Physics of Soft Colloidal Matter

–Interaction potentials and colloidal stability–

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Contents

1 Interactions

1.1 Molecular Interactions

As the interaction energy between large bodies like colloidal particles is composed of the interaction between their atomic or molecular constituents we will first briefly discuss interactions between molecular

- a charge and a permanent dipole
- permanent dipoles
- induced dipoles
- fluctuating dipoles

1.1.1 Interaction between a charge and a dipole

Fixed Orientation

According to Figure 1.1, a point particle with charge $Q = \mathcal{Z}e$ ($\mathcal{Z}$ is the number of elementary charges e)at position A shall interact with a permanent dipole at distance

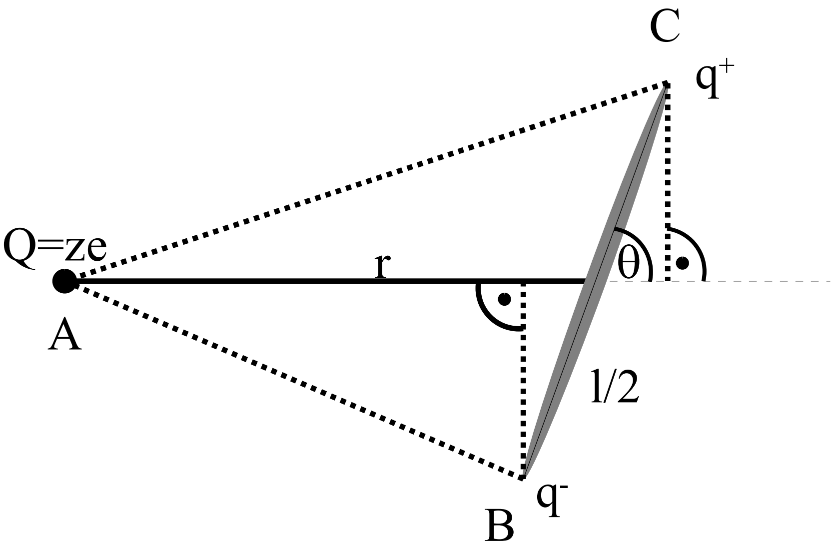

Figure 1.1: For the calculation of the interaction between a point charge and a permanent dipole

r with the length l and two partial charges of equal magnitude but opposite sign. The partial charges q^- and q^+ are located at the positions B and C respectively. The total interaction is the sum of the Coulombic interactions between the point charge Q and the partial charges

$$u(r) = \frac{Qq}{4\pi\varepsilon_0}\left|\frac{1}{\overline{AB}} - \frac{1}{\overline{AC}}\right| \tag{1.1}$$

The distances are given by

$$\begin{aligned} \overline{AB} &= \left[(r - l/2\cos\theta)^2 + (l/2\sin\theta)^2\right]^{1/2} \\ \overline{AC} &= \left[(r + l/2\cos\theta)^2 + (l/2\sin\theta)^2\right]^{1/2}, \end{aligned} \tag{1.2}$$

which reduces to

$$\overline{AB} \approx r - l/2\cos\theta \tag{1.3}$$

$$\overline{AC} \approx r + l/2 \cos\theta$$

for large r/l.

With this the interaction energy is

$$u(r) = \frac{Qq}{4\pi\varepsilon_0} \left| \frac{1}{r - l/2\cos\theta} - \frac{1}{r + l/2\cos\theta} \right|, \tag{1.4}$$

which can be rewritten as

$$u(r) = \frac{Qq}{4\pi\varepsilon_0} \left| \frac{l\cos\theta}{r^2 - (l/2\cos\theta)^2} \right| \tag{1.5}$$

and reduces to

$$u(r) = Q \left| \frac{m\cos\theta}{4\pi\varepsilon_0 r^2} \right| \tag{1.6}$$

for small $l/2$. Here m is the dipole moment $m = lq$.

According to eq. 1.6 the interaction is zero if the dipole is oriented perpendicular to r. For positive z it will be repulsive (i.e. $u(r) > 0$) in the range of $-\pi/2 < \theta < \pi/2$, attractive otherwise and vice versa for negative z. A measure for the interaction range can be estimated from the distance at which it will decay to one thermal unit $k_BT = 4.14 \cdot 10^{-21}$ J. For a point charge with $\mathcal{Z} = 1$ and a dipole with the moment $m = 3.33 \cdot 10^{-30}$ Cm (i.e. 1 Debye unit) this distance is $r = 1.08$ nm.

Freely Rotating Dipole

If the interaction potential is smaller than k_BT we may assume that the dipole is able to rotate more or less freely. The potential averaged over all orientations is non–zero since the orientations with lower potentials will have a higher weight (given by a Boltzmann–factor) than orientations with high potential. The averaged free energy $w(r)$ of an orientation dependent potential $u(\Omega, r)$ is in general given by the so–called potential distribution theorem (Landau, Lifschitz, 1980, Chap. III)

$$\exp\left\{-\frac{w(r)}{k_BT}\right\} = \left\langle \exp\left\{-\frac{u(\Omega,r)}{k_BT}\right\}\right\rangle = \frac{\int d\Omega \exp\left\{-\frac{u(\Omega,r)}{k_BT}\right\}}{\int d\Omega} \tag{1.7}$$

where the integration is over all orientations with $d\Omega = d\phi \sin\theta d\theta$ and accordingly the normalization is

$$\int d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta = 4\pi. \tag{1.8}$$

At sufficiently high separation distances where $u(r,\Omega) < k_BT$ the exponentials can be approximated by a Taylor expansion

$$\exp\left\{-\frac{w(r)}{k_BT}\right\} \approx 1 - \frac{w(r)}{k_BT} + ... = \left\langle 1 - \frac{u(r,\Omega)}{k_BT} + ...\right\rangle, \tag{1.9}$$

which leads to

$$w(r) = \left\langle u(r,\Omega) - \frac{u(r,\Omega)^2}{2k_BT}...\right\rangle. \tag{1.10}$$

For the interaction of a point charge with a freely rotating dipole we get therefore the approximation

$$\begin{aligned} w(r) &\approx -\frac{Qm}{4\pi\varepsilon_0 r^2}\langle\cos(\theta)\rangle - \left(\frac{Qm}{4\pi\varepsilon_0 r^2}\right)^2 \frac{1}{2k_BT}\langle\cos^2(\theta)\rangle \\ &= \left(\frac{Qm}{4\pi\varepsilon_0 r^2}\right)^2 \frac{1}{6k_BT} \end{aligned} \tag{1.11}$$

where we made use of the spatial average

$$\langle\cos^2(\theta)\rangle = \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \cos^2(\theta) = 1/3 \tag{1.12}$$

(Tabulated integrals: $\int dx \sin(ax)\cos^m(ax) = -\cos^{m+1}(ax)/(ma+a)$)

Figure 1.2: For the calculation of the interaction between two permanent dipoles. Note that the angles are defined differently from Fig.1.1

Note that according to eq. 1.11 the interaction between a point charge and a dipole is negative, i. e. attractive, it is temperature dependent and it decays with r^{-4}.

1.1.2 Dipole–Dipole Interactions

The interaction energy between two permanent dipoles, which are oriented as sketched in Figure 1.2, can be calculated in a similar (though more tedious) way. The result is

$$u(r, \theta_1, \theta_2, \phi) = -\frac{m_1 m_2}{4\pi\varepsilon_0 r^3}\left[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi\right] \tag{1.13}$$

A brief look to eq. 1.13 shows that the interaction energy at constant r is the smallest when the dipoles are oriented anti–parallel. In this case the energy is exactly half of the value for the in–line orientation, i. e.

$$u(r, 0, 0, 0) = 2u(r, 90, 90, 180) \tag{1.14}$$

If the dipoles are allowed to rotate freely in space the energy weighted average of all possible orientations has to be calculated in a simmilar procedure as in the preceding section. Eventually the spatially averaged free energy is obtained as

$$w_{orient}(r) = -\frac{m_1^2 m_2^2}{3k_B T(4\pi\varepsilon_0)^2}\frac{1}{r^6}. \tag{1.15}$$

The superscript $_{orient}$ refers to the fact that this is the energy a pair of dipoles gains by orienting with respect to each other, it will be called orientation interaction furthermore. Note that the interaction is attractive and decays extremely fast in this case with r^{-6}, and that it is inversely proportional to temperature.

1.1.3 Induced Dipolar Interactions

Additionally to their direct interaction, which is described by equation 1.15 permanent dipoles will induce additional dipole moments in other molecules if those are polarisable. This causes a further contribution to the interaction energy, which is proportional to the permanent moments squared of the interacting molecules, like the orientation interaction. Further the induced dipolar interaction is linearly proportional to the respective polarizabilities α_j. The final expression for the induced dipolar interaction between two different molecules is given by

$$w_{ind}(r) = -\frac{m_1^2\alpha_2 + m_2^2\alpha_1}{(4\pi\varepsilon_0)^2}\frac{1}{r^6}. \tag{1.16}$$

Note that the induced dipolar interaction decays with $1/r^6$ like the orientation interaction. For a comprehensive derivation of eq. 1.16 the reader is referred to the book by

Israelachvily.

1.1.4 Dispersion Interactions

The types of interaction described so far are basically electrostatic interactions, which require that the particle taking part carry charges or dipole moments. There is however a third type, which contributes to the interaction between all atoms and molecules even if they are completely non–polar like noble gas atoms: the so–called dispersion energy. This type of interaction has been first treated by London in 1937. They are of quantum mechanical origin and a rigorous treatment would require thorough knowledge of quantum electrodynamics. For our purposes an intuitive description based the on classical model of a Bohr atom will be sufficient. A Bohr atom consists of a positively charged nucleus and an electron travelling around it on an orbit with fixed radius R_B. In the classical picture the electron and the nucleus form a dipole, the moment of which fluctuates depending on the instantaneous position of the electron with respect to the core. Thus, two nearby Bohr atoms will interact, like induced dipoles, via their fluctuating moments. The instantaneous dipole moment of either atom is $m_j = eR_B$ and the polarizabilties are $\alpha_j = 4\pi\varepsilon_0 R_B^3$, thus

$$w_{disp}(r) = -\frac{R_B^2 e^2 4\pi\varepsilon_0 R_B^3}{(4\pi\varepsilon_0)^2 r^6} \tag{1.17}$$

The Bohr radius, R_B is the radius at which the Coulombic force between core and electron is balanced by the centrifugal force which the electron experiences.

$$\frac{mv^2}{R_B} = \frac{e^2}{4\pi\varepsilon_0 R_B^2} \tag{1.18}$$

Here v is the tangential velocity of the electron and m is its mass. The force balance may be rewritten as the balance between twice the kinetic and the Coulombic energy of the electron

$$mv^2 = \frac{e^2}{4\pi\varepsilon_0 R_B} = -E_C, \tag{1.19}$$

which allows us to relate R_B to the ionization energy of the Bohr atom, $I = E_{kin} + E_C = E_C/2$.

$$R_B = \frac{e^2}{8\pi\varepsilon_0 I} \tag{1.20}$$

I is the total energy the system gains by the approach of electron and nucleus from infinite separation distance to R_B. With eq. 1.20 the expression for the interaction energy simplifies to

$$w_{disp}(r) = -\frac{4\alpha^2 I}{(4\pi\varepsilon_0)^2 r^6}. \tag{1.21}$$

Apart from a factor this is equal to the expression London derived on the basis of quantum mechanical perturbation calculations. For two different atoms London's expression is

$$w_{disp}(r) = -\frac{3}{2}\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2 r^6}\frac{I_1 I_2}{I_1 + I_2} \tag{1.22}$$

which simplifies for two identical atoms to

$$w_{disp}(r) = -\frac{3}{4}\frac{\alpha^2 I}{(4\pi\varepsilon_0)^2 r^6} \tag{1.23}$$

It is important to note that dispersion energies scale with $1/r^6$ like orientation interactions and induced dipolar interactions.

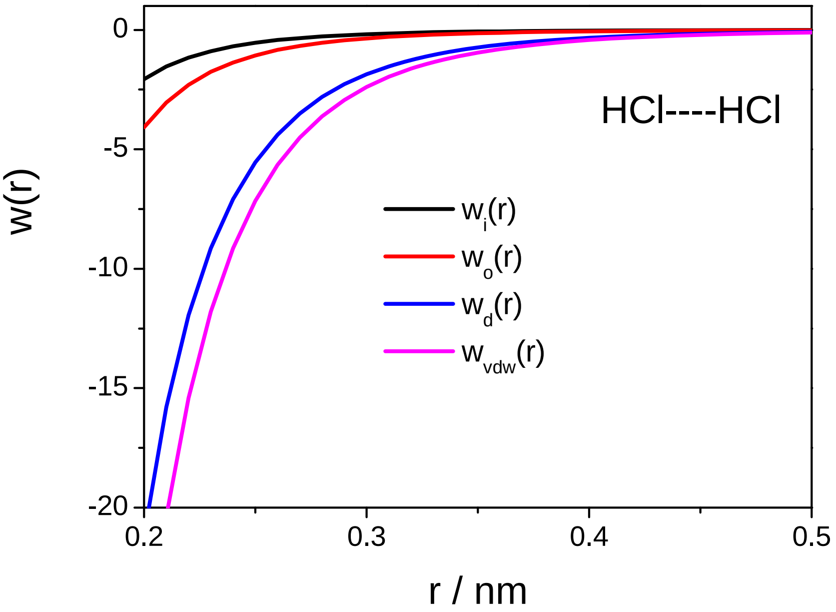

Figure 1.3: Distance profiles for the orientation contribution w_o, the contribution of polarizability w_i and the dispersion contribution w_d to van der Waals interactions w_{vdW} between two HCl–molecules.

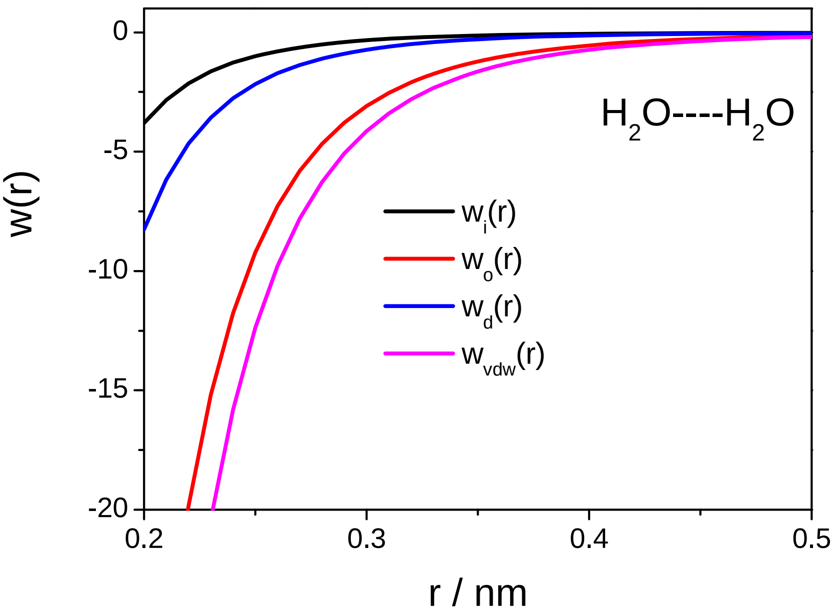

Figure 1.4: Distance profiles for the orientation contribution w_o, the contribution of polarizability w_i and the dispersion contribution w_d to van der Waals interactions w_{vdW} between two H_2O–molecules.

Table 1.1: Numerical values for the orientation contribution C_{orient}, the contribution of poarizability C_{ind} and the dispersion contribution C_{disp} to van der Waals interactions of like molecules.

	$\alpha/(4\pi\varepsilon_0)$	m	I	C_{orient}	C_{ind}	C_{disp}	C_{vdW}	C_{disp}/C_{vdW}
	10^{-30} m	Cm	10^{-18} J	10^{-79} Jm^6				
HCl	2.36	3.6	1.35	11	6	106	123	0.86
CH_3Cl	4.56	6.24	1.2	101	32	282	415	0.68
NH_3	2.26	4.9	1.08	38	10	63	111	0.57
H_2O	1.48	6.17	1.34	96	10	33	139	0.24

1.1.5 Van der Waals Interactions

From the preceding sections 1.1.2 through 1.1.4 we saw that there are three types of interaction contributing to the total interaction energy between two atoms or molecules, which all scale with $1/r^6$. The sum of these contributions is called the van der Waals interaction energy

$$w_{vdW}(r) = -\frac{1}{r^6}\left(C_{orient} + C_{ind} + C_{disp}\right) \tag{1.24}$$

where the parameters C_{orient}, C_{ind} and C_{disp} are defined by eqs. 1.15,1.16 and 1.22 respectively. Numerical values for these parameters are listed in Table 1.1, which show a maybe unexpected general trend.

$$C_{disp} \gg C_{orient} > C_{ind} \tag{1.25}$$

In most cases the dispersion forces are the dominating contribution, as is displayed in the distance profile of the van der Waals interaction shown in Fig. 1.3 for hydrogen chloride. Only in cases where the permanent molecular dipoles are very large and the polarizability is very low, like in the case of water, the contribution of the dispersion forces is smaller than fifty percent. In these cases the orientational contribution will be the largest one, as shown for the case of water molecule in Fig. **??**.

1.2 Van der Waals Interaction Between Colloidal Bodies

1.2.1 Interaction between a single molecule and a wall

In the preceding sections we discussed the attractive interactions between atomic and molecular constituents of colloidal particles. The forces and energies acting between colloidal particles are of the same nature and in a first approach to calculate the interaction between colloidal particles we assume simple pair wise additivity of the molecular interaction potentials. First we will calculate the potential between a single atom or molecule with a solid wall consisting of the same kind of atoms or molecules. As sketched in Figure 1.5 $r = \sqrt{x^2 + z^2}$ is the distance between any molecule in the wall and an outside molecule which has the shortest distance D from the wall. To calculate the interaction energy between the outside molecule and the entire wall, $W_{MW}(D)$ we have to sum over all N molecule–molecule interactions, which is

$$W_{MW}(D) = -\sum_{j=1}^{N} \frac{C_{vdw}}{r_j^6}. \tag{1.26}$$

We replace the sum by an integral and define the number density of molecules in the wall as $\rho = N/V = dN/dV$, and consider cylindric shells of molecules with radius x, thickness dx and length dz. Then the volume element $dV = 2\pi x dx dz$ and the total interaction potential may be written as

$$W_{MW}(D) = -2\pi\rho C_{vdw} \int_D^\infty dz \int_0^\infty dx \frac{x}{(z^2 + x^2)^{6/2}}. \tag{1.27}$$

In tables one finds the general solution for the integral over dx as $\int dx \frac{x}{(a+x^2)^{m+1}} = -\frac{1}{2m(a+x^2)^m}$, which in the present case with $m = 2$ and $a = z^2$ yields

$$\begin{aligned} W_{MW}(D) &= -2\pi\rho C_{vdw} \int_D^\infty dz \frac{1}{4z^4} \\ &= -\frac{\pi\rho C}{6} \frac{1}{D^3}. \end{aligned} \tag{1.28}$$

Note that the interaction of a molecule with a macroscopic body, in this case a planar wall, decays much slower than the interaction between two molecules.

1.2.2 Interaction between two planar walls

To calculate the interaction between two planar walls at distance D, $W_{WW}(D)$, we consider the single molecule in Fig. 1.5 to be part of a slice of a second wall as sketched in Fig. 1.6 with thickness dz. We have now to integrate over the molecule–wall interactions of all molecules in the second wall, which is

$$W_{WW}(D) = \int dN \rho W_{MW}(r). \tag{1.29}$$

If this second wall was infinitely extended like the first one, it is immediately obvious that the integration would lead to an infinitely large attraction. Therefore, we have to integrate over slices with a finite extension, h, in the x–direction. In this case all molecules in the slice have a smallest distance to the first wall $r = z$, and the volume of

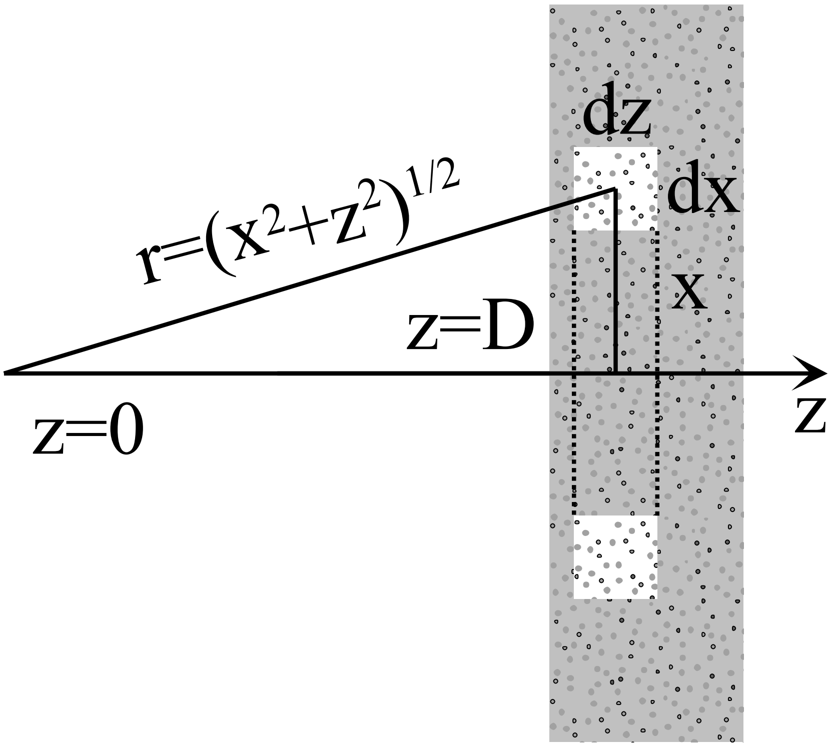

Figure 1.5: For the calculation of the interaction of a molecule with a wall.

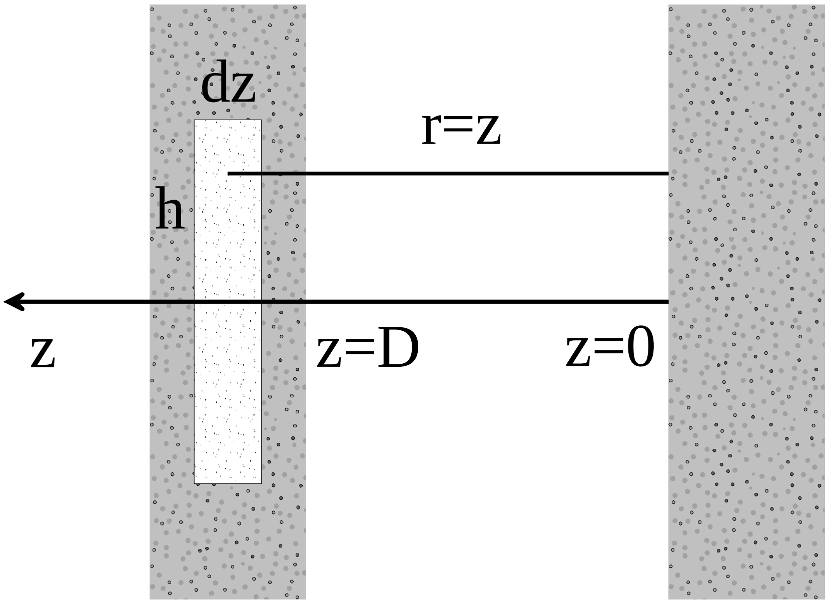

Figure 1.6: For the calculation of the interaction between two planar walls.

a slice is $dV = 2\pi x dx dz$. With this the integration writes

$$\begin{aligned} W_{WW}(D,h) &= \int_D^\infty dz \int_0^h dx 2\pi x \rho W_{MW}(z) \\ &= -\frac{\pi^2 h^2 \rho^2 C}{6} \int_D^\infty dz \frac{1}{z^3}. \end{aligned} \tag{1.30}$$

With the area of the second wall being $a = \pi h^2$ the wall–wall interaction per unit area finally is

$$W_{WW}^a(D) = \frac{W_{WW}(D,h)}{a} = -\frac{\pi \rho^2 C}{12 D^2}. \tag{1.31}$$

This would hold strictly only for a wall of unit area interacting with an infinitely extended wall. However, for $D << h$ the same expression holds for the interaction between two walls of unit area.

1.2.3 Interaction between a sphere and a wall

The interaction between a sphere and a wall can be calculated in principle along the same route as the interaction between two planar walls. The difficulty is that the height of the slice, h, is not a constant but depends on it's z–position. However, considering the blue triangle in Fig.1.7 it can be easily shown that $h^2 = (2R - z')z'$. With this the volume of a slice with thickness dz at position z' is $dV = 2\pi(2R - z')z'dz$. Since every molecule in the sphere has the smallest separation $r = D + z'$ to the wall and the Jacobian $dz/dz' = 1$ the interaction between the sphere and the (infinitely extended) wall is now

$$\begin{aligned} W_{SW}(D) &= \int dV \rho W_{MW}(D + z') \\ &= -\frac{\pi^2\rho^2 C}{6}\int_0^{2R} dz' \frac{(2R - z')z'}{(D + z')^3} \end{aligned} \tag{1.32}$$

Since the molecule–wall interaction drops off with the inverse third power of distance we may assume that only molecules at $z' << 2R$ contribute significantly to the sphere–wall interaction. In this case the numerator in the integrand of eq. 1.32 is $(2R - z')z' \approx 2Rz'$ and the integral attains the general form

$$\int dx x^m (a+bx^n)^p = \frac{1}{a(m+1)}\left[x^{m+1}(a+bx^n)^{p+1} - (m+n+1+np)b\int dx x^{m+n}(a+b^n)^p\right]. \tag{1.33}$$

Identifying $m = n = b = 1$, $p = -3$, $a = D$ and $x = z'$ we obtain

$$\int_0^{2R} dz' \frac{z'}{(D + z')^3} = \frac{1}{2D}\frac{z'^2}{(D + z')^2}\Big|_0^{2R} \tag{1.34}$$

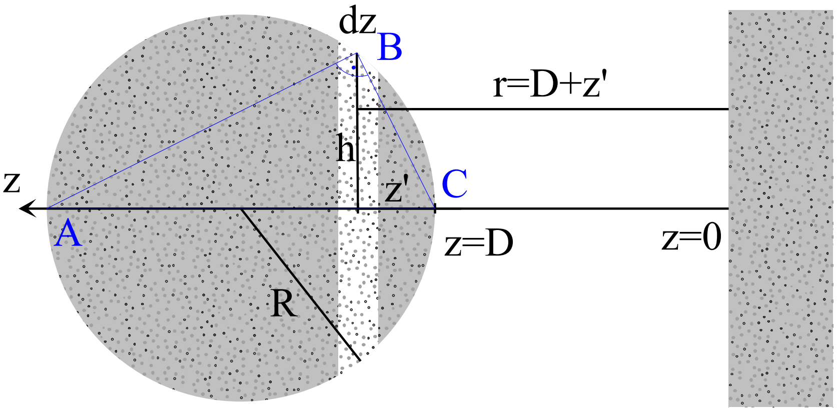

Figure 1.7: For the calculation of the interaction of a sphere with a wall.

which reduces to $1/(2D)$ in the limit of $R >> D$. Finally the sphere-wall interaction becomes

$$W_{SW}(D) = -\frac{\pi^2 \rho^2 C R}{6D}. \tag{1.35}$$

Note that the interaction between a sphere and a wall decays only linearly with the reciprocal distance.

The van der Waals force between a sphere and a wall is according to eq. 1.35

$$F_{SW}(D) = -\frac{\partial W_{SW}(D)}{\partial D} = -\frac{\pi^2 \rho^2 C R}{6D^2} \tag{1.36}$$

Comparison of the r.h.s of eq. 1.36 with the expression for the interaction between two planar walls of unit area shows that

$$F_{SW}(D) = 2\pi R W_{WW}^{a} \tag{1.37}$$

This important relation is known as the Derjaguin approximation and holds for $D <<$ R. It relates the force between curved surfaces to the interaction energy between two planar walls at the same distance.

1.2.4 Interaction between two spheres

The formulation of the Derjaguin approximation introduced in the previous section can be generalized for two curved surfaces. Consider both of the spheres as consisting of cylindrical shells with which it faces the other sphere with an area $a = 2\pi x dx$ over a distance Z. In this case the force between two such shells is $2\pi x dx f^a_{WW}(Z)$, where $f^a_{WW}(Z)$ is the force per unit area between two planar walls. The total force between the two spheres is obtained by integration over all $f^a_{WW}(Z)$

$$F_{SS}(D) = \int da f^a_{WW}(Z) = \int dx f^a_{WW}(Z) 2\pi x \tag{1.38}$$

For large spheres we assume that only the cylindrical shells at small z_1+z_2, i. e. $x >> z_{1,2}$ contribute significantly to the total force. Then we may approximate $Z = D + z_1 + z_2 \approx D + (1/R_1 + 1/R_2)x^2/2$, the Jacobian dZ/dx becomes $x(R_1 + R_2)/(R_1 R_2)$ and the total force becomes

$$\begin{aligned} F_{SS}(D) &= 2\pi \frac{R_2 R_1}{R_1 + R_2} \int_D^\infty dZ f^a_{WW} \\ &= -2\pi \frac{R_2 R_1}{R_1 + R_2} W^a_{WW}(D). \end{aligned} \tag{1.39}$$

Finally, to obtain the interaction energy between two spheres we have to integrate the force from distance D to infinity which gives the general formulation of the Derjaguin approximation

$$W_{SS}(D) = 2\pi \frac{R_1 R_2}{R_1 + R_2} \int_D^\infty dZ W^a_{WW}(Z) \tag{1.40}$$

Note that this approximation may be applied to any kind of interaction, as long as $D << R_{1,2}$. For the case of van der Wals interaction between two spheres where $W^a_{WW}(D) = -\pi\rho^2 C/(12D^2)$ it yields

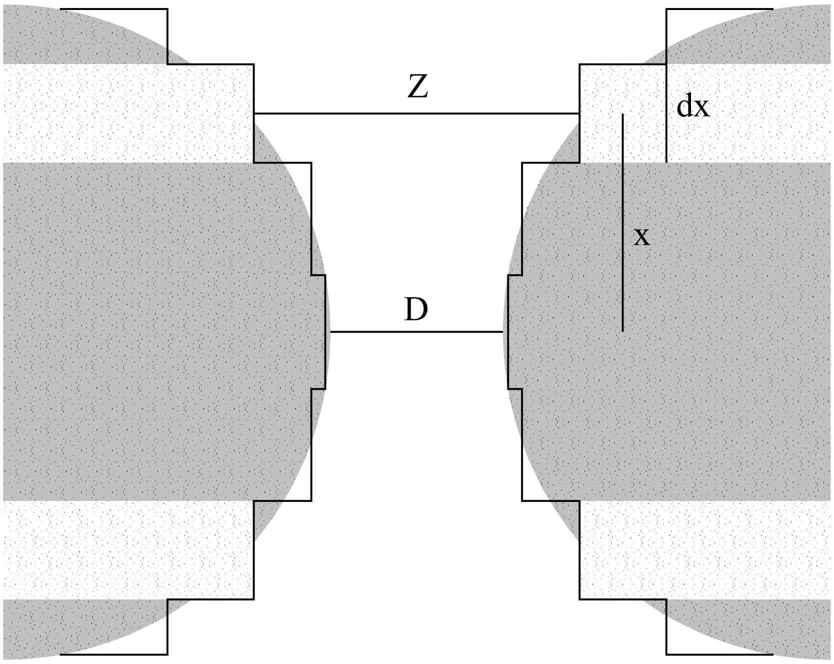

Figure 1.8: For the calculation of the interaction of a sphere with a wall.

$$W_{SS}(D) = -\frac{\pi^2\rho^2 C}{6D}\frac{R_1 R_2}{R_1 + R_2}. \tag{1.41}$$

Note that the sphere–wall interaction (eq. 1.35) can be obtained from the sphere-sphere interaction for the limiting case where either of the radii is set to infinity.

1.2.5 The Hamaker constant and the Lifshitz continuum theory

Summarizing the expressions for the van der Waals interaction between macroscopic bodies

$$W^a_{WW}(D) = -\frac{A_H}{12\pi D^2}. \tag{1.42}$$

$$W_{SW}(D) = -\frac{A_H R}{6D}. \tag{1.43}$$

$$W_{SS}(D) = -\frac{A_H}{6D}\frac{R_1 R_2}{R_1 + R_2}. \tag{1.44}$$

we realize that they all can be expressed in terms of a constant named in the honor of Hamaker

$$A_H = \pi^2 \rho_1 \rho_2 C. \tag{1.45}$$

In deriving these expression we assumed pairwise additivity of the dipole–dipole interactions. This is of course a very strong restriction, for example it neglects the influence of a third atom on the dispersion interaction between an other pair of atoms. This may by a valid approximation in highly dilute systems, i. e. gases, but not in condensed materials. Further this approximation can not be readily extended to the situation where two large particles are interacting through a dielectric medium. These problems are avoided in the Lifshitz theory where the particles are treated as a continuum neglecting their atomic structure. In this theory the forces are calculated on the basis of the particles' dielectric bulk properties. Fortunately we do not have to deal with the Lifshitz theory in detail, because the analytic form of eqs. 1.42 through 1.44 remains the same. The only thing that changes is the Hamaker constant which becomes a function of the dielectric constants of the media involved. For two particles of refractive index n_1 and

n_2 interacting across a dielectric medium with n_3 this is given approximately as

$$A_H \approx \frac{3}{4} k_B T \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h\nu_e}{8\sqrt{2}} \frac{\left(n_1^2 - n_3^2\right)\left(n_2^2 - n_3^2\right)}{\left(n_1^2 + n_3^2\right)^{1/2}\left(n_2^2 + n_3^2\right)^{1/2}\left[\left(n_1^2 + n_3^2\right)^{1/2} + \left(n_2^2 + n_3^2\right)^{1/2}\right]}. \tag{1.46}$$

For the simple case of two particles consisting of the same material with refractive index n_1 this simplifies to

$$A_H \approx \frac{3}{4} k_B T \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{\left(n_1^2 - n_3^2\right)^2}{\left(n_1^2 + n_3^2\right)^{3/2}}. \tag{1.47}$$

As a rough estimate, the Hamaker constant for most materials is in the range of 10^{-19} to 10^{-21} J, that is between 25 and 0.25 $k_B T$ at ambient temperature.It is very instructive to have a look at certain limiting cases of eq. 1.46. As can be seen from table 1.2 the potential between two bodies interacting through vacuum is always attractive, as is the potential between to bodies of the same material interacting across any medium. Repulsive van der Waals attraction are found between particles with different refractive index n_1 and n_2 interacting through a medium, the refractive index of which is intermediate between n_1 and n_2. This is very often the case when a vapor phase $n_1 \approx 1$ interacts across a liquid phase $1.3 \lesssim n_3 \lesssim 1.5$ with glass $n_2 \gtrsim 1.5$. The repulsive van der Waals potential between the vapor/liquid and the liquid/glass interface is the reason why most liquid tend to form a positive meniscus at the glass wall of a beaker or a test tube.

1.3 Repulsive interaction and Colloidal Stability

In section 1.2.5 we have seen that the van der Waals potential between colloidal bodies consisting of the same material is attractive across any medium. This would lead to an

Table 1.2: Limiting cases for eq. 1.46

	A_H	W_{vdW}
$n_1 \neq n_2$,$n_3 = 1$	> 0	< 0
$n_1 = n_2 \neq n_3$	> 0	< 0
$n_1 < n_3 < n_2$	< 0	> 0

aggregation and eventual precipitation of any colloid in solution. Since a lot of biological material, like proteins, red blood cells etc., is of colloidal size, this would be fatal for any living organism. However, our every day experience luckily shows that these materials form stable suspensions in body fluids, i. e. water, which forces the conclusion that there has to be an additional contribution to colloidal interaction, which is repulsive and by this prevents aggregation. There are basically two types of repulsive interaction: steric repulsion and electrostatic repulsion. In this course we will mainly discuss electrostatic interactions, while the steric interactions will be described only very briefly.

1.3.1 Electrostatic Repulsion in the Debye–Hückel Limit

Electrostatic interaction without electrolyte

Imagine a particle carrying ionizable surface groups, i. e. chemical groups which are able to dissociate if immersed in water, as sketched in Figure 1.9 for two planar surfaces. In this case the surface groups dissociate positive counter–ions into the solution leaving negative charges at the wall's surface. Between two plates a density profile $\rho(\delta)$ will build up which is determined by the electrostatic potential, $\psi(\delta)$, acting from the plates on the counterions via Botzman's law. Note that δ is the distance from either of the plates while their separation distance is $z = D$ with $z = 0$ at the surface of one of the plates. For symmetry reasons, the electric field $E = d\psi(\delta)/d\delta$ in the midplane is zero. For this reason we will call the counterion density and the electric potential in the mid plane ρ_0 and ψ_0 respectively. It is important to note that $\rho_0 \neq 0$ and $\psi_0 \neq 0$ in general.

For the sake of clarity we will discuss the details of the potential and the density profile at a later stage, and calculate the interaction potential between the two walls first. For this purpose we start with calculating the osmotic pressure Π between the parallel plates, from which we can calculate the interaction energy by integration over distance. In an equilibrium system the osmotic pressure is related to the the chemical potentials μ_i of the components by the Gibbs–Duhem equation. For the one component system, which we are considering, this reads:

$$\mu N = U + \Pi V - TS \tag{1.48}$$

where N is the number of counter–ions, U the internal energy, V the system volume and S the entropy. At constant temperature, volume and composition, the total differential of eq. 1.48 reduces to $d\mu N = d\Pi V$ or $d\Pi = \rho d\mu$. In the problem at hand ρ is the density of the counterions $\rho(\delta)$. With the definition of the chemical potential of the counterions

$$\mu(\delta) = \mathcal{Z} e\psi(\delta) + k_B T \ln \rho(\delta) \tag{1.49}$$

we obtain

$$d\Pi = \rho(\delta)\left[\mathcal{Z} e d\psi(\delta) + k_B T \frac{1}{\rho(\delta)} d\rho(\delta)\right] \tag{1.50}$$

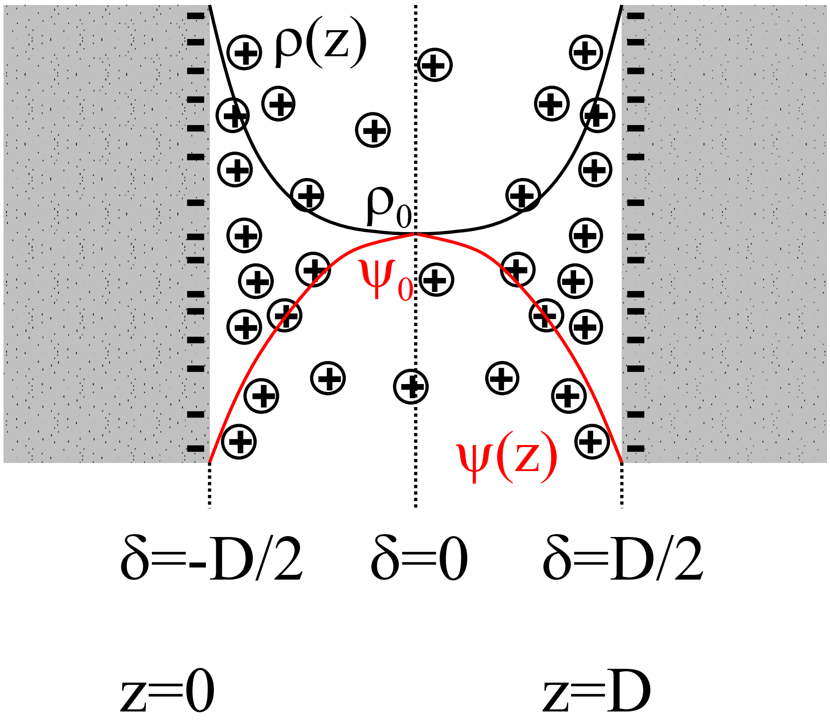

Figure 1.9: Two walls with ionizable groups immersed in a solvent without additional ions

where $\mathcal{Z}$ is the valency of the ions. To calculate the pressure between the two plates at distance $z = D$ we have to integrate eq. 1.50 from $z \to \infty$ to D

$$\int_{z\to\infty}^{z=D} d\Pi(\delta) = \mathcal{Z}e \int_{\infty}^{D} dz\rho(\delta)\frac{d\psi(\delta)}{d\delta} + k_BT \int_{z\to\infty}^{z=D} d\rho(\delta). \tag{1.51}$$

Here we used $d\psi(\delta) = d\psi(\delta)/d\delta dz$, because $d\delta/dz = 1$. To solve the first integral on the r.h.s. we have to relate the counterion density to the electric field, $d\psi(\delta)/d\delta$, which can be done using the one dimensional form of the Poisson equation

$$\frac{d^2\psi(\delta)}{d\delta^2} = -\frac{\mathcal{Z}e\rho(\delta)}{\varepsilon\varepsilon_0}. \tag{1.52}$$

With this we obtain

$$\mathcal{Z}e \int_{\infty}^{D} dz\rho(\delta)\frac{d\psi(\delta)}{d\delta} = -\frac{\varepsilon\varepsilon_0}{2}\int_{\infty}^{D} d\left(\frac{d\psi(\delta)}{d\delta}\right)^2 \tag{1.53}$$

where we used the general relation

$$\frac{d\left(\frac{df(u)}{du}\right)^2}{du} = 2\frac{df(u)}{du}\frac{d^2f(u)}{du^2}. \tag{1.54}$$

Now the pressure at separation distance $z = D$ can be calculated for any position δ between the plates as

$$\Pi(\delta)_{z=D} = -\frac{\varepsilon\varepsilon_0}{2}\left(\frac{d\psi(\delta)}{d\delta}\right)^2_{z=D} + k_BT\rho(\delta)_{z=D} \tag{1.55}$$

because $\Pi(\delta)_\infty = 0$ and $\rho(\delta)_\infty = 0$. To calculate the squared electric field we use again the Poisson equation, which in combination with Botzmann's law gives the Poisson–Boltzman differential equation

$$\frac{d^2\psi(\delta)}{d\delta^2} = -\frac{\mathcal{Z}e\rho_0}{\varepsilon\varepsilon_0}\exp\left\{-\frac{\mathcal{Z}e(\psi(\delta)-\psi_0)}{k_BT}\right\}. \tag{1.56}$$

Using the derivative of Boltzmann's law (note that $d\psi_0/d\delta = 0$) we can replace the factor

$$\mathcal{Z}e\rho_0 = -\frac{d\rho(\delta)}{d\delta} k_B T \exp\left\{+\frac{\mathcal{Z}e(\psi(\delta)-\psi_0)}{k_B T}\right\}\left(\frac{d\psi(\delta)}{d\delta}\right)^{-1} \tag{1.57}$$

in eq. 1.56 to obtain

$$\frac{d\psi(\delta)}{d\delta}\frac{d^2\psi(\delta)}{d\delta^2} = \frac{d\rho(\delta)}{d\delta}\frac{k_B T}{\varepsilon\varepsilon_0} \tag{1.58}$$

which relates the total differential of the counterion density to the total differential of the squared electric field by

$$d\rho(\delta) = \frac{\varepsilon\varepsilon_0}{2k_B T} d\left(\frac{d\psi(\delta)}{d\delta}\right)^2 . \tag{1.59}$$

Integration from zero to any value of δ yields

$$\rho(\delta) - \rho_0 = \frac{\varepsilon\varepsilon_0}{2k_B T}\left(\frac{d\psi(\delta)}{d\delta}\right)^2 , \tag{1.60}$$

which can be introduced into eq. 1.55 to obtain the final expression for the pressure

$$\Pi(D) = k_B T(\rho_0)_{z=D} \tag{1.61}$$

The subscript $_{z=D}$ indicates that the density in the midplane is a function of the separation distance. It is important to note that the r.h.s. expression does not anymore depend on the position δ, which is expected, since the osmotic pressure in a solution should be a constant. On the basis of the latter argument the pressure could also be calculated in a more heuristic way. If we treat the counterions as an ideal gas, the osmotic pressure is directly given by the ideal gas law. Due to symmetry reasons, we can argue that the electrostatic force between the two plates is zero at $\delta = 0$, because the two half systems at $\delta < 0$ and $\delta > 0$ are electroneutral on average. Consequently the force between the two plates in the midplane is the osmotic pressure multiplied with the plates' surface area. Since the pressure is independent of position we arrive directly at eq. 1.61. This is an important finding because is shows that the repulsion is an *entropic* effect governed by the counterion distribution, although it is generally referred to as electrostatic repulsion.

Electrostatic interaction in the presence of additional electrolyte

So far we have considered the pressure between two plates for the case when only counterions are present in the gap between the surfaces. This is however a very unrealistic scenario, because even if pure water was used as a solvent, the self dissociation would lead to an ion concentration of 2×10^{-7} mol/L. Therefore, in the following, we shall calculate the interaction between two surfaces in the presence of additional electrolyte, applying commonly used approximations. In this case we have to consider that $\rho(\delta)_\infty \neq 0$, it is rather the density of the additional electrolyte ρ_{salt}. Therefore we obtain

$$\Pi(\delta)_{z=D} = -\frac{\varepsilon\varepsilon_0}{2}\left(\frac{d\psi(\delta)}{d\delta}\right)^2_{z=D} + k_B T\left(\rho(\delta)_{z=D} - \rho_{salt}\right) \tag{1.62}$$

when solving the integrals of eq. 1.51

If we define the electric potential outside the gap as $\psi_\infty = 0$ and noting that the electric field outside the plates $(d\psi(\delta)/d\delta)_\infty = 0$, we get the final equation for the osmotic pressure

$$\Pi(D) = k_B T\left(\rho_0(D) - \rho_{salt}\right). \tag{1.63}$$

along the same line of argumentation as in the previous section. We have however to note that the ion density is now governed by the additional electrolyte and that either

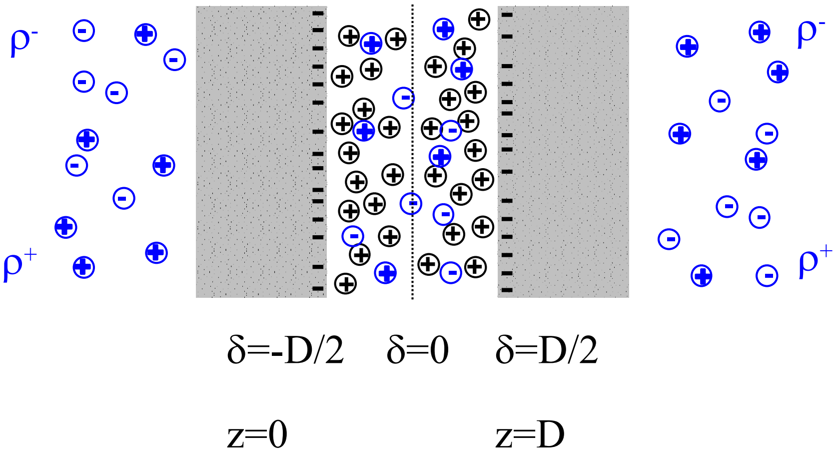

Figure 1.10: Two walls with ionizable groups immersed in a solution containing additional electrolyte

species of ions contributes to the pressure by

$$\begin{aligned} \rho_{salt} &= \sum_i \rho_i \\ \rho_0(D) &= \sum_i \rho_i \exp\left\{-\frac{\mathcal{Z}_i e\psi_0}{k_B T}\right\}. \end{aligned} \tag{1.64}$$

For the latter expression we used Botzmann's law to relate the ion density outside the gap to the density at the midplane. Here the index i refers to the individual species of ions. Combining eqs. 1.63 and 1.64 gives

$$\Pi(D) = k_B T \rho_{salt}\left[\left(\exp\left\{-\frac{e\psi_0}{k_B T}\right\} - 1\right) + \left(\exp\left\{+\frac{e\psi_0}{k_B T}\right\} - 1\right)\right] \tag{1.65}$$

for a 1 : 1 electrolyte. The first term in the curled brackets refers to the cation–contribution while the second term is due to the anions. If the electric potentials are small enough to grant that $\psi_0 << 25$ mV, the argument of the exponential is small compared to 1 and we may approximate this expression as a Taylor series truncated after the second terms

$$\Pi(D) \approx \rho_{salt} k_B T \left[\left(1 - \frac{e\psi_0}{k_B T} + \frac{(e\psi_0)^2}{2(k_B T)^2} - 1 \right) + \left(1 + \frac{e\psi_0}{k_B T} + \frac{(e\psi_0)^2}{2(k_B T)^2} - 1 \right) \right] . \quad (1.66)$$

This is the essential approximation in the Debye–Hckkel theory of electrolyte solutions. The linear terms cancel due to the electroneutrality condition and we obtain

$$\Pi(D) \approx \rho_{salt} \frac{(e\psi_0)^2}{k_B T} . \quad (1.67)$$

According to the Gouy–Chapman theory the electric potential at any distance δ from a charged surface is

$$\psi(\delta) \approx \frac{4k_B T}{e} \gamma \exp\{-\kappa\delta\} \quad (1.68)$$

with

$$\gamma = \tan\mathrm{h} \left(\frac{e\psi_S}{4k_B T} \right)$$

where ψ_S is the potential at the surface. The meaning of the constants γ and the so–called screening length κ, will be discussed in the following section in detail. If we assume that the potential between two plates can be regarded as the superposition of two potentials originating from either of the surfaces, the potential in the midplane will be twice the Gouy–Chapman value for symmetry reasons. Thus, we obtain for the pressure between two plates

$$\begin{aligned} \Pi(D) &\approx \frac{\rho_{salt} e^2}{k_B T} \left[\frac{8k_B T}{e} \gamma \exp\left\{ -\frac{\kappa D}{2} \right\} \right]^2 \\ &= 64 \rho_{salt} k_B T \gamma^2 \exp\{-\kappa D\} . \end{aligned} \quad (1.69)$$

Integrating the pressure with respect to distance we obtain the electrostatic interaction potential per unit area between two flat walls as

$$W^{a,es}_{WW} = 64\rho_{salt} k_B T \gamma^2 \frac{1}{\kappa} \exp\left\{-\kappa D\right\}, \tag{1.70}$$

and with the Derjaguin approximation we can easily calculate the interaction potential between two spheres

$$W^{es}_{SS} = \frac{2\pi R_1 R_2}{R_1 + R_2} 64\rho_{salt} k_B T \gamma^2 \frac{1}{\kappa^2} \exp\left\{-\kappa D\right\}. \tag{1.71}$$

The surface potential and the Gouy–Chapman theory

In this section we shall discuss the parameters γ and κ, and their relation to experimentally accessible quantities. As we have shown above, the counterion density at a given position between two charged surfaces is related to the square of the electric field at this position by

$$\rho(\delta) = \rho_0 + \frac{\varepsilon\varepsilon_0}{2k_B T}\left(\frac{d\psi(\delta)}{d\delta}\right)^2 \tag{1.72}$$

where ρ_0 is the density at a position where the electric field is zero. If we transfer this definition to a single surface in the presence of additional electrolyte, we have to realize that the electric field goes to zero at infinite distance and there the ion density of each species is that of the additional electrolyte. Thus

$$\sum_i \rho_i(\delta) = \sum_i \rho_{i,\infty} + \frac{\varepsilon\varepsilon_0}{2k_B T}\left(\frac{d\psi(\delta)}{d\delta}\right)^2, \tag{1.73}$$

which with Boltzmann's law gives

$$\frac{\varepsilon\varepsilon_0}{2k_B T}\left(\frac{d\psi(\delta)}{d\delta}\right)^2 = \rho_{salt}\left(\exp\left\{-\frac{e\psi(\delta)}{k_B T}\right\} - 1 + \exp\left\{+\frac{e\psi(\delta)}{k_B T}\right\} - 1\right) \tag{1.74}$$

for a 1:1 electrolyte. With the definition of the hyperbolic cosine and the relation $(2\cosh(u) - 2) = (2\sinh(u/2))^2$ we can rewrite this relation as

$$\frac{d\psi(\delta)}{d\delta} = \pm\sqrt{\frac{8k_BT\rho_{salt}}{\varepsilon\varepsilon_0}}\sinh\left(\frac{e\psi(\delta)}{2k_BT}\right). \tag{1.75}$$

It is important to note that only the solution with the negative sign is physically meaningful, because sinh is an asymmetric function and the gradient of ψ has to be positive for $\psi < 0$ and vice versa. This differential equation enables to relate the electric potential at any position to the potential at the surface, ψ_S, by integration. For this purpose we substitute $e\psi(\delta)/(2k_BT) \equiv \Phi(\delta)$ the derivative of which is

$$\begin{aligned}\frac{d\Phi(\delta)}{d\delta} &= \frac{d\Phi(\delta)}{d\psi(\delta)}\frac{d\psi(\delta)}{d\delta} \\ &= -\frac{e}{2k_BT}\sqrt{\frac{8k_BT\rho_{salt}}{\varepsilon\varepsilon_0}}\sinh(\Phi(\delta)).\end{aligned} \tag{1.76}$$

After separation of variables and integration we get

$$\ln\left(\frac{\tanh(\Phi(\delta)/2)}{\tanh(\Phi_S/2)}\right) = -\delta\sqrt{\frac{2\rho_{salt}e^2}{\varepsilon\varepsilon_0 k_BT}} \tag{1.77}$$

where $\Phi_S = e\psi_S/(2k_BT)$ and we used the tabulated integral

$$\int\frac{du}{\sinh(u)} = \ln\left[\tanh\left(\frac{u}{2}\right)\right]. \tag{1.78}$$

With the definition of the area hyperbolic tangent $\tanh^{-1}(u) = 0.5\ln((1+u)/(1-u))$, $\gamma \equiv \tanh(\Phi_S/2)$ (compare eq. 1.68) and $\kappa = \sqrt{2\rho_{salt}e^2/(\varepsilon\varepsilon_0 k_BT)}$ we get

$$\Phi(\delta) = \ln\left(\frac{1+\gamma\exp\{-\kappa\delta\}}{1-\gamma\exp\{-\kappa\delta\}}\right) \tag{1.79}$$

If $\gamma\exp\{-\kappa\delta\} << 1$ the argument of the logarithm is approximately $1 + 2\gamma\exp\{-\kappa\delta\}$, and a Taylor expansion of the logarithm, truncated after the linear term gives

$$\Phi(\delta) \approx 2\gamma\exp\{-\kappa\delta\}. \tag{1.80}$$

After resubstitution of Φ we obtain the final expression of the Gouy–Chapman theory

$$\psi(\delta) \approx \frac{4k_BT}{e}\tanh\left(\frac{e\psi_S}{4K_BT}\right)\exp\left\{-\kappa\delta\right\}, \tag{1.81}$$

which relates the potential at any distance δ to the potential at the surface. Note that $\psi(\delta)$ depends on the salt concentration only through the parameter κ, which has the units of an inverse length. Therefore κ^{-1} is often referred to as the (Debye–) screening length. Note that $\tanh(u) \approx u$ for small arguments. In this case eq. 1.81 reduces to the so called Debye–Hückel equation

$$\psi(\delta) \approx \psi_S \exp\left\{-\kappa\delta\right\}, \tag{1.82}$$

and κ^{-1} is the relaxation distance of the potential.

With equations 1.81 and 1.82 it is possible to express the the electrostatic interaction potential between colloids as a function of surface potential. By replacing γ^2 in eq. 1.70 we obtain

$$W_{WW}^{a,el} = 2\varepsilon\varepsilon_0\psi_S^2\kappa\exp\left\{-\kappa D\right\} \tag{1.83}$$

and for the interaction potential between two spheres of equal radius we get

$$W_{SS}^{el} = 2\pi R\varepsilon\varepsilon_0\psi_S^2\exp\left\{-\kappa D\right\} \tag{1.84}$$

from eq. 1.71.

The surface charge density and the Grahame equation

Instead of expressing the the electrostatic interaction potential between colloids as a function of the surface potential it can be written as a function of the surface charge density, σ. For this purpose we have to establish a relation between ψ_S and σ. If we define σ as the number of elementary charges per unit area we can identify

$$\sigma = -\int_0^{D/2} d\delta \rho(\delta) \mathrm{Z} e, \tag{1.85}$$

because the number of charges in the volume defined by $0 < \delta < D/2$ has to be equal to the number of opposite charges on the surface. Note that $\rho(\delta)$ and $\mathcal{Z}$ are the counterion density and valency respectively. The properties of the additional electrolyte do not enter into this consideration. According to the Poisson equation the integrand can be replaced by $\varepsilon\varepsilon_0 d^2\psi(\delta)/d\delta^2$, which gives

$$\sigma = \varepsilon\varepsilon_0 \left(\frac{d\psi(\delta)}{d\delta}\right)_{\delta=D/2} \tag{1.86}$$

Introducing this result into eq. 1.73 results

$$\sum_i \rho(\delta) = \sum_i \rho_{i,\infty} + \frac{\sigma^2}{2\varepsilon\varepsilon_0 k_B T} \tag{1.87}$$

and applying Boltzmann's law to each kind of ions we find for a 1:1 electrolyte

$$\begin{aligned} \sigma^2 &= 2\varepsilon\varepsilon_0 \rho_{salt} k_B T \left[\exp\left\{-\frac{e\psi_S}{k_B T}\right\} + \exp\left\{+\frac{e\psi_S}{k_B T}\right\} - 2\right] \\ &= 2\varepsilon\varepsilon_0 \rho_{salt} k_B T \left[2\cosh\left(\frac{e\psi_S}{k_B T}\right) - 2\right] \\ &= 8\varepsilon\varepsilon_0 \rho_{salt} k_B T \left[\sinh\left(\frac{e\psi_S}{2k_B T}\right)\right]^2 . \end{aligned} \tag{1.88}$$

Finally the relation between the surface charge density and the surface potential becomes

$$\sigma = \sqrt{8\varepsilon\varepsilon_0 \rho_{salt} k_B T} \sinh\left(\frac{e\psi_S}{2k_B T}\right), \tag{1.89}$$

which is known as the Grahame equation.

For electrolytes other than 1:1, the Grahame equation becomes more complicated, though it can be still written in an analytically closed form. However, for small potentials, if the exponentials in eq. 1.88 may be approximated by a Taylor–series which is truncated after the quadratic term we get for the general case

$$\begin{aligned}\sigma^2 &= 2\varepsilon\varepsilon_0 k_B T \sum_i \rho_{i,\infty}\left[\exp\left\{-\frac{\mathcal{Z}_i e\psi_S}{k_B T}\right\}-1\right] \\ &\approx 2\varepsilon\varepsilon_0 k_B T\left[\sum_i \rho_{i,\infty}^{anions}\frac{1}{2}\left(\frac{\mathcal{Z}_i e\psi_S}{k_B T}\right)^2+\sum_i \rho_{i,\infty}^{cations}\frac{1}{2}\left(\frac{\mathcal{Z}_i e\psi_S}{k_B T}\right)^2\right].\end{aligned} \tag{1.90}$$

Note that the linear terms cancel due to the electroneutrality condition. Thus, in the Debye–Hückel approximation, we get for all kinds of additional electrolytes

$$\begin{aligned}\sigma &= \psi_S\varepsilon\varepsilon_0\sqrt{\frac{\sum_i \rho_{i,\infty}\mathcal{Z}_i^2 e^2}{\varepsilon\varepsilon_0 k_B T}} \\ &= \psi_S\varepsilon\varepsilon_0\kappa.\end{aligned} \tag{1.91}$$

With this approximation we can also write the interaction potential per unit area between two flat surfaces as

$$W_{WW}^{a,el} = 2\frac{\sigma^2}{\varepsilon\varepsilon_0\kappa}\exp\{-\kappa D\} \tag{1.92}$$

and the interaction potential between two spheres of equal radius as

$$W_{SS}^{el} = 2\pi R\frac{\sigma^2}{\varepsilon\varepsilon_0\kappa^2}\exp\{-\kappa D\} \tag{1.93}$$

according to eqs. 1.83 and 1.84 respectively.

It is important to note, that the electrolyte concentration does enter into these equations only via the Debye screening length. It is therefore useful to memorize a rule of thumb for the calculation of κ. If the electrolyte concentration, c, is expressed in mol/L

Table 1.3: Rules of thumb for the calculation of κ for different types of electrolytes. The salt concentration, c has to be introduced in the unit *mol/L*

Type of electrolyte	example	κ^{-1}/ nm
1:1	NaCl	$\frac{0.304}{\sqrt{c}}$
1:2 or 2:1	$CaCl_2$	$\frac{0.176}{\sqrt{c}}$
2:2	$MgSO_4$	$\frac{0.152}{\sqrt{c}}$

and the constants entering into κ are given in SI–units, one obtains the screening length in nanometers as

$$\kappa^{-1} = \frac{0.304}{\sqrt{c}}[\mathrm{nm}]. \tag{1.94}$$

For some other types of electrolytes the corresponding results are listed in Table 1.3.

1.3.2 Addition of Van der Waals and Electrostatic Potential: The DLVO Theory

In calculating the electrostatic potential between particles, we have neglected van der Waals interactions completely, which is of course incorrect, since we have seen how charges interact with dipoles in section 1.1.1. However instead of calculating the interactions of individual charges with the spheres, we assume that the ions are evenly distributed and consequently produce a net zero mean force onto the particles. Further the electrostatic and the van der Waals potential between the particles are assumed to be additive. This is the basis of the so called DLVO–theory (named in the honor of

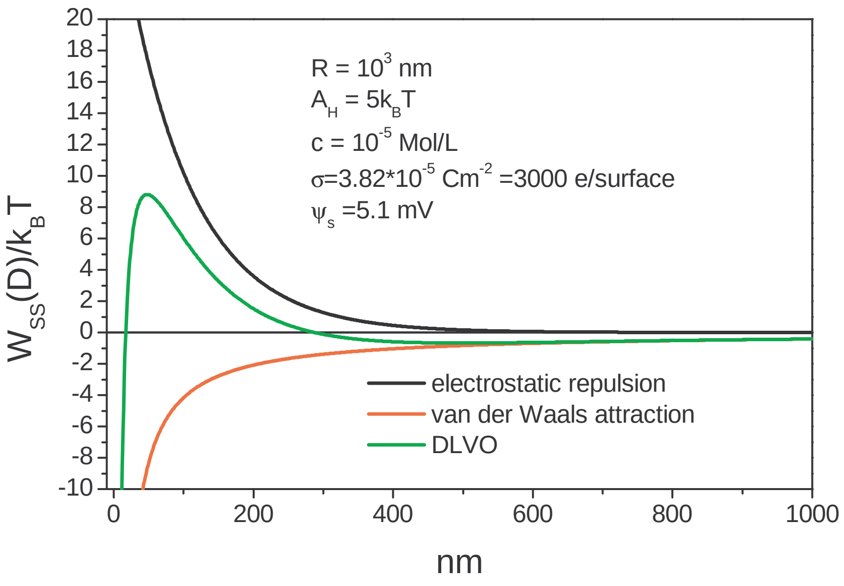

Figure 1.11: Contributions to the total interaction energy between two spheres

Derjaguin, Landau, Vervey and Overbeeck) of colloidal stability. The basic features of this theory are displayed in Figures 1.11 through 1.13.

Due to the fact that the electrostatic contribution increases epxonentially on approaching the interface and the van der Waals potential decay with $1/D$, the latter will always dominate at very small distances. However, if the repulsion is strong enough the total interaction may have a high barrier, which prevents the particles from coming close enough for the van der Waals attraction to be effective. In this case the suspension is considered to be stable. The barrier may be lowered by either increasing the salt concentration (see Figure 1.12) or by decreasing the surface charge (see Figure 1.13) of the particles. In both cases the solution is considered to be unstable if the barrier is not any more higher than several $k_B T$.

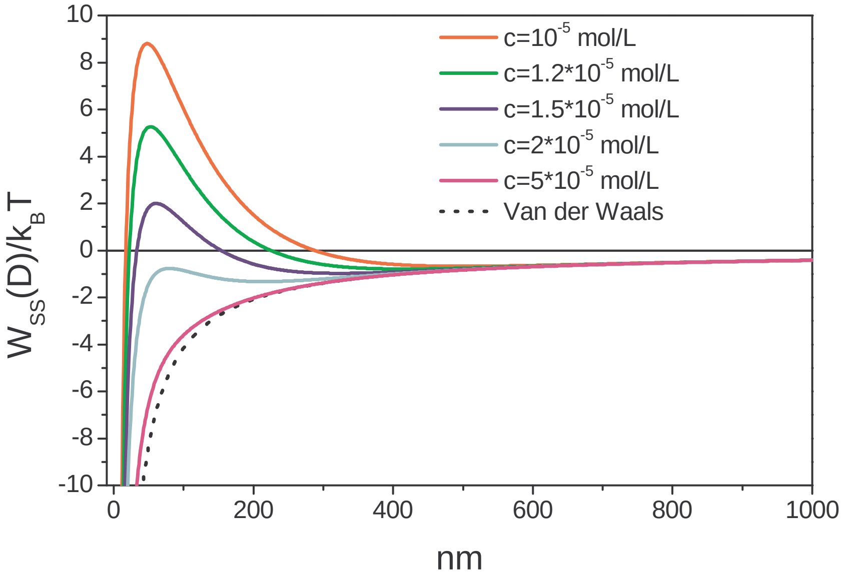

Figure 1.12: DLVO–potentials at constant surface charge density with varying salt concentration. The particle parameters are the same as in Fig. 1.11

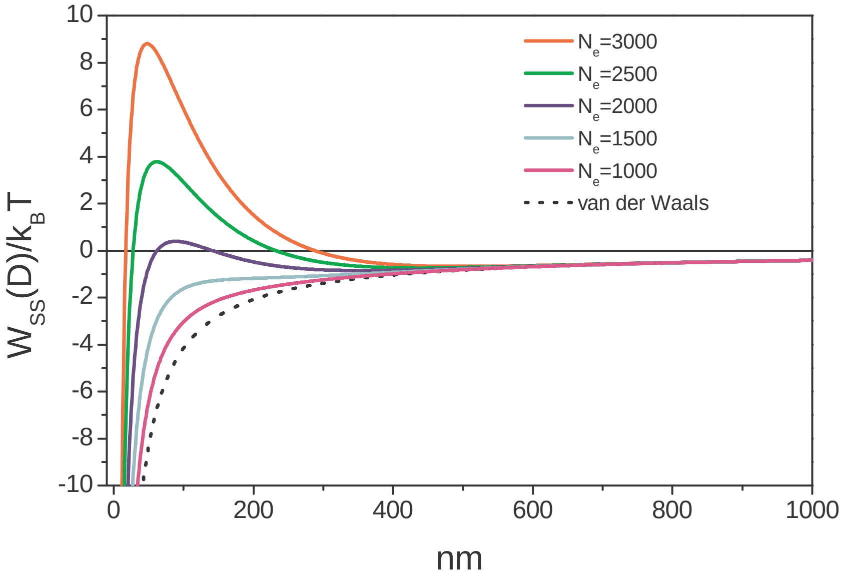

Figure 1.13: DLVO–potentials at constant salt concentration with varying surface charge density. The other particle parameters and the salt concentration are the same as in Fig.1.11

1.4 Non DLVO Interactions

1.4.1 Depletion interaction

Spherical depletants

If colloidal particles are dispersed in a solution which contains further a kind of solute, which has a typical length scale in the colloidal regime, an additional interaction has to be considered. Imagine two plates immersed in a solution containing small spheres of radius r as sketched in Figure 1.14. Then, the center of mass of any sphere can not get closer than a separation distance r to the plate. In other words in front of either plate there is a zone of thickness r which is depleted from spheres. The total volume, which for this is reason is not accessible to the spheres is called the excluded volume V_{ex}. We will see in the following that this depletion leads to an attractive interaction between the two plates, which for obvious reasons is referred to as depletion interaction.

The effective interaction potential between the two plates W_{WW}^{depl} may be regarded as the change in Helmholtz free energy ΔH of the whole system, when the plates are brought from an infinite distance to their final separation D. For a system at constant temperature and composition, $\Delta H = -\Pi \Delta V$, with Π the osmotic pressure and ΔV the negative change of excluded volume, ΔV_{ex}. If we treat the spheres as an ideal gas, we may immediately write down an expression for the depletion interaction between the two plates.

$$W_{WW}^{depl} = \rho k_B T \left[V_{ex}(D) - V_{ex}(D \to \infty) \right] \tag{1.95}$$

where we made use of $\Pi = \rho k_B T$ with ρ the sphere number density. The excluded volume

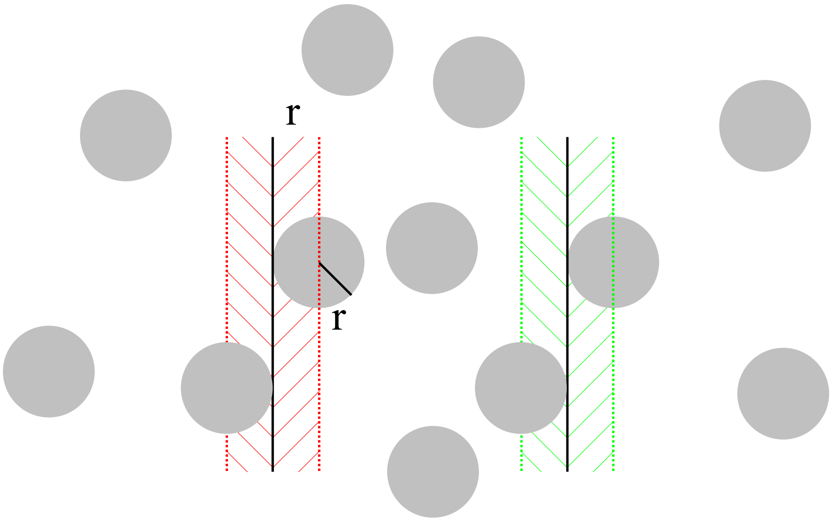

Figure 1.14: Two plates in a solution of spheres. The small spheres can enter the gap between the plates.

at a given separation distance is easily calculated from geometrical considerations. If the plates are further apart than a sphere diameter

$$V_{ex}(D \to \infty) = 4Ar \tag{1.96}$$

where A is the area of a single plate surface (note that there are four surfaces). If the two plates get closer together then $D < 2a$ their depletion zone overlap and the spheres can not get into the gap between the plates. This leads to a density difference, which causes an osmotic pressure imbalance that presses the plates together. For the quantitative description of the resulting interaction potential we need to calculate $V_{ex}(D)$. Which is

$$V_{ex}(D) = 2Ar + DA \tag{1.97}$$

as can be easily seen from Fig.1.15. Note, that the gain in accessible volume, is equal to the volume where the two depletion zones overlap (see green and red hatched areas in

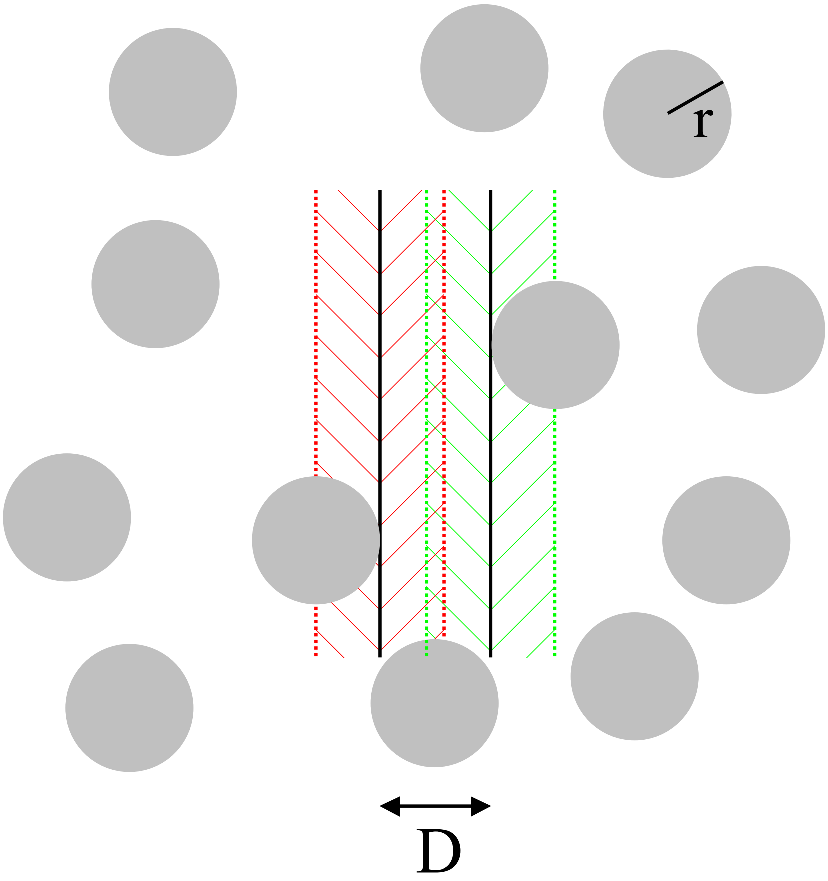

Figure 1.15: Two plates in a solution of spheres. The small spheres can not enter the gap between the plates if their distance is $D < 2r$

Fig. 1.15, i. e. $V_{ol} = -\Delta V_{ex}$. The combination of eqs. 1.95, 1.96 and 1.97 gives

$$\frac{W_{WW}^{depl,a}(D)}{k_B T} = -\rho\,(2r - D)\,. \tag{1.98}$$

Although, this equation yields finite values for the interaction if $D > 2r$, it is important to note that this is not a physical meaningful result. From Figs. 1.14 and 1.15 it is evident that $\Delta V_{ex} = 0$, if $D > 2r$ and consequently eq. 1.95 results $W_{WW}^{depl} = 0$ in this case.

It is important to note that eq. 1.95 holds in general independently whether the surfaces under consideration are curved or not. Consequently there are two ways to calculate the sphere–sphere depletion interaction. First we use the Derjaguin approximation for two spheres, which gives

$$\begin{aligned} \frac{W_{SS}^{depl}(D)}{k_B T} &\approx -2\pi\frac{R_1 R_2}{R_1 + R_2}\rho\int_D^{2r} dZ\,(2r - Z) \\ &= -2\pi\frac{R_1 R_2}{R_1 + R_2}\rho\left(2r^2 - 2rD + \frac{D^2}{2}\right). \end{aligned} \tag{1.99}$$

The upper limit for the integration has to be $2r$ because, the depletion interaction between two flat surfaces is zero beyond this separation distance.

It is very instructive to compare the approximate solution of eq. 1.99 to the exact solution, which one obtains, if the overlap volume between two spherical depletion zones is calculated from exact geometrical considerations. For two large spheres of equal radius R we get

$$V_{ol}^{SS} = -\Delta V_{ex}^{SS} = \frac{2\pi r^3}{3}\left(1 - \frac{D}{2r}\right)^2\left(2 + \frac{3R}{r} + \frac{D}{2r}\right), \tag{1.100}$$

which with we can immediately write

$$\frac{W_{SS}(D)}{k_B T} = -\rho\frac{2\pi r^3}{3}\left(2 + \frac{3R}{r} + \frac{D}{2r}\right)\left(1 - \frac{D}{2r}\right)^2 \tag{1.101}$$

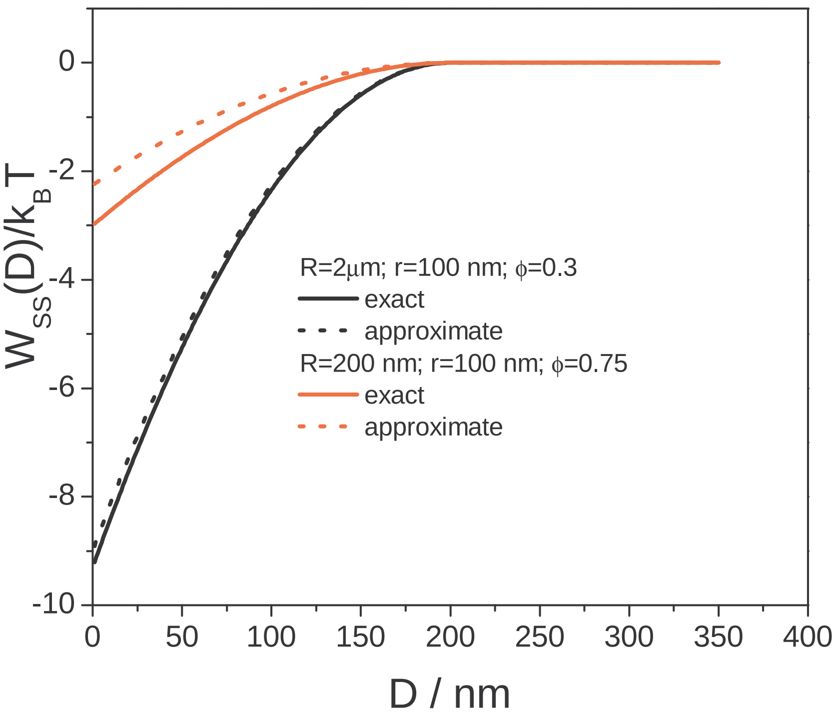

Figure 1.16: Comparison of the exact sphere–sphere depletion interaction with the Derjaguin approximation for two sphere sizes.

$$= \quad -2\pi\rho R\left(\frac{2r^3}{3R}+r^2+\frac{Dr^2}{6R}\right)\left(1-\frac{D}{2r}\right)^2,$$

For Large R/D and R/r this gives the same expression as eq. 1.99 for the case of $R_1 = R_2 = R$.

The effect of the Derjaguin approximation is illustrated in Figure 1.16. If $R >> r$ the approximation gives good agreement with the exact solution, while for smaller spheres the approximation gives values which are significantly too small.

From eqs. 1.99 or1.101 it can be seen that the depth of the potential depends on the volume fraction $\phi = \rho 4\pi r^3/3$ of the small spheres at constant R/r. This is shown in Figure 1.17. If the volume fraction is fixed, the depth of the potential increases with

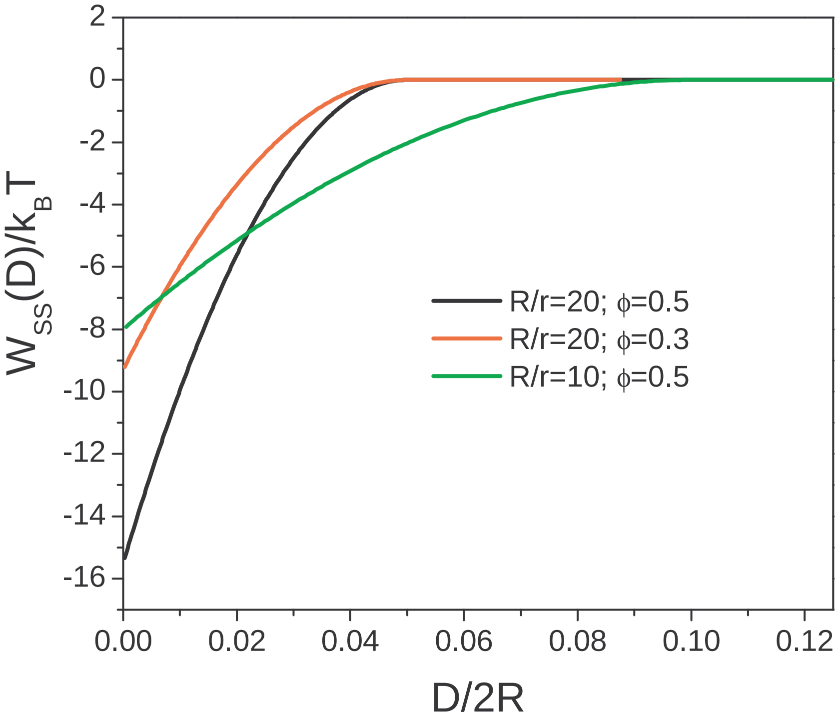

Figure 1.17: Depletion interaction between two spheres mediated by small spheres for different size ratios of the two species and different volume fractions of the small spheres

R/r and the range of the potential increases with r in any case.

Rod-shaped depletants

The depletion potential between two flat walls mediated by an ensemble of rods, W_{WW}^{depl}, is the change in free energy ΔF due the approximation of two wall from infinite separation to a distance D smaller than the rod length L. At constant temperature $\Delta F = -\Pi \Delta V$ where Π is the osmotic pressure in the system and ΔV is the change of the volume which

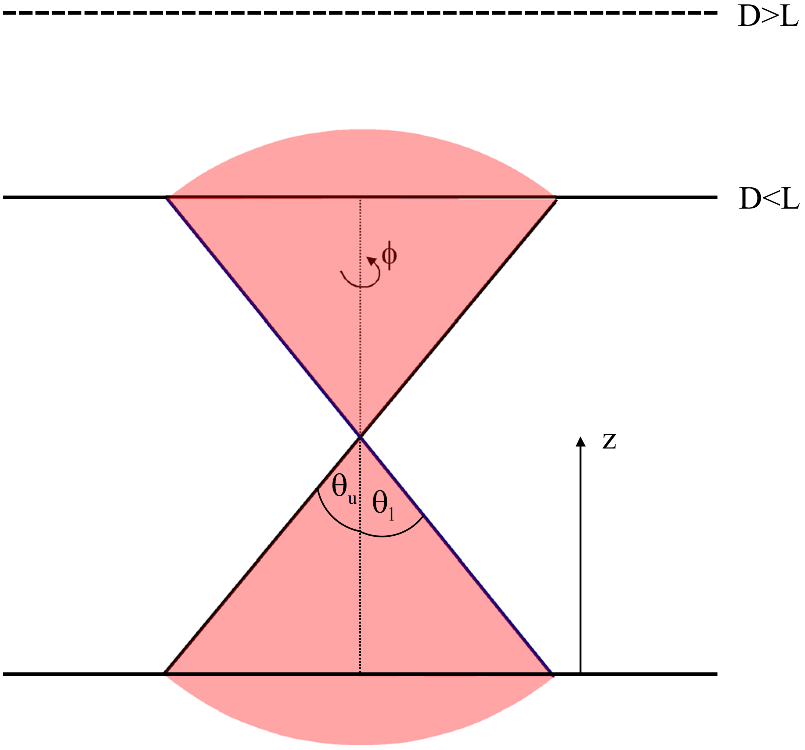

Figure 1.18: For the calculation of the depletion interaction between two walls mediated by a stiff rod.

is available to the rods. The latter is the negative change of excluded volume, thus

$$W_{WW}^{depl} = F(D) - F(D \to \infty) = \Pi(V_{ex}(D) - V_{ex}(D \to \infty)) \tag{1.102}$$

and V_{ex} is the volume from which the rods are excluded by hard body interaction with the walls.

The volume which is excluded for a single rod of length L by a single surface can be calculated as

$$V_{ex} = \int d^3\mathbf{r} \int d\mathbf{\Omega} \frac{1}{4\pi} \left(1 - \exp\left\{-\frac{u(\mathbf{r}, \mathbf{\Omega})}{k_B T}\right\}\right) \tag{1.103}$$

where $u(\mathbf{r}, \mathbf{\Omega})/k_B T$ is the hard body potential between the rod and the wall. Consequently, the Meyer–like function ($1 - \exp\{-u/k_BT\} = 1$) if the rod would touch the wall and zero otherwise. The conditions for the rod touching the wall are $z \leq L/2$ and $0 \leq \theta \leq \theta_l$ or $\theta_u \leq \theta \leq \pi$. The first integral in eq.1.103 represents the integration over all possible positions of the rod center and the second integral is the fraction of a spherical unit volume, which is not accessible to the rod, because of the restricted rotation around the angles θ and ϕ (see area marked red in Fig. 1.18.

Thus, the excluded volume caused by two walls is

$$\begin{aligned} V_{ex}(D) &= 2\frac{A}{4\pi}\int_0^{L/2} dz 2\pi\left[\int_0^{\theta_l} d\theta\sin\theta + \int_{\theta_u}^{\pi} d\theta\sin\theta\right] \text{for} D > L \\ V_{ex}(D) &= \frac{A}{4\pi}\int_0^{D} dz 2\pi\left[\int_0^{\theta_l} d\theta\sin\theta + \int_{\theta_u}^{\pi} d\theta\sin\theta\right] \text{for} D \leq L. \end{aligned} \quad (1.104)$$

Here A is the wall area resulting from the integrations over x and y and the factor 2π results from the integration over $d\phi$, because of the cylindrical symmetry of the problem. For $z < D/2$ $cos\theta_{l,u} = 2z/L$, while $cos\theta_{l,u} = 2(D-)z/L$ for $z > D/2$. This would make the z–integration a unnecessary complicated. It is more convenient replace the integration up to D by twice the integration up to $D/2$, which is allowed because the problem is mirror–symmetrical. With this the integration over dz yields $2(1-2z/L)$ in both cases. Therefore

$$\begin{aligned} V_{ex}(D) &= 2A(z - \frac{z^2}{L})|_0^{L/2} = A\frac{L}{2}\text{for} D > L \\ V_{ex}(D) &= 2A(z - \frac{z^2}{L})|_0^{D/2} = A\left(D - \frac{D^2}{2L}\right)\text{for} D \leq L. \end{aligned} \quad (1.105)$$

Introducing this into eq. 1.102 we find

$$W_{WW}^{depl}(D) = -\Pi A\left(\frac{L}{2} - D + \frac{D^2}{2L}\right), \quad (1.106)$$

which can be rewritten as

$$\frac{W_{WW}^{a,depl}(D)}{k_B T} = -\rho \left(\frac{L}{2} - D + \frac{D^2}{2L} \right), \tag{1.107}$$

if we treat the rods as an ideal gas, i. e. $\Pi = \rho k_B T$ where ρ is the number density of the rods. Note that eq. 1.107 yields finite attractive potentials for $D > L$, but this is a non–physical mathematical artifact. Actually, $W_{WW}^{a,depl} = 0$, because $V_{ex}(D) = V_{ex}(D \to \infty)$ for $D > L$.

The depletion interaction between two spheres can again be calculated using Derjaguin's approximation according to

$$\frac{W_{SS}^{depl}(D)}{k_B T} = 2\pi \frac{R_1 R_2}{R_1 + R_2} \int_D^L dZ \frac{W_{WW}^{a,depl}(Z)}{k_B T}. \tag{1.108}$$

The upper limit of the integration is chosen to be L because the range of the depletion interaction between flat walls levels off to zero at $Z = L$ according to eq. 1.107. With this we finally obtain

$$\begin{aligned} \frac{W_{SS}^{depl}(D)}{k_B T} &= -2\pi\rho \frac{R_1 R_2}{R_1 + R_2} \frac{L}{2} (L - D) - \frac{1}{2} \left(L^2 - D^2 \right) + \frac{1}{6L} \left(L^3 - d^3 \right) \\ &= -2\pi\rho \frac{R_1 R_2}{R_1 + R_2} L^2 \left(1 - \frac{D}{L} \right)^3 \end{aligned} \tag{1.109}$$

1.5 Exercises

1. Consider a charged sphere in aqueous NaCl solution, which is large enough to sediment significantly in the field of gravity. If this sphere approaches the bottom of a vessel, which we shall approximate as a planar wall of the same material as the sphere carrying like charges, electrostatic repulsion will prevent the sphere from settling completely. The sphere will rather float at a distance z_{min} above the glass, which corresponds to the position of a minimum in the potential curve that is given by a superposition of gravitational energy and electrostatic repulsion as sketched in Figure 1.19. Assume that $z_{min} = 120$ nm and that van der Waals interactions may be neglected a this distance. The spheres has a radius $R = 5\mu$m, and a density difference to the solvent of $\Delta\rho = 0.5$ mg/mL, the salt concentration is $c = 0.5$ mmol/L. The dielectric constant of the solution is $\varepsilon = 80$ and $\varepsilon_0 = 8.85 \cdot 10^{-12}$ $\mathrm{C}^2(\mathrm{Jm})^{-1}$. Calculate the number of elementary charges on the surface of the sphere. Use the Debye–Hückel expression for the electrostatic repulsion (is this justified ?) and make use of the fact that the potential has a single minimum

2. The depletion interaction between two planar walls immersed in a solution of small spheres at distance D is given by

   $$\frac{W^a_{WW}(D)}{k_B T} = -\rho(2r - D) \tag{1.110}$$

   where r is the radius of the small spheres, i. e. the thickness of the depletion zone and ρ is the number density of the spheres.

   The exact expression for the depletion interaction between two large spheres of

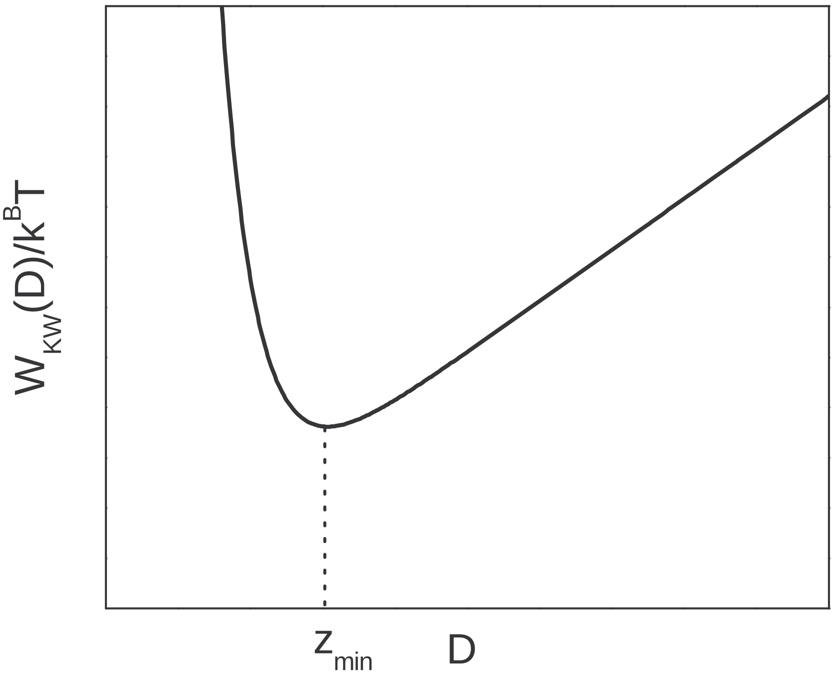

Figure 1.19: Superposition of gravitational energy and electrostatic repulsion of a sphere floating above the bottom of a vessel

equal radius R is given by

$$\frac{W_{SS}(D)}{k_B T} = -\phi_p \left(\frac{3R}{2r} + 1 + \frac{D}{4r} \right) \left(1 - \frac{D}{2r} \right)^2 \tag{1.111}$$

where the volume fraction of the small spheres $\phi = \rho 4\pi r^3/3$. Calculate the sphere–sphere interaction in the Derjaguin approximation and show that the approximate solution is a limiting case of the exact expression for $R >> D$ and $R >> r$.

1.6 Solutions to Exercises

1. The expression for the repulsive part of the potential hast the form

$$W_{SW}^{ER} = B\exp\{-\kappa D\} \tag{1.112}$$

where the amplitude

$$B = 4\pi R\frac{\sigma^2}{\varepsilon\varepsilon_0\kappa^2}. \tag{1.113}$$

The net weight of the sphere is $G = mg = g4\pi R^3\Delta\rho/3$ and the total potential is therefore

$$W_{SW}B = B\exp\{-\kappa D\} + GD. \tag{1.114}$$

By the minimum definition $\partial(W_{SW}(D))/\partial D = 0$ the position of the potential minimum is related to B by

$$z_{min} = \kappa^{-1}\ln\frac{\kappa B}{G}. \tag{1.115}$$

Introducing the given numbers one obtains $G = 0.257$ pN, $\kappa^{-1} = 13.6$ nm and $B = 2.38\cdot 10^{-17}$ J $= 5789k_BT$ and finally

$$\sigma = \sqrt{\frac{B\varepsilon\varepsilon_0\kappa^2}{4\pi R}} = 1.2\cdot 10^{-3}\mathrm{Cm}^{-2}, \tag{1.116}$$

which correspond to a number density of elementary charges per square meter of $\mathcal{N} \approx 7.5\cdot 10^{15}$ m^{-2} and the net number of charges per sphere is $N = \mathcal{N}4\pi R^2 = 2.36\cdot 10^6$.

With $\psi_0 = \sigma/(\varepsilon\varepsilon_0\kappa)$ the calculated charge density corresponds to a surface potential of $\psi_0 = 23$ mV, that is the Debye–Hückel approximation is just valid.

2. See section 1.4.1