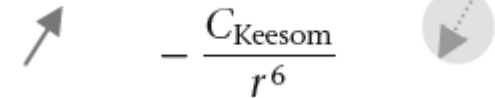# Van der Waals Forces between Polar Molecules
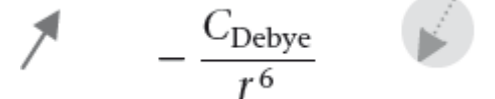
Van der Waals force:

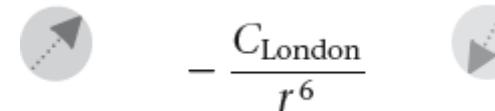- **the orientation force**: Keesom interactions of permanent dipoles

$$-\frac{C_{\text{Keesom}}}{r^6}$$

- **the induction force**: Debye interactions: a permanent dipole induces a dipole in another nonpolar molecule

$$-\frac{C_{\text{Debye}}}{r^6}$$

- **the dispersion force:** London dispersion interactions between transient dipoles of nonpolar but polarizable molecules

$$-\frac{C_{\text{London}}}{r^6}$$

Only the dispersion interaction contributes if both molecules are nonpolar.

For two dissimilar polar molecules:

$$
\begin{aligned}
w_{\text{VDW}}(r) &= -C_{\text{VDW}}/r^6 = -[C_{\text{ind}} + C_{\text{orient}} + C_{\text{disp}}]/r^6 \\
&= -\left[(u_1^2\alpha_{02} + u_2^2\alpha_{01}) + \frac{u_1^2 u_2^2}{3kT} + \frac{3\alpha_{01}\alpha_{02}h\nu_1\nu_2}{2(\nu_1+\nu_2)}\right]\bigg/(4\pi\varepsilon_0)^2 r^6
\end{aligned}
$$

(18)

Table 6.3 Induction, Orientation, and Dispersion Free Energy Contributions to the Total Van der Waals Energy in a Vacuum for Various Pairs of Molecules at 293K

Similar Molecules				Van der Waals Energy Coefficients C (10^{-79} J m^6)			Total VDW Energy C_{VDW}		
Interacting Molecules	Electronic Polarizability $\frac{\alpha_0}{4\pi\varepsilon_0}$ (10^{-30}m^3)	Permanent Dipole Moment u (D) [a]	Ionization Potential $I = h\nu_1$ (eV) [b]	C_{ind} $\frac{2u^2\alpha_0}{(4\pi\varepsilon_0)^2}$	C_{orient} $\frac{u^4}{3kT(4\pi\varepsilon_0)^2}$	C_{disp} $\frac{3\alpha_0^2 h\nu_1}{4(4\pi\varepsilon_0)^2}$	Theoretical Eq. (6.17)	From Gas Law Eq. (6.14)	Dispersion Energy Contribution to Total (Theoretical) (%)
Ne–Ne	0.39	0	21.6	0	0	4	4	4	100
CH$_4$–CH$_4$	2.60	0	12.6	0	0	102	102	101	100
HCl–HCl	2.63	1.08	12.7	6	11	106	123	157	86
HBr–HBr	3.61	0.78	11.6	4	3	182	189	207	96
HI–HI	5.44	0.38	10.4	2	0.2	370	372	350	99
CH$_3$Cl–CH$_3$Cl	4.56	1.87	11.3	32	101	282	415	509	68
NH$_3$–NH$_3$	2.26	1.47	10.2	10	38	63	111	162	57
H$_2$O–H$_2$O	1.48	1.85	12.6	10	96	33	139	175	24

Dissimilar Molecules	$\frac{u_1^2\alpha_{02}+u_2^2\alpha_{01}}{(4\pi\varepsilon_0)^2}$	$\frac{u_1^2 u_2^2}{3kT(4\pi\varepsilon_0)^2}$	$\frac{3\alpha_{01}\alpha_{02}h\nu_1\nu_2}{2(4\pi\varepsilon_0)^2(\nu_1+\nu_2)}$			
Ne–CH$_4$	0	0	19	19[c]	—	100
HCl–HI	7	1	197	205	—	96
H$_2$O–Ne	1	0	11	12	—	92
H$_2$O–CH$_4$	9	0	58	67	—	87

[a] 1 D = 3.336 × 10^{-30} Cm.

[b] 1 eV = 1.602 × 10^{-19} J.

[c] This approximate value may be compared with the ab initio calculation by Fowler et al., (1989) that gives 23 × 10^{-79} J m^6.

hydrophobic effect

Van der Waals Forces between Polar Molecules

$$w_{\mathrm{VDW}}(r) = -C_{\mathrm{VDW}}/r^6$$

(18)

(18) has limited validity:
- should consider quadrupolar and higher-order multipole interactions
- in rigid media the dipole–dipole interaction is proportional to $1/r^3$
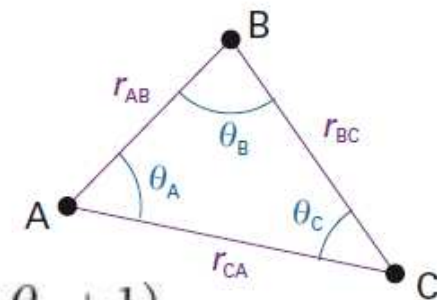
- should consider the interaction of three (or more) molecules

$$V = -\frac{C_6}{r_{AB}^6} - \frac{C_6}{r_{BC}^6} - \frac{C_6}{r_{CA}^6} + \frac{C'}{(r_{AB}r_{BC}r_{CA})^3}$$

(19)

Axilrod–Teller formula

$$C' = a(3\cos\theta_A \cos\theta_B \cos\theta_C + 1)$$

$$a = \tfrac{3}{4}\alpha' C_6$$

Van der Waals Forces between Polar Molecules

•molecules are squeezed together: the nuclear and electronic repulsions dominate the attractive forces

hard-sphere potential:
σ van der Waals packing radius

$$V(R) = \begin{cases} \infty & r \le \sigma \\ -\epsilon & \sigma < r \le a\sigma \\ 0 & r > a\sigma \end{cases}$$
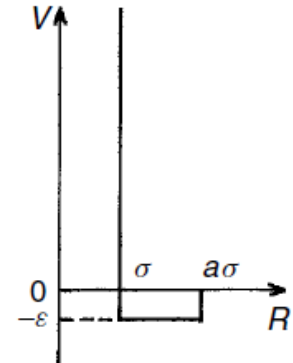
Mie potential: $\quad V = \dfrac{C_n}{r^n} - \dfrac{C_m}{r^m} \qquad n > m.$

     Repulsions   Attractions

e^{-r/r_0} exp-6 potential

Lennard-Jones potential: $\quad V = 4\varepsilon\left\{ \left(\dfrac{r_0}{r}\right)^{12} - \left(\dfrac{r_0}{r}\right)^{6} \right\}$
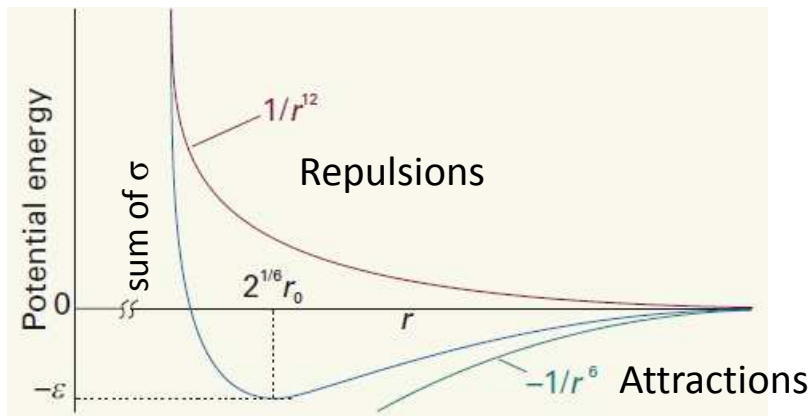
	r_0/pm
Ar	362.3
CCl_4	624.1
N_2	391.9
Xe	426.0

Retardation effects of dispersion forces

b Casimir–Polder (waves/retardation)

Wave effects

A

B
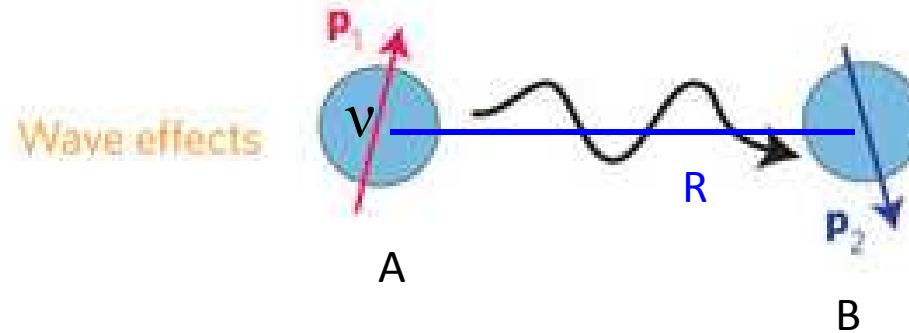
$2R/c \gg (\Delta E/h)^{-1}$ dispersion interaction is weakened

$R \sim 100$ nm,

$$w(r) \approx -\left(\frac{23\hbar c}{4\pi}\right)\frac{\alpha'_A \alpha'_B}{R^7}$$

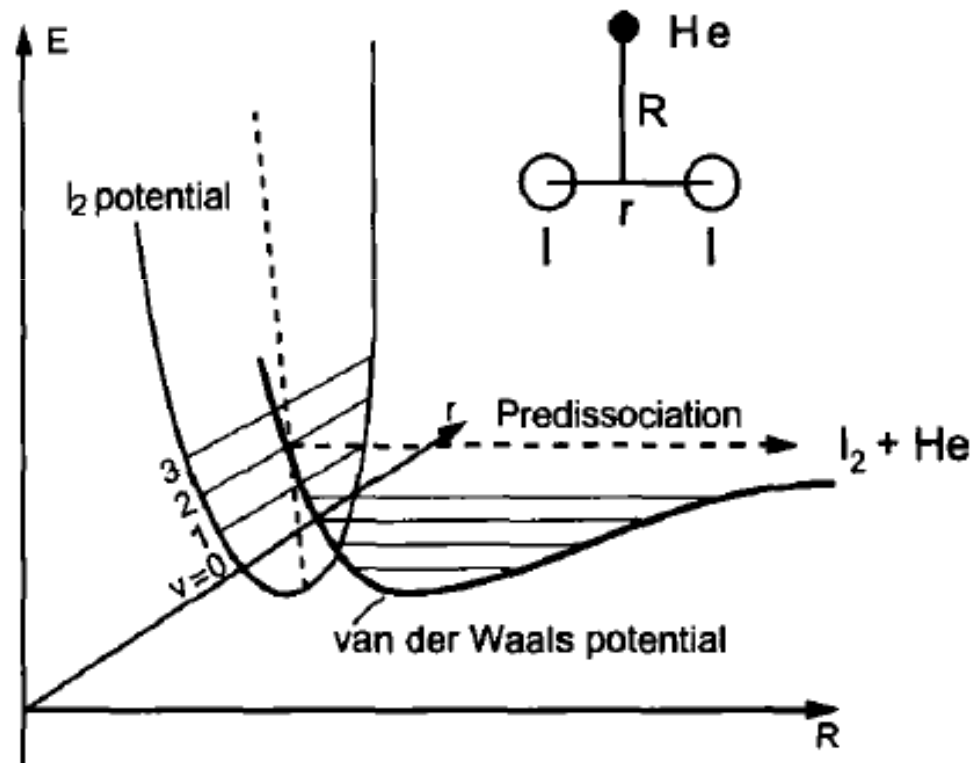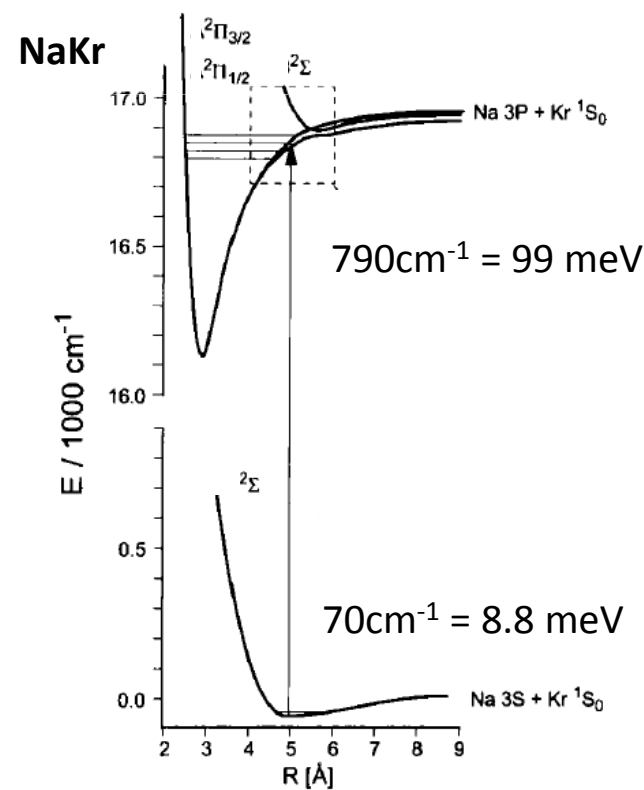$2R/c \ll (\Delta E/h)^{-1}$ the correlation of the dipoles is perfect

Van der Waals Molecules

van der Waals molecules:
He_2, Ne_2, Ar_2, $XeCl$, ArF, $NaAr$, $Ar-CO$
dimers$(NH_3)_2$, $(C_6H_6)_2$, $(C_6H_6)Ar$.

He$_2$
$R_e = 3.0$ Å
$< R > = 50$ Å !

$D_e = 1$ meV, $D_o = 1.1 \cdot 10^{-4}$ meV
$E_{kin}(v = 0) = 0.9999$ meV
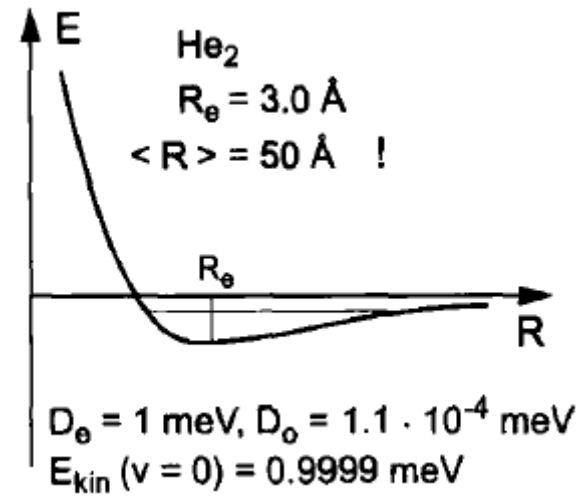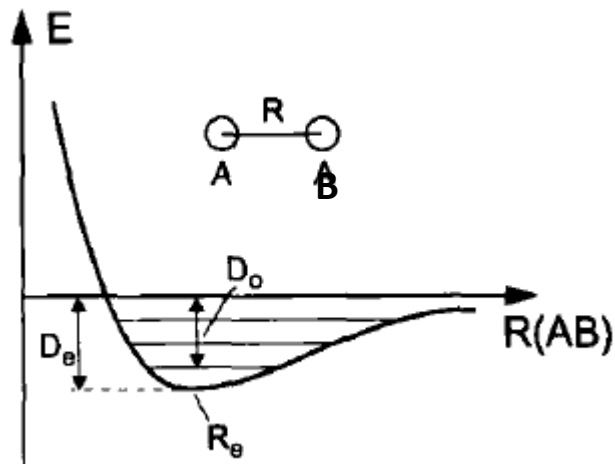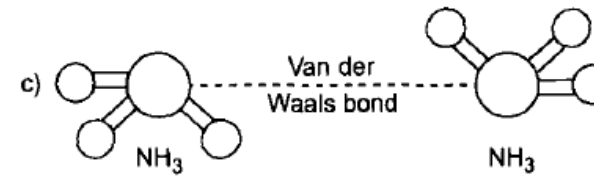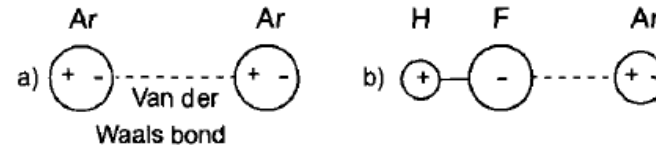
Van der Waals Molecules

Van der Waals Molecules

Molecule	Bond type	D_e / cm^{-1}	D_e / eV	R_e / Å
He$_2$	van der Waals	7.6	9×10^{-4}	3.0
Ne$_2$	van der Waals	30	3.6×10^{-3}	3.1
ArCO	van der Waals	110	1.4×10^{-2}	3.3
(NH$_3$)$_2$	van der Waals &	1000	0.12	3.4
CO	covalent	90500	11.2	1.1

bond energy:
three orders of magnitude larger

NaKr

790cm^{-1} = 99 meV

70cm^{-1} = 8.8 meV
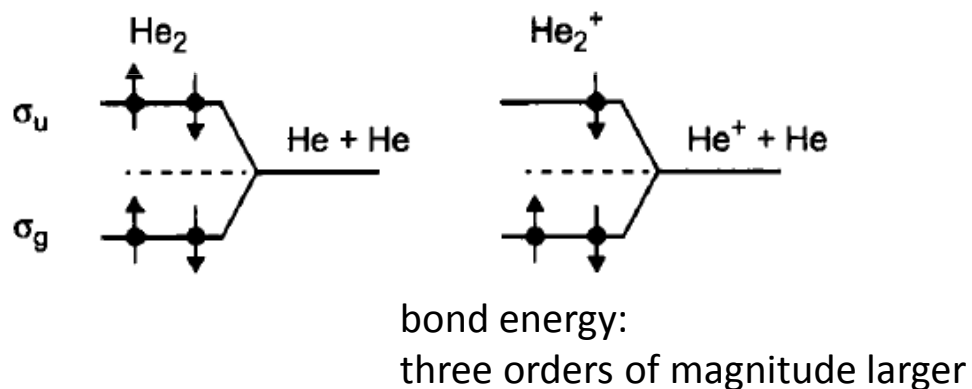
Van der Waals Molecules

van der Waals molecules often exhibit nonrigid structures: can alter their nuclear framework periodically.

There exist several isomers with slightly different ground-state energies
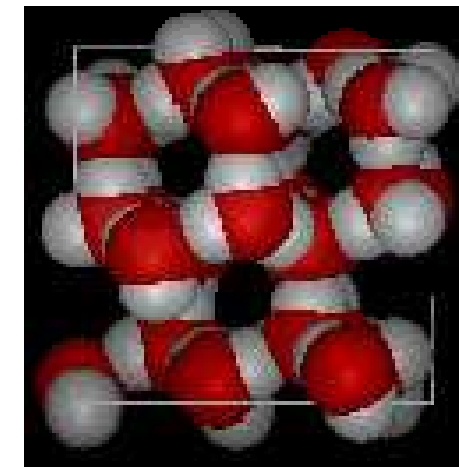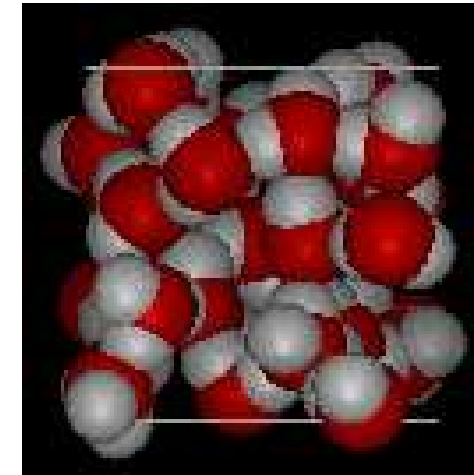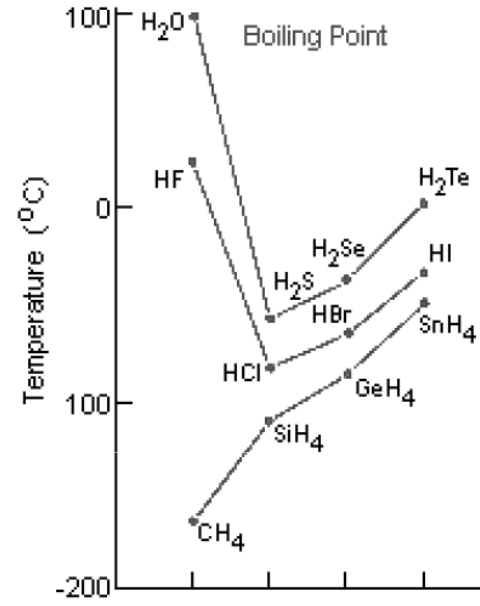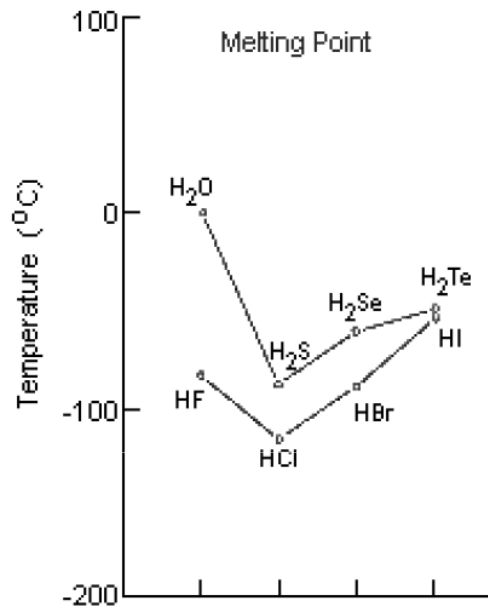

$(NH_3)_2$
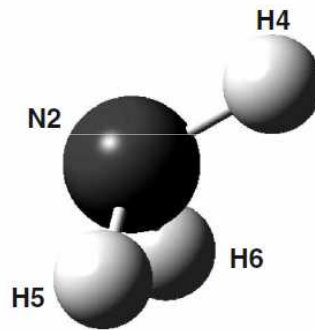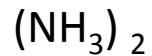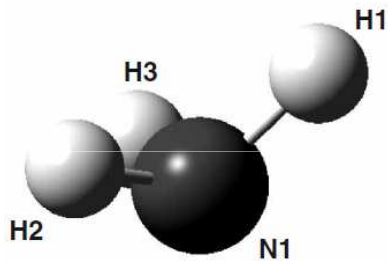
$(O_2)_2$:
the rectangular structure has the largest binding energy
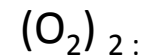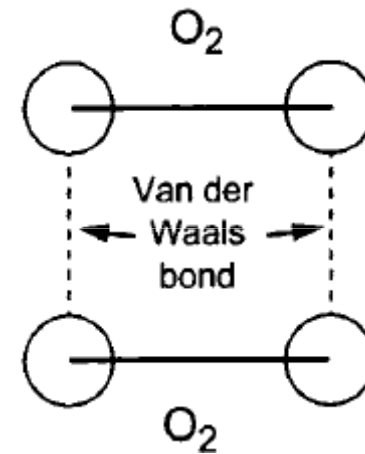
Large mean internuclear distance: large moments of inertia are large, and small rotational constants: low temperatures are needed to resolve the closely spaced rotational lines

The Unique Properties of Water

liquid

ice

- high melting and boiling points
- density maximum at 4°C exhibited by liquid water
- very low compressibility
- unusual solubility properties both as a solute and as a solvent

These properties of water point to the existence of an intermolecular interaction that is stronger than that expected for ordinary, even highly polar, liquids.

The Unique Properties of Water: Cohesion
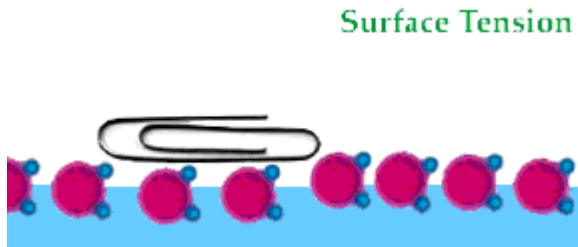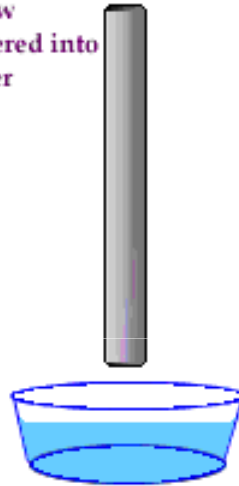

Surface Tension

- Attraction between particles of the same substance (why water is attracted to itself)
- Results in Surface tension (a measure of the strength of water's surface)
- Produces a surface film on water that allows insects to walk on the surface of water

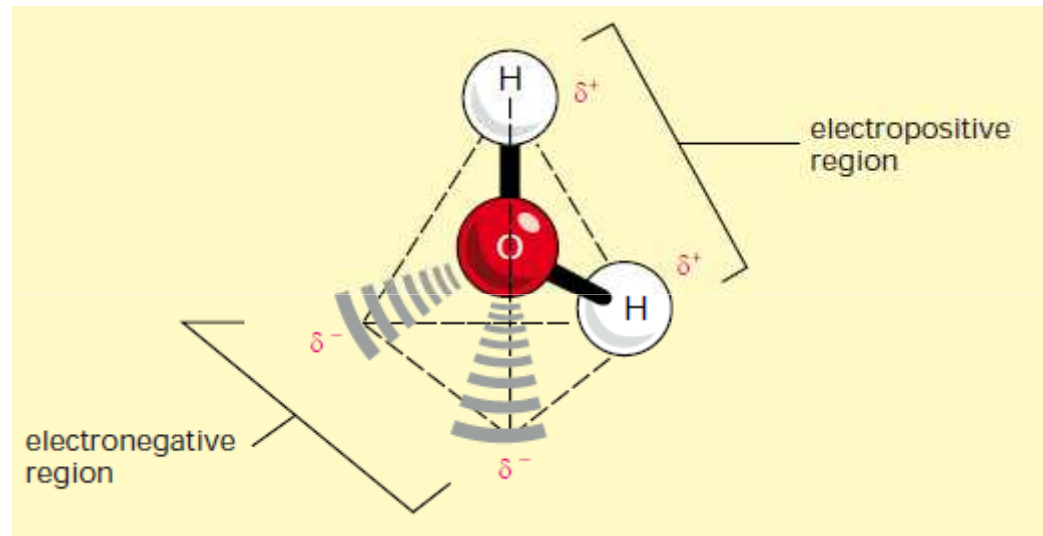# The Unique Properties of Water: Adhesion
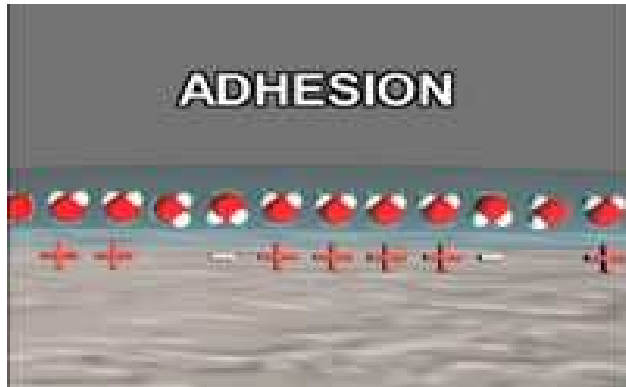
- Attraction between two different substances.
- Capillary action-water molecules will "tow" each other along when in a thin glass tube.
- Example: transpiration process which plants and trees remove water from the soil, and paper towels soak up water.
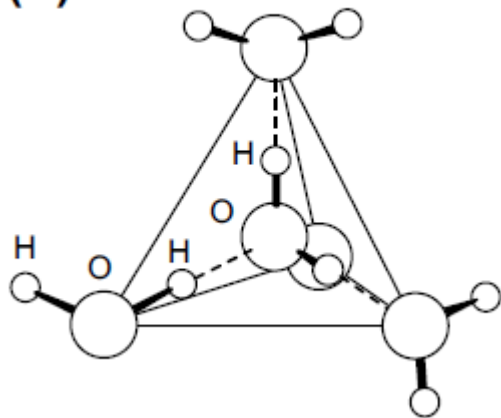
Water Molecule

Watermolecule is very polar, and gets even more polar in the condensed phase.
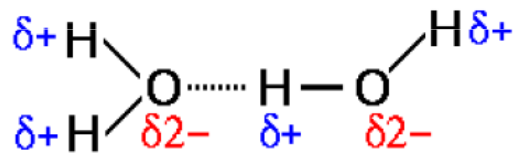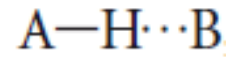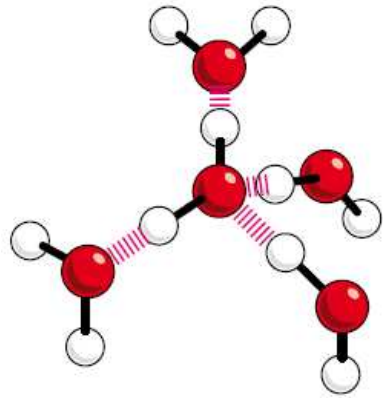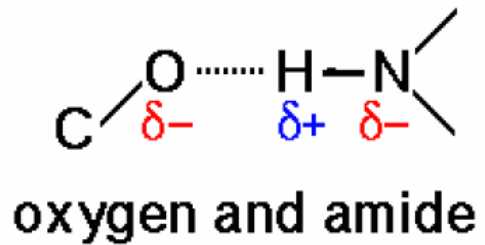
Condensed Water
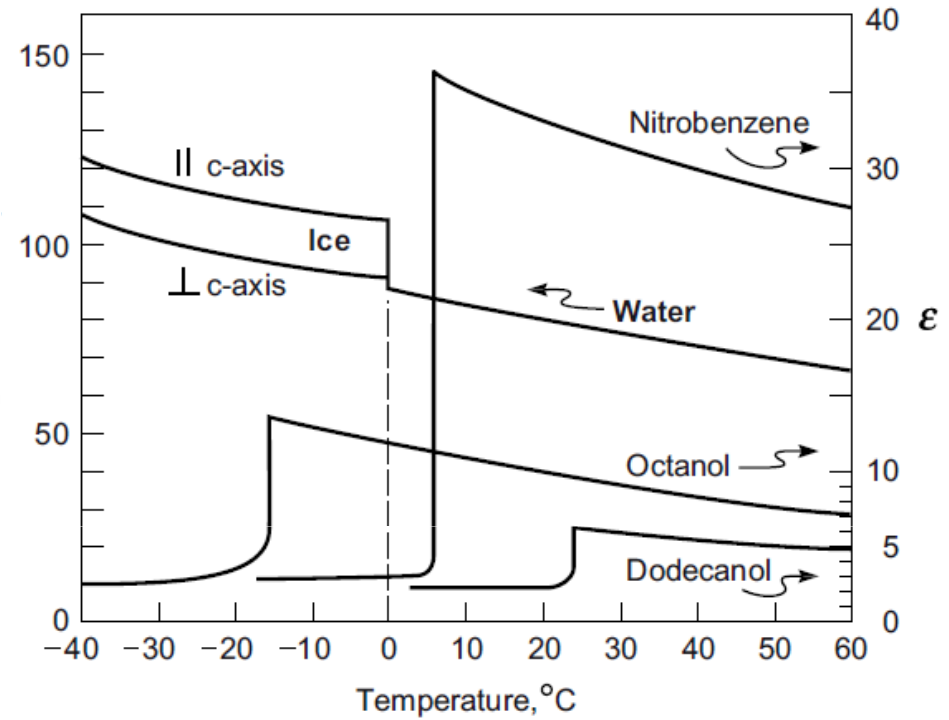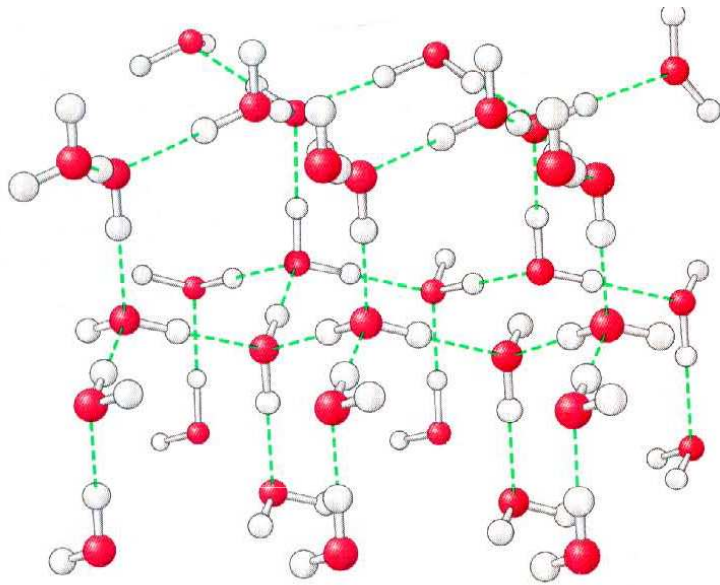
(a)

The proton conductivity and mobility in ice is higher than in the liquid: the ice lattice affords pathways for the movement of charges-hydrogen bonding network .

Hydrogen bond

$$A-H\cdots B$$

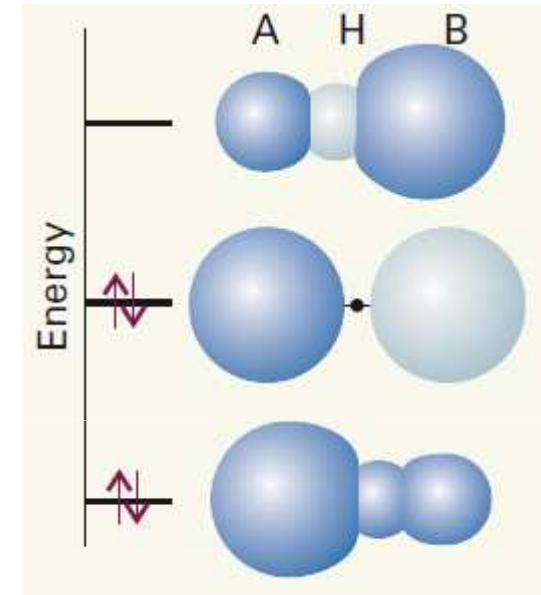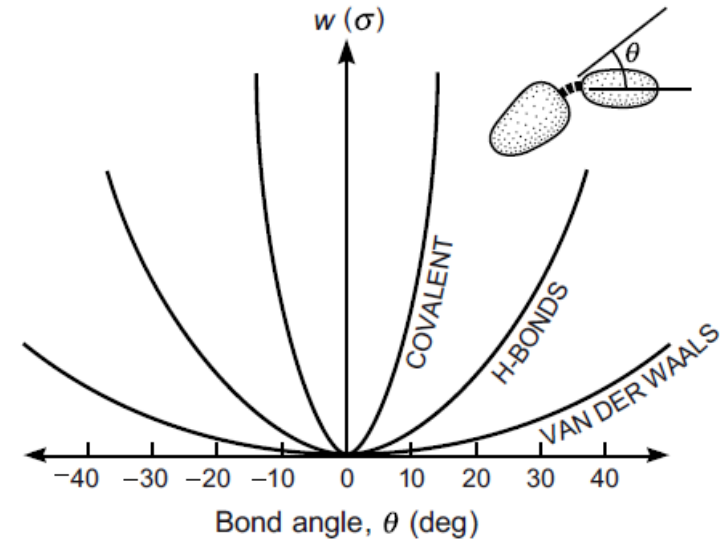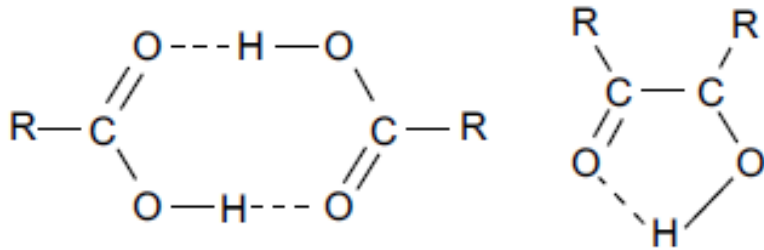$$\psi = c_A \psi_A + c_H \psi_H + c_B \psi_B$$

$\delta+$H, H$\delta+$

$\delta+$H, $\delta 2-$ O $\cdots$ H — O $\delta 2-$
$\delta+$H, $\delta 2-$ $\delta+$ $\delta 2-$

water

C, O $\cdots$ H — N
$\delta-$ $\delta+$ $\delta-$

oxygen and amide

Hydrogen bond

intermolecular H-bond   intramolecular H-bond

covalent bond   > H-bond   > van der Waals

$\Delta H = 400 \text{ kJmol}^{-1}$ $\Delta H = 15\text{-}20 \text{ kJmol}^{-1}$ $\Delta H = 1\text{-}5 \text{ kJmol}^{-1}$

$\Delta H \approx 4 \text{ eV}$ $\Delta H \approx 0.2 \text{ eV}$ $\Delta H \approx 0.01 \text{ eV}$
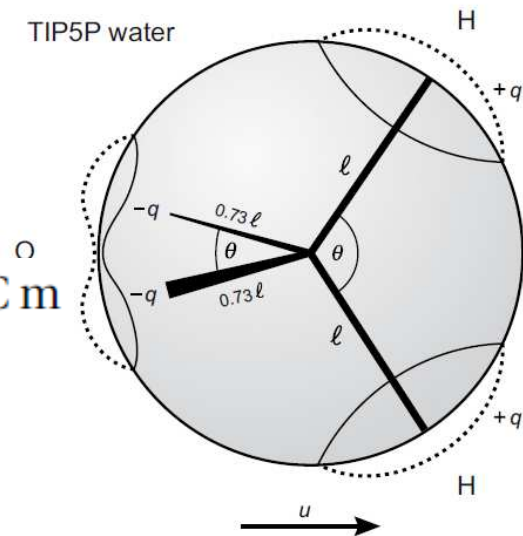
$$w(r) = -Q_{\text{H}^+} u \, \cos \theta / 4\pi\varepsilon_0\varepsilon r^2$$

$Q = 0.24e = 0.4 \times 10^{-19} \text{ C}$ $u_{\text{H}_2\text{O}} = 1.5 \text{ D} = 5 \times 10^{-30} \text{ C m}$

$r = 0.176 + (0.100/2) = 0.226 \text{ nm}$ $\theta = 0$, and $\varepsilon = 1$

$w(r) \approx -3.4 \times 10^{-20} \text{ J} = 20.4 \text{ kJ mol}^{-1} = 4.9 \text{ kcal/mole}$
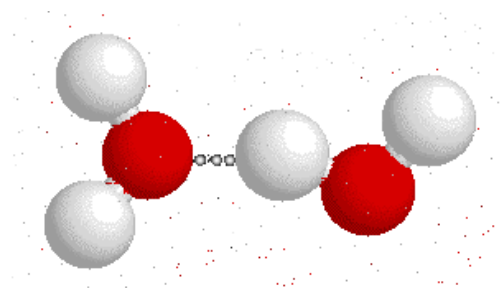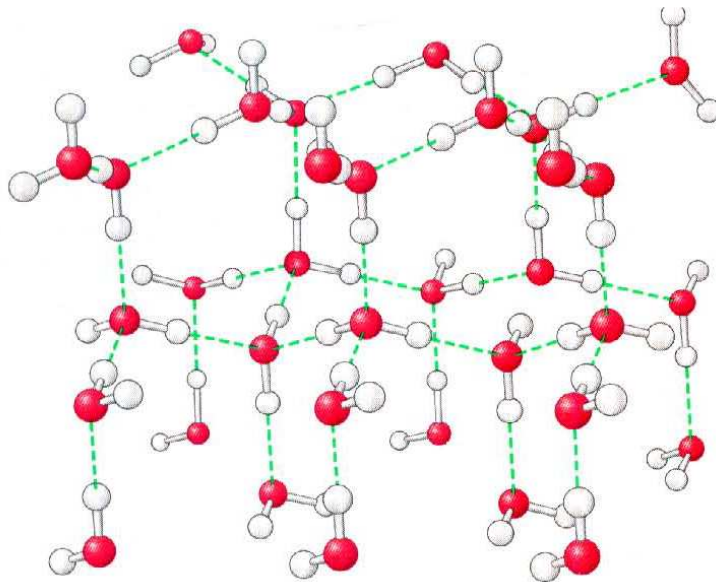
Literature: 4.5 kcal/mole

Hydrogen bond

bond	d[Å]
O-H ••• O	2.7
O-H ••• O⁻	2.6
O-H ••• N	2.9
N-H ••• O	3.0
N⁺-H ••• O	2.9
N-H ••• N	3.1

- The shorter the H-bond, the stronger the bond; typical distances between donor and acceptor are 2.6 to 3.1 Å (depends on the involved atoms and their charge).
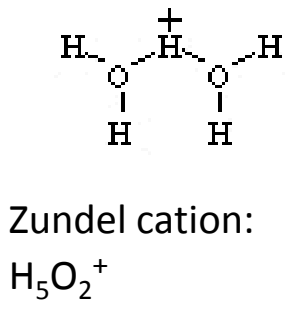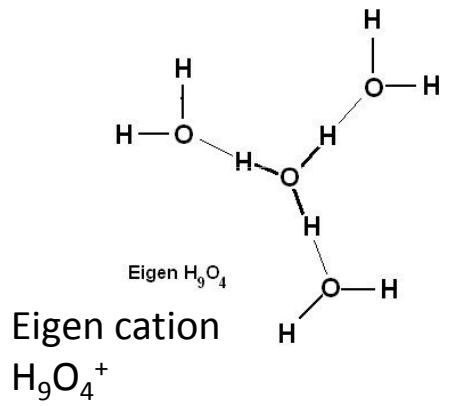
Structure of ice

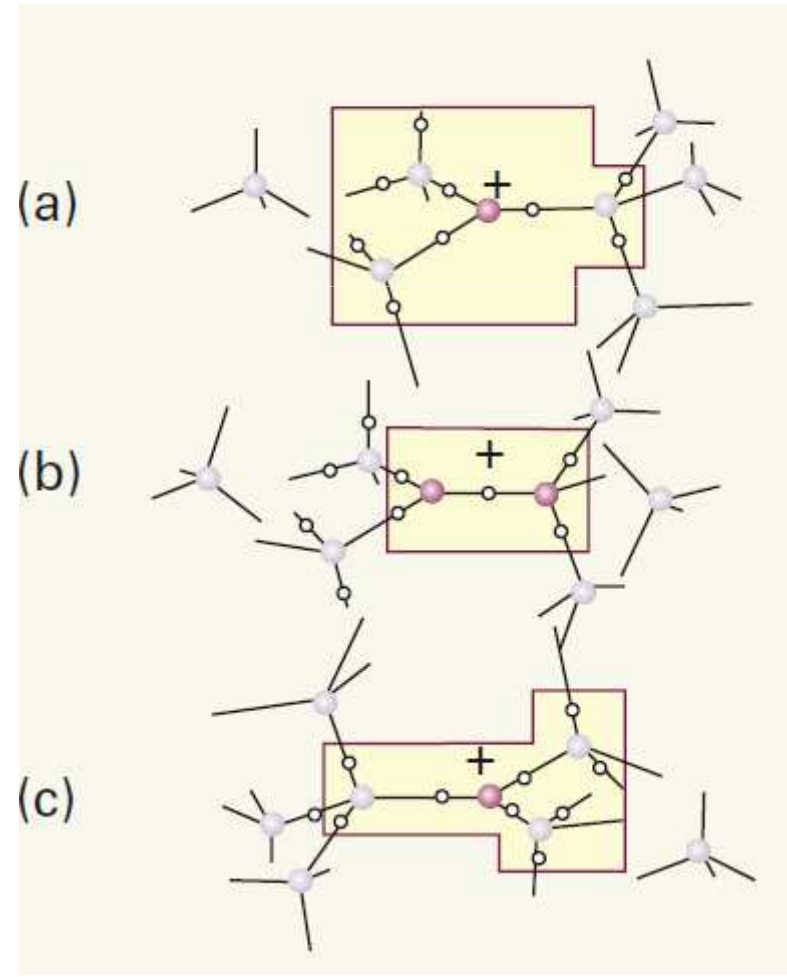The hydrogen bonds are shorter in ice (2.7 Å) than between isolated H_2O dimers (2.82 Å) because of cooperativity.

Protonated Water Molecules

Cation	Mobility / cm² V⁻¹ s⁻¹
NH_4^+	0.763×10^{-3}
Na^+	0.519×10^{-3}
K^+	0.762×10^{-3}
H^+	3.62×10^{-3}

proton hops: 1.5 ps

Eigen cation
$H_9O_4^+$

Zundel cation:
$H_5O_2^+$

(a)

(b)

(c)

Protonated Water Molecules

Zundel cation: $H_5O_2^+$

$(H_2O)_D - H^+$ $H^+ - (H_2O)_A$

potential energy

reaction coordinate
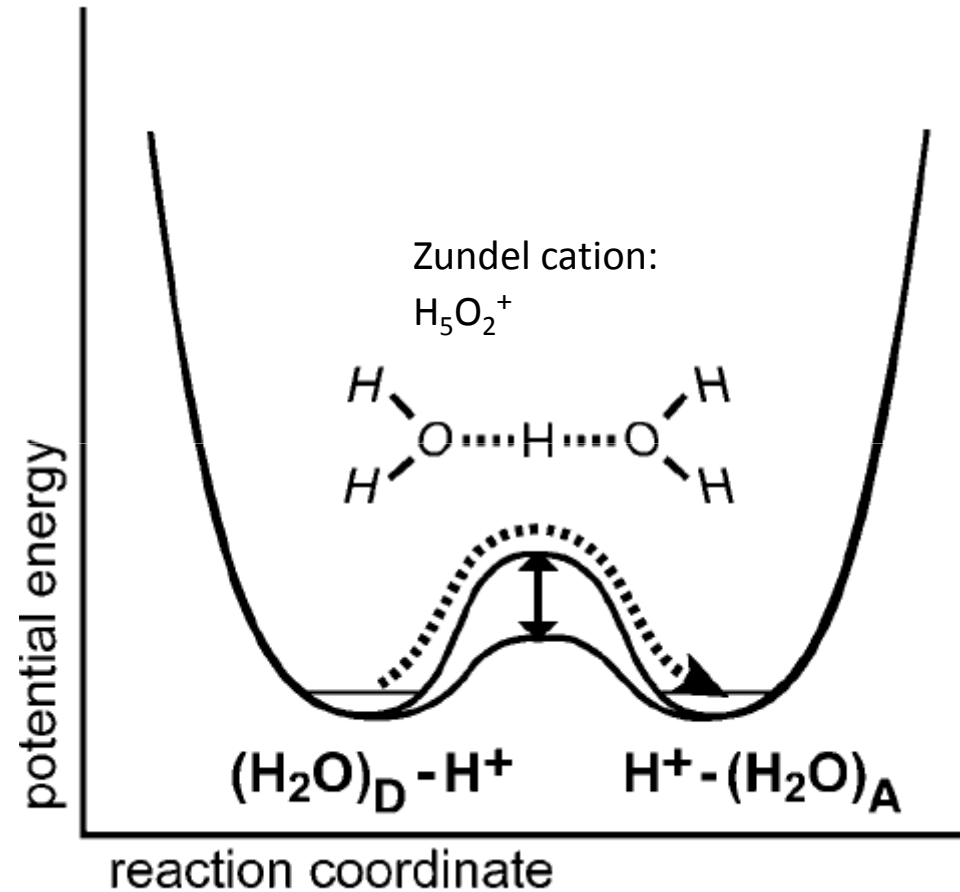
The
de Broglie wavelength of the proton is 1.5 A°: ~ distances of proton transfer reactions:
tunneling ?

Hydrophobic interaction

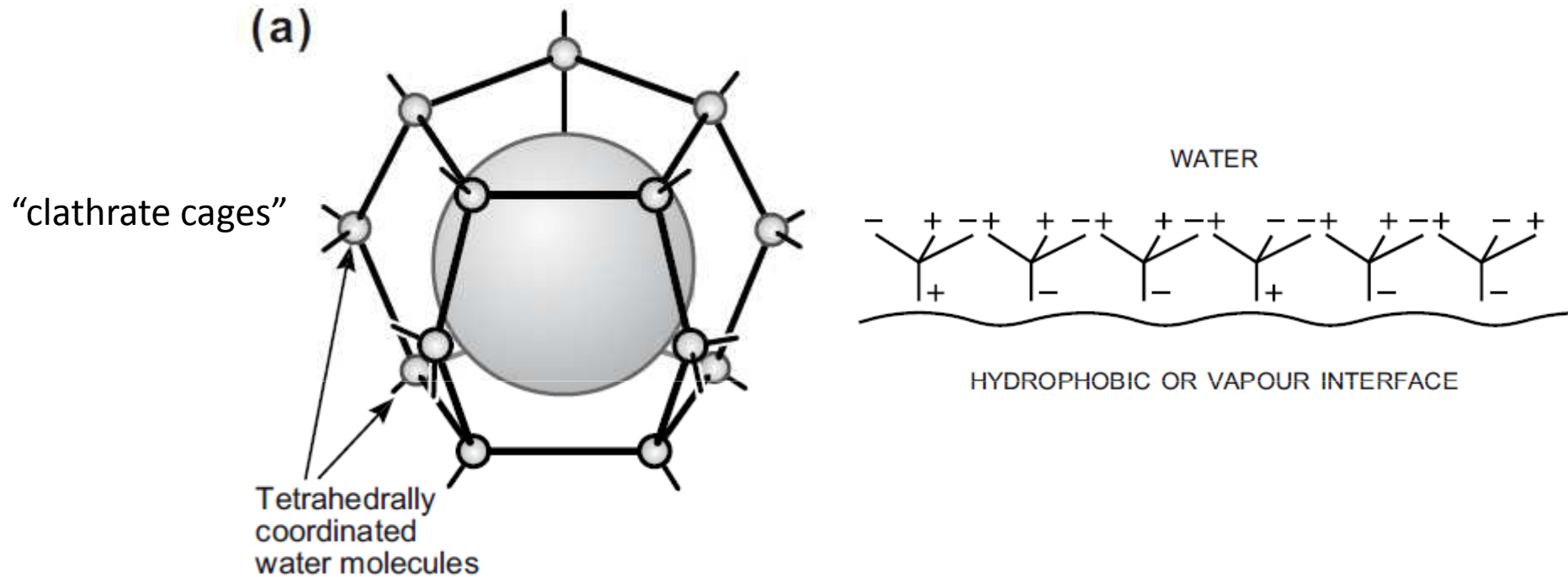- electrostatic, H-bond and van der Waals interactions between molecules in an aqueous environment are competed by the interactions between molecules and the water surrounding them.

- but: nonpolar molecules make unfavorable interactions with water.

- **hydrophobic interaction**: the preference of nonpolar molecules for nonaqueous environments

n-butane (C_4H_{10}) $\Delta G_{transfer} = \Delta H - T\Delta S = -4.3 + 28.7 = +24.5 \text{ kJ mol}^{-1}$.

- driven by entropy: interaction of hydrophobic (nonpolar) residues with water is less favorable as water –water interactions

- major factor in the stabilities of proteins

The „hydrophobic" effect

"clathrate cages"

(a)

WATER

Tetrahedrally
coordinated
water molecules

HYDROPHOBIC OR VAPOUR INTERFACE

- result of the unfavorable change in entropy
- reorientation or restructuring of the water molecules so they can participate in H-bond formation
- water-ordering effect