Forces in colloidal systems and self-assembly

- Why and which forces are important?
- Electrostatic interactions
- van der Waals forces
- Hydrophobic effect
- Depletion forces
- Steric forces
- Self-assembly process
- Introduction in surfactants, self-assembly of surfactants
Why and which forces are important?

Colloids are stabilized by a balance of competing forces, which act:

- to *repel* the colloidal particles

- to *attract* the colloidal particles > aggregation

Interparticle interactions are important.

Why are these interparticle interactions important?
Which forces are important?

- Dynamic balance:
  - gravity
  - thermal motion of colloidal particles
- Example: one particle ($\rho < \rho_{H_2O}$) with radius R is suspended in water.

Arhimeke force

$$F_a = \rho_{H_2O} \left( \frac{4}{3} \pi R^3 \right) g$$

Gravity force

$$G = m_p g = \rho \left( \frac{4}{3} \pi R^3 \right) g$$

Stockes force

$$F_s = 6\pi \eta R v$$

$$\Delta \rho = \rho_{H_2O} - \rho$$

Stockes force

$$F_s = 6\pi \eta R v$$

\[\eta \] viscosity

\[v \] velocity of the particle
Which forces are important?

- Example: one particle (\( \rho < \rho_{H_2O} \)) with radius R is suspended in water.

Sedimentation velocity of the particle:

\[
F_s = F \\
\nu = \frac{2R^2 \Delta \rho g}{9 \eta}
\]

\( \nu < \nu_B \) Colloidal particles remain in solution

\( \nu > \nu_B \) Colloidal particles sediment

Difusion coefficient of a particle, D

\[
D = \frac{k_B T}{6\pi \eta R} \\
\nu = \left(\frac{4}{3}\pi R^3\right) \frac{D \Delta \rho g}{k_B T}
\]
Do you know that…?

- 26°C is the minimal temperature for life

- The molecules have a $T = -173^\circ C$ (100K) in the external region of the Horse Nebula, and -258°C (15K) in its core.

- $T$ inside the core of the Sun is $+15.7$ milions of °C. $T$ at the external region of the Sun is $5800^\circ C$. 
Intermolecular/interparticle forces

- Intermolecular/interparticle forces are expressed by the potential energy:

\[ F(r) = -\frac{dV(r)}{dr} \]

- **Attractive** forces: -
- **Repulsive** forces: +

- Importance of the intermolecular/interparticle forces

Interfacial tension
Electrostatic forces between molecules

- The elements of a soft phase are charged (particles, surface) → the distribution of charges can lead to *assembly* in solution.

- **Example:** 2 oppositely charged particles \((q_1, q_2)\) are interacting due to the Coulomb force, \(F_c\):

\[
F_c = \frac{q_1 q_2}{4 \pi \varepsilon_0 r^2}
\]

Coulomb force (charges in *vacuum*)

Coulomb force (charges in a *medium*)

\[
F_c = \frac{q_1 q_2}{4 \pi \varepsilon_0 \varepsilon r^2}
\]

\[
\varepsilon = \frac{\varepsilon_{\text{material}}}{\varepsilon_0}
\]

- \(\varepsilon_0\) Permittivity of vacuum
- \(r\) Distance between charges
- \(\varepsilon\) Relative permittivity
- \(\varepsilon_{\text{medium}}\) Permittivity in medium
Electrostatic forces between molecules

- Coulomb force is related to the potential energy:

\[ V(r) = \frac{q_1q_2}{4\pi\varepsilon_0 r} = \frac{z_1z_2e^2}{4\pi\varepsilon_0 r} \]

- Coulomb forces are long range forces.

\[ F_c \gg F_{vdW} \]

\[ F_c = 100 - 600 \text{ kJ/mol} \]

\[ F_{vdW} < 1 \text{ kJ/mol} \]

\[ F_{H-bonds} = 10 - 40 \text{ kJ/mol} \]

- Coulomb forces represent the basis of the electrostatic repulsive forces between colloidal particles > disperse the particles
Electrostatic forces between molecules

- Example: 2 ions, Cl\(^+\) and Na\(^-\) in contact (\(r = 0.276\, \text{nm}\)), in vacuum and in water:
  
  a) vacuum: \( V_{1,2} = -8.36 \cdot 10^{-19} \, \text{J} \)
  
  b) water: \( V_{1,2} = -0.106 \cdot 10^{-19} \, \text{J} \)

\( \text{NaCl} \) dissociates in water

- Comparison between Coulomb potential energy and thermal energy (300K):

\[ k_B T = 4.1 \cdot 10^{-21} \, \text{J} \quad \Rightarrow \quad V_{1,2} \approx 203k_B T \]

\( V_{1,2} < k_B T \)

Coulomb forces are strong forces

\( r > 56 \, \text{nm} \)
Electrostatic interaction between an ion and a dipole

- Potential energy of the electrostatic interaction between an ion and a polar molecule (dipole)
  a) vacuum:
\[ V(r) = \frac{q_1 \mu_2 \cos \theta}{4\pi\varepsilon_0 r^2} \]

b) medium:
\[ V(r) = \frac{q_1 \mu_2 \cos \theta}{4\pi\varepsilon_0 \varepsilon r^2} \]

- In colloidal systems: the sum of all Coulomb interactions between the ion and each dipole.
Electrostatic Interaction Energies Between Molecules in the Gas Phase

<table>
<thead>
<tr>
<th>n</th>
<th>Name</th>
<th>Interaction Energy</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Coulomb ion–ion</td>
<td>$\frac{q_1 q_2}{4\pi \varepsilon_0 R_{12}}$</td>
<td>See Figure 3.1</td>
</tr>
<tr>
<td></td>
<td>Ion–dipole</td>
<td>$\frac{q_1 m_2 \cos \theta}{4\pi \varepsilon_0 R_{12}^3}$</td>
<td>See Figure 3.2</td>
</tr>
<tr>
<td></td>
<td>Dipole–dipole</td>
<td>$\frac{-m_1 m_2 f(\theta, \phi)}{4\pi \varepsilon_0 R_{12}^3}$</td>
<td>$f(\theta, \phi) = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_2 - \phi_1)$ See Figure 3.3</td>
</tr>
<tr>
<td></td>
<td>Ion-induced dipole</td>
<td>$\frac{-\alpha q_1^2}{2(4\pi \varepsilon_0)^2 R_{12}^4}$</td>
<td>Attractive</td>
</tr>
<tr>
<td></td>
<td>Dipole-induced dipole (Debye)</td>
<td>$\frac{-m_1^2 \alpha (1 + 3 \cos^2 \theta)}{2(4\pi \varepsilon_0)^2 R_{12}^6}$</td>
<td>Attractive</td>
</tr>
<tr>
<td></td>
<td>Thermally averaged dipole–dipole (Keesom)</td>
<td>$\frac{-2m_1^2 m_2^2}{3(4\pi \varepsilon_0)^2 kT R_{12}^6}$</td>
<td>Attractive</td>
</tr>
</tbody>
</table>
Electrostastic induced interactions

- **ion** - induced dipole ($\mu$)
- **dipol** - induced dipole ($\mu$)

- Polarizability of an atom $\alpha$:

$$\mu_{ind} = \varepsilon E$$

**Example:** $H_2O \quad \alpha / \varepsilon_0 = 1.86 \cdot 10^{-29} \text{ m}^3$
Electrostatic induced interactions

- Electrostatic interactions: ion-ion → STRONG

  Electrolytes

  Charged colloidal solutions

- How to treat colloidal systems?  The full description never solved !!!

- Most distances $\gg$ molecular size $\rightarrow$ AVERAGE
Van der Waals forces

- between molecules: rather short range

- Potential energy:
  \[ V_{12} = -\frac{C}{r^6} = -\frac{C^{\text{disp}} + C^p + C^{\text{ind}}}{r^6} \]

  - London:
    \[ V_{12} = -\frac{C^{\text{disp}}}{r^6} = -\frac{3}{2} \frac{\alpha_{01} \alpha_{02}}{(4\pi \varepsilon_0)^2} \left( \frac{I_1 I_2}{I_1 + I_2} \right) \]

  - Kesson:
    \[ V_{12} = -\frac{C^p}{r^6} = -\frac{1}{3} \frac{\mu_1^2 \mu_2^2}{k_B T (4\pi \varepsilon_0)^2} \]

  - Debye:
    \[ V_{12} = -\frac{C^{\text{ind}}}{r^6} = -\frac{\alpha_{01} \mu_1^2 + \alpha_{02} \mu_2^2}{(4\pi \varepsilon_0)^2} \]
Van der Waals forces

Other forces:
- **Quadrupol** forces: not important for Colloid & Surface
- **Repulsive** forces:  
  \[ V^{rep} = -\frac{C}{r^n} \quad n \in [8-16] \]

Van der Waals forces:
- **Size & Shape** to be taken into account
- Potential Energy integrate van der Waals forces over shape & particles geometry & surface.
  \[ V_A(H) \]
  \[ H \rightarrow \text{distance (notation)} \]
### Table 2.2  Van der Waals interaction (potential) energies between particles/surfaces; $V_A$ is the potential energy (in [J/m$^2$] for the interaction between two surfaces), $H$ is the interparticle/intersurface distance and $R$ is the radius (for spherical particles); $A$ is the Hamaker constant (see Equations 2.6–2.8 and Hamaker, 1937) and, depending on the application, is evaluated under conditions of either vacuum/air or a dielectric (i.e. a liquid medium, in which case an effective Hamaker constant must be used). $C$ is defined in Equation 2.6 and $\rho$ is the number density (molecules/volume).

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Expression for the potential energy $V_A (H)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface-molecule</td>
<td>$V_A = -\frac{\pi C \rho}{6H^3}$</td>
</tr>
<tr>
<td>Two equal-sized spheres ($H \ll R$)</td>
<td>$V_A = -\frac{AR}{12H}$</td>
</tr>
<tr>
<td>Two equal-sized spheres, valid at all distances</td>
<td>$V_A = -\frac{AR}{12H} \left[ \frac{4R}{(H+4R)} + \frac{4RH}{(2R+H)^2} + \frac{2H}{R} \ln \left( \frac{H(H+4R)}{(2R+H)^2} \right) \right]$</td>
</tr>
<tr>
<td>Two unequal-size spheres (radii $R_1$ and $R_2$) ($H \ll R_1$, $R_2$)</td>
<td>$V_A = -\frac{A}{6H} \left( \frac{R_1 R_2}{R_1 + R_2} \right)$</td>
</tr>
<tr>
<td>Two spherical particles of unequal/equal radii, valid at all separations. In the equation, use $r = R_1 + R_2 + H$.</td>
<td>$V_A = -\frac{A}{6} \left[ \frac{2R_1 R_2}{r^2 - (R_1 + R_2)^2} + \frac{2R_1 R_2}{r^2 - (R_1 - R_2)^2} \right]$</td>
</tr>
<tr>
<td>Two flat plates/surfaces of “infinite” thickness (per unit area, J m$^{-2}$)</td>
<td>$V_A = -\frac{A}{12 \pi H^2}$</td>
</tr>
<tr>
<td>Two flat plates/surfaces per unit area of surface (J m$^{-2}$) (finite thickness $t$)</td>
<td>$V_A = -\frac{A}{12 \pi} \left[ \frac{1}{t^2} + \frac{1}{(H+2t)^2} - \frac{2}{(H+t)^2} \right]$</td>
</tr>
<tr>
<td>Two parallel cylinders with radii $R_1$ and $R_2$ ($H \ll R_1$, $R_2$) (per unit length, J m$^{-1}$)</td>
<td>$V_A = -\frac{A}{12 \sqrt{2} H^{3/2}} \left( \frac{R_1 R_2}{R_1 + R_2} \right)^{1/2}$</td>
</tr>
<tr>
<td>Cylinder–cylinder (crossed at 90°) interactions (radii $R_1$, $R_2$, respectively)</td>
<td>$V_A = -\frac{A}{6H} \sqrt{R_1 R_2}$</td>
</tr>
<tr>
<td>Sphere or macromolecule of radius $R$ near a flat surface ($H \ll R$)</td>
<td>$V_A = -\frac{AR}{6H}$</td>
</tr>
<tr>
<td>Cylinder of radius $R$ near and parallel with a flat surface (per unit length, J m$^{-1}$) ($H &lt; R$)</td>
<td>$V_A = -\frac{A\sqrt{R}}{12 \sqrt{2} H^{3/2}}$</td>
</tr>
</tbody>
</table>
Van der Waals forces

- The previous formulas: particles $R > 0.5 \text{ nm}$

- **Hamaker** constant $\to f(C)$

$$ A = \pi \rho^2 C \quad \text{with} \quad C = \text{London coefficient} $$

Other medium $\to A_{\text{eff}}$

**Example:** $H_2O$ - particles 1,3 & medium 2

$$ A_{123} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)\left(\sqrt{A_{33}} - \sqrt{A_{22}}\right) \quad 1 = 3 $$

$$ A_{121} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2 $$
Van der Waals forces

- Total interaction: \[ \sum \text{(interactions - pairs } ij, \text{ central potential)} \]

- **Lifshitz theory**: more appropriate

\[ A_{123} = A_{\nu=0} + A_{\nu>0} \]

\[
A_{\nu=0} = \frac{3k_B T}{4} \left( \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left( \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right)
\]

\[ n_i = \text{refractive index of particle } i \]

\[
A_{\nu>0} = \frac{3h \nu_e}{8\sqrt{2}} \frac{\left( n_1^2 - n_3^2 \right) \left( n_2^2 - n_3^2 \right)}{\sqrt{\left( n_1^2 + n_3^2 \right) \left( n_2^2 + n_3^2 \right) \left[ \sqrt{\left( n_1^2 + n_3^2 \right)} + \sqrt{\left( n_2^2 + n_3^2 \right)} \right]}}
\]
Van der Waals forces

- **Lifshitz:**
  - **Case:** particle 1 = particle 3

\[
A_{121} = \frac{3k_B T}{4} \left( \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^2 + \frac{3\hbar \nu_e}{16\sqrt{2}} \left( \frac{n_1^2 - n_2^2}{n_1^2 + n_2^2} \right)^{3/2}
\]

- **Case:**
  - Medium 2 = vacuum (air) \(\rightarrow\) \(\varepsilon_2 = 1\), \(n_2 = 1\)

\[
A_{121} = \frac{3k_B T}{4} \left( \frac{\varepsilon_1 - 1}{\varepsilon_1 + 1} \right)^2 + \frac{3\hbar \nu_e}{16\sqrt{2}} \left( \frac{n_1^2 - 1}{n_1^2 + 1} \right)^{3/2}
\]
- Smooth $f(n_i)$ for a large number of compounds: acetone, ethanol, polymers, $\text{H}_2\text{O}$, ceramics, etc.
- No trend $f(\varepsilon_i)$

**Lifshitz formula** → Nanoparticles & medium = continuous phases.
Van der Waals forces

- **Estimate the Hamaker constant in other media:**
  - Hamaker constant of water: \( A_{22} = 3.7 \cdot 10^{-20} J \)

  - **Example:** Polystyrene in water: \( A_{11} = 7.0 \cdot 10^{-20} J \) \( \text{Exp: } (6.1 + 7.9)/2 = 7.0 \)
    
    \[
    A_{121} = \left( \sqrt{7.0 \cdot 10^{-20}} - \sqrt{3.7 \cdot 10^{-20}} \right)^2 = 0.52 \cdot 10^{-20} J
    \]

  - **Example:** \( Al \) nanoparticles in water: \( A_{11} = 14.0 \cdot 10^{-20} J \)
    
    \[
    A_{121} = \left( \sqrt{14.0 \cdot 10^{-20}} - \sqrt{3.7 \cdot 10^{-20}} \right)^2 = 3.31 \cdot 10^{-20} J
    \]

  - **Example:** \( Zr \) nanoparticles in water: \( A_{11} = 17.0 \cdot 10^{-20} J \)
    
    \[
    A_{121} = \left( \sqrt{17.0 \cdot 10^{-20}} - \sqrt{3.7 \cdot 10^{-20}} \right)^2 = 4.83 \cdot 10^{-20} J
    \]
Van der Waals forces

- **Estimate the Hamaker constant** when we know another constants:

- **Example**: Octane in water:

  - Hamaker constant of water: $A_{22} = 3.7 \cdot 10^{-20} J$
  
  - Octane in air (vacuum) $\rightarrow \epsilon_2 = 1.90$, $n_2 = 1.39$
  
  - $\nu_e = 3 \cdot 10^{15}$ Hz

  $$A_{11} = \frac{3k_B T}{4} \left( \frac{\epsilon_1 - 1}{\epsilon_1 + 1} \right)^2 + \frac{3h \nu_e}{16\sqrt{2}} \left( \frac{n_1^2 - 1}{n_1^2 + 1} \right)^{3/2}$$

  $$A_{11} = \frac{3 \cdot 1.38 \cdot 10^{-23} \cdot 300}{4} \left( \frac{0.9}{2.9} \right)^2 + \frac{3 \cdot 6.62 \cdot 10^{-34} \cdot 3 \cdot 10^{15}}{16\sqrt{2}} \frac{0.93^2}{2.93^{3/2}} = 4.57 \cdot 10^{-20} J$$

  $$A_{121} = \left( \sqrt{4.57 \cdot 10^{-20}} - \sqrt{3.7 \cdot 10^{-20}} \right)^2 = 0.045 \cdot 10^{-20} J$$

  $$A_{121} = 0.36 \cdot 10^{-20} J \quad \text{← Hamaker const (Lifshitz theory)}$$

  - Experimental:

  $$A_{121} = 0.41 \cdot 10^{-20} J$$
### Refractive Indices / Permittivities

#### Table 121. Refractive Indices for Wavelengths Corresponding to Selected Fraunhofer Lines

<table>
<thead>
<tr>
<th>Fraunhofer Line</th>
<th>A</th>
<th>B</th>
<th>D</th>
<th>F</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength, nm</td>
<td>759</td>
<td>687</td>
<td>589</td>
<td>486</td>
<td>397</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>1.610</td>
<td>1.617</td>
<td>1.629</td>
<td>1.654</td>
<td>1.702</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>1.339</td>
<td>1.360</td>
<td>1.363</td>
<td>1.367</td>
<td>1.374</td>
</tr>
<tr>
<td>Glass (light crown)</td>
<td>1.510</td>
<td>1.512</td>
<td>1.545</td>
<td>1.521</td>
<td>1.531</td>
</tr>
<tr>
<td>Water</td>
<td>1.332</td>
<td>1.331</td>
<td>1.333</td>
<td>1.337</td>
<td>1.344</td>
</tr>
</tbody>
</table>

#### Table 122. Refractive Indices of Selected Gases

<table>
<thead>
<tr>
<th>Gas or vapour</th>
<th>(n-1)×10⁻⁴</th>
<th>Gas or vapour</th>
<th>(n-1)×10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>0.06</td>
<td>Hydrogen sul-</td>
<td>6.19</td>
</tr>
<tr>
<td>Air</td>
<td>2.92</td>
<td>phide</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>3.77</td>
<td>Mercury</td>
<td>9.33</td>
</tr>
<tr>
<td>Benzene</td>
<td>7.48</td>
<td>Methane</td>
<td>4.31</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>4.50</td>
<td>Nitrogen</td>
<td>2.87</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>17.63</td>
<td>Selenium</td>
<td>8.95</td>
</tr>
<tr>
<td>Chloroform</td>
<td>14.55</td>
<td>Sulphur dioxide</td>
<td>7.37</td>
</tr>
<tr>
<td>Helium</td>
<td>0.35</td>
<td>Tellurium</td>
<td>9.91</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.38</td>
<td>Water vapour</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zinc</td>
<td>20.50</td>
</tr>
</tbody>
</table>

**Note.** The values of the refractive indices in the table are for a wavelength corresponding to the yellow line of sodium (D) and have been reduced to a density corresponding to 0°C and standard pressure (101.325 kPa) using the relationship (n - 1)/ρ = const (for a given gas).

#### Table 74. Permittivities of Selected Pure Liquids

<table>
<thead>
<tr>
<th>Substrate</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>23.3</td>
<td>22.5</td>
<td>21.4</td>
<td>20.9</td>
<td>20.5</td>
<td>19.5</td>
<td>18.7</td>
</tr>
<tr>
<td>Benzene</td>
<td>-</td>
<td>2.30</td>
<td>2.29</td>
<td>2.27</td>
<td>2.26</td>
<td>2.25</td>
<td>2.22</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>-</td>
<td>2.31</td>
<td>2.30</td>
<td>-</td>
<td>2.20</td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>27.88</td>
<td>25.41</td>
<td>23.08</td>
<td>21.25</td>
<td>23.52</td>
<td>22.16</td>
<td>20.87</td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>8.50</td>
<td>4.58</td>
<td>4.38</td>
<td>4.27</td>
<td>4.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glycerin</td>
<td>-</td>
<td>-56.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kerosene</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>87.63</td>
<td>83.86</td>
<td>80.08</td>
<td>78.25</td>
<td>76.47</td>
<td>74.47</td>
<td>72.06</td>
</tr>
</tbody>
</table>

**Note.** Small amounts of impurities have a negligible effect on the value of the permittivity.
Importance of the van der Waals forces

- **dispersion** forces → universal
- **polar** & **induction** forces → \( f(\text{material}) \)
  
  only polar forces = \( f(T) \)

- Dispersion forces → **additive**: \( \sum \) (attraction - pairs \( ij \))

  \[ \text{Dominate} \rightarrow \text{nanoparticles & surfaces} \]

- Example:
  - van der Waals between **molecules**: \( V_{12} = -\frac{C^{\text{disp}}}{r^6} \)
  - van der Waals between **nanoparticles**: \( H \ll R \)

  \[ V_{1,2} = -\frac{AR}{12H} \]
Importance of the van der Waals forces

- van der Waals forces between particles:
  → **attractive**: - medium is vacuum, air
    - molecules / nanoparticles: identical
  → **repulsive**: - molecules / nanoparticles: different in a 3\textsuperscript{rd} medium

\[ n_3 \in (n_1, n_2) \]

predict immiscibility in polymer blends

- van der Waals forces: decrease in a medium different from vacuum/air
- van der Waals forces \rightarrow theory of colloids **stability**
Importance of the van der Waals forces

**Example**: relative importance of polar/dispersion forces – $H_2O \leftrightarrow$ alkanes:

$-H_2O \leftrightarrow$ methan $\rightarrow \quad \varepsilon_{water} = 80, \ n_{water} = 1.33$

$\quad \varepsilon_{methan} = 2, \ n_{methan} = 1.30$

2 molecules (methan) $\rightarrow$ polar forces have the **major** contribution
Importance of the van der Waals forces

- electrostatic quantum field theory (McLachlan)

\[ V_{v=0} = -\frac{3k_B T}{r^6} R_1^3 R_2^3 \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + 2\varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + 2\varepsilon_3} \right) \]

\[ V_{v>0} = -\frac{\sqrt{3} h \nu_e R_1^3 R_2^3}{2r^6} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{(n_1^2 + 2n_3^2)(n_2^2 + 2n_3^2)}} \left[ \sqrt{n_1^2 + 2n_3^2} + \sqrt{n_2^2 + 2n_3^2} \right] \]

- Example: \( H_2O \leftrightarrow \text{methan} \)

\[ V_{v>0} = -\frac{\sqrt{3} h \nu_e R_1^3 R_2^3}{2r^6} \frac{(-0.08)(-0.08)}{\sqrt{(5.23)(5.23)}} \left[ \sqrt{(5.23)} + \sqrt{(5.23)} \right] = -\frac{\sqrt{3} h \nu_e R_1^3 R_2^3}{2r^6} \cdot 0.000267 \]

\[ V_{v=0} \gg V_{v>0} \Rightarrow V = V_{v=0} + V_{v>0} \approx V_{v=0} \]
Importance of the van der Waals forces

- van der Waals dispersion forces → London interaction
- derived from quantum mechanics: attractive

- correlation between $e^-$ → instantaneous dipoles

- dipole-dipole interaction

→ dispersion interaction: ⇒ cohesion in liquids & solids

approximation: $\sum (\text{pairs } ij \text{ of molecules})$

$\neq f(T)$
# Importance of the van der Waals forces

## Table 5.1

| Material                          | M|Air|M | M|Water|M | M|Water|Air  | M|Air|Water |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Water                            | 3.7             | 0.0             | 0.0             | 3.7             |                 |                 |                 |                 |                 |                 |                 |
| Alkanes                           |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| $n = 5$                           | 3.8             | 0.3             | 0.15            | 3.6             |                 |                 |                 |                 |                 |                 |                 |
| $n = 6$                           | 4.1             | 0.4             | 0.0             | 3.8             |                 |                 |                 |                 |                 |                 |                 |
| $n = 10$                          | 4.8             | 0.5             | -0.3            | 4.1             |                 |                 |                 |                 |                 |                 |                 |
| $n = 14$                          | 5.1             | 0.5             | -0.5            | 4.2             |                 |                 |                 |                 |                 |                 |                 |
| $n = 16$                          | 5.2             | 0.5             | -0.5            | 4.3             |                 |                 |                 |                 |                 |                 |                 |
| Fused quartz                     | 6.5             | 0.8             | -1.0            | 4.8             |                 |                 |                 |                 |                 |                 |                 |
| Fused silica                     | 6.6             | 0.8             | -1.0            | 4.8             |                 |                 |                 |                 |                 |                 |                 |
| Sapphire                          | 16.0            | 5.0             | -3.8            | 7.4             |                 |                 |                 |                 |                 |                 |                 |
| Polymethyl methacrylate          | 7.1             | 1.1             | -1.3            | 5.0             |                 |                 |                 |                 |                 |                 |                 |
| Polystyrene                       | 6.6             | 1.0             | -1.1            | 4.8             |                 |                 |                 |                 |                 |                 |                 |
| Polyisoprene                      | 6.0             | 0.7             | -0.8            | 4.6             |                 |                 |                 |                 |                 |                 |                 |
| Polytetrafluoroethylene           | 3.8             | 0.3             | 0.1             | 3.7             |                 |                 |                 |                 |                 |                 |                 |
| Mica (green)                     | 10.0            | 2.1             |                 |                 |                 |                 |                 |                 |                 |                 |                 |
Hydrogen bonds & Hydrophobic Effect

- H bonds $\rightarrow H \leftrightarrow F, O, N$ atoms $\rightarrow$ Lewis acid – Lewis base interactions
  $\rightarrow$ when present: dominate the properties

**Example:** Ethanol $\rightarrow T_{boiling} = 79^\circ C$
Isomeric dimethylether $\rightarrow T_{boiling} = -25^\circ C$

- H bonds $\gg$ van der Waals interactions
  $\rightarrow (8 - 40) \text{ kJ/mol} \ll$ covalent interactions: $(150 - 900) \text{ KJ/mol}$
  $\rightarrow$ electrostatic attraction: $O^- \leftrightarrow H^+$
Hydrogen bonds & Hydrophobic Effect

$H_2O \rightarrow \text{dipol}$

- Hydrophyllic molecule: polar molecule $\rightarrow$ H bonds with $H_2O$
- Hydrophobic molecule: nonpolar molecule $\rightarrow$ NO H bonds with $H_2O$

$H_2O$ - form a „cage-like“ structure

Entropically unfavorable
Hydrogen bonds & Hydrophobic Effect

- decrease local entropy

- give energy → incorporate a hydrophobic molecule in a $H_2O$ solution

- Hydrophobic surface
Hydrogen bonds & Hydrophobic Effect

Amphiphilic $\rightarrow$ **Hydrophobic** + **Hydrophilic**
Hydrogen bonds & Hydrophobic Effect

Hydrophobic effect → $H_2O$ molecules: connected with H bounds

non-polar molecules added

more structured cavities

Example: $H_2O$ → $T_{boiling} = 100 \, ^{\circ}C$

$(3 \text{-} 3.5 \text{ H bound/molecule})$

$CH_4$ → $T_{boiling} = -167 \, ^{\circ}C$

$H_2O$ + alcanes $\rightarrow$ $S$ decreases $\rightarrow$ $\Delta G > 0$
Hydrogen bonds & Hydrophobic Effect

**Hydrophobic interaction** = strong attraction forces between non-polar molecules and surfaces in water


Depends on the size of the hydrophobic clusters
Hydrogen bonds & Hydrophobic Effect

\[ T \text{ increase} \Rightarrow \text{Hydrophobic forces increase} \]

Induce order in the \( H_2O \) molecule arrangement

\( \text{Hydrophobic forces} \rightarrow \) entropic \( \Rightarrow \) decrease \( S \)

Near a small hydrophobic unit

- only remainants of a clathrate structure of \( H_2O \) molecules
Hydration of small / large hydrophobic solutes

Hydrophobic solutes $\Rightarrow$ “cavities” in $H_2O$ : do not exists $H$ bounds.

Van der Waals interactions

Affect the position of an interface between $H_2O$ molecules & solute units

Strong attractive forces (hydrophilic) $\rightarrow$ amphiphilic nature

Affect the arrangement of the assemblies relative to interface
Hydration of small hydrophobic units

Each $H_2O$ molecule $\rightarrow$ 4 $H$ bounds

$d < 0.5 \text{ nm}$

Do not break the $H$ bounds of $H_2O$
Hydration of small hydrophobic units

\[ \Delta G \rightarrow W \text{ reversible for the solvent to reorganize and solvate the solute molecule} \]

\[ P \approx e^{\frac{ \Delta G }{ k_B T }} \]

\[ \Delta G = \Delta H - T \Delta S \]

H bonds breaking \( \rightarrow \Delta H \) is dominant: \( \frac{\Delta G}{T} \) decrease when \( T \) increase

\( \Delta S > 0 \Rightarrow \text{High } T \ (25 \degree C) \)

\( H_2O \) arrangements \( \rightarrow \Delta S \) is dominant: (\( \Delta S < 0 \)) \( \rightarrow \Delta G \) increase when \( T \) increase
Hydration of big hydrophobic units

The solute \textbf{surface} → extent with \textit{low curvature} for $A \gg 1 \text{ nm}^2$

H bonds of $H_2O$ molecules → broken → each $H_2O : 3 \text{ H bonds}$

$H_2O$ molecules tends to move away

$H_2O$ \textbf{interface} around the hydrophobic units → simular to interface between \textit{liquid - vapour}

Hydration of big hydrophobic units

\[ \Delta G \approx 4\pi R^2 \gamma + \frac{4}{3} \pi R^3 p \approx 4\pi R^2 \gamma \]

The H\textsubscript{2}O interface $\rightarrow \Delta G \sim$ surface area

\[ \Delta G = f(R) \]

H bonds breaking $\rightarrow \Delta H$ is dominant:

$\Delta G/T$ decrease when $T$ increase

**Small Hydrophobic unit:** $\Delta G \approx \frac{4}{3} \pi R^3$

**Big Hydrophobic unit:** $\Delta G \approx R^2$
Depletion forces

Solution of *big colloidal* particles → add *small nanoparticles*

The *big particles* are aggregating

Net force → *isotropic* (from all directions)

*Depletion forces* → Effect of *small nanoparticles* added to a solution of *big particles*

Origin of depletion attraction: *thermal motion* of small molecules
Depletion forces

*big colloidal* particles → random movement

can approach each other

\[ d \approx 2r \]

small particles do **not enter between** big particles

*Depletion forces* \(\rightarrow\) **Net force \rightarrow anisotropic**
Depletion forces

Depletion forces → do not determine permanent aggregates

change of solution conditions

redispersion

Adding a polymer → aggregation of big particles

\[ d \approx 2R_g \]

\[ R_g = f(T) \rightarrow \Delta T \text{ can be used to control the dispersion} \]
Depletion forces

Polymer $\rightarrow$ **change conformation** in a confined space $\rightarrow$ chain of «blobs»

The size of polymer $\rightarrow$ the range of depletion

**Example:** PEG $\rightarrow$ fusion of biological cells
Depletion forces

- \( F_{depl} = f(z) \) → depends on the concentration profile

- polymers → density peak outside the depletion zone

- oscillations in the solute concentration
Steric repulsion

Modify the **particle surface** → control the force between particles

**Steric modification**

Entropic energy barrier → **Brush** configuration

„Interlocked“ chains → **Lower number of configurations**

$S$ decrease

**Interlocking ≅ packing**
Steric repulsion

Example: PEG $\rightarrow$ brushes

Do not allow protein adsorption

Range repulsion forces $\rightarrow$ greater than van der Waals forces

Repulsive forces $\rightarrow$ greater difficulty of packing connected objects
Assembly in colloidal systems

Attractive & repulsive forces

Spontaneous assembly of particles

Assembly process

Phase thermodynamically stable
Diffusive process → structure aggregation
Assembly in colloidal systems

Self assembly = $f$ (how particles come together)

Process of association $\rightarrow$ aggregates

Small clusters $\rightarrow$ diffuse at: $v = f(\text{size})$ [Stokes-Einstein]

$D = \frac{k_B T}{6\pi \eta R}$

Small clusters $\rightarrow$ grow in size $\rightarrow$ aggregate
Assembly in colloidal systems

Particles do not interact \(\rightarrow\) high dissociation rate

Particles interact \(\rightarrow\) stick permanently

- Reaction-limited aggregation

\[
\text{Probability to } \textit{stick together} + \text{Probability of } \textit{dissociation}
\]

Dispersed particles are randomly added \(\rightarrow\) cluster growths

Inside the cluster volume \(\rightarrow\) vacancies \(\rightarrow\) fractal structure
Assembly in colloidal systems

- **Reaction-limited aggregation**
  - Fairly dense

- **Diffusion-limited aggregation**
  - High fraction of free space
  - *Open cluster structure* → particle coming from outside cannot fill any interior gap

- **Cluster-cluster aggregation** → small clusters → large clusters
Assembly in colloidal systems

Example: flocculation process of water purification

Small impurities → not filtered

Addition of flocculants (charged particles)

Particles + impurities → clusters → can be filtered
Assembly of big hydrophobic particles in $H_2O$

Big hydrophobic particles → cluster in $H_2O$

$\Delta G = f(R)$

- $n$ particles solvated separately (one at a time) → overall solvation $\Delta G$ → linear

Linear $\rightarrow f(\text{excluded volume of hydrophobic particles})$

$\Delta G \approx n\Delta G_i$

- $n$ particles → hydrophobic unit

cluster in $H_2O \rightarrow \Delta G \sim \text{surface area}$
Assembly of big hydrophobic particles in $H_2O$

$\Delta G$ for assembling → cluster in $H_2O$

- $n$ particles high → big cluster

$\Delta G < n\Delta G_i$ → favour cluster formation

$\Delta G_{assembly} \sim \Delta G_{particles} - \Delta G_{cluster}$

Reality

$\Delta G \approx 4\pi R^2 \gamma + \frac{4}{3} \pi R^3 \rho \approx 4\pi R^2 \gamma$
Assembly of amphiphilic particles → surfactants

Strong interactions between *hydrophilic molecules* $\leftrightarrow H_2O$

- Limit fluctuations

- Partially stabilized by *hydrophobic* forces

**Amphiphilic molecules**

- Small molecular weight: *surfactants, lipids*
- Big molecular weight: *polymer, proteins*
Assembly of amphiphilic particles $\rightarrow$ surfactants

Self assembly process

\[ f(\text{concentration amphiphilic molec}) \]

\textbf{supramolecular} assemblies

different \textbf{shapes}
Surfactants

**Surfactant** - molecule that localize at the **interface** between:
- 2 *immiscible* fluids
- liquid-air surface

![Chemical structures of various surfactants](image)
Forces in colloidal systems and self-assembly

- Why and which forces are important?
- Electrostatic interactions
- van der Waals forces
- Hydrophobic effect
- Depletion forces
- Steric forces
- Self-assembly process
- Introduction in surfactants, self-assembly of surfactants