

* Welcome, Introduction (handout)

* PowerPoint Intro

Moore's Law 2x 18 mo.

100x / 10 years

* Book - Molecular Model(l)ing / Hutchings

Molecular Modeling: determining properties
from microscopic-level computations

• Quantum Mechanics:
rates of reactions
intermolecular forces
conformations, ΔH_{form} , optical props

} Single molecules
or a few
interacting
molecules

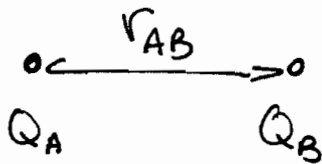
• Statistical Mechanics:
given interactions among parts of system,
predict properties observable at macroscopic scales

• Mesoscale Modeling:
for complex systems (e.g., polymer ^{nano-}composites)
model at intermediate level between
molecular + macroscopic

Properties : Melting and boiling points
(examples) Viscosities, diffusion coefficients
 κ -values for separations
 Conformations of proteins,
 nucleic acids

Coulomb's Law

Most interaction forces at the molecular level arise because of electrostatics, or quantum mechanical exclusion / bonding.



$$U(r_{AB}) = \frac{1}{4\pi\epsilon\epsilon_0} \cdot \frac{Q_A Q_B}{r_{AB}}$$

electrostatic interaction energy ↑ relative permittivity

$$\epsilon_0 = 8.854 \cdot 10^{-12} \frac{C^2}{Nm^2}$$

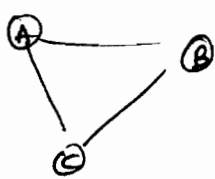
$$e = 1.602 \cdot 10^{-19} C \text{ (elementary charge)}$$

$$\epsilon = \begin{cases} 1 & \text{in vacuum,} \\ 78 & \text{in H}_2\text{O @ 300 K, } 1g/cm^3 \end{cases}$$

[Units] ? [Energy] = $\frac{C^2 Nm^2}{C^2 m} = J$ ✓

Force $F = -\frac{du}{dr} = -\frac{1}{4\pi\epsilon\epsilon_0} \frac{Q_A Q_B}{r_{AB}^2}$ (sign: + is on A, in neg r direction)

Electrostatic forces are pair-wise additive.



$$U(ABC) = U(AB) + U(BC) + U(AC)$$

Charge-charge interactions important for strong electrolytes, e.g. $Na^+ Cl^-$, salts, biophysics etc.

Note that Coulombic interactions fall off very slowly with distance, $u(r) \propto r^{-1}$

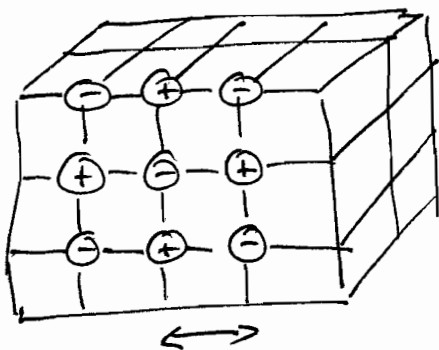


interaction of central ion with uniform charge cloud at r:

$$du(r) = 4\pi r^2 \rho \cdot \frac{Q}{4\pi\epsilon_0 r^2} dr$$

$\int_{R_c}^{\infty} u(r) dr$ diverges (galaxies do not have thermodynamics)

Ionic Crystals



- 6 neighbors at l , opp. Q
- 12 " at $\sqrt{2}l$, same Q
- 8 " at $\sqrt{3}l$, opp. Q
- \vdots \vdots \vdots \vdots

Total interaction:

$$u = \frac{-e^2}{4\pi\epsilon_0 l} \cdot \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \dots \right]$$

converges because of \pm cancellation, slowly


$$= -1.748 \frac{e^2}{4\pi\epsilon_0 l}$$

$\uparrow\uparrow$

"Madelung constant" depends on lattice type
 - this value is for NaCl-type lattice.

Born Energy

Even isolated ions have electrostatic energy - required to put together the ion from elementary charges initially at infinite distance.



$$dw = \frac{q dq}{4\pi\epsilon\epsilon_0 a}$$

$$w = \int_0^Q \frac{q dq}{4\pi\epsilon\epsilon_0 a} = \frac{Q^2}{8\pi\epsilon\epsilon_0 a}$$

} unfavorable
} $w \rightarrow \infty$
} as $a \rightarrow 0$

$Q = ze$ $z = \text{valence}$

Δw of transfer from solvent of permittivity ϵ_1 to ϵ_2

$$\Delta w = \frac{z^2 e^2}{8\pi\epsilon\epsilon_0 a} \left[\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right]$$

e.g. for $a = 0.14 \text{ nm}$ (Cl^-) from vacuum ($\epsilon_1 = 1$)
to water ($\epsilon_2 = 78$) @ $\Delta w = -1,000 \frac{\text{kJ}}{\text{mol}} \approx 40kT$
@ 300K

Solubility of ions in Solvents

Despite the high lattice ^{binding} energies, ionic crystals such as NaCl are soluble in water because the transfer free energy for moving ions from $\epsilon = 1$ to $\epsilon = 78$ overwhelms the binding energy.