Chapter 11

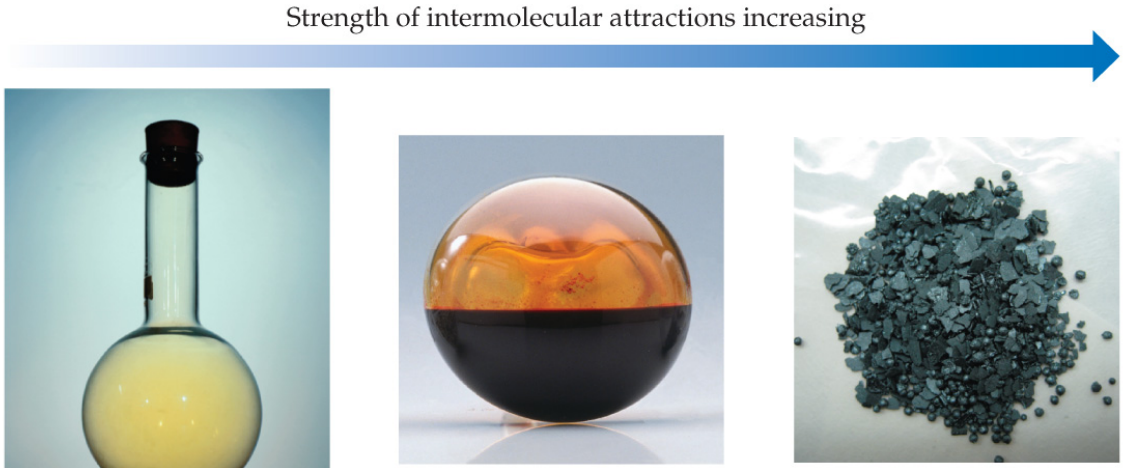
Intermolecular Forces

States of Matter

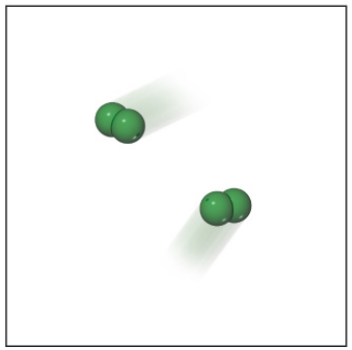
Dependent on 2 things:

Closeness

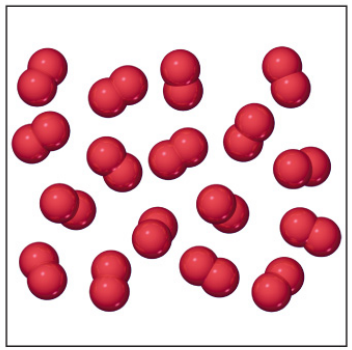
Motion



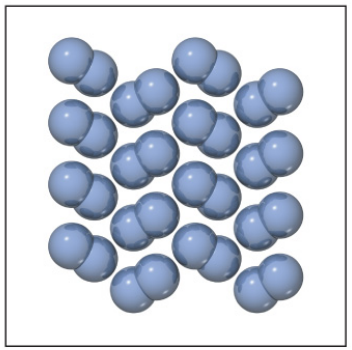
Gas | **Liquid** | **Crystalline solid**



Chlorine, Cl_2
Particles far apart; possess complete freedom of motion



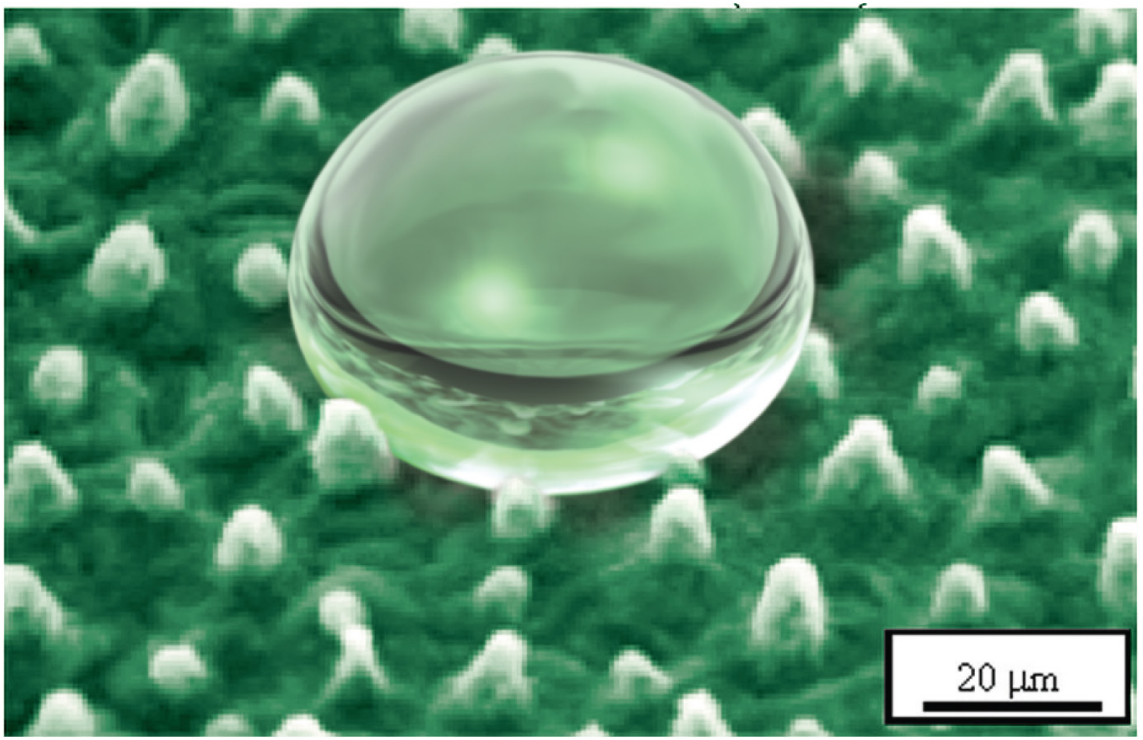
Bromine, Br_2
Particles are closely packed but randomly oriented; retain freedom of motion; rapidly change neighbors



Iodine, I_2
Particles are closely packed in an ordered array; positions are essentially fixed

States of Matter

Liquid & solid: atoms/molecules/ ions perpetually touching. **condensed phases**.



Droplet of water on a solid surface
Shows how liquid molecules stick together

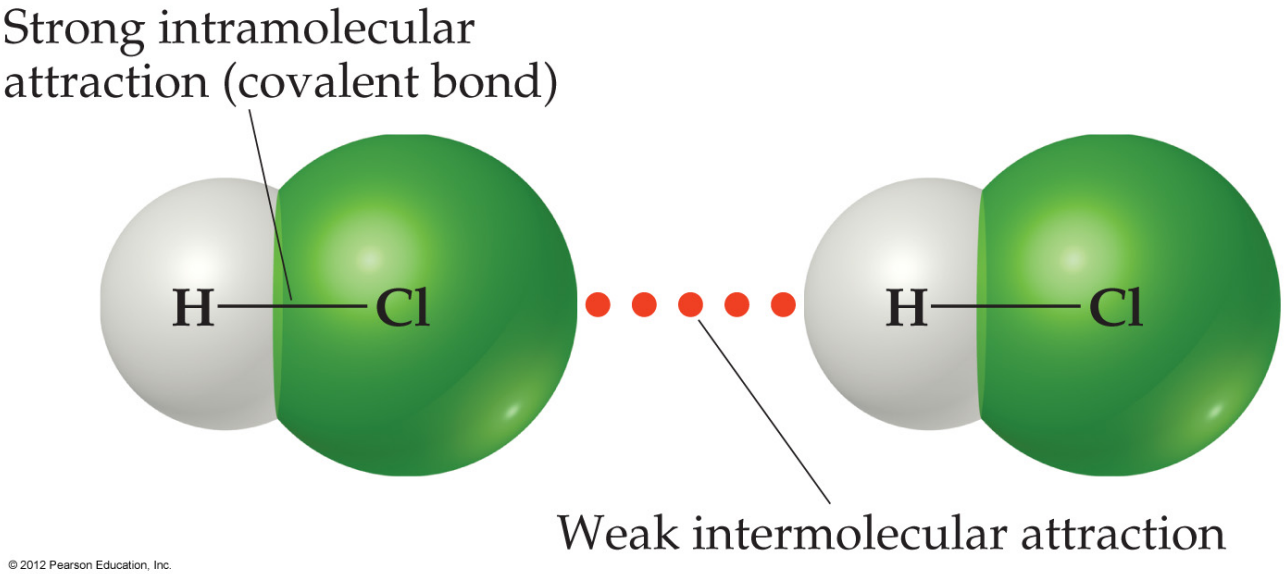
The States of Matter

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* of matter depends on:
  - temperature
  - pressure
  - The kinetic energy of the particles.
  - The strength of the attractions between the particles.

Intermolecular Forces



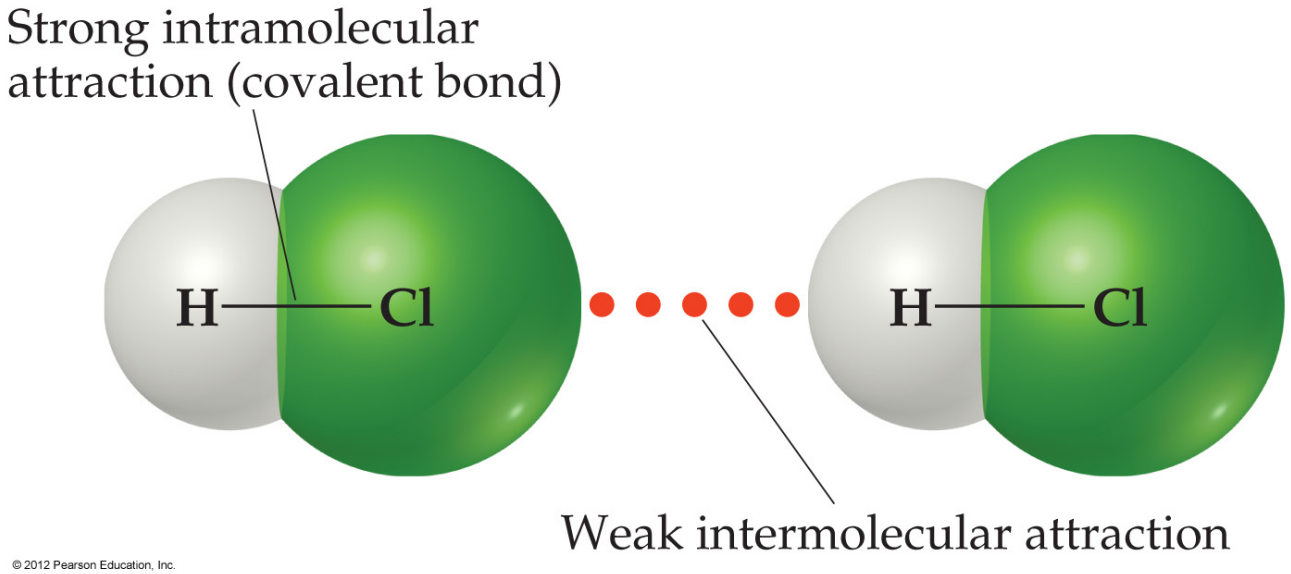
Molecules/atoms can stick to each other.

But much more weakly than a bond.

Covalent bond strength: 50-200 kJ/mole

Intermolecular force: 1-12 kJ/mole

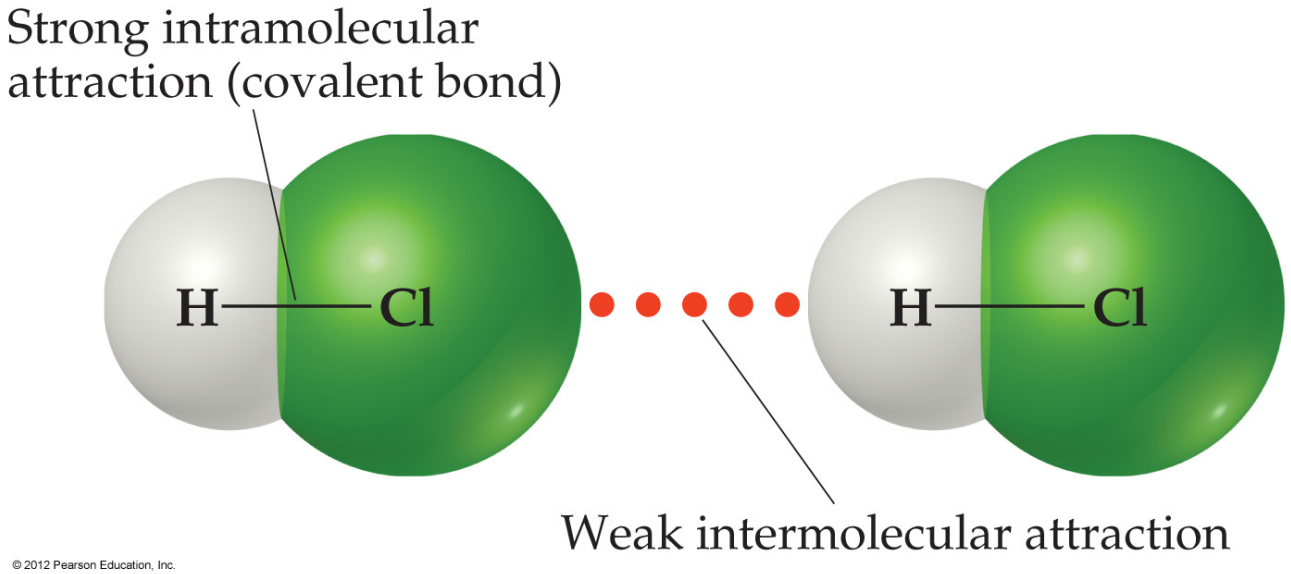
Intermolecular Forces



But these weak interactions control many critical properties:

- boiling and melting points,
- vapor pressures
- viscosities, etc.

Intermolecular Forces



All weak intermolecular forces are called:

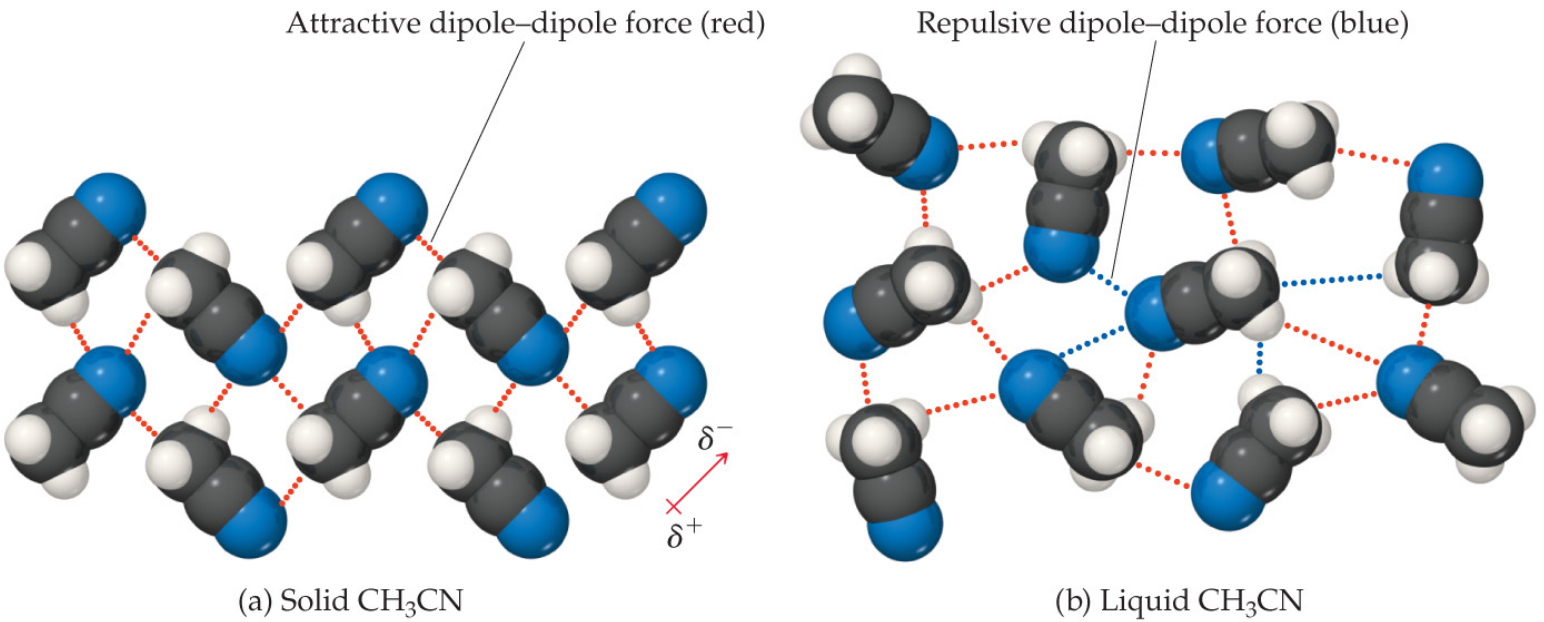
van der Waals forces.

van der Waals Forces
Two major forms:

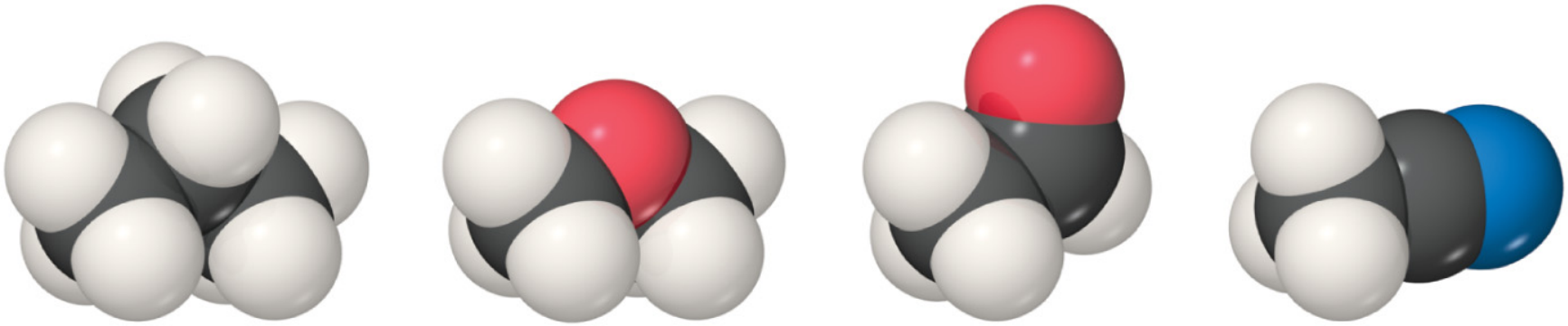
- Dipole–dipole interactions
  - Hydrogen bonding
- London dispersion forces

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



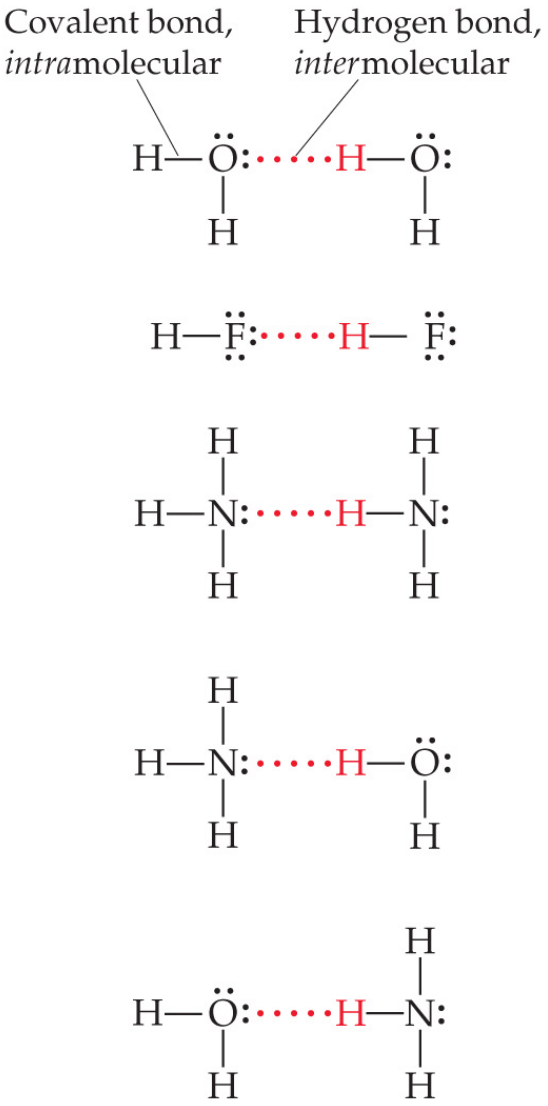
Propane	Dimethyl ether	Acetaldehyde	Acetonitrile
$CH_3CH_2CH_3$	CH_3OCH_3	CH_3CHO	CH_3CN
MW = 44 amu	MW = 46 amu	MW = 44 amu	MW = 41 amu
μ = 0.1 D	μ = 1.3 D	μ = 2.7 D	μ = 3.9 D
bp = 231 K	bp = 248 K	bp = 294 K	bp = 355 K

Increasing polarity
Increasing strength of dipole–dipole forces

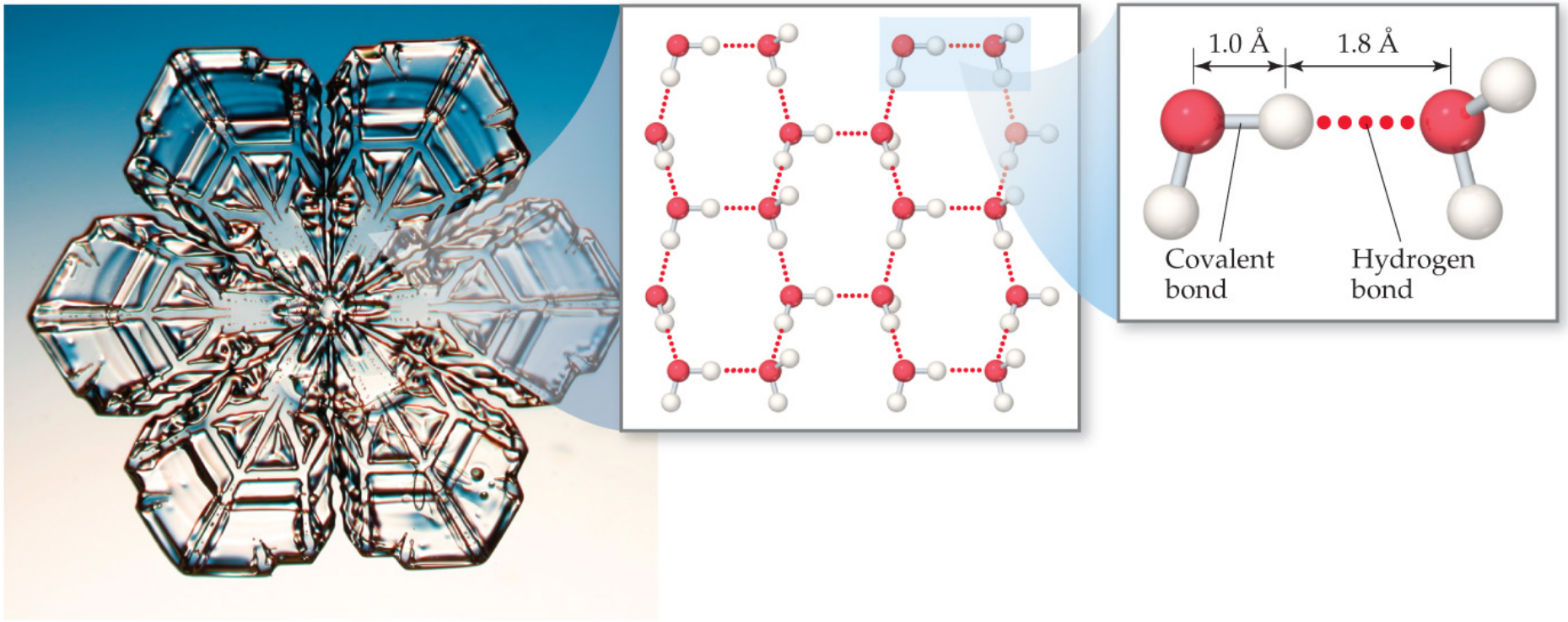
The more polar the molecule, the higher its boiling point.

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**.



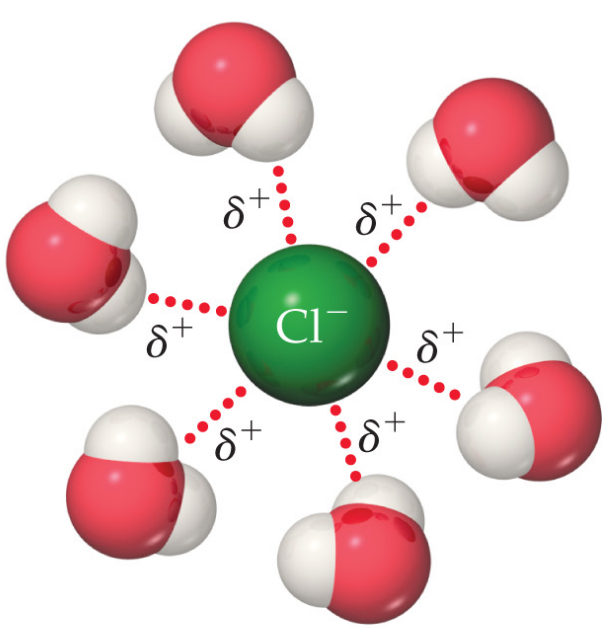
Hydrogen Bonding



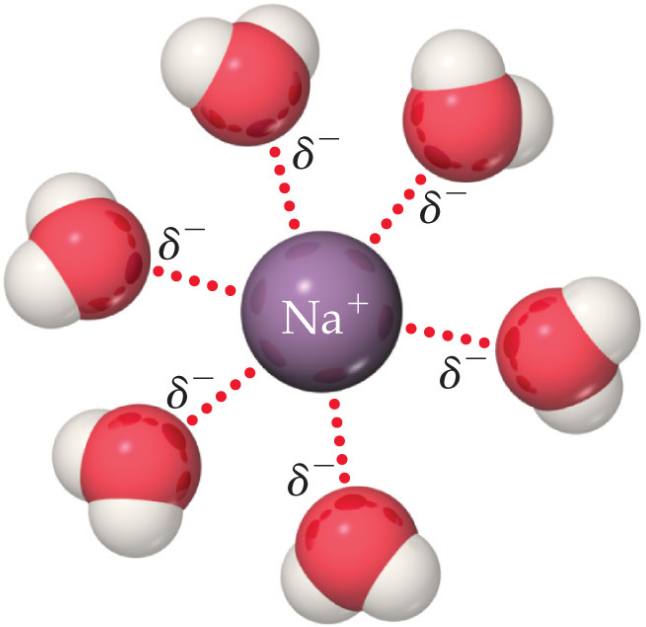
- Hydrogen bonding result of high electronegativity of nitrogen, oxygen, and fluorine.

Ion–Dipole Interactions

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

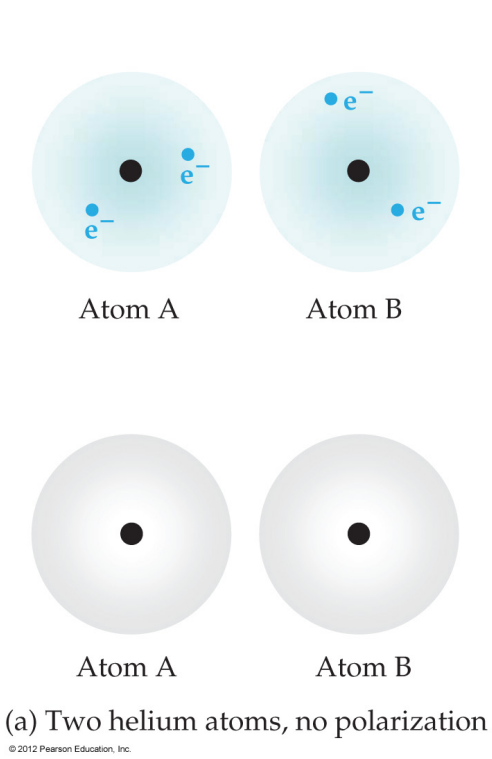


Positive ends of polar molecules are oriented toward negatively charged anion



Negative ends of polar molecules are oriented toward positively charged cation

London Dispersion Forces

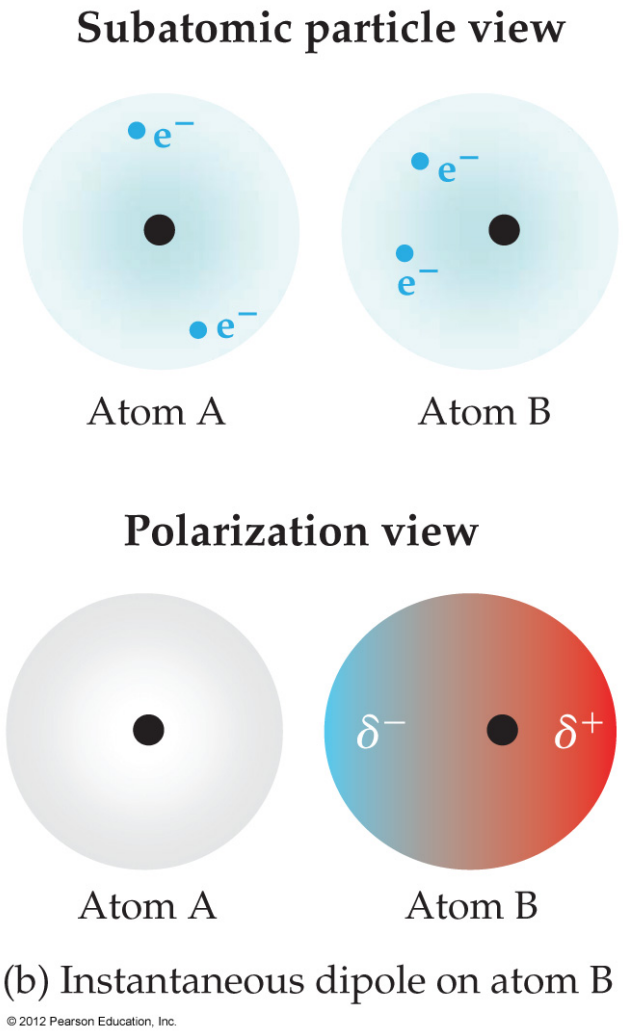


(a) Two helium atoms, no polarization

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

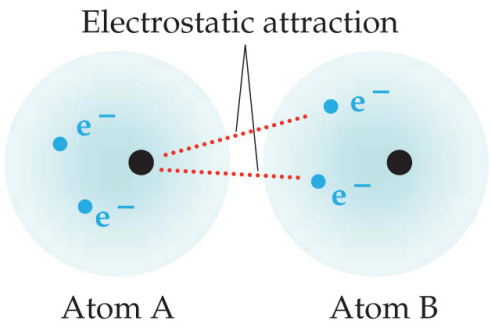
At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.



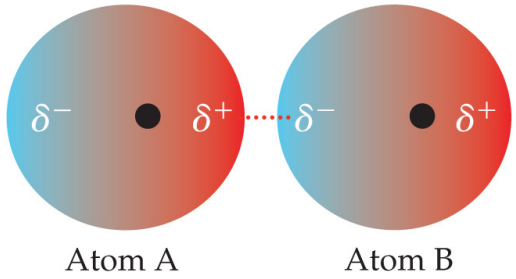
(b) Instantaneous dipole on atom B

London Dispersion Forces

Subatomic particle view



Polarization view

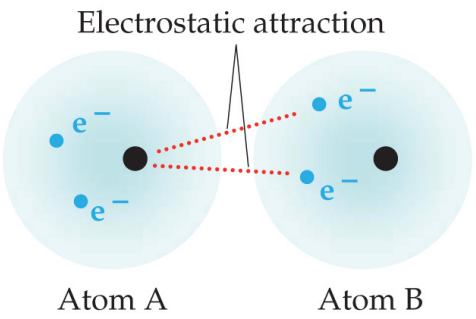


(c) Induced dipole on atom A

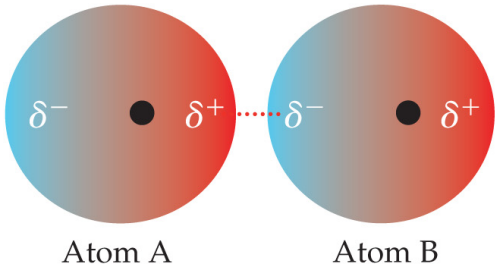
Another helium atom nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

London Dispersion Forces

Subatomic particle view



Polarization view



(c) Induced dipole on atom A

London dispersion forces

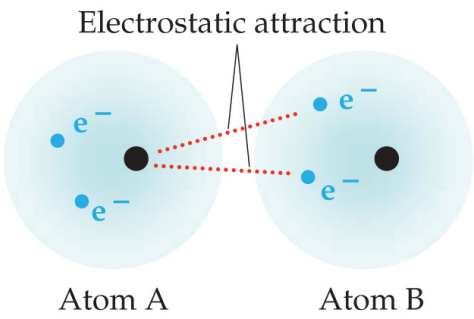
attractions between an instantaneous dipole and:

an induced dipole.

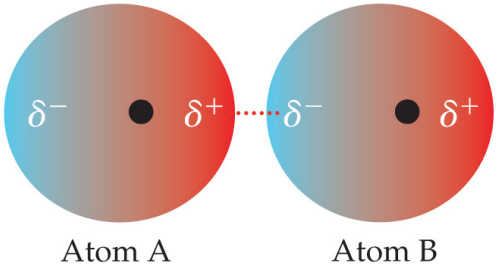
London Dispersion Forces

- present in *all* molecules,
  - polar or nonpolar.
- Tendency of an electron cloud to distort in this way is called **polarizability**.

Subatomic particle view

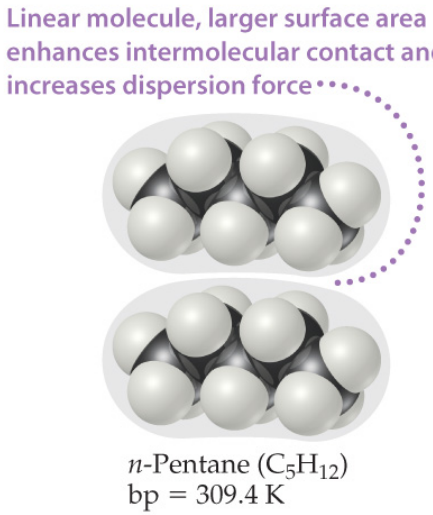


Polarization view

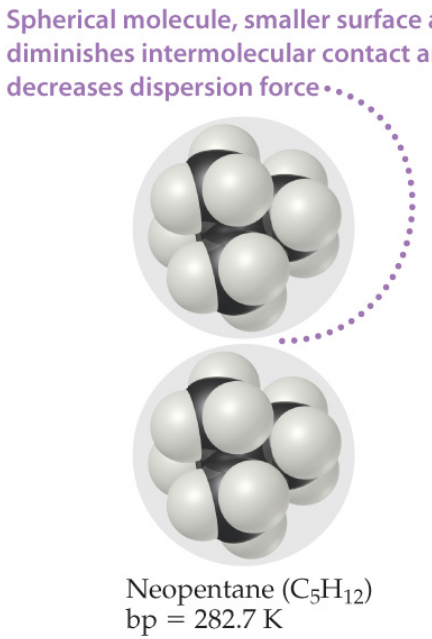


(c) Induced dipole on atom A

Factors Affecting London Forces

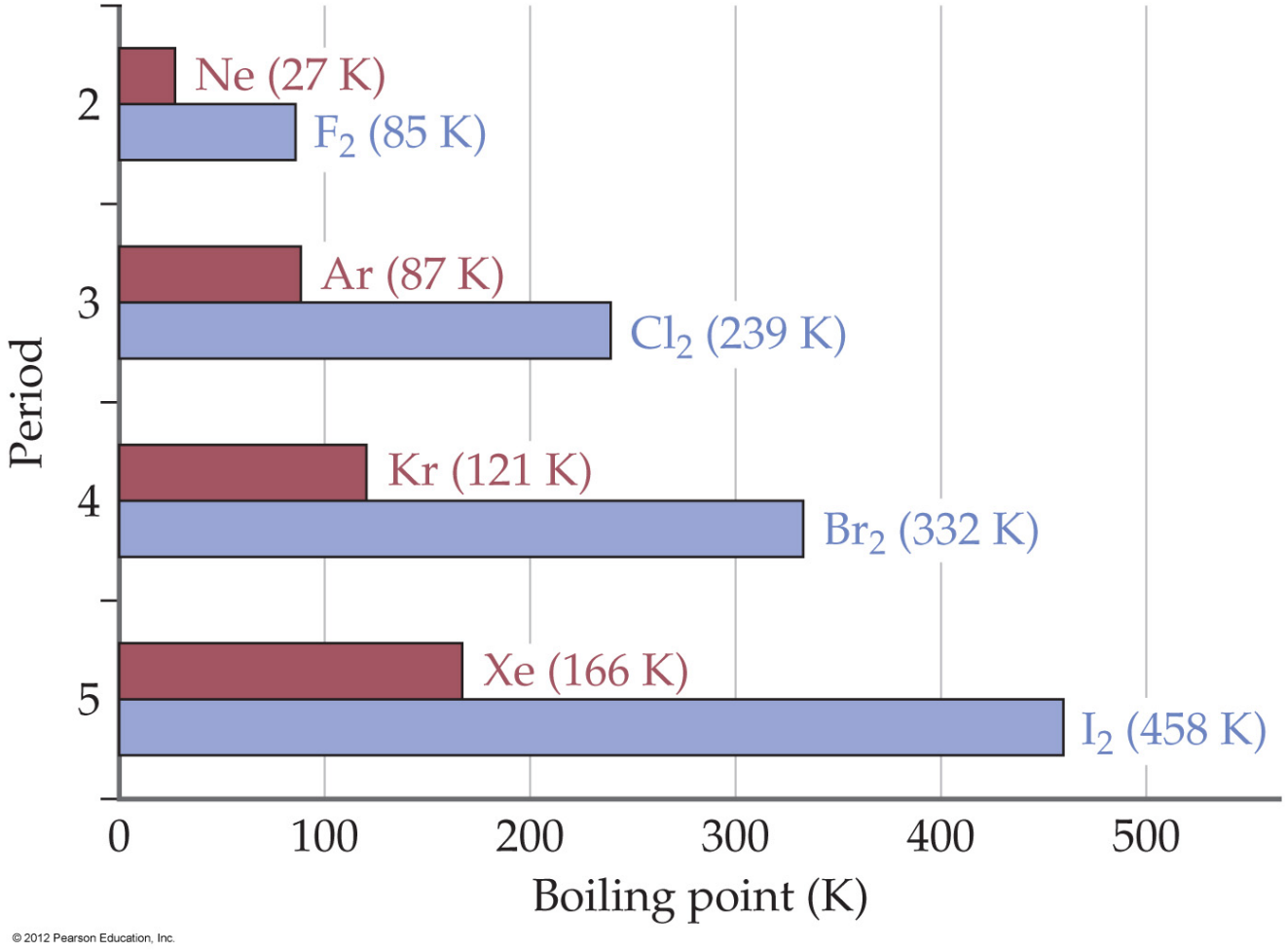


- Shape matters. long, skinny molecules (like *n*-pentane) pack together more efficiently.
  - Stronger interaction



- Short fat ones pack less well
  - Weaker interaction

Factors Affecting London Forces



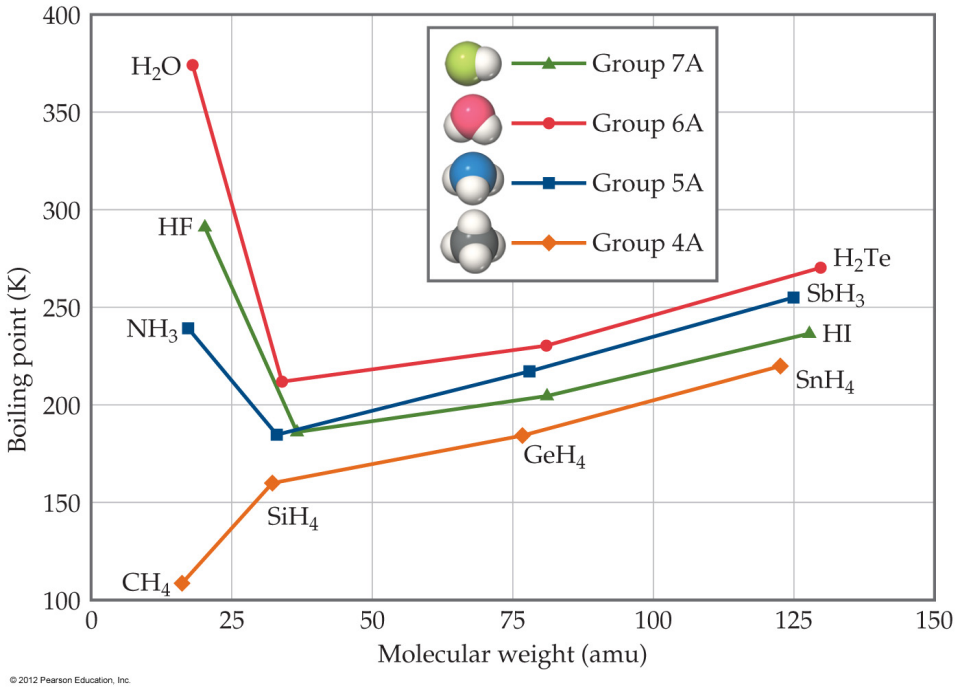
- increases with increased molecular weight.
- Larger atoms more electrons to slosh around easier to polarize.

Which Have a Greater Effect?

Dipole–Dipole Interactions or Dispersion Forces

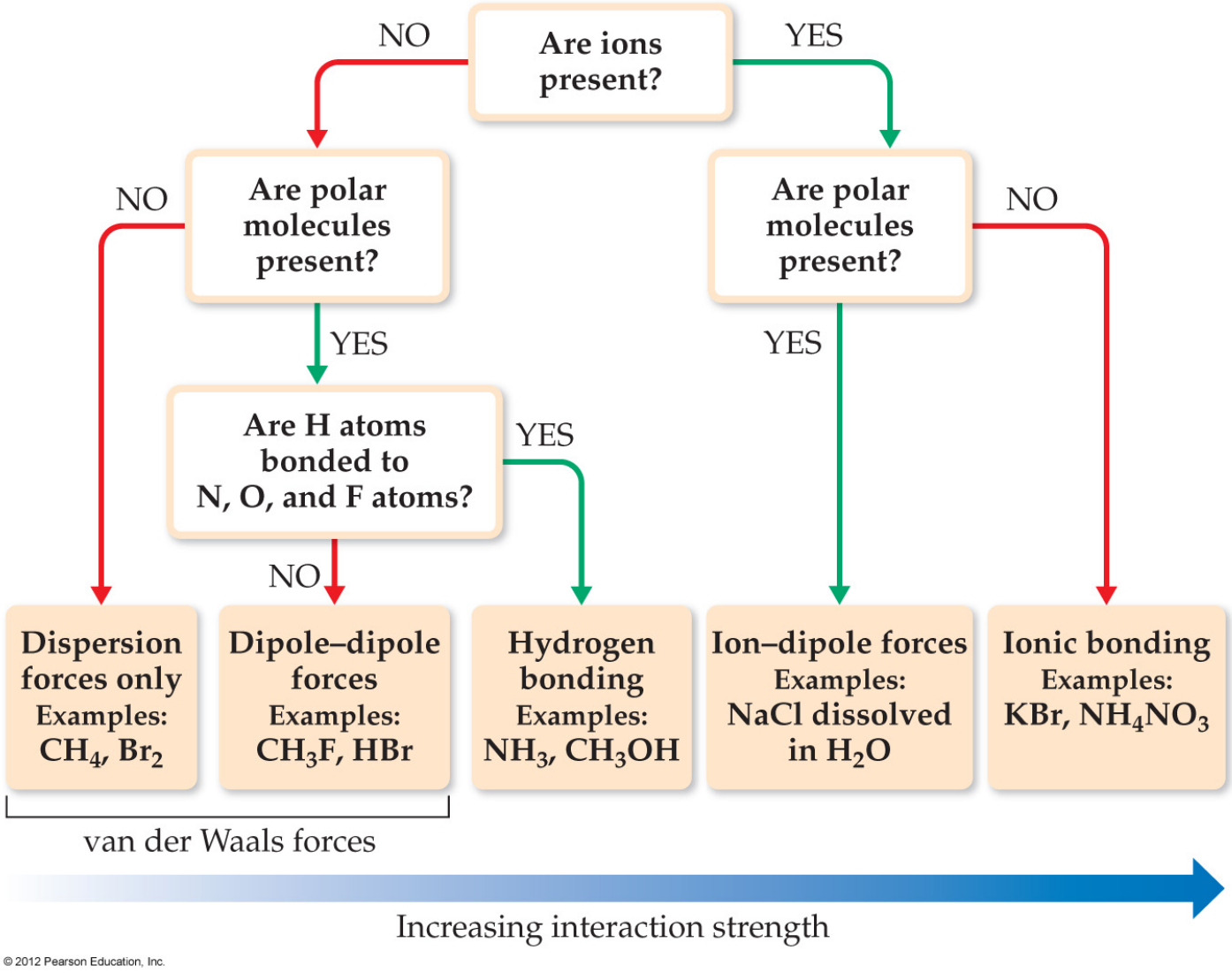
- If two molecules are of comparable size and shape, dipole–dipole interactions will likely be the dominating force.
- If one molecule is much larger than another, dispersion forces will likely determine its physical properties.

How Do We Explain This?

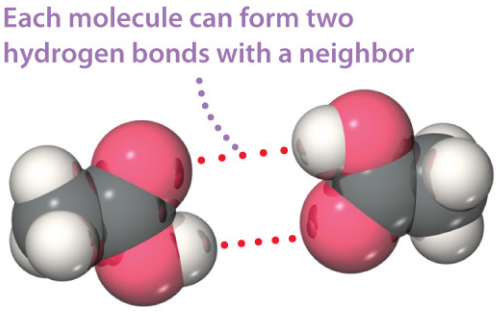


- The nonpolar series (SnH_4 to CH_4) follow the expected trend.
- The polar series follow the trend until you get to the smallest molecules in each group.

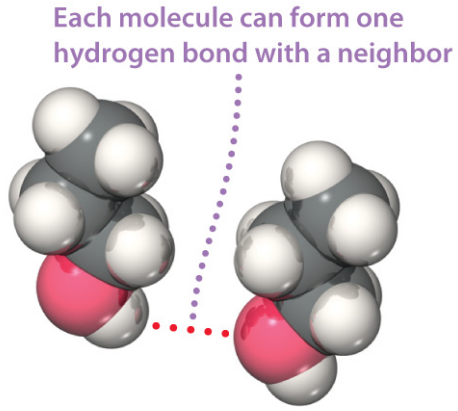
Summarizing Intermolecular Forces



Intermolecular Forces Affect Many Physical Properties



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



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

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.

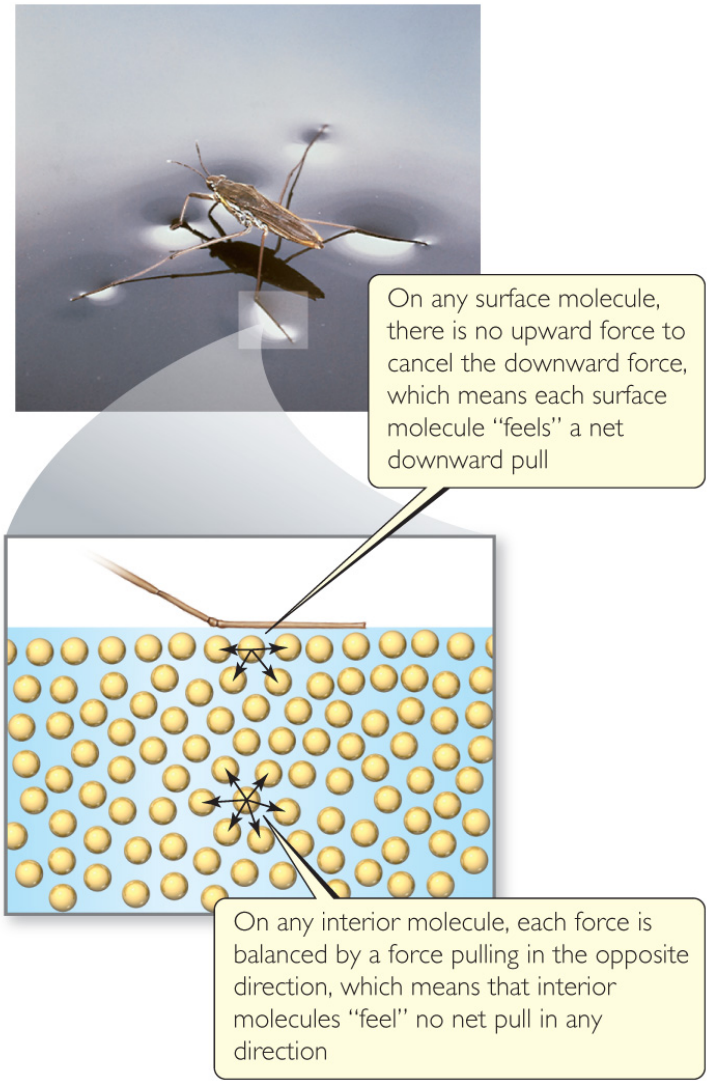
SAE 40
higher number
higher viscosity
slower pouring

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.