

Electronic and entropic interactions



Carsten Svaneborg, Department of Chemistry,
Aarhus University, Langelandsgade 140,
DK-8000 Århus C, Denmark



Relevant interactions?

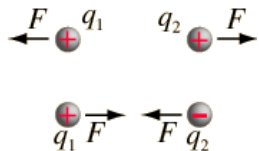
Microscopic due to electrons/quantum mech.

- ▶ Covalent bonds
- ▶ Hydrogen bonds
- ▶ Coloumbic interactions
- ▶ van der Waals interactions

Mesoscopic forces due to free energy

- ▶ hydrophobic/hydrophilic
- ▶ depletion interactions
- ▶ excluded-volume interactions
- ▶ polymers molecular-springs
- ▶ effective interactions between colloids
- ▶ counter-ion cloud entropy

Coulombic interactions



Attraction or repulsion between charges in vacuum.

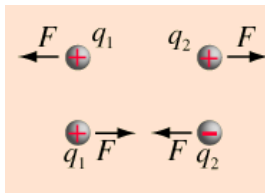
$$U = \frac{q_1 q_2}{4\pi\epsilon_0} \frac{1}{r} \quad (1)$$

Strong and long range interaction.

Ions in a crystal $U \sim 250k_B T$.

Equivalently ions have to be separated to $l_B \sim 60nm$ before the $U \sim k_B T$.

Coulombic interactions



Attraction or repulsion between charges in a medium.

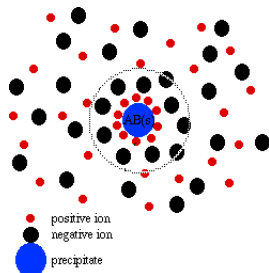
$$U = \frac{q_1 q_2}{4\pi\epsilon_r\epsilon_0} \frac{1}{r} \quad (1)$$

$\epsilon_r = 78.5$ for water.

Ions in pure water $U \sim 3k_B T$ and

$l_B \sim 0.7 \text{ nm}$.

Coulombic interactions



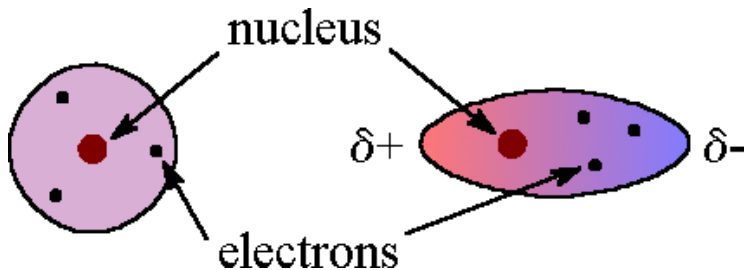
Attraction or repulsion between charges in a solution with ions.

$$U = \frac{q_1 q_2}{4\pi\epsilon_r\epsilon_0} \frac{1}{r} \exp(-\kappa r) \quad (1)$$

$\kappa^{-1} = 0.304 \text{ nm} (I \times L/\text{mol})^{-1/2}$ the Debye or screening length. Where I is the concentration of NaCl.

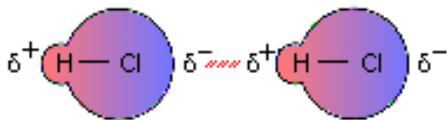
Strong attraction at short distance, but weak interaction at long distances!

Dipole interactions



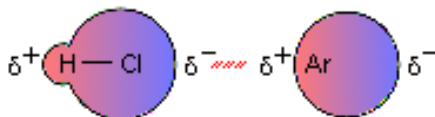
Neutral atom. Symmetric distribution has no dipole moment, however, the asymmetric charge distribution does. This can for instance happen if an atom is close to a charge.

Dipole interactions



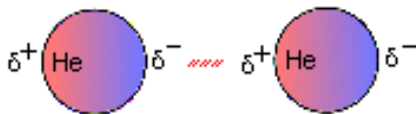
Attraction between two HCl molecules with permanent dipole moments due to the electronegative Cl atom. (Keesome interaction)

Dipole interactions



Permanent dipole HCl interacting with an induced dipole (Ar).
(Debye interaction)

Dipole interactions



Quantum fluctuations in leading to a weak interactions between the fluctuating dipoles of two He atoms without a permanent dipole moment. (London dispersion interaction). Energy $\sim k_B T$

Overview¹

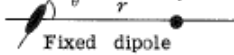
Charge-charge



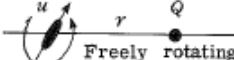
$$Q_1 Q_2 / 4\pi\epsilon_0 r$$

(Coulomb energy)

Charge-dipole



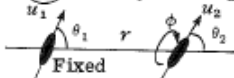
Fixed dipole

$$-Qu \cos \theta / 4\pi\epsilon_0 r^2$$


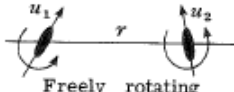
Freely rotating

$$-Q^2 u^2 / 6(4\pi\epsilon_0)^2 k T r^4$$

Dipole-dipole



Fixed

$$-u_1 u_2 [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi] / 4\pi\epsilon_0 r^3$$


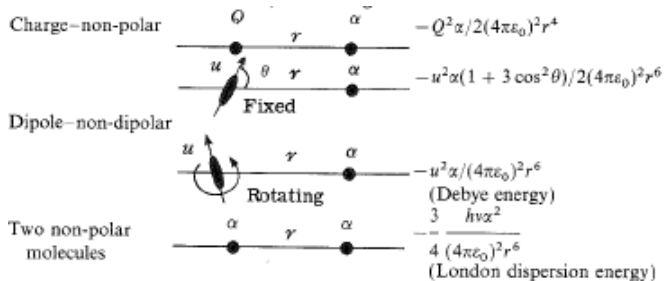
Freely rotating

$$-u_1^2 u_2^2 / 3(4\pi\epsilon_0)^2 k T r^6$$

(Keesom energy)

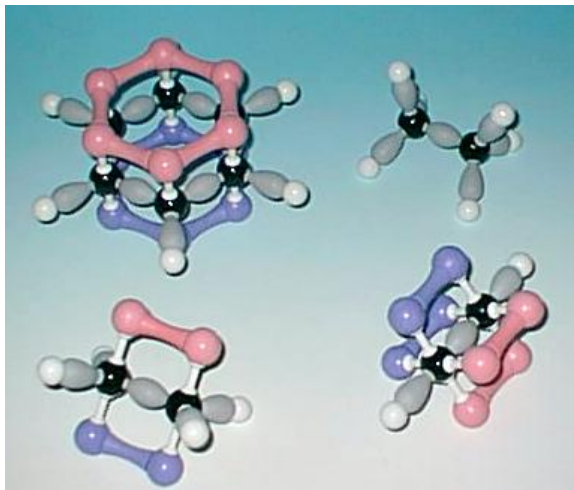
¹(J.N. Israelachvili - Intermolecular and surface forces)

Overview¹

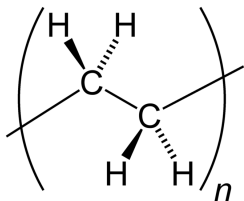


¹(J.N. Israelachvili - Intermolecular and surface forces)

Quantum effects



Covalent bonds



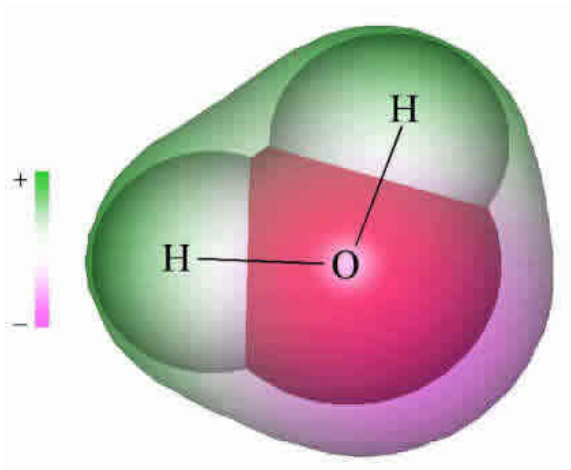
For instance C-C bonds in polyethylene. Electrons are shared between multiple atoms. Directional bond. Typical energies per bond $100 - 300k_B T$, very short range $0.1 - 0.2nm$.

Covalent bonds are strong and permanent.

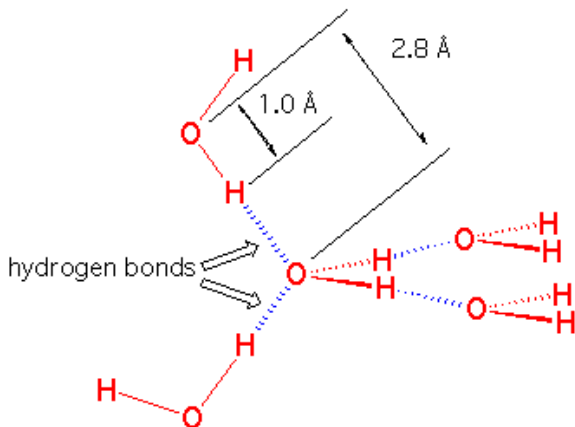
N.b. $k_B T = 4 \times 10^{-21} J$ at room temperature.

Hydrogen bonds - covalent+dipole

25 – 100 $k_B T$ per molecule. Directional dependence.



Structure of water



Structure of water

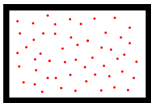
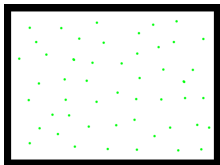


Summary

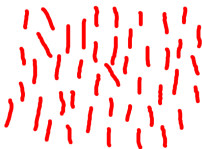
- ▶ Chemical bonds are much stronger than $k_B T$, and can not be broken by thermal fluctuations.
- ▶ van der Waals interactions between molecules, aggregates and surfaces makes them stick together, but is a much weaker interaction

Sources of entropy

Position



Orientation



Configuration



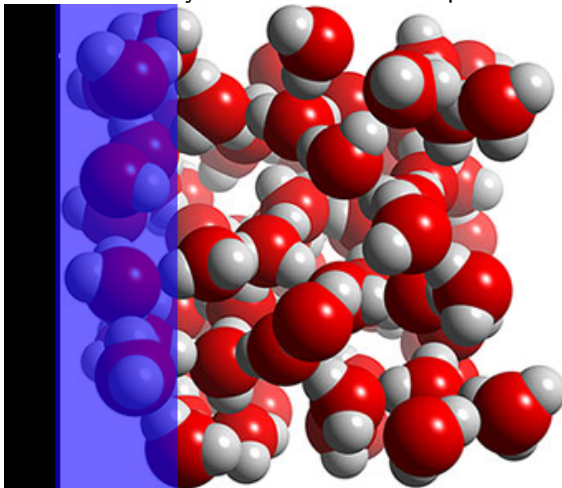
Hydrophobic effect

Water in the vicinity of a surface or non-polar molecule.

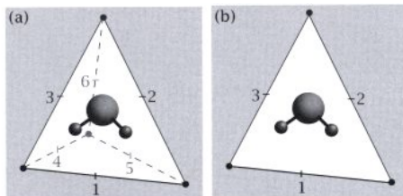


Hydrophobic effect

Water in the vicinity of a surface or non-polar molecule.



Simple stat.mech. calculation



"Free" water 6, "surface" water only 3 configs.

$$\Delta S = k_B \ln(W_{surf}) - k_B \ln(W_{free}) = k_B (\ln 3 - \ln 6) = -k_B \ln 2$$

Free energy cost $\approx 0.7 k_B T$ per molecule. 90% of the hydrophobic effect! More entropy lost in water configs. than gained by the translational entropy of e.g. dissolved alkanes.

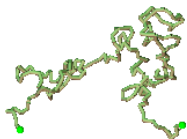
ref:

http://www.bio.brandeis.edu/classes/biochem104/hydrophobic_effect.pdf

Stretching a polymer

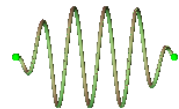
Microstates with end-to-end distance r and mean end-to-end distance $\langle R_{ee}^2 \rangle = Nb^2$

$$W(r) \propto \exp\left(-\frac{3r^2}{2\langle R_{ee}^2 \rangle}\right)$$



Free energy

$$F(r) = -TS(r) = -k_B T \ln W(r) = \frac{3B T}{2\langle R_{ee}^2 \rangle} r^2 + c$$



Force

$$f(r) = -\partial F(r)/\partial r = -\frac{3k_B T}{\langle R_{ee}^2 \rangle} r$$

Stretching a polymer molecule = an entropic



A polymer

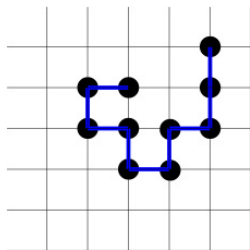
Number of conformations W
with z directions per step in (6
on cubic lattice) after
 N $10^3 - 10^6$ steps.

$$W = z^N$$

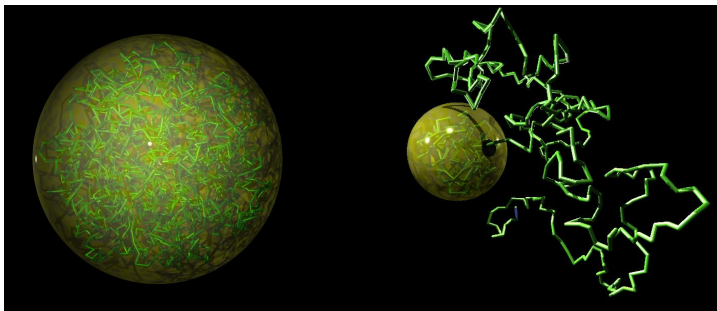
$$S_{config} = k_B N \log z$$

$$S_{trans} = k_B \log V$$

$$F = -k_B T (N \log z + \log V)$$

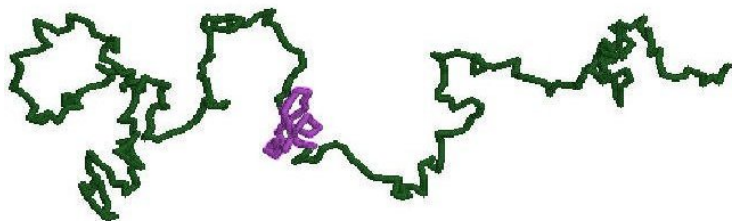


A Confined Polymer



ref: <http://ariadne.mse.uiuc.edu/Group/cacciuto/home.html>

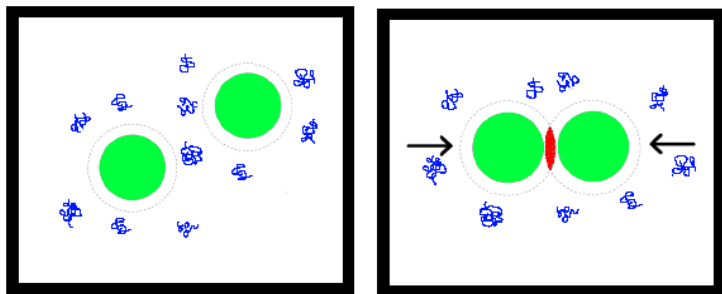
A Polymer Knot



ref: O Farago, Y Kantor, M Kardar - Europhysics Letters, 2002

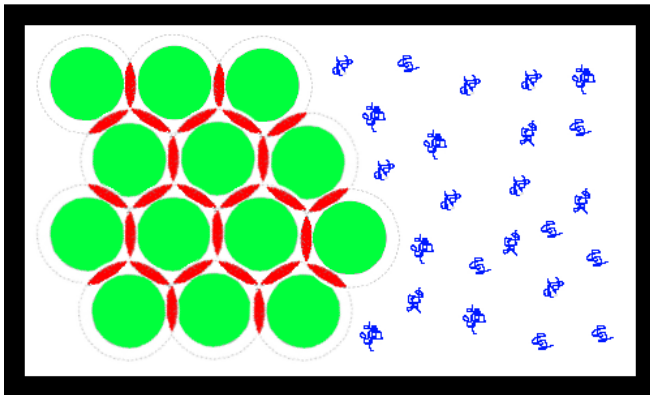


Depletion interaction³

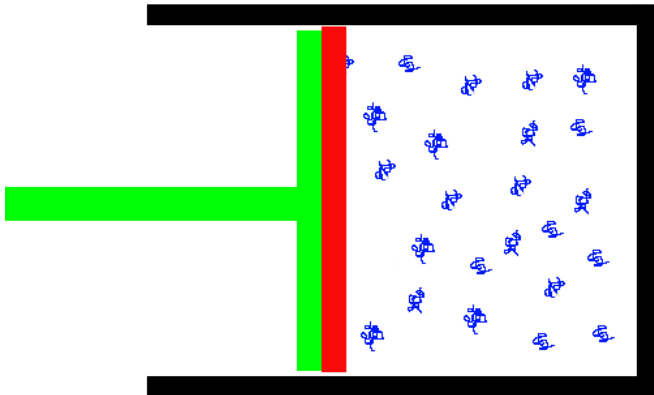


³R. Tuinier et al. Adv. Coll. Interface Sci. 103, 1 (2003)

Depletion interaction



Depletion interaction



Summary

- ▶ Electronic interactions are relevant on the microscopic scale.
- ▶ Entropy can be due to position, orientation, or configurational degrees of freedom.
- ▶ Entropic interactions are important on the mesoscopic scale, and for the hydrophobic effect.
- ▶ Soft-matter systems are dominated by entropic interactions, hence their characteristic energy is typically $k_B T$.