Syllabus:

- Introduction / Thermodynamic Aspects

- Strong intermolecular forces
- Interactions of polar molecules
- Van der Waals forces
- Repulsive Forces
- Hydrogen bonding

PART I

- Intermolecular and Interparticle forces

① Van. der Waals, ② electrostatic, ③ solvation, ④ steric

Adhesion

PART II

- Self-Assembly (Thermodynamics)
- Aggregation to biologically relevant superstructures
- Membranes

PART III

1: Introduction

① ②

* forces of nature : - weak and strong interactions:
neutrons/protons/electrons
range of action $< 10^{-5}$ nm !

↳ nuclear/high energy physics

③ ④

- electromagnetic forces & gravitation:

range of action: subatomic → 'infinity'
⇒ govern behavior of everyday things

⟹ ! electromagnetic forces determine:
properties of solids/liquids/gases
chemical reactions
behavior of particles in solution
biological structure organisation

gravitational forces: - tidal motion,
- cosmological phenomena

sometimes work together:
- height, a liquid rises in a capillary
- maximum size of animals and plants
- contemporary belief: forces are related to gravitation

Historical developments

- greeks : fundamental forces → love/hate

  love ↓ bring together

  hate ↓ bring apart

  Knew magnets, action at a distance

  Empedocles, Aristotle : basis of chemical theory in Europe until ~1600 (including imagination)

early science

- Newton, 'molecules' might be linked to physical properties of matter

- Clairaut : capillarity work, investigated liquid/liquid and liquid/glass attraction found that glass wall thickness is irrelevant, → short ranged

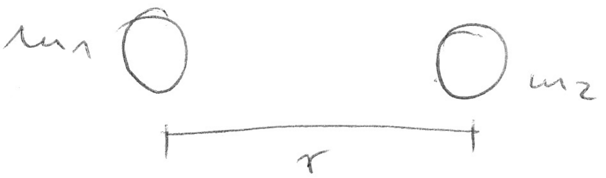
19th century quest for a single universal force law (like Newton's gravitational force)

~~putative~~ interaction potential like

$$w(r) = -C\, m_1 m_2 / r^n$$

and the resulting force law:

$$F(r) = dw(r)/dr = -n\, C m_1 m_2 / r^{n+1}$$



C= constant

n= integer to be 4 or 5

n = 1 for gravitational interaction

$$w(r) = -G\, m_1 m_2 / r \qquad G = 6.67 \cdot 10^{-11} \left[N m^2 kg^{-2} \right]$$

choice of n: intermolecular forces do not exceed over large distances if n>3

why? let $w(r) = -C/r^n$ n= integer

density of molecules = ρ

$\Rightarrow$ number of molecules in a region $(r + dr)$ equals to $\underset{\substack{\uparrow \\ \text{volume of a shell: thickness } dr \\ \text{radius: } r}}{\rho \cdot 4\pi r^2 dr}$

⇒ Total interaction energy

$$\int_{\sigma}^{L} w(r)\,\rho\,4\pi r^{2}\,dr = -4\pi C\rho \int_{\sigma}^{L} r^{2-n}\,dr$$

σ = diameter of molecule

L = size of system

$$= \frac{4\pi C\rho}{(n-3)\sigma^{n-3}}\left[1-\frac{\sigma}{L}\right]^{n-3}$$

$\lim_{\sigma - L \to 0} = 0$

$$= \frac{4\pi C\rho}{(n-3)\sigma^{n-3}}$$

for $n > 3$, $L \gg \sigma$

if $n > 3$: large distance contributions dissapear (as demanded)

f $n < 3$: greater second term → size L has to be accounted for as occurs for gravitational forces

⇒ **Consequence**: bulk properties of solids/liquids/gases to not depend on volume!!

- long range interactions rarely exceed 100 nm

19.th century: no candidate for all-embracing force found!

however: modern concept of surface tension forces developed

further developments: from work on gases

First successful theories

v. d. Waals equation

$$\underset{\substack{\swarrow \\ \text{accounting for attractive intermolecular (v. d. Waals) forces}}}{\left(p+\frac{a}{V^2}\right)}\underset{\substack{\searrow \\ \text{accounting for finite molecule size}}}{(V-b)} = RT$$

early 20th century: intermolecular forces were found not to be of simple nature

→ semi empirical expressions,

e.g. Mie, 1903: pair potential

$$w(r) = \underset{\substack{\uparrow \\ \text{attractive}}}{-A/r^n} + \underset{\substack{\uparrow \\ \text{repulsive}}}{B/r^m}$$

still used today

at this time adjustable parameters n, m and the underlying force ~~nature~~ still unclear

"Modern view of the origin of intermolecular forces"

- electronic structure is discribed by quantum theory
  ↳ derivation of expressions for interaction potentials (which are all essentially electrostatic)

Hellman-Feynman theorem:

① Solving the Schrödinger eq. → spatial distribution of the electron cloud

② Intermolecular can then be calculated on the bassis of classical electrostatics;

charge-charge interaction: Coulomb's force $F \sim 1/r^2$

moving charge: electromagnetic forces

fluctuating charge distributions in/around atoms result in various interatomic/intermolecular forces

HOWEVER: No exact solution for $H_2 \leftrightarrow H_2$ interaction in vacuum available

⇒ approximations for certain categories of interactions

e.g. ionic bonds, metallic, van der Waals, hydrophobic, hydrogen bonding

strong weak short-range long range

1.6. recent trends

areas of activity

① forces acting between simple molecules and atoms in gases: quantum mechanical and statistical mechanical calculations: account for many physical properties

② ions, atoms, molecules in solids

③ long-range interactions between surfaces and colloidal particles suspended in liquids: colloid science

④ – liquid structure, surface/thin-film phenomena, complex fluids: surfactant/polymer self-assembling systems, material properties, biological macromolecules

not only static but also dynamic forces
(equilibrium) (viscous/time-dependent)

→ MC simulation + molecular dynamics

Chemistry/: dominated by short-range interactions
biology (binding sites, lock & key mechanisms)

closely related: <u>colloid science</u>: long-range forces dominate
(electric double layer / van der Waals...)