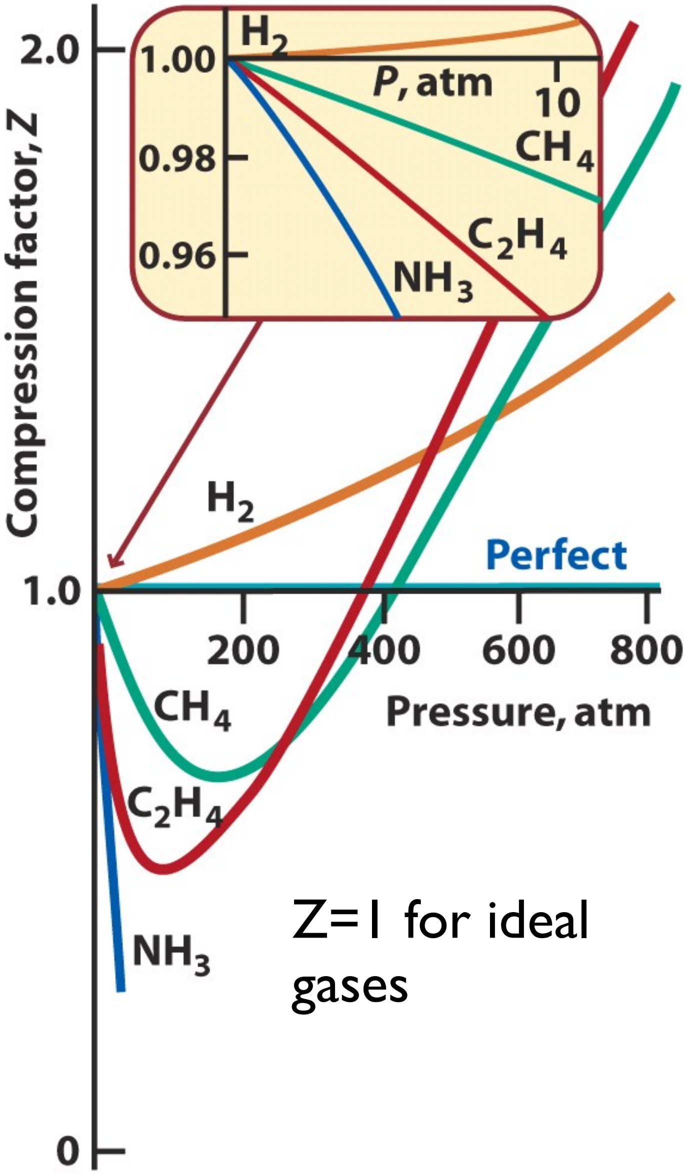
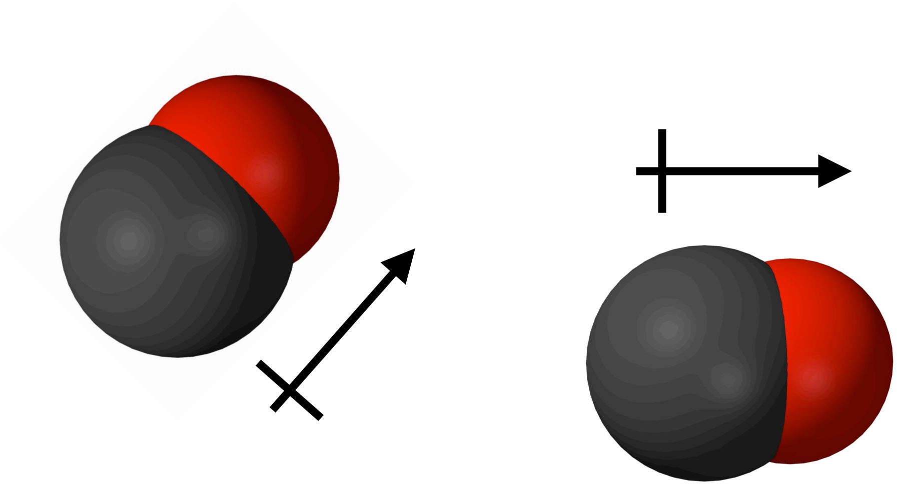
Lecture C2
Microscopic to Macroscopic, Part 2: Intermolecular Interactions

Let's get together.

Most gases are NOT ideal except at very low pressures:

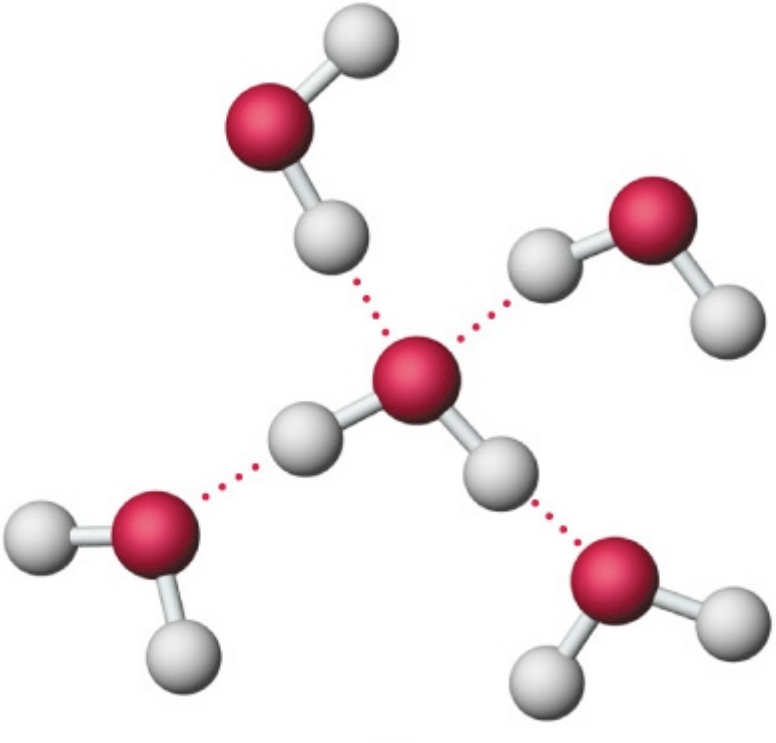


Z=1 for ideal gases

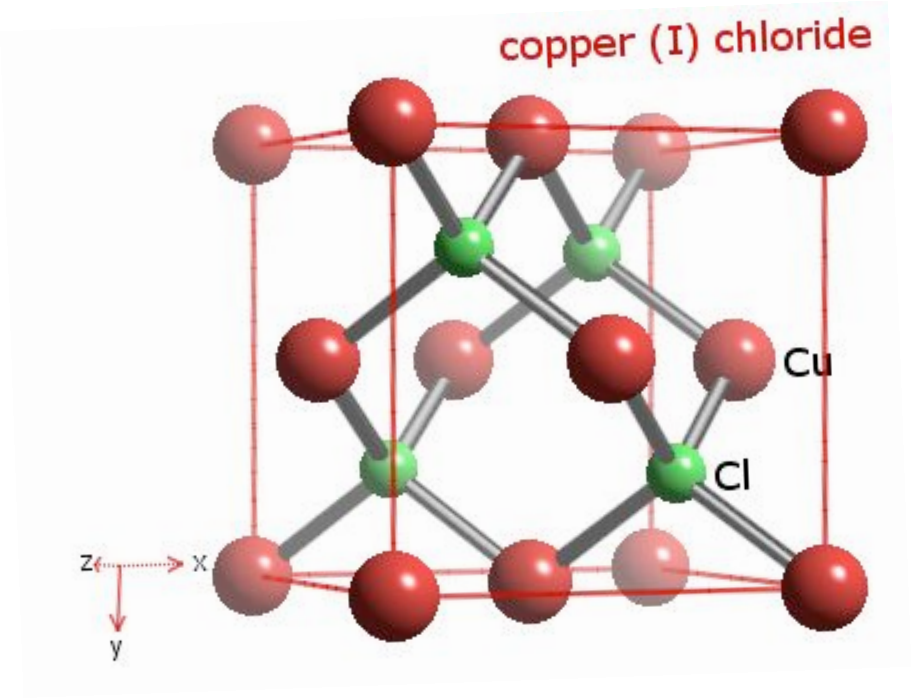


Intermolecular interactions come into play at higher pressures -- molecules interact!

Intermolecular interactions are important in gases, but even MORE so in determining the material properties of liquids and solids!



liquid water



CuCl crystal

A list of some of the intermolecular interactions that control macroscopic material properties:

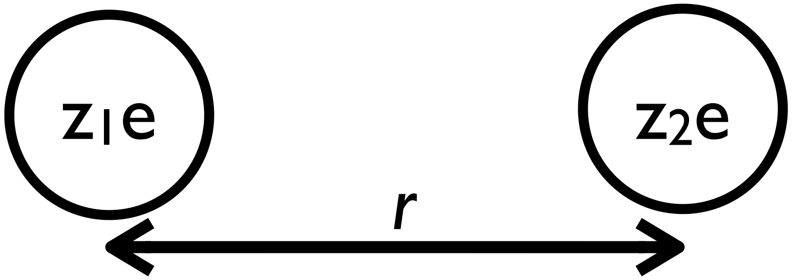
a. ion-ion
b. ion-dipole
c. dipole-dipole (electric)
d. dipole-dipole (magnetic)
e. dispersion forces (induced dipoles)
f. hydrogen bonding
g. metal-ligand bonding

"Noncovalent Intermolecular Interactions"

Noncovalent Intermolecular Interactions

a. ion-ion interactions: Coulomb's Law

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{z_1 z_2 e^2}{r}$$



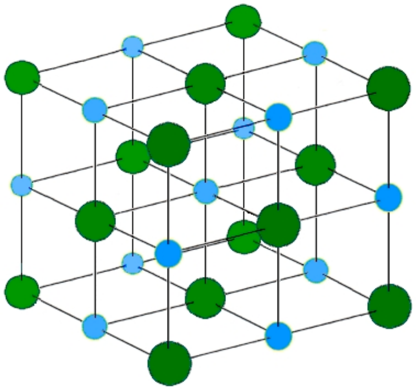
Noncovalent Intermolecular Interactions

a. ion-ion interactions:

$$V(r) = \frac{1}{4\pi\varepsilon_0} \frac{z_1 z_2 e^2}{r}$$

Sodium Chloride

Melting Point: 801 C
Boiling Point: 1465 C
Lattice: fcc
Lattice Parameter a = 564 pm

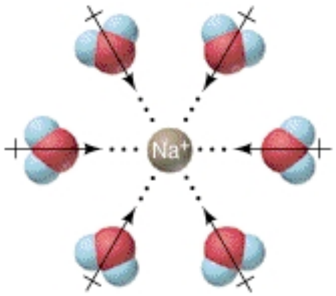


Blue: Na^+
Green: Cl^-

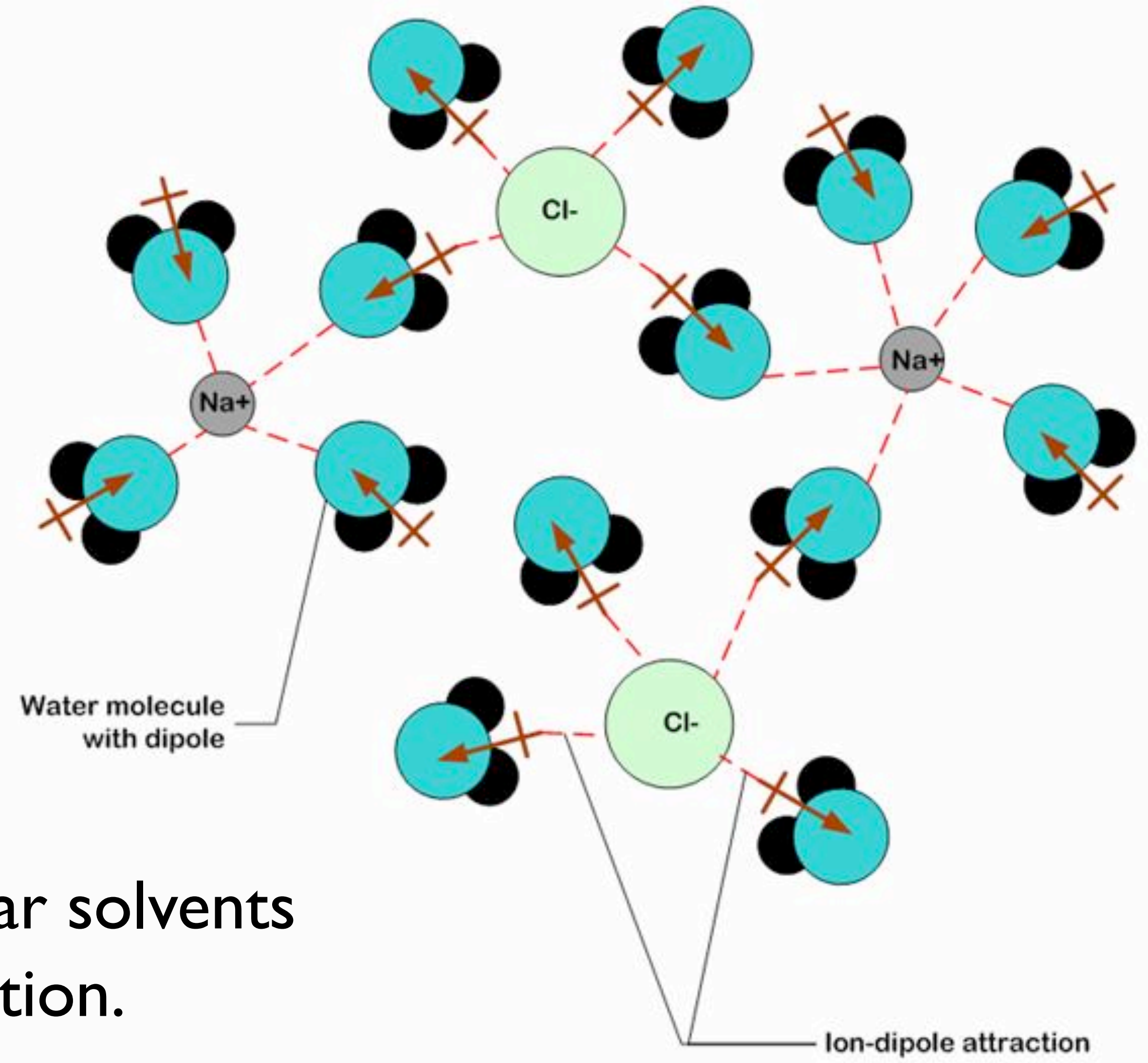
We call these "ionic solids."

Noncovalent Intermolecular Interactions

b. ion-dipole interactions



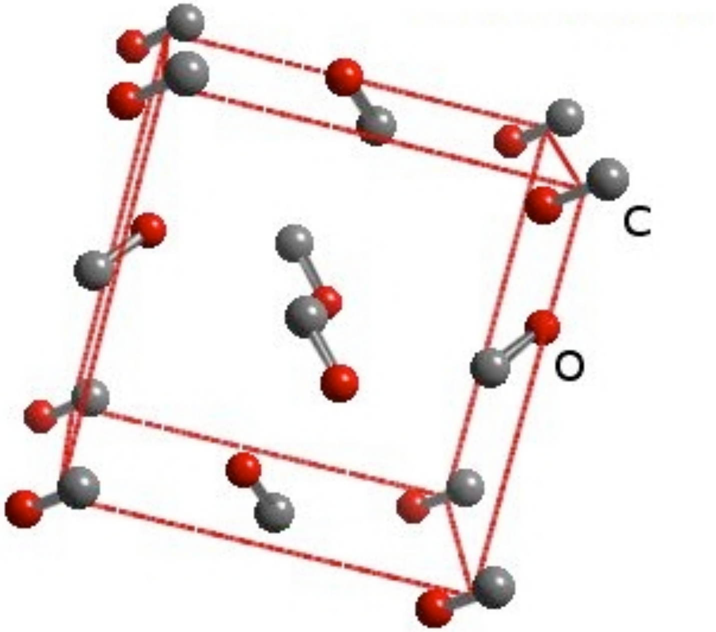
solvation shell



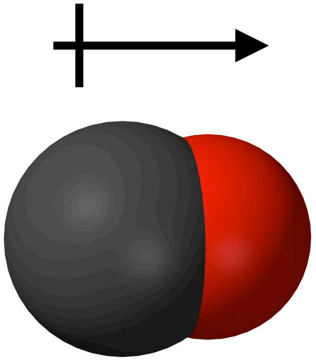
Ion solvation in polar solvents leads to salt dissolution.

Noncovalent Intermolecular Interactions

c. dipole-dipole interactions (electric)



CO μ=0.112D

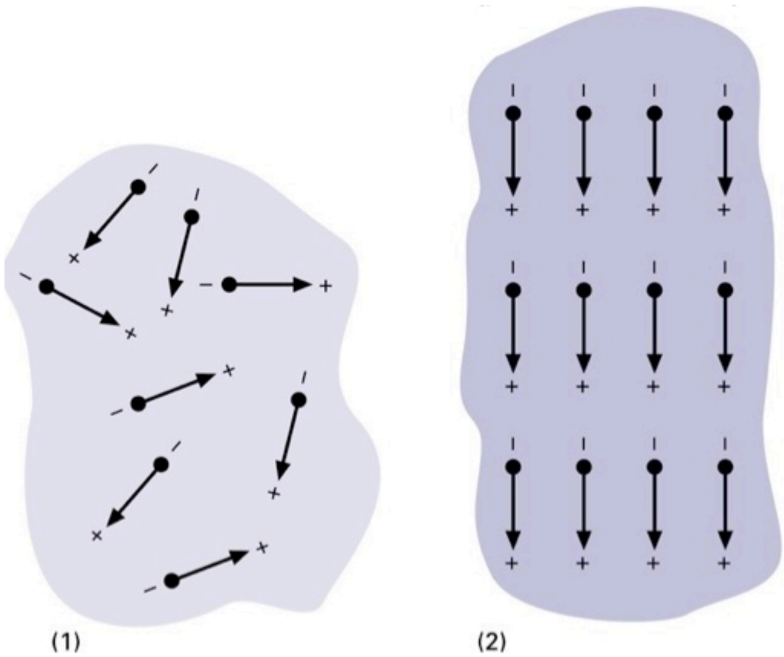


The CO molecules in solid CO align to cancel out the net dipole moment in the unit cell.

Noncovalent Intermolecular Interactions

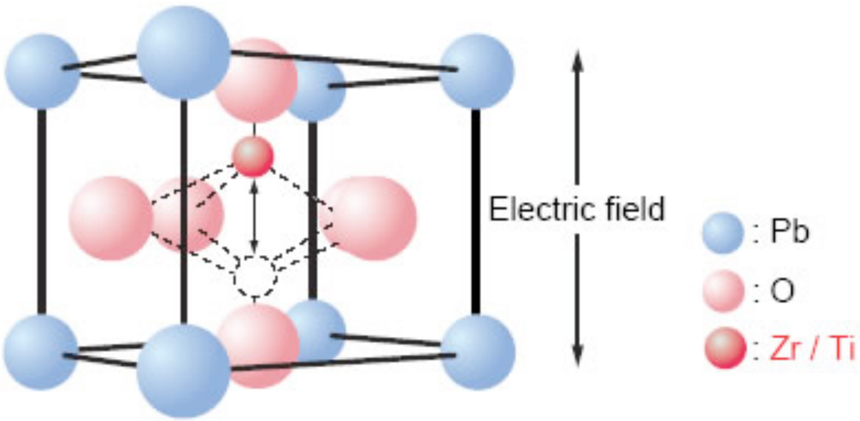
c. dipole-dipole interactions (electric)

The dipole moments in some materials can be aligned (poled) with an external electric field: Ferroelectrics



before poling

after poling



$PbZrO_3$ or $PbTiO_3$

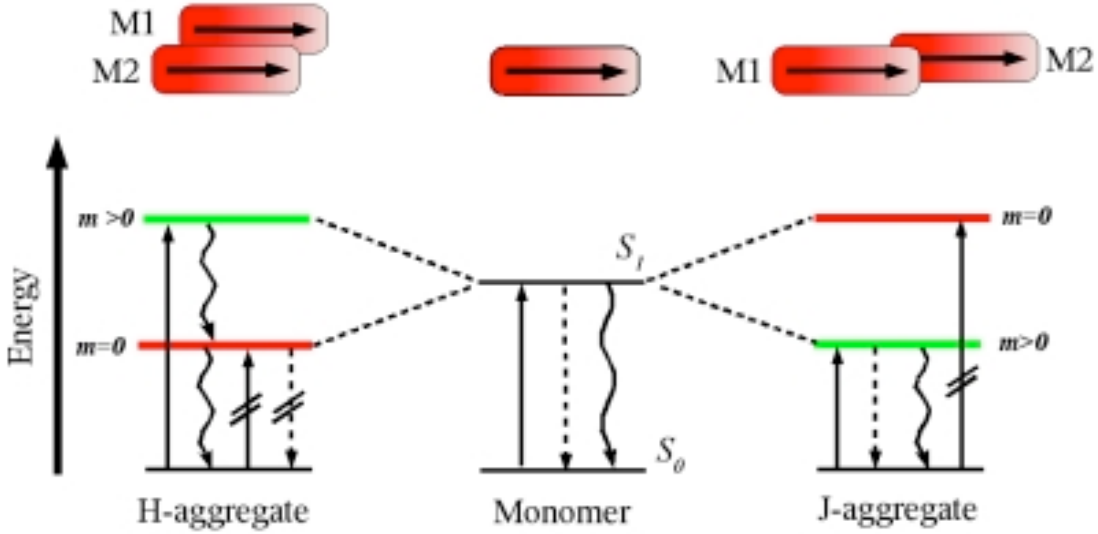
Noncovalent Intermolecular Interactions

c. dipole-dipole interactions (electric)

Excited state dipoles are transient (nanosecond lifetimes), but can couple as well: solvatochromism is the change in color of a molecule when placed in different polar solvents.

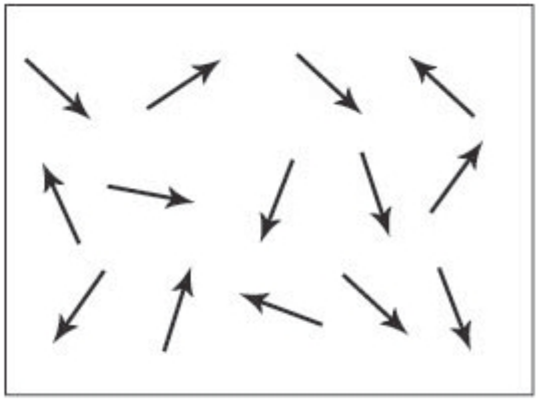
Also, dye molecules can interact via Exciton Coupling: The coupling of two or more dye molecules via transition dipole-transition dipole interactions.

(H aggregates and J aggregates)



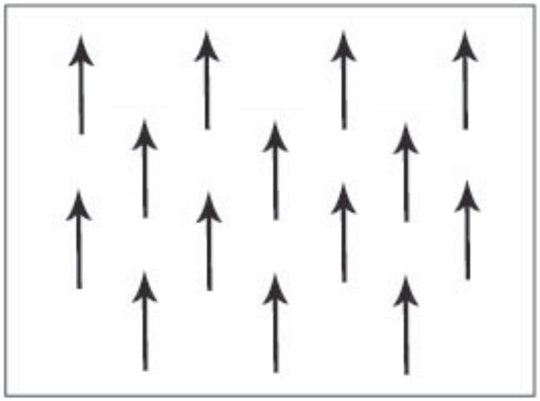
Noncovalent Intermolecular Interactions

d. magnetic dipole-magnetic dipole



Paramagnetism

O_2



Ferromagnetism

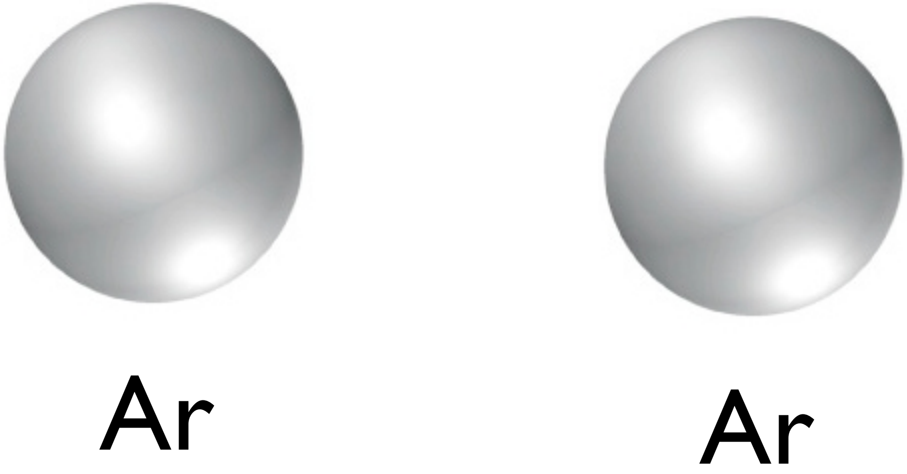
Fe, Co, Ni

We've looked at magnetic dipole coupling via spin interactions in ferromagnetic materials before.

(There are no magnetic monopoles).

Noncovalent Intermolecular Interactions

e. induced dipoles and dispersion forces



Argon atoms have no net charge or dipole moment.
Yet Argon forms a liquid and a solid phase. Why?

Noncovalent Intermolecular Interactions

e. induced dipoles and dispersion forces

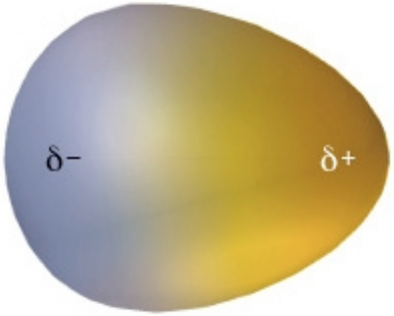
Ar Cl^-

ion-induced dipole interactions

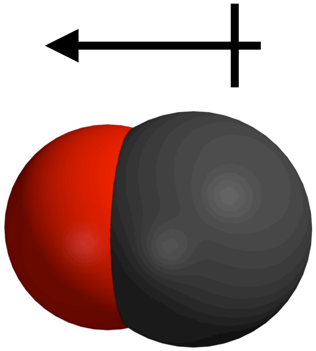
"Van der Waals Interactions"

Noncovalent Intermolecular Interactions

e. induced dipoles and dispersion forces



Ar



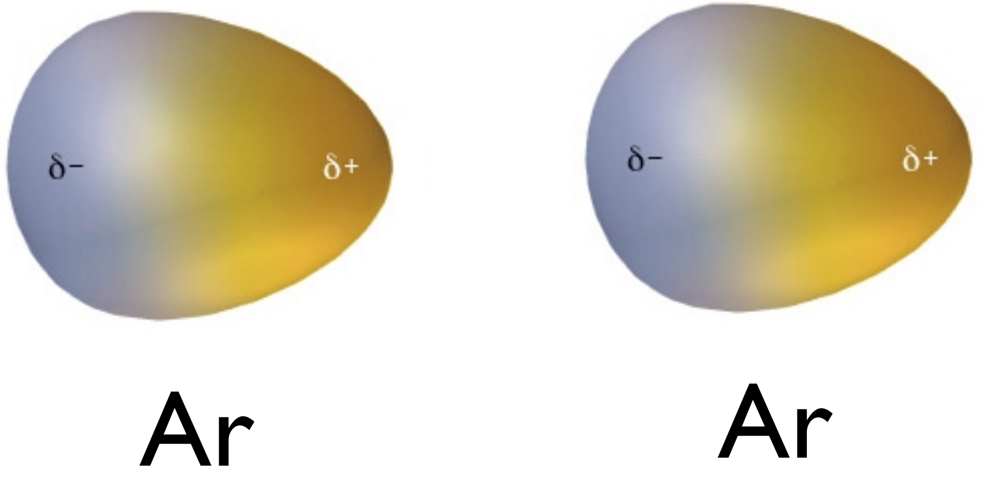
CO

dipole-induced dipole interactions

"Van der Waals Interactions"

Noncovalent Intermolecular Interactions

e. induced dipoles and dispersion forces



instantaneous induced dipole-induced dipole interactions

"Van der Waals Interactions" "London dispersion forces"

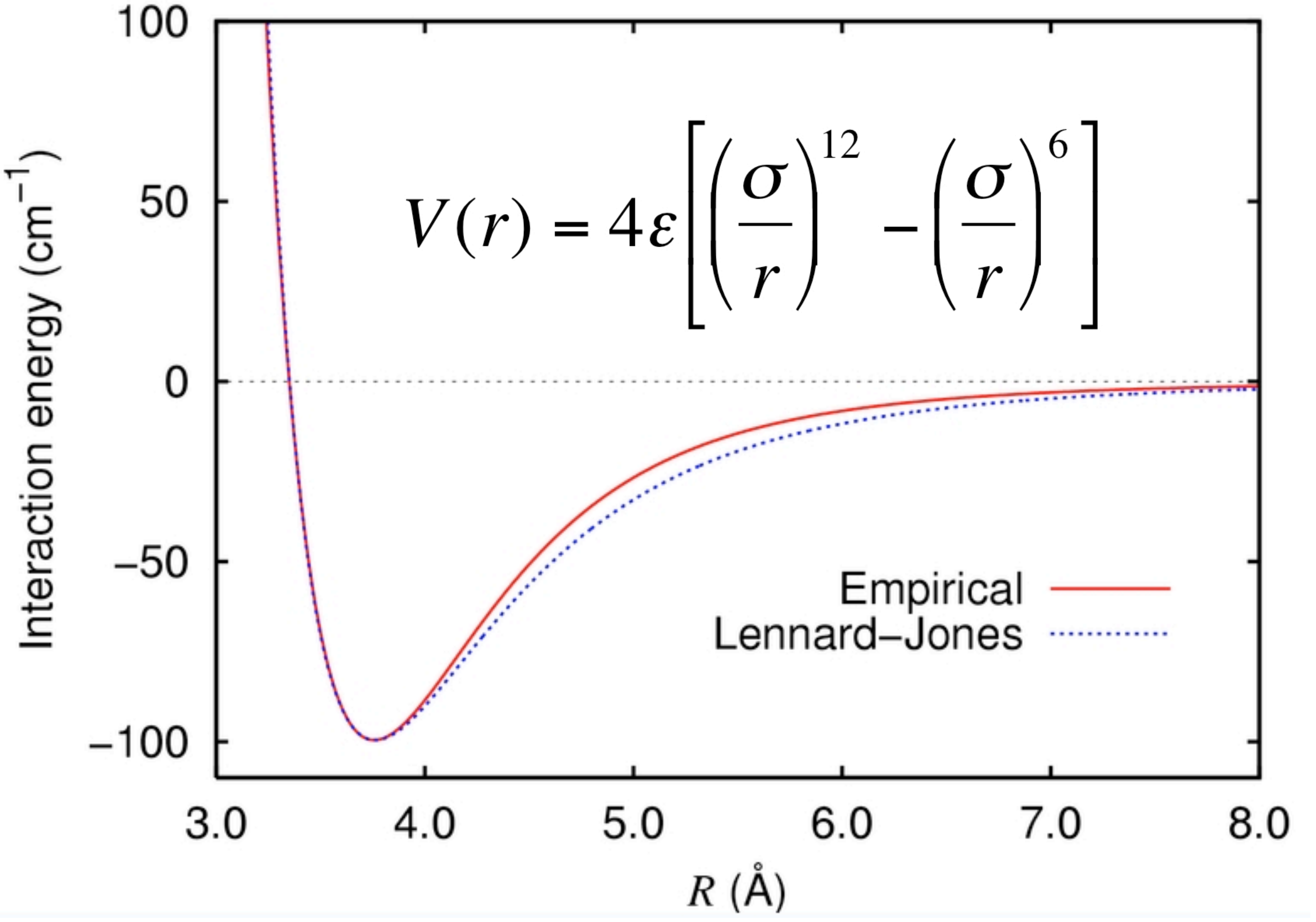
London dispersion forces are attractive ($-1/r^6$).
There are also repulsive forces that prevent the Ar atoms from getting to close (e.g., electron overlap).

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

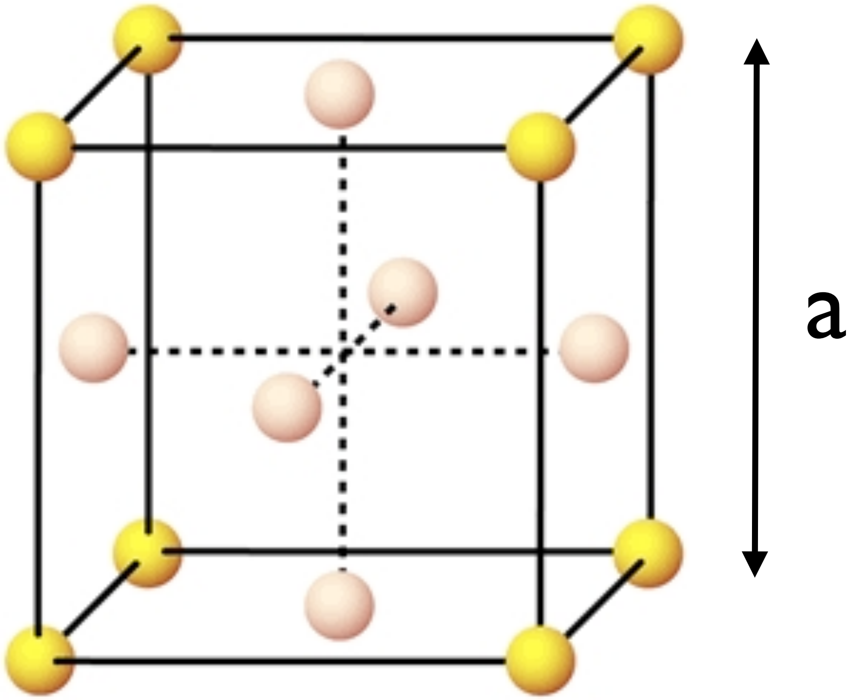
Lennard-Jones potential

The Lennard-Jones potential (also referred to as the L-J potential or 6-12 potential) is a simple mathematical model that describes the interaction between a pair of neutral atoms or molecules. It was proposed in 1924 by John Lennard-Jones.

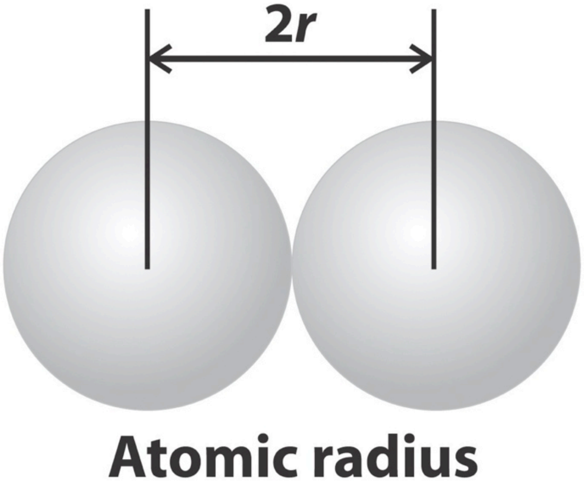
London dispersion forces are attractive ($-1/r^6$).
There are also repulsive forces that prevent the Ar atoms from getting to close (e.g., electron overlap).



The LJ potential helps us understand the forces that make solid Argon crystallize into an FCC lattice with a = 526.0 pm.



FCC Argon
a = 526.0 pm



r = 186.0 pm

"*van der Waals radius*"

$r = (\sqrt{2}/4)a$

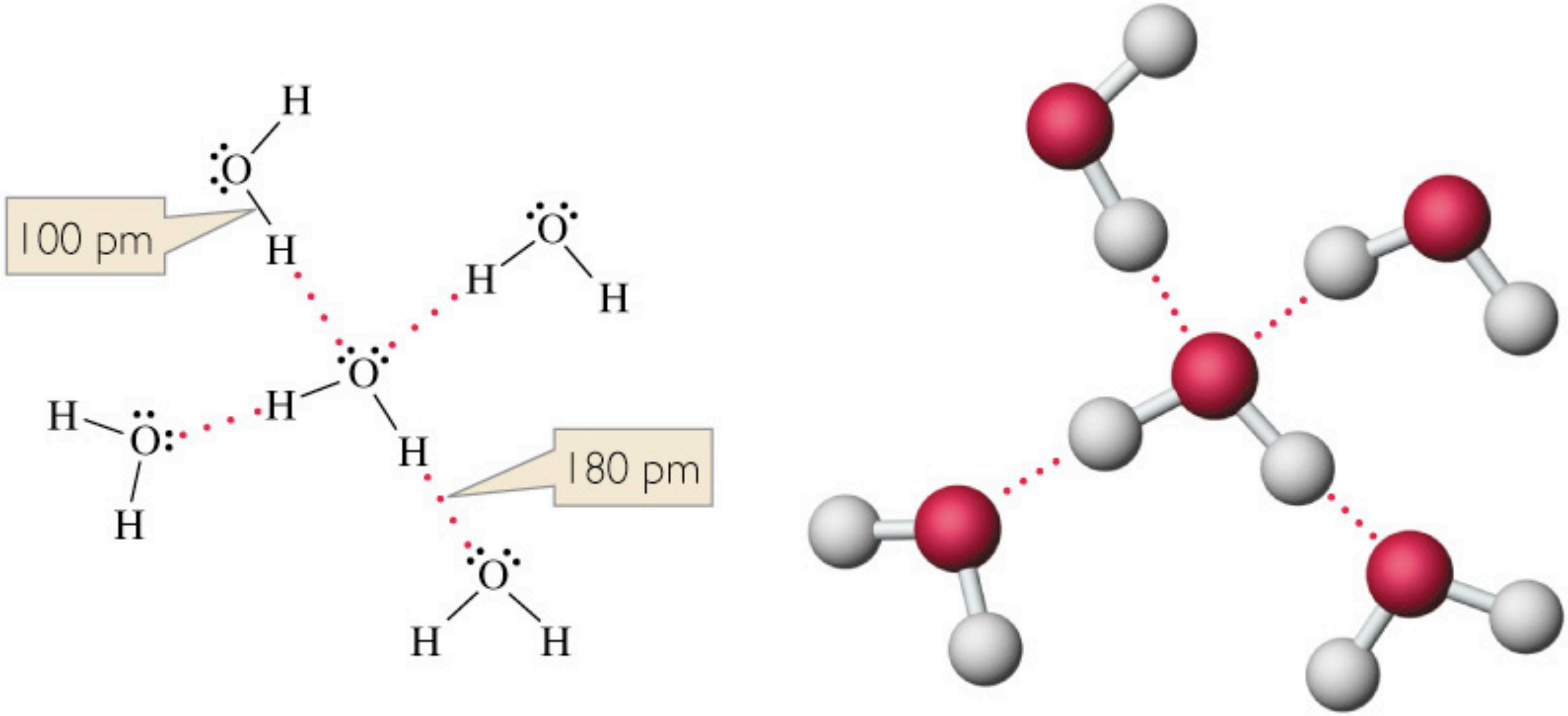
Noncovalent Intermolecular Interactions

a. ion-ion
b. ion-dipole
c. electric dipole-electric dipole
d. magnetic dipole-magnetic dipole
e. dispersion forces
f. hydrogen bonding
g. metal-ligand bonding

The last two are bonding types that do involve electron overlap, but are typically not as strong as covalent bonds.

Noncovalent Intermolecular Interactions

f. hydrogen bonding



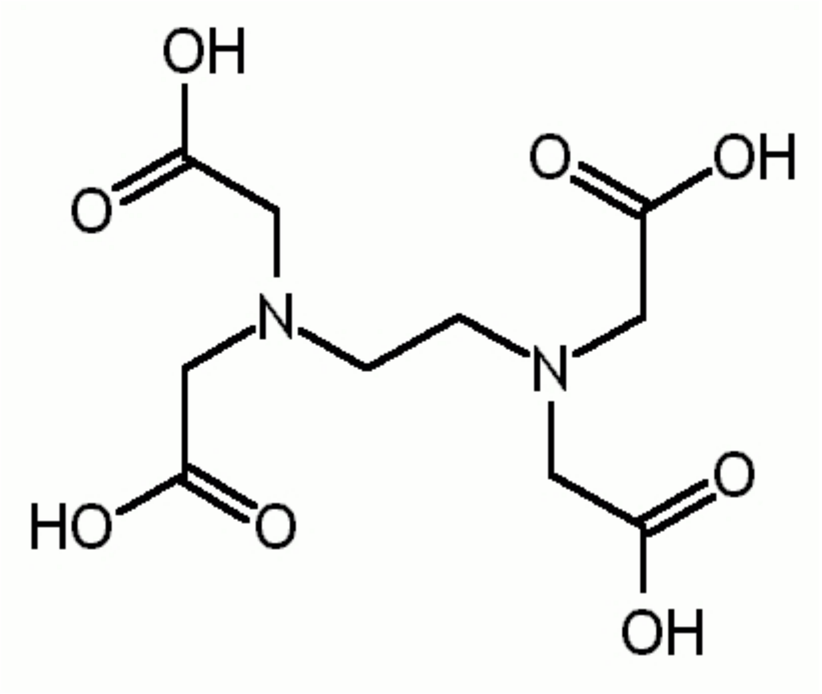
(a)

(b)

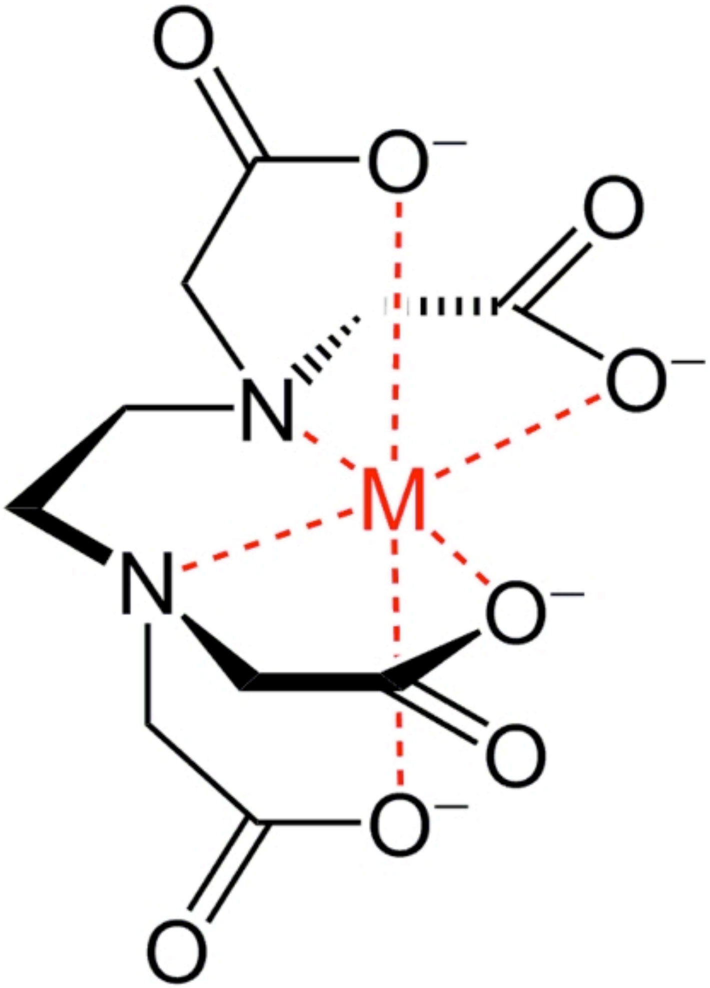
hydrogen bond energy - 20 kJ mol^{-1}

Noncovalent Intermolecular Interactions

g. metal-ligand bonding



EDTA - H_4Y



MY^{n-4}

Noncovalent Intermolecular Interactions

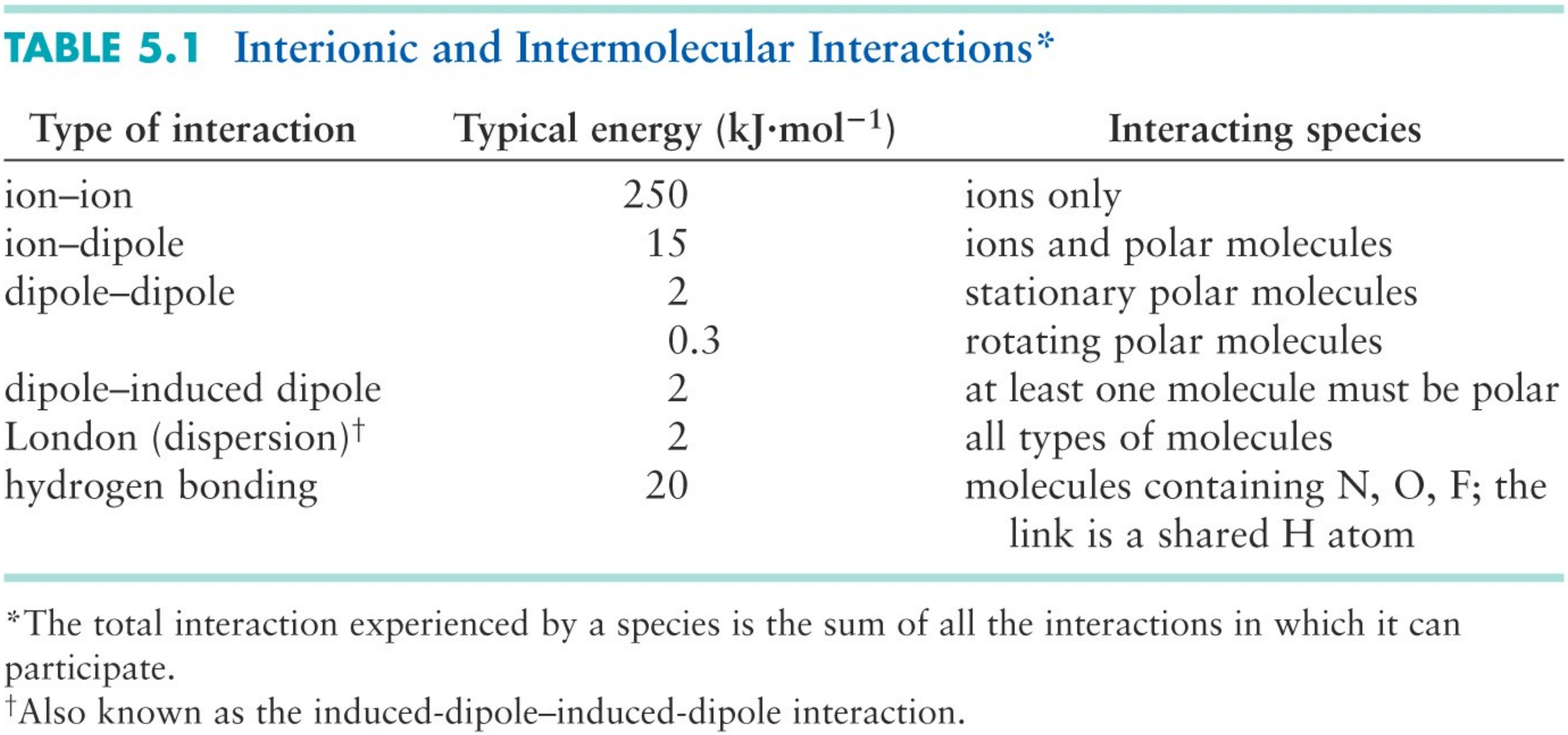


TABLE 5.1 Interionic and Intermolecular Interactions*

Type of interaction	Typical energy ($kJ \cdot mol^{-1}$)	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)†	2	all types of molecules
hydrogen bonding	20	molecules containing N, O, F; the link is a shared H atom

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

†Also known as the induced-dipole–induced-dipole interaction.

C-H covalent bond in CH_4 = 440 kJ mol^{-1}

Which has the higher boiling point?

$H_3C\text{-}CH_2\text{-}CH_3$

propane

$H_3C\text{-}CO\text{-}CH_3$

dimethyl ketone

Let's list the types of IM forces - from strong to weak - between molecules in the liquid form:

$H_3C\text{-}CH_2\text{-}CH_3$	$H_3C\text{-}CO\text{-}CH_3$
propane	dimethyl ketone
VdWs	dipole-dipole VdWs

Which has the higher boiling point?

$H_3C\text{-}CH_2\text{-}CH_3$	$H_3C\text{-}CO\text{-}CH_3$
propane	dimethyl ketone
VdWs	dipole-dipole VdWs
$T_B = -42°C$	$T_B = 102°C$

Which has the higher boiling point?

$H_3C\text{-}CH_2\text{-}OH$

ethanol

$H_3C\text{-}O\text{-}CH_3$

ethyl ether

Let's list the types of IM forces - from strong to weak - between molecules in the liquid form:

$H_3C\text{-}CH_2\text{-}OH$	$H_3C\text{-}O\text{-}CH_3$
ethanol	ethyl ether
hydrogen bonding dipole-dipole VdWs	dipole-dipole VdWs

Which has the higher boiling point?

$H_3C\text{-}CH_2\text{-}OH$	$H_3C\text{-}O\text{-}CH_3$
ethanol	ethyl ether
hydrogen bonding dipole-dipole VdWs	dipole-dipole VdWs
T_B = 78.4°C	T_B = 34.5°C

Which has the higher boiling point?

$H_3C\text{-}CH_2\text{-}CH_3$

propane

$H_3C\ \text{-}CH_2\text{-}CH_2\text{-}CH_3$

butane

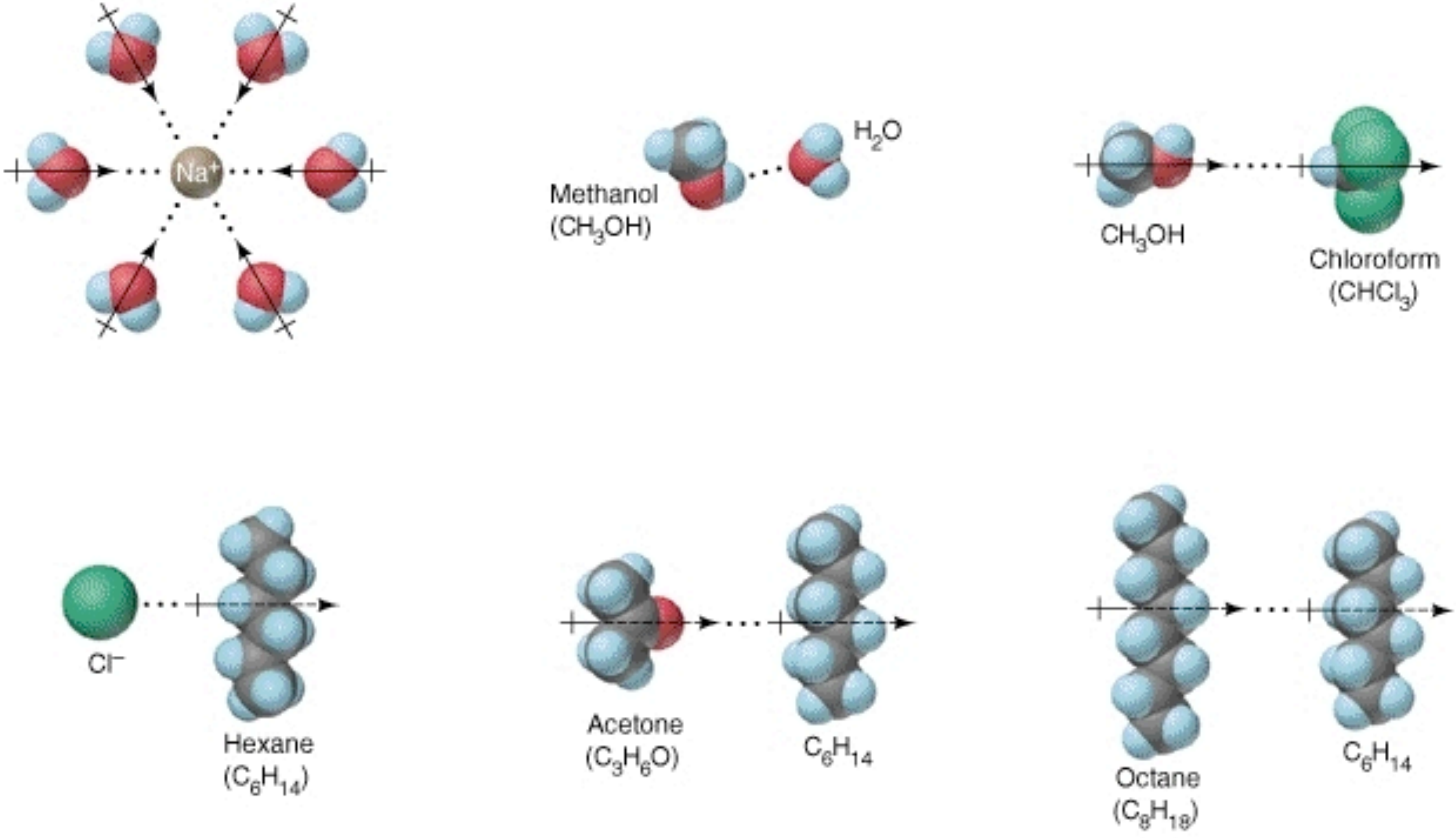
Let's list the types of IM forces - from strong to weak - between molecules in the liquid form:

$H_3C\text{-}CH_2\text{-}CH_3$	$H_3C\ \text{-}CH_2\text{-}CH_2\text{-}CH_3$
propane	butane
VdWs	VdWs

Which has the higher boiling point?

$H_3C\text{-}CH_2\text{-}CH_3$	$H_3C\ \text{-}CH_2\text{-}CH_2\text{-}CH_3$
propane	butane
VdWs	VdWs
$T_B = -42°C$	$T_B = -11.7°C$

Noncovalent Intermolecular Interactions



Can you name the type of interaction?