

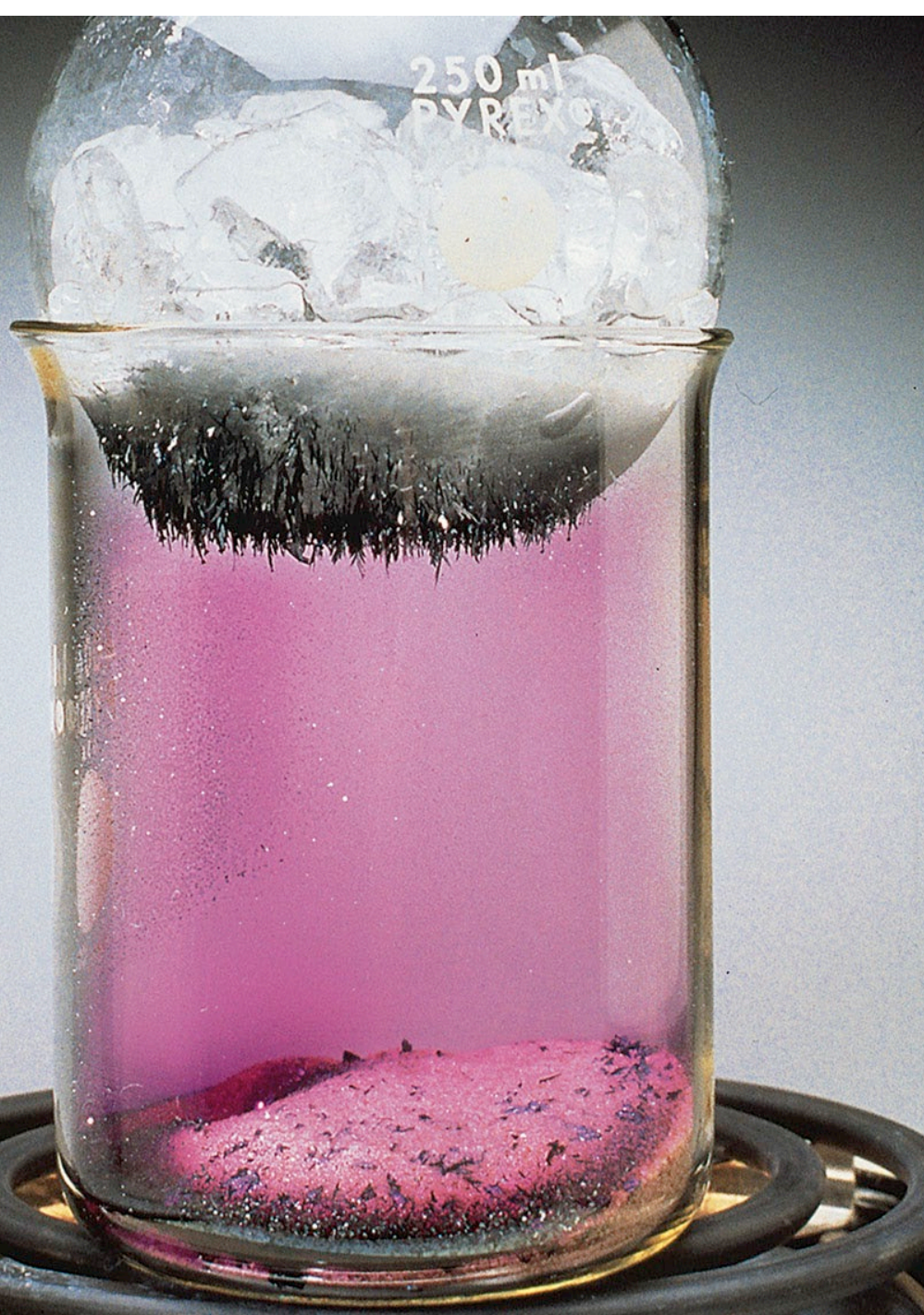
## 10

## CHAPTER

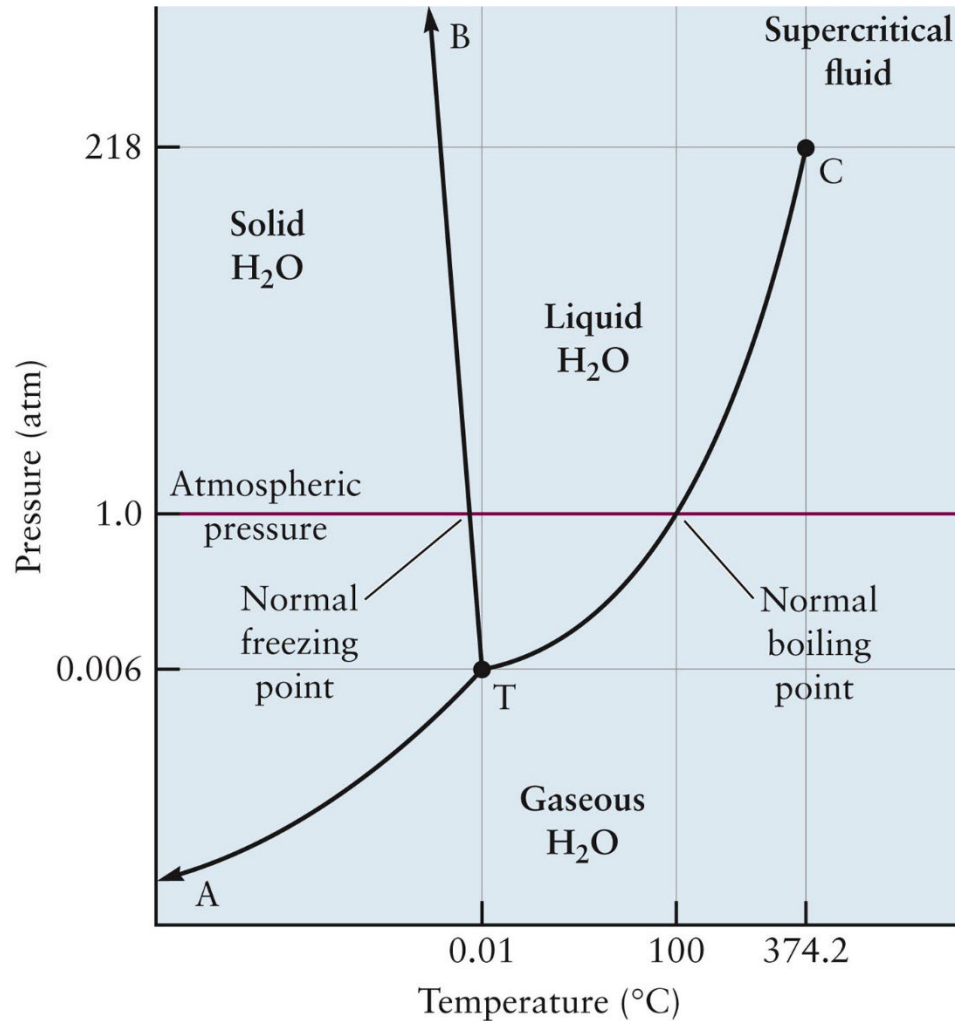
# SOLIDS, LIQUIDS, AND PHASE TRANSITIONS

→ The average separation between molecules, and the nature of the intermolecular forces, determine the local structure and therefore the properties of the bulk.

- 10.1** Bulk Properties of Gases, Liquids, and Solids: Molecular Interpretation
- 10.2** Intermolecular Forces: Origins in Molecular Structure
- 10.3** Intermolecular Forces in Liquids
- 10.4** Phase Equilibrium
- 10.5** Phase Transitions
- 10.6** Phase Diagrams

 $I_2(s)$  $I_2(g)$  $I_2(s)$ 

## Key question: what is the origin of phase transitions?



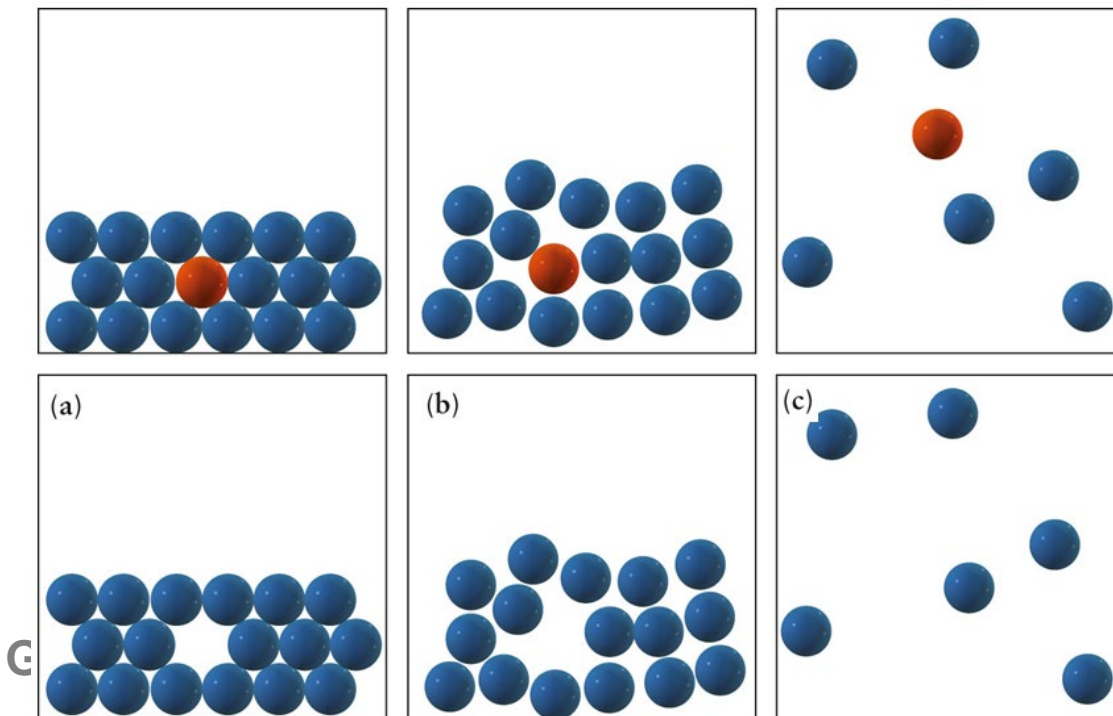
→ The following macroscopic measurements clearly distinguishes gases, liquids, and solids from each other and also probes the strength of the intermolecular forces, albeit indirectly

## 10.1 BULK PROPERTIES OF GASES, LIQUIDS, AND SOLIDS: MOLECULAR INTERPRETATION

### ➤ Molar Volume

Solids, liquids:  $10\text{--}100\text{ cm}^3/\text{mol}$ ,  $3\text{--}5\text{ \AA}$  between molecules  
(*cf.* bond lengths;  $0.5\text{--}2.5\text{ \AA}$ )

Gases:  $24000\text{ cm}^3/\text{mol}$ ,  $\sim 30\text{ \AA}$  between molecules



**Fig. 10.1** Intermolecular forces create structure in liquids and solids.  
(a) Solid (b) Liquid (c) Gas

## ➤ Compressibility

❖ **Isothermal compressibility,**  $\kappa_T = -\frac{1}{V} \left( \frac{dV}{dP} \right)_T$

~ Fractional volume decrease against the pressure increase

Solids, liquids: nearly incompressible, (nearly) in contact,  
strong intermolecular forces

Gases: highly compressible, space between molecules

## ➤ Thermal Expansion

❖ **Thermal Expansion Coefficient,  $\alpha$**

~ Fractional volume increase against the temperature increase

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

## ➤ Ideal gas

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left( \frac{\partial (nRT/P)}{\partial T} \right)_P = \frac{1}{V} \frac{nR}{P} \frac{dT}{dT} = \frac{nR}{nRT} = \frac{1}{T}$$

At 0°C,  $\alpha = \frac{1}{T} = \frac{1}{273.15} = 0.00366 \rightarrow 0.366\%$  volume increase

**T A B L E 10.1**

**Isothermal Compressibility<sup>†</sup> and Thermal Expansion Coefficients**

Compound	$\kappa / (10^{-6} \text{ atm}^{-1})$	$\alpha / (10^{-4} \text{ K}^{-1})$
<b>Liquids</b>		
Benzene	92.1	12.4
Ethanol	76.8	11.2
Mercury	38.7	1.82
Water	49.7	2.1
<b>Solids</b>		
Copper	0.735	0.501
Diamond	0.187	0.030
Iron	0.597	0.354
Lead	2.21	0.861

General<sup>†</sup> Values at 20°C.



## ➤ Fluidity and Rigidity

- Fluidity of gases and liquids vs. rigidity of solids
- **shear viscosity**: the resistance of a material to macroscopic flow  
most liquids 16 orders of magnitude smaller than those of solids

## ➤ Diffusion

- Molecules of one type migrate into regions initially occupied only by the other type.
- **diffusion constant**: measuring the rate of diffusive mixing
- In liquids, quickly changing the neighbors and finding new interactions due to low shear viscosity  
In solids, a durable arrangement of neighbors

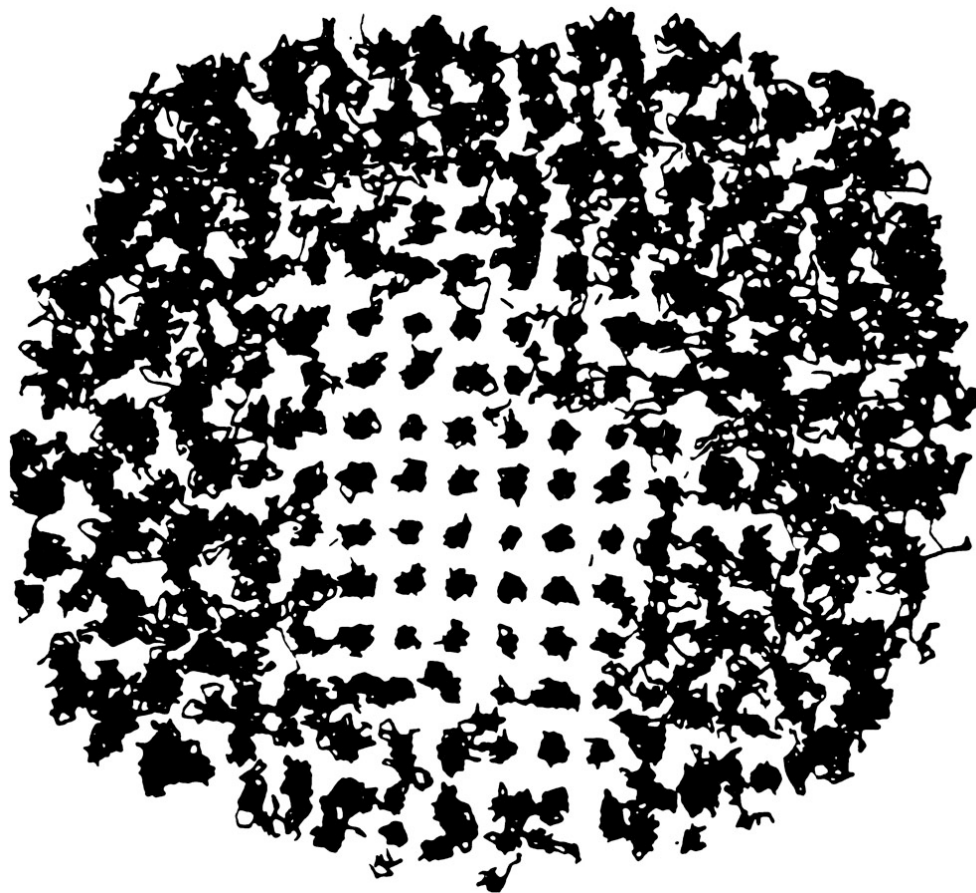
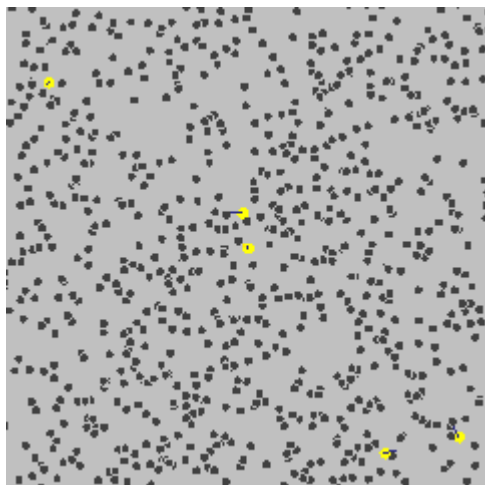
<https://www.youtube.com/watch?v=Bz02z4GSS0k>

TABLE 10.2

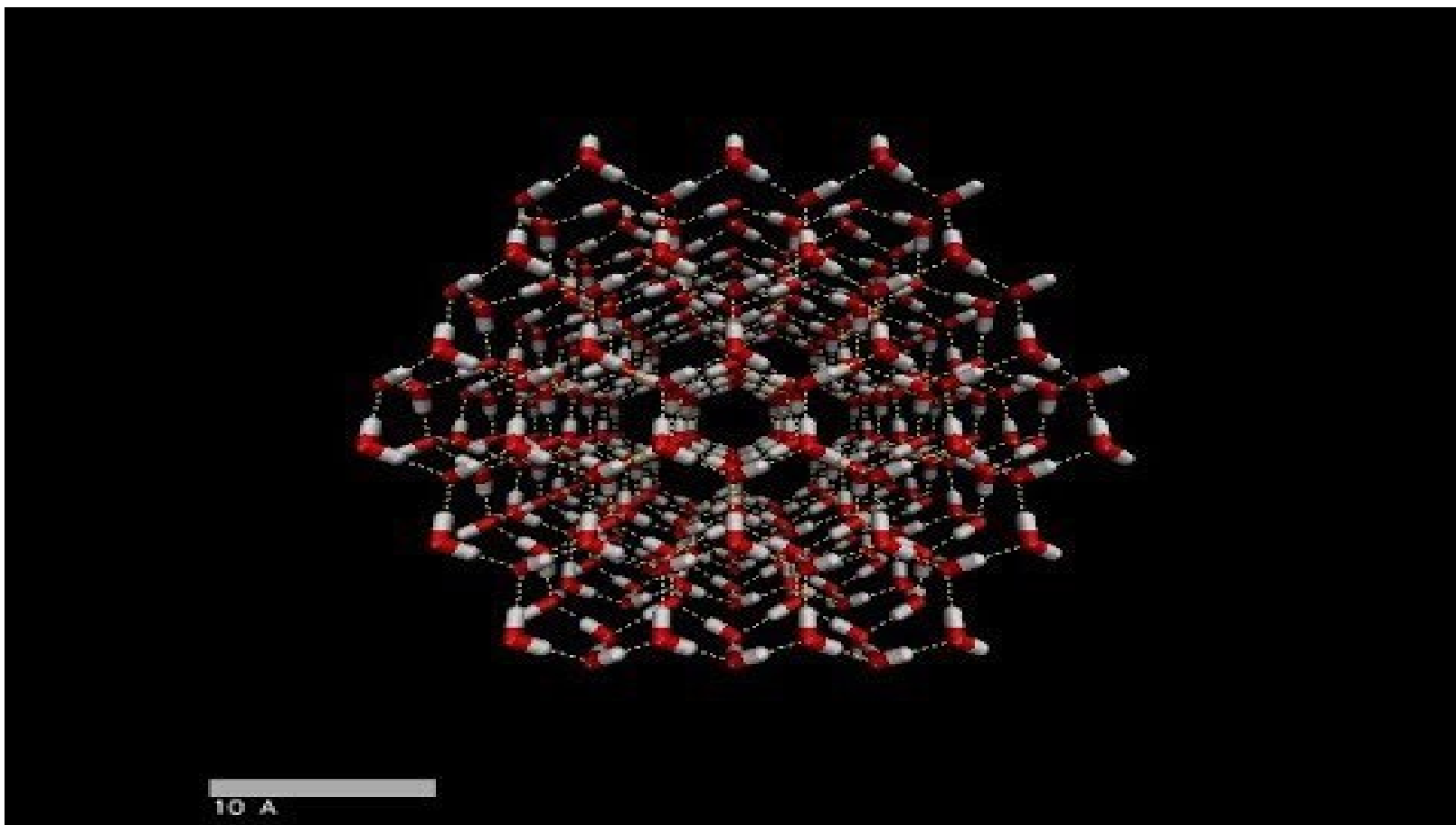
## Diffusion Constants

Diffusing Species	Host Material	Diffusion Constant ( $\text{m}^2 \text{s}^{-1}$ )	Temperature (K)
Ar	Ar	$2.3 \times 10^{-6}$	100
Ar	Ar	$1.86 \times 10^{-5}$	300
N <sub>2</sub>	N <sub>2</sub>	$2.05 \times 10^{-5}$	300
O <sub>2</sub>	O <sub>2</sub>	$1.8 \times 10^{-5}$	273
CH <sub>4</sub>	CH <sub>4</sub>	$2.06 \times 10^{-5}$	273
HCl	HCl	$1.24 \times 10^{-5}$	295
Cu	Cu	$4.2 \times 10^{-19}$	500
Al	Al	$4.2 \times 10^{-14}$	500
Cu	Al	$4.1 \times 10^{-14}$	500
Cu	Ni	$1.3 \times 10^{-22}$	500
Fe	Fe	$3.0 \times 10^{-21}$	500
Fe	Fe	$1.8 \times 10^{-15}$	900
C	Fe	$1.7 \times 10^{-10}$	900





**Fig. 10.2** Computer simulated picture of the motion of atoms in a tiny melting crystal, the atoms at the center (in the solid) moves erratically about the particular sites. The atoms at the surface (in the liquid) move much greater distance.

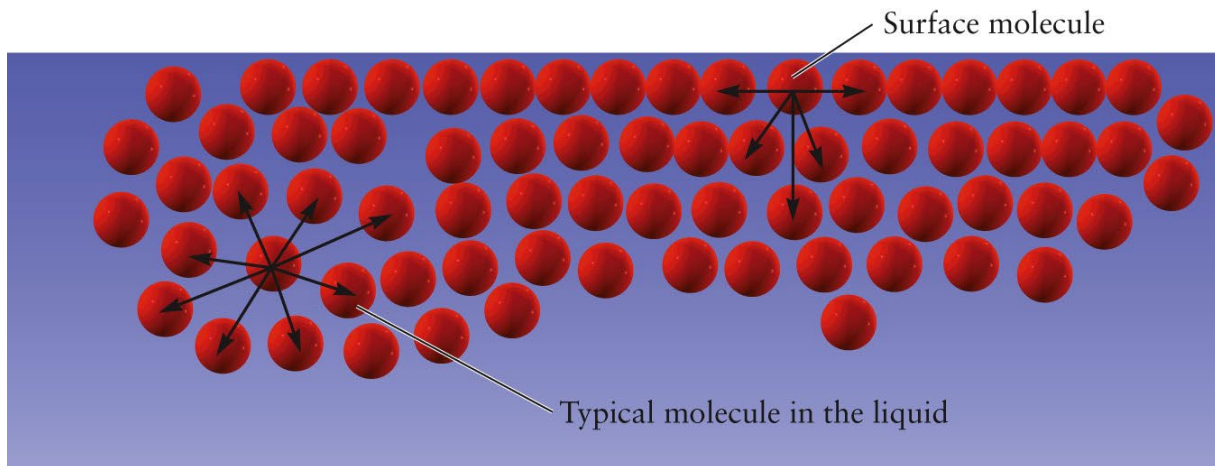


<https://www.youtube.com/watch?v=NQhjAtCKghE>

Molecular dynamics simulation of ice crystal melting

## ◆ Surface tension, $\gamma$

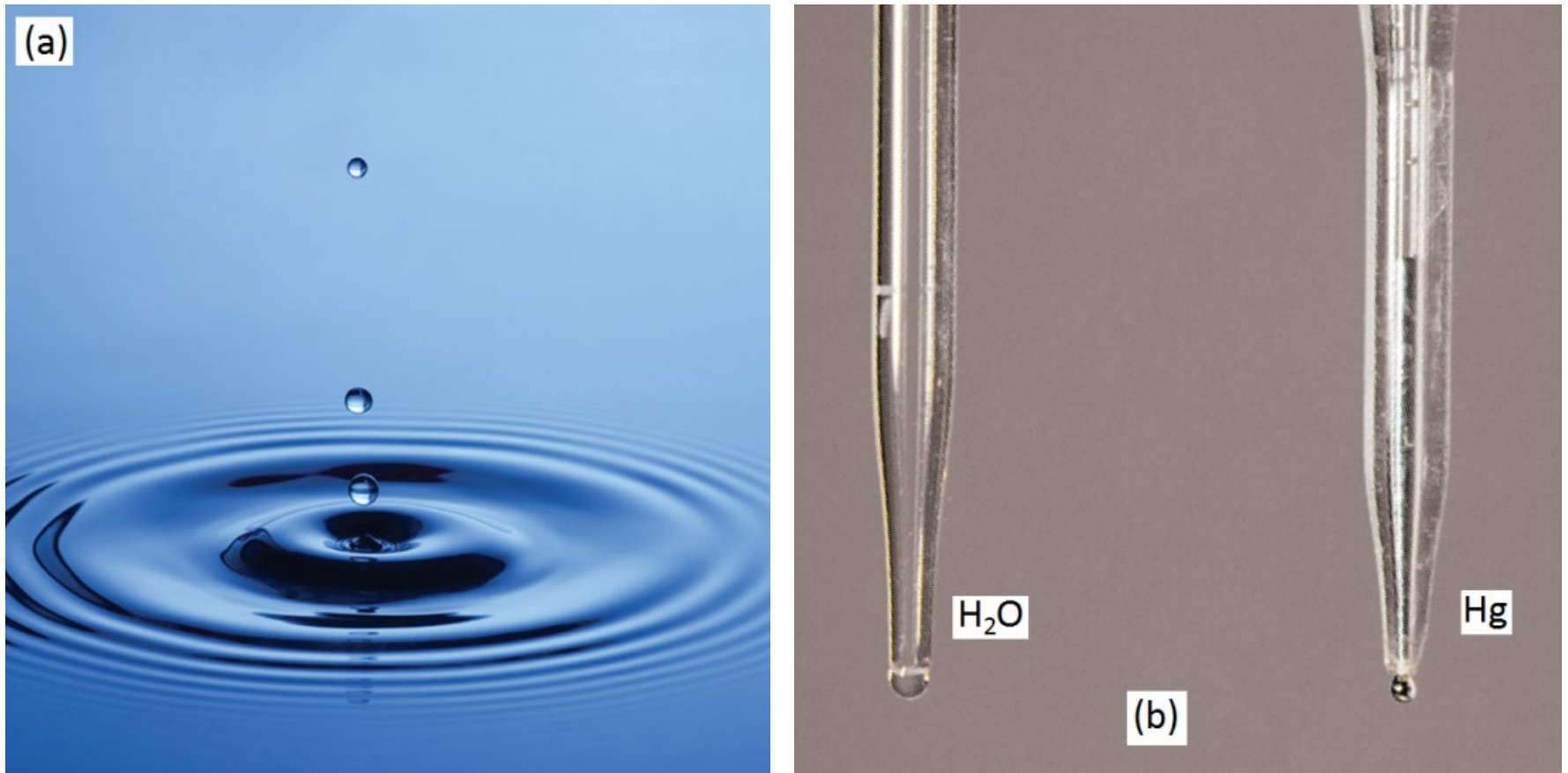
- Resistance of the surface of a liquid to an increase in its area in unit of  $\text{N}\cdot\text{m}^{-1}$  or  $\text{J}\cdot\text{m}^{-2}$
- Surface tension is the net inward pull of surface molecules.
- Liquids with strong intermolecular interaction have high surface tension.



**TABLE** Surface Tensions of Liquids at 25°C

Liquid	Surface tension, $\gamma$ ( $\text{mN}\cdot\text{m}^{-1}$ )
benzene	28.88
carbon tetrachloride	27.0
ethanol	22.8
hexane	18.4
mercury	472
methanol	22.6
water	72.75
	58.0 at 100°C

~ Tendency of a liquid toward minimal surface area → sphere



**Fig. 10.3** (a) Spherical shape of a water droplet after it hits the surface of a pool and bounced up. (b) A water drop and a mercury drop at the dropper tip. The mercury drop is a perfect sphere whereas the water drop sags slightly due to difference in the surface tension.



## 10.2 INTERMOLECULAR FORCES: ORIGINS IN MOLECULAR STRUCTURE

→ Vs intramolecular forces: weaker, less directional, at longer range

### ◆ Ion-Ion Forces

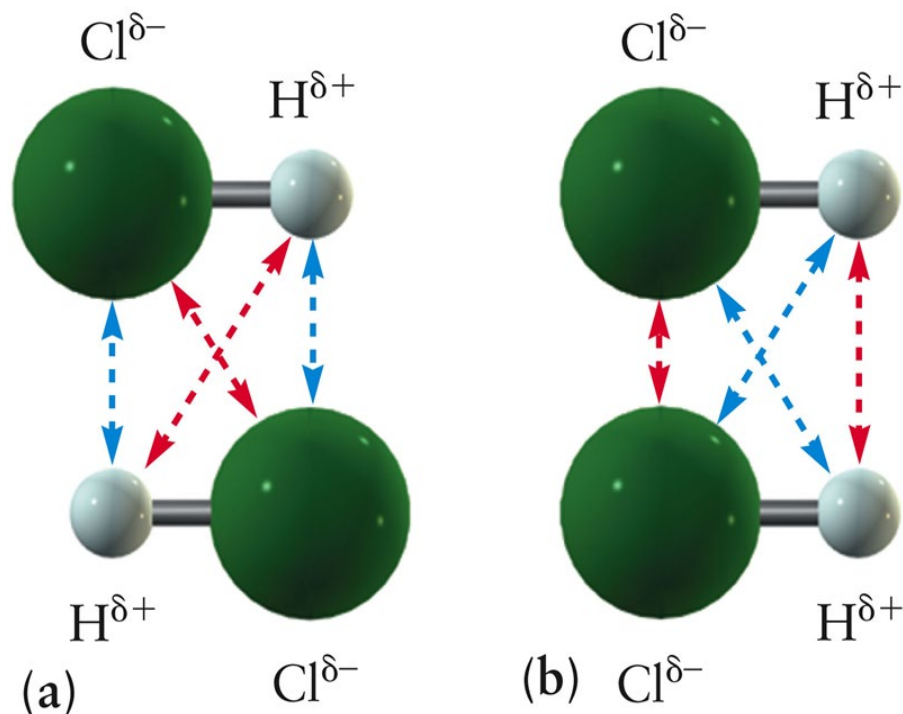
- Strong, Long-range, Not directional

$$U \propto \frac{1}{R} \quad \text{Coulombic potential}$$

### ◆ Dipole-Dipole Forces

- Depends on orientations of two dipolar molecules.
- Potential energy between two dipoles  $\propto \frac{1}{R^3}$   
~ shorter range than Coulomb potential

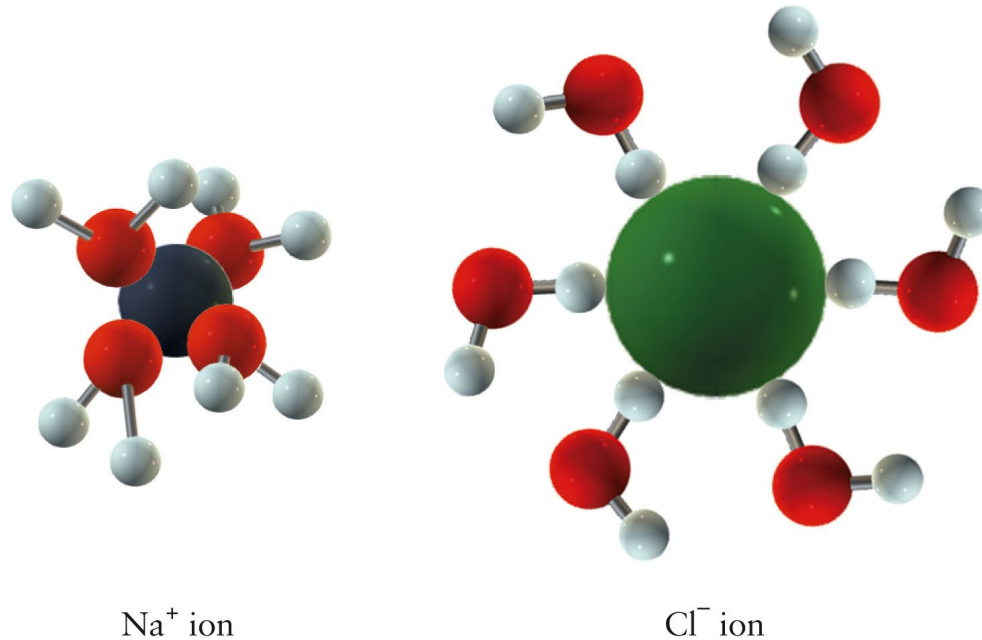
- Weaker than thermal energy:
  - ~ Can not hold a rigid molecular assembly
- Strong enough to influence b.p., m.p., and molecular orientations



**Fig 10.5** The dipole-dipole forces between two HCl molecules depend on their orientations.

## ◆ Ion-Dipole Forces

- Potential energy between ion and dipole  $\propto \frac{1}{R^2}$
- Dissolution of salts in water (polar solvent)



**Fig 10.6** Na<sup>+</sup> and Cl<sup>-</sup> ions are surrounded by water dipoles. Orientation of water molecules are reversed.

## ◆ Charge-Induced Dipole Forces

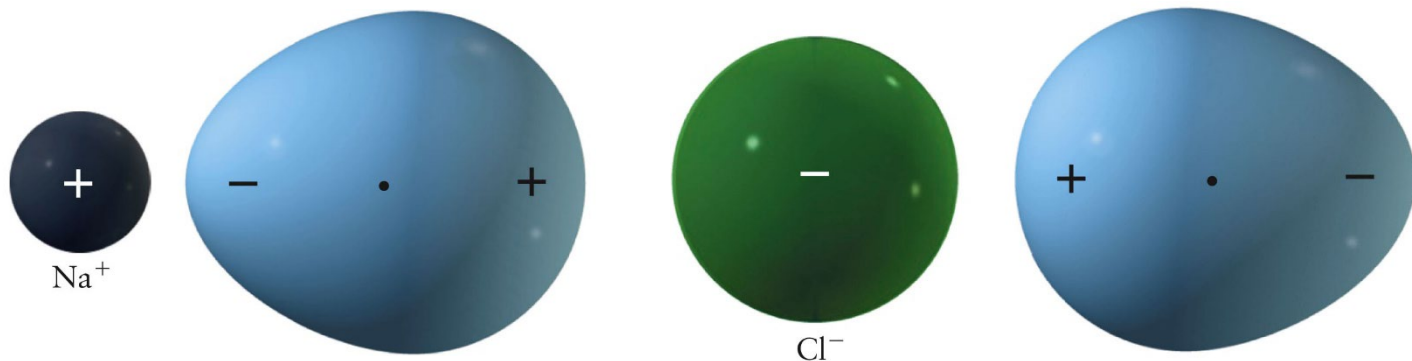
➤ Potential energy between ion and induced dipole  $\propto \frac{1}{R^4}$

➤ Weak and short range

➤ Electrical **polarizability**

~ Relative tendency of a charge distribution to be distorted from its normal shape by an external electric field

~ Measure by the magnitude of the induced dipole moment



**Fig. 10.7** Distortion of electron distribution of Ar as an ion is approached.





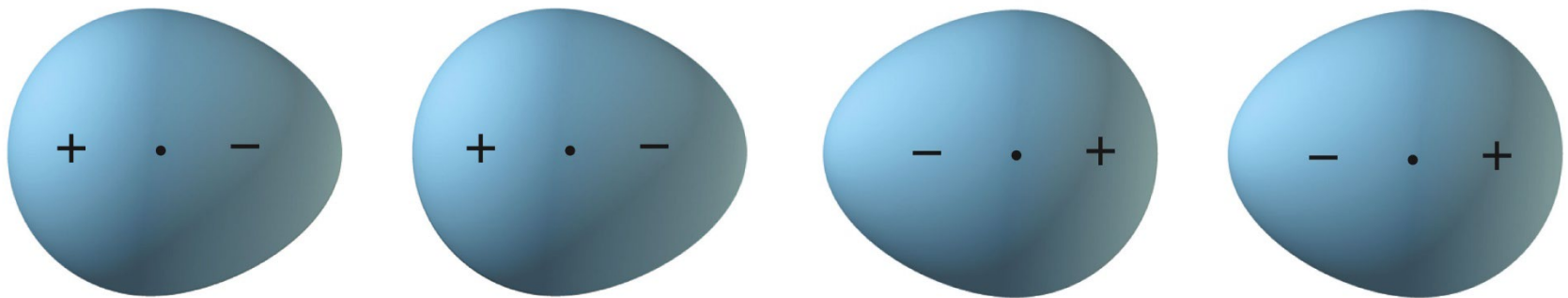
## ◆ Induced Dipole-Induced Dipole Forces

- Potential energy between two induced dipoles  $\propto \frac{1}{R^6}$
- Weak ( $\sim 1$  kJ/mol) and short range,
- Attraction between Ar atoms: **London dispersion force**

Fluctuation of electron distribution in one molecule

→ Temporary dipole

Second temporary dipole in the other → ...

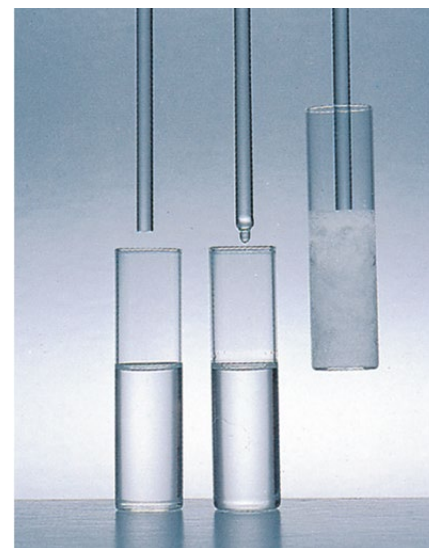


**Fig. 10.8** A fluctuation of the electron distribution on one atom induces a corresponding temporary dipole moment on a neighboring atom.

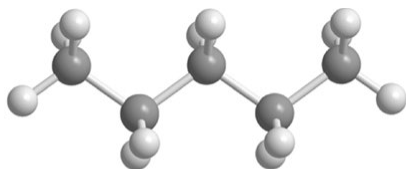


- A large molecule is likely to have a stronger London interactions than a smaller one.

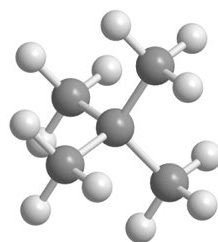
$C_5H_{12}$ ; mobile liquid  
 $C_{15}H_{32}$ ; viscous liquid  
 $C_{18}H_{38}$ ; waxy solid



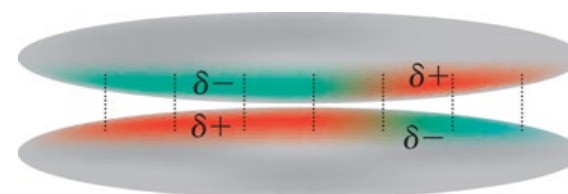
- Halogens: gases ( $F_2$ , and  $Cl_2$ ); liquid ( $Br_2$ ); solid ( $I_2$ )
- Rod-shaped (pentane;  $T_b = 36\text{ }^\circ\text{C}$ ) vs. spherical (2,2-dimethylpropane;  $T_b = 10\text{ }^\circ\text{C}$ )



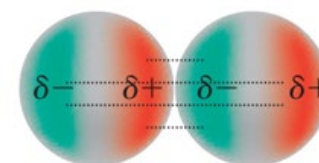
8 Pentane,  $C_5H_{12}$



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



(a)



(b)

# ◆ INTERACTIONS

▶ Ion – Ion (Coulomb):  $E_P = \frac{Q_1 Q_2}{4\pi\epsilon_0 r}$

▶ Ion – Dipole:  $E_P \propto -\frac{|z|\mu}{r^2}$

▶ Dipole – Dipole:  $E_P \propto -\frac{\mu_1 \mu_2}{r^3}$

▷ Rotating polar gas molecules\*:

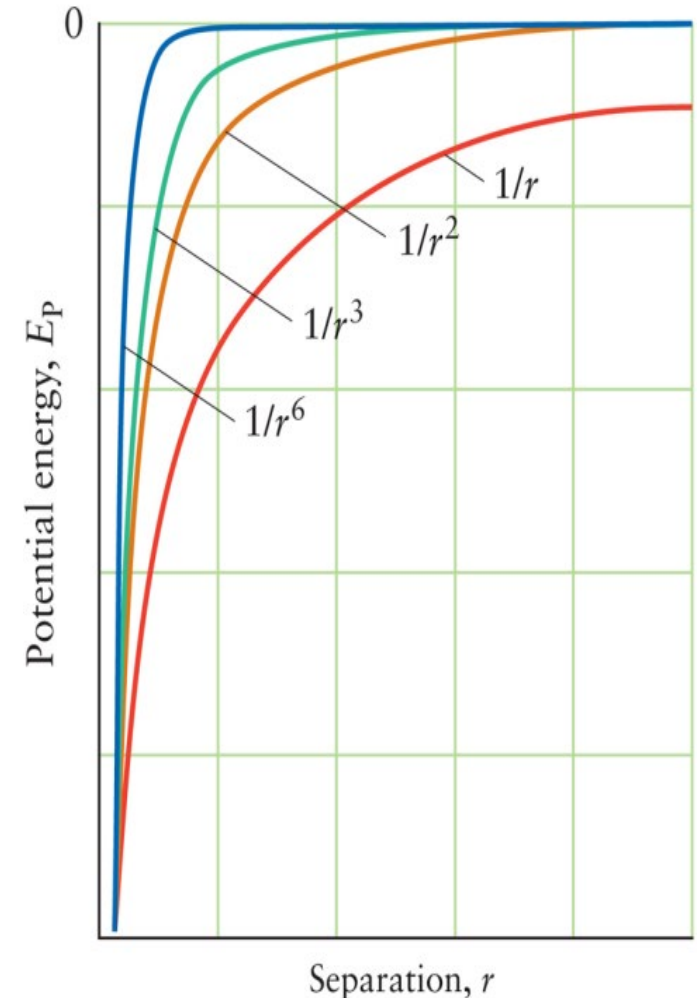
$$E_P \propto -\frac{\mu_1 \mu_2}{r^6}$$

▶ Dipole – Induced dipole\*:  $E_P \propto -\frac{\mu_1^2 \alpha_2}{r^6}$

▶ London (dispersion)\*:  
(Induced dipole –  
Induced dipole)  $E_P \propto -\frac{\alpha_1 \alpha_2}{r^6}$

\* Van der Waals interactions  $E_P \propto -\frac{C}{r^6}$

General Chemistry I



Potential Energies  
between ions,  
ions and dipoles,  
stationary dipoles, and  
rotating dipoles.

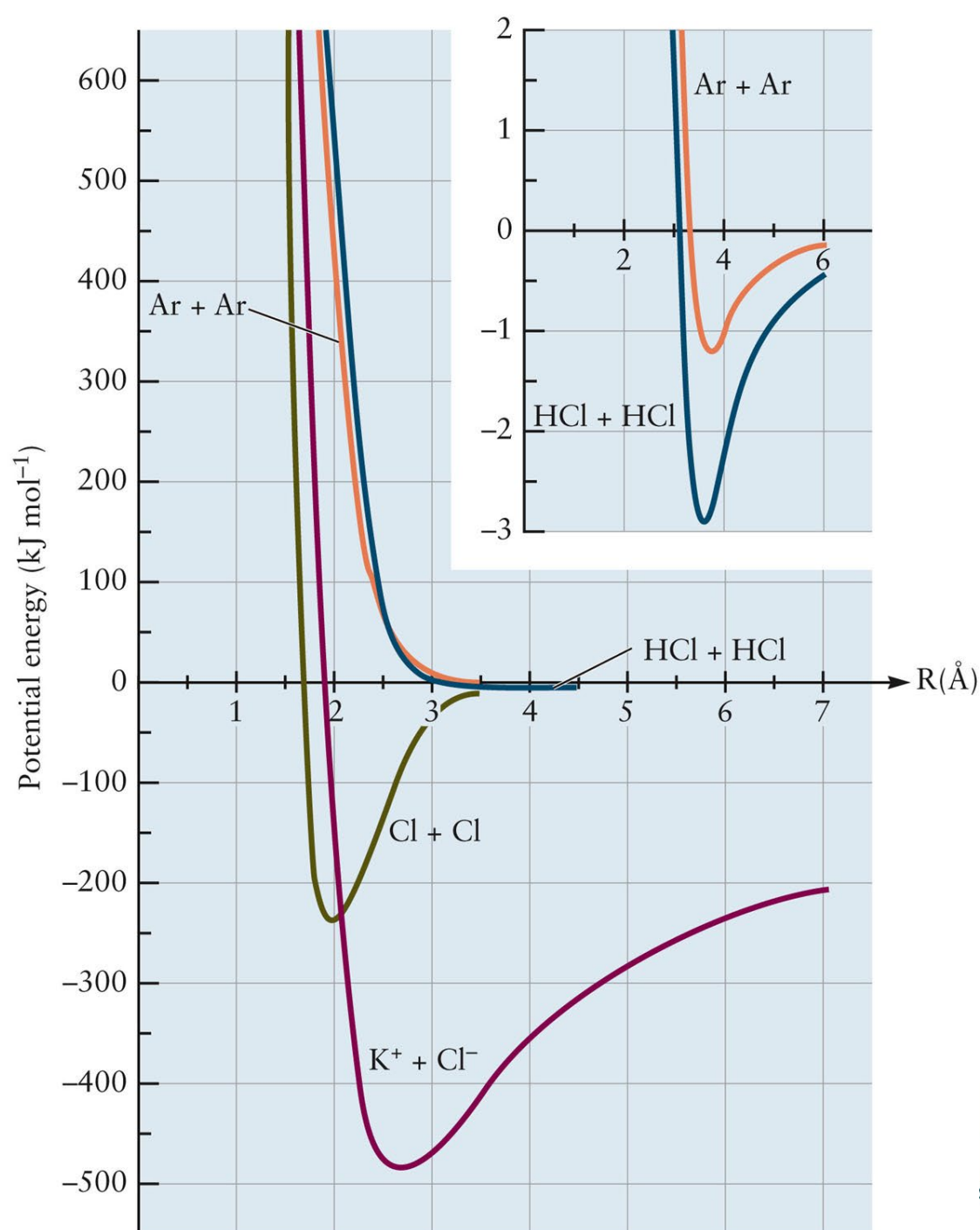
Ar + Ar : dispersion only

HCl + HCl : dipole-dipole  
and dispersion

Cl + Cl : covalent interaction

$K^+ + Cl^-$  : ion-ion interaction

General Chemistry I



## TABLE. Interionic and Intermolecular Interactions

Type of interaction	Typical energy (kJ·mol <sup>-1</sup> )	Interacting species
ion–ion	250	ions only
ion–dipole	15	ions and polar molecules
dipole–dipole	2	stationary polar molecules
	0.3	rotating polar molecules
dipole–induced-dipole	2	at least one molecule must be polar
London (dispersion) <sup>†</sup>	2	all types of molecules
hydrogen bonding	20	molecules containing an N–H, O–H, or F–H bond; a shared H atom links the molecules

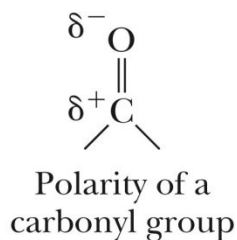
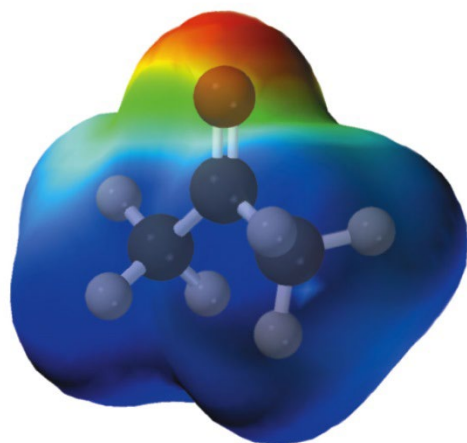
\*The total interaction experienced by a species is the sum of all the interactions in which it can participate.

<sup>†</sup>Also known as the induced-dipole–induced-dipole interaction.

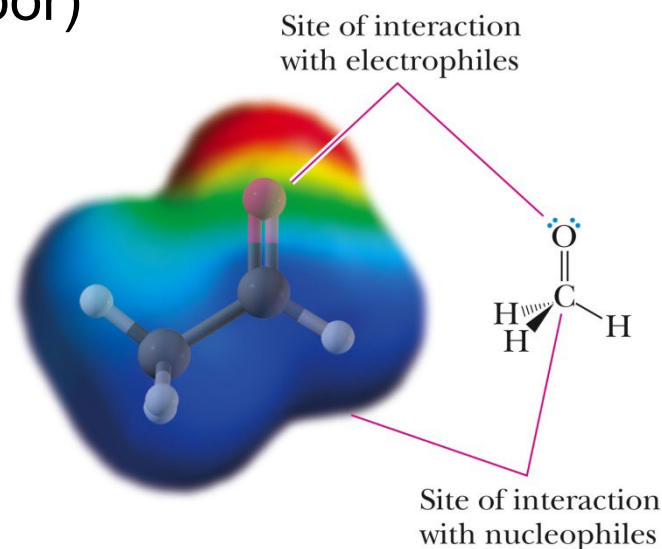
## ◆ Shape of Molecules and Electrostatic Forces

### ➤ Electrostatic potential energy map

~ Shows the shape and size of the molecule, the sign and magnitude of the electrostatic potential at the “surface” of the molecule. (electron rich/poor)



**Fig. 10.10** Electrostatic potential energy map of acetone.



**Fig. 10.11** Electrostatic potential energy map of acetaldehyde.

→ The dipole moment and charge separation are shown in both figures.

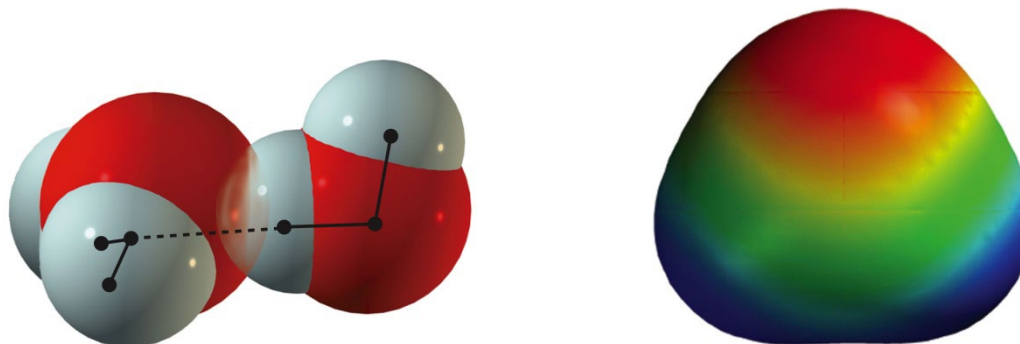
## 10.3 INTERMOLECULAR FORCES IN LIQUIDS

### ◆ Hydrogen bonding, $\sim 20 \text{ kJmol}^{-1}$

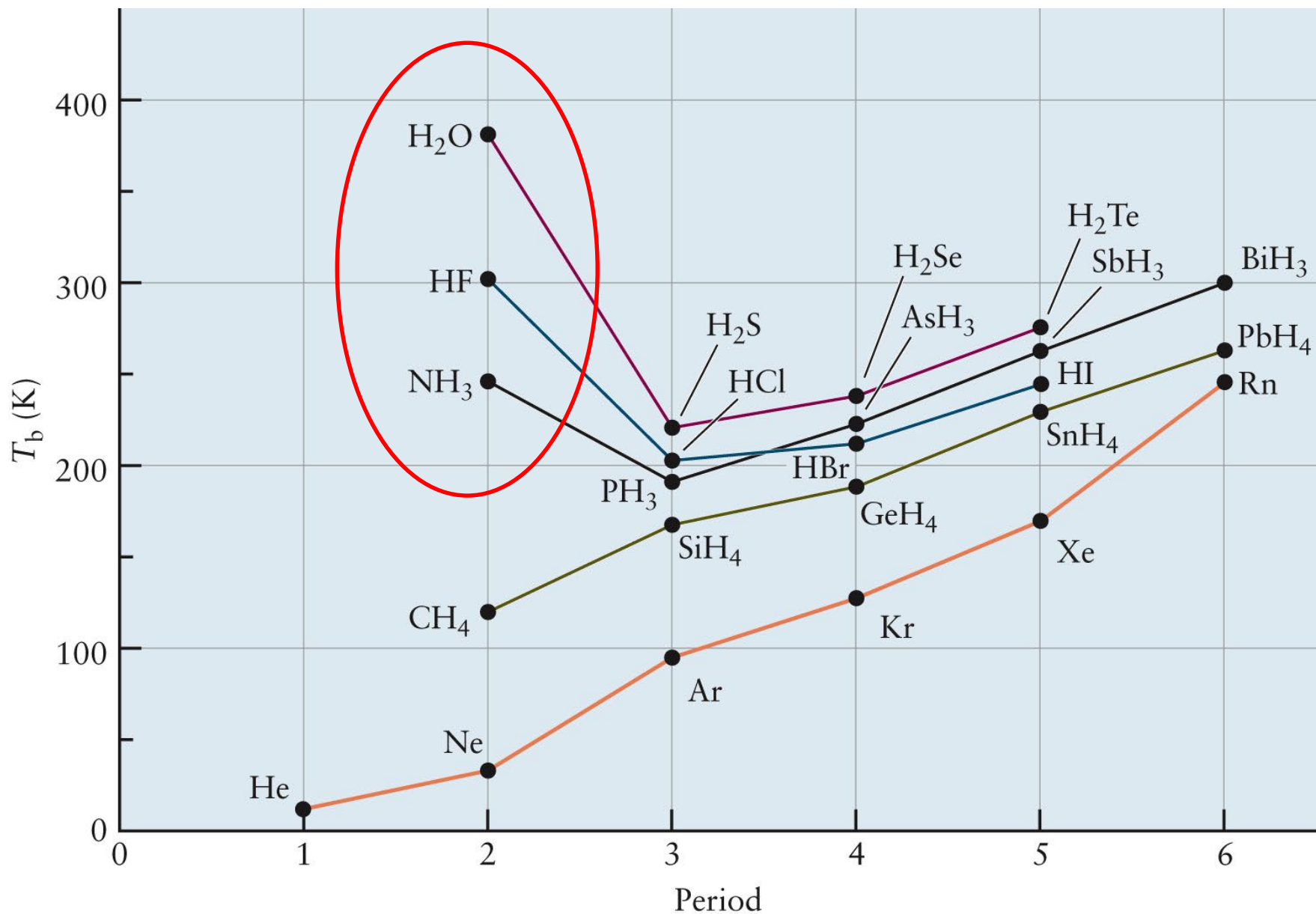
H bonded to O, N, F (electronegative, lone-pair) interacts with a lone electron pair of another nearby O, N, or F



Strong **electrostatic** interaction; stronger than most intermolecular interactions Ex.  $\text{H}_2\text{O}$ , HF,  $\text{NH}_3$



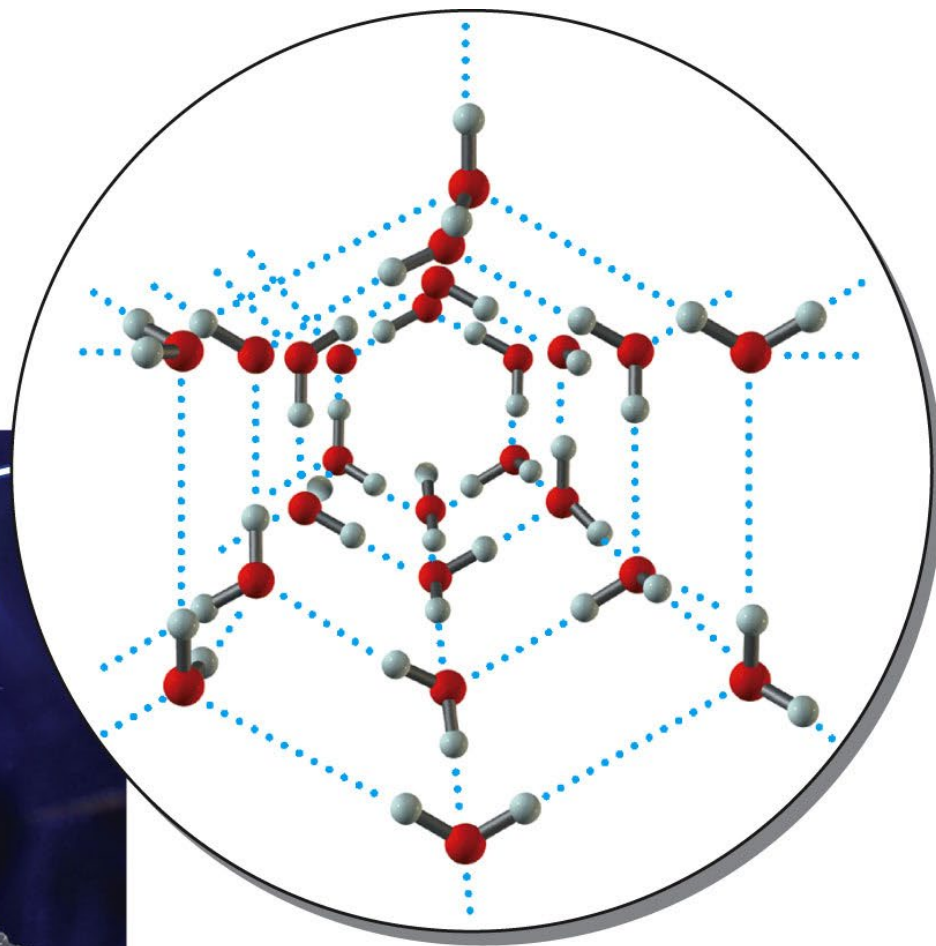
**Fig. 10.13** A single hydrogen bond between water molecules forms a dimer and the electrostatic potential energy map for  $\text{H}_2\text{O}$ .



**Fig. 10.12** The boiling points of hydrides of some main group elements and the noble gases.

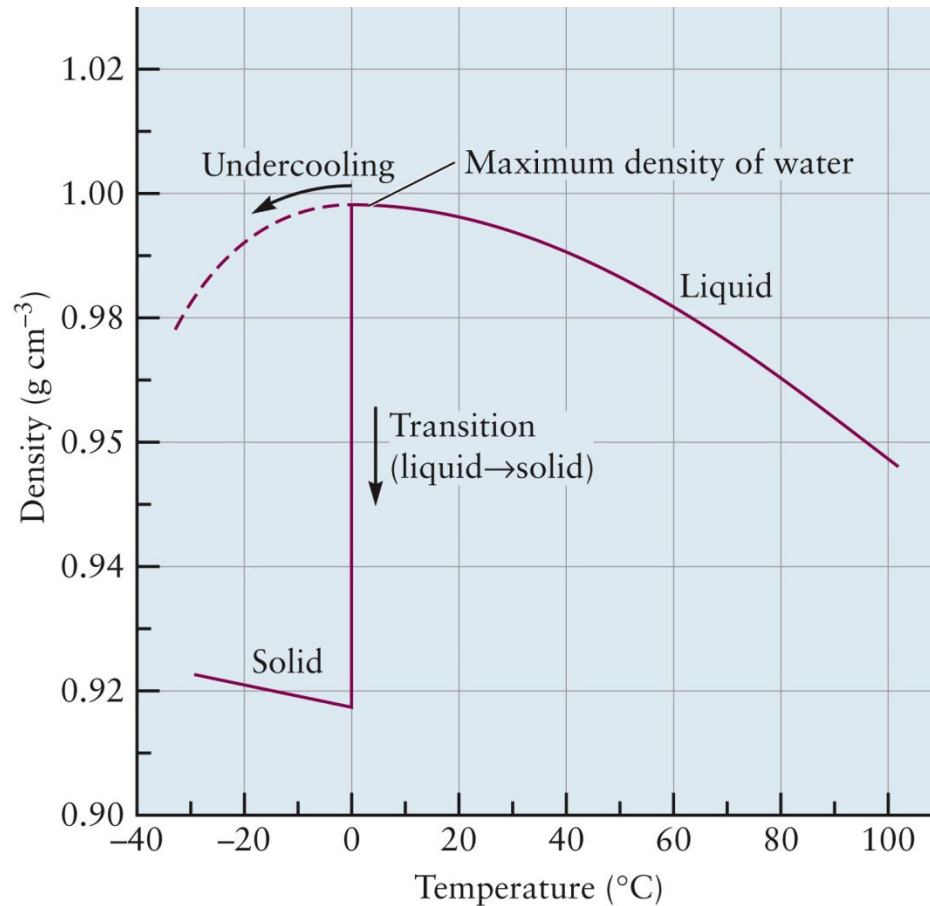


## The structure of ice



## ➤ Special Properties of Water

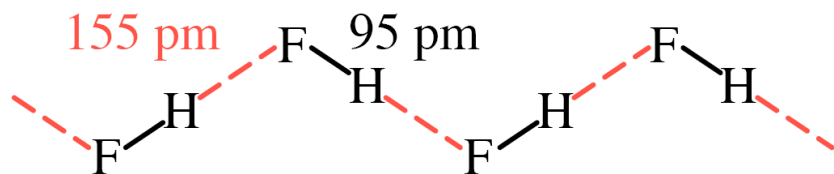
Maximum density at 3.98°C, high  $T_b$ , high heat capacity



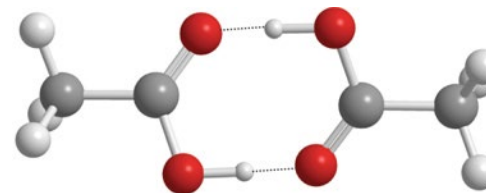
Density of ice is smaller than water!

Gen Ice remains at the surface. Warm water under the ice.

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



- Acetic acid dimer (vapor)

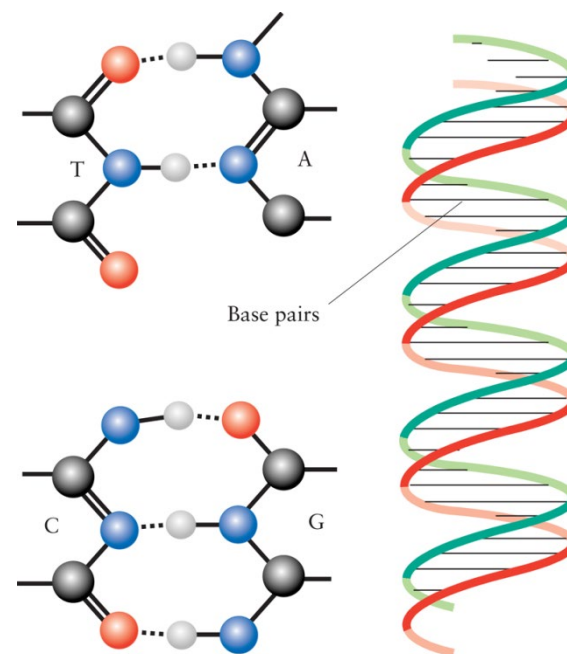


12 Acetic acid dimer

- upright trees

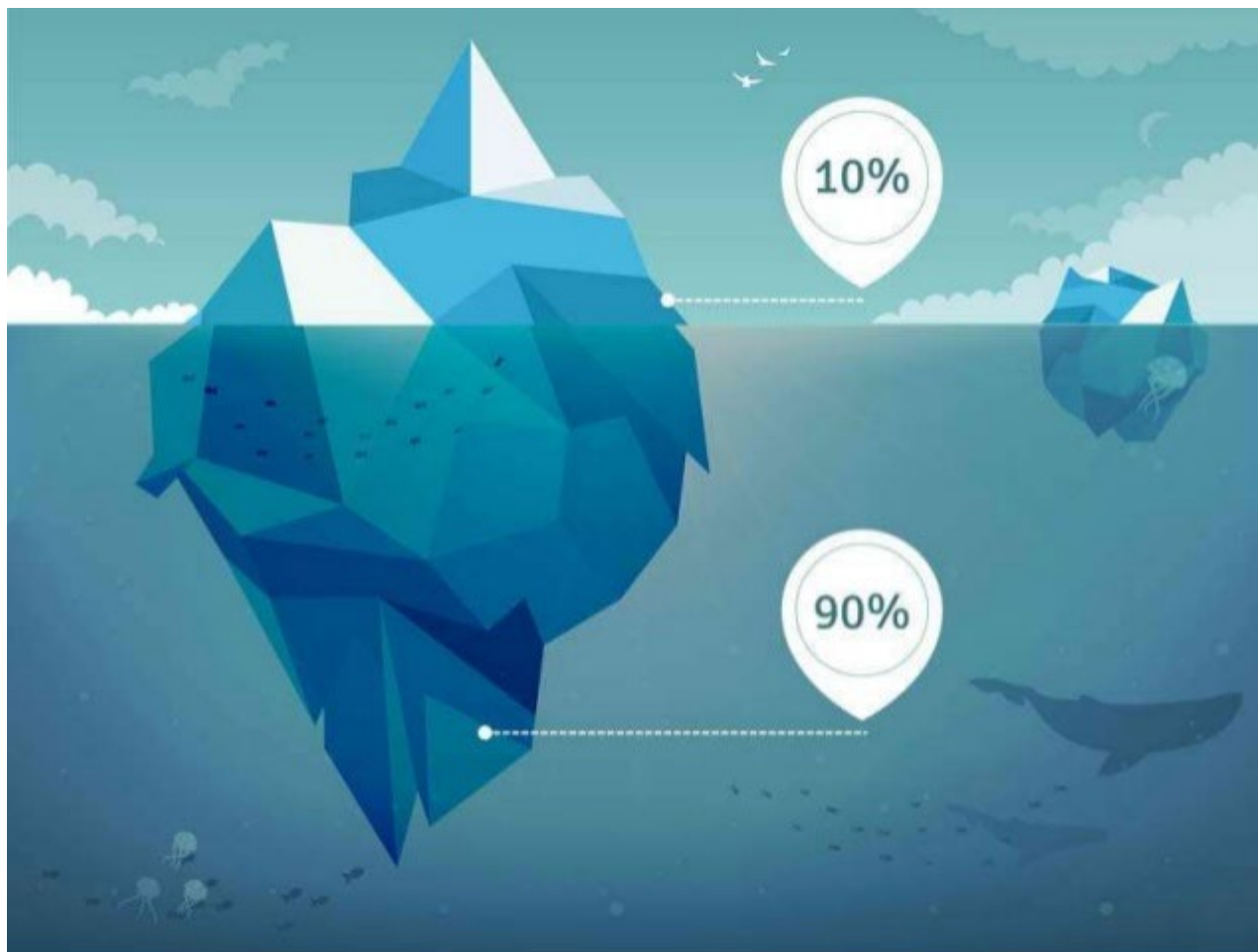


- DNA double strand





General Chemistry I



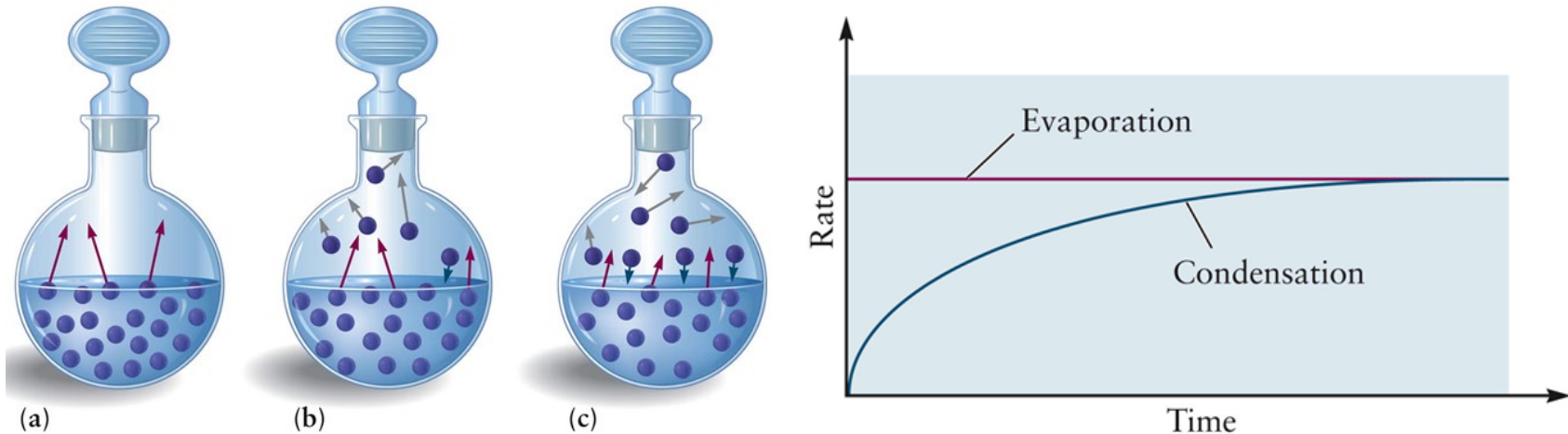
## 10.4 PHASE EQUILIBRIUM

❖ **Phase** ~ a sample of matter uniform throughout in both chemical and physical states

➤ **Phase Equilibrium**

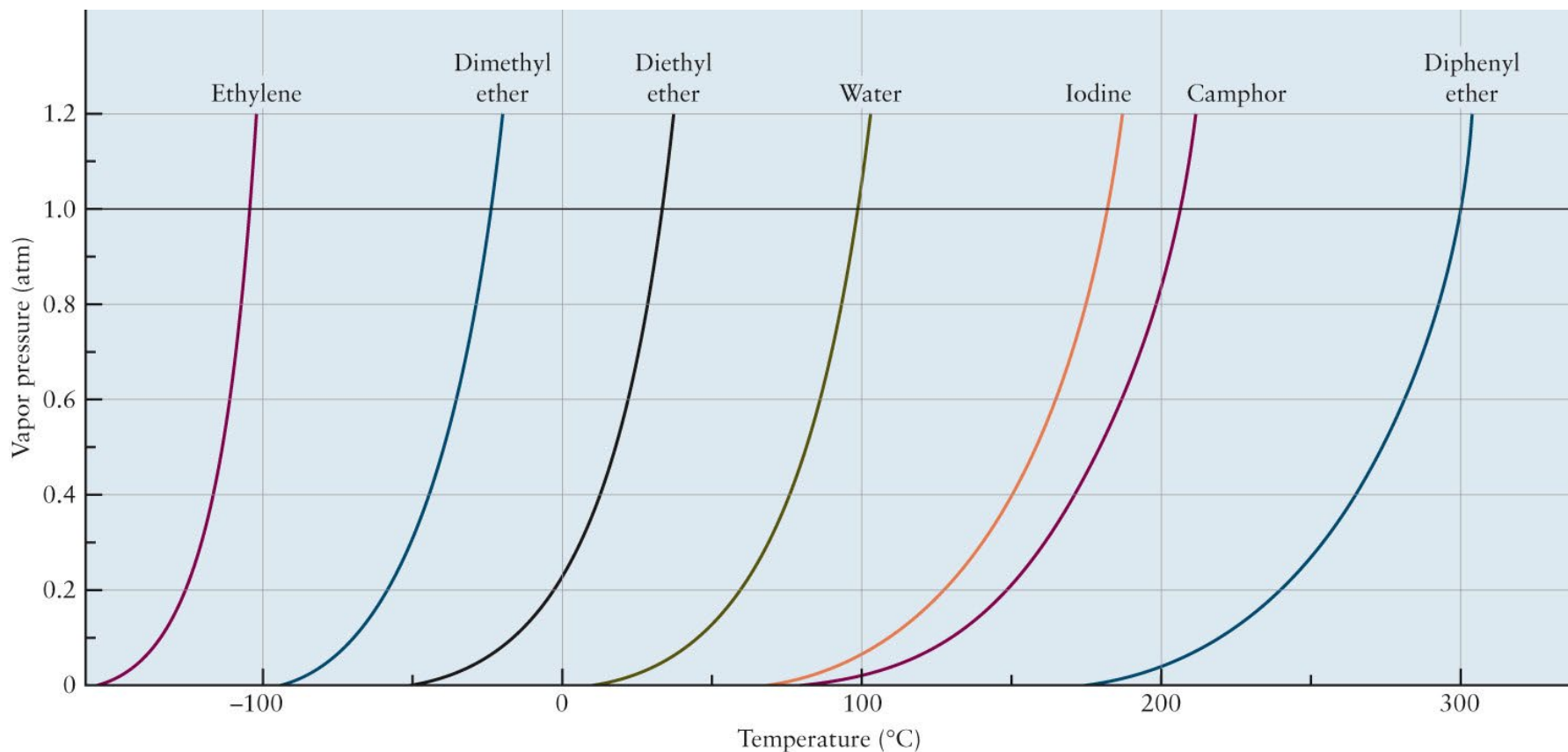
dynamic process; no net flow of matter between phases  
*rate of evaporation = rate of condensation*

independent of the direction (with enough material)



Gen **Fig. 10.16** Approach to equilibrium in evaporation and condensation.





**Fig. 10.17** Vapor pressure vs. temperature. The temperature at which the vapor pressure becomes 1 atm defines the **normal boiling point** of liquid and the **normal sublimation point** of a solid.

$$P_{\text{vapor}}(\text{water}) = 0.03126 \text{ atm (at } 25^{\circ}\text{C)}$$

$$= 1 \text{ atm (at } 100^{\circ}\text{C)}$$

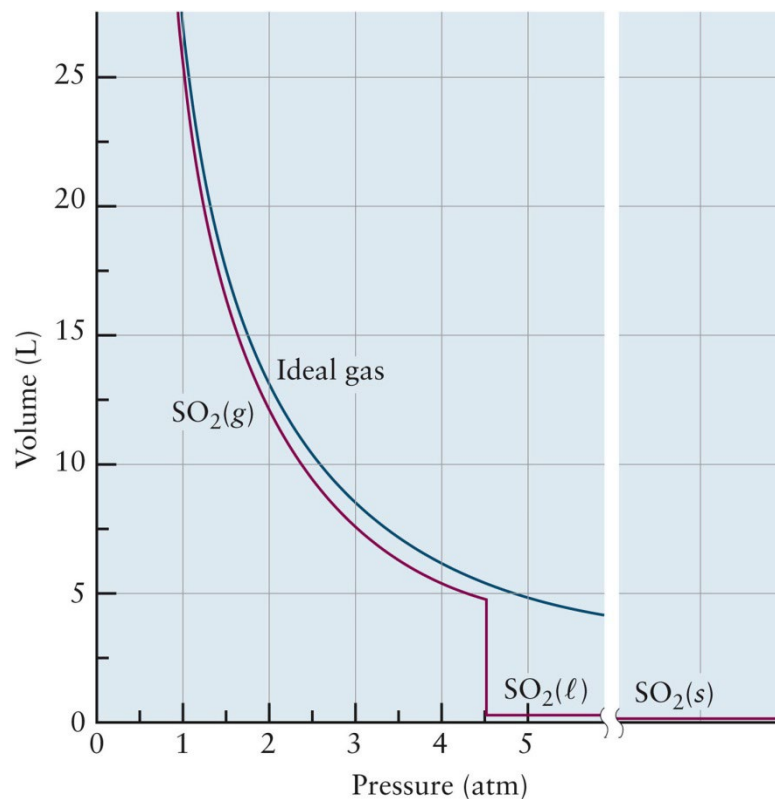
← normal boiling point

$$P_{\text{vapor}}(\text{CO}_2) = 1 \text{ atm (at } -78.5^{\circ}\text{C)}$$

← normal sublimation point

## 10.5 PHASE TRANSITIONS

~ Transformation of a thermodynamic system from one phase or state of matter to another



$$P = 4.52 \text{ atm}$$

$$V = 5.50 \text{ L (Ideal gas: } PV = nRT) \\ = 4.74 \text{ L (van der Waals Eq.)}$$

$$P > 4.52 \text{ atm}$$

liquefying (*l*), freezing (*s*)

❖ Liquefying:

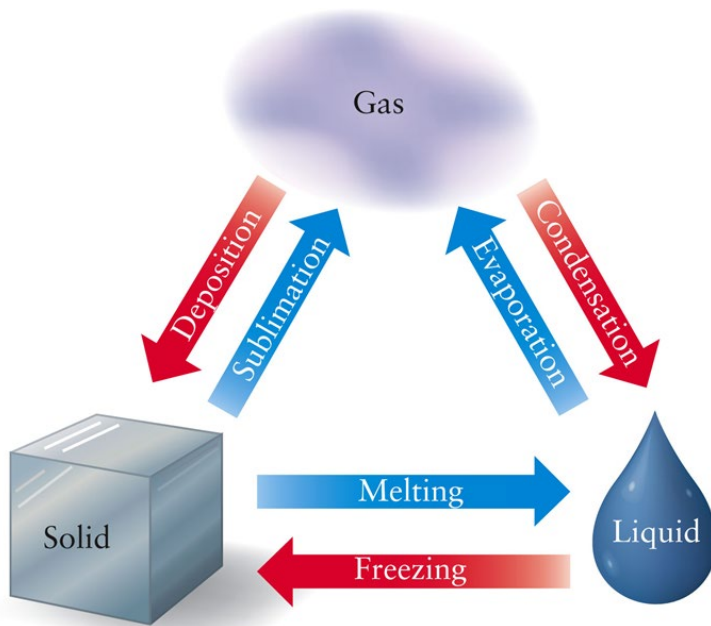
**inter**molecular attractions  
> kinetic energy ( $3/2 RT$ )

**Fig. 10.18.** Compression of 1 mol SO<sub>2</sub> at 30°C.



## ➤ Phase transitions between three states

Gas	$\xrightleftharpoons[\text{Evaporation}]{\text{Condensation}}$	Liquid	Boiling point, $T_b$
Liquid	$\xrightleftharpoons[\text{Melting}]{\text{Freezing}}$	Solid	Melting (Freezing) point, $T_f$
Gas	$\xrightleftharpoons[\text{Sublimation}]{\text{Deposition}}$	Solid	Sublimation point, $T_s$



**Fig. 10.19** Six phase transitions.

### ❖ Superheating

~ Raising the temperature of a liquid above its b.p. without it becoming a gas

### ❖ Supercooling (undercooling)

~ Lowering the temperature of a liquid or a gas below its f.p. without it becoming a solid

➔ Substances whose chemical identities change before their physical state changes do not have normal melting or boiling points.

## 10.6 PHASE DIAGRAMS

### ➤ Phase Diagram

A plot of  $P$  vs.  $T$  showing the stable state of a substance

Phase boundaries, Triple point, Critical point

### ➤ Triple point

Three phases coexist in equilibrium

$$T = 0.01^\circ\text{C}, P = 0.006 \text{ atm for water}$$

### ➤ Critical point

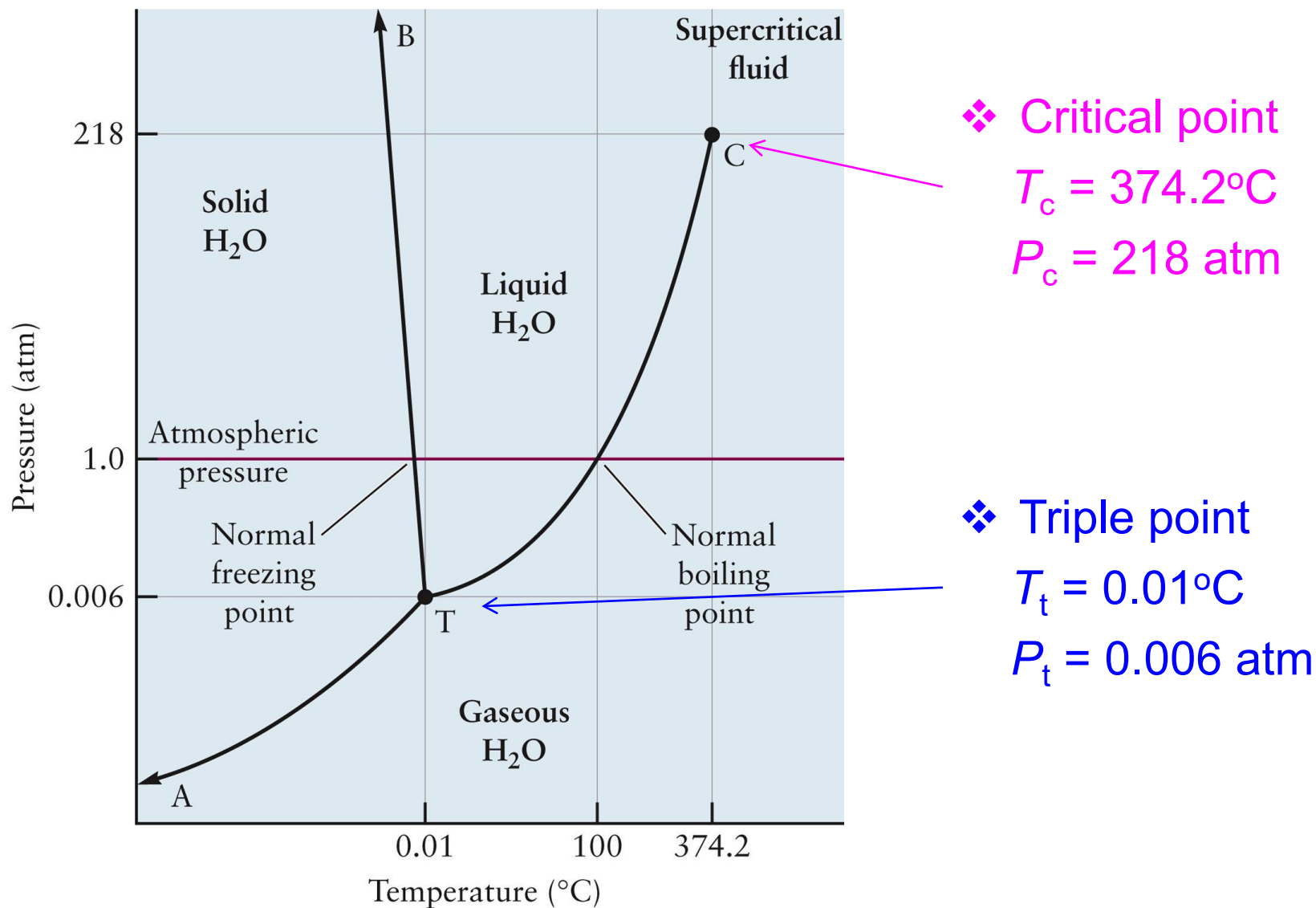
Terminal point of liquid-gas boundary

Supercritical fluid ~ no phase boundary (no meniscus)

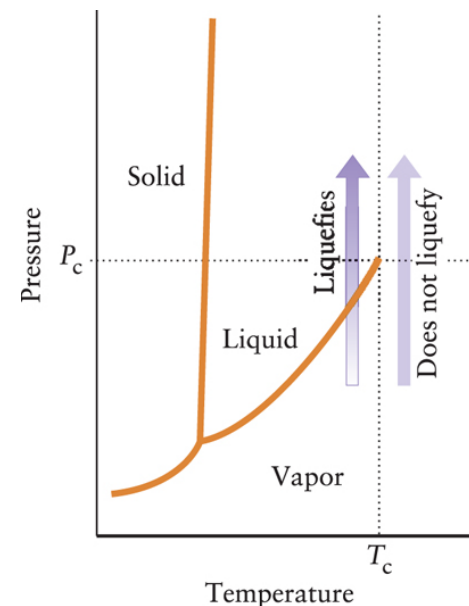
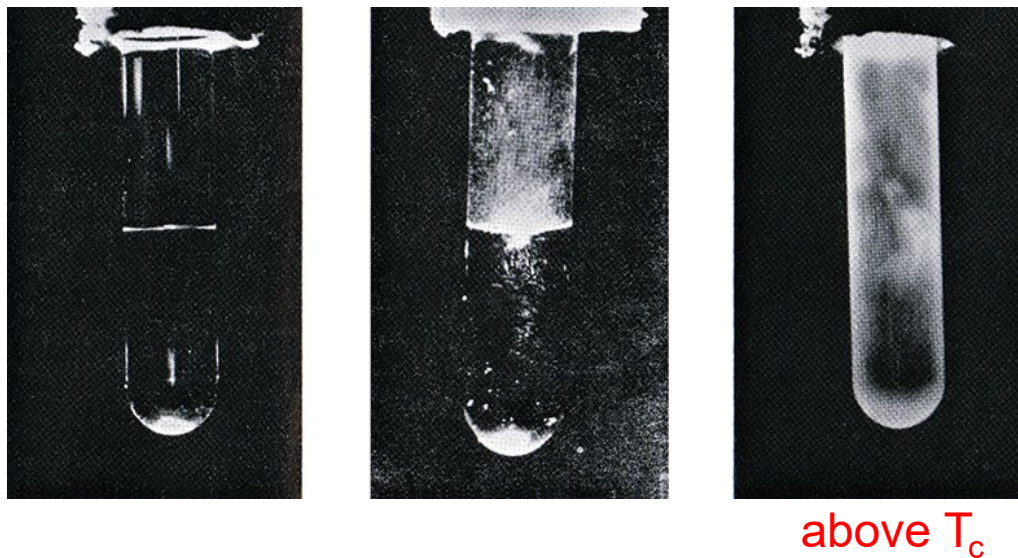
~ critical opalescence

$$T_c = 374.2^\circ\text{C}, P_c = 218 \text{ atm for water}$$

→ The differences between the properties of the liquid and the gas become smaller as the critical point is approached and disappear altogether at that point.



**Fig. 10.21** Phase diagram for water.

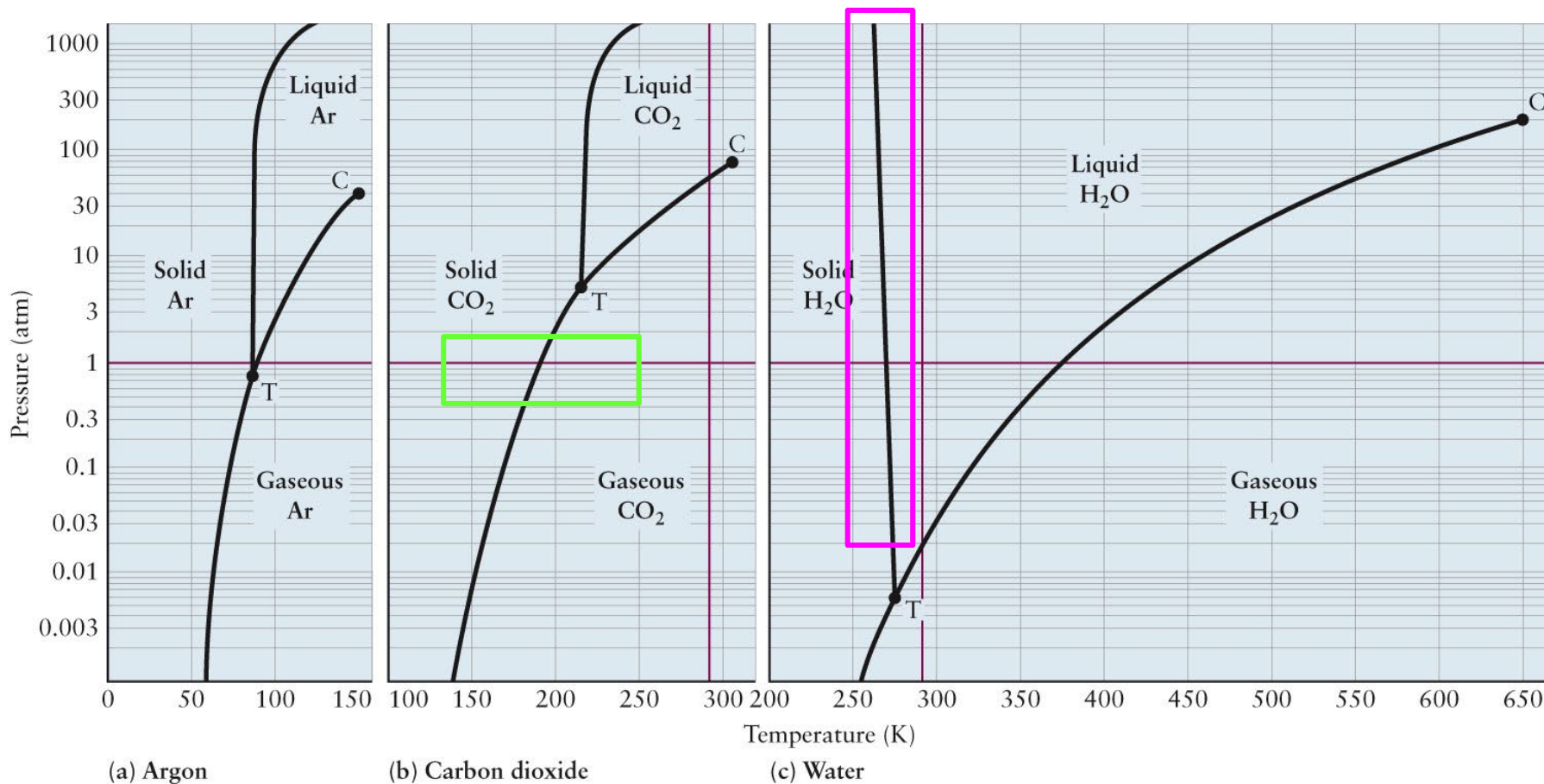


- **Supercritical fluid** – formally a gas, but is dense as a liquid phase and can act as a solvent for liquids and solids.

➔ **supercritical CO<sub>2</sub>**: solvents for green chemical reactions; no use of harmful solvents and rapid extraction due to high mobility

i.e.) removing caffeine from coffee beans

Substance	Critical temperature (°C)	Critical pressure (atm)
He	-268 (5.2 K)	2.3
Ne	-229	27
Ar	-123	48
Kr	-64	54
Xe	17	58
H <sub>2</sub>	-240	13
O <sub>2</sub>	-118	50
H <sub>2</sub> O	374	218
N <sub>2</sub>	-147	34
NH <sub>3</sub>	132	111
CO <sub>2</sub>	31	73
CH <sub>4</sub>	-83	46
C <sub>6</sub> H <sub>6</sub>	289	49



**Fig. 10.23** Phase diagrams of Ar, CO<sub>2</sub>, and water.

- ❖ Phase boundary between ice (s) and water (l) → negative slope
- ❖ Sublimation of dry ice to CO<sub>2</sub>(g) at 1 atm

## Key question: what is the origin of phase transitions?

