Matt Lang, MIT

Forces at the Molecular Level

Covalent Interactions

Here electrons are truly shared between atoms. To do this properly we need to know the wavefunctions describing the electron probability density around the atoms. Lets assume a model of a bond as a spring to make some approximations.

Examples of typical energy of covalent bonds:

Carbon Carbon single bond ~140kT

Carbon Carbon double bond ~240kT

Force on a spring ~ kx

$$F_{spring} := k_{stiff} \cdot x$$

integrate to get the energy, Mathcad does this for us

Energy in a spring = $\int F_{spring}\, dx \rightarrow \frac{1}{2} \cdot k_{stiff} \cdot x^2$

$E_{bond} := 140 \cdot 4.$ units of pN*nm

A reasonable dissociation distance for this bond is 0.5 angstroms

set this value $x := \frac{0.5}{10}$ converted to nm

We can now estimate an approximate stiffness for the bond:

$$k_{stiff\_estimate} := 2 \cdot \frac{E_{bond}}{x^2}$$

$k_{stiff\_estimate} = 4.592 \times 10^5$ units of pN/nm

now generate a characteristic force required to rupture a covalent bond

$$characteristic\_force\_covalent := k_{stiff\_estimate} \cdot x$$

$characteristic\_force\_covalent = 2.296 \times 10^4$ units of pN   this = 23 nN or so

These bonds are strong you couldn't break for example with an optical trap, need more force

Matt Lang, MIT

Ionic bonding/interactions

develop using the physics of the coulombic interaction

Thermal Energy "kT"

$kT := 4.1 \cdot 10^{-21}$ J

4.1 pN*nm

distance separation, "r"

$r := 2.3 \cdot 10^{-10}$

typical NaCl separation
is 2.3 angstroms

charge on an electron

$q_1 := 1.60 \times 10^{-19}$

$q_2 := q_1$

$\varepsilon_0 := 8.85 \cdot 10^{-12}$

$\varepsilon := 1$

epsillon for water =80,
for oils, it is ~3

$$E_{coulomb} := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon \cdot r \cdot kT}$$

$E_{coulomb} = 244.104$ kT

units in kT

do salt, then do salt in water,
also show salt in non-polar

$$E_{water} := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot 80 \cdot r \cdot kT} \qquad E_{oil} := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot 3 \cdot r \cdot kT}$$

$E_{water} = 3.051$

$E_{oil} = 81.368$

Energy in units of kT

Coulombic Force

Coulombic force goes as $1/r^2$

$$F_{coulomb} := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon \cdot r^2}$$

$F_{coulomb} = 4.351 \times 10^{-9}$ N

Lets add up an array of work elements

create a range of r values increasing to infinity

$it := 0, 1 .. 50000 \qquad rin_{it} := r + it \cdot 0.2 \cdot 10^{-10}$

$rin_0 = 2.3 \times 10^{-10}$

$rin_3 = 2.9 \times 10^{-10}$

$$F_{cou}(ri) := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon \cdot ri^2}$$

sum over the force, multiply times the distance, add these all up to get the energy. basically integrate

$$EF_{total} := \sum_{it} \left(F_{cou}\left(rin_{it}\right) \cdot \frac{0.2 \cdot 10^{-10}}{kT} \right)$$

from summation

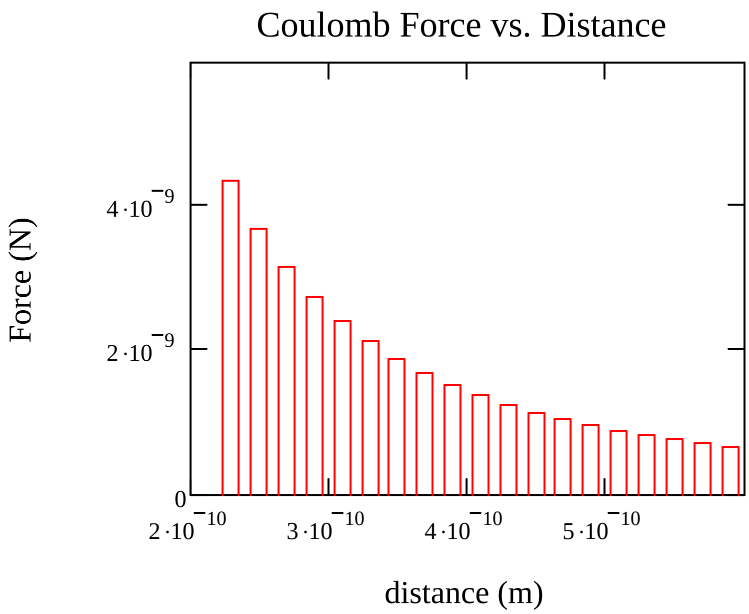
$EF_{total} = 254.968$

units of kT

from equation

$E_{coulomb} = 244.104$

Matt Lang, MIT



try making the boxes smaller, approach the integration limit

Instead of doing this by hand, we can do the integral in Mathcad to get the 1/r dependence:

$$F_{cou} := \frac{q_{11} \cdot q_{22}}{4 \cdot \pi \cdot \varepsilon_{00} \cdot \varepsilon_{11} \cdot r_3^{\,2}}$$

Energy = $\displaystyle\int -F_{cou}\, dr_3 \rightarrow \frac{1}{4} \cdot q_{11} \cdot \frac{q_{22}}{\pi \cdot \varepsilon_{00} \cdot \varepsilon_{11} \cdot r_3}$

Bjerrum length

Ask: How close do ions need to be to have a stable interaction?

solve coulombic interaction for a "kT" characteristic length

set for water

$\varepsilon := 80$

$$L_b := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon \cdot kT}$$

$L_b = 7.018 \times 10^{-10}$

units of meters

Should be about 7 angstroms in water

Matt Lang, MIT

Hydrogen Bond Examples

distance separation, "r"

$r := 3.0 \cdot 10^{-10}$

$\varepsilon := 1$

put in partial charges

$E_{hydrogenbond} := (0.2) \cdot (0.3) \cdot \dfrac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon \cdot r \cdot kT}$ $\quad E_{hydrogenbond} = 11.229$ units of kT

Debye Length

The coulomb potential is normally nice and long, but ions can screen this. We can calculate an ionic strength and a screening parameter that leads to a characteristic screening length called the Debye Length.

$i := 0 .. 1$

Ionic Strength

Make a table with concentrations and valency

concentration Molar — charge or valency

Dataconc :=

	0	1
0	1·10-4	1
1	1·10-4	-1

concentrations in a cell ~150mM plug this in and look at the Debye length

$C_{conc} := Dataconc^{\langle 0 \rangle}$ concentration

$z := Dataconc^{\langle 1 \rangle}$ charge on ion

$C_{conc} = \begin{pmatrix} 1 \times 10^{-4} \\ 1 \times 10^{-4} \end{pmatrix}$

$z = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$

formula for ionic strength

the higher the ionic strength, the more things are screened

$I_{str} := \left(\dfrac{1}{2}\right) \cdot \sum_i \left[C_{conc_i} \cdot \left(z_i\right)^2 \right]$

$I_{str} = 1 \times 10^{-4}$

$\varepsilon := 78.54$ $\quad \varepsilon_0 = 8.85 \times 10^{-12}$ $\quad n_o := 6.022 \cdot 10^{26}$

$k_{screen} := \sqrt{2 \cdot \dfrac{q_1^{\,2} \cdot n_o}{\varepsilon \cdot \varepsilon_0 \cdot kT}} \cdot \sqrt{I_{str}}$

this equation is approximate, valid in a limit of dilute species

$k_{screen} = 3.289 \times 10^{7}$

screening parameter (units of inverse length)

Debye Length

Will a charge "see" the full other charge? The ions in solution, reduce a charge, effectively the molecule "sees" less of the original charge.

$\dfrac{1}{k_{screen}} \cdot 10^{10} = 304.021$

screening length, units of Angstroms

these are short range, contact interactions

Matt Lang, MIT

$\lambda_D := \frac{1}{k_{screen}}$ $\quad \lambda_D = 3.04 \times 10^{-8}$

$\varepsilon = 78.54 \quad r = 3 \times 10^{-10}$

$\varepsilon := 1 \quad r := 300 \cdot 10^{-10}$

$E_{cou\_debye} := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon \cdot r \cdot kT} \cdot e^{\frac{-r}{\lambda_D}}$ $\quad E_{coulomb2} := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon \cdot r \cdot kT}$

$E_{cou\_debye} = 0.698 \quad E_{coulomb2} = 1.871$

Lennard-Jones potential

(Carbon example)

units in kcal/mole converted to kT units

$C_{12} := 2.75 \cdot 10^6 \cdot \frac{4.1}{0.59}$ repulsive term

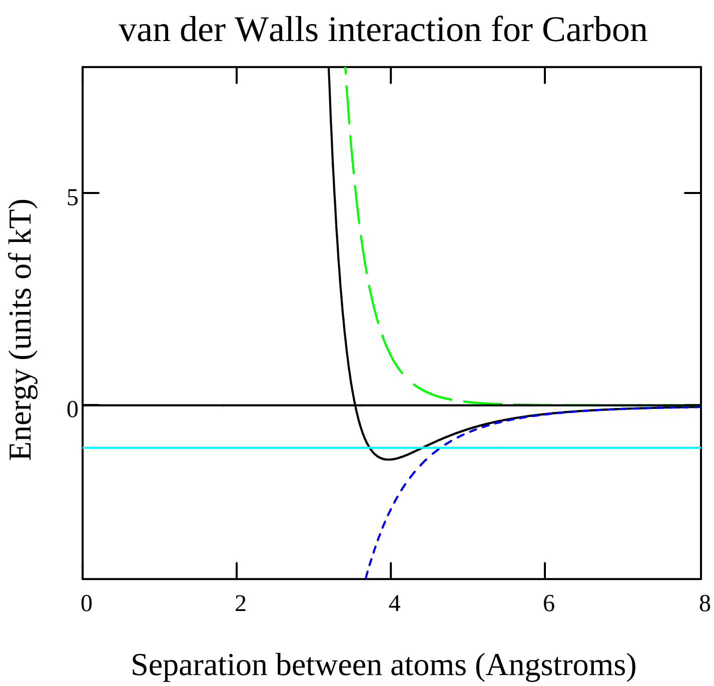
$C_6 := 1425 \cdot \frac{4.1}{0.59}$ attractive terms

$E_{LJ}(x) := \frac{C_{12}}{x^{12}} - \frac{C_6}{x^6}$

conversion factor is 4.1 (kT)/0.59 (kcal/mole)

$E_{AttrLJ}(x) := \frac{-C_6}{x^6} \quad E_{RepLJ}(x) := \frac{C_{12}}{x^{12}} \quad E_{base}(x) := x \cdot 0 \quad E_{kT}(x) := x \cdot 0 - 1$

$d := 0.001, 0.01 .. 8$



green is repulsive potential

dark blue is attractive

black is sum

light blue is kT level

example parameters from Creighton