4_Forces_and_Interactions

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0.1 Forces and Interactions in Soft Matter

While we have discussed in the previous sections the thermodynamics of systems and the kinetics of phase transitions, we have made as few as possible assumptions on the interactions between the, i.e., liquid components of a mixture to highlight the importance of entropic and other effects. Now, we would like to have a close look at the possible types of interactions and their order of magnitude in soft matter systems. We may classify the interactions in the following way: - covalent interaction (chemical binding) - electrostatic (Coulomb) - dipolar (vdW) - dispersion (vdW) - fluctuation, depletion (entropic)

These interactions deliver the forces that hold soft matter together, even though the phases are characterized by *density*, *free energy* and *entropy*, but not by the forces.

Pairwise interaction energy – Before we go into further details, we may have a look at some general behavior again. Let us assume that the interaction energy between two atoms/molecules is given by

$$w(r) = -\frac{C}{r^n} \tag{1}$$

with C being an interaction specific constant, then the force between the two species at a distance r is given by

$$F(r) = -\frac{\mathrm{d}w(r)}{\mathrm{d}r} = -\frac{nC}{r^{n+1}}. \tag{2}$$

For a material, which has a number density and thus the total number $\rho 4\pi r^2 dr$ molecules in a shell between $r, r + dr$ around a molecule, we obtain the following total interaction energy per molecule (the standard chemical potential)

$$\mu^0 = \int_\sigma^L w(r)\rho 4\pi r^2 \mathrm{d}r = \frac{-4\pi C\rho}{(n-3)\sigma^{n-3}}\left[1 - \left(\frac{\sigma}{L}\right)^{n-3}\right]. \tag{3}$$

The total interaction energy, and thus also the property of the system will thus depend on the size L of the system, except we assume $n > 3$ and$ L>> $, where σ is the size of the molecule. This states nothing else, that long range interactions may yield system dependent properties or bulk properties do not depend on the volume size only if objects become small. Obviously Coulomb interactions, or dipolar interactions may not satisfy the above assumptions. We can find out some general rule about the cohesive energy of molecule with its neighbors in a liquid, when comparing

the molar gas and molar liquid volumes. A typical gas molar volume is 22.400 cm^3/mol, while this is only 20 cm^3/mol for a liquid. If liquid and gas coexist at a certain temperature T,then the chemical potential of gas and liquid have to be the same, i.e.,

$$\mu_{\text{gas}}^0 + k_{\text{B}}T \ln(X_{\text{gas}}) = \mu_{\text{liq}}^0 + k_{\text{B}}T \ln(X_{\text{liq}}) \tag{4}$$

or

$$\mu_{\text{gas}}^0 - \mu_{\text{liq}}^0 \approx -\mu_{\text{liq}}^0 = k_{\text{B}}T \ln\left(\frac{X_{\text{liq}}}{X_{\text{gas}}}\right) \approx 7k_{\text{B}}T \tag{5}$$

assuming that there is essentially no cohesive energy in the gas phase. At the vaporization temperature, the energy required to release one mole of molecules from its cohesion with its neighboring molecules to the gas phase is thus

$$U_{\text{vap}} = -N_A\mu_{\text{liq}}^0 = 7N_A k_{\text{B}}T. \tag{6}$$

This allows us to estimate the latent heat of vaporization

$$\Delta H_{\text{vap}} = U_{\text{vap}} + pV \approx 7RT_{\text{B}} + RT_{\text{B}} \tag{7}$$

According to that, the ratio of latent heat of vaporization and boiling temperature is $\frac{\Delta H_{\text{vap}}}{T_B} \approx 8R \approx 80\frac{\text{J}}{\text{K mol}}$ per mole, or $9k_{\text{B}}T$ per molecule. If we assume that each molecule has on average 6 neighbors in a liquid, than we obtain a value of $\frac{3}{2}k_{\text{B}}T$ as energy molecular pair. The about rough rule is called **Troutons rule** and gives only a very rough estimate of the cohesive energy, as it completely neglects the details of the interactions. However, it demonstrates why the thermal energy is important in soft matter.

0.1.1 Coulomb forces, charge–charge interactions

The simplest form but at the same time, also one of the most important types of interaction is the electrostatic interaction, e.g., of simple charges. This type of interaction is important not only due to its relevance in biological systems, but the electrostatic interaction is in principle the only one delivering a long range repulsive forces.

Charge–charge interactions Charge–charge interactions are mediated by the electric fields. Assume that we have a charge Q_1 that creates an electric field

$$E_1 = \frac{Q_1}{4\pi\epsilon_0\epsilon r^2}. \tag{8}$$

We neglect the vectorial character of the electric field to avoid further complications. The electric field is creating a force on a second charge Q_2

$$F(r) = Q_2 E_1 = \frac{Q_1 Q_2}{4\pi\epsilon_0\epsilon r^2}. \tag{9}$$

In this charge assembly at a distance r is an energy stored, which is the potential energy of assembling these two charges from infinity. The free energy of the two charges thus reads

$$w(r) = \int_{\infty}^{r} -F(r)\mathrm{d}r = -\int_{\infty}^{r} \frac{Q_1 Q_2}{4\pi\epsilon_0 \epsilon r^2}\mathrm{d}r = \frac{Q_1 Q_2}{4\pi\epsilon_0 \epsilon r}. \tag{10}$$

If we evaluate this energy, for example, for a sodium and a chlorine ion at a distance of $r = 0.276\,\mathrm{nm}$ we find a free energy of interaction of $w = -8.4 \cdot 10^{-19}\,\mathrm{J}$, which corresponds to about $200\,k_{\mathrm{B}}T$ at 300 K temperature. This is on the same order of magnitude than covalent interactions. It requires about 3 nN to break this bond and the long range character of electrostatics becomes clear when evaluating the distance at which this interaction becomes comparable to $k_{\mathrm{B}}T\,(r = 56\,\mathrm{nm})$. This is only considering a pair of ions. In a NaCl crystal, multiple neighbors contribute to the interaction energy of one sodium ion with its surrounding. One sodium ion has 6 Cl– neighbors at a distance of $r = 0.276\,\mathrm{nm}$, 12 Na+ neightbors at $\sqrt{2}r$, and further 8 Cl– neighbors at $\sqrt{3}r$ and so on. We have to sum up all the interaction energies for the total cohesive energy of the sodium ion in the crystal

$$\mu^0 = -\frac{e^2}{4\pi\epsilon_0 r}\left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + ...\right] = -1.748\frac{e^2}{4\pi\epsilon_0 r}. \tag{11}$$

The factor in front of the Coulomb term (the one in the square brackets) is termed Madelung constant and is known from solid state physics. It is characteristic for specific lattice types such as a simple cubic lattice in this case. Note that the cohesive energy of one sodium ion therefore is about $350\,k_{\mathrm{B}}T$ and is thus much larger than the thermal energy keeping the NaCl crystal stable. Yet it can be dissolved in water very easily.

Born energy of solvation The Born energy of solvation calculates the free energy of assembling a charge inside a dielectric medium of dielectric constant ϵ. Let us shortly reconsider the free energy

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W \tag{12}$$
$$\mathrm{d}U = T\mathrm{d}S + \mathrm{d}W \tag{13}$$
$$\mathrm{d}W = \mathrm{d}U - T\mathrm{d}S \tag{14}$$

which leads to

$$\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S = \mathrm{d}W. \tag{15}$$

Therefore, the free energy change is related to the energy to assemble a charge

$$\Delta F = \frac{\epsilon\epsilon_0}{2}\int_V E^2\mathrm{d}V. \tag{16}$$

To find the free energy we, therefore, integrate the square of the electric field over the volume (this is actually the same as adding tiny charge elements against previously assembled parts of the charge). According to that, the free energy of a charge in a medium with dielectric constant ϵ is

$$\mu^0 = \frac{z^2 e^2}{8\pi\epsilon\epsilon_0 a} \tag{17}$$

if the charge has a radius a. If we look now at the difference of assembling the charge in vacuum (with $\epsilon = 1$) and in a medium with ϵ, we find the following difference in the chemical potential (free energy)

$$\Delta\mu^0 = \frac{z^2 e^2}{8\pi\epsilon_0 a}\left(\frac{1}{\epsilon} - 1\right) = -\frac{28z^2}{a}\left(\frac{1}{\epsilon} - 1\right). \tag{18}$$

This is the Born free energy of solvation of a single ion. The molar free energy is then obtained by multiplication with the Avogadro number N_A

$$\Delta G = N_A \Delta\mu^0 = -\frac{69z^2}{a}\left(\frac{1}{\epsilon} - 1\right) \tag{19}$$

$$\Delta\mu^0 \approx \frac{e^2}{4\pi\epsilon_0\epsilon(a_+ + a_-)} \tag{20}$$

The mole fraction that is dissolved in water is then found by the Boltzmann factor

$$X_s = e^{-\frac{\Delta\mu^0}{k_B T}} \tag{21}$$

which is a measure for the solubility of the ions. Inserting the formula for the chemical potential delivers the proportionality $X_s \propto \exp(-\mathrm{const}/\epsilon)$. This dependency on the dielectric constant of the solvent is indeed observed in the experiment, even though this is only a trend and there are solvents with marked deviations. The reason for that is essentially that the theory just assumes 1) continuous changes in the interactions, despite the fact that there is a near order and 2) that additional interactions like hydrogen bonds exist.

Interactions involving polar molecules

Many molecules exhibit dipole or even higher moments due to the fact that the charges are not evenly distributed over the molecular structure. Some of the atoms exhibit a stronger tendency to accept charges than others. This is typically measured by electronegativity and provides an idea of whether atoms rather donate or accept a charge when binding to other atoms. While homo-atomic bonds therefore do not have dipole moments heteroatomic bonds do (see table).

Bond	Dipole moment
C-C	0
C-N	0.22

The dipole moment of a molecule is measured by the displacementlof two charges $\pm q$ from each other

$$\vec{u} = q\vec{l}. \tag{22}$$

Its direction is from the negative to the positive side. It creates an electric field that is given by

$$\vec{E} = \frac{3(\vec{u} \cdot \hat{r})\hat{r} - \vec{u}}{4\pi\epsilon_0\epsilon r^3}. \tag{23}$$

The dipole self-energy, i.e., the energy to create the dipole in a solvent is given by

$$\mu^0 = \frac{1}{4\pi\epsilon_0\epsilon} \left[\frac{q^2}{2a} + \frac{q^2}{2a} - \frac{q^2}{l} \right]. \tag{24}$$

F or $l = 2a$ this yields $\mu^0 = q^2/(8\pi\epsilon_0\epsilon a) = u^2/(4\pi\epsilon_0\epsilon l^3)$ and thus yields a similar dependence of the chemical potential on the dielectric function ϵ as in the case of a single charge. The result is a similar dependence of the solubility on the dielectric function.

Ion–dipole interaction

The interaction energy of a dipole with a charge can be calculated by

$$w(r) = -\frac{qQ}{4\pi\epsilon_0\epsilon} \left[\frac{1}{r - \frac{1}{2}l\cos(\theta)} - \frac{1}{r + \frac{1}{2}l\cos(\theta)} \right] = -\frac{qQ}{4\pi\epsilon_0\epsilon r^2}\cos(\theta) = -uE\cos(\theta), \tag{25}$$

where the last two equations are assuming that the distance between both objects r is much larger than the extent of the dipole l itself. From equation (**??**), we see that the interaction can be either attractive or repulsive. An angle $\theta = 0°$ results in an attractive interaction, while $\theta = 180°$ yields repulsive interaction. Using a single chargee(Na+ ion) and a dipole of $u = 1.85\,\mathrm{D}$ (water molecule) results in an interaction energy of about $39\,k_\mathrm{B}T$. Ions align and bind polar molecules like water, for example. For arbitrary polar molecules this is called solvation, while for water the term hydration is used. The strength of the hydration can effect the mobility of ions in solution as it makes them effectively charges and is of interest, for example, for the study of ion transport through ion channels, as this requires stripping the hydration shell.

Dipole–dipole interactions

The interactions of two dipoles (u_1, u_2) in the solution can be also calculated following the above scheme

$$w(r, \theta_1, \theta_2, \phi) = -\frac{u_1 u_2}{4\pi\epsilon_0\epsilon r^3} \left[2\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1\sin(\theta_2)\cos(\phi)) \right]. \tag{26}$$

Also in this case the dipole–dipole interaction yields an orientation dependence with either repulsive or attractive interactions. The figure below shows the distance dependence for two configurations where the dipoles are arranged parallel but either along the connecting line or perpendicular to it.

Rotating dipoles, angle averaged Potential

0.1.2 van der Waals interactions

0.1.3 Depletion Forces

Depletion force between two plates

Depletion force between two spheres – To describe the depletion interaction between two spheres (radius R) in a solution of smaller spheres (radius $\sigma/2$), we may use the same approach of assuming an isotropic osmotic pressure of the smaller spheres. The smaller spheres can actually not approach a spherical shell of thickness $\sigma/2$ around the larger spheres or a total volume of $4\pi(R+\sigma/2)^3/3$. The pressure on the large spheres has no consequences except in the case where the two spheres approach closer than $r \leq 2(R+\sigma/2) = 2R_d$. In this case the two excluded volumes around each sphere overlap to a lens-like volume. Due to this overall, the forces which create the pressure on the spherical surface up to an angle θ_0 are unbalanced from the other side of the surface (see image) and result in an attractive interaction.
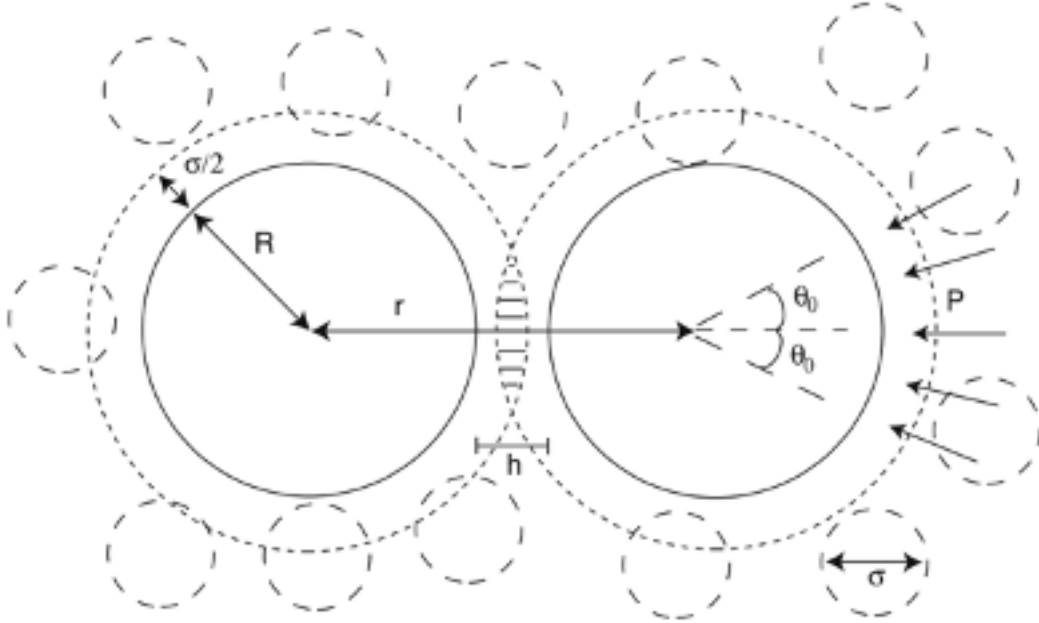
The total force is then calculated from the osmotic pressure times the surface area of the spherical cap by just taking into account the force components along the connecting line. This the read

$$F(r) = -2nk_\mathrm{B}T\pi(R+\sigma/2)^2 \int\limits_0^{\theta_0} \sin(\theta)\cos(\theta)\mathrm{d}\theta \tag{27}$$

resulting in

$$F(r) = -nk_\mathrm{B}T\pi(R_d)^2 \left[1 + \left(\frac{r}{2R_d}\right)^2\right] \tag{28}$$

which is valid if the distance between the centers of the large spheres is $r < 2(R + \sigma/2)$. For $r \geq 2(R + \sigma/2)$ there is no depletion of the smaller spheres from the region between the larger spheres and the force is zero, i.e., $F(r) = 0$.

General description – A more general description of the depletion interaction may be obtained based on our introduction into statistical physics at the beginning of the course. There we stated that the probability of finding a system in a stet of energy E is

$$p(E) = \frac{e^{-\beta E}}{Z}, \tag{29}$$

where $\beta = 1/k_{\mathrm{B}}T$ and the partition function Z is

$$Z = \sum_i e^{-\beta E_i} \tag{30}$$

for a system with a discrete number of states numbered by the indexi.For a single particle with a continuous number of energies the energy may look like

$$E = \frac{p^2}{2m} + U(q), \tag{31}$$

where q is some general coordinate. The classical partition function for a system of N particles is then

$$Z = \frac{1}{N! h^{3N}} \int \mathrm{d}^3 p^N \int \mathrm{d}^3 q^N \exp\left(-\beta \left[\sum_i \frac{p^2}{2m} + U(q^N)\right]\right), \tag{32}$$

where we use the notation p^N and q^N to denote the whole set of variables. The prefactor is appropriate for indistinguishable particles and the phase space normalization factor h (Planck's constant) for every pair of p and q. Since there is no issue of the non-commutation of positions and momenta we can perform the momentum integrals exactly, yielding

$$Z = \frac{1}{N!} \frac{1}{\Lambda^{3N}} \int \mathrm{d}^3 q^N \exp(-\beta U(q^N)), \tag{33}$$

where the thermal de Broglie wavelength Λ is

$$\Lambda = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}}. \tag{34}$$

In the case of two interacting large spheres in a solution of small spheres with all spheres being hard spheres, the integration over the exponential function yields

$$Z = \frac{V_A^N}{N! \Lambda^{3N}} \tag{35}$$

with V_A being the volume available to the small spheres, i.e., $V_A = V - V_E'$ for $r < D + d$ and $V_A = V - V_E$ for $r > D + d$ with $V_E = \pi(D+d)^3/3$ and $V_E' = V_E - (2\pi l^2)/3[3(D+d)/2 - l]$ and $l = (D+d)/2 - r/2$. The calculation then yields the free energy

$$G = -k_\mathrm{B}T \ln(Z) = -k_\mathrm{B}T \ln\left(\frac{V_A^N}{N!\Lambda^{3N}}\right).$$ (36)

Using Stirling's formula again this can be turned into

$$G = G_\mathrm{ideal} - Nk_\mathrm{B} \ln\left(\frac{V_A}{V}\right).$$ (37)

The ideal contribution to the free energy is constant with the separation of the large sphere, so it does not contribute to the depletion force. It reads

$$G_\mathrm{ideal} = -Nk_\mathrm{B}T\left(1 - \ln\left(\frac{N\Lambda^3}{V}\right)\right).$$ (38)

The distance-dependent part still contains the logarithm which we can approximate by

$$\ln\left(\frac{V_A}{V}\right) \approx -\frac{V_E}{V} + \frac{\pi}{6V}(D+d-r)^2(D+d+r/2)$$ (39)

for the case of the overlapping excluded volumes. This gives then finally a force

$$F = -\frac{N}{4V}k_\mathrm{B}T\pi(D+d-r)(D+d+r)$$ (40)

for $r < d + D$. For all other distances of the two centers of the spheres, the depletion force is zero.