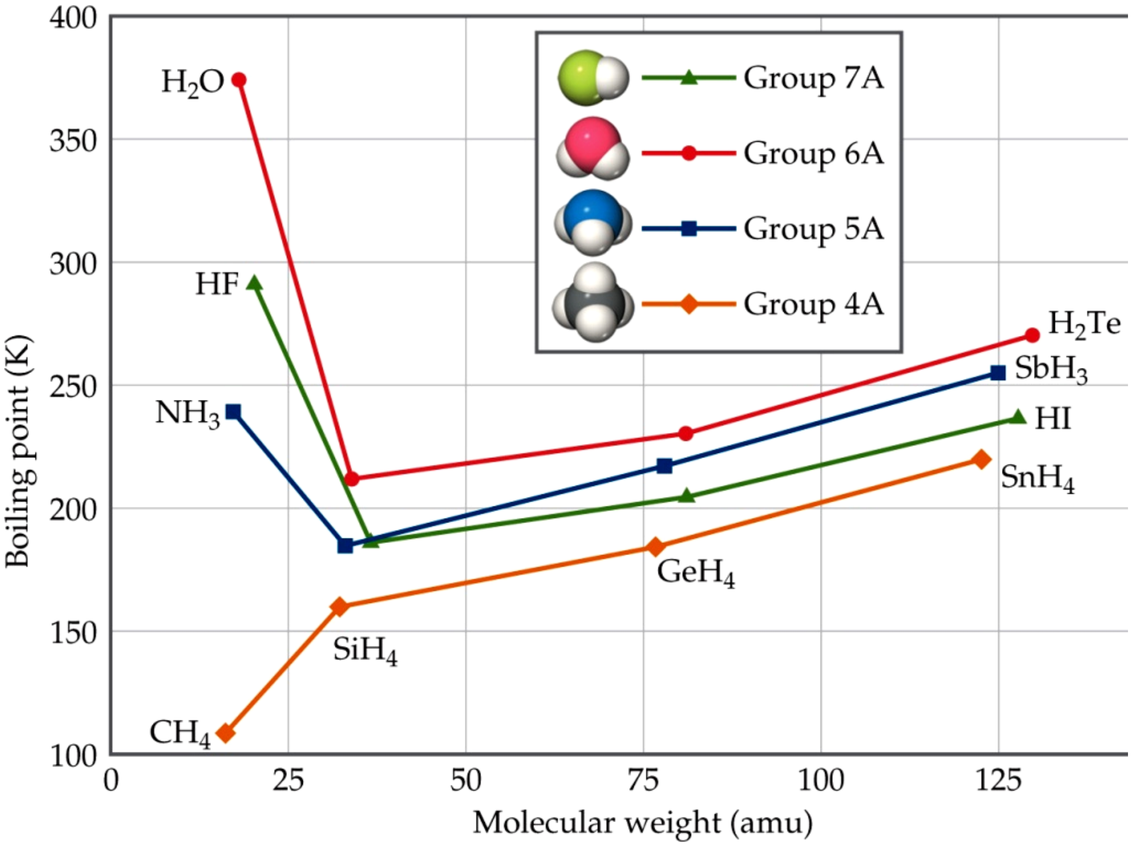
1. the strength of intermolecular **attraction increases** with **increasing polarity**.
2. the **more polar** the molecule, the **higher its boiling point**.

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.

How Do We Explain This?



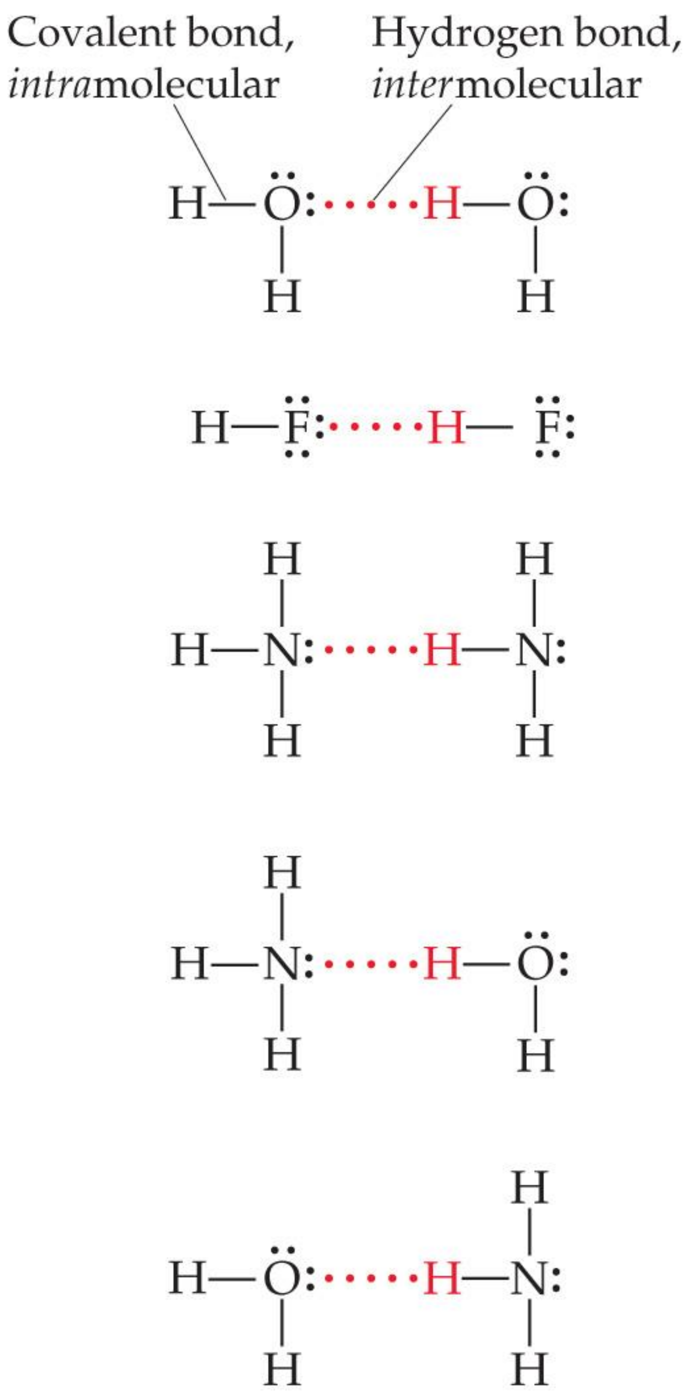
- The **nonpolar series** follow the expected **trend**: **higher B.P.** as the group member gets **larg**er.
- The **polar series follow the trend except** for the **smallest** molecules in each group.

H_2O: a high melting point, specific heat & heat of vaporization. → Intermolecular forces between H_2O are very strong. **(Hydrogen bonding)**

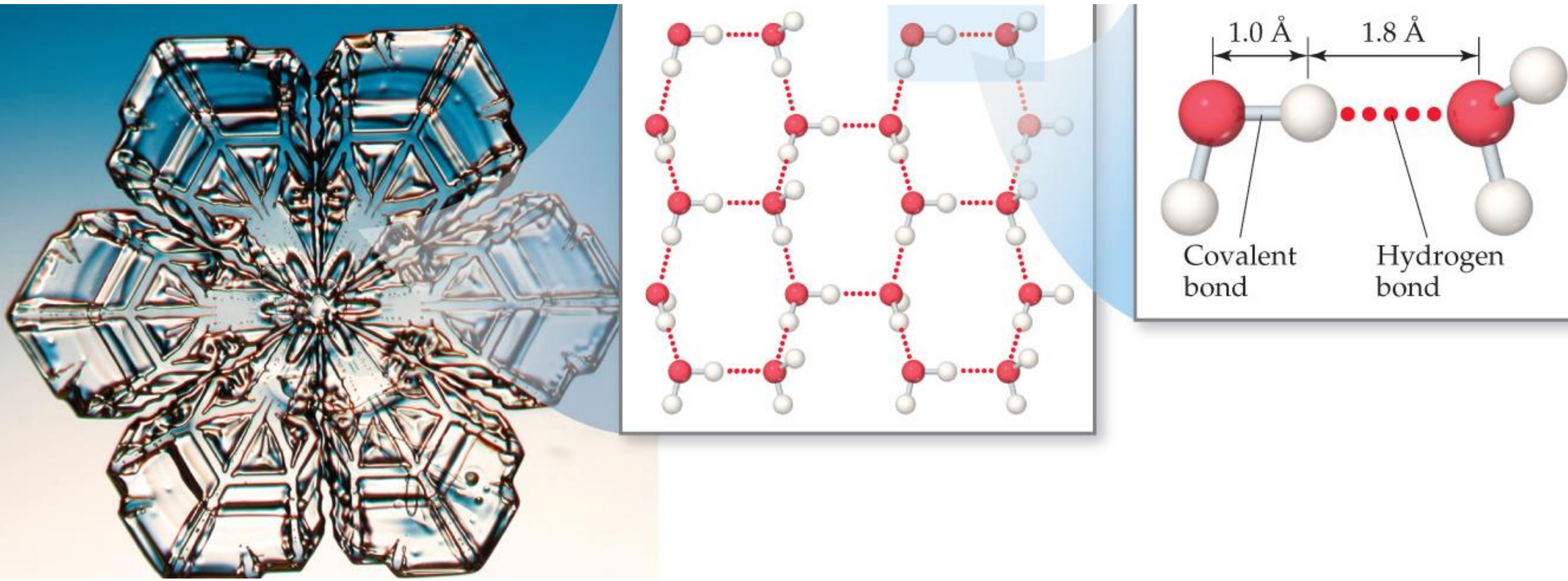
Hydrogen Bonding

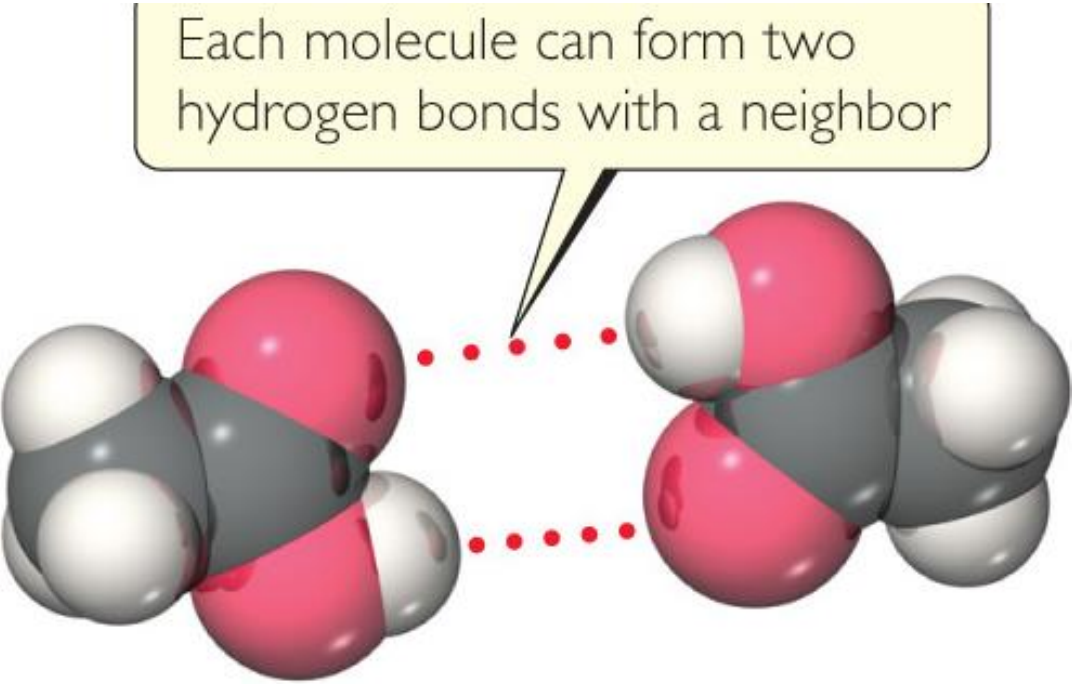
• The **dipole–dipole interactions** experienced are unusually strong, when H is bonded to **N, O, or F**.

• 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**

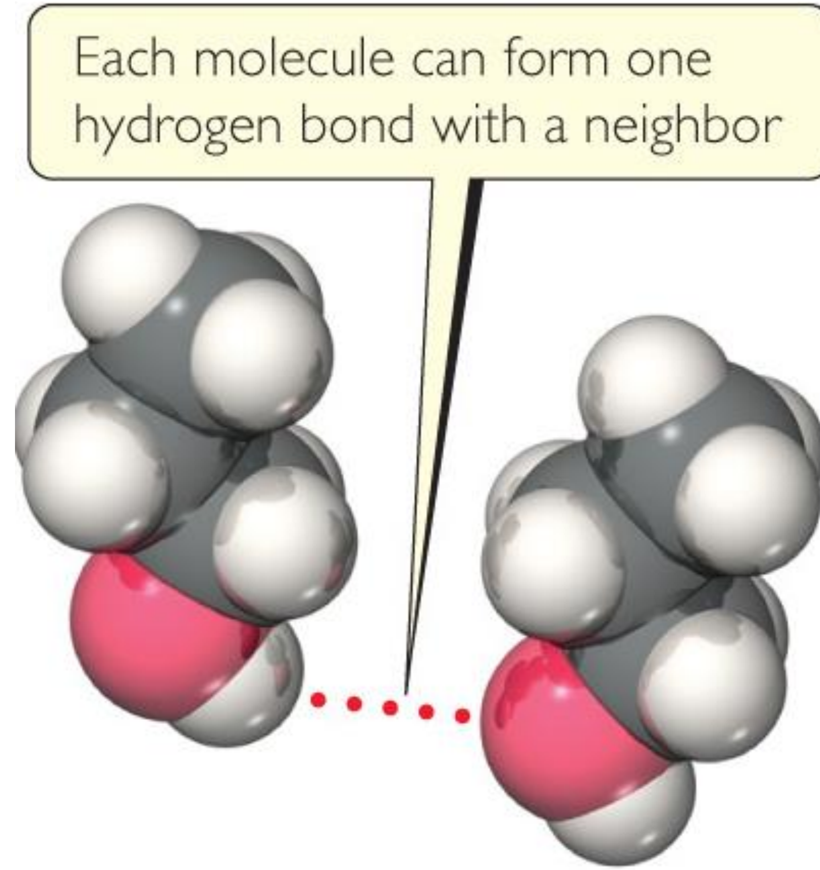


• The high electronegativity of N, O, and F interact with a nearly bare nucleus (H, which contains one proton).

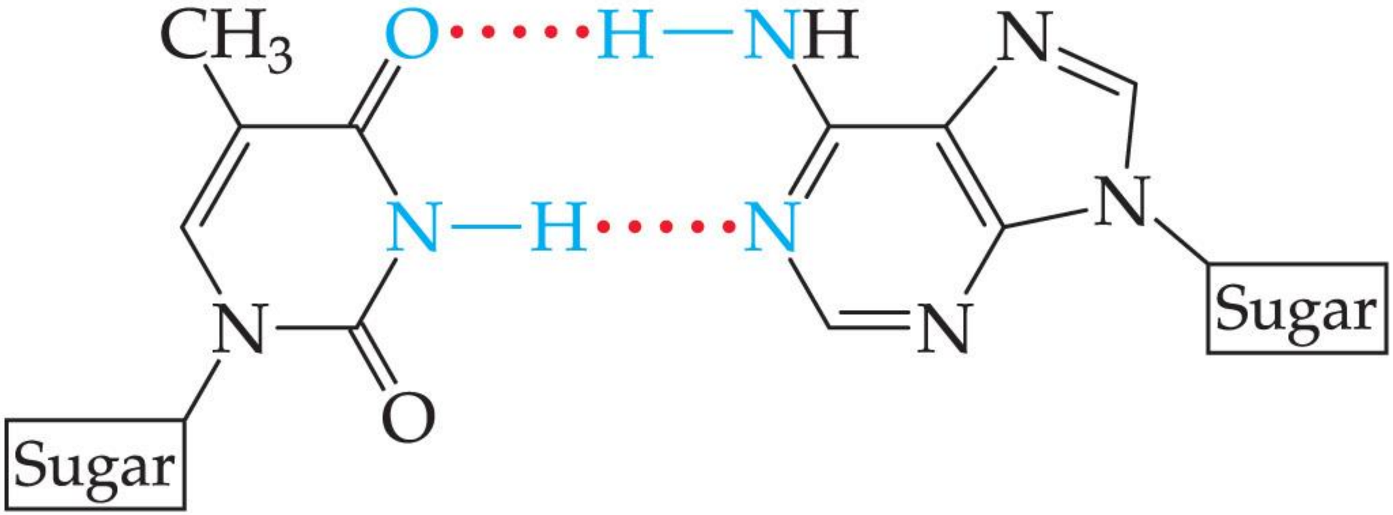




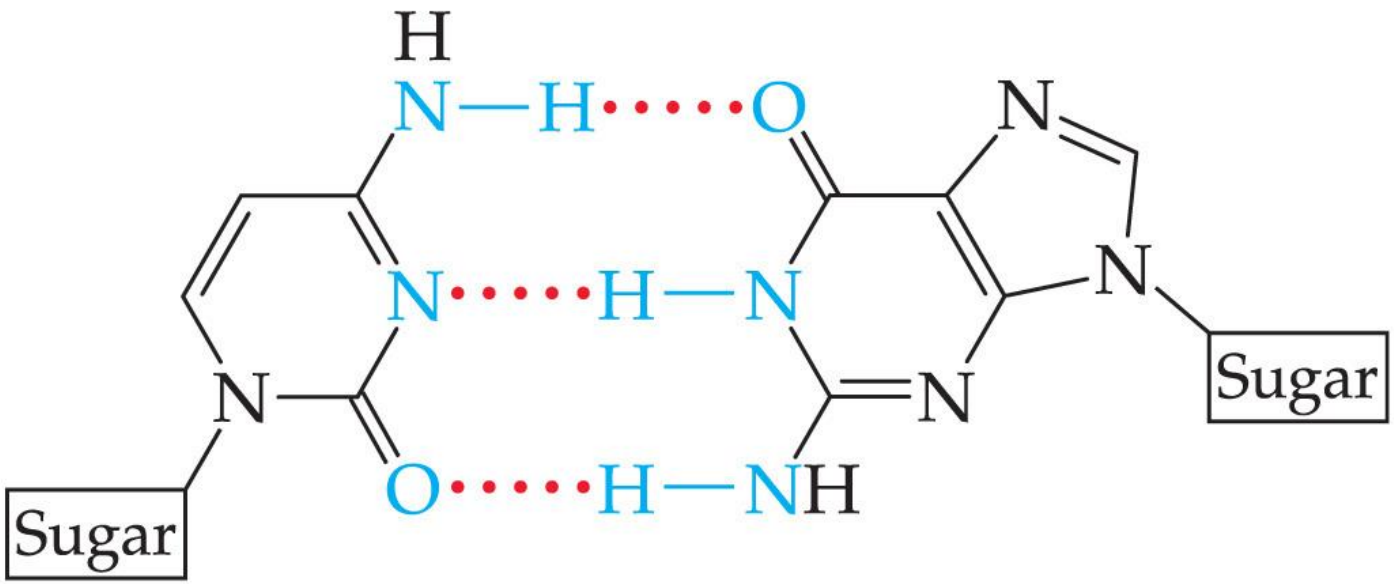
Acetic acid, CH_3COOH
MW = 60 amu
bp = 391 K



1-Propanol, $CH_3CH_2CH_2OH$
MW = 60 amu
bp = 370 K



Thymine Adenine



Cytosine Guanine

(Extra Info.)

Table 2. Strong, moderate, and weak hydrogen bonds following the classification of Jeffrey.[6] 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 [$kcal\,mol^{-1}$]	15–40	4–15	< 4
relat. IR shift $\Delta\tilde{\nu}_{XH}$ [cm^{-1}]	25 %	10–25 %	< 10 %
^{1}H downfield shift	14–22	< 14	

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

Dimer	Energy
$[F{-}H{-}F]^-$	39
$[H_2O{-}H{-}OH_2]^+$	33
$[H_3N{-}H{-}NH_3]^+$	24
$[HO{-}H{-}OH]^-$	23
$NH_4^+ \cdots OH_2$	19
$NH_4^+ \cdots Bz$	17
$HOH \cdots Cl^-$	13.5
$O{=}C{-}OH \cdots O{=}C{-}OH$	7.4
$HOH \cdots OH_2$	4.7; 5.0
$N{\equiv}C{-}H \cdots OH_2$	3.8
$HOH \cdots Bz$	3.2
$F_3C{-}H \cdots OH_2$	3.1
$Me{-}OH \cdots Bz$	2.8
$F_2HC{-}H \cdots OH_2$	2.1; 2.5
$NH_3 \cdots Bz$	2.2
$HC{\equiv}CH \cdots OH_2$	2.2
$CH_4 \cdots Bz$	1.4
$FH_2C{-}H \cdots OH_2$	1.3
$HC{\equiv}CH \cdots C{\equiv}CH^-$	1.2
$HSH \cdots SH_2$	1.1
$H_2C{=}CH_2 \cdots OH_2$	1.0
$CH_4 \cdots OH_2$	0.3; 0.5; 0.6; 0.8
$C{=}CH_2 \cdots C{=}C$	0.5
$CH_4 \cdots F{-}CH_3$	0.2

(Extra Info.)

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

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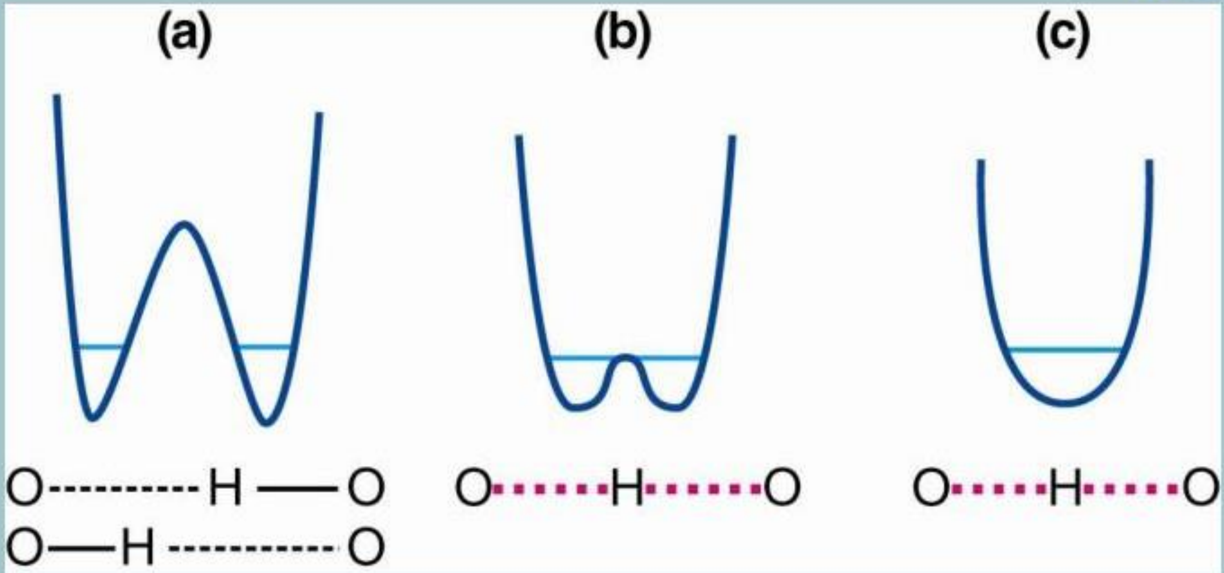
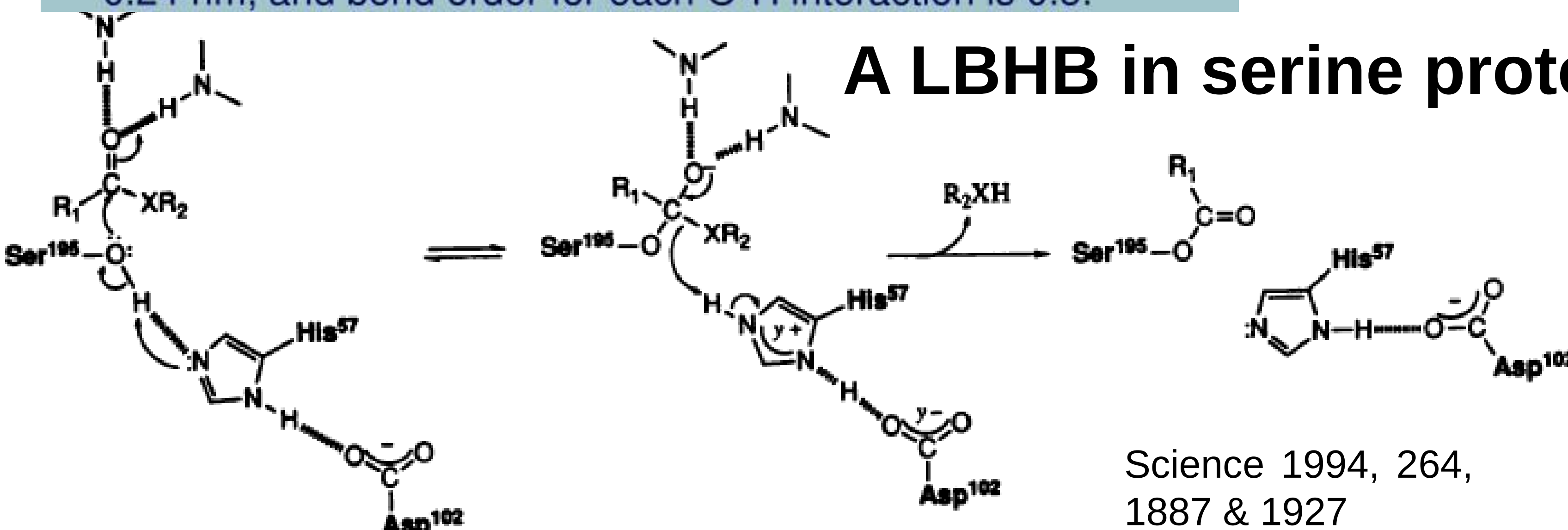
Low-Barrier Hydrogen Bonds (LBHBs)

(Extra Info.)

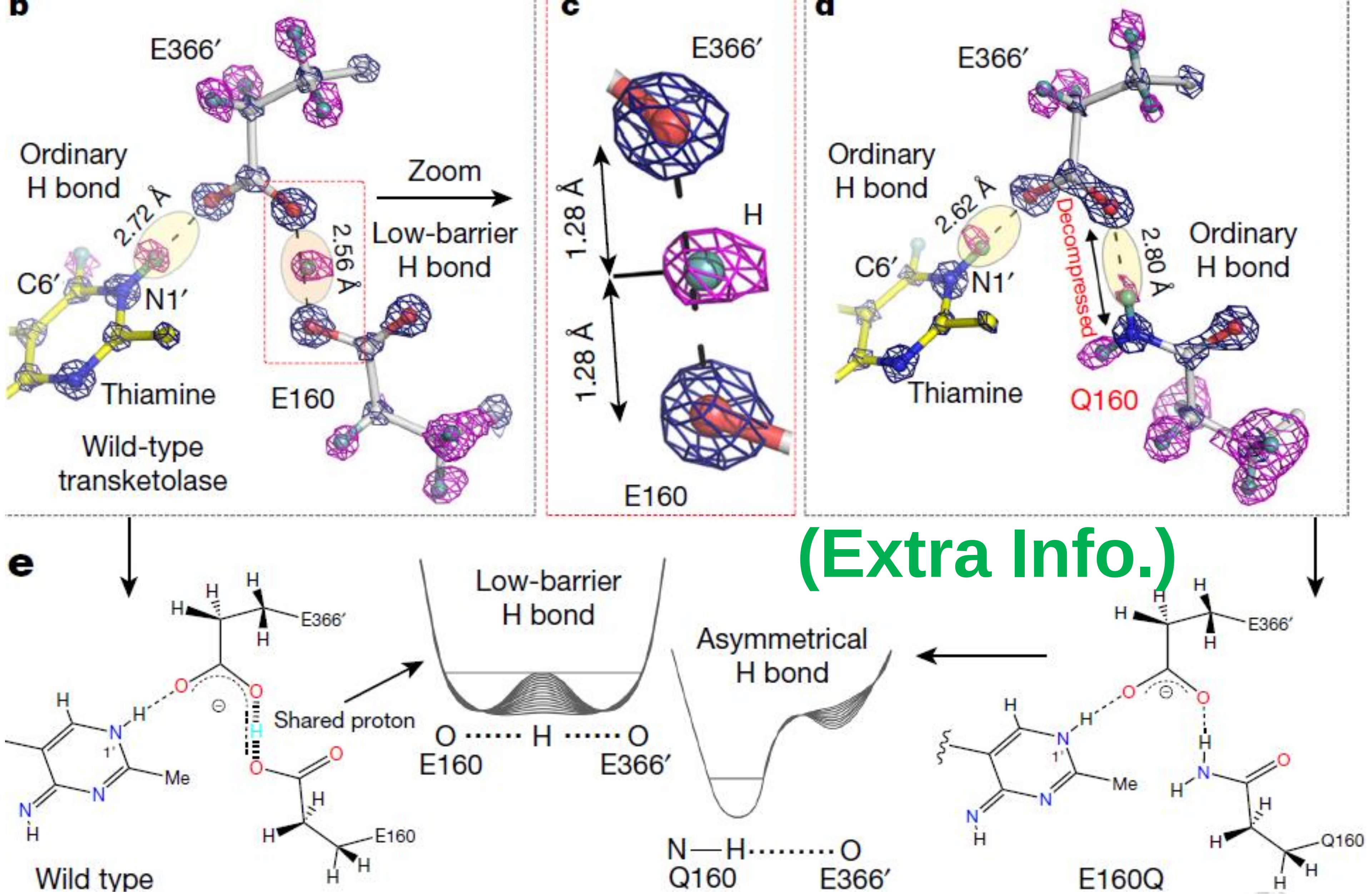


Energy diagrams for conventional H bonds (a), and low-barrier hydrogen bonds (b and c). In (c), the O-O distance is 0.23 to 0.24 nm, and bond order for each O-H interaction is 0.5.

A LBHB in serine proteases



Science 1994, 264, 1887 & 1927



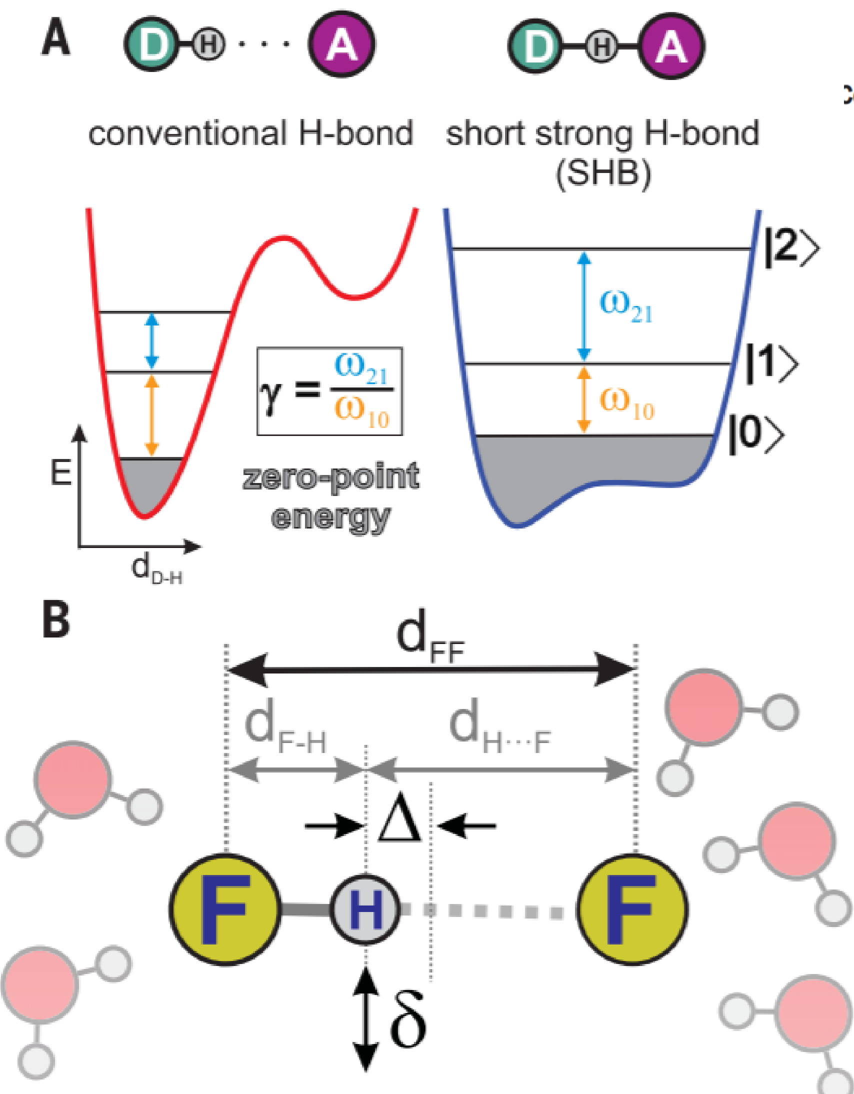
(Extra Info.)

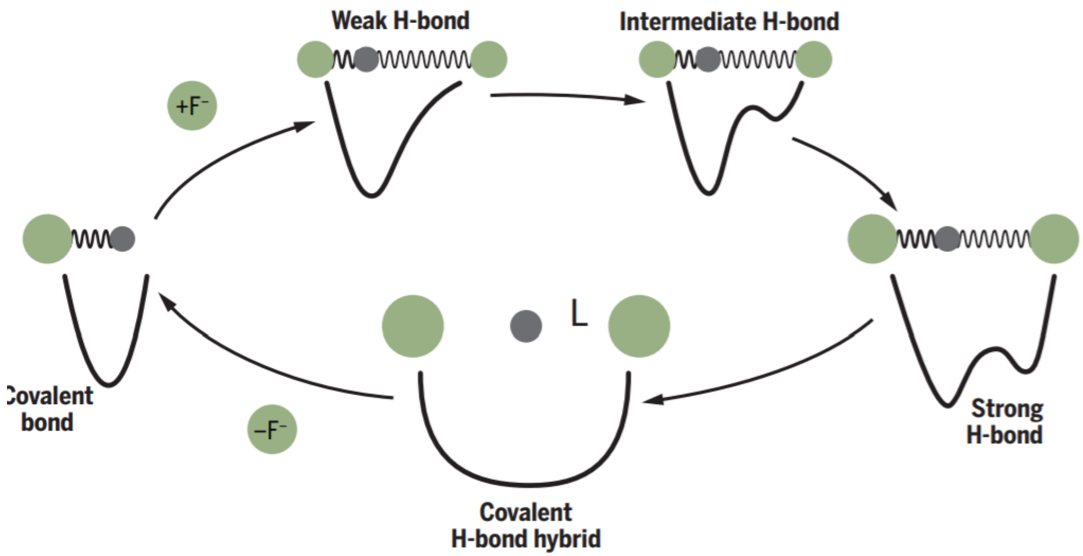
LBHB in human transketolase

Nature 2019, 573, 609

Intermolecular Forces

(Extra Info.)



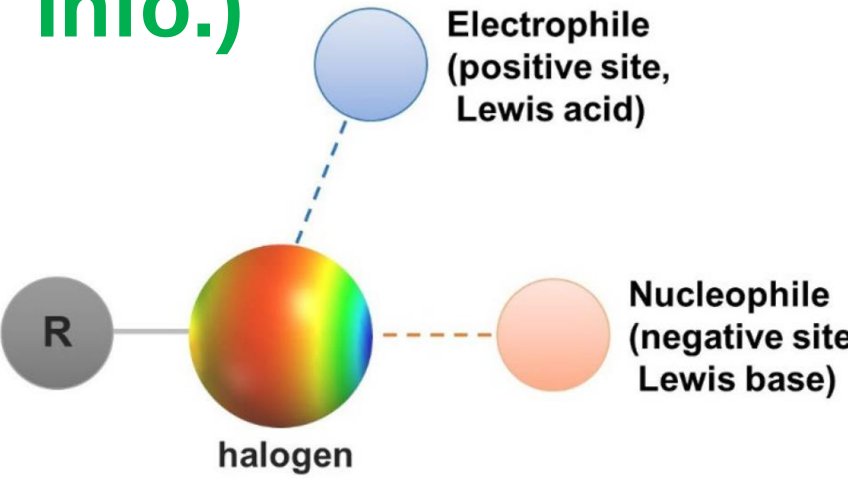


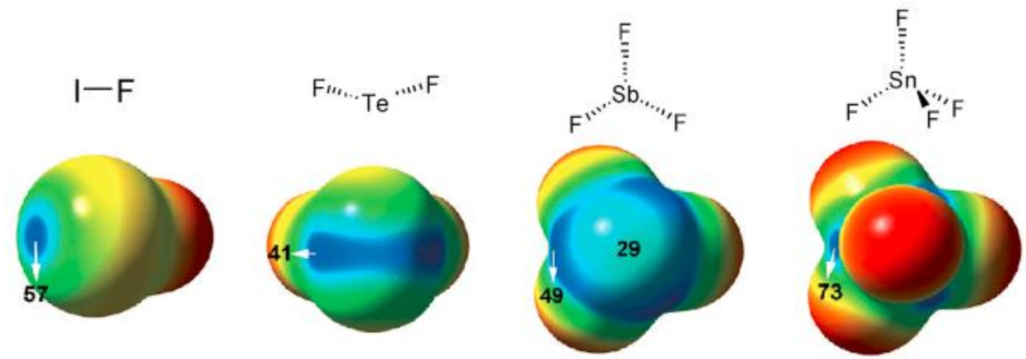
Strong H-bond for $F\text{-}H\text{-}F^-$

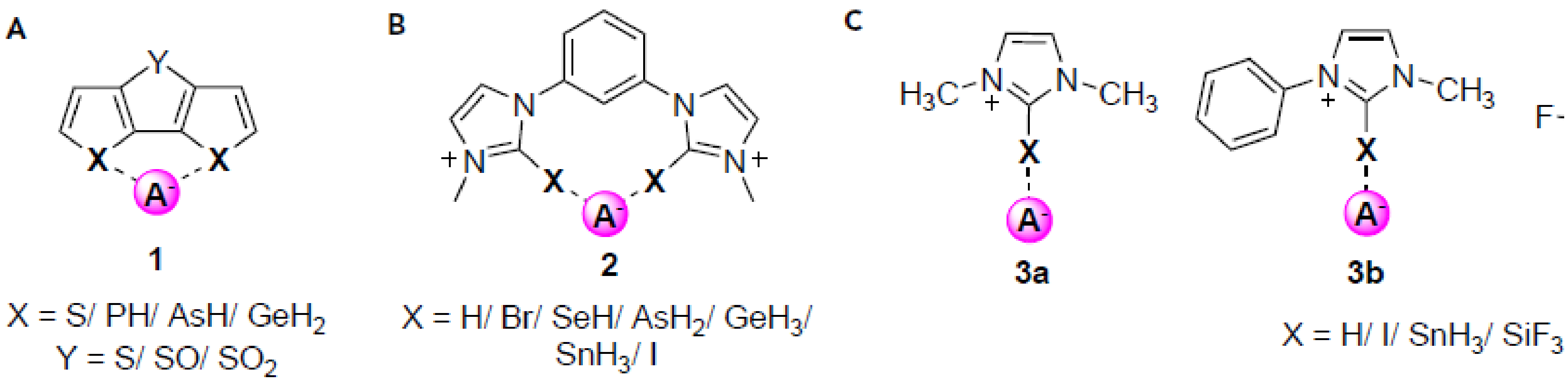
Science **2011**, 371, 123 & 160

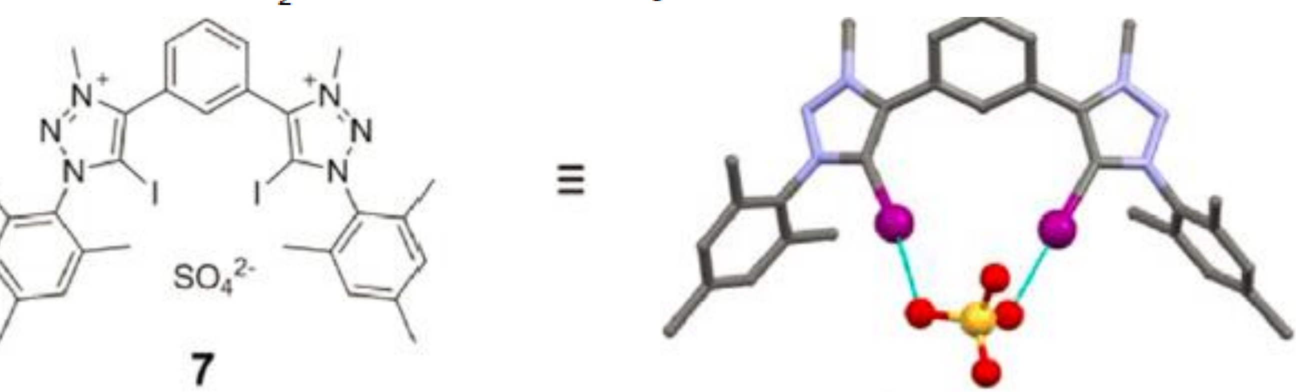
Intermolecular Forces

σ-Hole Interactions, Halogen Bond (Extra Info.)









A^- = halide ion

Intermolecular Forces

Chem 2018, 4, 733

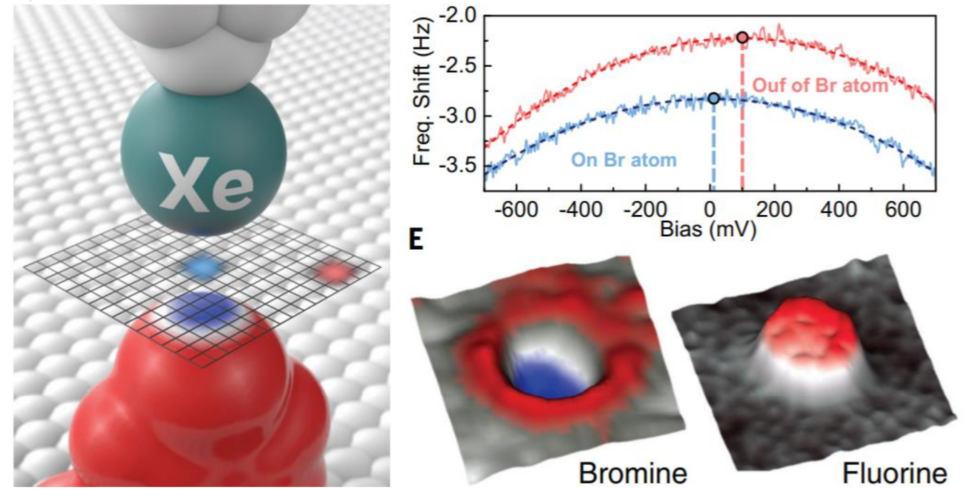
SPECTROSCOPY

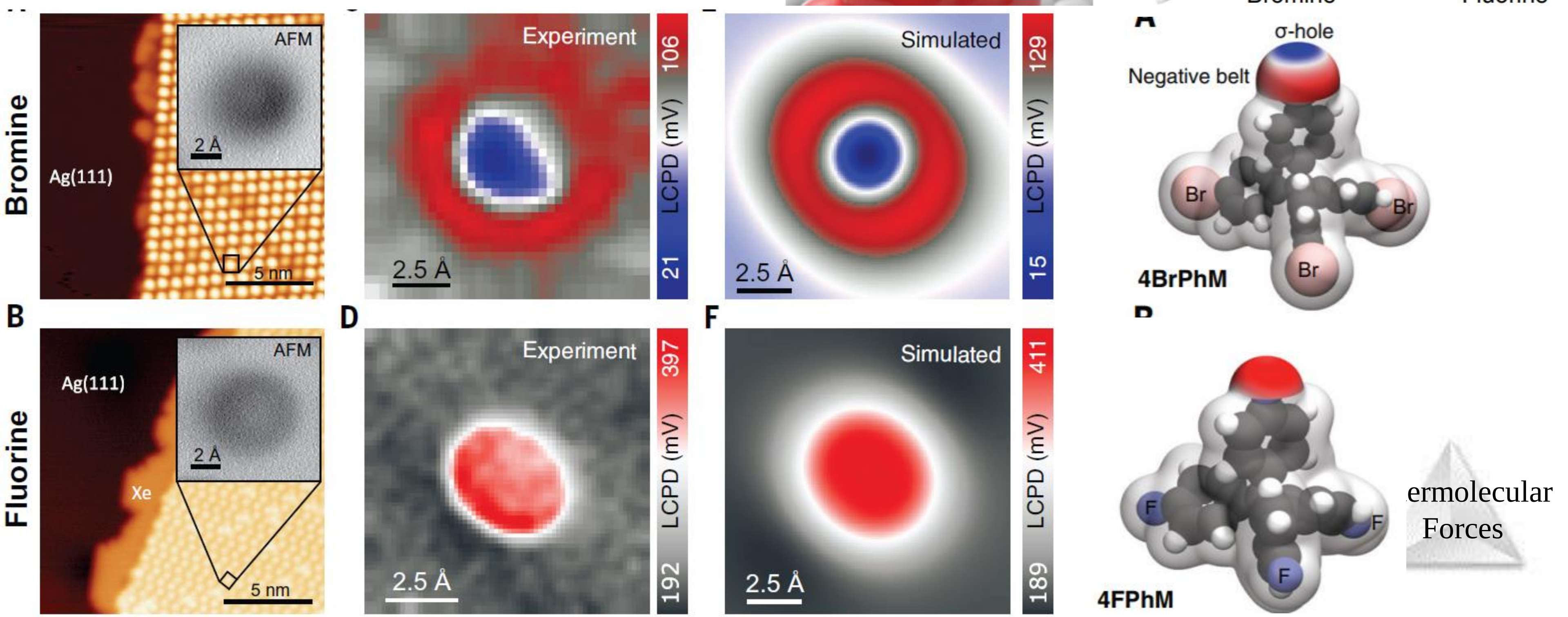
(Extra Info.)

Real-space imaging of anisotropic charge of σ-hole by means of Kelvin probe force microscopy

B. Mallada[1,2,3]†, A. Gallardo[2,4]†, M. Lamanec[3,5]†, B. de la Torre[1,2], V. Špirko[5,6], P. Hobza[5,7]*, P. Jelinek[1,2]*

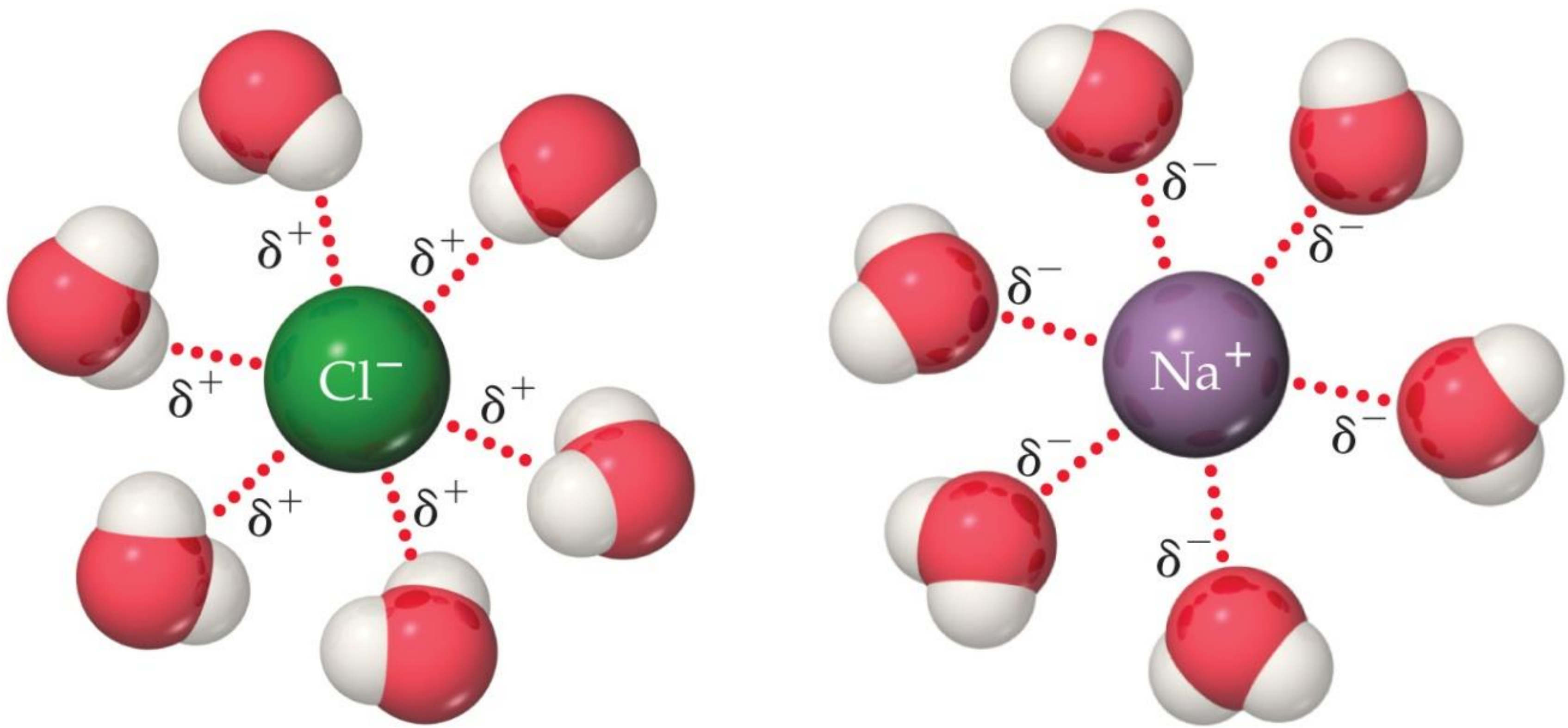
Science 2021, 374, 863





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 π-systems

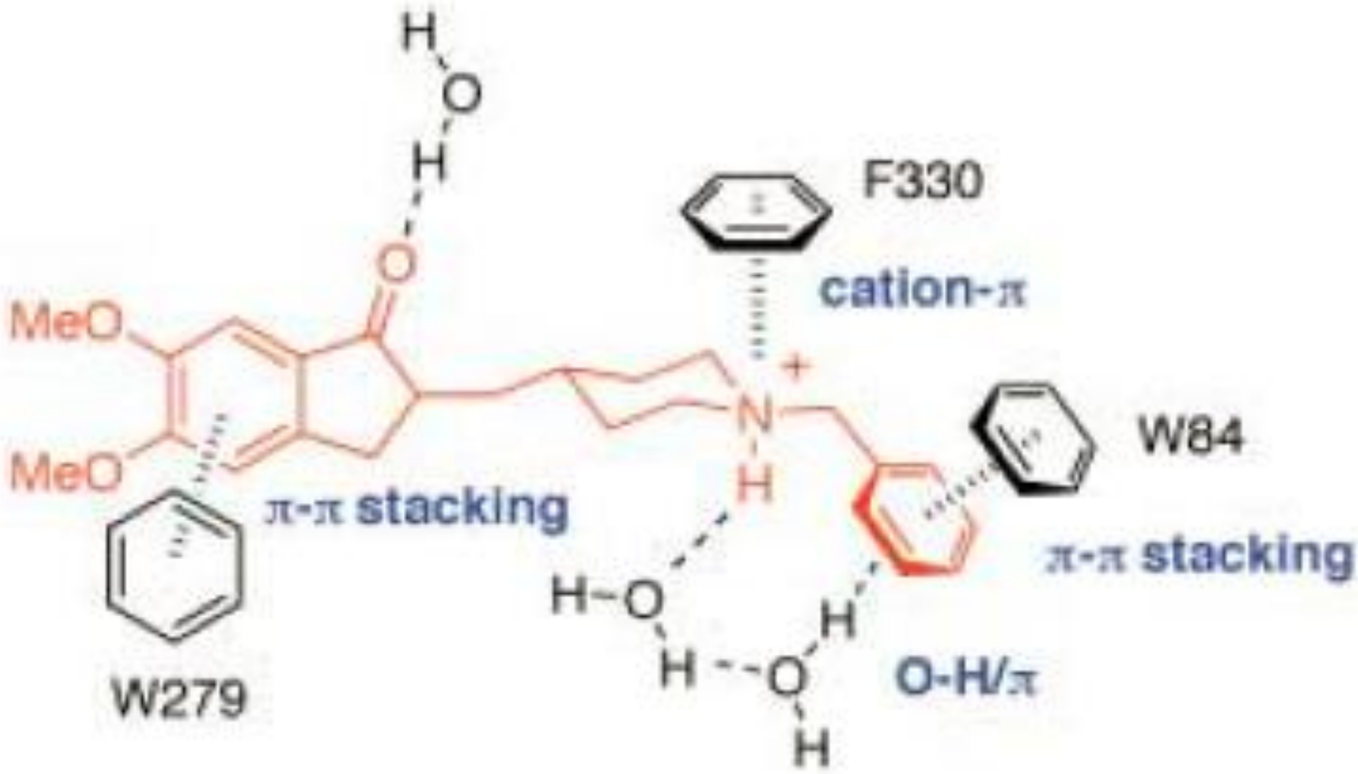


Figure 1. Binding mode of the anti-Alzheimer drug E2020 within the active site of acetylcholinesterase from *Torpedo californica* (PDB code: 1EVE).[1]

Angew. Chem. Int. Ed. 2003, 42, 1210

(extra info.) Interactions with π-systems

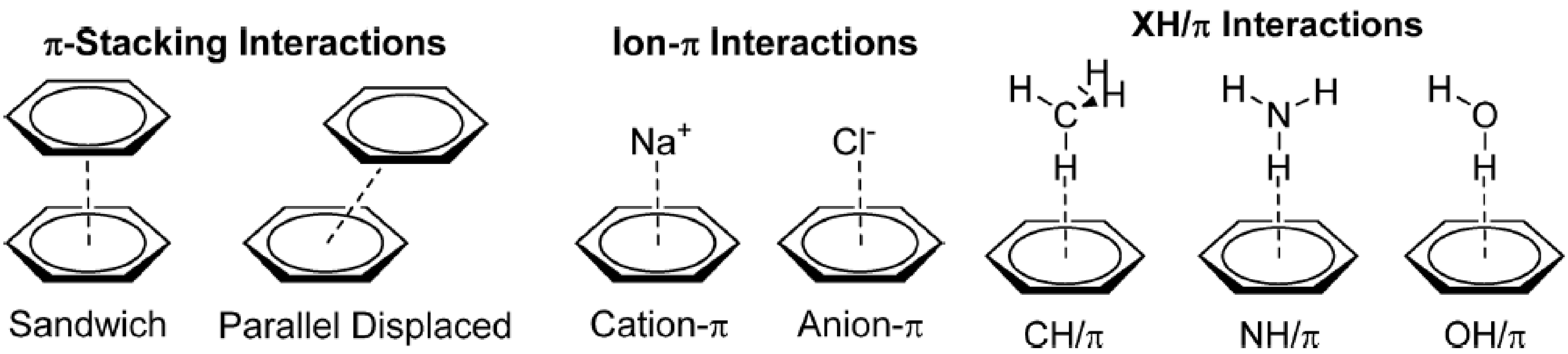


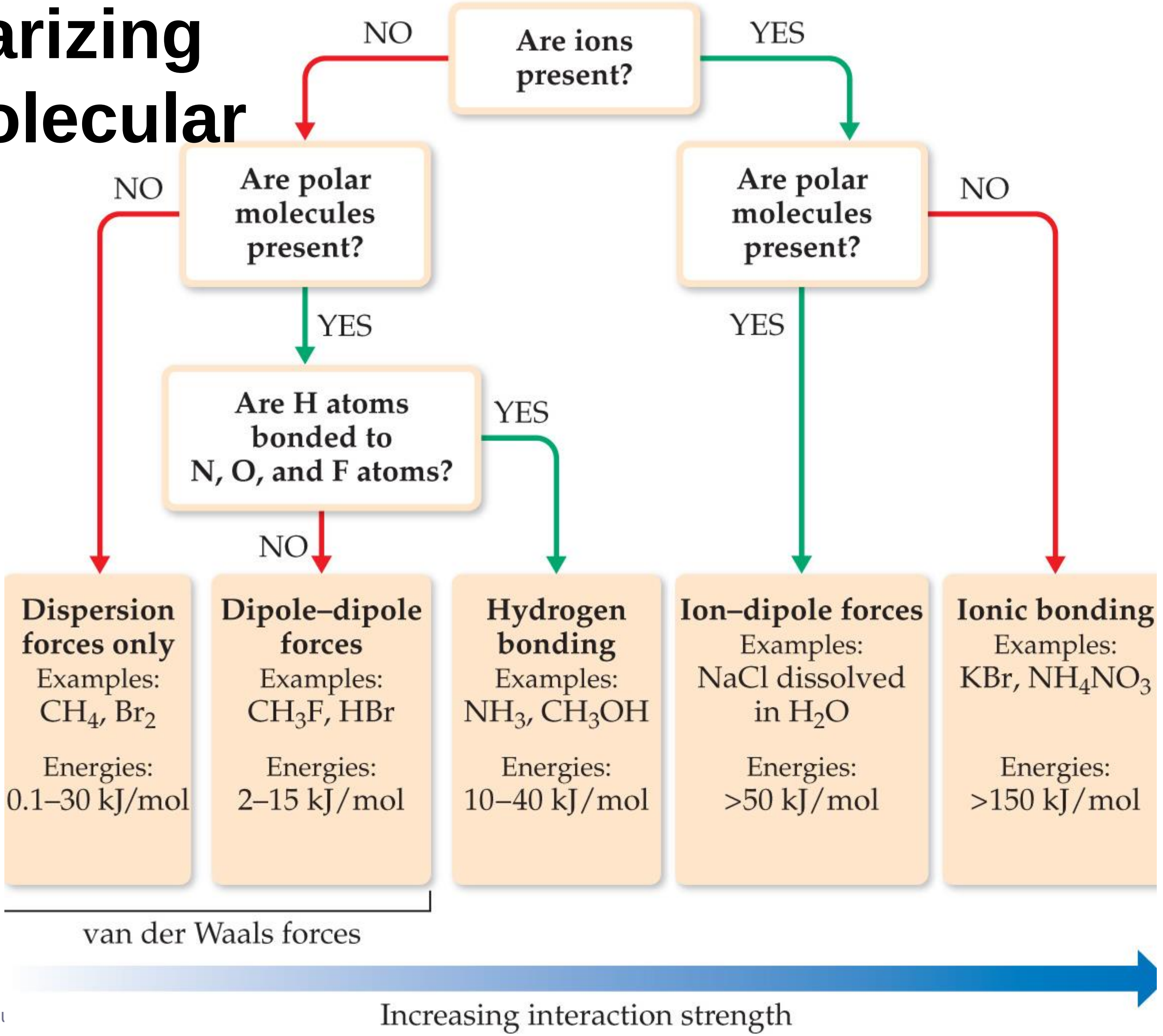
Table 1. Gas-Phase Ion Molecule Binding Energies[a] (kcal/mol)

A. Experimental Measurements

ion	molecule	binding energy[b]	ref	ion	molecule	binding energy[b]
Li^+	C_6H_6	38.3[c]	11	NH_4^+	C_6H_5F	(14.4)[l]
Na^+	C_6H_6	28.0	8	NH_4^+	1,4-$C_6H_4F_2$	(13.0)[l]
K^+	C_6H_6	19.2	2	NH_4^+	C_2H_4	10.0
$K^+\cdot C_6H_6$	C_6H_6	18.8	2	$CH_3NH_3^+$	C_6H_6	18.8
$K^+\cdot(C_6H_6)_2$	C_6H_6	14.5	2	$CH_3NH_3^+$	cyclohexene	11.6
$K^+\cdot(C_6H_6)_3$	C_6H_6	12.6	2	$CH_3NH_3^+$	pyrrole	(18.6)[l]
K^+	H_2O	17.9	2	$(CH_3)_3NH^+$	C_6H_6	15.9
Al^+	C_6H_6	35.2	26	NMe_4^+	C_6H_6	9.4
NH_4^+	C_6H_6	19.3	13	NMe_4^+	$C_6H_5CH_3$	9.5
NH_4^+	1,3,5-$C_6H_3(CH_3)_3$	21.8	13	$C_2H_5OH_2^+$	C_6H_6	21.0

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

Summarizing Intermolecular Forces

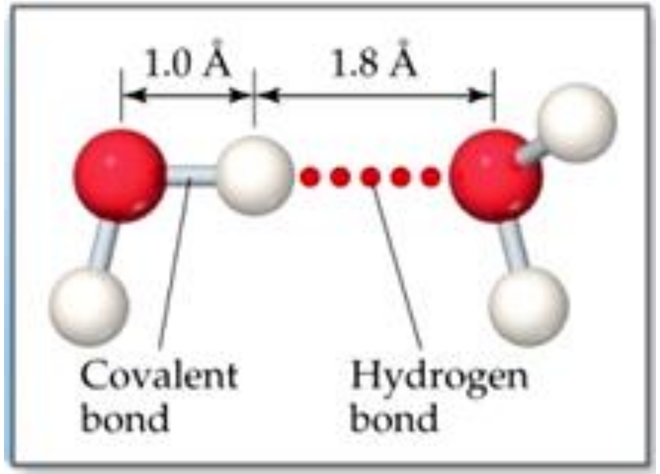


List the substances CCl_4, CBr_4, and CH_4 in order of increasing boiling point.

A. $CH_4 < CBr_4 < CCl_4$
B. $CCl_4 < CH_4 < CBr_4$
C. $CH_4 < CCl_4 < CBr_4$
D. $CBr_4 < CCl_4 < CH_4$

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

A. Approximately 90°
B. Approximately 109°
C. Approximately 120°
D. Approximately 180°



Intermolecular Forces

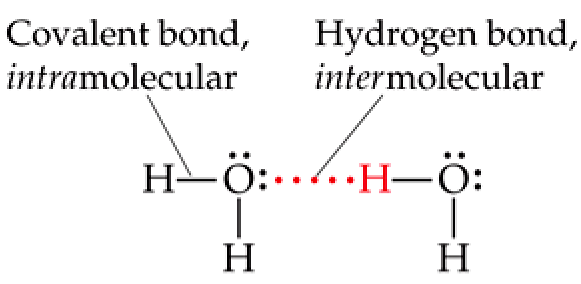
To form a hydrogen bond what must the non-hydrogen atom (N, O, or F) involved in the bond possess?

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.



Lone pair

In which mixture do you expect to find ion–dipole forces: CH_3OH in water or $Ca(NO_3)_2$ in water?

A. CH_3OH in water, because CH_3OH is a strong electrolyte and forms ions.

B. $Ca(NO_3)_2$ in water, because $Ca(NO_3)_2$ is a strong electrolyte and forms ions.

C. CH_3OH in water, because CH_3OH is a weak electrolyte and forms ions.

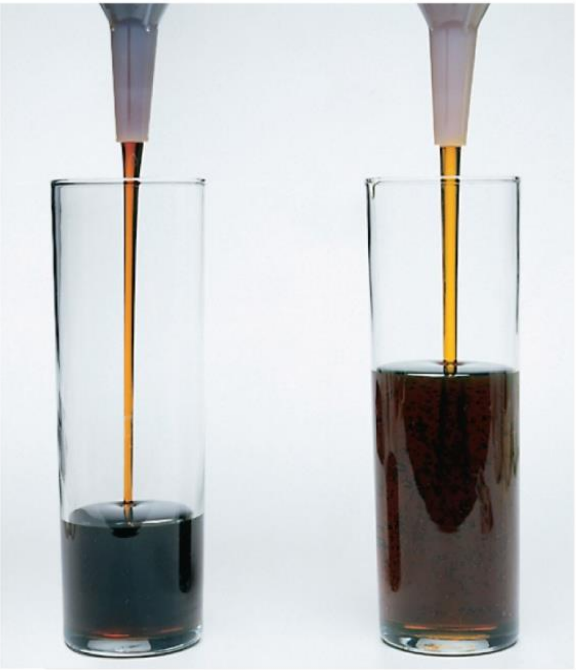
D. $Ca(NO_3)_2$ in water, because $Ca(NO_3)_2$ is a weak electrolyte and forms ions.

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**.



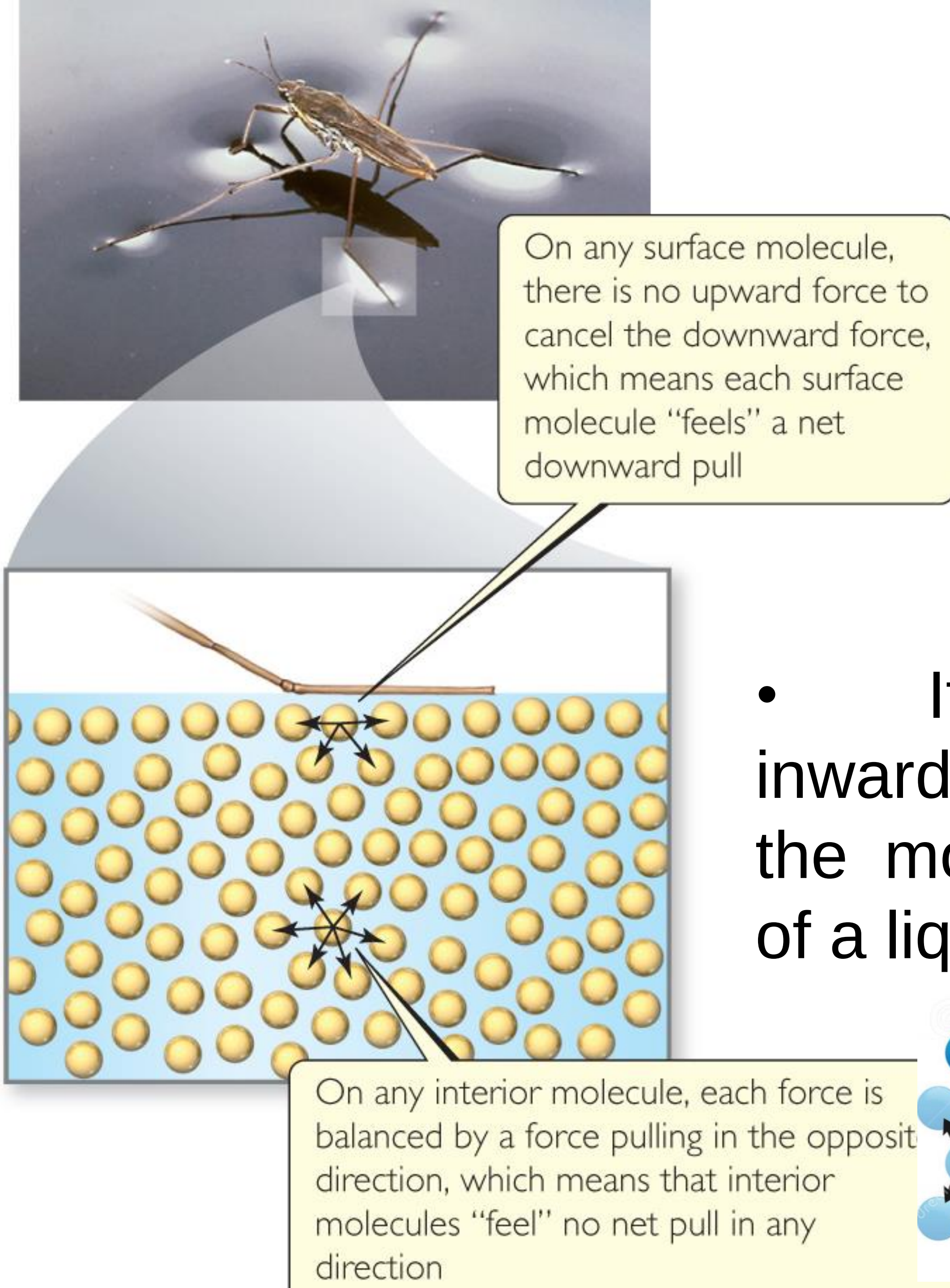
SAE 40
higher number
higher viscosity
slower pouring

SAE 10
lower number
lower viscosity
faster pouring

Substance	Formula	Viscosity (kg/m-s)
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	3.26×10^{-4}
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	4.09×10^{-4}
Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	5.42×10^{-4}
Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	7.11×10^{-4}
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	1.42×10^{-3}

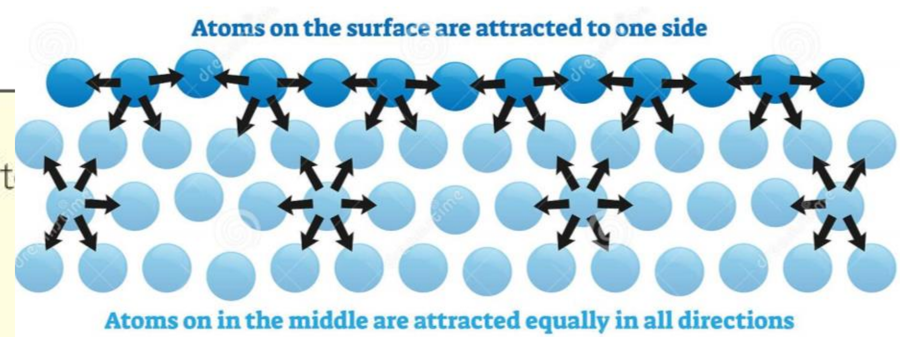
Viscosity

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.



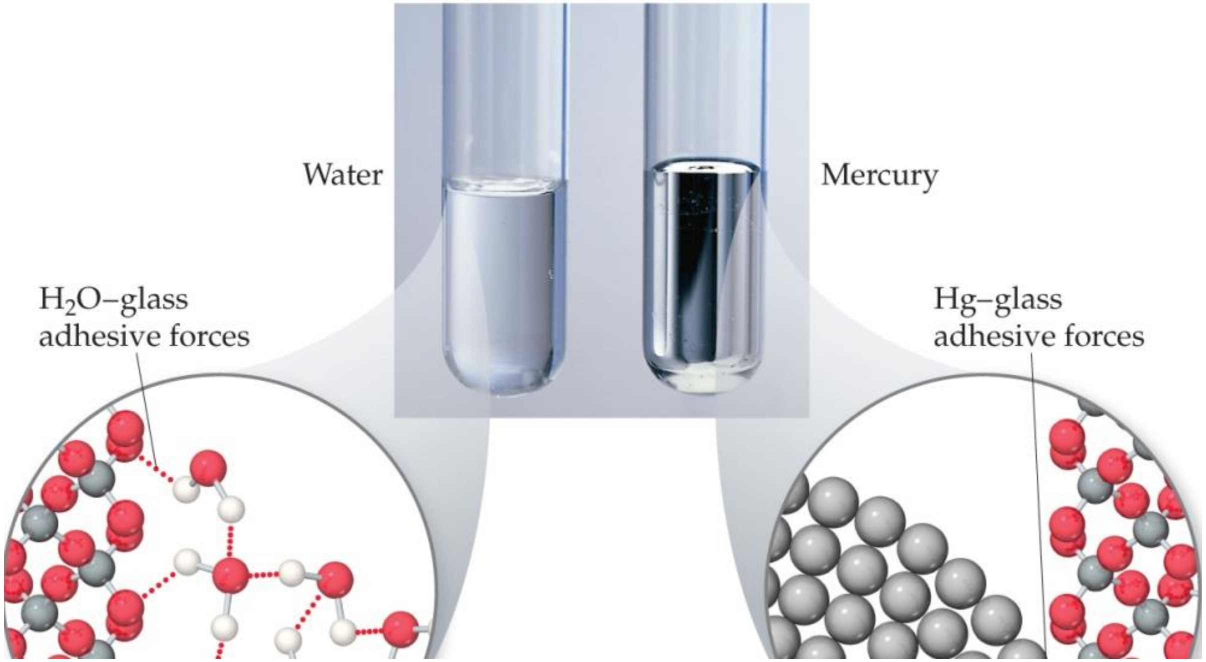
Cohesion (内聚力) & Adhesion (黏附力)

- **Intermolecular** forces that bind **similar molecules** to one another are called *cohesive forces*.

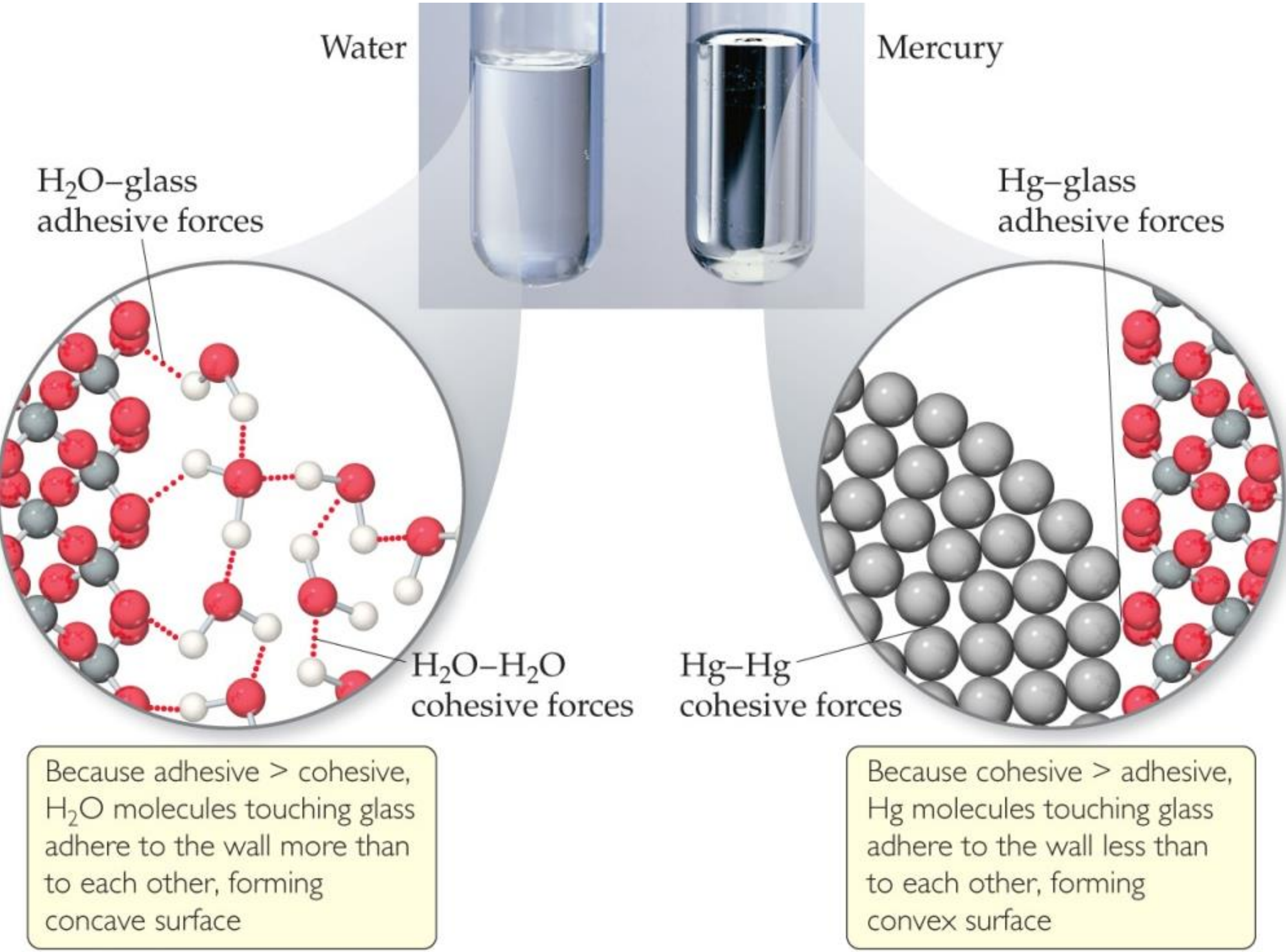
- **Intermolecular** forces that bind a substance to a **surface** are called *adhesive forces*.

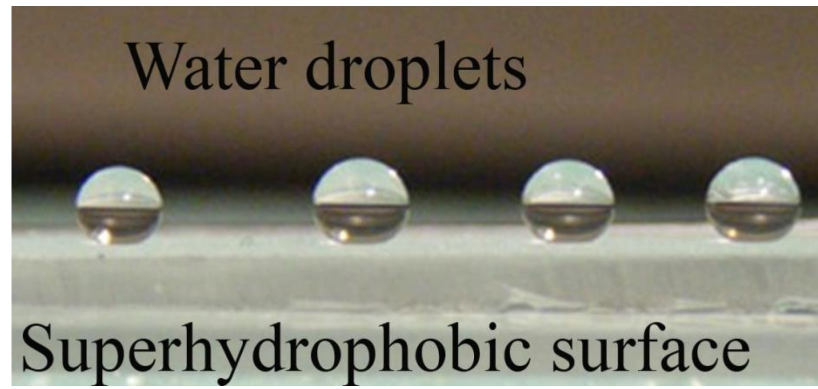
- These forces are important in capillary action.

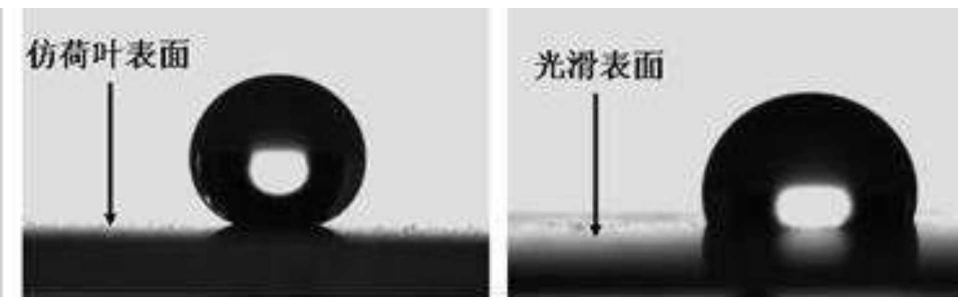
Capillary Action



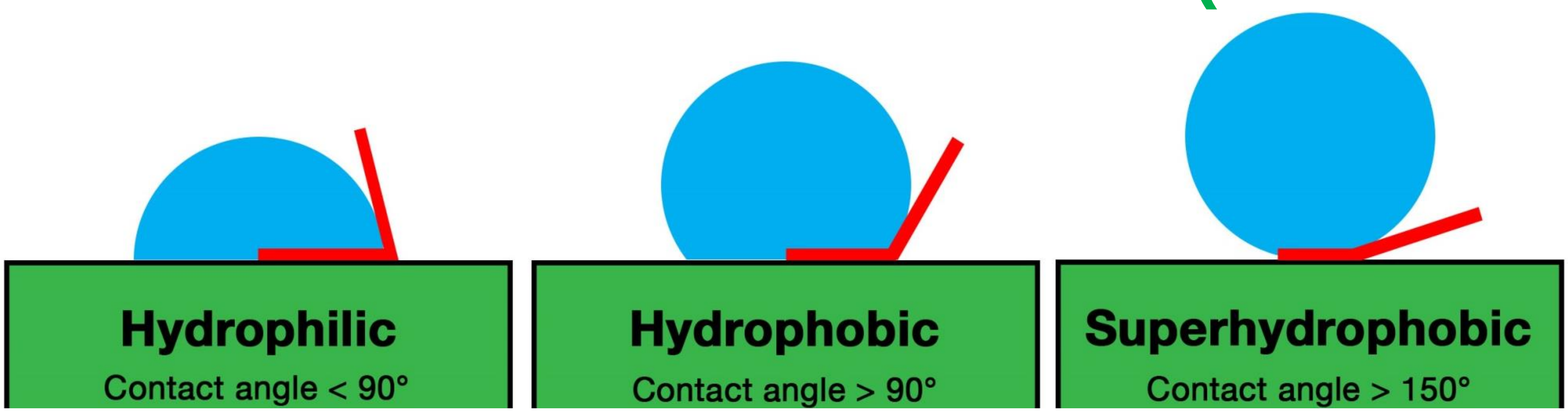
- The rise of liquids up **narrow** tubes.
- **Adhesive forces** attract the **liquid** to the **wall** of the tube.
- **Cohesive forces** attract the **liquid to itself**.
- Water has stronger adhesive forces with glass; mercury has stronger cohesive forces with itself.


Water
Mercury
H_2O–glass adhesive forces
Hg–glass adhesive forces
H_2O–H_2O cohesive forces
Hg–Hg cohesive forces
Because adhesive > cohesive, H_2O molecules touching glass adhere to the wall more than to each other, forming concave surface
Because cohesive > adhesive, Hg molecules touching glass adhere to the wall less than to each other, forming convex surface





(extra info.)

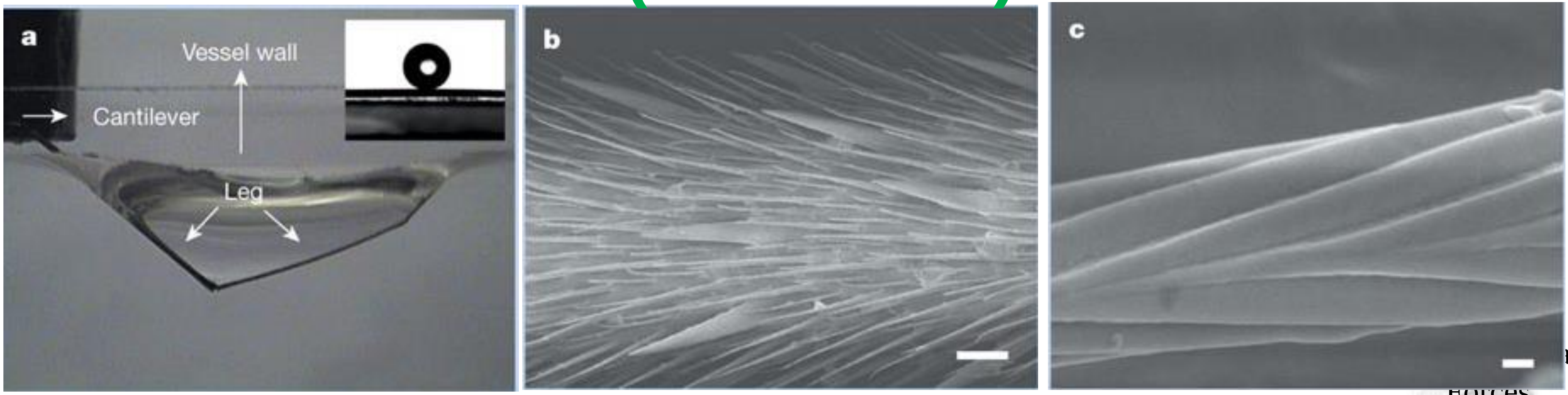


ecular
es

Water-Repellent Legs of Water Striders

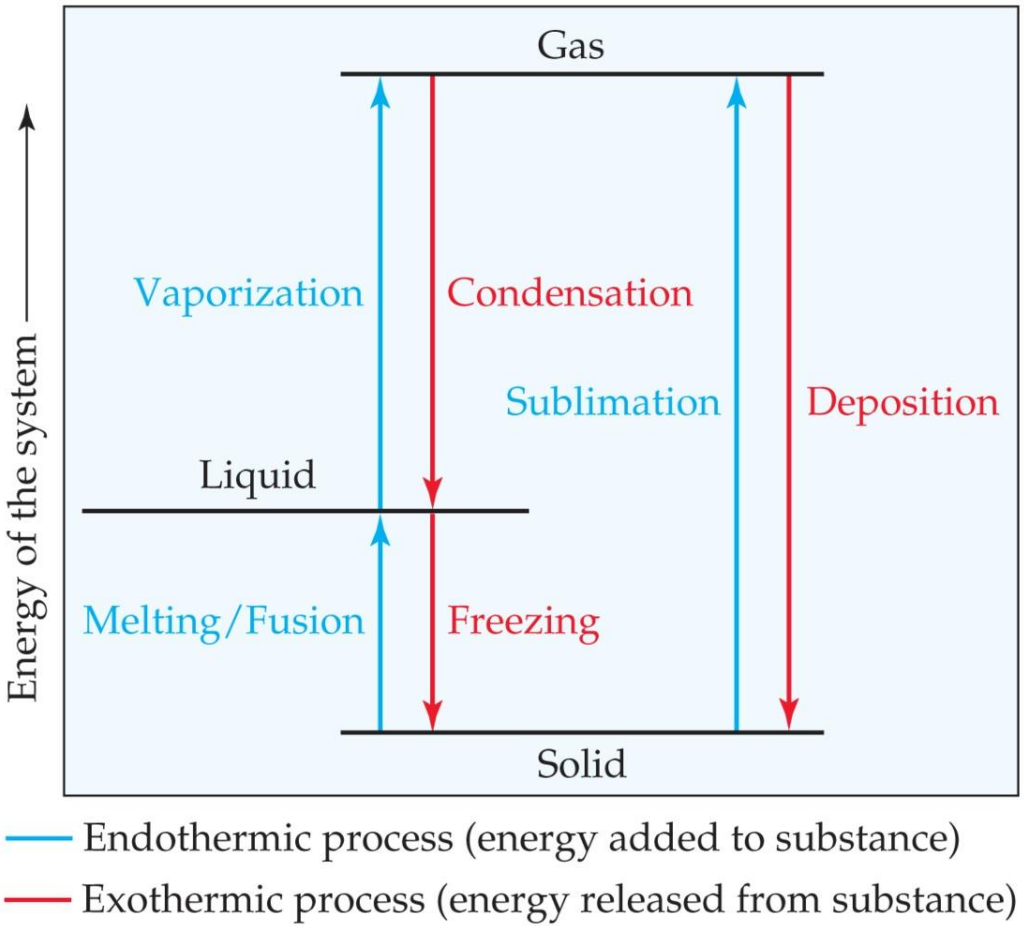
- Water striders (*Gerris remigis*) have remarkable non-wetting legs that enable them to stand effortlessly and move quickly on water, a feature believed to be due to a surface-tension effect caused by secreted wax.
- Jiang L and *et al.* show that it is the special hierarchical structure of the legs, 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.)



L. Jiang, et al., *Nature* **2004**, *432*, 36.

Phase Changes



- 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).**

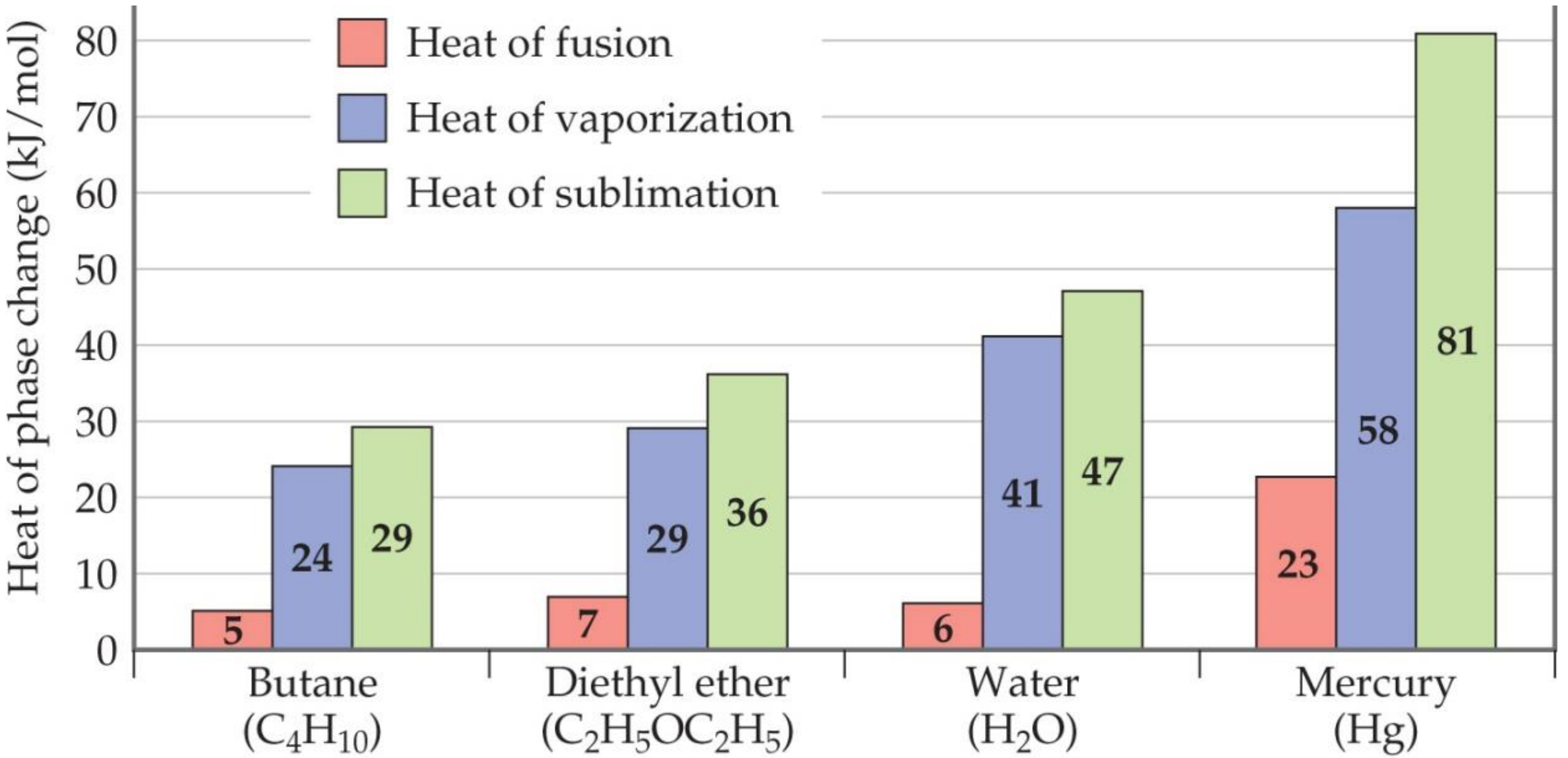
Phase Change of Chlorine from Gas to Liquid

Phase Change of Bromine from Liquid to Gas to Solid

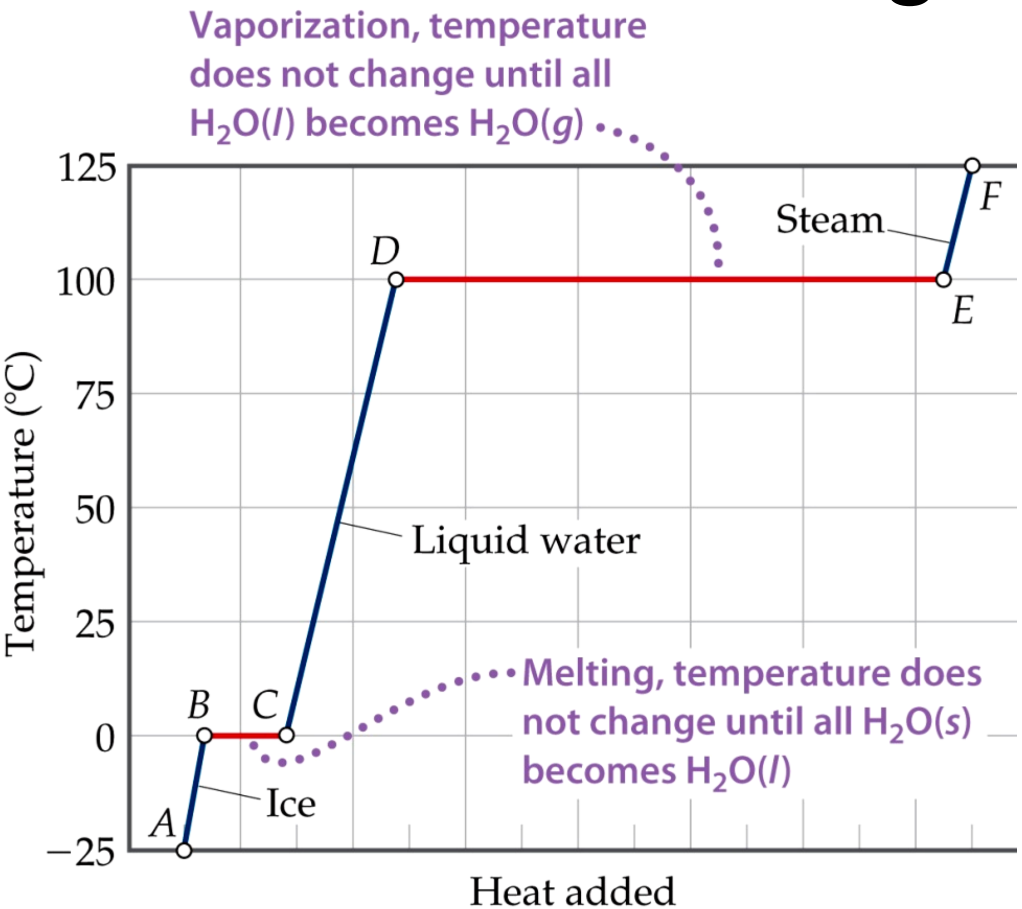
Phase Change of Iodine from Solid to Gas to Solid

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*ΔT**).

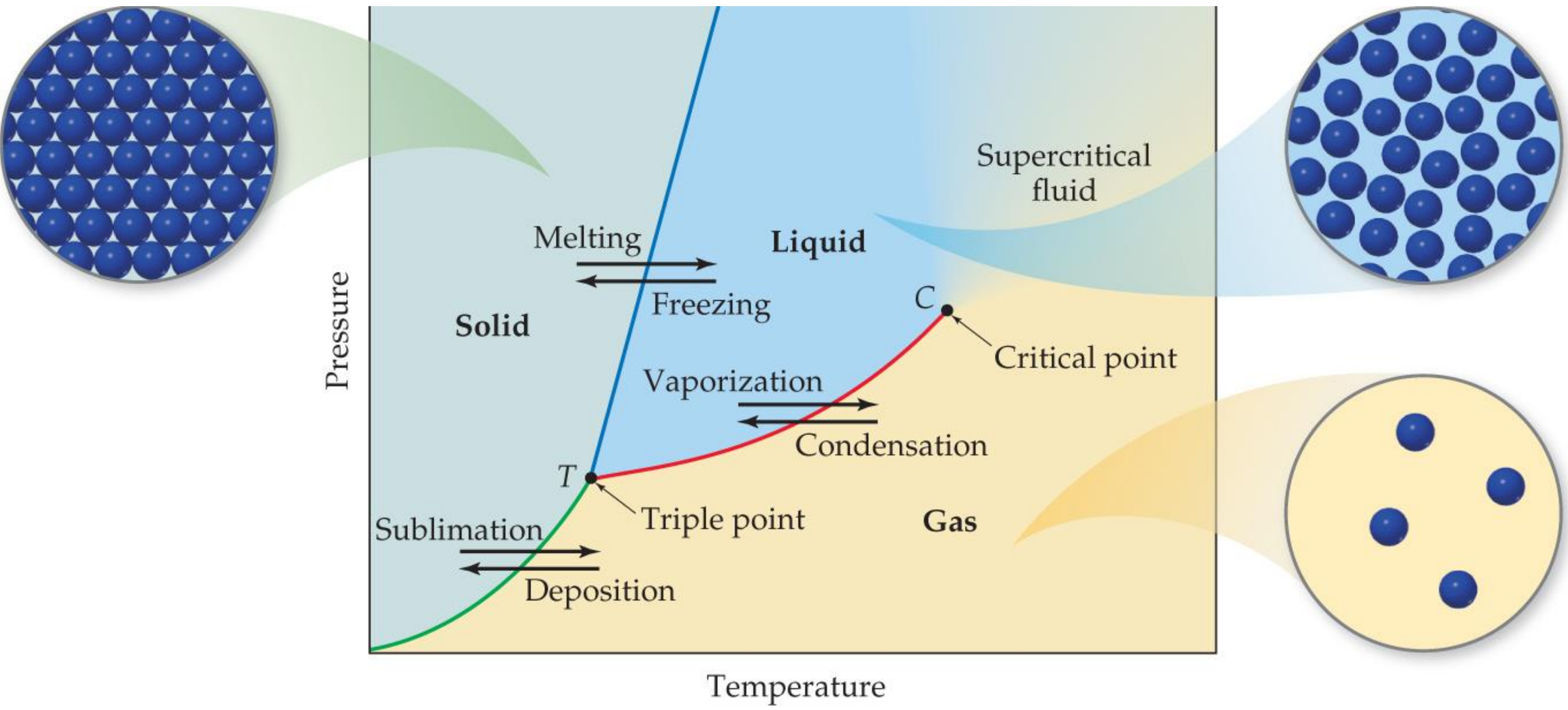
- The **temperature** of the substance does **not rise during a phase change**.

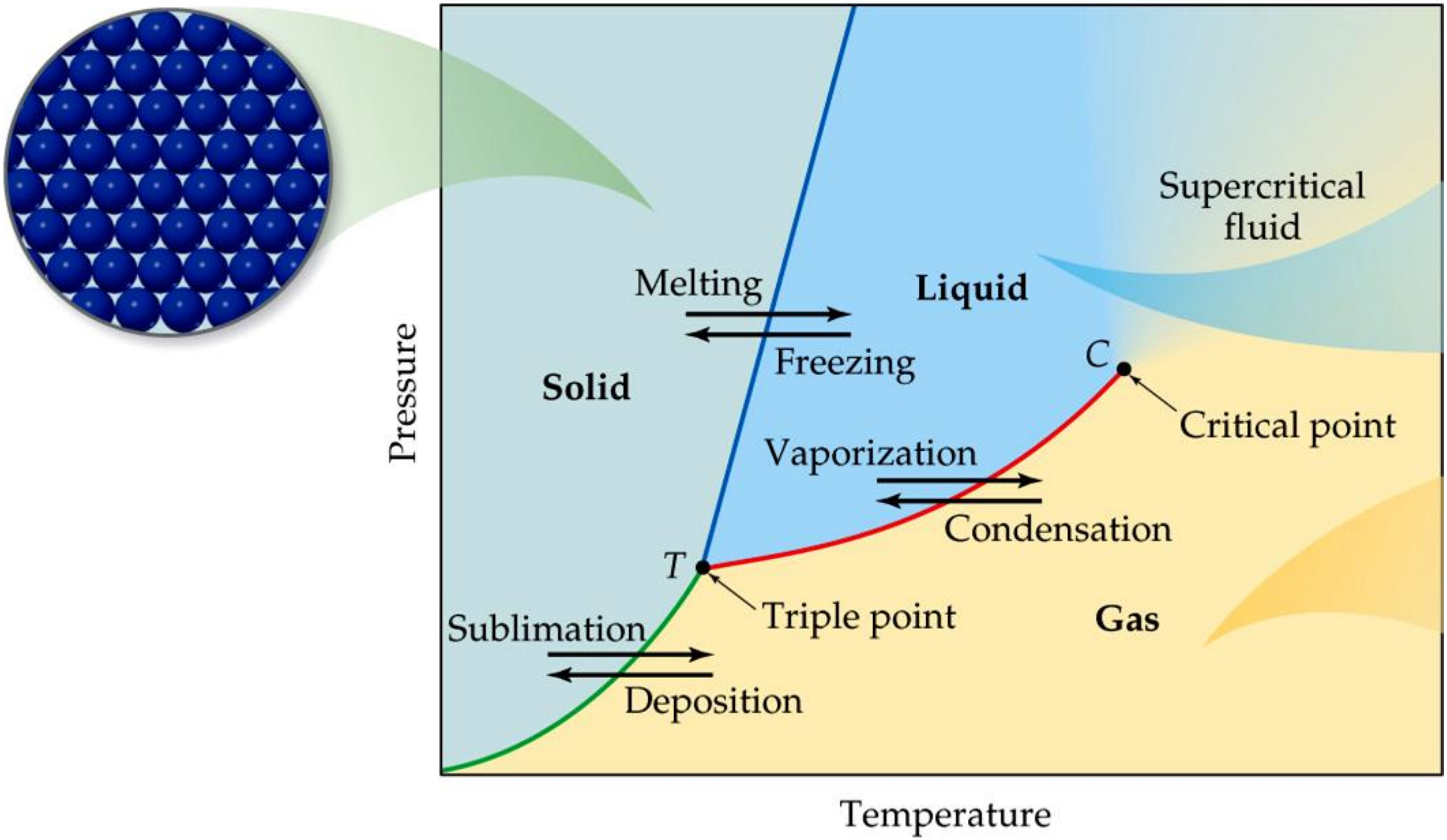
- For the phase changes, the **product of mass & heat of fusion or vaporization is heat**. The heat added to the system at the melting or boiling point goes into **pulling the molecules farther apart** from each other.

Phase Diagram

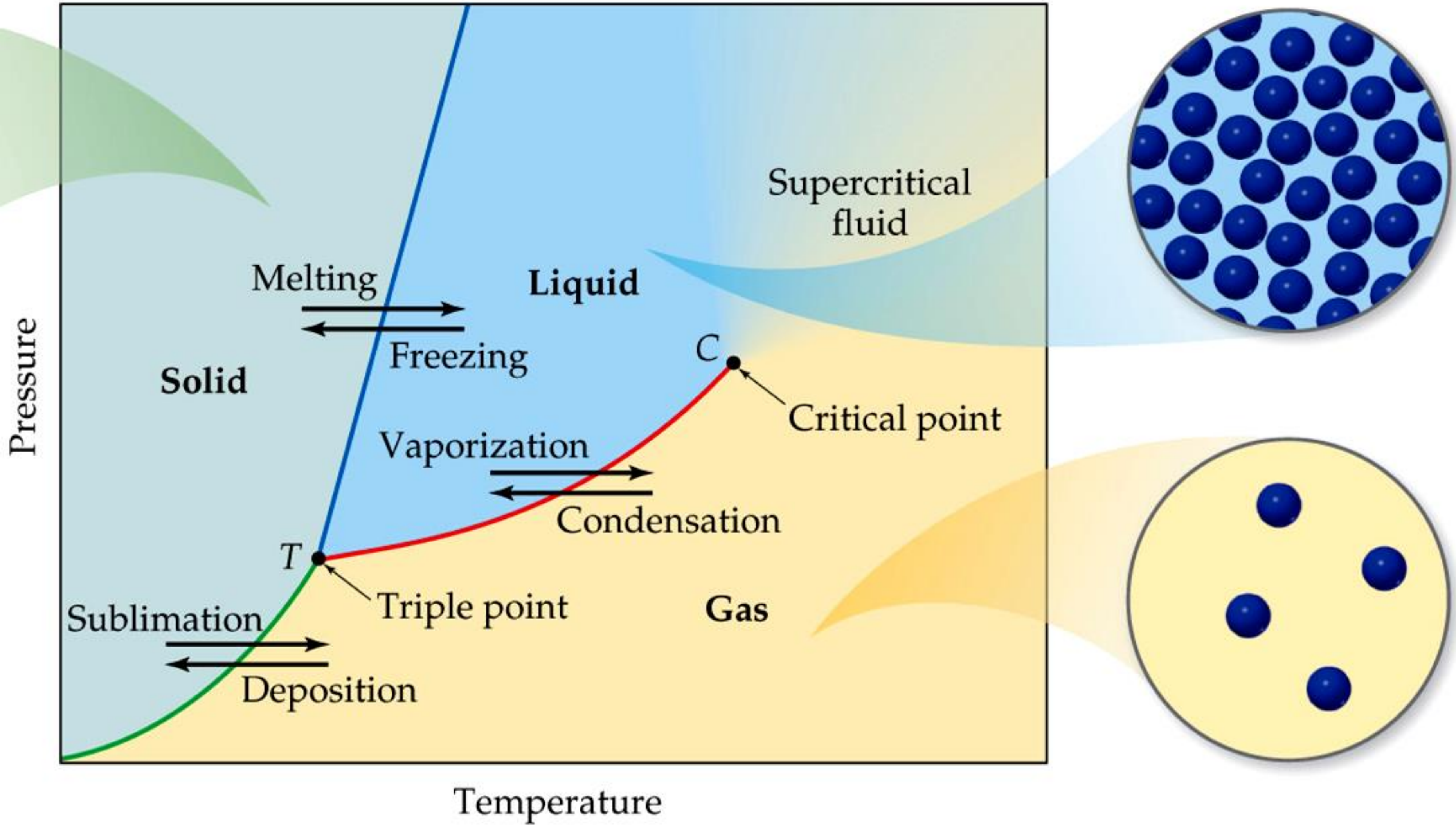
• A graph of pressure vs. temperature for a substance & the places where **equilibrium exist between phases**.

• It shows **(i) melting, boiling, & sublimation points at different pressures; (ii) the triple point and critical point**.

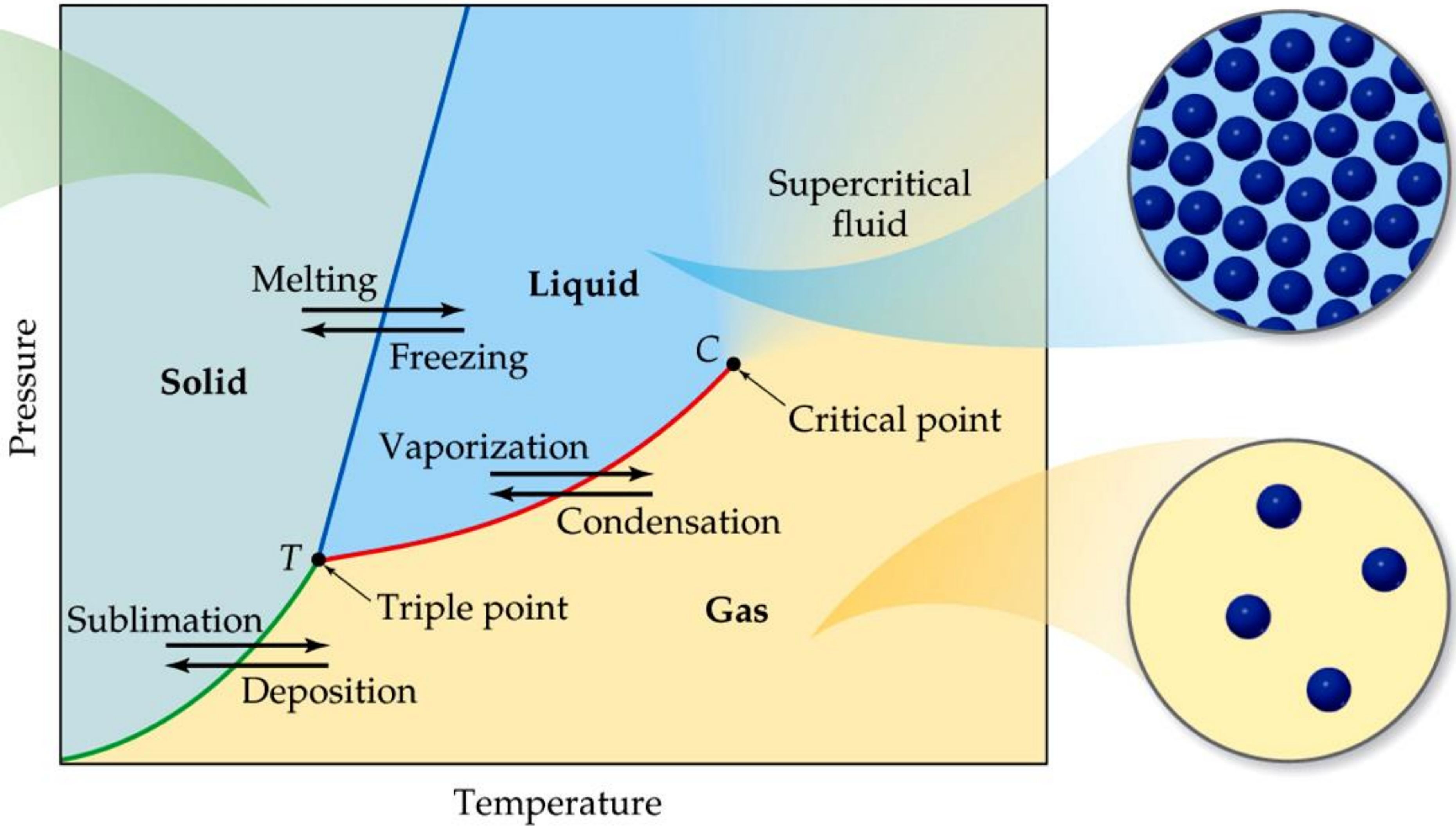




Green Curve: sublimation curve, **separates the solid phase from the gas phase** and represents the **change in the vapor pressure** of solid as it sublimes at different temperature. the sublimation point at each pressure.

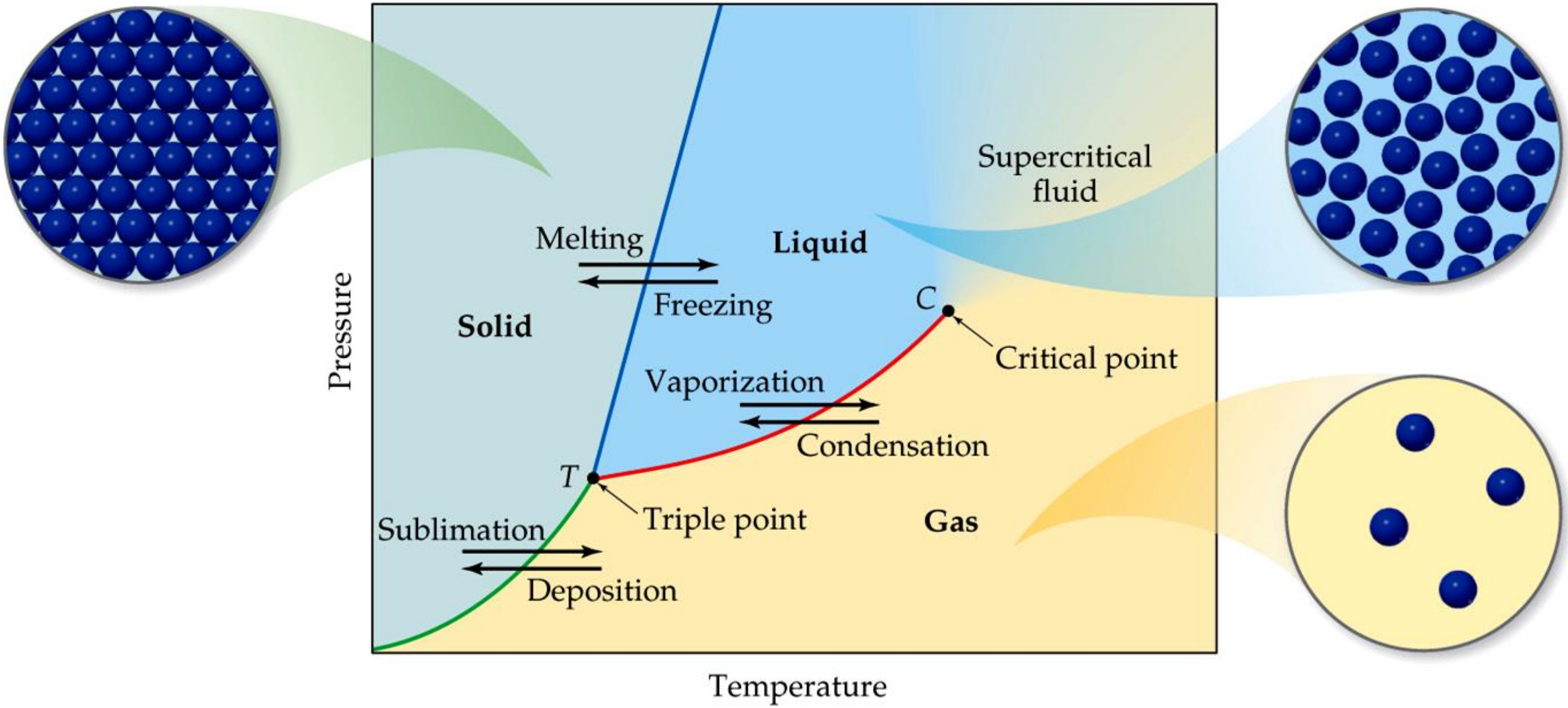


Red Curve: vapor-pressure curve of the liquid, representing equilibrium between the **liquid and gas ends at critical point** & the **change in boiling point** with increasing pressure.



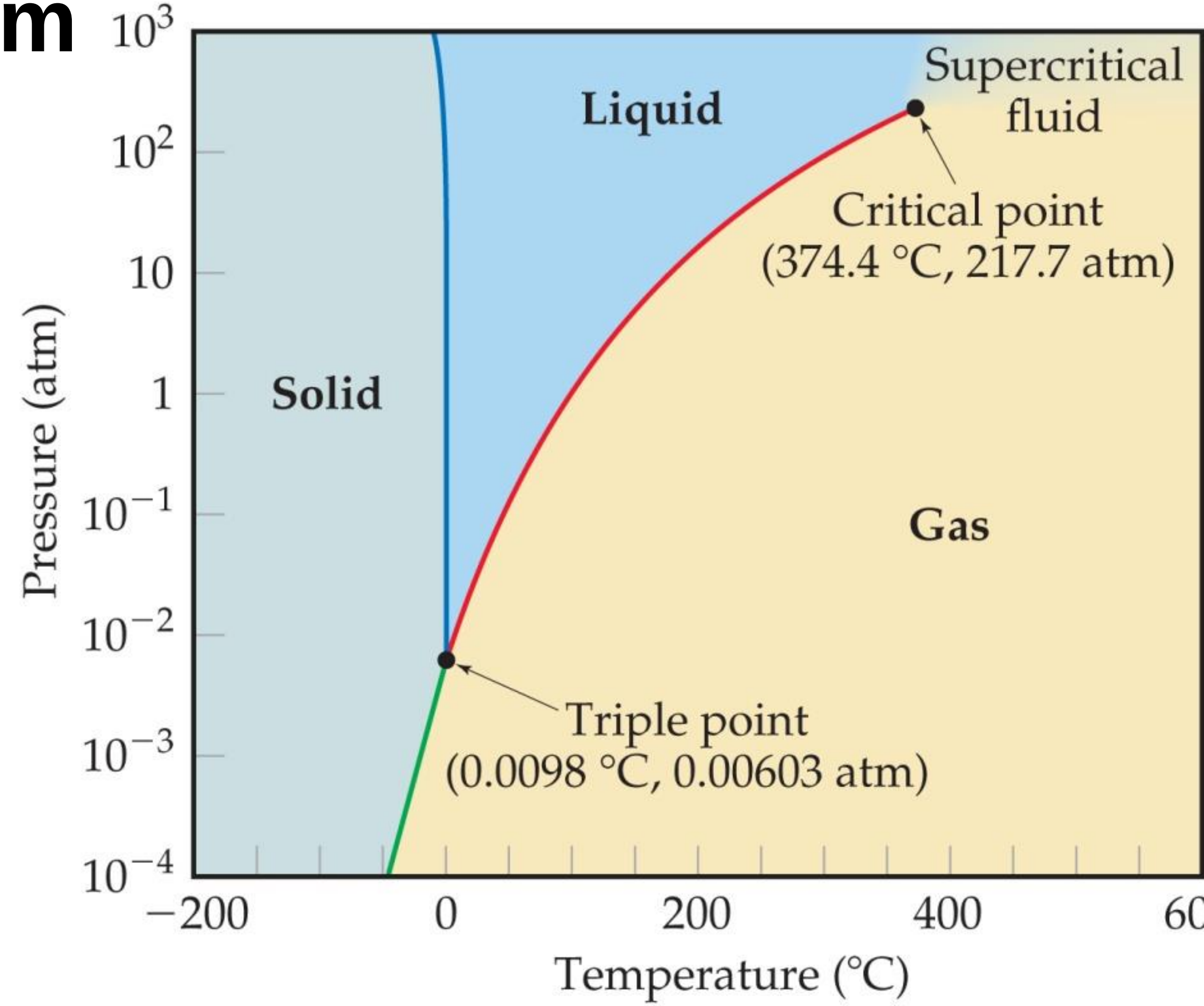
Blue Curve: melting curve, **separates the solid phase from the liquid phase** and represents the **change in melting point** of the solid with increasing pressure.

Intermolecular Forces

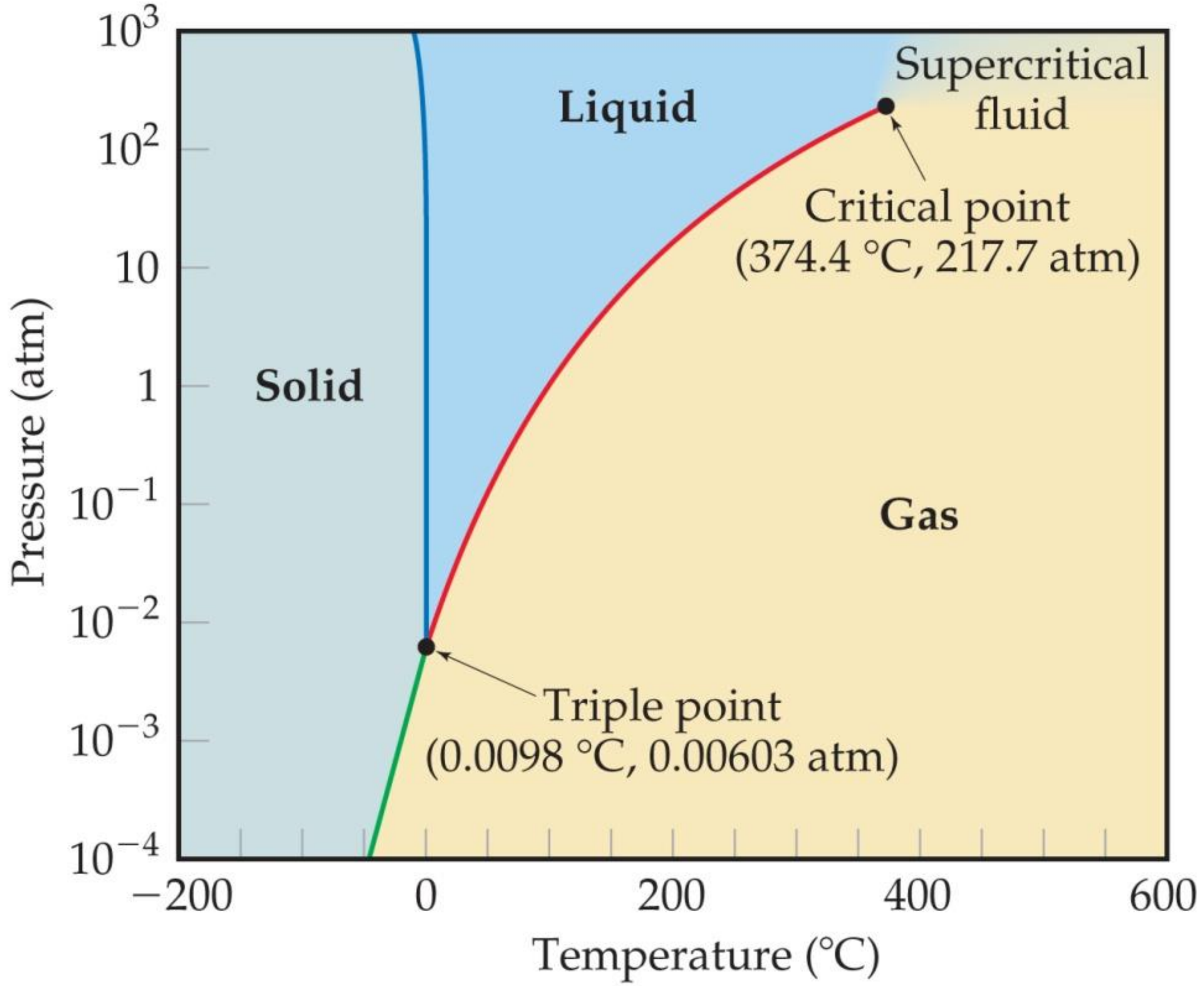


• The liquid–vapor interface starts at the **triple point (*T*)**, at which **all three states are in equilibrium**, and ends at the **critical point (*C*)**, above which the **liquid & vapor** are **indistinguishable** from each other.

Phase Diagram of Water



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



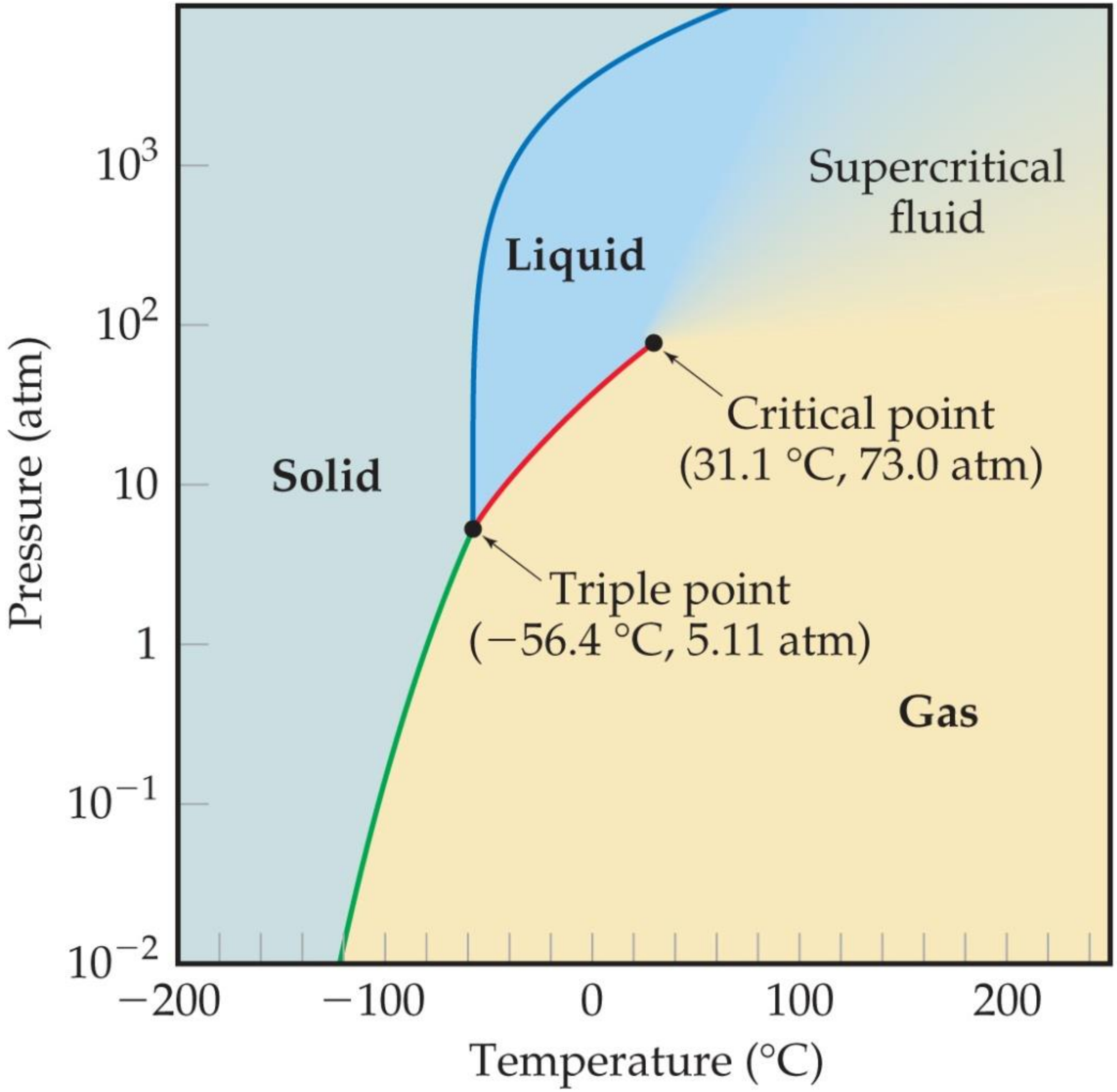
- **Unusual features**:

➢ 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 atm (triple point).
  - ➔ CO_2 sublimes at normal pressures.

Critical Temperature and Pressure

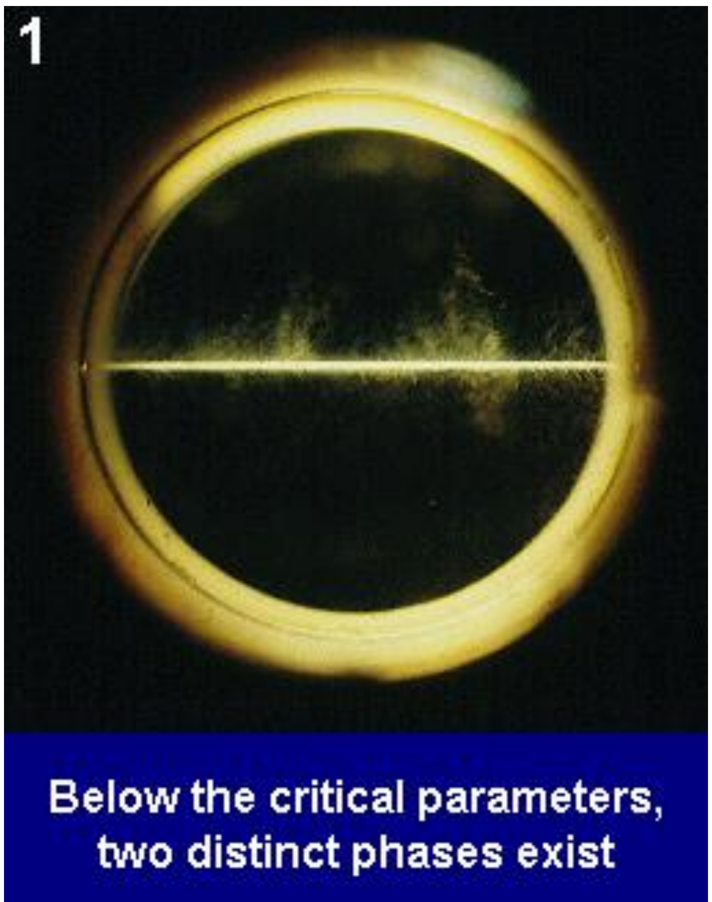
- The highest temperature at which a distinct liquid phase can form: critical temperature.
- Critical pressure: The pressure needed to compress the liquid at this critical temperature.

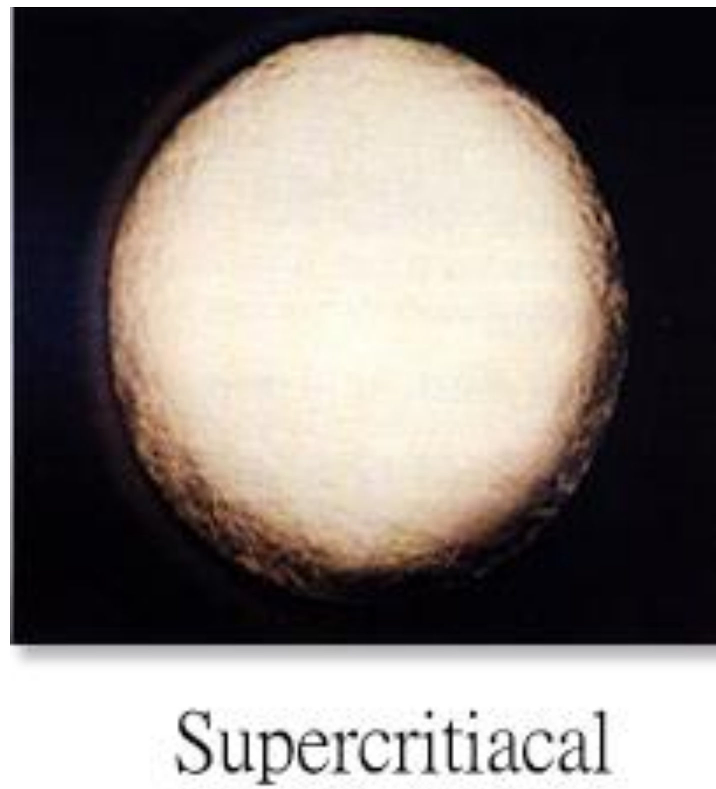
Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen, N_2	126.1	33.5
Argon, Ar	150.9	48.0
Oxygen, O_2	154.4	49.7
Methane, CH_4	190.0	45.4
Carbon dioxide, CO_2	304.3	73.0
Phosphine, PH_3	324.4	64.5
Propane, $CH_3CH_2CH_3$	370.0	42.0
Hydrogen sulfide, H_2S	373.5	88.9
Ammonia, NH_3	405.6	111.5
Water, H_2O	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.





ntermolecular
Forces

Critical Point of Benzene

Forces

Critical Point of Benzene

Critical Point of Benzene

Forces

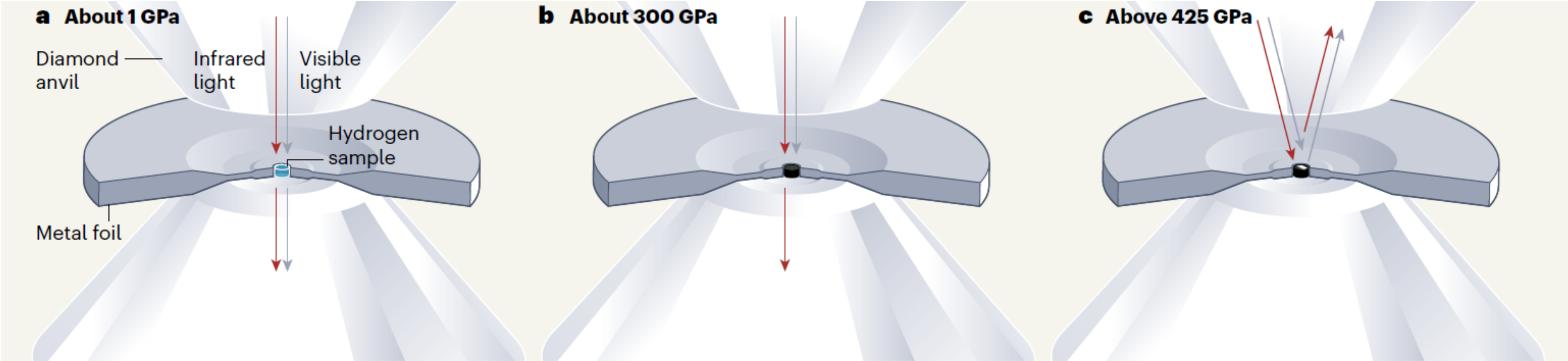
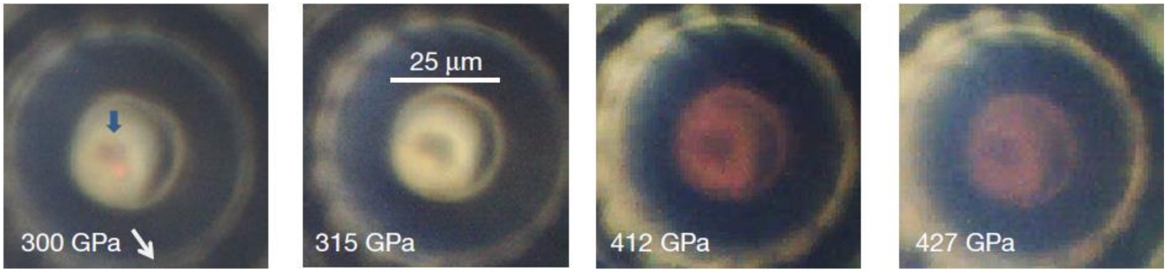
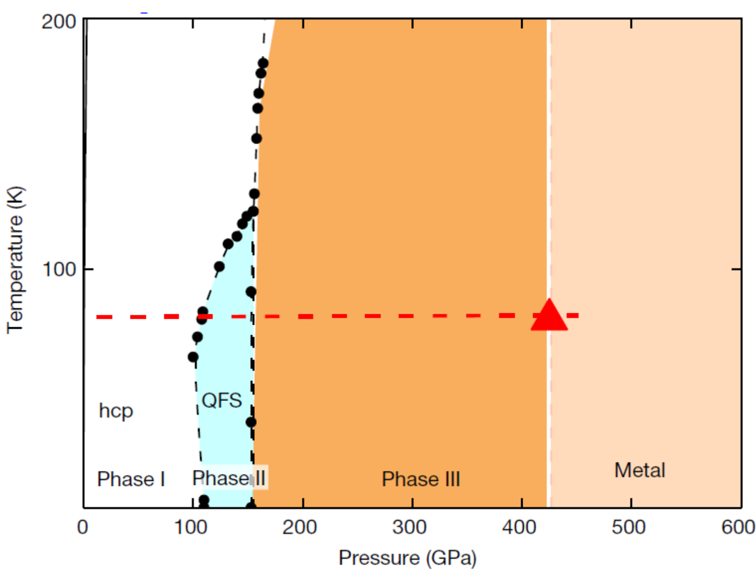


Figure 1 | Effect of increasing pressure on cold solid hydrogen. a, Loubeyre *et al.*[5] have studied solid hydrogen at extreme pressure and low temperature using a device known as a diamond anvil cell. This device compresses a sample of the material, which is confined to a microscopic chamber in a thin 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

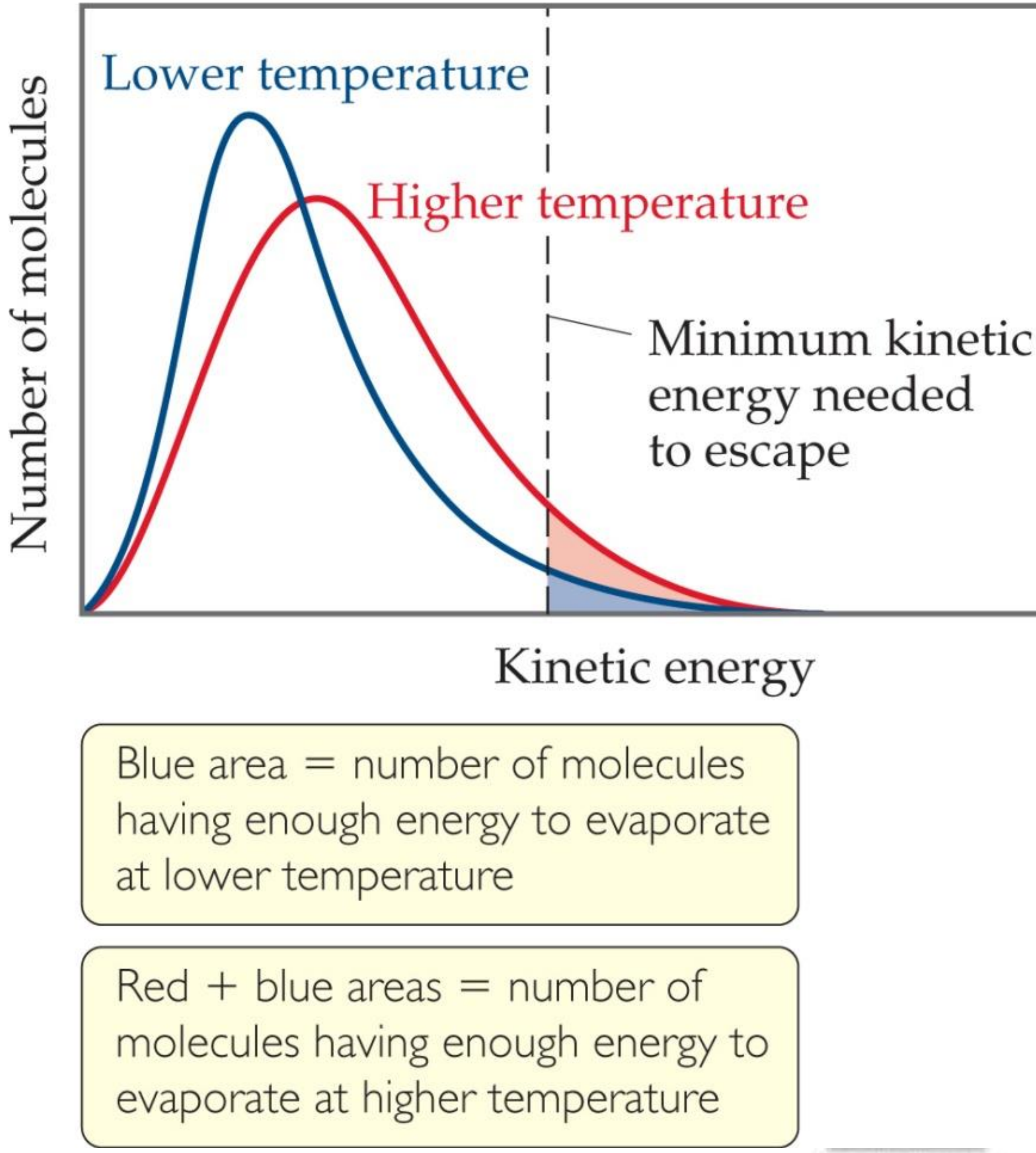
Nature | Vol 577 | 30 January 2020 | **631**

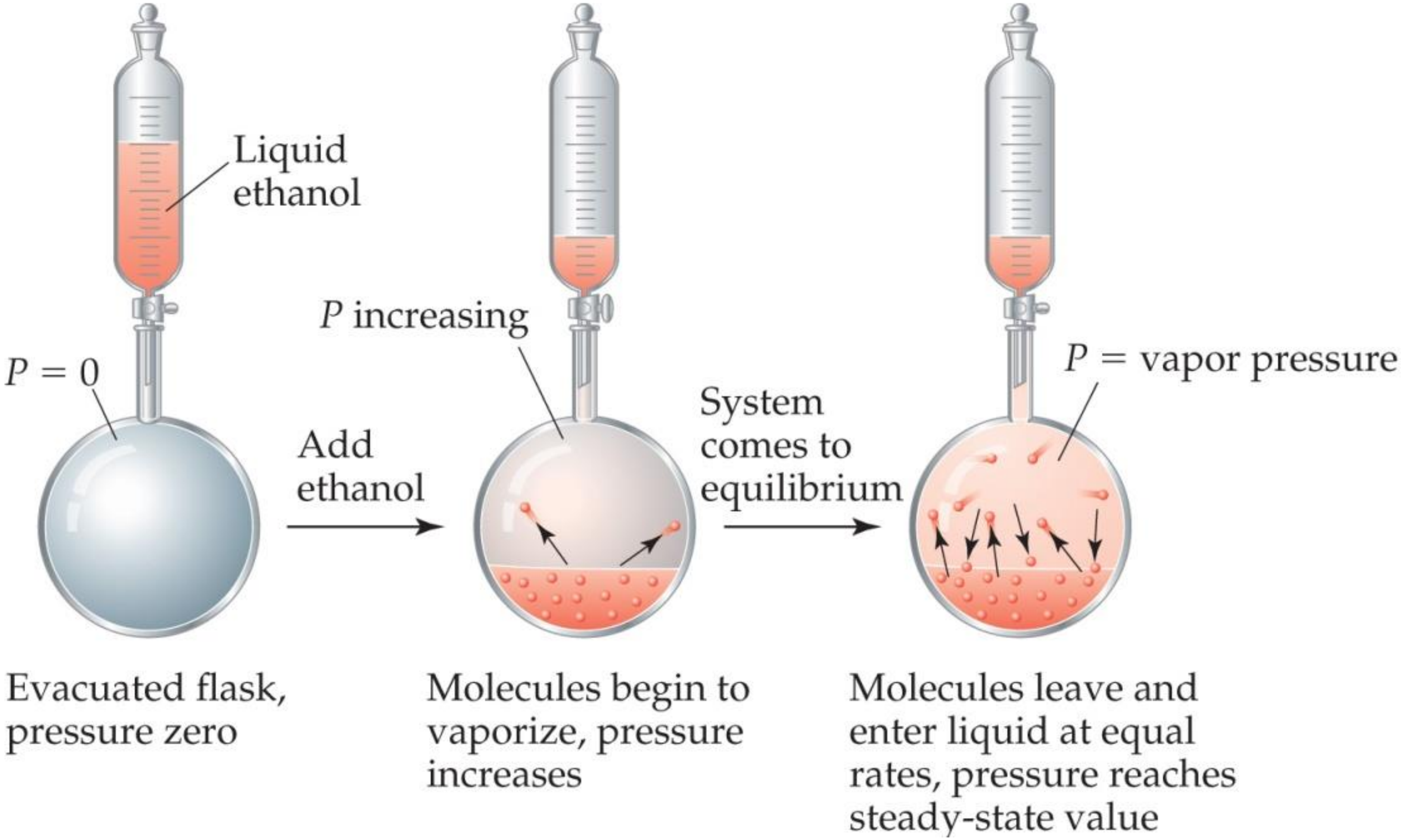
Fig. 4 | Low-temperature phase diagram of solid hydrogen. The red dashed

Vapor Pressure

- At *any temperature*, **some liquid molecules** have enough energy to **escape the surface** and **become** a **gas**.

- When the pressure of the vapor becomes constant, we call **vapor pressure**.





- 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*.

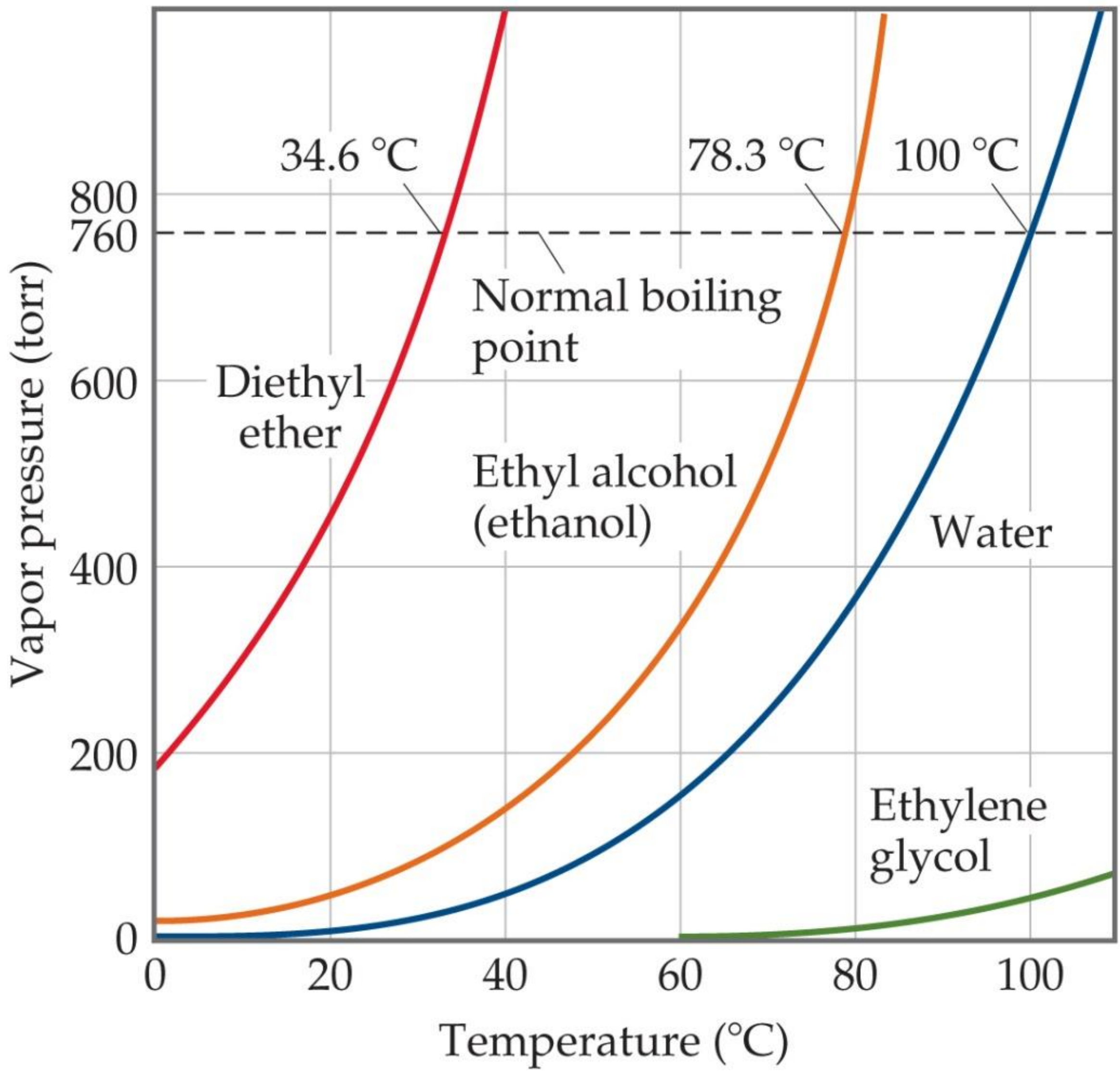
Vapor Pressure

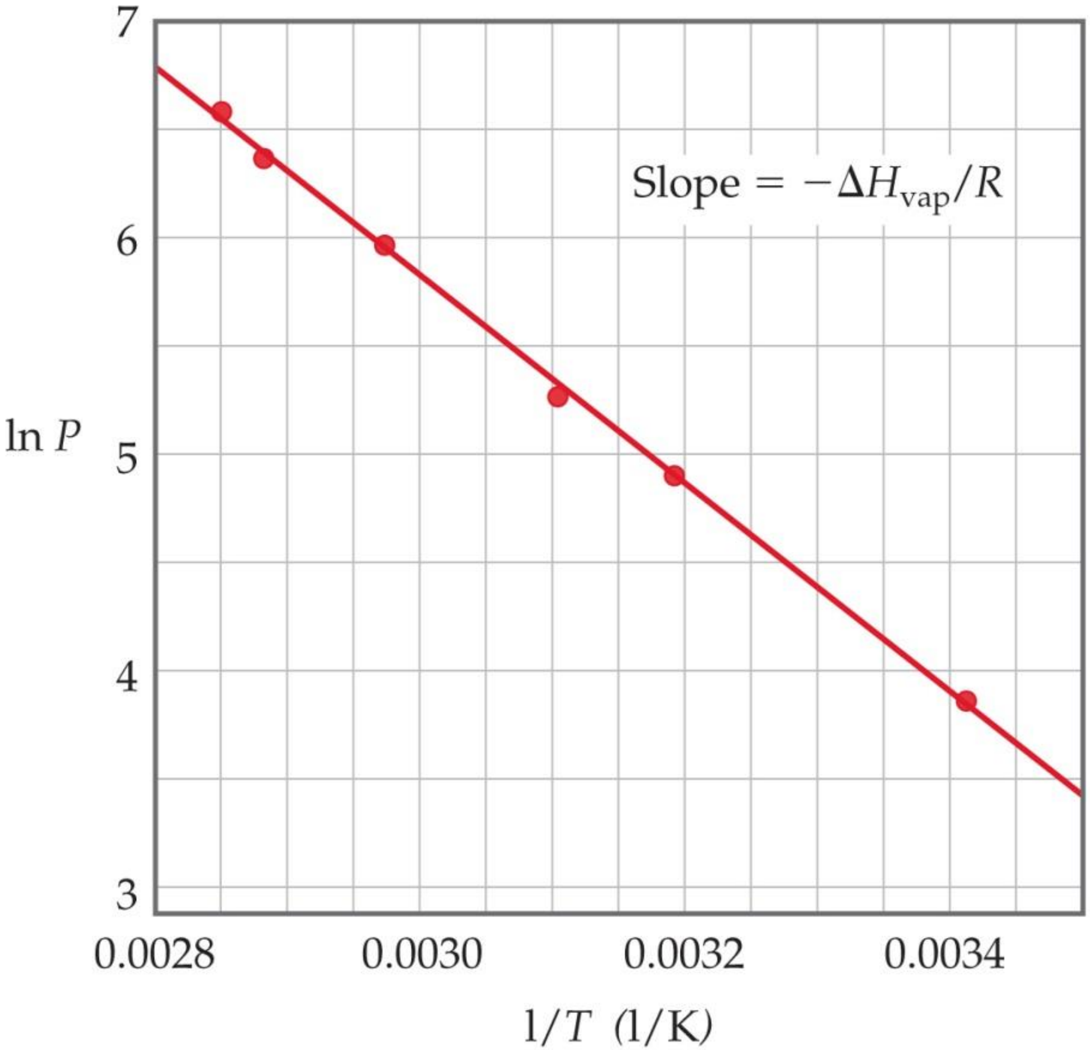
Vapor Pressure (torr)	10.0	40.0	100.0	400.0
T for CH_2Cl_2 (°C)	−43.3	−22.3	−6.3	24.1
T for CH_3I (°C)	−45.8	−24.2	−7.0	25.3

- 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**.

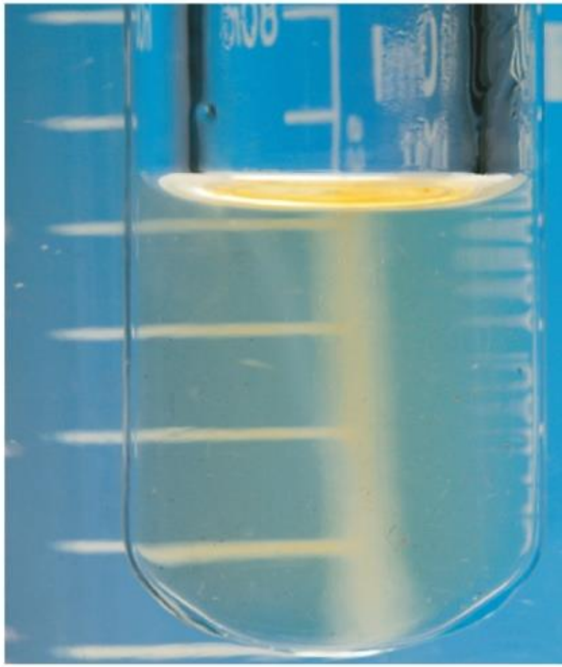
- **Clausius–Clapeyron equation**:

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

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

Liquid Crystals

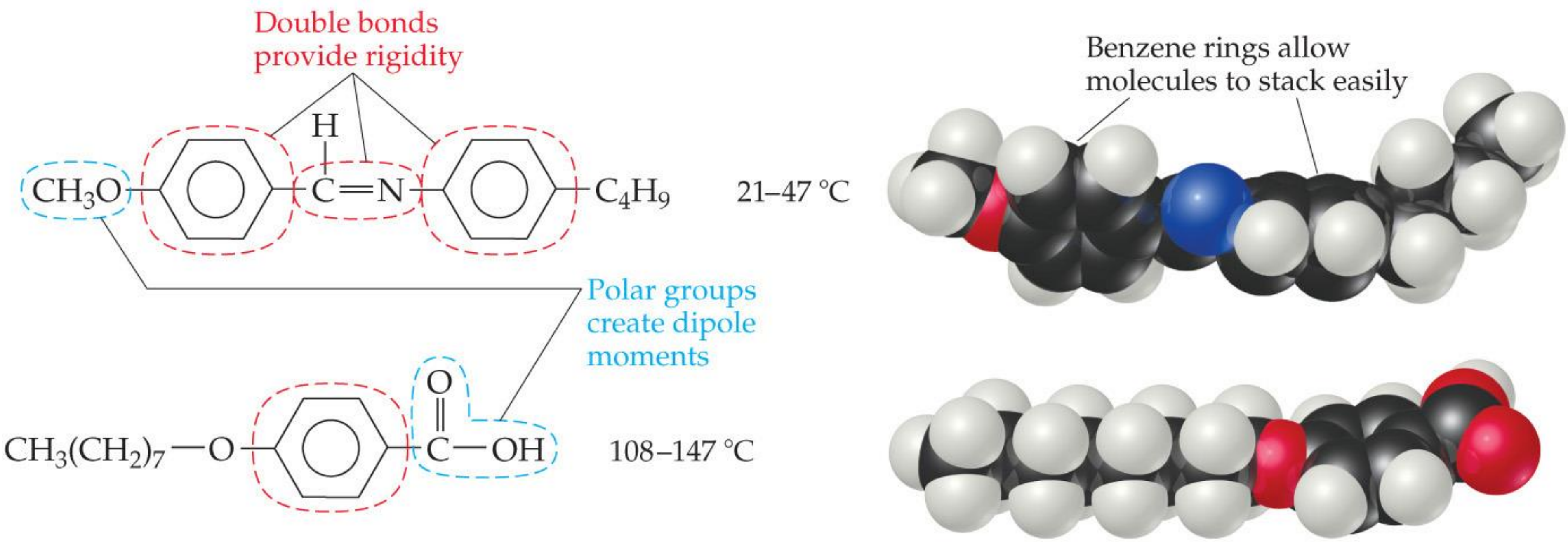
145 °C < *T* < 179 °C
Liquid crystalline phase



T > 179 °C
Liquid phase

- Some substances do not go directly from the solid state to the liquid state.

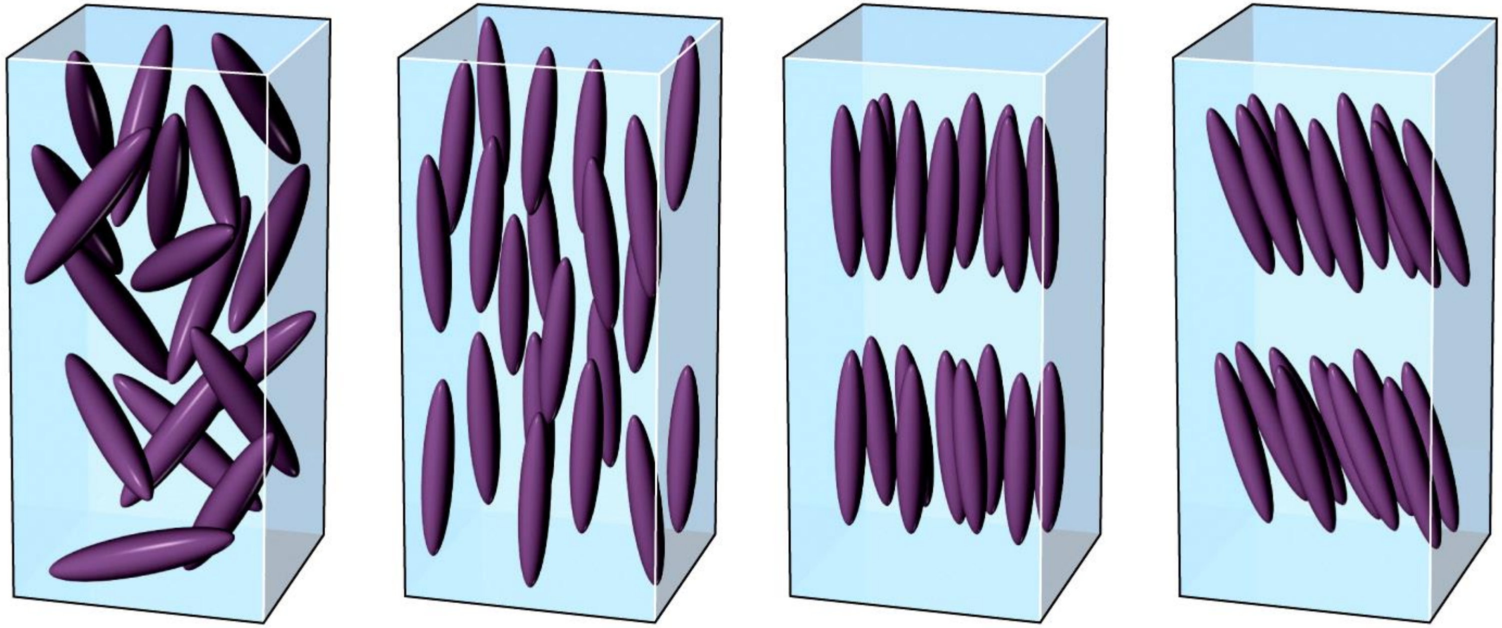
- In this **intermediate state**, liquid crystals **have some traits of solids and some of liquids**.



- 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

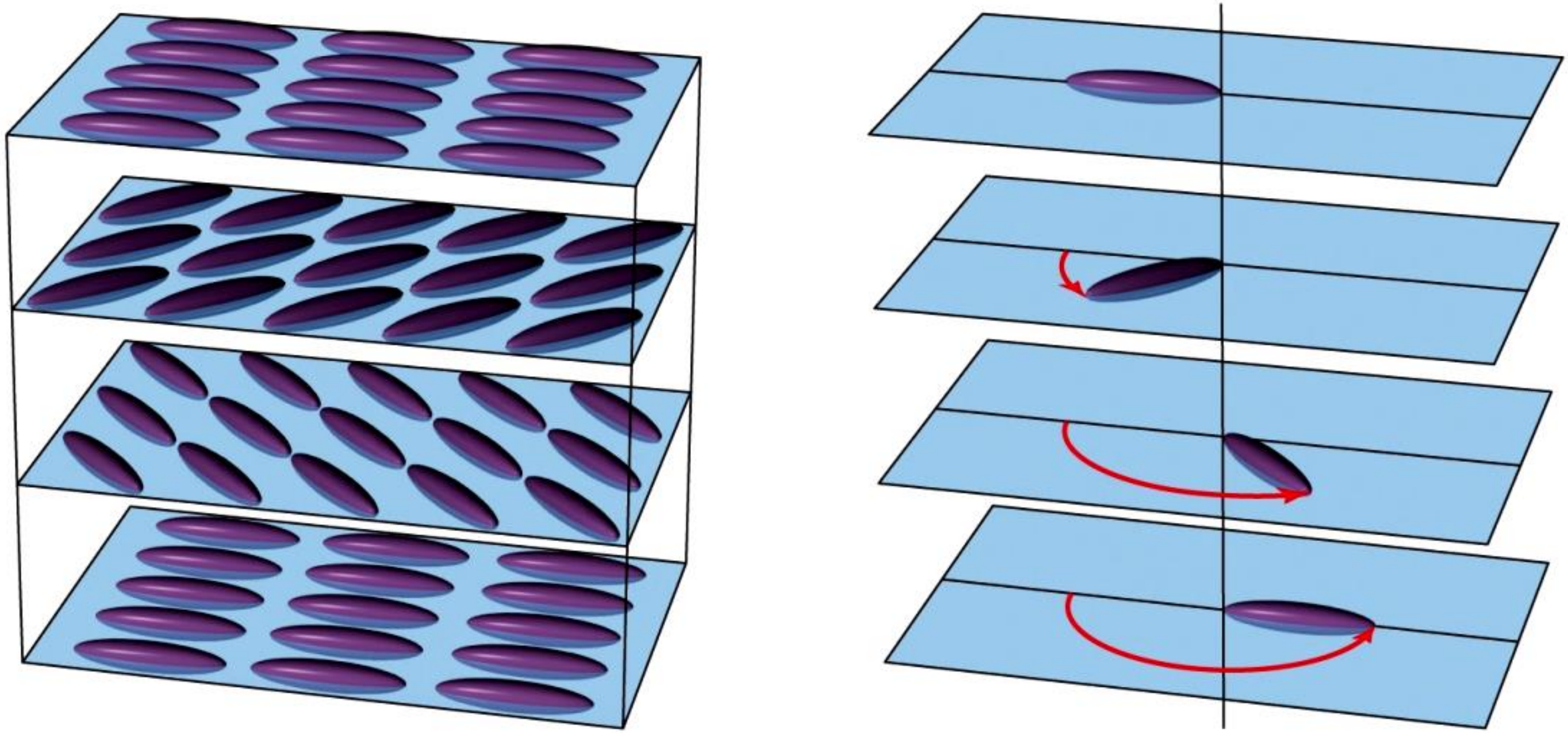
Smectic A liquid crystalline phase

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

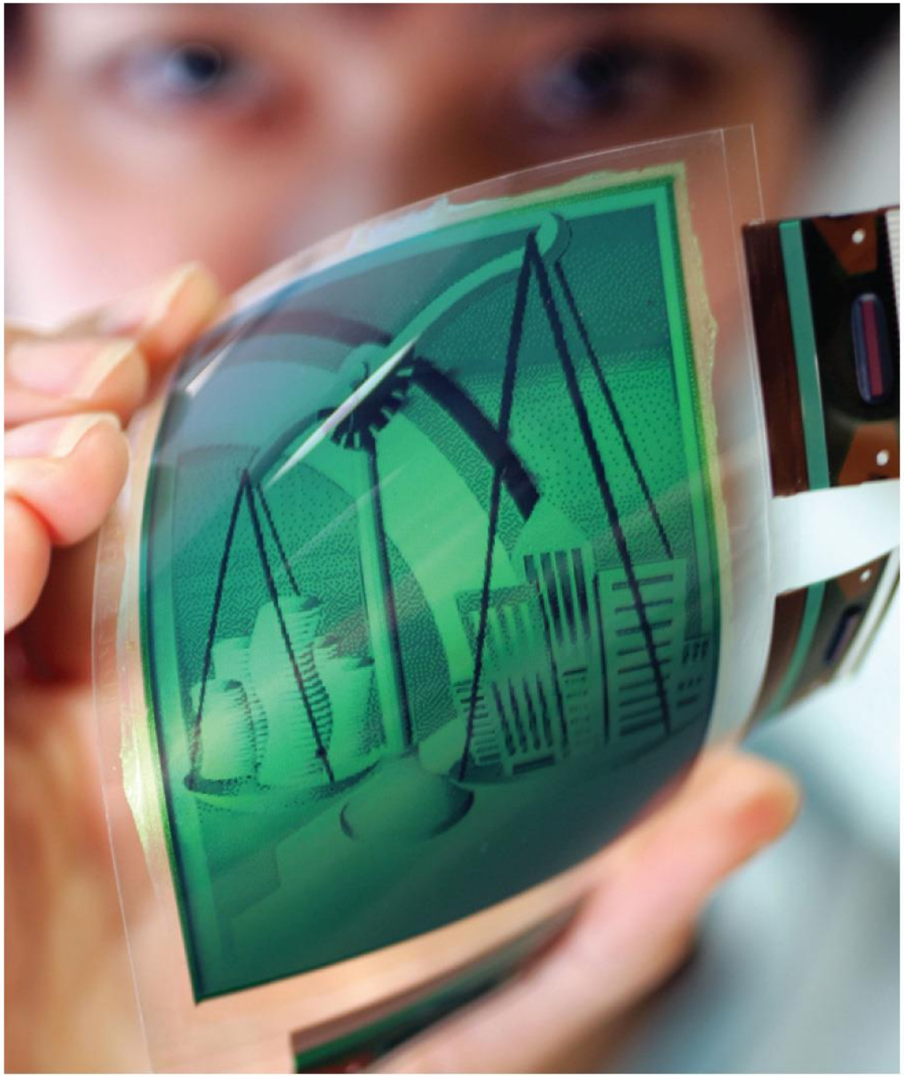
- In **nematic liquid crystals**, molecules are only **ordered in 1D**, along the long axis.
- In **smectic liquid crystals**, molecules are **ordered in 2Ds**, along the long axis & in layers.

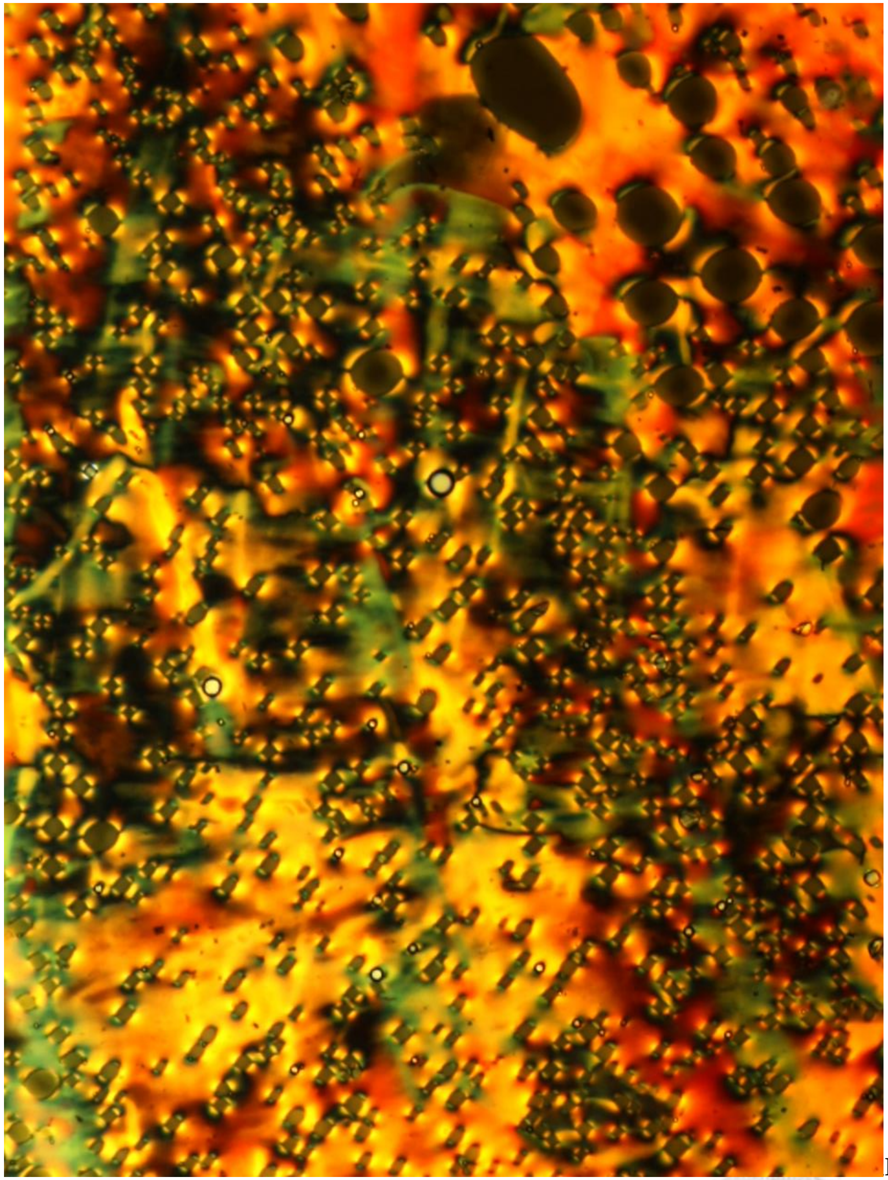


In a cholesteric liquid crystal the molecules pack into layers; the long axis of each molecule is oriented parallel to its neighbors within the same layer

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)





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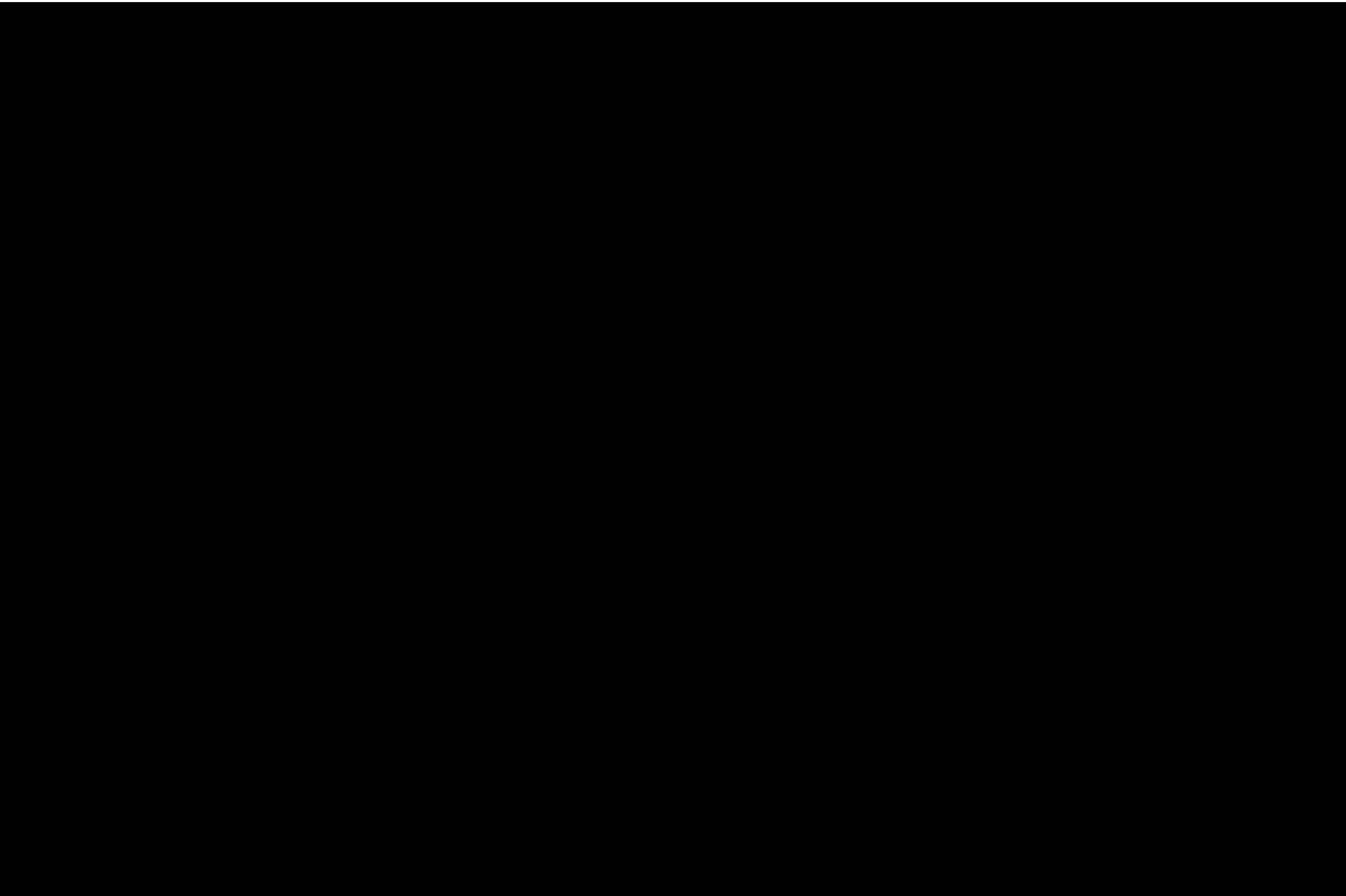
Forces

Liquid Crystal Display



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.

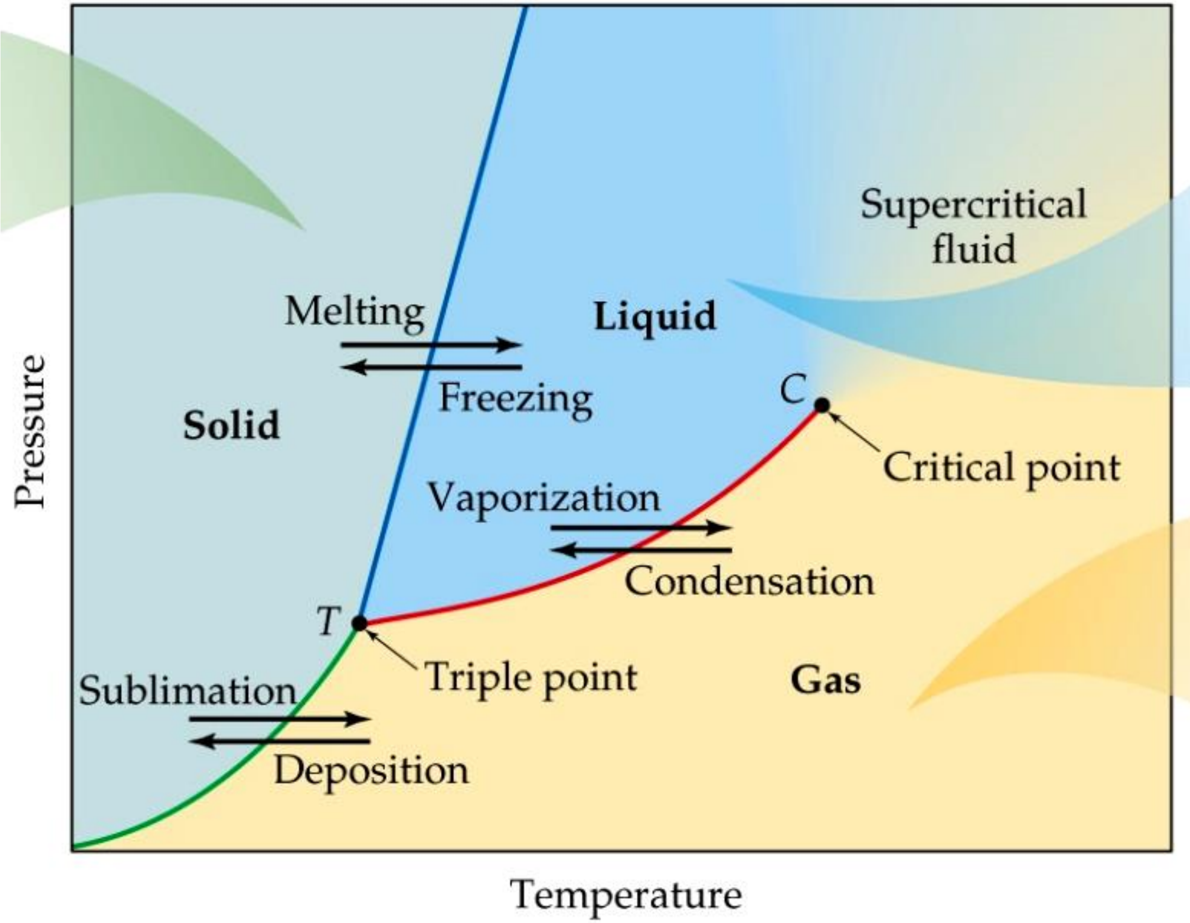
D. Both viscosity and surface tension decrease as intermolecular forces increase and temperature increases.

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	Shape of Hg Meniscus
A. Yes, Inverted U	Yes, downward U
B. No change	Yes, downward U
C. No change	No change
D. Yes, Inverted U	No change

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. CH_4
b. NH_3
c. H_2O
d. HF

Which compound below has the highest boiling point?

a. H_2O
b. H_2S
c. H_2Se
d. H_2Te

Which element below has the highest boiling point?

a. Kr
b. F_2
c. Cl_2
d. Br_2

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 Attractions: List the substances $BaCl_2$, H_2, CO, HF, and Ne in order of increasing boiling point.

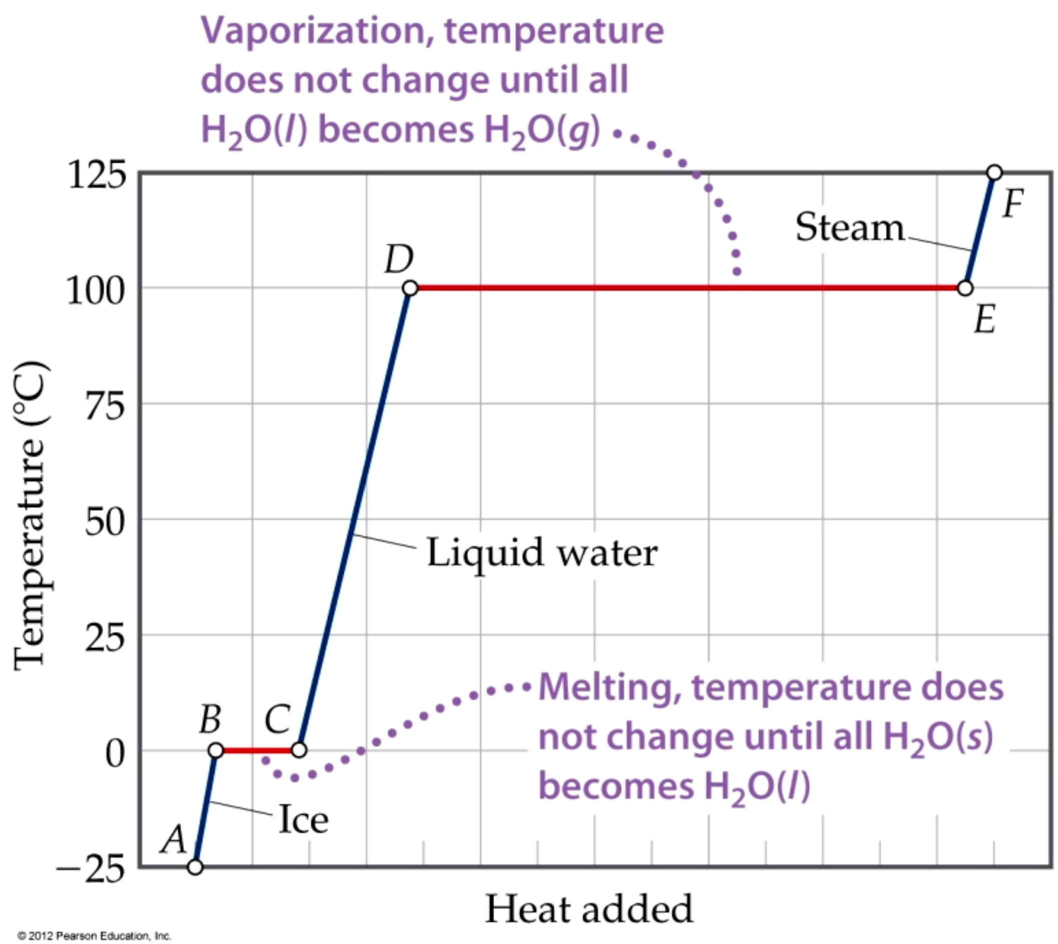
$H_2 < Ne < CO < HF < BaCl_2$

The boiling points reported in the literature are H_2 (20 K), Ne (27 K), CO (83 K), HF (293 K), and $BaCl_2$ (1813 K).

Calculate the enthalpy change upon converting 1.00 mol of ice at –25 °C to steam at 125 °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 H_2O, ΔH_{fus} = 6.01 kJ/mol and ΔH_{vap} = 40.67 kJ/mol

AB:
ΔH = (1.00 mol)(18.0 g/mol)(2.03 J/g-K)(25 K)
= 914 J = 0.91 kJ

BC: ΔH = (1.00 mol)(6.01 kJ/mol)
= 6.01 kJ

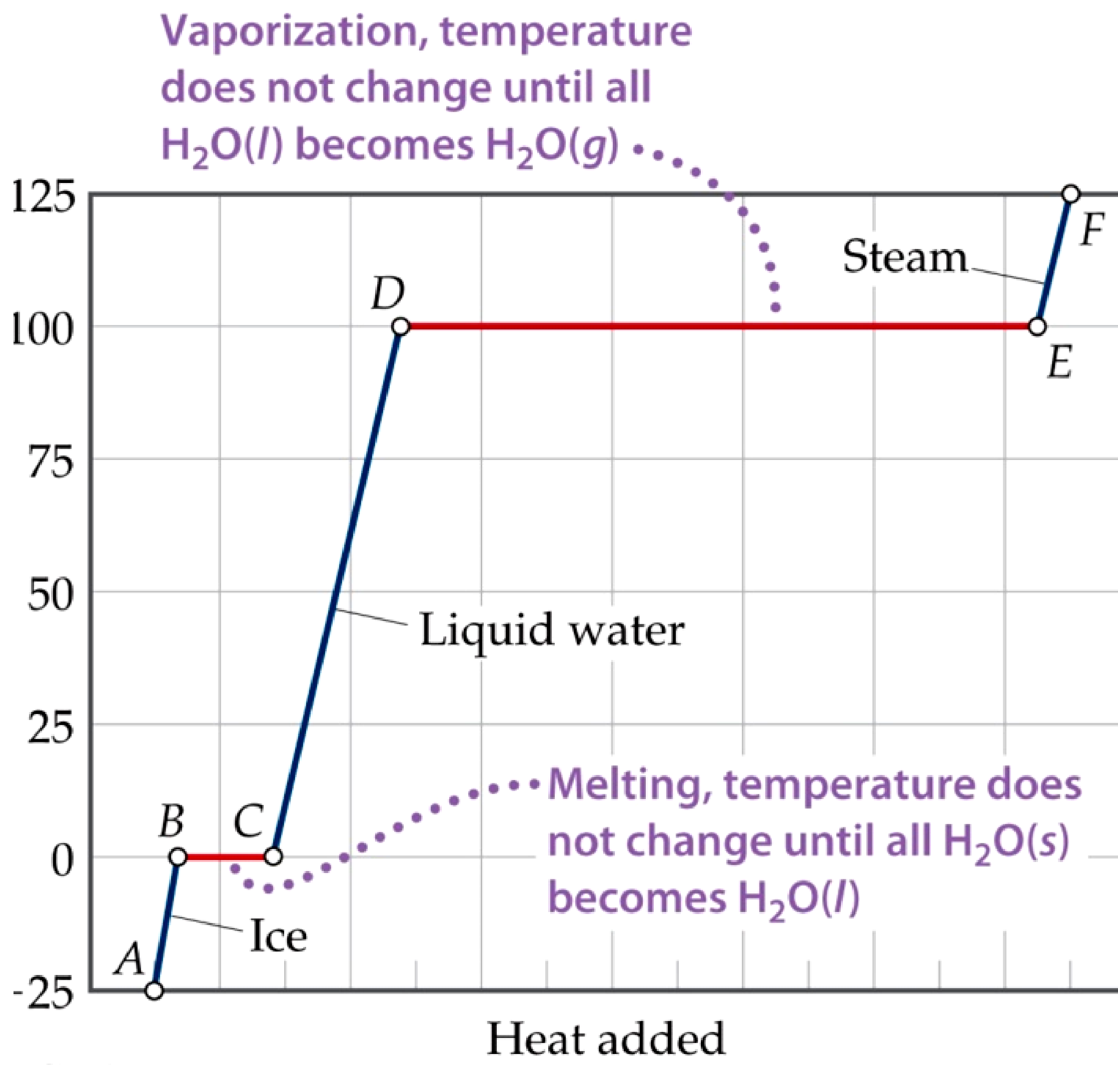


CD: ΔH = (1.00 mol)(18.0 g/mol)(4.18 J/g-K)(100 K) = 7520 J = 7.52 kJ

DE: ΔH = (1.00 mol)(40.67 kJ/mol) = 40.7 kJ

EF: ΔH = (1.00 mol)(18.0 g/mol)(1.84 J/g-K)(25 K) = 830 J = 0.83 kJ

ΔH = 0.91 kJ + 6.01 kJ + 7.52 kJ + 40.7 kJ + 0.83 kJ = 56.0 kJ



Intermolecular Forces

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?