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. Let's assume a model of a bond as a spring to make some approximations.

Examples of typical energy of covalent bonds:

- Carbon Carbon single bond \( \sim 140kT \)
- Carbon Carbon double bond \( \sim 240kT \)

Force on a spring \( \sim kx \)

\[ F_{\text{spring}} := k_{\text{stiff}} \cdot x \]

Integrate to get the energy, Mathcad does this for us

\[ E_{\text{bond}} := \int F_{\text{spring}} \, dx \rightarrow \frac{1}{2} k_{\text{stiff}} \cdot x^2 \]

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:

\[ k_{\text{stiff estimate}} := 2 \cdot \frac{E_{\text{bond}}}{x^2} \]

\[ k_{\text{stiff estimate}} = 4.592 \times 10^5 \text{ units of pN/nm} \]

Now generate a characteristic force required to rupture a covalent bond

\[ \text{characteristic force covalent} := k_{\text{stiff estimate}} \cdot x \]

\[ \text{characteristic force covalent} = 2.296 \times 10^4 \text{ units of pN} \quad \text{this} = 23 \text{ nN or so} \]

These bonds are strong you couldn't break for example with an optical trap, need more force.
Ionic bonding/interactions
develop using the physics of the coulombic interaction

Thermal Energy "kT"

\[ kT := 4.1 \times 10^{-21} \text{ J} \]

4.1 pN*nm

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

\[ E_{\text{coulomb}} = 244.104 \text{ kT} \]
units in kT

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

\[ E_{\text{water}} := \frac{q_1 q_2}{4\pi \varepsilon_0 \cdot 80 \cdot r \cdot kT} \]

\[ E_{\text{water}} = 3.051 \text{ kT} \]

\[ E_{\text{oil}} := \frac{q_1 q_2}{4\pi \varepsilon_0 \cdot 3 \cdot r \cdot kT} \]

\[ E_{\text{oil}} = 81.368 \text{ units in kT} \]

\[ \varepsilon := \frac{1}{1} \]

epsilon for water =80,
for oils, it is \( \varepsilon \approx 3 \)

distance separation, "r"

\[ r := 2.3 \times 10^{-10} \]

typical NaCl separation

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

is 2.3 angstroms

\[ q_2 := q_1 \]

\[ \varepsilon_\text{w} := 8.85 \times 10^{-12} \]

Coulombic Force

Coulombic force goes as \( 1/r^2 \)

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

\[ F_{\text{coulomb}} = 4.351 \times 10^{-9} \text{ N} \]

\[ F_{\text{coul}}(ri) := \frac{q_1 q_2}{4\pi \varepsilon_0 \cdot \varepsilon \cdot ri^2} \]

\[ \text{sum over the force, multiply times the distance, add these all up to get the energy.} \]

\[ \text{basically integrate} \]

\[ EF_{\text{total}} := \sum_{it} \left( F_{\text{coul}}(rin) \cdot \frac{0.2 \times 10^{-10}}{kT} \right) \]

from summation

\[ EF_{\text{total}} = 254.968 \text{ units of kT} \]

\[ E_{\text{coulomb}} = 244.104 \text{ from equation} \]
Coulomb Force vs. Distance

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

\[
F_{\text{cou}} := \frac{q_1 q_2}{4 \pi \varepsilon_0 \varepsilon_1 r^2}
\]

\[
\text{Energy} = \int -F_{\text{cou}} dr \rightarrow \frac{1}{4} q_1 q_2 \frac{\varepsilon_2}{\pi \varepsilon_0 \varepsilon_1 r^3}
\]

**Bjerrum length**

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

Set for water $\varepsilon = 80$

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

$L_b = 7.018 \times 10^{-10}$ units of meters

Should be about 7 angstroms in water
Hydrogen Bond Examples

\[ r := 3.0 \times 10^{-10} \]

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.

\[ I_{\text{str}} := \left( \frac{1}{2} \right) \sum_i C_{\text{conc}} (\text{conc}) (z_i)^2 \]

\[ C_{\text{conc}} := \text{Dataconc} (\text{conc}) \]

\[ z := \text{Dataconc} (\text{z}) \]

<table>
<thead>
<tr>
<th>( \text{conc} )</th>
<th>( \text{charge} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1 ( \times 10^{-4} )</td>
</tr>
<tr>
<td>1</td>
<td>1 ( \times 10^{-4} )</td>
</tr>
</tbody>
</table>

[I_{\text{str}} = 1 \times 10^{-4}]

Debye Length

\[ k_{\text{screen}} := 2. \frac{q_1^2 n_o}{e \varepsilon_0 kT} \sqrt{I_{\text{str}}} \]

\[ k_{\text{screen}} = 3.289 \times 10^7 \]

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

Debye Length

\[ \frac{1}{k_{\text{screen}}} \times 10^{10} = 304.021 \]
\[ \lambda_D := \frac{1}{k_{\text{screen}}} \quad \lambda_D = 3.04 \times 10^{-8} \]

\[ \epsilon = 78.54 \quad r = 3 \times 10^{-10} \]

\[ d := 0.001, 0.01 .. 8 \]

\[ E_{\text{coulomb}} := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \epsilon_0 \cdot \epsilon \cdot r \cdot kT} \]

\[ E_{\text{coulomb2}} := \frac{q_1 \cdot q_2}{4 \cdot \pi \cdot \epsilon_0 \cdot \epsilon \cdot r \cdot kT} \]

\[ E_{\text{coulomb2}} = 0.698 \quad E_{\text{coulomb2}} = 1.871 \]

**Lennard-Jones potential**

(Carbon example)

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

\[ E_{\text{AttrLJ}}(x) := -\frac{C_6}{x^6} \quad E_{\text{RepLJ}}(x) := \frac{C_{12}}{x^{12}} \]

\[ E_{\text{base}}(x) := x \cdot 0 \quad E_{kT}(x) := x \cdot 0 - 1 \]

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**van der Walls interaction for Carbon**

- green is repulsive potential
- dark blue is attractive
- black is sum
- light blue is kT level

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example parameters from Creighton