Short-ranged attractions in real solutions of colloids and reverse micelles

Colloids and micelles are *mesoscopic* particles of dimensions 10-10^4 Å

Real solutions are fluid *mixtures* made of *solute* species (big particles) and *solvent* species (small particles)

In an *effective fluid* approach we determine a *mean or effective* potential $W_{ij}(r)$ for the interaction between the solute particles

We will discuss,

- dispersion forces

- depletion forces

- polymer-coated colloids

- hydrophobic interactions

- reverse micelles in water in oil (W/O) microemulsions

I. Direct interactions

a. Dispersion forces

The interaction between two *neutral molecules* far apart is dominated by *dipolar forces*.

The simplest model potential, suggested by the London forces, corresponds to a mixture of *hard spheres* (HS) of diameters $\{\sigma_i\}$ with dispersion attractions (polarizable hard spheres),

$$
\phi_{ij}^{PHS}(r) = \begin{cases} +\infty & r < \sigma_{ij} \\ -A_{ij}\sigma_i^3\sigma_j^3/r^6 & r \geq \sigma_{ij} \end{cases}
$$

with $A_{ij} > 0$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

Since the ionization energies of most molecules are of the same order of magnitude, the interaction between unlike molecules is related to the interaction between like molecules as

$$
A_{ij} = \sqrt{A_{ii}A_{jj}},
$$

known as the *Berthelot mixing rule*.

b. Hamaker's macroscopic approximation

Mesoscopic particles are formed by a very large number of molecules ($\sim 10^{10}$ in particles of μm dimensions).

Hamaker proposed to estimate the energy of interaction of two macroscopic bodies i and j, of densities ρ_i and ρ_j, occupying volumes V_i and V_j, in vacuum, as

$$\phi_{ij}^H(r; \sigma_i, \sigma_j) = \sum_{\substack{m \in \text{molecule } i \\ n \in \text{molecule } j}} \phi_{m,n}^{disp}$$

$$\approx \rho_i \rho_j \int_{V_i} d\mathbf{r} \int_{V_j} d\mathbf{r}' \, \phi_{ij}^{disp}(|\mathbf{r} - \mathbf{r}'|) \ ,$$

with $\phi^{disp}(r) = -C_{ij}/r^6$.

The following scale invariance holds,

$$\phi_{ij}^H(\gamma r; \gamma \sigma_i, \gamma \sigma_j) = \phi_{ij}^H(r; \sigma_i, \sigma_j) \ .$$

II. Solvent-mediated indirect interactions

Indirect solute-solute interactions depend on both the solute-solvent and solvent-solvent interactions.

a. Excluded volume depletion forces in colloidal mixtures

The potential of average force $W_{ij}(r)$ acting between particles i and j is related to the radial distribution function as

$$g_{ij}(r) = e^{-\beta W_{ij}(r)} \ ,$$

with

$$W_{ij}(r) = \phi_{ij}^{direct}(r) + \phi_{ij}^{indirect}(r) \ ,$$

where the *direct* pair potential is the one related to the Mayer function between a particle of species i and one of species j,

$$f_{ij}(r) = e^{-\beta \phi_{ij}^{direct}(r)} - 1 \ .$$

Consider then a mixture of solute HS diluted in a sea of small *depletant* spheres of species 0. Expanding $W_{ij}(r)$ in a power series of the density ρ_0 one finds,

$$W_{ij}(r) = \phi_{ij}^{direct} + \rho_0 \omega_{ij}^{(1)}(r) + O(\rho_0^2) \ ,$$

with

$$-\beta \omega_{ij}^{(1)}(r) = \int d\mathbf{r}' f_{i0}(r') f_{0j}(|\mathbf{r} - \mathbf{r}'|) = V^{overlap}(\sigma_{i0}, \sigma_{j0}, r) \ ,$$

the volume of the region of space delimited by the overlap of two spheres of radii σ_{i0} and σ_{j0} a distance r apart.

b. Polymer-coated colloids or hairy spheres

If the intermolecular attractive forces are strong enough, a colloidal suspension phase-separates or even flocculates or gels (see paint or yogurt)

Stability against flocculation may be ensured by *steric stabilization* or charge stabilization.

In steric stabilization the colloidal molecules are coated with polymer brushes (the "hair") whose length is much smaller than the colloidal diameter.

Changing the solvent or temperature may turn the effective interaction from attractive to repulsive:

- in a *good* solvent for the brushes, the solutes behave as HS independently of temperature,

- in a *poor* solvent, there exists a temperature Θ (the Flory's "theta temperature") characteristic of the given polymer-solvent pair, such that:
  - the solute are HS for $T > \Theta$,
  - an attraction occurs for $T < \Theta$.

In a poor solvent the polymer-solvent attractions are weaker than the polymer-polymer ones. A "Θ-solvent" is a poor solvent at $T = \Theta$.

Duits proposed the following interaction potential between two hairy hard spheres (HHS) i and j,

$$\beta\phi_{ij}^{HHS}(r) = \begin{cases} +\infty & r < \sigma_{ij} \\ -F(T)cV^{overlap}(R_i + l, R_j + l, r) & r > \sigma_{ij} \end{cases}$$

with,

$$F(T) = \begin{cases} \Theta/T - 1 & T < \Theta \\ 0 & T > \Theta \end{cases}$$

the Flory's temperature function, $R_i = \sigma_i/2$, l the thickness of the polymeric layer, and c a constant.

c. Solvation forces and Gurney potential

An indirect interaction between solute particles may arise from solvation.

Gurney and Frank introduced the concept of *cosphere* or *solvation layer*

cosphere made of
solvent with different
properties than the
bulk solvent

solute
particle

ω
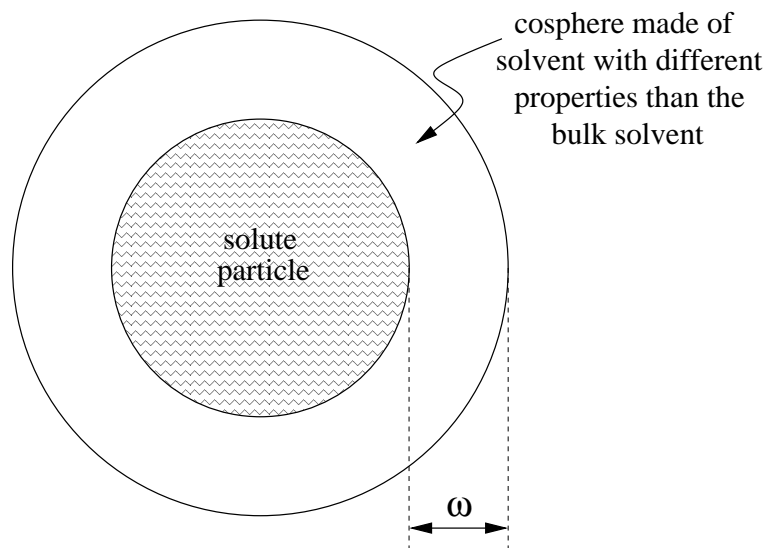
Friedman proposed that the free energy change accompanying the cosphere overlapping of the two HS solute particles i and j gives rise to the Gurney potential,

$$\beta\phi_{ij}^{Gurney}(r) = A_{ij}(T,P)\frac{V^{overlap}(R_i + \omega, R_j + \omega, r)}{v_0} \ ,$$

where A_{ij} is the molar free energy of transfer of solvent from the overlapping region of the cospheres to the bulk (which may depend on temperature and pressure) and v_0 is the molar volume of the bulk solvent.

d. Hydrophobic interaction

Solvation forces are well understood when the solvent is water, whose molecules have the known tendency to associate forming hydrogen bonds.

Polar (i.e. carrying a permanent electric dipole moment) molecules or groups, of a solute, feel strong attraction towards water molecules and thus are said *hydrophilic*.

Non-polar molecules or groups dislike water and are called *hydrophobic*.

The *hydrophobic effect* means that non-polar particles have an extremely weak solubility in water (increasing with temperature) and manifest itself through:

- hydrophobic *attraction* between non polar molecules

- hydrophobic *bonding*

The water molecules close to the foreign solute non-polar particle re-orient themselves so as to create as many hydrogen bonds as possible. The result is the formation of an *hydration-layer*, around the solute, with more rigid hydrogen bonds than in the bulk.

The hydrophobic interaction arises when overlap of hydration-layers occurs and becomes increasingly negative as the distance between the two solute particles decreases.

e. Reverse micelles in water-in-oil microemulsions

Molecules having both hydrophilic and hydrophobic parts are said to be *amphiphilic*.

head group
(ionizable or polar)

tail group
(non–polar)   surfactant
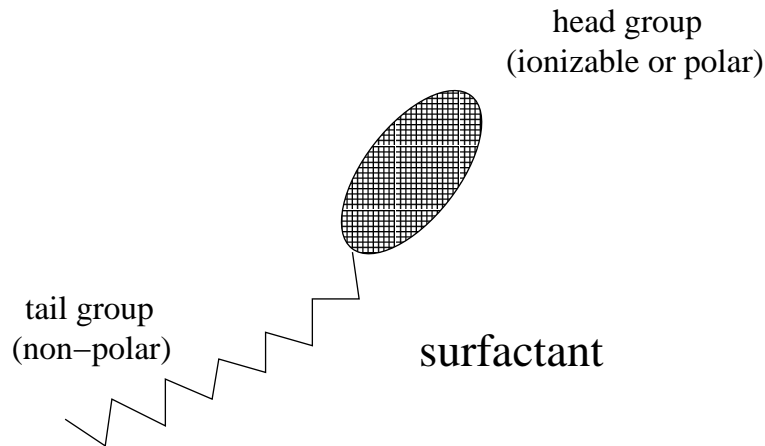
When immersed in water the head group may become negatively or positively charged or neutral. Accordingly the *surfactant* are classified as *anionic*, *cationic*, or *non-ionic*.

When added to a water in oil (an organic liquid immiscible with water) *microemulsion* (a two-phase suspension of finely divided droplets) a surfactant forms monolayers at every water-oil interface.

(reverse) micelle

continuum of oil

penetrable surfactant layer

water

$l=l(T)$
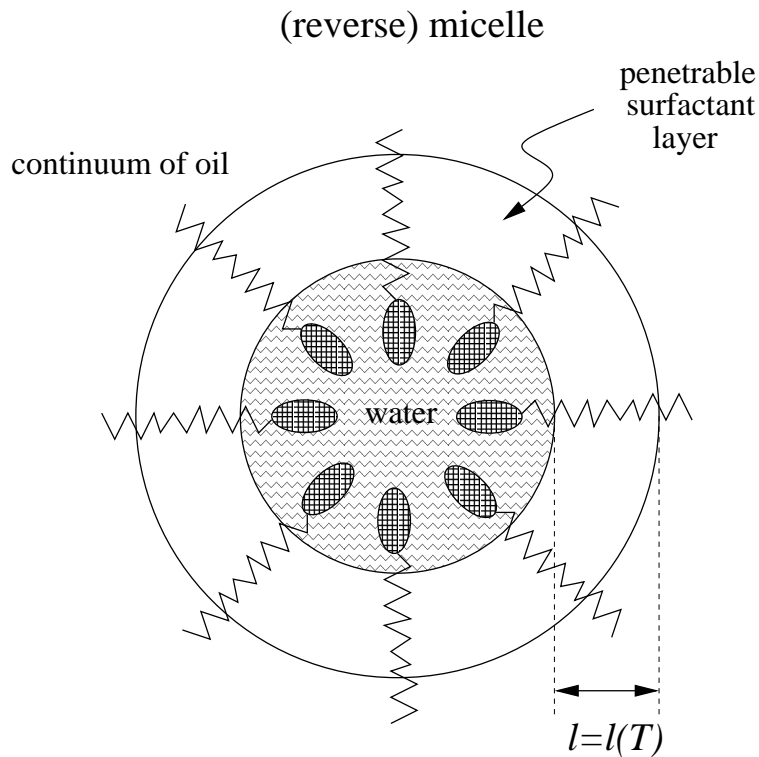
The short-ranged attraction between reverse micelles seems to be mainly determined by the overlapping of the penetrable surfactant-layers which induces oil removal. The molar volume of oil inside the surfactant layer is expected to be larger than that in the bulk.

The simplest model for the interaction potential between micelle i and j would then be

$$\beta\phi_{ij}(r) = \begin{cases} +\infty & r < \sigma_{ij} \\ -\Delta\rho V^{overlap}(R_i + l, R_j + l, r) & r \geq \sigma_{ij} \end{cases}$$

where $\Delta\rho$ is an adjustable parameter which depends only on the oil.