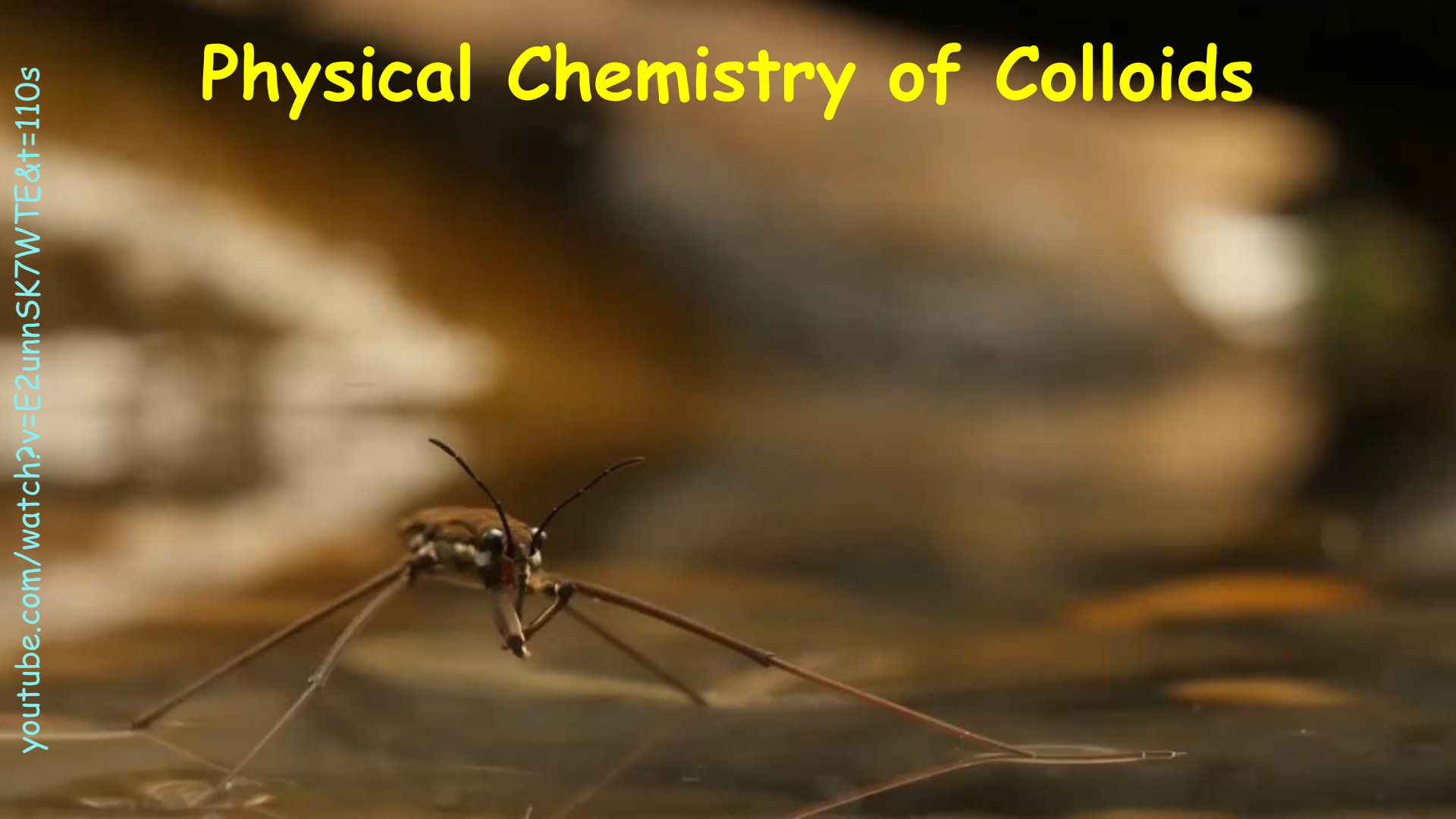# Physical Chemistry of Colloids

Lecture 2

February 27, 2019

Manos Anyfantakis
Physics & Materials Science Research Unit

Previously in ColloidsPhysChem…(I)

Colloids/Colloidal Systems/Colloidal Dispersions

Sols
fluid continuous phase

Lyophobic
thermodynamically unstable, not spontaneous

Suspensions solid in liquid	**Emulsions** liquid in liquid
Aerosols solid/liquid in gas	**Fluid foams** gas in liquid

Lyophilic
solutions, stable, spontaneous

Association colloids

Macromolecular colloids

Solid colloids
solid continuous phase
insulating foam, styrofoam…

IUPAC: International Union of Pure & Applied Chemistry

Previously in ColloidsPhysChem...(II)

100 mL of olive oil in 1L of water:
i) macroscopic phase separation
ii) emulsion in a beaker with 2R= 10 cm

Colloids & **Interfaces** are two
concepts that are interrelated !

imgcop.com

dreamstime.com

$A_{int, i}$ = 7.85x10^{-3} m^2

$A_{int, ii}$ = 6.03x10^2 m^2

PS spheres, 2R= 1 μm
dispersed in water, T= 20 ^{o}C

Stokes-Einstein-Sutherland

$$D = \frac{k_B T}{6\pi\eta R}$$

random walk in 3D

$$\langle l^2 \rangle = 6Dt$$

Time scale (Brownian motion): t = 0.86 ms   microscopic systems: ~ 10^{-12} – 10^{-10} s

Length scale: 1 μm ~ λ of visible light   microscopic systems: ~ 10^{-10} – 10^{-9} m
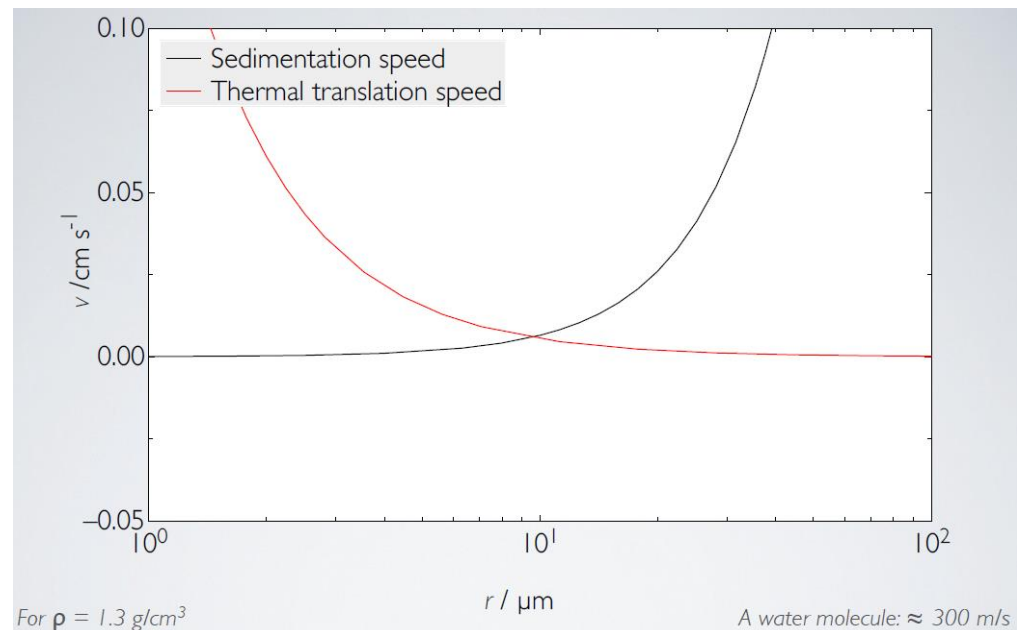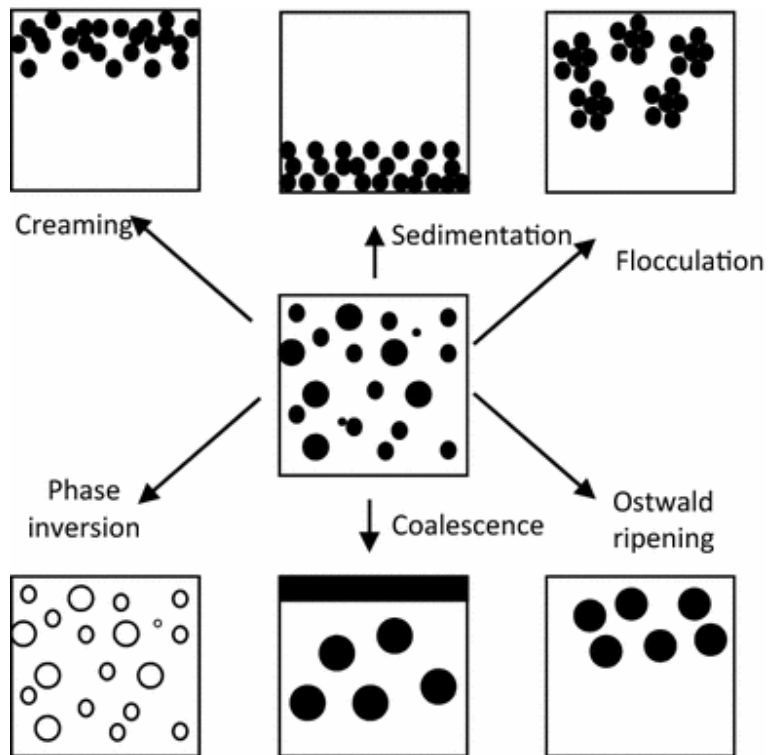
Colloids belong to the class of **mesoscopic systems** (typical for Soft Matter)

3

Previously in ColloidsPhysChem…(III)

Thermal energy

internal energy present in a system in a state of thermodynamic equilibrium by virtue of its temperature

@ room T (=20 ºC): $E_{th} = k_B T_{room} \approx 4 \times 10^{-21}$ J

Creaming

Sedimentation

Flocculation

Phase inversion

Coalescence

Ostwald ripening

Sedimentation speed

Thermal translation speed

v / cm s^{-1}

r / μm

For $\rho = 1.3$ g/cm^3

A water molecule: ≈ 300 m/s

Interfaces & interfacial tension

fluid-fluid interfaces
- far simpler than F-S or S-S interfaces
- we can assume mechanical & diffusional equilibrium
- morphologically & energetically homogeneous
- shear stress-free @ rest

the simplest fluid interface: **water-air**

stratum of inhomogeneity very thin: **~ few Å to nm**
→ treated as a **membrane with zero thickness**

a fluid interface contracts → **minimum area**

zero-thickness membrane model to quantify the **"contractile tendency"** of fluid interfaces (**Thomas Young**, 1805)

interfacial tension
force/length along the dividing line @ P

wikipedia

$$\sigma = \frac{d|F|}{dl}$$

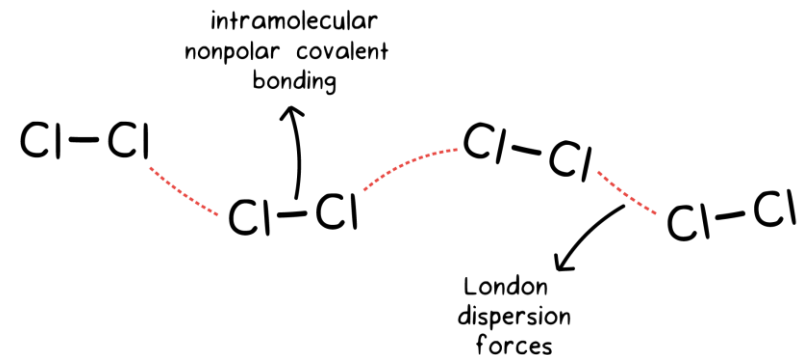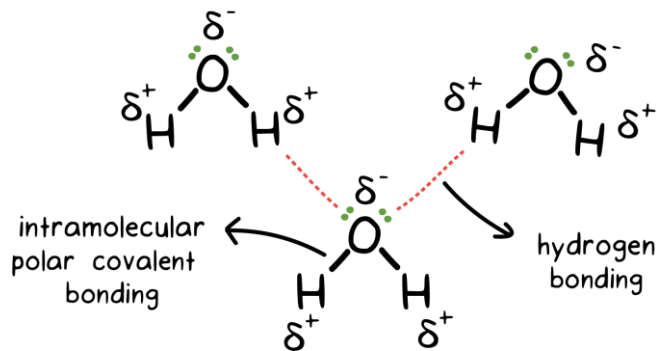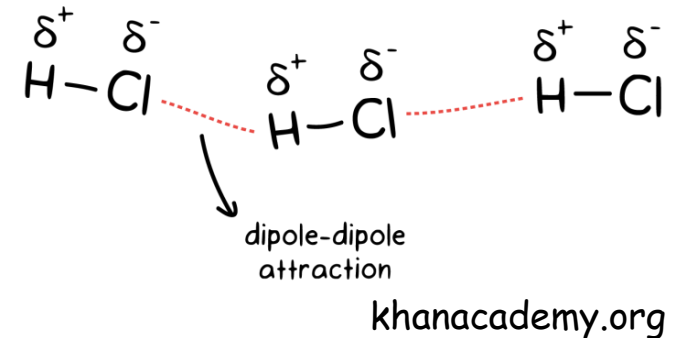$$\delta W = \sigma dA$$

unit (SI): N/m or J/m²
more common: mN/m

5
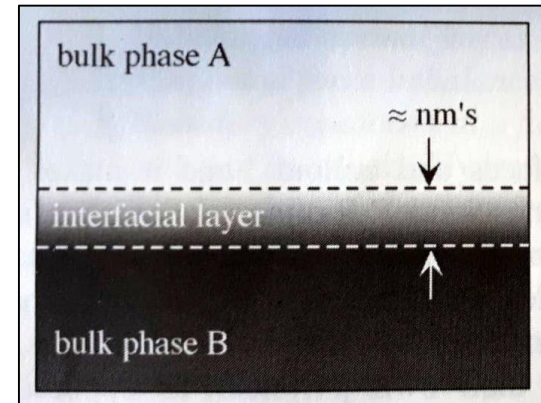
Intermolecular forces

Intermolecular forces

- they mediate interactions between molecules; can be attractive or repulsive

- responsible for physical properties of substances (e.g. T_{melt} & T_{boil}, density)

- weak compared to *intra*molecular forces

Types of attractive intermolecular forces

- dipole-dipole forces
- hydrogen bonding
- van der Waals forces
  (Keesom, Debye, London dispersion)

dipole-dipole attraction

khanacademy.org

intramolecular polar covalent bonding

hydrogen bonding

intramolecular nonpolar covalent bonding

London dispersion forces

Intermolecular forces & interfacial tension

Interfacial tension may be interpreted in terms of unbalanced intermolecular forces
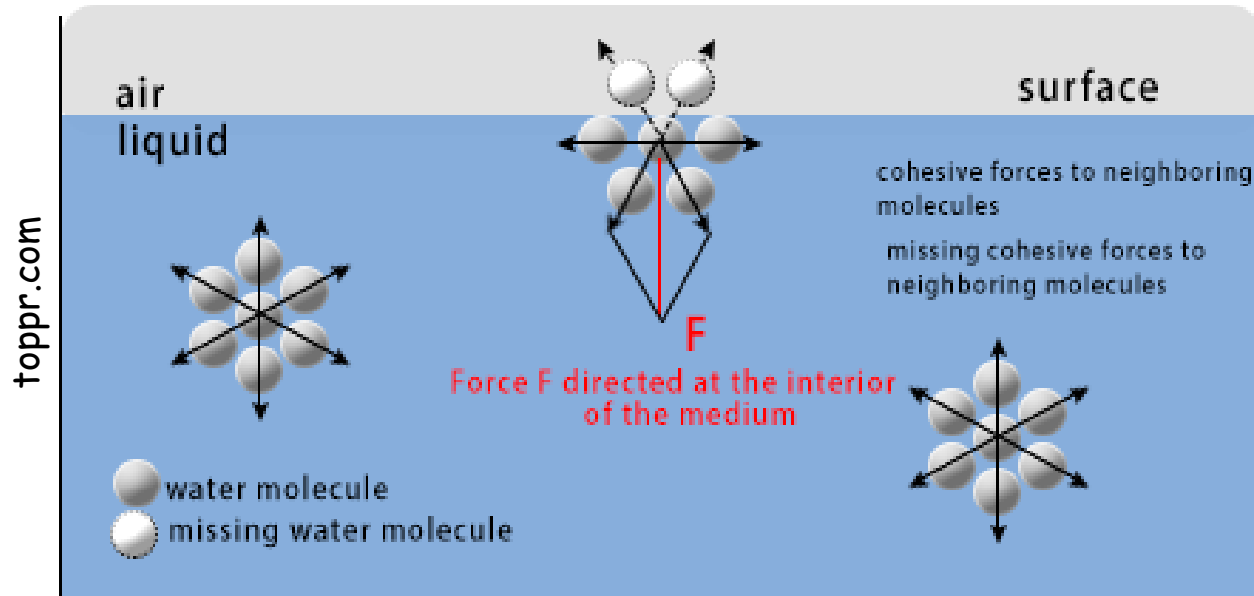
forces @ in the bulk: acted upon equally in all directions

forces @ the liquid surface: directed inward toward the interior

→ net inward attraction pulls surface molecules toward the interior; surface tries to minimize its area

interfacial tension increases with increasing intermolecular forces

Air-liquid interfacial tension of simple liquids

"surface tension" typically used when one of the fluid phases is gas

lowest σ values for liquefied gases

common solvents: σ = 20 -70 mN/m (except silicone oils & fluorocarbons)

Table 2-1: Surface tension values for various liquids		
Liquid	T	Surface Tension
Helium	-272 °C	0.16 mN/m
Hydrogen	-254	2.4
Perfluoropentane	20	9.9
Oxygen	-183	13.2
Silicone (HMDS)	25	15.9
n-Heptane	20	20.3
Ethanol	20	22.0
Benzene	20	28.9
Olive oil	18	33.1
Ammonia	-33	34.1
Nitric acid	21	41.1
Glycerol	20	63.4
Methylene iodide	20	67.0
Water	20	72.7
Sodium chloride	801	114.
Lithium	181	394.
Zinc	360	877.
Iron	1530	1700.

Fig. 2-3: Surface tension dependence on temperature for a variety of liquids: (1) water, (2) furfural, (3) chlorobenzene, (4) acetic acid, (5) carbon tetrachloride, (6) ethanol, (7) n-octane. Dashed line has slope: -0.1 mN/m·K, in reasonable agreement with that for most liquids.

simple liquids: σ = **f(T)**

typically: $d\sigma/dT \approx$ -0.1 mN/m K

8
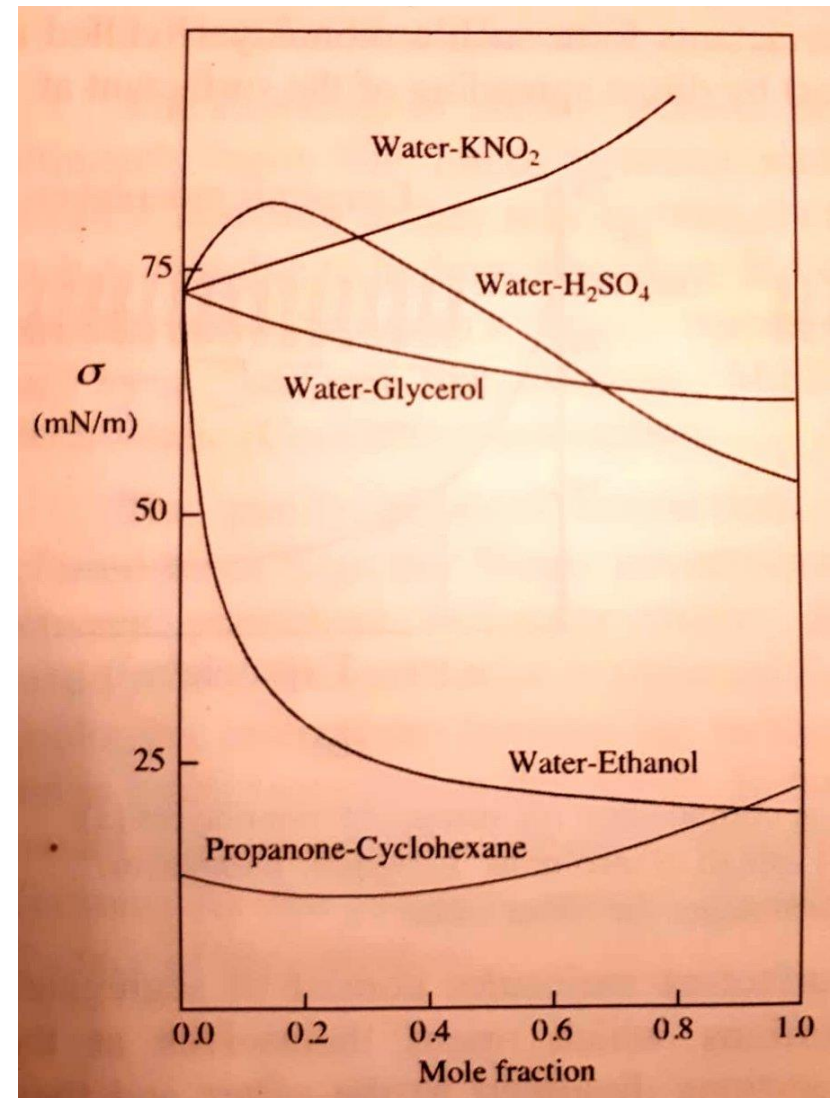
Air-liquid interfacial tension of solutions

the surface tension of solutions depends both on T & composition

usually in-between σ of the pure components (but less than the mole-fraction-average value)

σ of water increases by dissolved salts (weakly for low [salt])

σ of water strongly decreases by organic solutes (especially surfactants)

van der Waals interactions (I)

Johannes van der Waals (1837-1923)

- Dutch theoretical physicist

- equation of state for gases & liquids

- Nobel prize in Physics (1910)

Ideal gas law (Clapeyron, 1834)

- assumes point particles & no interactions between molecules

$$PV = nRT$$

- the same for all gases

wikipedia

van der Waals equation of state (1873)

- takes into account molecular size & interaction forces

- a, b > 0; characteristic of each gas

- **b:** correction for finite molecular size
  a: correction for intramolecular forces
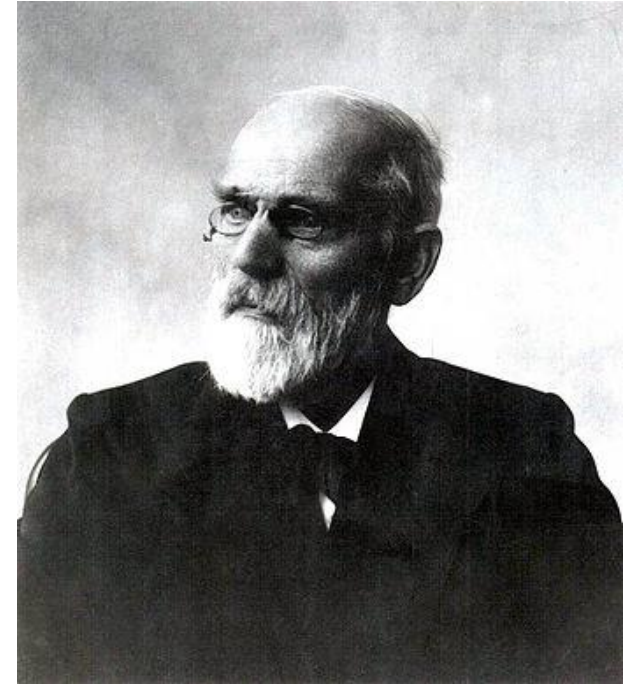
$$\left[P + a\left(\frac{n}{V}\right)^2 \right]\left(\frac{V}{n} - b\right) = RT$$

Coffee break

ign.com

pinterest.com/pin/181199584981085462/

What would be the consequence(s) of water having σ = 72 N/m instead of 72 mN/m ?

van der Waals interactions (II)

van der Waals (vdW) interations: a general term to describe a "family"
of intermolecular forces

Keesom interactions

- permanent dipole – permanent dipole

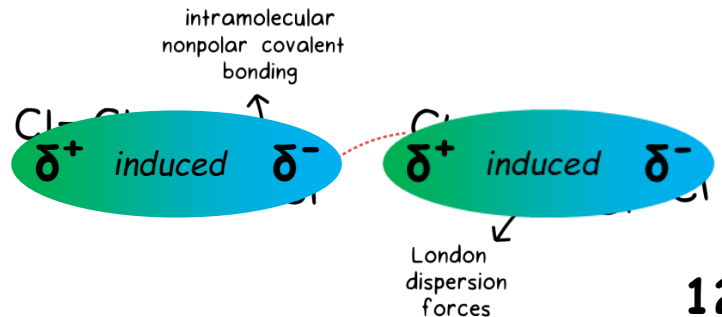- net effect after averaging over different relative orientations: *attraction*
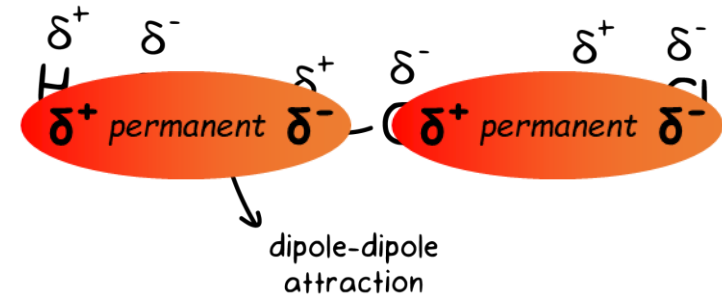
Debye interactions

- permanent dipole – induced dipole

- the latter is induced by the permanent dipole

London dispersion forces

- induced dipole – induced dipole

- e⁻ densities in nearby molecules redistribute *via* fluctuations to minimize energy

van der Waals interactions (III)

$$V_{Keesom} = \frac{-\mu_1^2\mu_2^2}{3(4\pi\varepsilon_0)^2 k_B T r^6}$$

$$V_{Keesom} = -\frac{B_{polar}}{r^6}$$

μ: dipole moment

ε_0: vacuum permittivity

k_B: Boltzmann's constant

$$V_{Debye} = \frac{-\mu_1^2\alpha_2^2}{(4\pi\varepsilon_0)^2 r^6}$$

$$V_{Debye} = -\frac{B_{induced}}{r^6}$$

T: temperature

r: interaction distance

α: polarizability

$$V_{London} = \frac{-3h\nu\mu_1^2\alpha^2}{4(4\pi\varepsilon_0)^2 r^6}$$

$$V_{London} = -\frac{B_{disp}}{r^6}$$

h: Planck's constant

ν: absorption frequency

All attractive vdW interactions vary as 1/r⁶

$$V_{attractive} = -\frac{B_{attractive}}{r^6}$$

Repulsive interactions

- strong repulsion when electron clouds overlap (hard-core repulsion)
- manifestation of Pauli's exclusion principle

$$V_{repulsive} = \frac{B_{repulsive}}{r^{12}}$$

13

van der Waals interactions (IV)

Total interaction between two molecules: $V_{attractive} + V_{repulsive}$

δ: r for which $V_{tot} = 0$
(molecular diemeter)

ε: depth of potential well

$$V_{tot} = 4\varepsilon \left[\left(\frac{\delta}{r}\right)^{12} - \left(\frac{\delta}{r}\right)^{6} \right]$$
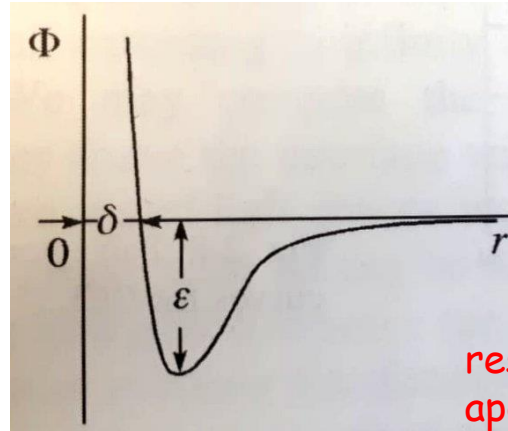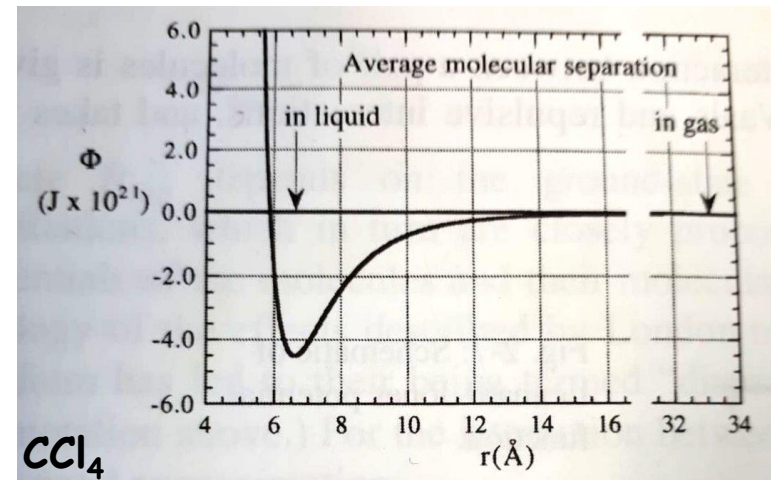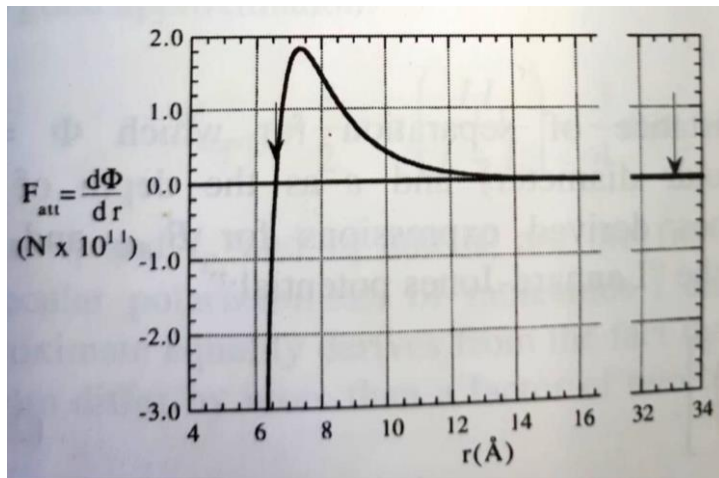

Fig. 2-7: Schematic of Lennard-Jones potential function.

restricted to approx. spherical, apolar or weakly polar molecules

force of interaction: $F_{tot} = \dfrac{dV_{tot}}{dr}$

14

van der Waals interactions (V)

General features of vdW forces

- non-directional but strongly dependent on relative orientation of interacting partners
- comparatively weak ($\sim 1 k_B T_{room}$)
- occur to some extent between any couple of molecules
- short range (attraction: r^{-6})

TABLE 10.2 Percentage of the Debye, Keesom, and London Contributions to the van der Waals Attraction Between Various Molecules

chemguide.co.uk

Compound	μ (debye)	$\frac{\alpha}{4\pi\epsilon_0} \times 10^{30}$ (m³)	$\beta \times 10^{77}$ (J m⁶)	Keesom (permanent-permanent)	Debye (permanent-induced)	London (induced-induced)
CCl_4	0.00	10.70	4.41	0.0	0.0	100.0
Ethanol	1.73	5.49	3.40	42.6	9.7	47.6
Thiophene	0.51	9.76	3.90	0.3	1.3	98.5
t-Butanol	1.67	9.46	5.46	23.1	9.7	67.2
Ethyl ether	1.30	9.57	4.51	10.2	7.1	82.7
Benzene	0.00	10.50	4.29	0.0	0.0	100.0
Chlorobenzene	1.58	13.00	7.57	13.3	8.6	78.1
Fluorobenzene	1.35	10.30	5.09	10.6	7.5	81.9
Phenol	1.55	11.60	6.48	14.5	8.6	76.9
Aniline	1.56	12.40	7.06	13.6	8.5	77.9
Toluene	0.43	11.80	5.16	0.1	0.9	99.0
Anisole	1.25	13.70	7.22	5.5	6.0	88.5
Diphenylamine	1.08	22.60	14.25	1.5	3.7	94.7
Water	1.82	1.44	2.10	84.8	4.5	10.5

Source: Dipole moments and polarizibilities from A. L. McClellan, *Tables of Experimental Dipole Moments*, W. H. Freeman, San Francisco, CA, 1963.

15

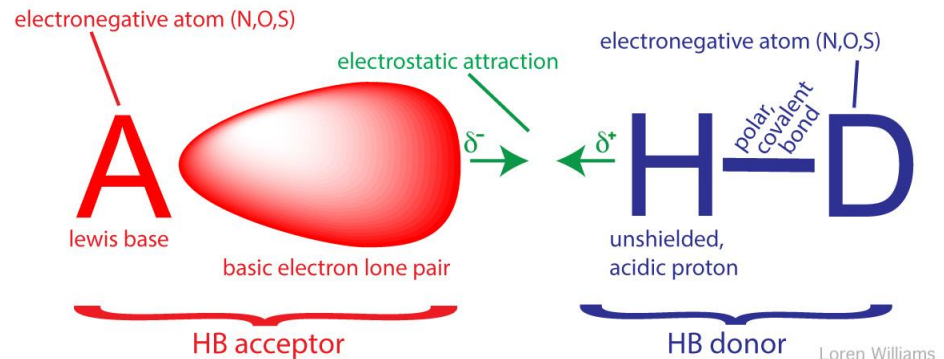# Hydrogen bonding (I)

IUPAC definition

H-bond is an attractive interaction between an H atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, & an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.

typically written: **D-H···A**

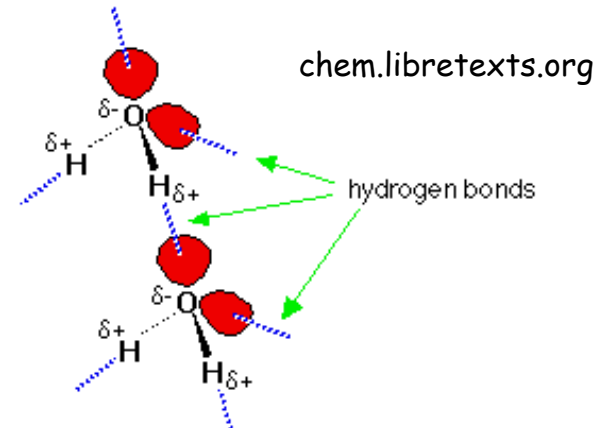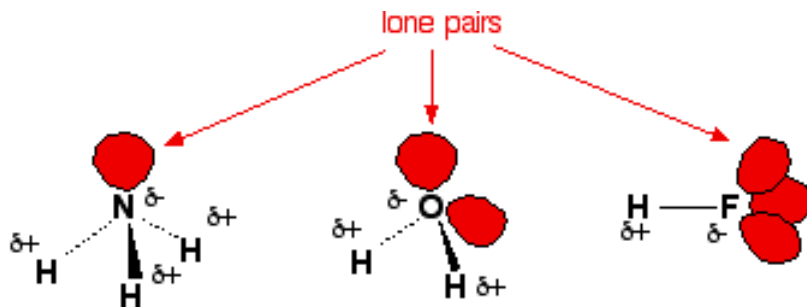**D:** H-bond donor (N, O, F, S)

A: H-bond acceptor (N, O, F, S) possesses a lone pair of e⁻

Anatomy of a Hydrogen Bond

electronegative atom (N,O,S)

electrostatic attraction

electronegative atom (N,O,S)

A

δ^- δ^+ H—D

polar, covalent bond

lewis base

basic electron lone pair

unshielded, acidic proton

HB acceptor

HB donor

Loren Williams

ww2.chemistry.gatech.edu/~lw26/structure/molecular_interactions/mol_int.html

lone pairs
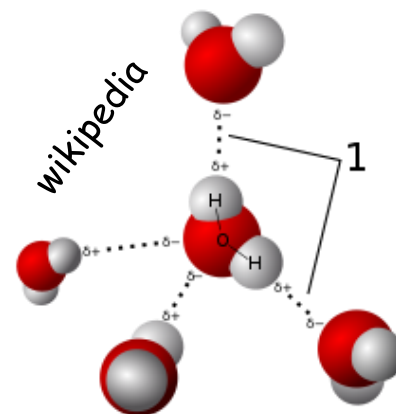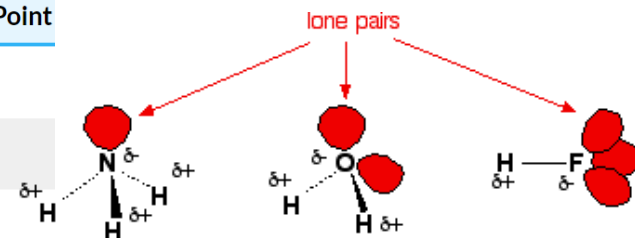

chem.libretexts.org

hydrogen bonds

Hydrogen bonding (II)

water: the perfect example of H-bonding

- each water molecule can form 4 H-bonds with surrounding water molecules

- 2 lone e$^-$ pairs + 2 δ^+ H

- reason for very high T_{boil}

wikipedia

Compound	Molar Mass	Normal Boiling Point
H_2O	18 g/mol	373 K
HF	20 g/mol	292.5 K
NH_3	17 g/mol	239.8 K

chem.libretexts.org

lone pairs

chem.ucla.edu/~harding/IGOC/H/hydrogen_bond_donor.html

Hydrogen bonding (III)

**often described as a dipole-dipole interaction,
but H-bonds also show features of covalent bonds**

- directional & with limited number of interaction partners

  - ideal bond angle: colinear with D-H axis

  - directionality → restricts number of neighbours
  water: max 4 neighbours; non-H-bonding liquids: many more

D—H⋯A linear (preferred, strongest)

D—H⋯A bent

D—H⋯A donating bifurcated
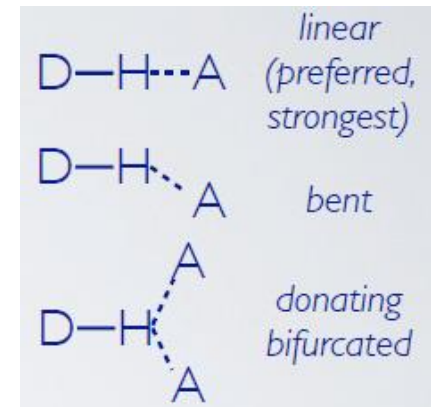
- strong

  - typical energies ~ 5-30 kJ/mol

  - $k_B T$ @ 25 °C = 2.47 kJ/mol

    → dynamically formed & broken

- F−H⋯:F (161.5 kJ/mol or 38.6 kcal/mol), illustrated uniquely by HF_2^-, bifluoride
- O−H⋯:N (29 kJ/mol or 6.9 kcal/mol), illustrated water-ammonia
- O−H⋯:O (21 kJ/mol or 5.0 kcal/mol), illustrated water-water, alcohol-alcohol
- N−H⋯:N (13 kJ/mol or 3.1 kcal/mol), illustrated by ammonia-ammonia
- N−H⋯:O (8 kJ/mol or 1.9 kcal/mol), illustrated water-amide
- HO−H⋯:OH_3^+ (18 kJ/mol[13] or 4.3 kcal/mol)

wikipedia

Comparison of intermolecular forces

Force	Model	Basis	E (kJ/mol)	Example
Ion-dipole		Ion charge–dipole charge	40–600	$Na^+ \cdots O \big\langle{}^H_H$
H bond	$-A-H\cdots:B-$	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$:\ddot{O}-H\cdots:\ddot{O}-H$
Dipole-dipole		Dipole charges	5–25	$I-Cl\cdots I-Cl$
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	$Fe^{2+}\cdots O_2$
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	$H-Cl\cdots Cl-Cl$
Dispersion (London)		Polarizable e^- clouds	0.05–40	$F-F\cdots F-F$

chem.fsu.edu/chemlab/chm1046course/interforces.html

Contribution of intermolecular forces to σ

Table 2-2: Components of surface tension (in mN/m at 23.±0.5°C).
From [Fowkes, F. M., Riddle, F. L., Pastore, W. E., and Webber, A. A., *Colloids Surfaces*, **43**, 367 (1990).]

Liquid	σ	σ^d	σ^{ab}	Type
Water	72.4	21.1	51.3	both
Glycerol	63.4	37.0	26.4	both
Formamide	57.3	28.0	29.3	both
Methyl iodide	50.8	50.8	0	Neither
a-Bromonaphthalene	44.5	44.5	0	Neither
Nitrobenzene	43.8	38.7	5.1	Both
Dimethylsulfoxide	43.5	29.0	14.5	Both
Aniline	42.5	37.3	5.1	Both
Benzaldehyde	38.3	37.0	1.3	Both
Pyridine	38.0	38.0	0	Basic
Formic acid	37.4	18.0	19.4	Both
Pyrrole	37.4	32.6	4.8	Both
Dimethylformamide	36.8	30.2	6.6	Both
1,4-Dioxane	33.5	33.5	0	Basic
cis-Decaline	32.2	32.3	0	Neither
Squalane	29.2	29.2	0	Neither
Acetic acid	27.6	22.8	4.8	Both
Chloroform	27.1	27.1	0	Acidic
Methylene chloride	26.6	26.6	0	Acidic
Tetrahydrofuran	26.5	26.5	0	Basic
Ethyl acetate	25.2	25.2	0	Basic
Acetone	23.7	22.7	1.0	Both
Ethanol	22.2	20.3	1.9	Both
Triethylamine	20.7	20.7	0	Basic
Ethyl ether	17.0	17.0	0	Basic

$$\sigma = \sigma^d + \sigma^p + \sigma^i + \sigma^H + \sigma^m + ...$$

σ^d: London force contribution

σ^p: Keesom force contribution

σ^i: Debye force contribution

σ^H: H-bond contribution

σ^m: metallic bond contribution

condensed-phase media:
Keesom & Debye negligible

example
σ_{water} = 72 mN/m
$\sigma^p + \sigma^i$ = 1.4 mN/m

for most liquids:

$$\sigma = \sigma^d + \sigma^{ab}$$

σ^{ab}: acid-base interactions