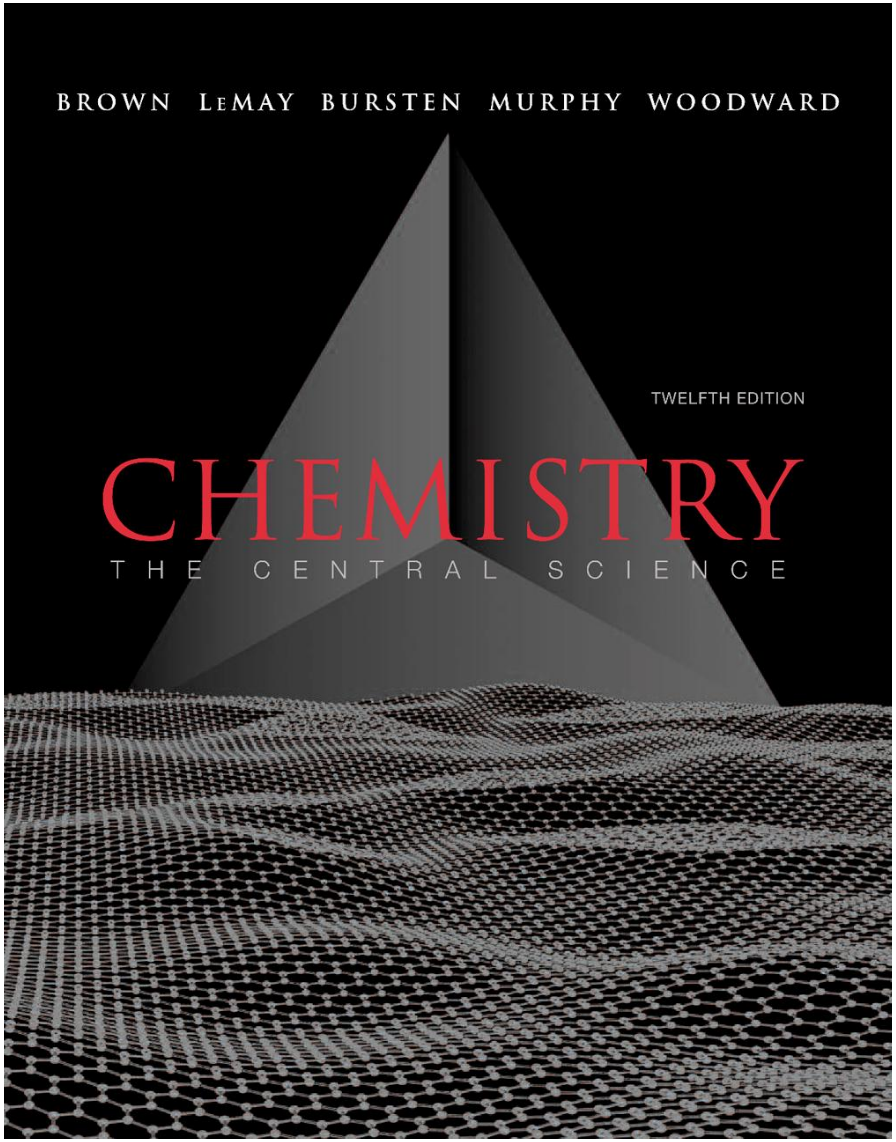

Lecture Presentation

Chapter 11

Liquids and Intermolecular Forces

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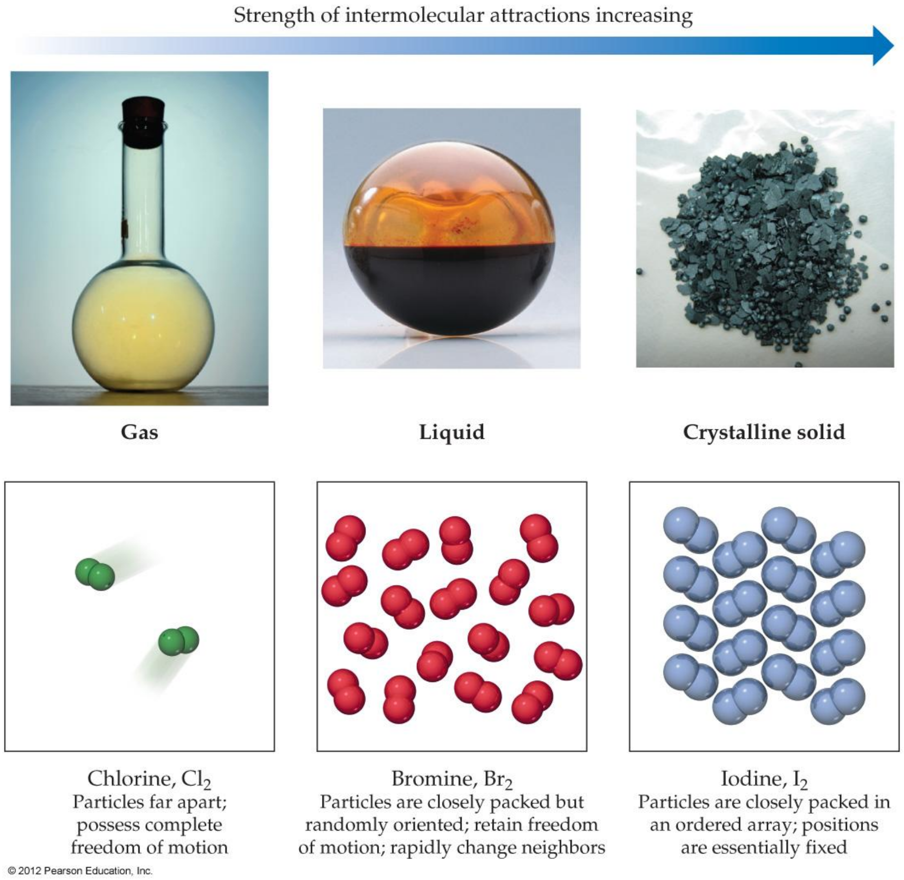
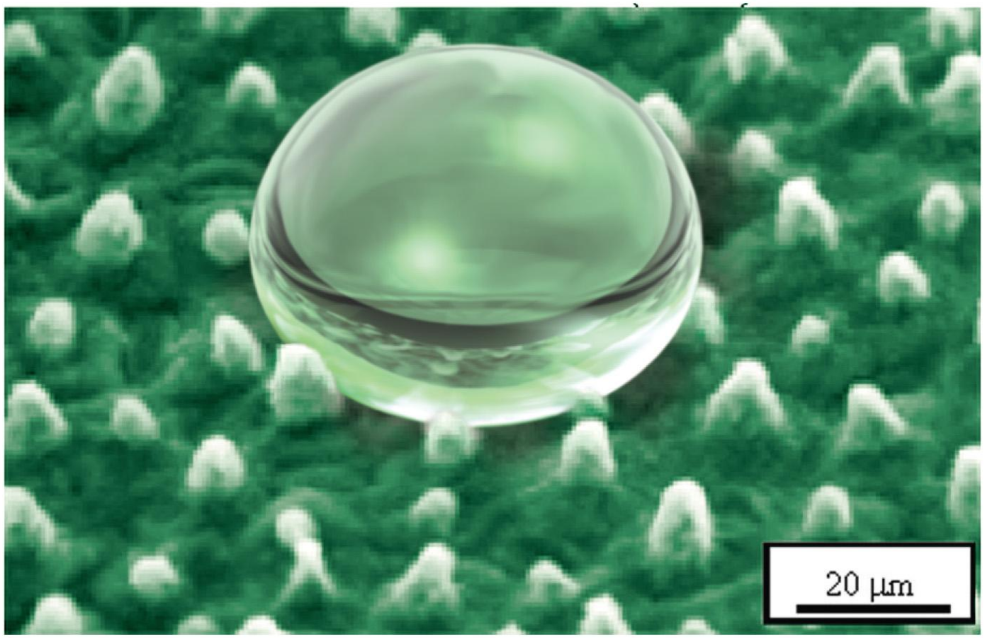
States of Matter

The fundamental difference between states of matter is the distance between particles.



States of Matter

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

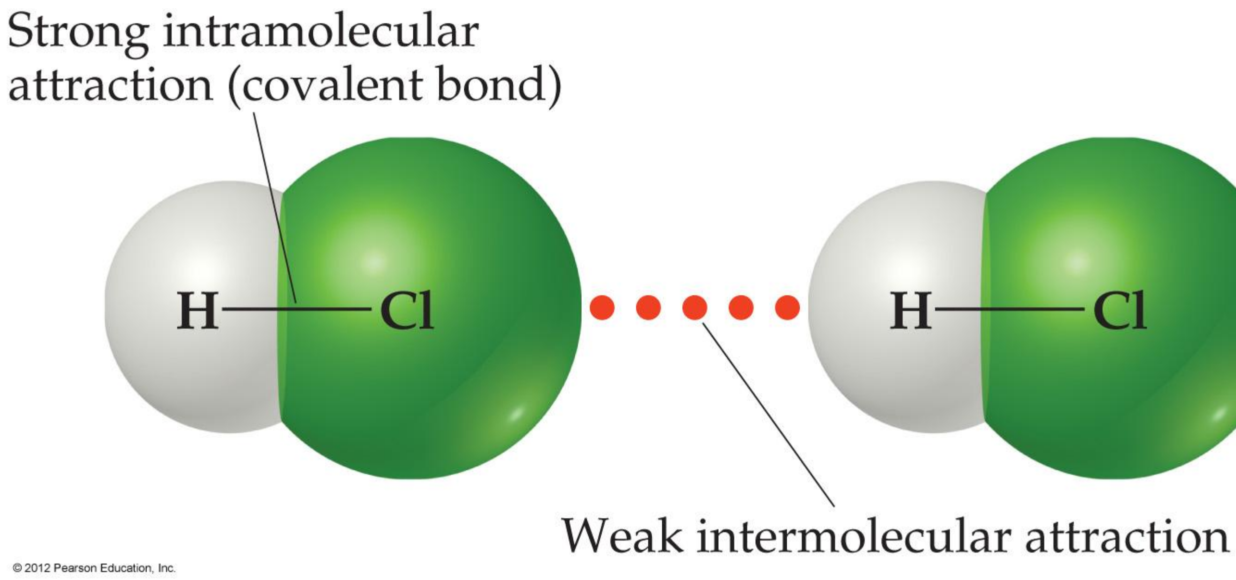


The States of Matter

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

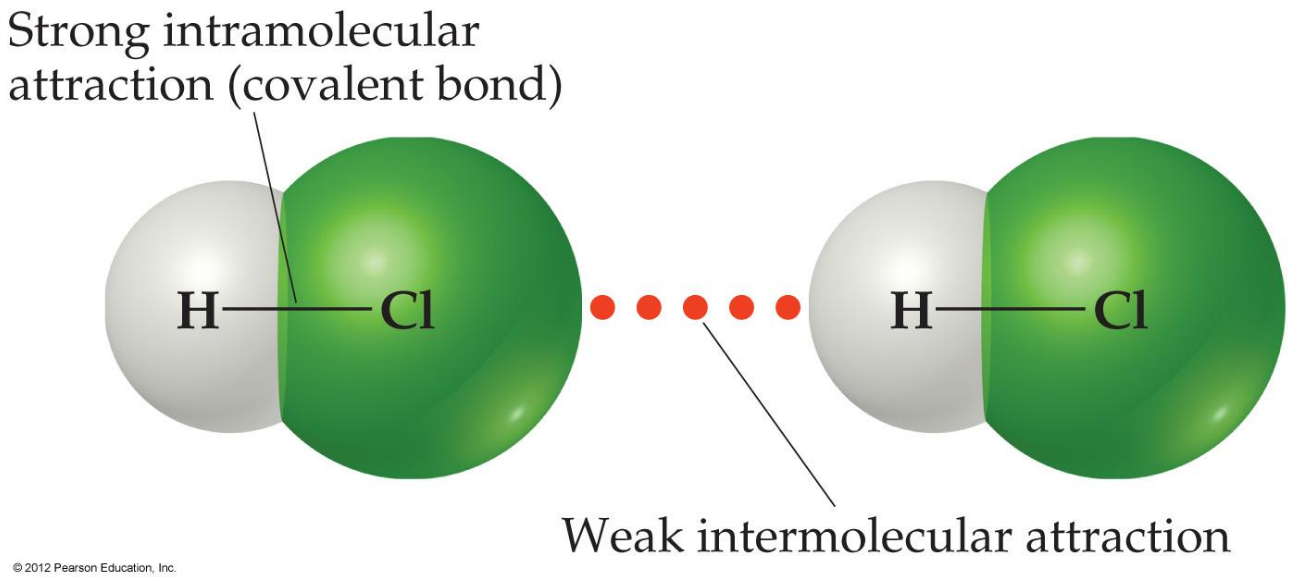
- The state a substance is in at a particular temperature and pressure depends on two antagonistic entities:
  - The kinetic energy of the particles.
  - The strength of the attractions between the particles.

Intermolecular Forces



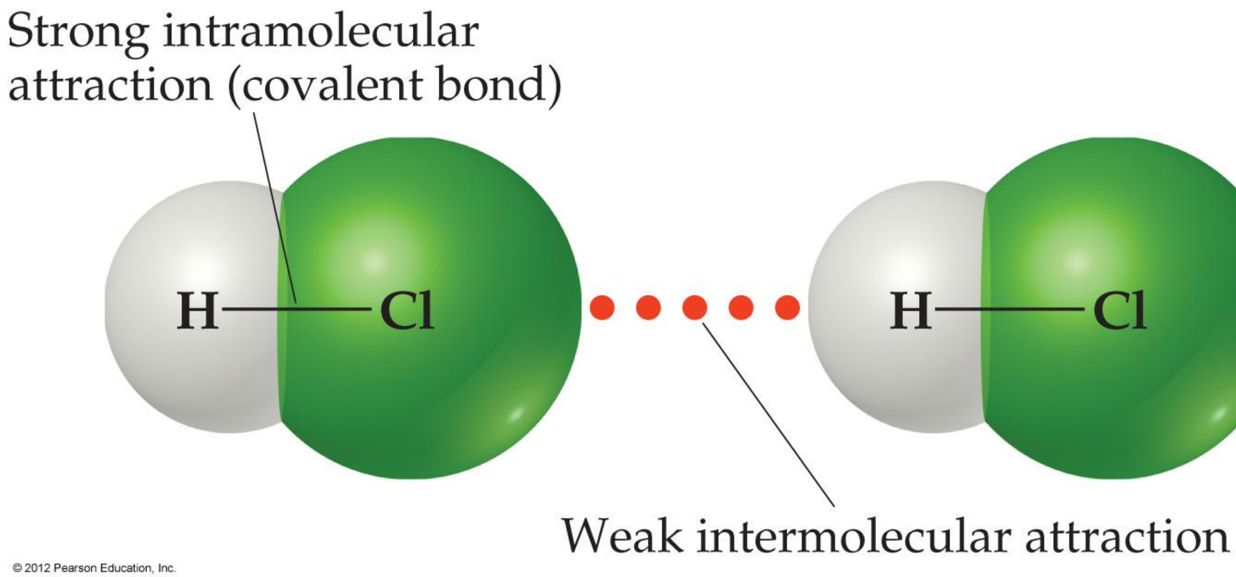
The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compounds together.

Intermolecular Forces



These intermolecular attractions are, however, strong enough to control physical properties, such as boiling and melting points, vapor pressures, and viscosities.

Intermolecular Forces

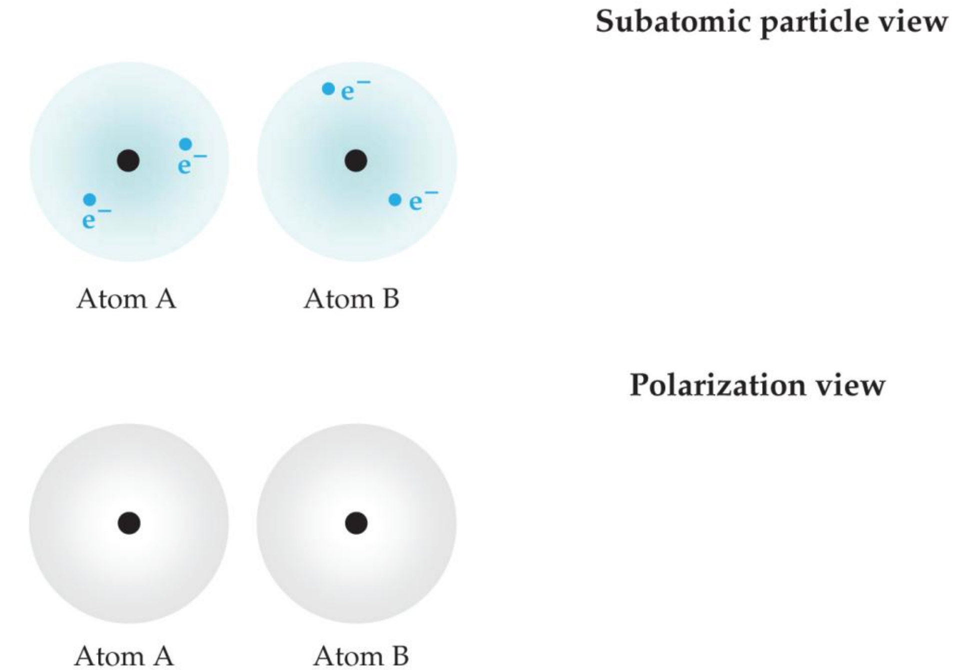


These intermolecular forces as a group are referred to as **van der Waals forces**.

van der Waals Forces

- Dipole–dipole interactions
- Hydrogen bonding
- London dispersion forces

London Dispersion Forces

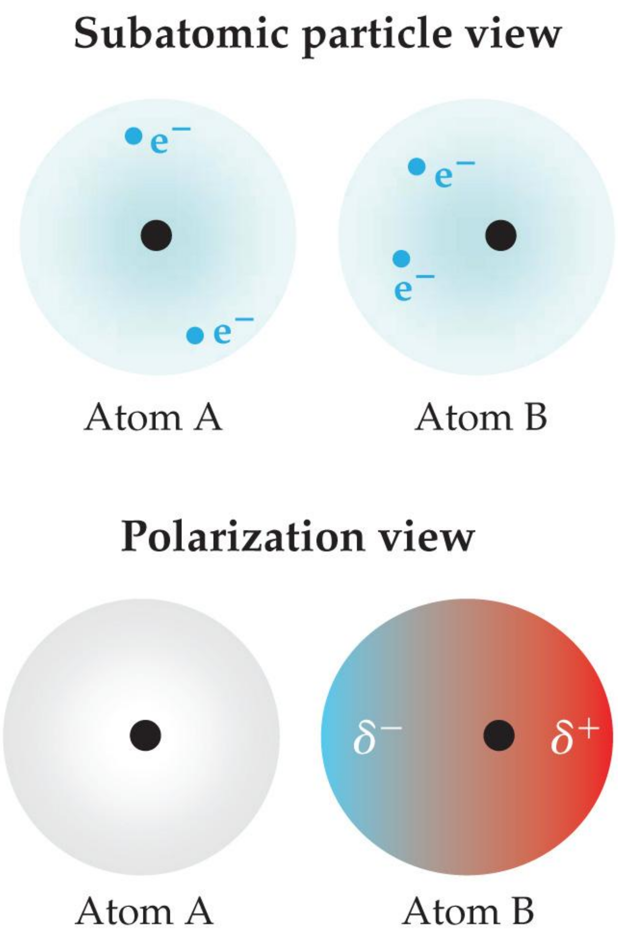


(a) Two helium atoms, no polarization

While the electrons in the 1*s* orbital of helium would repel each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom.

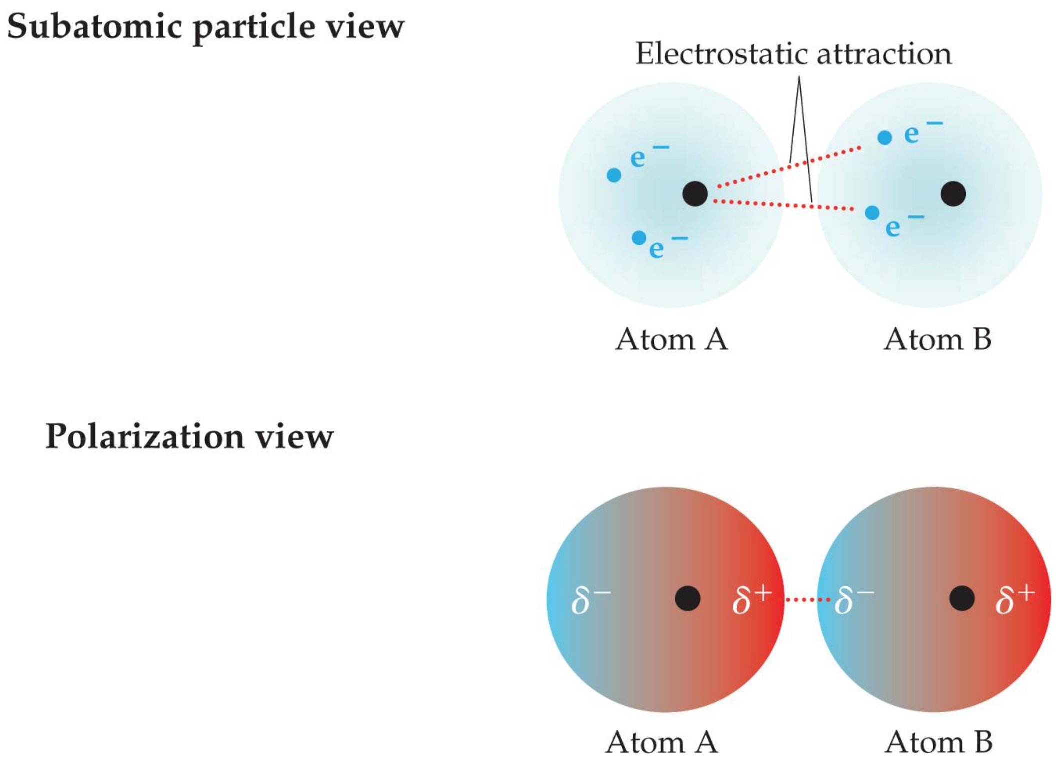
London Dispersion Forces

At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.



(b) Instantaneous dipole on atom B

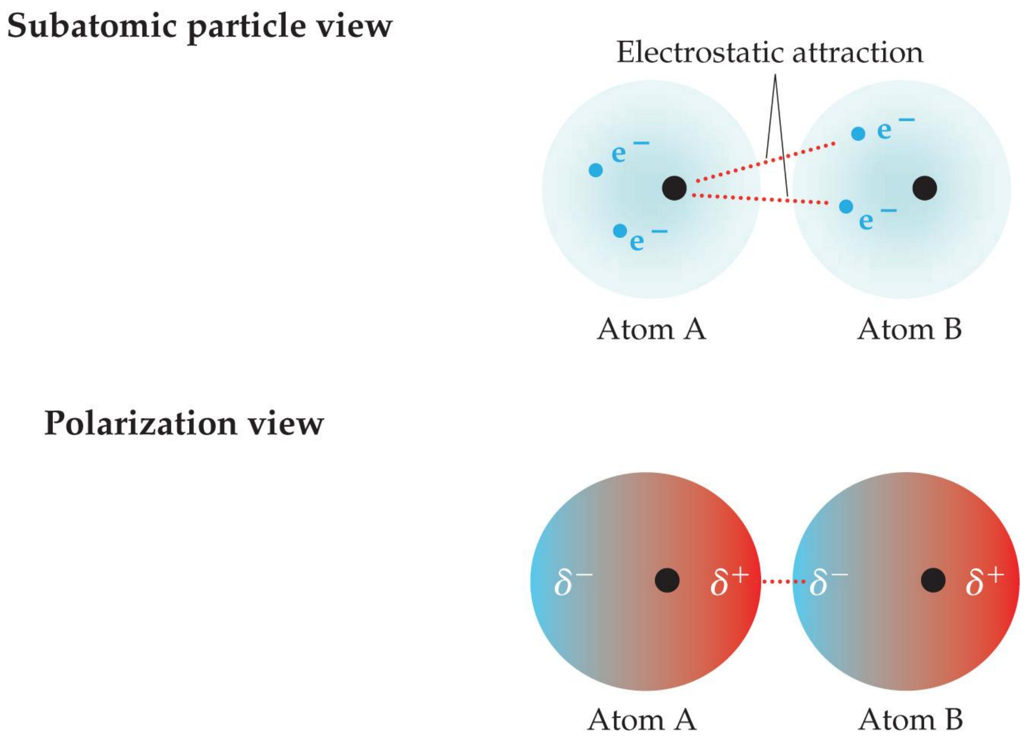
London Dispersion Forces



(c) Induced dipole on atom A

Another helium atom nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

London Dispersion Forces

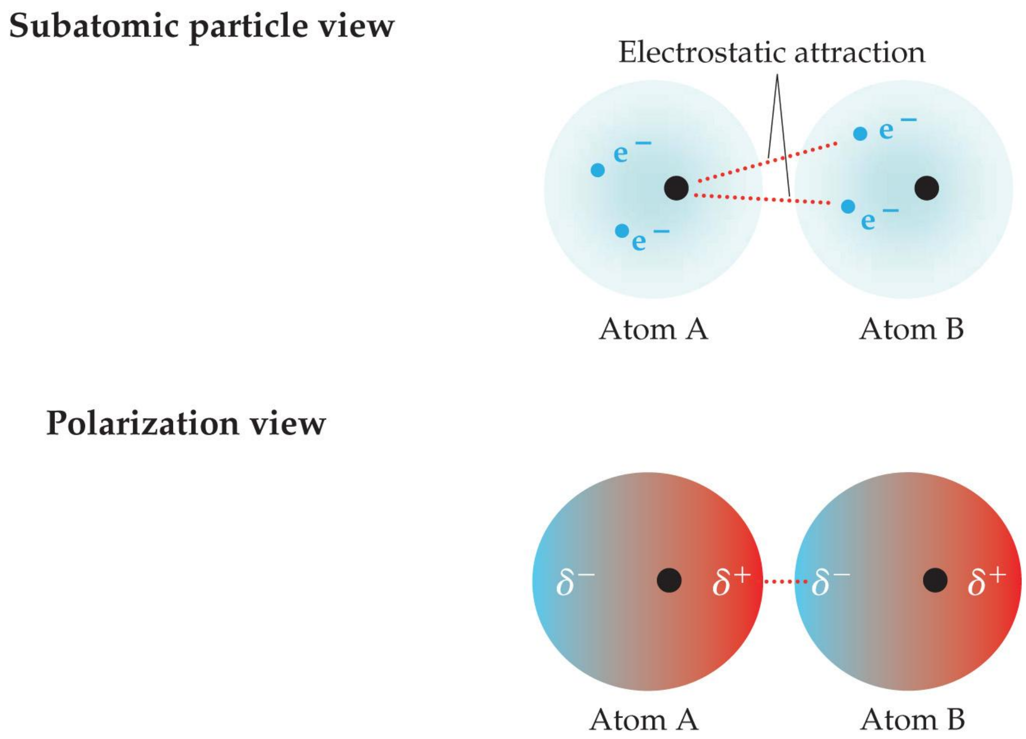


(c) Induced dipole on atom A

London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole.

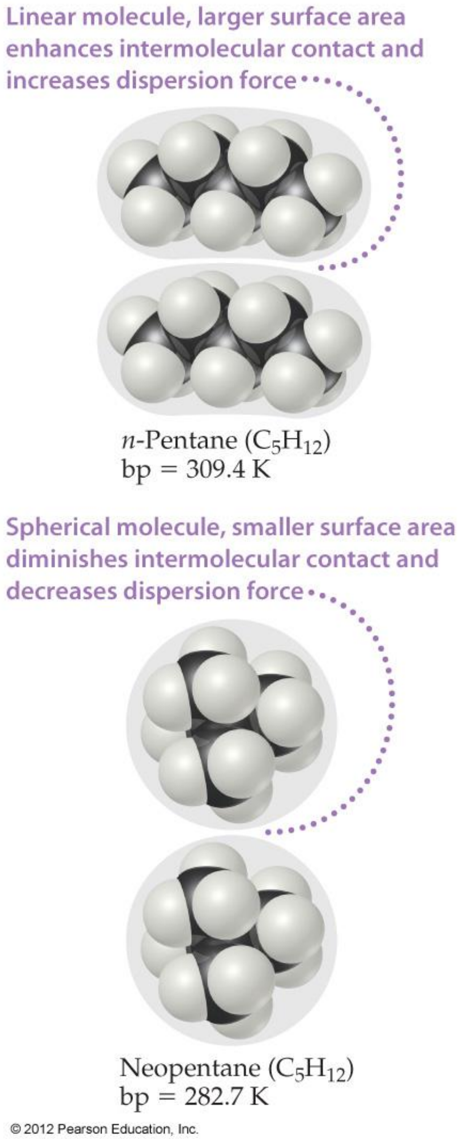
London Dispersion Forces

- These forces are present in *all* molecules, whether they are polar or nonpolar.
- The tendency of an electron cloud to distort in this way is called **polarizability**.



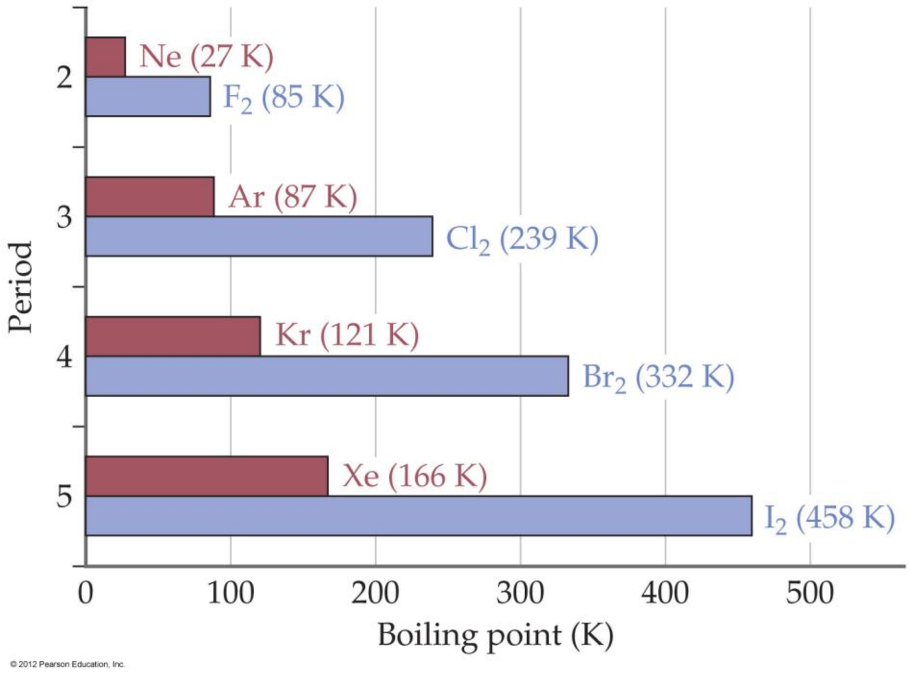
(c) Induced dipole on atom A

Factors Affecting London Forces



- The shape of the molecule affects the strength of dispersion forces: long, skinny molecules (like *n*-pentane) tend to have stronger dispersion forces than short, fat ones (like neopentane).
- This is due to the increased surface area in *n*-pentane.

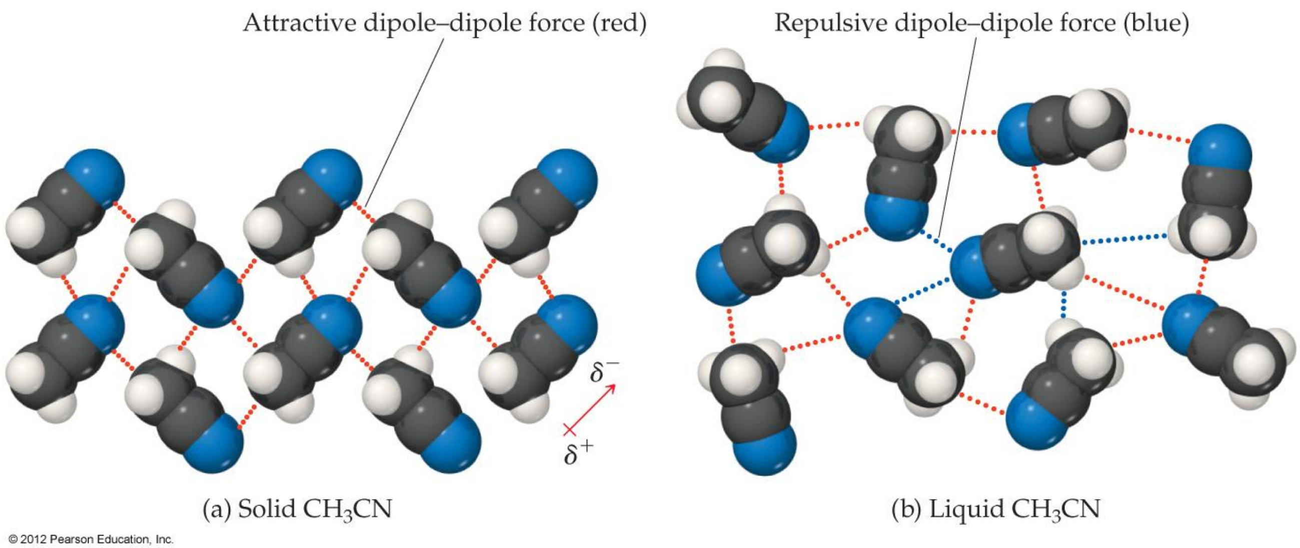
Factors Affecting London Forces



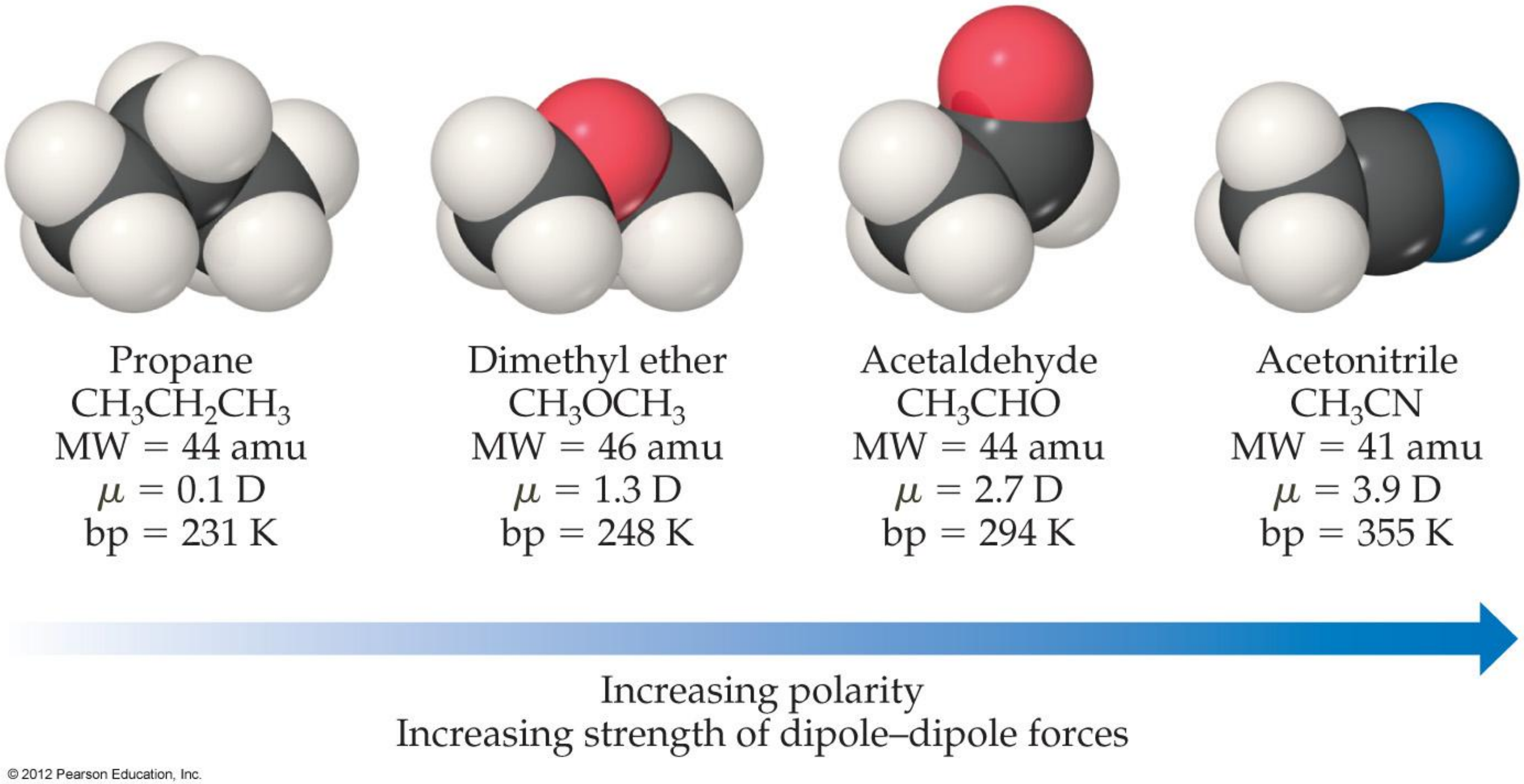
- The strength of dispersion forces tends to increase with increased molecular weight.
- Larger atoms have larger electron clouds that are easier to polarize.

Dipole–Dipole Interactions

- Molecules that have permanent dipoles are attracted to each other.
  - The positive end of one is attracted to the negative end of the other, and vice versa.
  - These forces are only important when the molecules are close to each other.



Dipole–Dipole Interactions



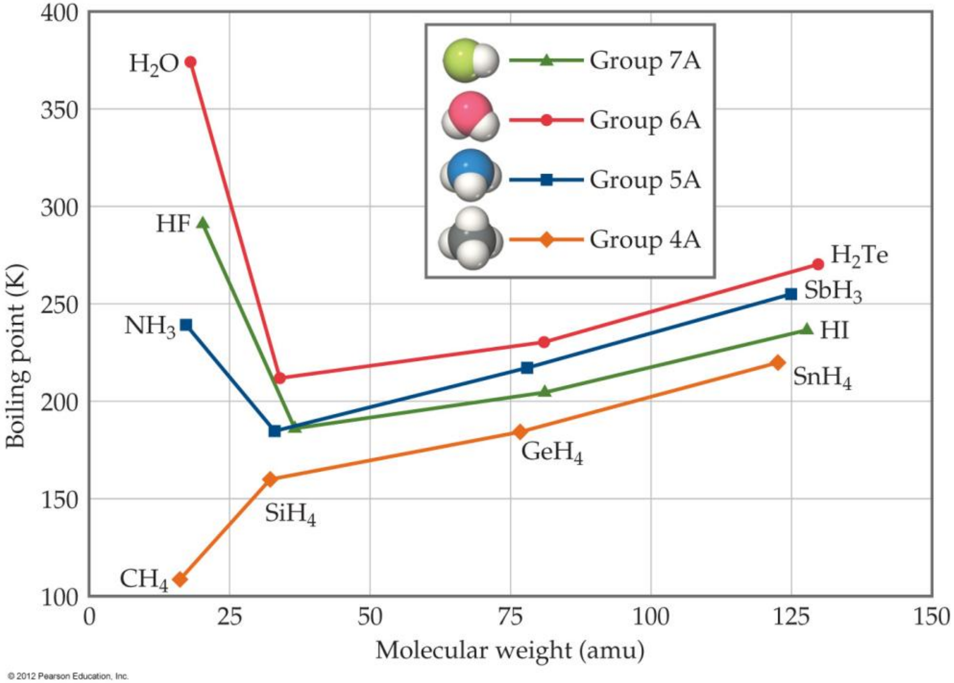
The more polar the molecule, the higher its boiling point.

Which Have a Greater Effect?

Dipole–Dipole Interactions or Dispersion Forces

- 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 likely determine its physical properties.

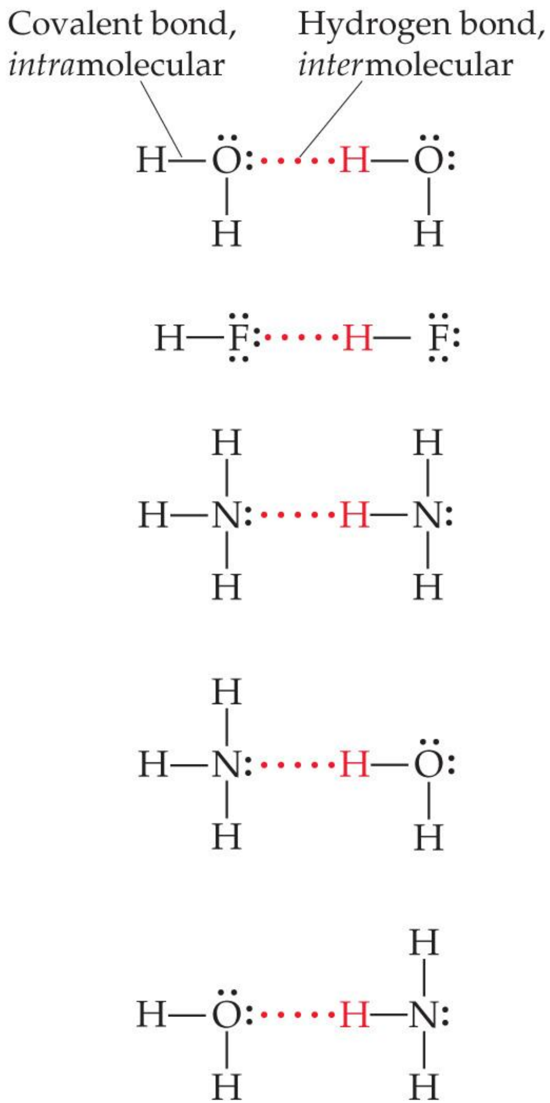
How Do We Explain This?



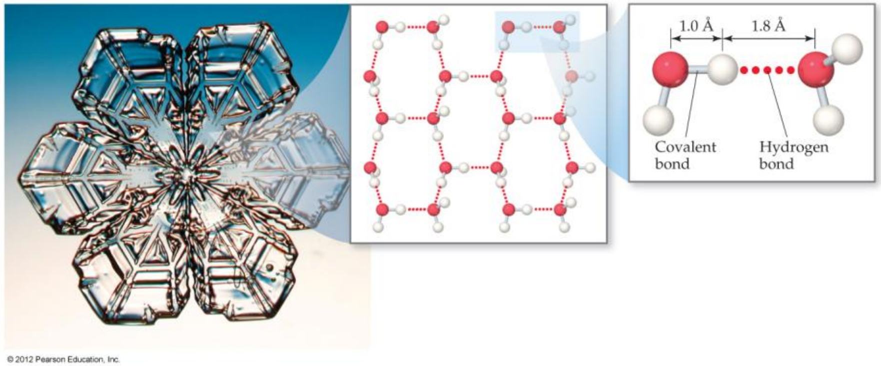
- The nonpolar series (SnH_4 to CH_4) follow the expected trend.
- The polar series follow the trend until you get to the smallest molecules in each group.

Hydrogen Bonding

- The dipole–dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions **hydrogen bonds**.



Hydrogen Bonding

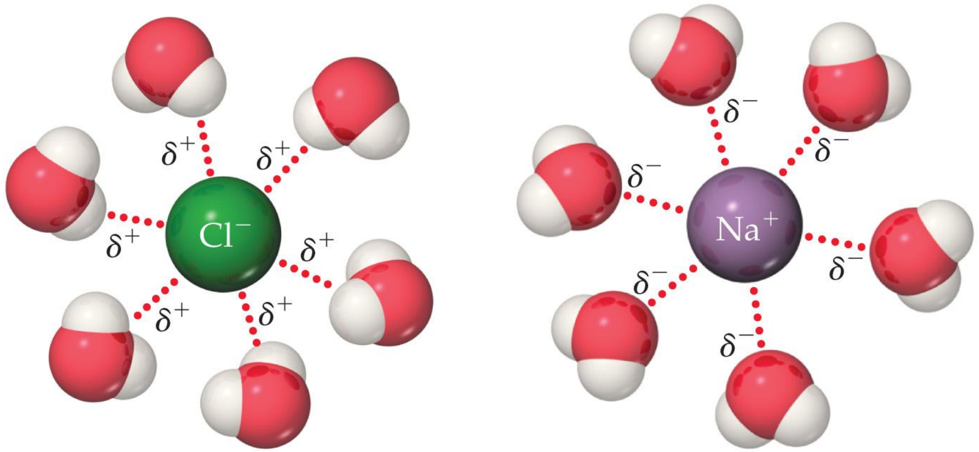


- Hydrogen bonding arises in part from the high electronegativity of nitrogen, oxygen, and fluorine.

Also, when hydrogen is bonded to one of those very electronegative elements, the hydrogen nucleus is exposed.

Ion–Dipole Interactions

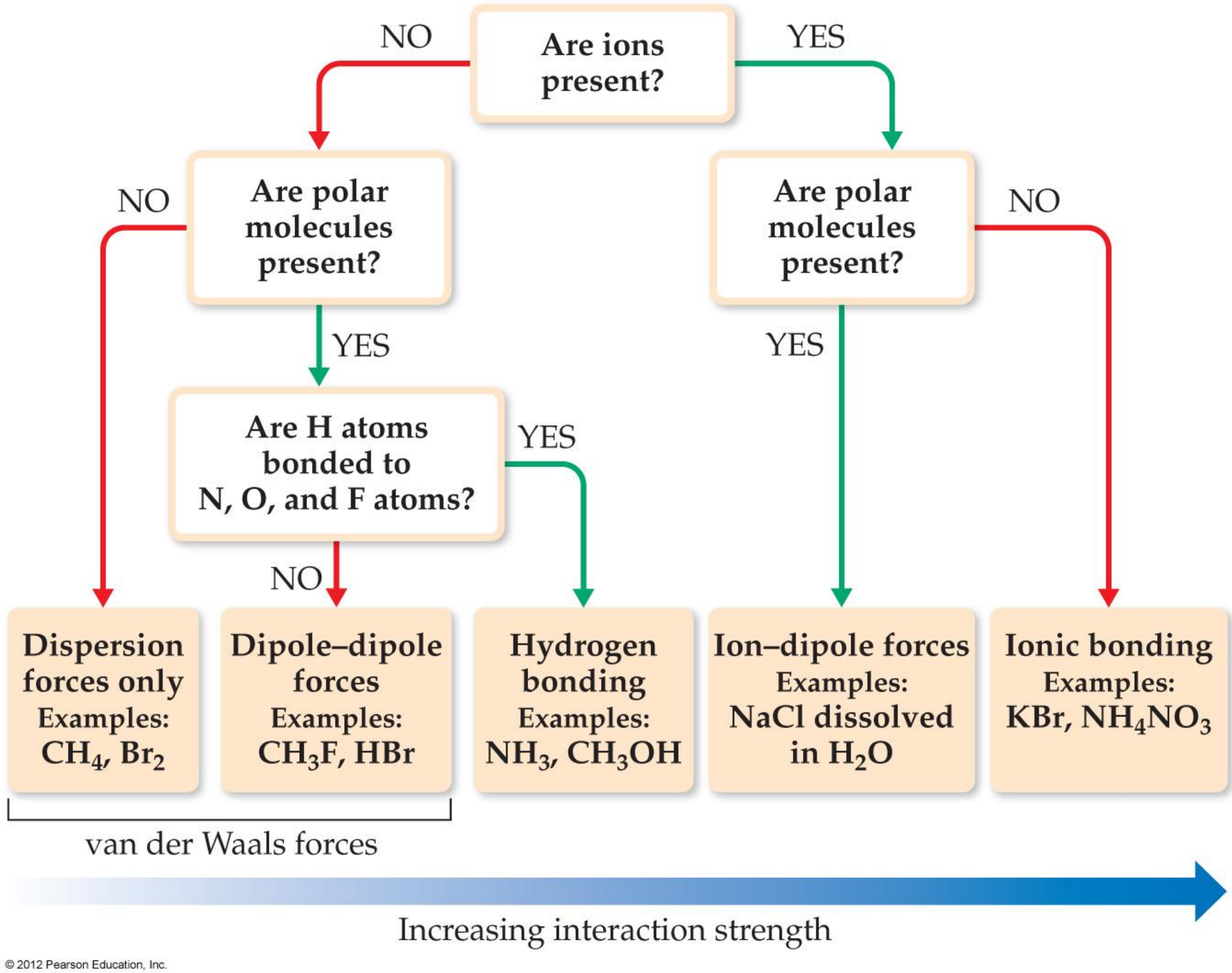
- Ion–dipole interactions (a fourth type of force) are important in solutions of ions.
- The strength of these forces is what makes it possible for ionic substances to dissolve in polar solvents.



Positive ends of polar molecules are oriented toward negatively charged anion

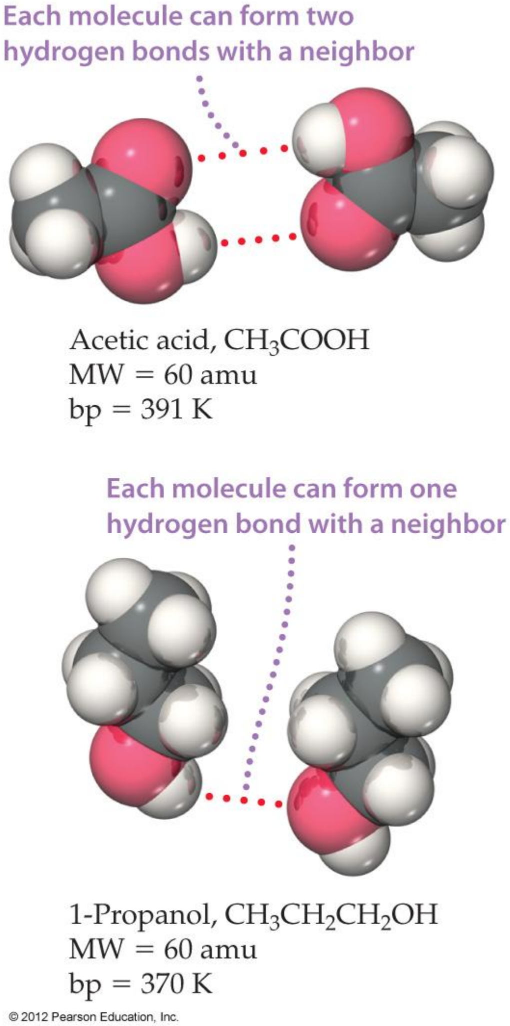
Negative ends of polar molecules are oriented toward positively charged cation

Summarizing Intermolecular Forces



Intermolecular Forces

Intermolecular Forces Affect Many Physical Properties



The strength of the attractions between particles can greatly affect the properties of a substance or solution.

Viscosity

- Resistance of a liquid to flow is called **viscosity.**
- It is related to the ease with which molecules can move past each other.
- Viscosity increases with stronger intermolecular forces and decreases with higher temperature.

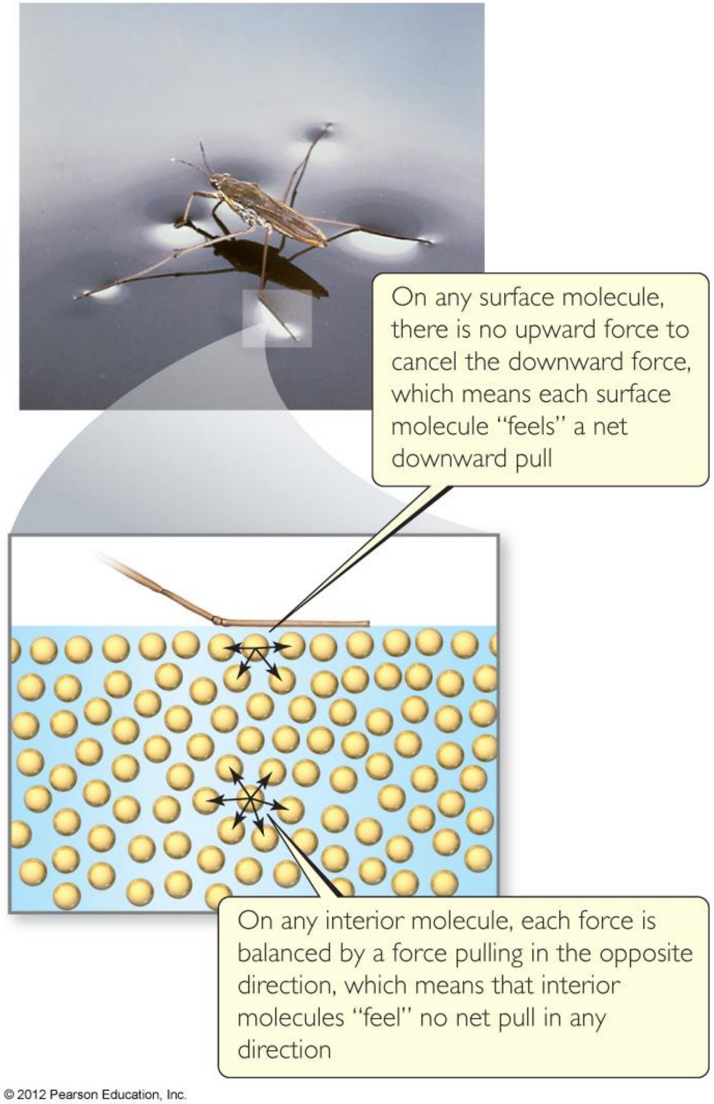
SAE 40
higher number
higher viscosity
slower pouring

SAE 10
lower number
lower viscosity
faster pouring

TABLE 11.4 • Viscosities of a Series of Hydrocarbons at 20 °C

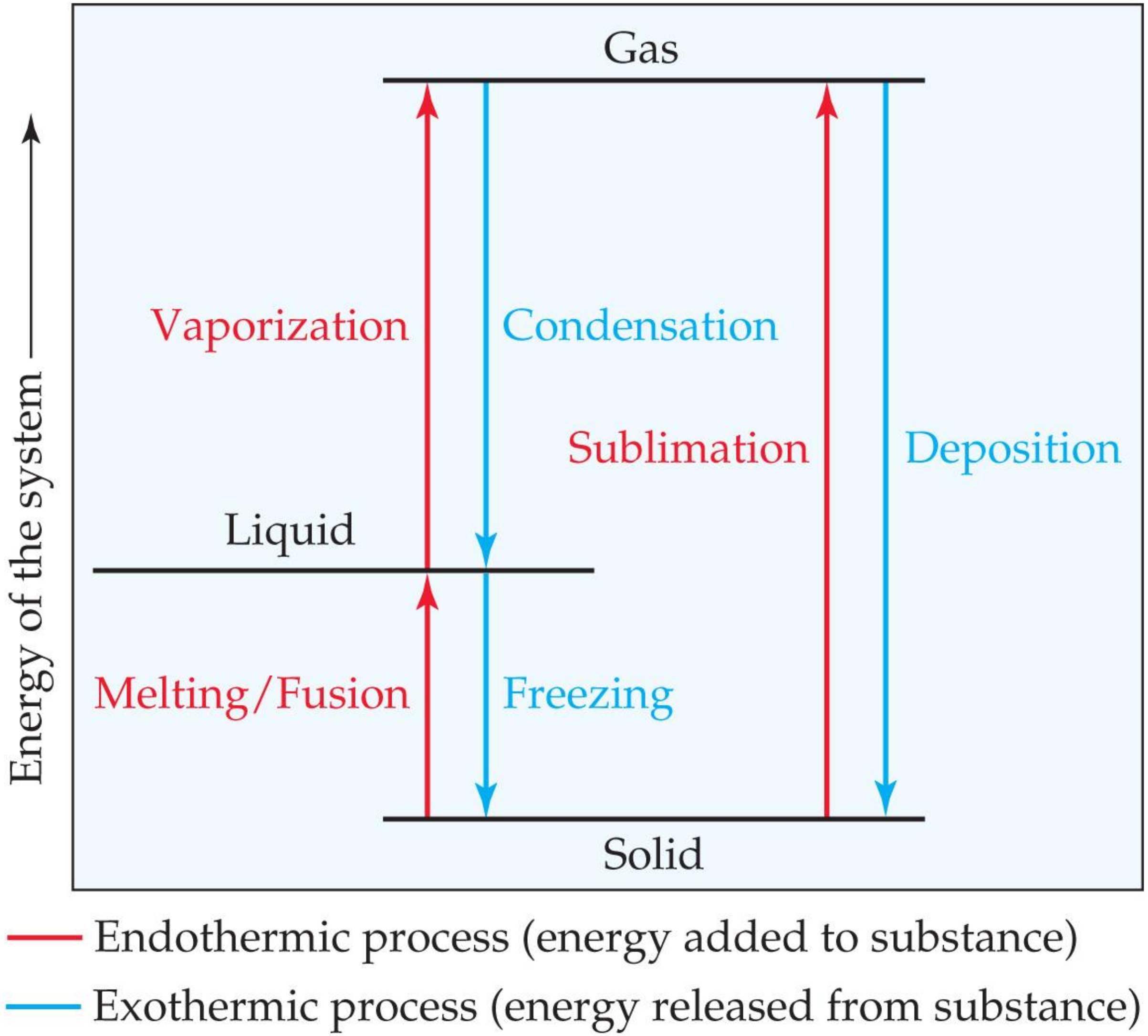
Substance	Formula	Viscosity (kg/m-s)
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	3.26×10^{-4}
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	4.09×10^{-4}
Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	5.42×10^{-4}
Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	7.11×10^{-4}
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	1.42×10^{-3}

Surface Tension

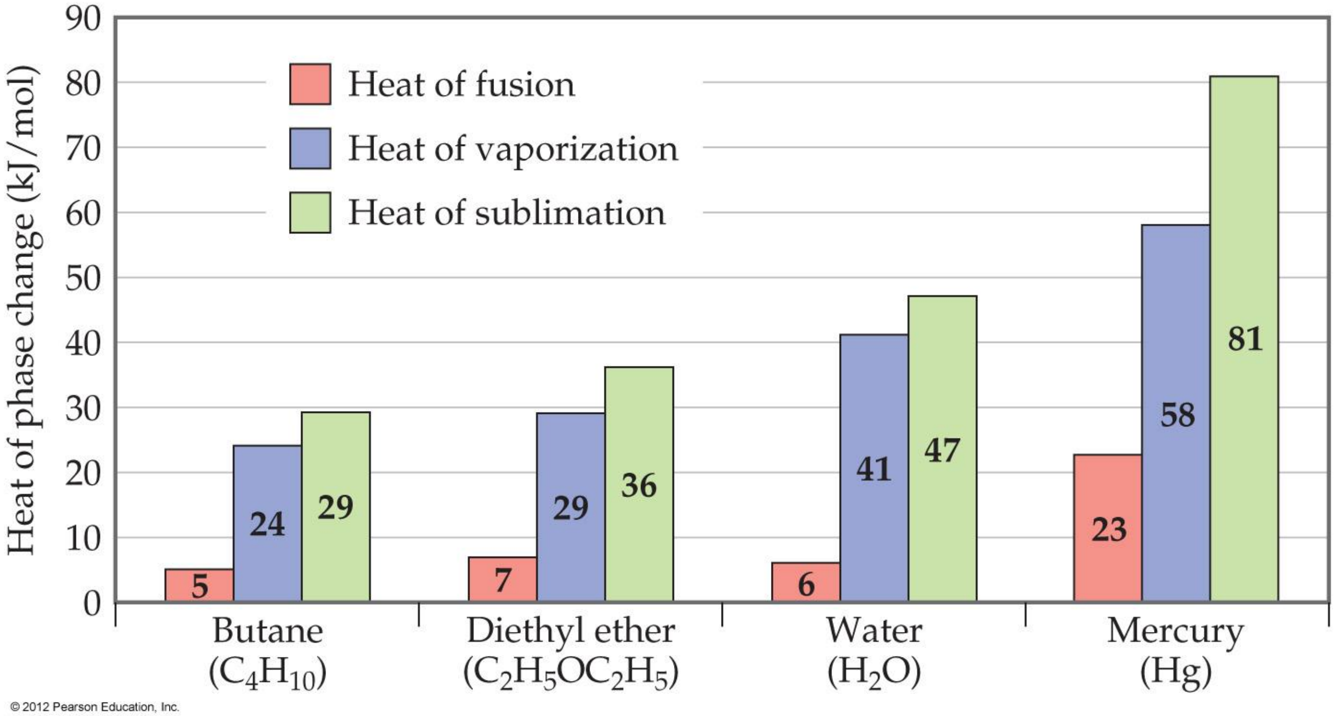


Surface tension results from the net inward force experienced by the molecules on the surface of a liquid.

Phase Changes

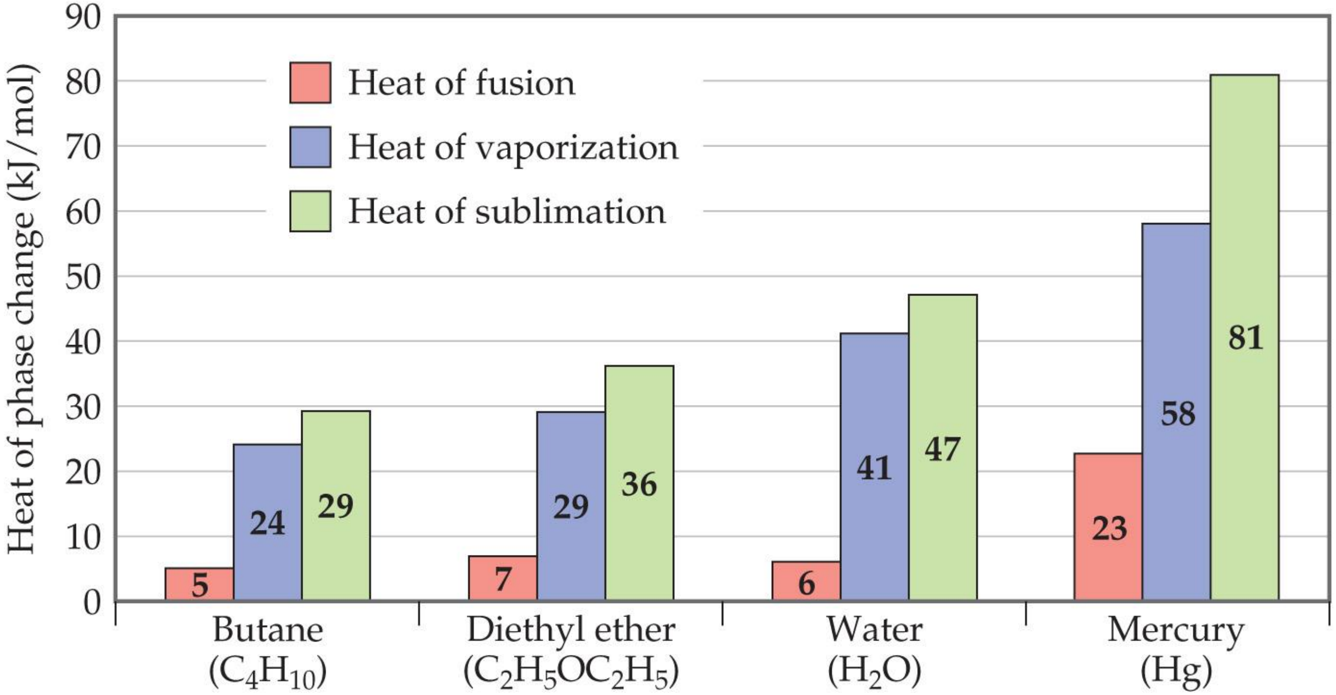


Energy Changes Associated with Changes of State



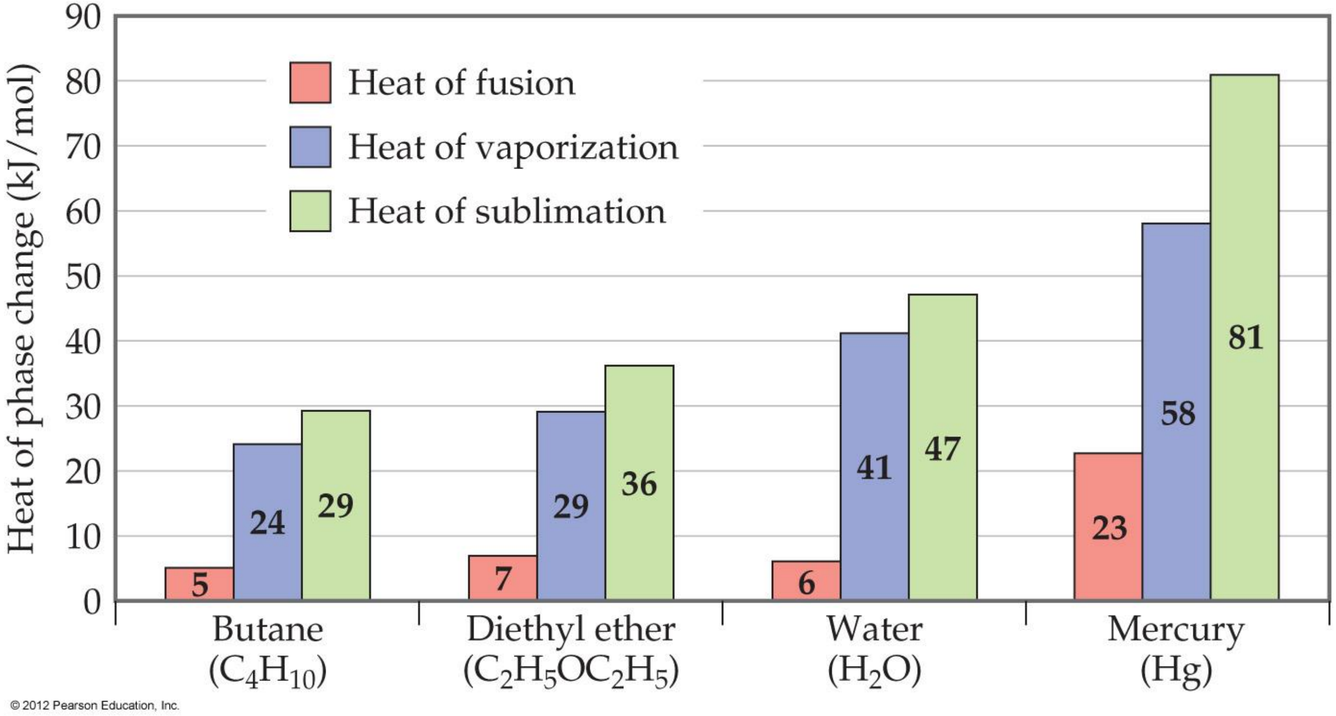
The **heat of fusion** is the energy required to change a solid at its melting point to a liquid.

Energy Changes Associated with Changes of State



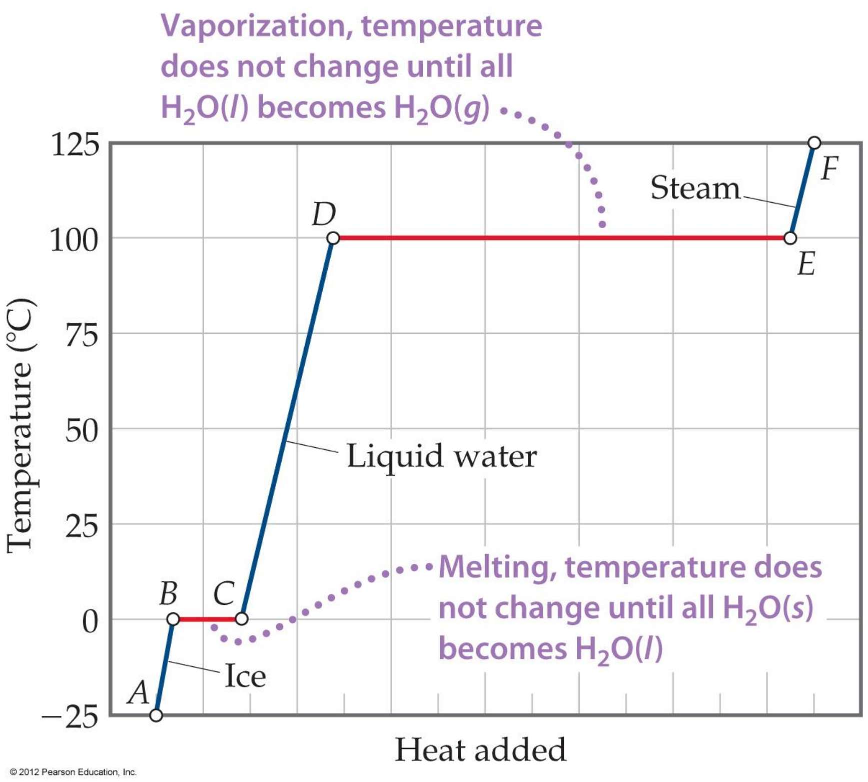
The **heat of vaporization** is defined as the energy required to change a liquid at its boiling point to a gas.

Energy Changes Associated with Changes of State



The **heat of sublimation** is defined as the energy required to change a solid directly to a gas.

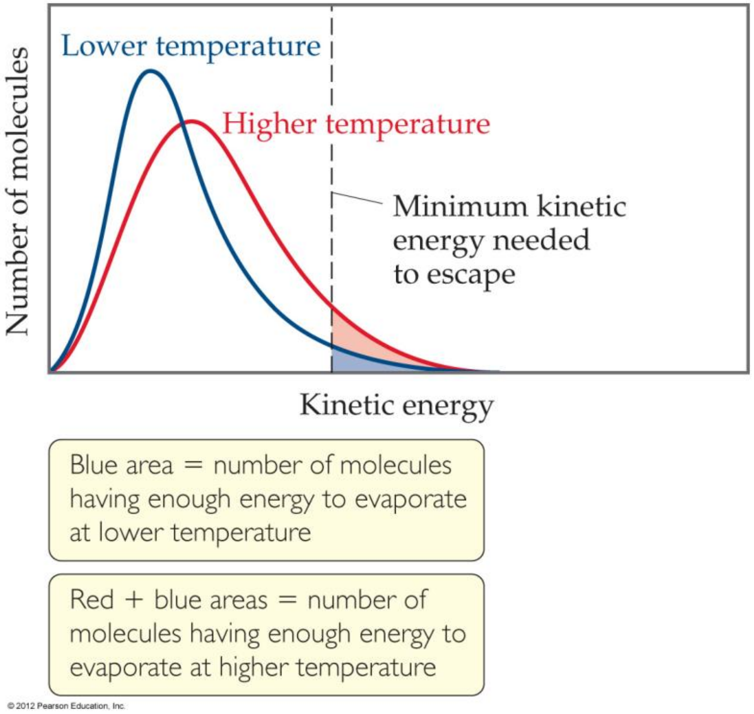
Energy Changes Associated with Changes of State



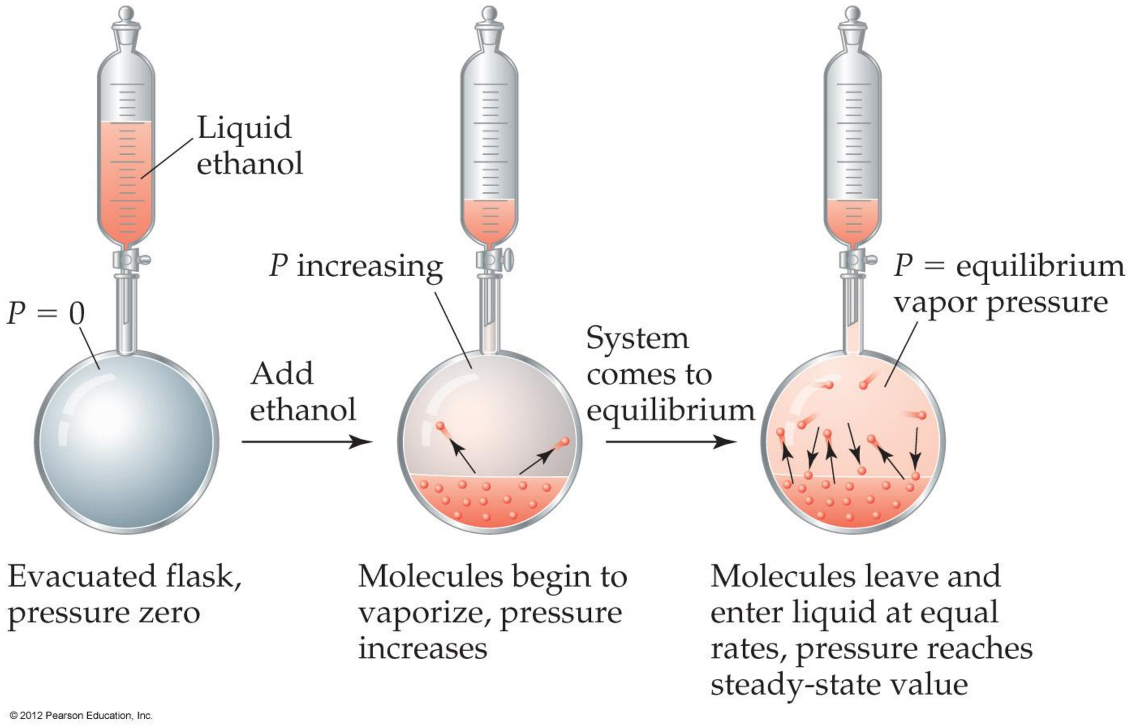
- The heat added to the system at the melting and boiling points goes into pulling the molecules farther apart from each other.
- The temperature of the substance does not rise during a phase change.

Vapor Pressure

- At any temperature some molecules in a liquid have enough energy to break free.
- As the temperature rises, the fraction of molecules that have enough energy to break free increases.

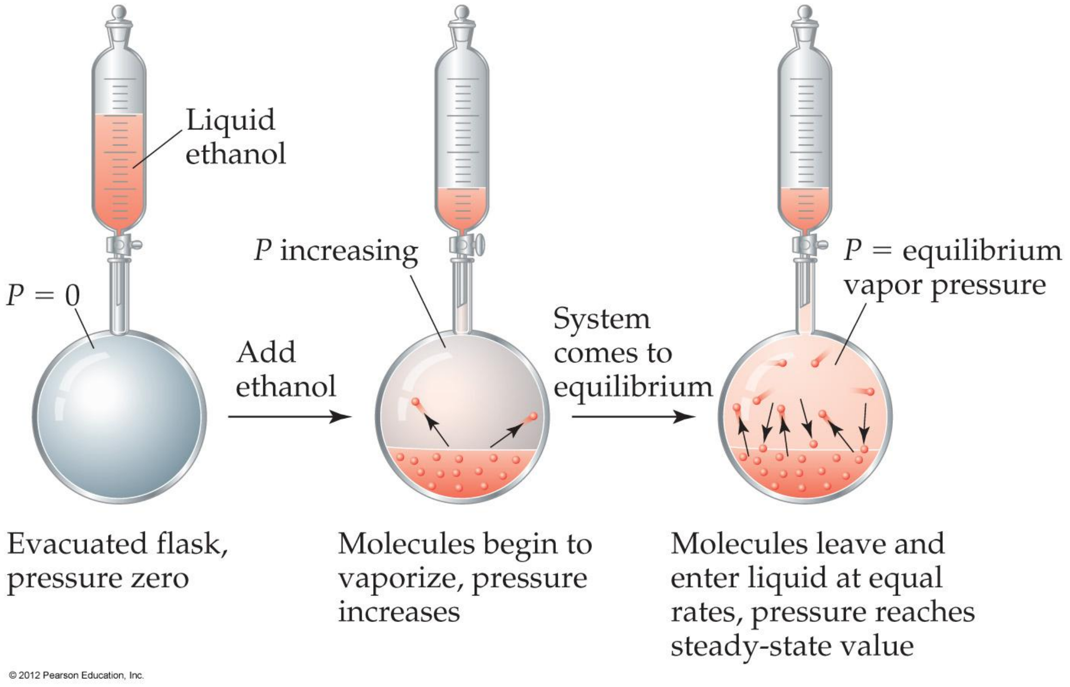


Vapor Pressure



As more molecules escape the liquid, the pressure they exert increases.

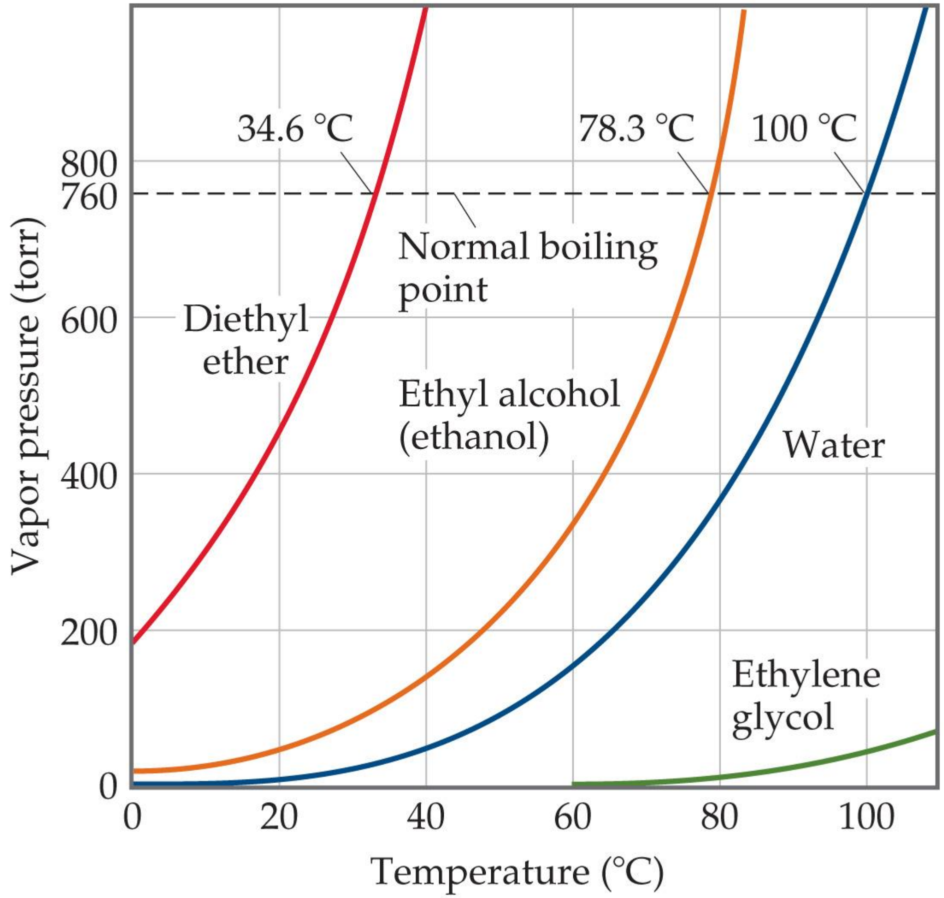
Vapor Pressure



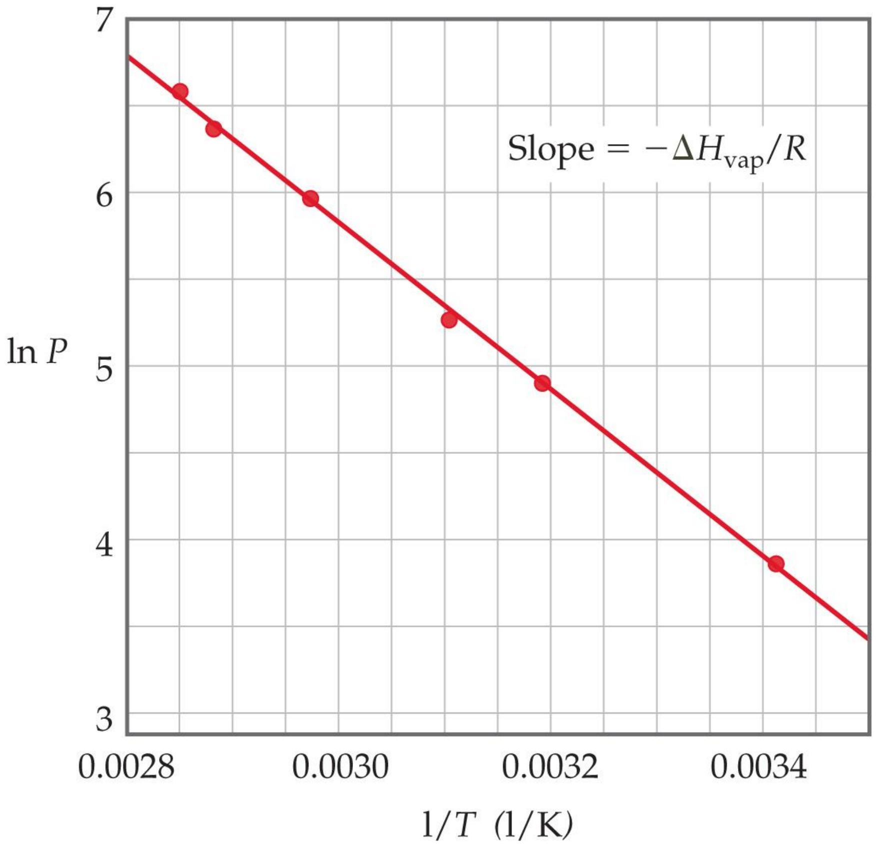
The liquid and vapor reach a state of dynamic equilibrium: liquid molecules evaporate and vapor molecules condense *at the same rate.*

Vapor Pressure

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

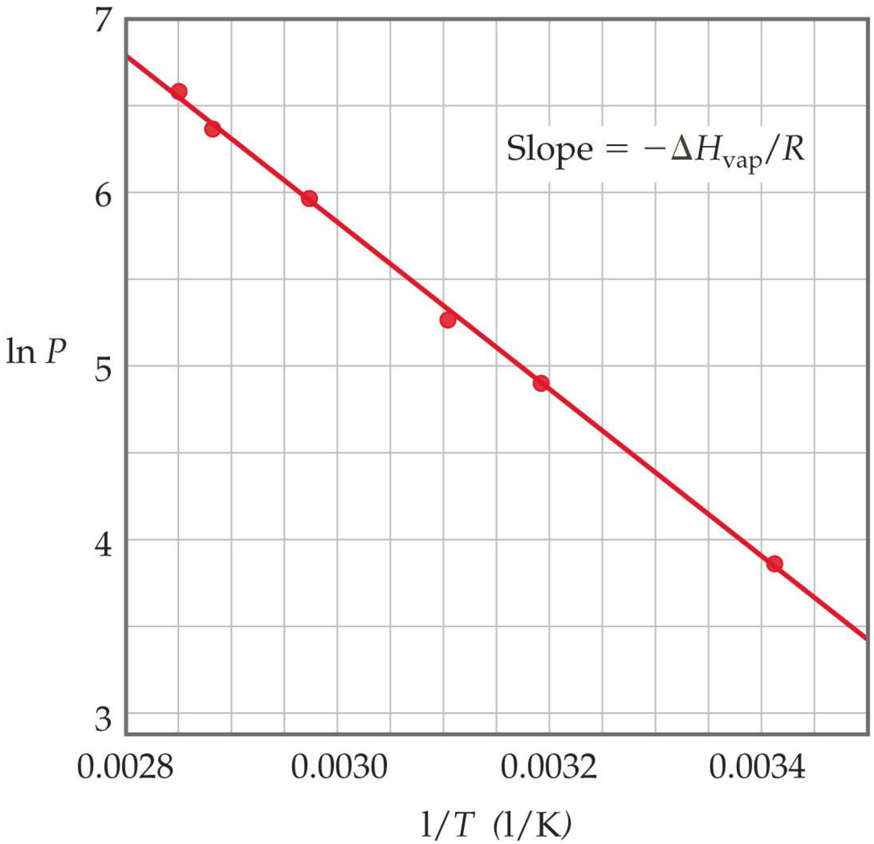


Vapor Pressure



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

Vapor Pressure



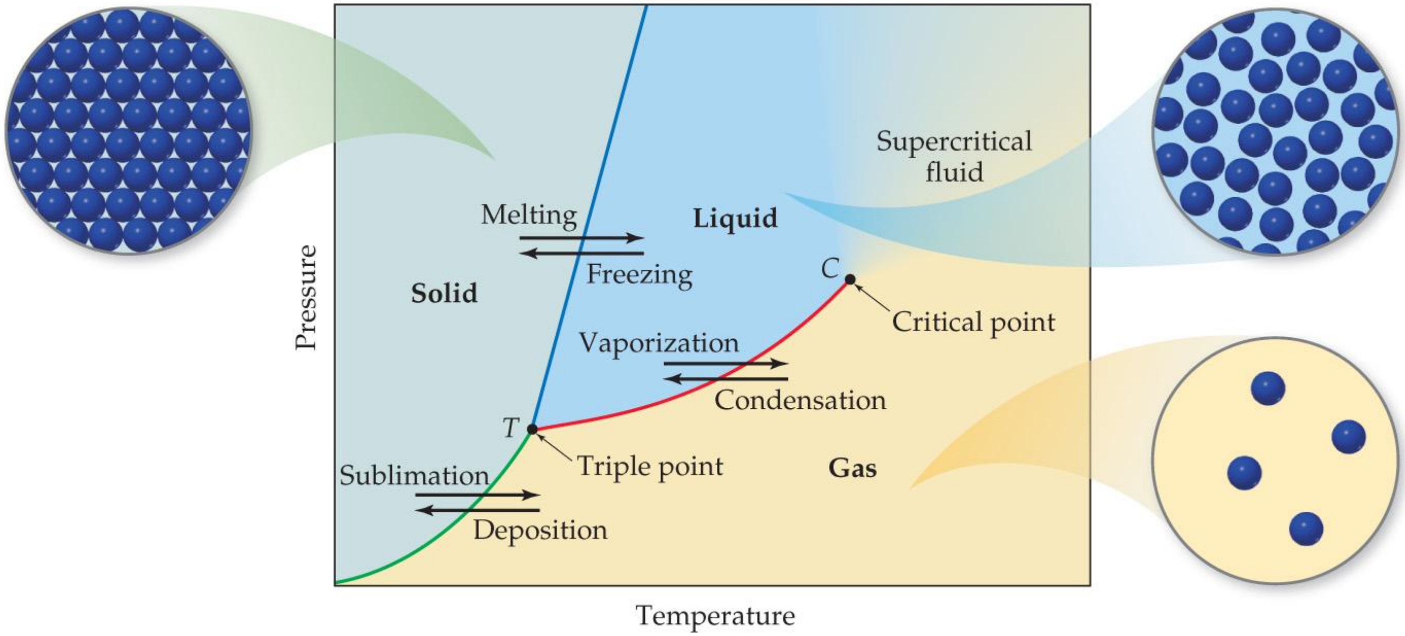
This relationship is quantified in the **Clausius–Clapeyron equation:**

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

where C is a constant.

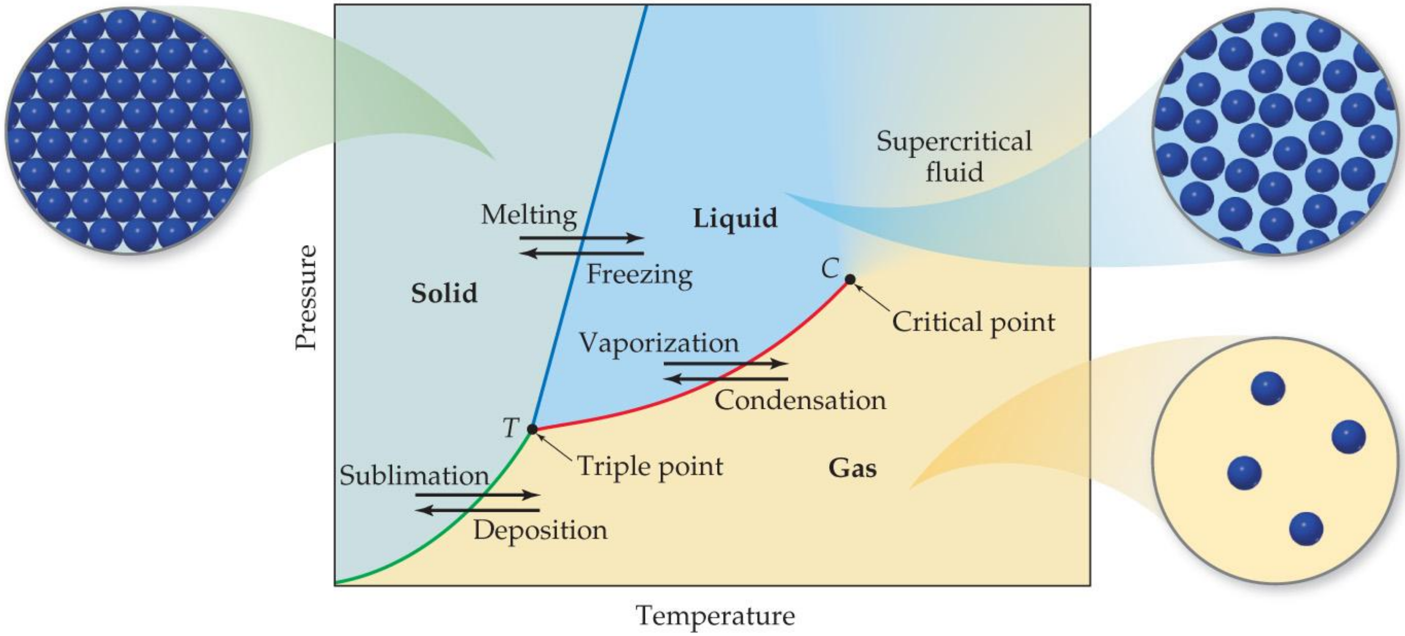
Phase Diagrams

Phase diagrams display the state of a substance at various pressures and temperatures, and the places where equilibria exist between phases.



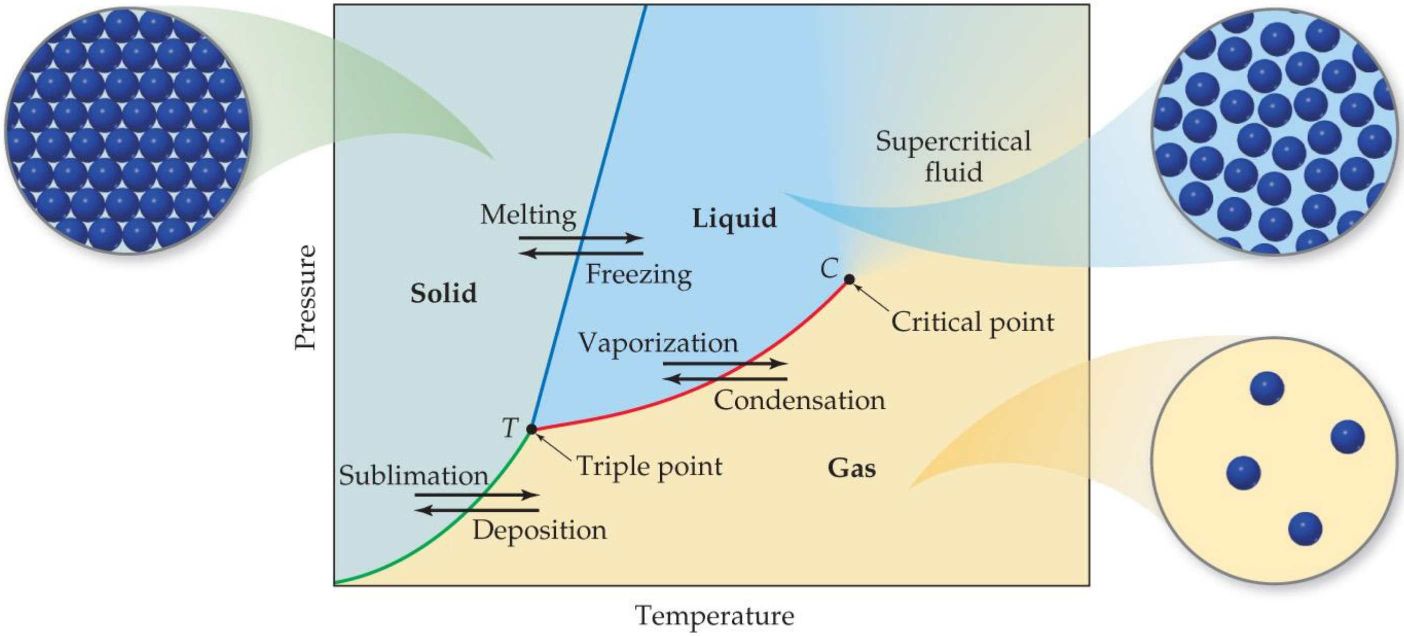
Phase Diagrams

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 and vapor are indistinguishable from each other.



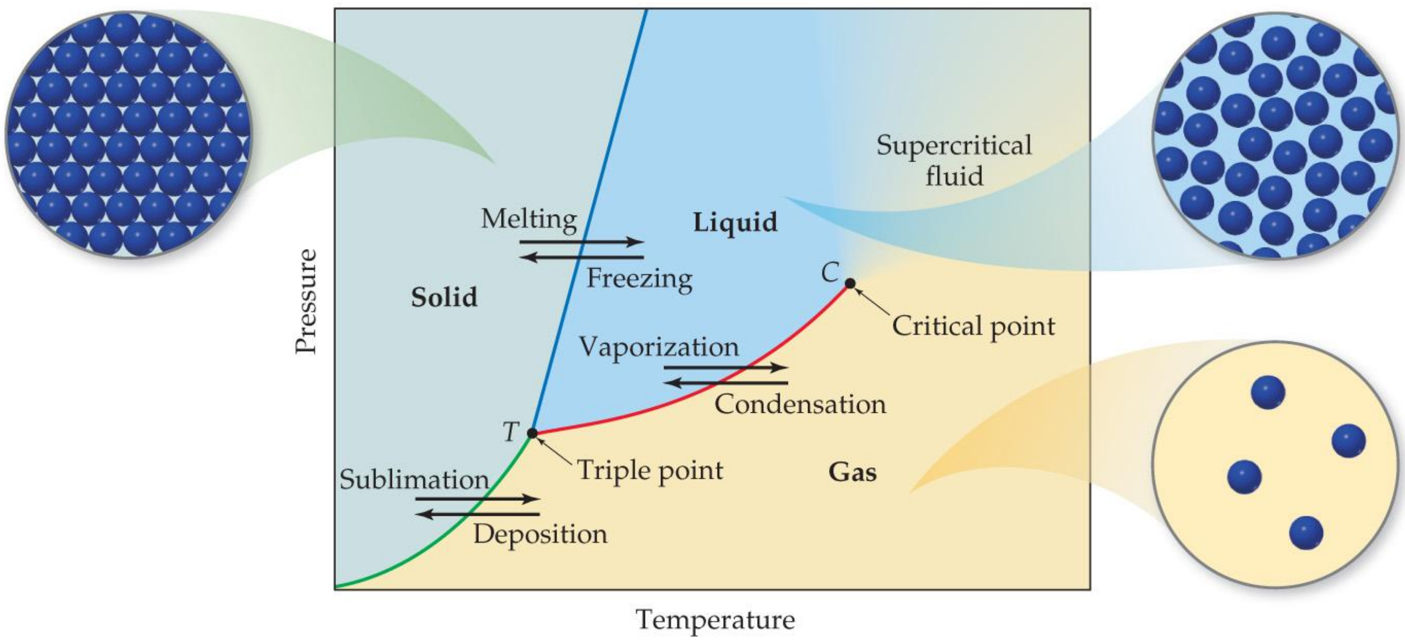
Phase Diagrams

Each point along this line is the boiling point of the substance at that pressure.



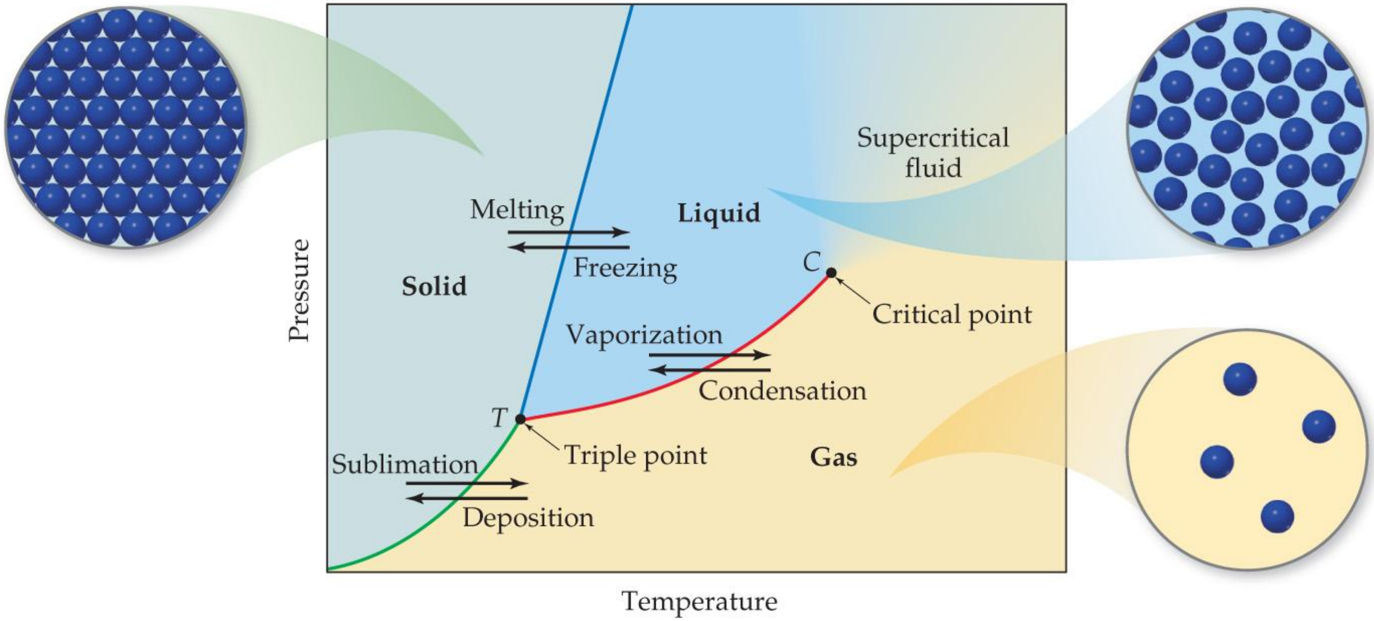
Phase Diagrams

The interface between liquid and solid marks the melting point of a substance at each pressure.

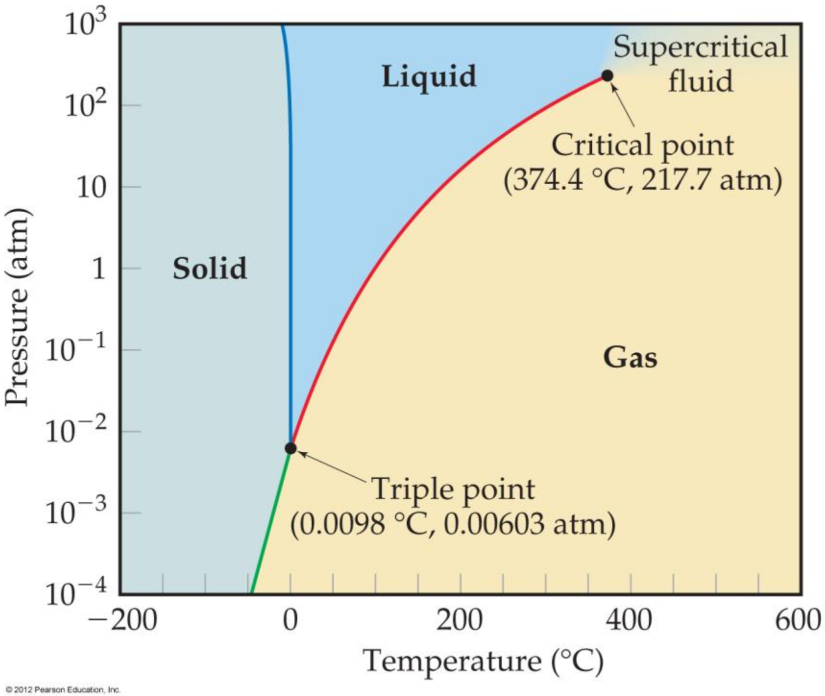


Phase Diagrams

- Below the triple point the substance cannot exist in the liquid state.
- Along the solid–gas line those two phases are in equilibrium; the sublimation point at each pressure is along this line.

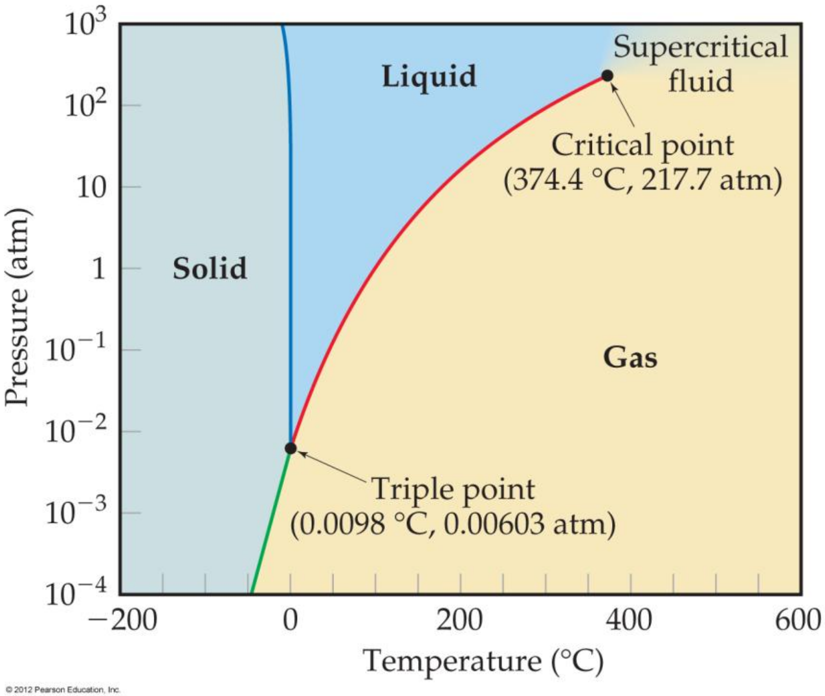


Phase Diagram of Water



- Note the high critical temperature and critical pressure.
  - These are due to the strong van der Waals forces between water molecules.

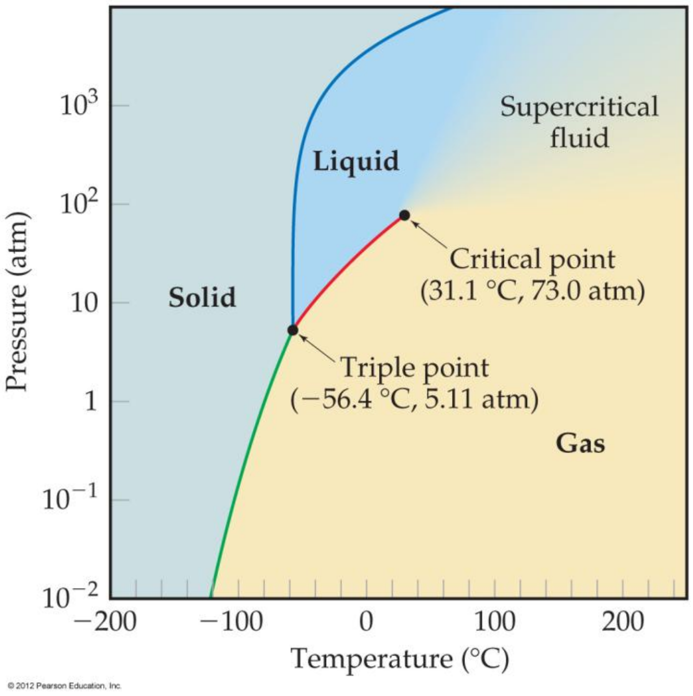
Phase Diagram of Water



- The slope of the solid–liquid line is negative.
  - This means that as the pressure is increased at a temperature just below the melting point, water goes from a solid to a liquid.

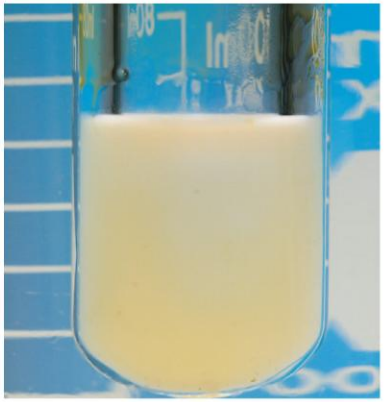
Phase Diagram of Carbon Dioxide

Carbon dioxide cannot exist in the liquid state at pressures below 5.11 atm; CO_2 sublimes at normal pressures.

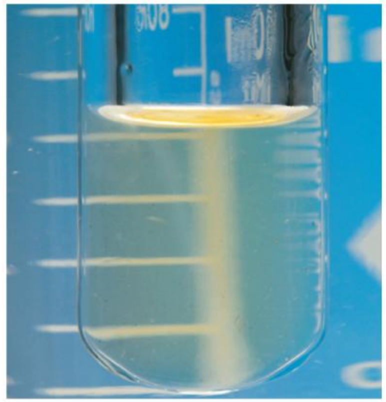


Intermolecular Forces

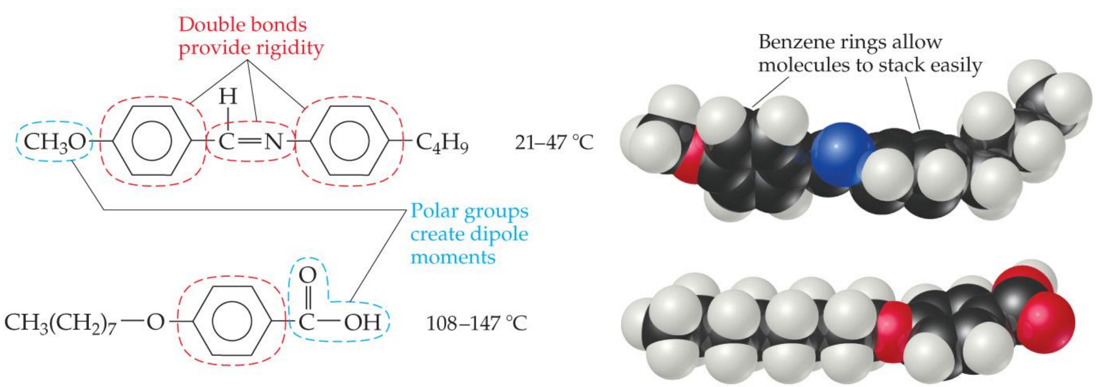
Liquid Crystals



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

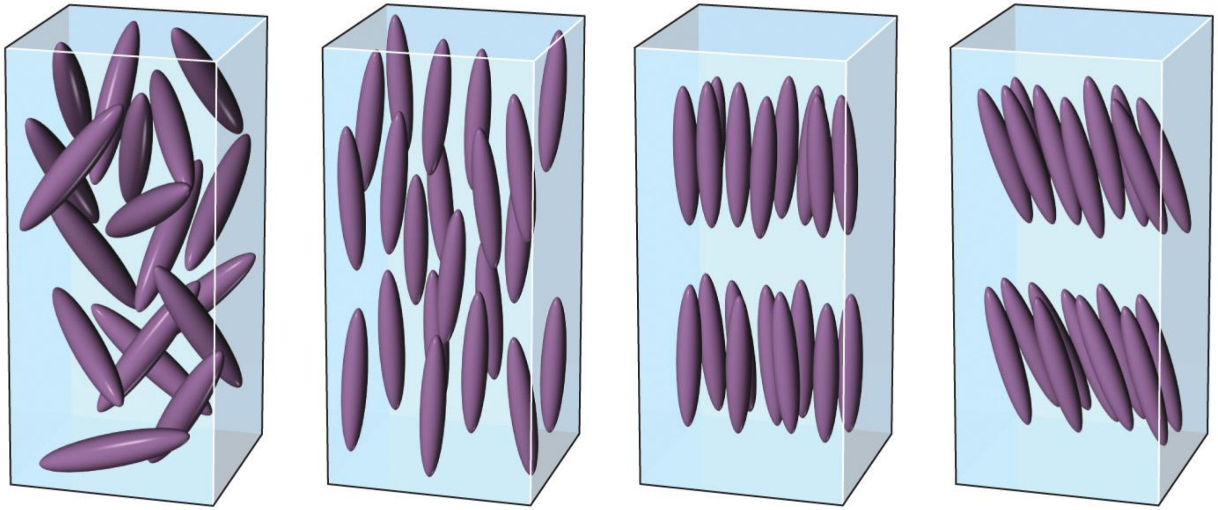


T > 179 °C
Liquid phase



- 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.

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

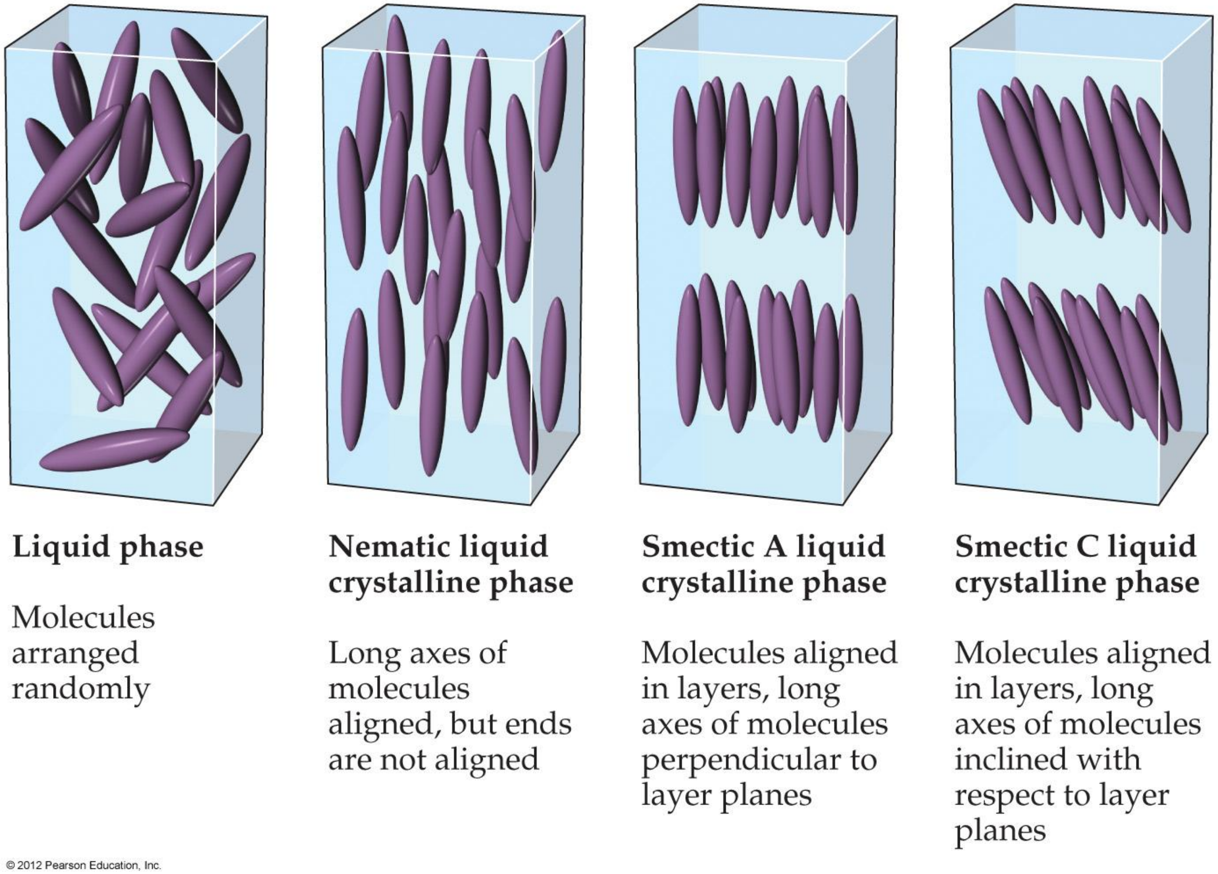
Molecules aligned in layers, long axes of molecules perpendicular to layer planes

Smectic C liquid crystalline phase

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

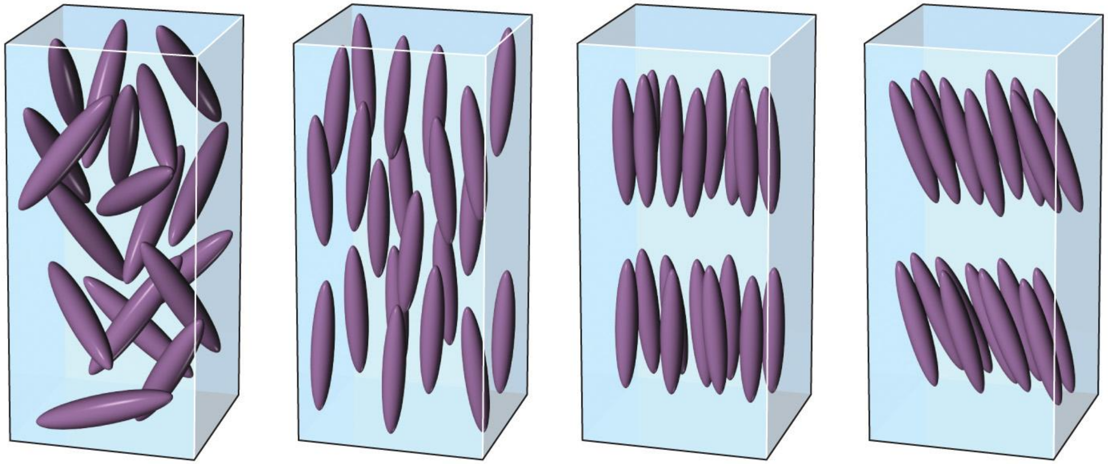
Unlike liquids, molecules in liquid crystals have some degree of order.

Liquid Crystals



In **nematic liquid crystals**, molecules are only ordered in one dimension, along the long axis.

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

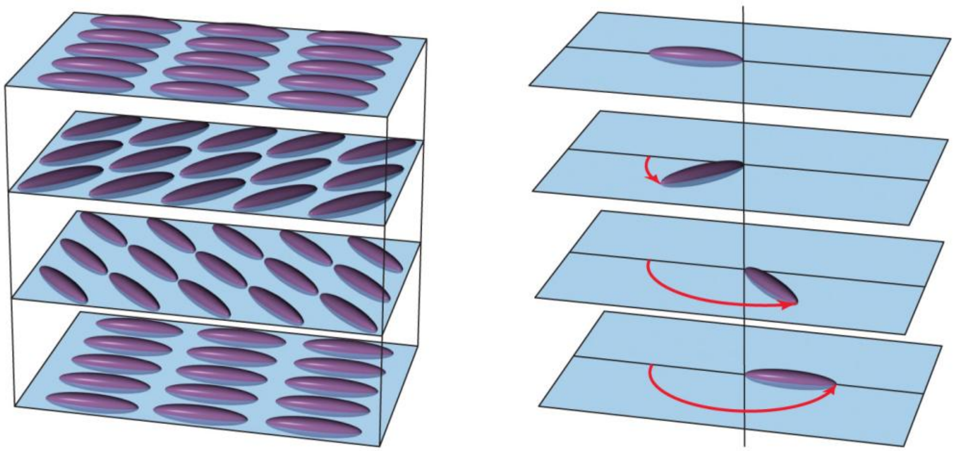
Smectic C liquid crystalline phase

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

In **smectic liquid crystals**, molecules are ordered in two dimensions, along the long axis and in layers.

Liquid Crystals

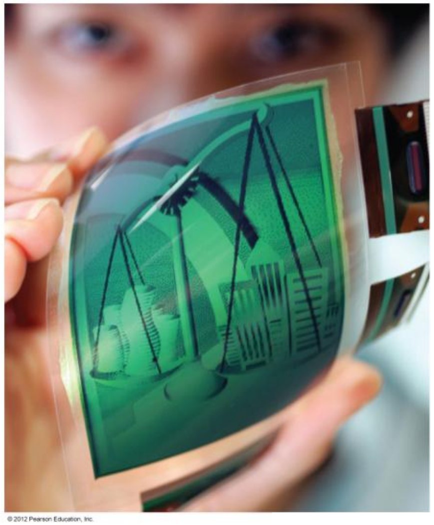
In **cholesteryl liquid crystals**, nematic-like crystals are layered at angles to each other.



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

Liquid Crystals



These crystals can exhibit color changes with changes in temperature.