Chapter 2
Depletion Interaction

In this chapter we consider the depletion interaction between two flat plates and between two spherical colloidal particles for different depletants (polymers, small colloidal spheres, rods and plates). First of all we focus on the depletion interaction due to a somewhat hypothetical model depletant, the penetrable hard sphere (phs), to mimic a (ideal) polymer molecule. This model, implicitly introduced by Asakura and Oosawa [1] and considered in detail by Vrij [2], is characterized by the fact that the spheres freely overlap each other but act as hard spheres with diameter $\sigma$ when interacting with a wall or a colloidal particle. The thermodynamic properties of a system of hard spheres plus added penetrable hard spheres have been considered by Widom and Rowlinson [3] and provided much of the inspiration for the theory of phase behavior developed in Chap. 3.

The depletion potential is a potential of mean force and, as stressed by Onsager [4, 5], the system is considered at a given chemical potential of the solvent (and other solution) components; the relevant pressure is the osmotic pressure.

2.1 Depletion Interaction Due to Penetrable Hard Spheres

2.1.1 Depletion Interaction Between Two Flat Plates

2.1.1.1 Interaction Potential Between Two Flat Plates Using the Force Method

The force per unit area, $K(h)$, between two parallel plates separated by a distance $h$, is the difference between the osmotic pressure $P_i$ inside the plates and the outside pressure $P_o$

$$K = P_i - P_o$$  \hspace{1cm} (2.1)
Since the penetrable hard spheres behave thermodynamically ideally the osmotic pressure outside the plates is given by the Van ’t Hoff law

\[ P_o = n_b kT, \]

where \( n_b \) is the bulk number density of the phs. When the plate separation \( h \) (see Fig. 2.1) is equal to or larger than the diameter \( \sigma \) of the penetrable hard spheres the osmotic pressure inside the plates is the same as outside:

\[ P_i = P_o = n_b kT. \]

On the other hand, when the plate separation is less than the diameter of the penetrable hard spheres, no particles can enter the gap and

\[ P_i = 0. \]

This means that

\[ K(h) = \begin{cases} -n_b kT & \text{if } h < \sigma \\ 0 & \text{if } h \geq \sigma. \end{cases} \quad (2.2) \]

This is the classical result derived by Asakura and Oosawa [1] more than 50 years ago.

Since \( K = -dW/dh \), integration from \( \infty \) to \( h \) yields the interaction potential per unit area \( W(h) \) between the plates

\[ W(h) = \begin{cases} -n_b kT(\sigma - h) & \text{if } h < \sigma \\ 0 & \text{if } h \geq \sigma. \end{cases} \quad (2.3) \]

### 2.1.1.2 Interaction Potential Between Two Flat Plates Using the Extended Gibbs Adsorption Equation

An alternative and insightful way to obtain the interaction potential is from the extended Gibbs adsorption equation [6–8]. The natural thermodynamic potential to describe the system depicted in Fig. 2.2 is the grand potential \( \Omega(T, V, \mu, h) \)
\[ \Omega = F - \mu N, \quad (2.4) \]

where \( F = F(T, V, N, h) \) is the Helmholtz (free) energy, \( N \) the number of penetrable hard spheres in the system and \( \mu \) their chemical potential. At constant temperature and volume we have \( dF = \mu dN - KA dh \), so \( d\Omega \) is given by

\[ d\Omega = -KA \, dh - N \, d\mu, \quad (2.5) \]

where \( K \) is again the force per unit area between the plates and \( A \) is the area of the plates.

From cross-differentiating (2.5) we obtain

\[ \left( \frac{\partial K}{\partial \mu} \right)_h = \frac{1}{A} \left( \frac{\partial N}{\partial h} \right)_\mu. \quad (2.6) \]

Combining this with

\[ K = -\left( \frac{\partial W}{\partial h} \right)_\mu \quad (2.7) \]

we obtain

\[ -\left( \frac{\partial}{\partial h} \left( \frac{\partial W}{\partial \mu} \right)_h \right)_\mu = \frac{1}{A} \left( \frac{\partial N}{\partial h} \right)_\mu. \quad (2.8) \]

Since the depletion potential \( W \) vanishes at infinite separation for all values of the chemical potential \( \mu \) of the depletion agent, integration over \( h \) gives

\[ -\left( \frac{\partial W}{\partial \mu} \right)_h = \frac{N(h) - N(\infty)}{A}, \quad (2.9) \]

where \( N(h) \) is the number of penetrable hard spheres in the system when the plates are at separation \( h \) and \( N(\infty) \) is that at infinite separation. The right-hand side of (2.9) can be conveniently written in terms of the surface adsorption

\[ -\left( \frac{\partial W}{\partial \mu} \right)_h = \Gamma(h) - \Gamma(\infty), \quad (2.10) \]
where

\[ \Gamma(h) = \int_0^h [n(x) - n_b] \, dx, \quad (2.11) \]

and

\[ \Gamma(\infty) = 2\Gamma_{\text{single wall}} = 2 \int_0^\infty [n(x) - n_b] \, dx. \quad (2.12) \]

In (2.12) \( n(x) \) refers to the polymer segment concentration profile near a single wall whereas in (2.11) \( n(x) \) is the profile between two walls. Expression (2.10) is the extension of the Gibbs adsorption equation for a single surface to the case of two surfaces at finite separation [6–8]. Integration of (2.10) gives

\[ W(h) = -\int_{-\infty}^\mu [\Gamma(h) - \Gamma(\infty)] \, d\mu. \quad (2.13) \]

The depletion thickness of penetrable hard spheres is \( \sigma/2 \) and \( A\Gamma(h) \) equals the overlap volume \( A(\sigma - h) \) times \( n_b \) (see Fig. 2.3)

\[ \Gamma(h) - \Gamma(\infty) = n_b(\sigma - h) \quad h < \sigma \]
\[ = 0 \quad h \geq \sigma. \quad (2.14) \]

The chemical potential of the penetrable hard spheres is

\[ \mu = kT \ln n_b. \quad (2.15) \]
Inserting (2.14) and (2.15) into (2.13) yields (again) the interaction potential given by (2.3). The conceptual advantage of the calculation with the extended Gibbs adsorption equation is that it provides a direct link between the depletion of particles with the depletion potential, which is highly illuminating. The method also offers advantages to obtain physically motivated approximate expressions for the depletion interaction where an exact calculation is not possible.

### 2.1.2 Depletion Interaction Between Two Spheres

#### 2.1.2.1 Interaction Potential Between Two Spheres Using the Force Method

When the depletion zones with thickness $\frac{\sigma}{2}$ around spherical colloidal particles with radius $R$ start to overlap, i.e., when the distance $r$ between the centers of the colloidal particles is smaller than $2R + \sigma = 2R_d$, a net force arises between the colloidal particles. For a convenient notation we defined an effective depletion radius $R_d$ \[ R_d = R + \frac{\sigma}{2}. \] (2.16)

This (attractive) force originates from an uncompensated (osmotic) pressure due to the depletion of penetrable hard spheres from the gap between the colloidal particles. This is depicted in Fig. 2.4 from which we immediately deduce that the uncompensated pressure acts on the surface between $\theta = 0$ and $\theta_0 = \arccos\left(\frac{r}{2R_d}\right)$. 

![Fig. 2.4](image)}
For obvious symmetry reasons only the component along the line connecting the centers of the colloidal spheres contributes to the total force. For the angle $\theta$ this component is $P \cos \theta$ where the pressure is $P = n_k T$. The surface on which this force acts between $\theta_0$ and $\theta_0 + d\theta$ equals $2\pi R^2 \sin \theta d\theta$. The total force between the colloidal spheres is obtained by integration over $\theta$ from 0 to $\theta_0$

$$
\frac{K_s(r)}{n_k T} = -2\pi(R + \sigma/2)^2 \int_{0}^{\theta_0} \sin \theta \cos \theta d\theta
$$

$$
= -\pi R^2 \left[ 1 - \left( \frac{r}{2R_d} \right)^2 \right] \quad 2R \leq r < 2R_d
$$

$$
= 0 \quad r \geq 2R_d.
$$

This result was also obtained by Asakura and Oosawa [1]. The minus sign in the right-hand side of (2.17) implies that the force is attractive.

Exercise

Show that (2.17) can also be written as the pressure times the area of the overlap of the depletion zones (see Fig. 2.4).

The depletion potential is now obtained by integration of the depletion force (2.17)

$$
W_s(r) = \int_{r}^{2R_d} K_s(r) \, dr
$$

$$
= -n_k T V_{ov}(r) \quad 2R \leq r < 2R_d
$$

$$
= 0 \quad r \geq 2R_d,
$$

with

$$
V_{ov}(r) = \frac{4\pi}{3} R_d^3 \left[ 1 - \frac{3}{4} \frac{r}{R_d} + \frac{1}{16} \left( \frac{r}{R_d} \right)^3 \right]
$$

which can also be written as

$$
V_{ov}(h) = \frac{\pi}{6} (\sigma - h)^2 (3R + \sigma + h/2)
$$

This result of (2.19a), in which $r$ is the variable, was first obtained by Vrij [2]. In (2.19b) the variable is $h$ and was already given (without explicit derivation) in (1.22). Both (2.19a) and (2.19b) are frequently used in the literature. Note that $W_s(r)$ in (2.18) is equal to pressure times the overlap volume $V_{ov}$. The reason for this simple form will become clearer after consideration of the interaction between two spheres using the extended Gibbs equation. In the limit that $\sigma/2 \ll R$ the force (2.17) and potential (2.18) between the spheres take very simple forms:
\[ K_s(h) = -\pi R (\sigma - h) \]  
\[ W_s(h) = -\pi R \frac{1}{2} (\sigma - h)^2, \]
for separations \( h = r - 2R \) smaller than \( \sigma \)

**Exercise**

Derive (2.20) and (2.21) from (2.17) and (2.18).

### 2.1.2.2 Interaction Potential Between Two Spheres from the Extended Gibbs Adsorption Equation

Applying exactly the same line of reasoning as for the derivation of the extended Gibbs adsorption equation for two flat plates, see (2.9), we now obtain

\[- \left( \frac{\partial W_s}{\partial \mu} \right) = N(r) - N(\infty),\]  
\[ N(r) = N(\infty) \]  
where \( N(r) \) is the number of penetrable hard spheres in the system when the colloidal spheres are at centre-to-centre separation \( r \) and \( N(\infty) \) that at infinite separation. Clearly, the difference between \( N(r) \) and \( N(\infty) \) is caused by the overlap of the depletion zones

\[ N(r) - N(\infty) = n_b V_{ov}(r) \]
\[ = 0 \quad 2R \leq r < 2R_d \]
\[ r \geq 2R_d \]

with \( V_{ov} \) defined in (2.19a, b). Integration of (2.22) using (2.23) and (2.15) immediately leads to the interaction potential (2.18). This route to the interaction potential makes it clear why the overlap volume of the depletion zones appears.

### 2.1.3 Depletion Interaction Between a Sphere and a Plate

The force method and the extended Gibbs adsorption equation can also be applied to obtain the depletion interaction between a sphere and a flat plate. For the Gibbs adsorption route we use (again)

\[- \left( \frac{\partial W_{sp}}{\partial \mu} \right) = N(h) - N(\infty),\]
where now \( N(h) \) is the number of penetrable hard spheres in the system when the colloidal sphere is at a separation \( h \) from the plate and \( N(\infty) \) is that at infinite
separation. Again the difference between \( N(h) \) and \( N(\infty) \) is caused by the overlap of the depletion zones, now of the sphere and of the plate (see Fig. 2.5)

\[
\frac{N(h) - N(\infty)}{n_b} = V_{ov}(h) = \frac{1}{3} \pi (\sigma - h)^2 \left( 3R + \frac{\sigma}{2} + h \right) \quad 0 \leq h < \sigma \\
= 0 \quad h \geq \sigma,
\]

Integration of (2.24) now leads to

\[
\frac{W_{sp}(h)}{n_b kT} = -\frac{1}{3} \pi (\sigma - h)^2 \left( 3R + \frac{\sigma}{2} + h \right) \quad 0 \leq h < \sigma \\
= 0 \quad h \geq \sigma. \tag{2.25}
\]

For \( R \gg \sigma \) (2.25) simplifies to

\[
W_{sp}(h) = -n_b kT \pi R (\sigma - h)^2 \quad 0 \leq h < \sigma, \tag{2.26}
\]

which is twice (2.21).

### 2.1.4 Derjaguin Approximation

Some of the above results also follow directly from the so called Derjaguin approximation. Derjaguin [10] showed that there exists a simple (approximate) relation for the force between curved objects and the interaction potential between two flat plates. In the Derjaguin approximation the spherical surface is replaced by a collection of flat rings. Consider two spheres with radius \( R \) at a center-to-center
distance \( r = 2R + h \). The distance \( H \) between the sphere surfaces at a distance \( z \) from the line joining the centers is \( H = h + 2\Delta \), where \((R - \Delta)^2 + z^2 = R^2\) (see Fig. 2.6). When the range of interaction is short it is sufficient to consider only small values of \( h/R \) or \( z/R \), see Fig. 2.7. For \( z \ll R \) we can write to a good approximation \( \Delta = z^2/2R \). Hence \( H = h + z^2/R \) and thus \( dH = (2z/R)dz \). The interaction between two spheres can now be written as the sum (integral) of the interactions of flat rings with radius \( z \) and surface \( 2\pi z \) at a distance \( H \) from each other (see Fig. 2.7). Assuming that the interaction is sufficiently short-ranged, the contribution of rings with high values of \( H \) may be neglected, and thus the integration may be extended to \( z = \infty \). We obtain

\[
W_s(h) = \int_0^\infty W(H)2\pi z \, dz
\]

\[
= \pi R \int_h^\infty W(H) \, dH
\]

(2.27)
and hence

\[ K_s(h) = -\frac{\partial W_s(h)}{\partial h} = \pi RW(h). \]  \hspace{1cm} (2.28)  

Here \( W(h) \) is the interaction potential between two flat plates at distance \( h \). Clearly this approximate relation between the force for spheres and the interaction potential for plates is more accurate the larger the radius of the spheres compared to the range of the interaction. In this chapter we shall frequently use this Derjaguin approximation. It is a useful tool which, under the right conditions (see above), is very accurate but one has to be careful and be aware of its limitations.

With respect to the depletion interaction the Derjaguin approximation becomes accurate when considering a depletion agent which is small compared to the radius of the colloidal spheres. For example, applying the Derjaguin approximation to (2.3), the case of penetrable hard spheres, using (2.28) immediately leads to (2.20).

Applying the Derjaguin approximation to the interaction between a sphere and a flat plate provides

\[ K_{sp}(h) = 2\pi RW(h). \]  \hspace{1cm} (2.29)  

This is an important relation as it allows one to obtain the interaction potential between two parallel plates from the measured force between a sphere and a wall (see Sect. 2.6)

**Exercise**

Derive equation (2.29).

From (2.29) it follows that

\[ W_{sp}(h) = 2\pi R \int_{h}^{\infty} W(h')dh'. \]  \hspace{1cm} (2.30)  

For the case of the penetrable hard sphere as depletion agent this leads to

\[ W_{sp}(h) = -n_b kT \pi R (\sigma - h)^2 \quad 0 \leq h < \sigma \]
\[ = 0 \quad h \geq \sigma, \]  \hspace{1cm} (2.31)  

in agreement with (2.26).
2.2 Depletion Interaction Due to Ideal Polymers

2.2.1 Depletion Interaction Between Two Flat Plates

2.2.1.1 Interaction Potential Between Two Flat Plates Using the Force Method

The simplest model to describe polymers is the ideal-chain model. For books on polymer physics where all the relevant background material can be found see [11–19]. In this model the polymer consists of \( M \) subunits, each with a fixed bond length \( b \), and their orientation is completely independent of the orientation and positions of previous monomers, even to the extent that two different monomers can occupy the same position in space: there is no excluded volume. This model plays the same role in polymer physics as an ideal gas in molecular physics. It allows to describe the polymer chain as a (Gaussian) random walk of \( M \) steps, as depicted in Fig. 2.8.

The average value \( \langle R \rangle \) of the end-to-end vector \( R \) joining one end of the polymer to the other is zero, as ‘negative’ steps have the same probability as ‘positive’ ones. Mathematically, the probability of the end-to-end vector being \( R \) is the same as it being \(-R\) so that, for symmetry reasons, the two contributions cancel in the average. A straightforward calculation (see any of the references [11–14, 17, 19]) shows that \( \langle R^2 \rangle \), the average of the square of \( R \) is given by

\[
\langle R^2 \rangle = M b^2.
\]  

This quantity is a measure of the size of the polymer chain. We see that the size of the ideal polymer chain, being proportional to \( \sqrt{M} \), is much smaller than the total unfolded contour length \( M b \) of the polymer.

Another commonly used and convenient quantity to describe the size of a polymer is the radius of gyration \( R_g \), the root-mean-square of the average monomer position from the center of mass which becomes

\[
R_g^2 = \frac{1}{6} M b^2.
\]  

Fig. 2.8 Sketch of a random walk chain consisting of monomers with length \( b \). For any given walk the end-to-end vector \( R = \sum r_i \)
The result $R_g = b\sqrt{M/6}$ holds for a Gaussian chain in the bulk solution.

We now consider an ideal Gaussian chain confined between two (large) flat plates with area $A$ at a plate separation $h$, see Fig. 2.9.

For the computation of segment density profiles in polymer solutions near interfaces one can use the fact that there is a close analogy between the diffusion of a Brownian particle and the flight of a random walk [20, 21]. A diffusion-like equation can be derived to evaluate the partition function of polymer chains. Given the boundary condition this ‘diffusion’ equation can be solved. The partition function $z(h)$ of one confined chain is given by [1, 22, 23]

$$z(h) = V\chi(h), \quad (2.34)$$

where $V = A \cdot h$ is the volume of the system and

$$\chi(h) = \frac{8}{\pi^2} \sum_{n=1,3,5,...} \frac{1}{n^2} \exp\left(-\frac{n^2\pi^2 R_g^2}{h^2}\right). \quad (2.35)$$

For a derivation of the above expression see for instance [24] or Chap. 2 in [14]. Note that since

$$\sum_{n=1,3,5,...} \frac{1}{n^2} = \frac{\pi^2}{8}$$

clearly

$$0 \leq \chi(h) \leq 1. \quad (2.36)$$

Exercise

Show that (2.35) can be approximated as [25]

$$\chi(h) = \frac{8}{\pi^2} e^{-\pi^2 R_g^2/h^2}, \quad 0 \leq h \leq \frac{8R_g}{\sqrt{\pi}},$$

$$= 1 - \frac{4R_g}{h\sqrt{\pi}}, \quad h > \frac{8R_g}{\sqrt{\pi}}. \quad (2.37)$$
Since the ideal chains do not interact the partition function for $N$ confined chains can be written as

$$Z(h) = \frac{z(h)^N}{N!}.$$  \hfill (2.38)

The Helmholtz energy is given by

$$F(h) = -kT \ln Z(h).$$  \hfill (2.39)

Hence the result

$$F(h) = NkT \left[ \ln \left( \frac{N}{V} \right) - 1 - \ln \chi(h) \right]$$  \hfill (2.40)

is obtained after insertion of (2.38). This free energy can be written as

$$F(h) = F_{\text{unconfined}} - T \Delta S(h),$$  \hfill (2.41)

where $\Delta S(h)$ is the entropy of confinement:

$$\Delta S(h) = N \Delta s(h) = N k \ln \chi(h).$$  \hfill (2.42)

From (2.36) it follows that the confinement entropy is negative, as expected, because confinement leads to a decrease of the entropy. From the free energy (2.39) we obtain for the pressure of the chains inside the plates

$$P_i = - \left( \frac{\partial F}{\partial V} \right) = kT n_i \left[ 1 + \frac{\hbar}{\chi} \frac{\partial \chi}{\partial h} \right]$$  \hfill (2.43)

where $n_i = (N/V)_i$ is the number density of the ideal chains between the plates. The first term $kT n_i$ corresponds to the Van ’t Hoff law. Likewise, the pressure of the ideal chains outside the plates is given by

$$P_o = n_b kT,$$  \hfill (2.44)

where $n_b$ is the bulk number density of the polymer chains. Using Einstein fluctuation theory [26, 27] it follows immediately that

$$n_i = e^{\Delta s/k} n_b = \chi n_b.$$  \hfill (2.45)

**Exercise**

Derive (2.45) by using the equality of the chemical potential of the ideal chains inside and outside the plates $\mu_i = \mu_o$.

Combining (2.1), (2.43), (2.44), and (2.45) we find for the force per unit area, $K(h)$, between the plates
Again this result was first derived by Asakura and Oosawa [1]. Integration of (2.46) yields the interaction potential per unit area $W(h)$ between the plates [28]

$$W(h) = -n_b kT \left[ \frac{4R_g}{\sqrt{\pi}} - h + h\chi(h) \right]. \quad (2.47)$$

Here we have used that

$$\lim_{h \to \infty} [h - h\chi(h)] = \frac{4R_g}{\sqrt{\pi}} \quad (2.48)$$

according to (2.37). Comparing (2.47) with the interaction potential (2.3) between flat plates due to penetrable hard spheres we find that the contact potentials ($h = 0$) match if we take $\sigma = 4R_g/\sqrt{\pi} = 2.26R_g$. A plot of the two potentials is given in Fig. 2.10. For small $h$, where $\chi(h)$ is negligible, the two potentials coincide: this is in the region $0 < h < 3R_g/2$. For $h > 2R_g$ the two potentials deviate because the discontinuous behaviour of (2.3) is replaced by the smooth crossover of (2.47). In the transition region ideal polymers have a longer range of attraction than penetrable hard spheres. Eisenriegler [29] has shown that (2.47) is identical to (2.3) (with $\sigma = 4R_g/\sqrt{\pi}$) up to and including terms of order $h^4$.

### 2.2.1.2 Interaction Potential Between Two Flat Plates from the Extended Gibbs Equation

From (2.45) and (2.11) it follows that

$$\Gamma(h) = [n_i(h) - n_b]h = n_b[\chi(h)h - h] \quad (2.49)$$
and hence, in view of (2.48)

$$\Gamma(\infty) = -n_b \frac{4R_g}{\sqrt{\pi}}$$  \hspace{1cm} (2.50)

Substituting (2.49) and (2.50) in (2.13) and using the fact that ideal chains show ideal thermodynamic behaviour, i.e.,

$$\mu = kT \ln n_b,$$

we obtain for the interaction potential per unit area $W(h)$ between two plates again the result given by (2.47). While the above thermodynamic route to the calculation of the adsorption is very efficient (as thermodynamics always is!) it is instructive (and useful for future reference) to consider the calculation of $\Gamma$ starting from the polymer segment concentration profile $\phi(x)$ near a single flat plate (with bulk concentration $\phi_b$) and between two flat plates. Eisenriegler [30], and later Marques and Joanny [31], calculated the polymer concentration near one flat plate for ideal Gaussian ($M \gg 1$) chains and found the following expression for the relative polymer segment concentration $f(x) = \phi(x)/\phi_b$:

$$f(x) = 2\psi(z) - \psi(2z),$$  \hspace{1cm} (2.51)

with

$$\psi(z) = \text{erf}(z) + \frac{2z}{\sqrt{\pi}} e^{-z^2} - 2z^2 \text{erfc}(z),$$  \hspace{1cm} (2.52)

where $z$ is defined as $x/(2R_g)$ and $x$ is the distance from the surface. The (Gauss) error function $\text{erf}(y)$ is defined as

$$\text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-t^2} dt,$$

and the complimentary error function $\text{erfc}(y) = 1 - \text{erf}(y)$.

One can characterize the negative adsorption by the depletion layer thickness $\delta$, which is defined as

$$\delta = \int_0^\infty dx(1 - f(x)).$$  \hspace{1cm} (2.53)

For the case of ideal polymer chains near a flat plate with the profile (2.51), we find

$$\delta = \frac{2R_g}{\sqrt{\pi}},$$  \hspace{1cm} (2.54)

This is in full agreement with (2.50) as $\Gamma(\infty) = 2\Gamma_{\text{single wall}} = -n_b 2\delta$. 
Exercise

Derive $\delta = 2R_g/\sqrt{\pi}$ for ideal chains starting from its definition (2.53) and using the profile (2.51).

A simple approximation for the rather involved (2.51) is [28, 32]

$$f(x) = \tanh^2\left(\frac{x}{\delta}\right)$$

(2.55)

with $\delta$ given by (2.54).

In Fig. 2.11 we depict the concentration profile of an ideal polymer near a flat wall and its replacement by a step profile with width $\delta = 2R_g/\sqrt{\pi}$ (dashed). The simple approximation (2.55) reproduces the exact result within an accuracy of 1%.

Exercise

Show that the profile $f(x) = \tanh^2(x/\delta)$ has a depletion thickness $\delta$.

For the concentration profile between two flat plates separated by a distance $h$ the following product function approximation has been proposed [28]

$$\frac{\varphi(x)}{\varphi_b} = f(x)f(h-x).$$

(2.56)

In (2.56), $\varphi(x)$ is the polymer segment concentration between the plates and $f(x)$ and $f(h-x)$ are the individual one plate profiles given by (2.51) or, more simply by (2.55). The concentration near a single plate, say plate 1, can be expressed by a Boltzmann factor as $f(x) = \exp[-W_{\text{wall}}(x)/kT]$, where $W_{\text{wall}}(x)$ is the free energy giving rise to the profile. For the second plate, located at a distance $h$, we can then write $f(h-x) = \exp[-W_{\text{wall}}(h-x)/kT]$. Subsequently, the product function (2.56) follows from the superposition approximation:

$$W_{\text{wall,tot}}(x) = W_{\text{wall}}(x) + W_{\text{wall}}(h-x),$$
which is expected to work well for sufficiently large \( h/R_g \). This is indeed supported by computer simulations [28], see the comparison in Fig. 2.12. For \( h/R_g < 3 \), the product function overestimates the segment concentration between the plates. In such narrow slits the configurations of an ideal chain are then affected by both walls, which is not accounted for by the superposition approximation. While the relative deviation of the production function is largest for small plate separation \( h \), for these distances \( \Gamma(h) \to 0 \) and hence the absolute error is small. The resulting adsorption is plotted in Fig. 2.13 (dashed curve). The exact result from (2.49) (with (2.35) for \( \chi(h) \)) is plotted as the solid curve. We conclude therefore that the product function gives overall a good prediction for the adsorption and we will use it to calculate the depletion interaction between two spheres due to ideal polymers using the extended Gibbs adsorption equation.
2.2.2 Interaction Between Two Spheres

2.2.2.1 Interaction Between Two Spheres from the Derjaguin Approximation

Using the Derjaguin approximation (2.27) for the force between two spheres the interaction potential between the spheres can be obtained from

\[
W_s = \pi R \int_{h}^{\infty} W(h') dh',
\]

(2.57)

where \(W(h)\) is the interaction potential per unit area between flat plates (2.47). The result for \(q = 0.01\) is plotted in Fig. 2.14. Eisenriegler [29] obtained the following analytical expression

\[
W_s(h) = -n_bkT R^2 g \left( 4\pi \ln \frac{2}{h} - 4\sqrt{\frac{\pi}{R_g}} \frac{h}{R_g} + \frac{\pi h^2}{2 R_g^2} \right)
\]

(2.58)

for small values of \(h\) valid up to and including terms of order \(h^4\). This equation matches the numerical results for \(R/R_g = 100\) presented in Fig. 2.14 very closely for \(h < (3/2)R_g\), see [28, 29].

Comparing the expression (2.21) for penetrable hard spheres and (2.58) for ideal chains reveals that we match the contact potentials for

\[
\sigma = \sqrt{8 \ln(2) R_g}
\]

The result \(\sigma = 2.35R_g\) agrees closely (within 5%) with the value \(\sigma = 4R_g/\sqrt{\pi} = 2.26R_g\) for flat plates. Hence in the limit \(R \gg R_g\) ideal polymers behave almost as penetrable hard spheres with a diameter \(\sigma \approx 2R_g\), just as for ideal chains between flat plates. In the next section we will see that this picture changes when \(R \lesssim R_g\).
2.2.2.2 Interaction Potential Between Two Spheres from the Extended Gibbs Equation

The limitation of the Derjaguin approximation is that it only provides reliable results for \( R \geq R_g \). To obtain results for the interaction potential between spheres for arbitrary \( q = R_g / R \) we use the extended Gibbs adsorption equation. Taniguchi et al. [33] and, independently, Eisenriegler et al. [34] found the concentration profile of Gaussian ideal polymer chains around a single hard sphere with radius \( R \) which reads

\[
fs(x) = \frac{(x/R)^2 + 2(x/R)\psi(z) + f(x)}{(x/R + 1)^2},
\]

where \( z \) again equals \( x/2R_g \) and \( x \) is now the distance from the surface of the sphere; the functions \( f(x) \) and \( \psi(z) \) are defined in (2.51) and (2.52). A simpler, yet accurate, form of (2.59) is [32]

\[
fs(x) = \left( \frac{x}{R} + \frac{x}{R} + \tanh(x/\delta) \right)^2.
\]

For various ratios of \( q = R_g / R \) we plotted the profiles \( fs(x) \) in Fig. 2.15. For \( R \ll R_g \), the Odijk [35] result

\[
fs(x) = \left( \frac{x}{x + R} \right)^2
\]

is recovered, which is independent of the polymer length scale. For large hard sphere radii (\( q = 0.1 \)) we see that the sphere profile approaches that of a flat plate.
However, for $R_g/R = 1$ the depletion layer thickness already becomes significantly smaller than $2R_g/\sqrt{\pi}$ and it further decreases with increasing $q$.

**Exercise**

(a) Show that in the limit $R \gg R_g$ the expression (2.59) for the profile around spheres becomes equal to the expression (2.51) for the profile at a flat plate.

(b) Give a physical argument why the concentration profile shifts towards the particle surface when $R_g/R$ increases.

Starting from (2.59) we can obtain an analytical expression for the depletion thickness around a sphere $\delta_s$, which is now defined by

$$
\frac{4\pi}{3} \left[ (R + \delta_s)^3 - R^3 \right] = \int_0^\infty 4\pi(R + x)^2(1 - f_s(x))dx.
$$

After carrying out the integration of the right-hand side of (2.61) we obtain

$$
\frac{\delta_s}{R_g} = \left[ \left( 1 + \frac{6q}{\sqrt{\pi}} + 3q^2 \right)^{1/3} - 1 \right] / q.
$$

Note that in the limit $q \to 0$, (2.62) yields, as expected, the flat plate result $\delta_s/R_g = 2/\sqrt{\pi}$. The result in (2.62) holds for Gaussian ideal chains, implying the segment size $b$ is smaller than all other length scales, $R_g$ and $R$. For freely-jointed ideal chains the depletion thickness also depends on the size ratio $b/R$ for $R \lesssim 50b$ [38].

**Exercise**

(a) Show that in the limit $R \gg R_g$ (and hence $R \gg \delta_s$) expression (2.61) for $\delta_s$ reduces to the flat plate equation (2.53) for $\delta_s$.

(b) Carry out the integrations in (2.61) and show that the result for $\delta$ is given by (2.62).

The result for the relative depletion thickness $\delta/R_g$ as a function of the size ratio $q = R_g/R$ is plotted in Fig. 2.16.

We showed in Sect. 2.2.1 that the product function (2.56) describes the polymer concentration profile between two flat plates quite well. Here we apply the product function Ansatz to calculate the concentration profile around two spheres. We assume that the local polymer concentration $n_s(r)$ in every point $P$ (see Fig. 2.17) outside the spheres is given by

$$
\frac{n_s(r)}{n_b} = f_s(x_1)f_s(x_2),
$$

(2.63)
where \( f_s(x_i) \) is the polymer concentration profile around a sphere given by (2.59) with \( x_i \) the closest distance to the surface of the sphere (see Fig. 2.17). The interaction between two spheres can now be calculated from (2.22), which for ideal chains becomes

\[
\frac{W_s(h)}{kT} = N(h) - N(\infty),
\]

(2.64)

where \( N(h) \) is the number of polymer molecules in the system when the colloidal particles are at a distance \( h \) (see Fig. 2.17) and \( N(\infty) \) that when the colloidal particles are infinitely far apart. The quantity \( N(h) \) can be calculated numerically from

\[
N(h) = \int d\mathbf{r} n_s(\mathbf{r})
\]

(2.65)
using the profile function (2.63) and obviously

\[ N(\infty) = n_b \left( V - 2 \frac{4\pi}{3} (R + \delta_s)^3 \right). \]

The result for \( q = 0.01 \) is plotted in Fig. 2.18 (dashed curve). We normalised the interaction curve by dividing by the absolute value at contact. The depth of the interaction at contact can be computed and it is first compared to the result \( W_s(0)/kT = -4\pi R R_g^2 \ln(2) \) that follows from applying the Derjaguin approximation. We find a numerical value for \( W_s(0)/kT \) of \(-4\pi R R_g^2(0.76)\), which is close. In Fig. 2.19 we plot the results for different values of the size ratio \( q \). We observe that the range of the interaction becomes smaller with decreasing colloid radius \( R \) in agreement with the decrease of the depletion thickness \( \delta_s \) with decreasing colloid radius. In fact, by replacing in (2.18) \( \sigma/2 \) by \( \delta_s \) given by (2.62) we obtain interaction curves in good agreement with the results presented in Fig. 2.19 obtained from the extended Gibbs adsorption equation using the product function (2.63).
This brings us to the conclusion that as far as the depletion interaction is concerned ideal polymer chains to a good approximation can be replaced by penetrable hard spheres with a diameter \( \sigma = 2\delta_s \), where the depletion thickness \( \delta_s \) now depends on the size ratio \( q = R_g / R \). In dilute polymer solutions the ideal chain description suffices to describe depletion effects. In Chap. 4 we shall see that for polymers with excluded volume the depletion thickness not only depends on the size ratio \( q \) but also on the polymer concentration, see also [36, 39–41]. Also the (osmotic) pressure is no longer given by the ideal (Van ‘t Hoff) expression. Both features significantly affect depletion effects.

2.3 Depletion Interaction Due to Colloid Hard Spheres

2.3.1 Concentration Profiles Near a Hard Wall and Between Two Hard Walls

We now consider the depletion interaction due to (small) colloidal hard spheres with diameter \( \sigma \). At very low concentration, where we may neglect the interaction between the spheres so the system can considered to be thermodynamically ideal, the results for the depletion interaction are identical to those for penetrable hard spheres. At higher concentrations, say at volume fractions larger than a few percent, the interactions between the spheres cannot be neglected. This has two important consequences for the depletion interaction. First of all the pressure and chemical potential are no longer given by the ideal expressions. The corrections to ideal behaviour can be written in terms of the virial series (see textbooks on statistical thermodynamics, e.g., Hill [42] or Widom [43]):

\[
P = \frac{1}{n_b kT} + B_2 n_b + \cdots \quad (2.66)
\]

\[
\mu = \frac{\ln n_b + 2B_2 n_b + \cdots}{kT} \quad (2.67)
\]

Now \( n_b \) is the bulk concentration of (small) hard spheres. The quantity \( B_2 \) is the second osmotic virial coefficient

\[
B_2 = \frac{2\pi \sigma^3}{3} = 4v_0, \quad (2.68)
\]

where \( v_0 = \pi \sigma^3 / 6 \) is the volume of a hard sphere. Secondly, the interactions between the particles among themselves and with a wall leads to a concentration profile near the wall. Obviously, in a layer at the wall with thickness \( \sigma / 2 \) no centers of the hard spheres can penetrate. In the case of penetrable hard spheres the concentration takes on the bulk value \( n_b \) outside the depletion layer. However, in the case of hard spheres the interactions lead to an effective attraction between a
sphere and the wall and the concentration profile at distance \(x = \sigma/2 + y\) from the wall can be written as

\[ n(x) = n_b \exp\left[-W_{\text{wall}}(x)/kT\right], \tag{2.69} \]

where \(W_{\text{wall}}(x)\) is the effective interaction between the hard sphere and the wall. In fact this is the potential of mean force between the sphere and the wall due to the other hard spheres. To lowest order in density we can write

\[ W_{\text{wall}}(x) = -n_b kT v(y) \tag{2.70} \]

where \(v(y)\) is the overlap volume of the depletion zone around the sphere and the depletion layer of the wall depicted in Fig. 2.20,

\[ v(y) = \frac{\pi}{3} \left(2\sigma^3 - 3\sigma^2 y + y^3\right) \quad 0 \leq y \leq \sigma. \tag{2.71} \]

or

\[ n_b v(y) = \phi \left(4 - 6 \frac{y}{\sigma} + 2 \frac{y^3}{\sigma^3}\right) \quad 0 \leq y \leq \sigma. \tag{2.72} \]

Here \(\phi = n_b \pi \sigma^3 / 6\) is the volume fraction of the (small) spheres.

From (2.69–2.71) we obtain the lowest order in density \(n(x)\)

\[ \frac{n(x)}{n_b} = \begin{cases} 0 & 0 \leq x < \sigma/2 \\ 1 + n_b v(y) & \sigma/2 \leq x \leq 3\sigma/2 \end{cases} \tag{2.73} \]

This profile of hard spheres at a single wall to order \(n_b^2\) is depicted in Fig. 2.21. We see that in addition to the depletion layer there is also an ‘accumulation’ layer, where \(n(x) > n_b\). The hard spheres located close to the depletion layer tend to ‘push’ one another into the layer next to the excluded depletion layer resulting in the accumulation. As we will see later this layer has important consequences for the depletion interaction. The concentration profile at a single wall to order \(n_b^3\) was calculated by Fisher [44].
For the calculation of the depletion interaction due to hard spheres we need the concentration profile between two confining walls. This problem was treated analytically by Glandt [45] and by Antonchenko et al. [46] using Monte Carlo computer simulations. Like for a single wall we present the calculation of the concentration profile between two confining walls to order \( n^2 \). For \( h < \sigma \), no spheres can penetrate between the walls and hence the concentration is zero. For \( \sigma < h < 2\sigma \), the depletion zone of a sphere overlaps with the depletion zones of both walls (see Fig. 2.22) and we can write

\[
\frac{n(x)}{n_b} = 1 + n_b v(y) + n_b v(h - \sigma - y), \quad 0 \leq y \leq h - \sigma,
\]

with \( n_b v \) defined in (2.72).

Fig. 2.21 Density profile \( n(x) \) of hard spheres with \( \phi = 0.1 \) as a function of the distance from the wall \( x \) (2.73)

Fig. 2.22 A sphere between two walls. Hatched areas are the overlap volume between the hard sphere and the hard walls.
The profile of hard spheres between two confining walls to order $n_b^{2}$ for $\sigma \leq h \leq 2\sigma$ is depicted in Fig. 2.23. For $h > 2\sigma$ there is no longer simultaneous overlap of the depletion layer of a sphere with the depletion layers of the confining walls. The profile then simply is the sum of the profiles of the two separate walls; there is no depletion-induced attraction.

### 2.3.2 Depletion Interaction Between Two Flat Plates

#### 2.3.2.1 Interaction Potential Between Two Flat Plates from the Force Method

We follow the work of Mao et al. [47]. The same results as presented here were obtained earlier by Walz and Sharma [48] using a somewhat different method. The starting point for our treatment is a result by Henderson [49] that the force per unit area between two parallel hard plates immersed in a suspension of hard spheres is given by

$$K = P_i - P_o = kT(n_i - n_o),$$

where $n_i$ and $n_o$ are the contact densities of the hard spheres inside and outside the plates. A contact density is ensemble-averaged the density at the surface. This result can be explained as follows. The particle velocities are separable degrees of freedom and therefore always obey the Maxwell–Boltzmann distribution. The force per unit area on a hard plate is therefore given rigorously by elementary kinetic theory as [50]

$$P = n^*kT,$$
where \( n^* \) is the number density of particles at a distance corresponding to the point of impact (the position at which a particle hits the surface). This is, of course, the contact density. This argument applies whenever there is a hard interaction between the particles and the plate [50]. The generality of (2.75) will also be exploited in Sects. 2.4 and 2.5, where we consider the depletion interaction due to hard rods and hard disks. Up to order \( n_b^2 \) we find from (2.73) that

\[
\frac{P_o}{kT} = n_o = n_b [1 + n_b v(0)]
\]

or, in terms of \( \phi \),

\[
\frac{P_o v_0}{kT} = \phi + 4\phi^2.
\]

This is in agreement with the virial series (2.66) using the second virial coefficient (2.68). Between the plates we find

\[
\frac{P_i}{kT} = 0 \quad 0 \leq h < \sigma
\]

\[
= n_b [1 + n_b v(0) + n_b v(h - \sigma)] \quad \sigma \leq h < 2\sigma
\]

\[
= n_b [1 + n_b v(0)] \quad h \geq 2\sigma
\]

Hence

\[\frac{K(h)}{n_b kT} = -1 - 4\phi \quad 0 \leq h < \sigma\]

\[= \phi [4 - 6\lambda + 2\lambda^3] \quad \sigma \leq h < 2\sigma\]

\[= 0 \quad h \geq 2\sigma\]

where \( \lambda = (h - \sigma)/\sigma \), which runs from 0 at \( h = \sigma \) to 1 at \( h = 2\sigma \).

The depletion force depicted in Fig. 2.24 jumps from negative (attractive) at \( h = \sigma^- \) to positive (repulsive) at \( h = \sigma^+ \). The key idea behind the origin of the repulsive part of the depletion force is that for small \( \lambda \) the mutual repulsion of spheres is substantially reduced due to the fact that the excluded volumes of the spheres are hidden behind the depletion zones of the walls. In the limit \( h = \sigma^+ \), the spheres behave effectively thermodynamically ideal. To match the chemical potential (2.67) of the spheres in the bulk the number density inside the gap must be

\[
n_i = n_b [1 + 2B_2 n_b],
\]

and hence for \( h = \sigma^+ \)

\[
P_i = kT n_b [1 + 2B_2 n_b],
\]
giving rise to a maximum repulsive depletion force

\[ K_{\text{max}}(h = \sigma^+) = P_i - P_o = 44kTn_b\phi \]  \hspace{1cm} (2.83)

**Exercise**

Derive (2.81)

Integrating the force (2.80) yields the interaction potential per unit area \( W(h) \) between the plates

\[
\frac{W(h)}{kTn_b} = \sigma \left( \lambda + \frac{3}{2} \phi + 4\lambda \phi \right) \hspace{1cm} 0 \leq h < \sigma
\]

\[
= \sigma \phi \left( \frac{3}{2} - 4\lambda + 3\lambda^2 - \frac{1}{2} \lambda^4 \right) \hspace{1cm} \sigma \leq h < 2\sigma \hspace{1cm} (2.84)
\]

\[
= 0 \hspace{1cm} h \geq 2\sigma
\]

In Fig. 2.25 we present the interaction potential which has a significant attraction at small separation distance \( h \), but also has a repulsive part of the potential.

**Exercise**

(a) Explain why, whereas the force \( K \) has a discontinuity at \( h = \sigma \), the interaction potential \( W \) is continuous at that point.

(b) Why is the interaction potential still repulsive for \( h \) just below \( \sigma \), while the force is attractive?
2.3.2.2 Interaction Potential Between Two Flat Plates from the Extended Gibbs Equation

From the depletion layer with thickness $\sigma/2$ and concentration profile (2.73) it follows that the adsorption on a single plate is given by

$$
\Gamma_{\text{single wall}} = -\frac{\sigma}{2} n_b + n_b^2 \int_0^{\sigma} v(x) dx
$$

(2.85)

Hence

$$
\Gamma(\infty) = 2\Gamma_{\text{single wall}}
$$

$$
= -\sigma n_b + n_b^2 \frac{\pi}{4} \sigma^4
$$

(2.86)

For two confining walls it is clear that for $h < \sigma$ no spheres can penetrate the gap between the walls. Hence

$$
\Gamma(h) = \sigma n_b (3\phi - 1)
$$

(2.87)

Using the concentration profile (2.74) we obtain for $\sigma \leq h < 2\sigma$

$$
\Gamma(h) = -\sigma n_b + n_b^2 \int_0^{\sigma} [v(x) + v(h - \sigma - x)] dx
$$

$$
= -\sigma n_b + \frac{2\pi}{3} n_b^2 \sigma^4 \left[ 2\lambda - \frac{3}{2} \lambda^2 + \frac{1}{4} \lambda^4 \right]
$$

(2.88)
or
\[
\frac{\Gamma(h)}{n_b \sigma} = \phi [8\lambda - 6\lambda^2 + \lambda^4] - 1
\]  
(2.89)

For \( h \geq 2\sigma \)
\[
\Gamma(h) = \Gamma(\infty).
\]  
(2.90)

Combining (2.86–2.90) gives
\[
\frac{\Gamma(h) - \Gamma(\infty)}{n_b \sigma} = 1 - \frac{h}{\sigma} - 3\phi; \quad 0 \leq h < \sigma
\]
\[
= -\phi [3 - 8\lambda + 6\lambda^2 - \lambda^4]; \quad \sigma \leq h < 2\sigma
\]
\[
= 0; \quad h \geq 2\sigma
\]  
(2.91)

Taking into account that the chemical potential is now given by (2.67) we obtain from (2.13)
\[
W(h) = -kT \int_0^{n_b} \left[ \Gamma(h) - \Gamma(\infty) \right] \left[ \frac{1}{n_b} + 2B_2 \right] \, dn_b.
\]  
(2.92)

Substituting (2.91) in (2.92) after some algebra yields (2.84). Note that in all cases considered so far (penetrable hard spheres, polymers) the quantity \([\Gamma(h) - \Gamma(\infty)]\) was always positive (or zero) for all values for \( h \). Here we see that due to accumulation effects in the concentration profiles \([\Gamma(h) - \Gamma(\infty)]\) is negative for a certain range of \( h \) values. This leads to a positive interaction energy as is clear from (2.92).

Such a repulsive contribution to the depletion interaction originates from excluded volume interactions between the depletants; in case of ideal polymers and penetrable hard spheres it is absent. One might expect accumulation effects also in the case of interacting polymers. From Monte Carlo simulation studies [51] and numerical self-consistent field computations [52, 53] it follows that interacting polymers do contribute to repulsive depletion interactions but with a strength of the repulsion that is nearly imperceptible.

### 2.3.3 Depletion Interaction Between Two (Big) Spheres

Using the Derjaguin approximation (2.27) we obtain the interaction between two big spheres due to the small spheres by integration:
\[
W_s(h) = \pi R \int_h^{2\sigma} W(h') \, dh'.
\]  
(2.93)
Using (2.84) for the interaction potential per unit area in (2.93) we obtain

\[
\frac{W_s(h)}{kT} = -\frac{R}{\sigma} \left[ 3\phi \lambda^2 - \phi^2 (12 - 45\lambda - 60\lambda^2) \right] \quad 0 \leq h < \sigma
\]

\[
= \frac{R\phi^2}{5\sigma} \left[ 12 - 45\lambda + 60\lambda^2 - 30\lambda^3 + 3\lambda^5 \right] \quad \sigma \leq h < 2\sigma
\]

\[
= 0 \quad h \geq 2\sigma,
\]

(2.94)

which has a positive maximum value of

\[
\frac{W_{s,\text{max}}}{kT} = \frac{12R}{5\sigma} \phi^2 \quad \text{at} \quad h = \sigma \left( 1 - \frac{3}{2} \phi \right),
\]

and a minimum value at contact

\[
\frac{W_{s,\text{min}}}{kT} = -\frac{3R}{\sigma} \left( \phi + \frac{1}{5} \phi^2 \right).
\]

(2.95)

In Fig. 2.26 we present the interaction potential between spheres (valid up to \(n_b^2\) or, equivalently, up to \(\phi^2\)). In [47] results are presented for the interaction valid up to \(n_b^3\) including a comparison with the computer simulation results of Biben et al. [54].

**Exercise**

(a) Derive the interaction potential between spheres (2.94) from the extended Gibbs adsorption equation in the limit \(R \gg \sigma\) (as is implicit when using the Derjaguin approximation).

(b) Show that (2.94) in the limit of first order \(\phi\) equals (2.21).
2.4 Depletion Interaction Due to Colloidal Hard Rods

Asakura and Oosawa [1, 55] already recognized that rod-like macromolecules are very efficient depletion agents. In retrospect the observations of Fåhraeus [56] that the rod-like protein fibrinogen has, on a weight basis, the strongest effect on the aggregation of red blood cells can be understood on the basis of its high efficiency as a depletion agent associated with its rod-like shape. Here we consider the interaction caused by rod-like colloids as depletants and focus on a simple case; infinitely thin hard rods of length \( L \). These rods have no excluded volume with respect to each other and hence behave thermodynamically ideally.

2.4.1 Depletion Interaction Between Two Flat Plates

2.4.1.1 Interaction Potential Between Two Flat Plates Using the Force Method

As we are dealing with hard plates and a hard wall we can again use (2.75) to calculate the force. The contact densities this time follow by considering the angles of the rods as a function of distance from the wall that lead to contact of an end point with the wall. First of all to make contact with the wall the distance of the center of the rod from the wall should be smaller than \( \frac{L}{2} \). At a distance from the wall \( x < \frac{L}{2} \) the angle that leads to contact is given by

\[
\theta_x = \arccos \left( \frac{x}{L/2} \right),
\]

(see Fig. 2.27). Outside the confining walls \( x \) runs from \( \frac{L}{2} \) to 0. Hence \( \theta_x \) runs from 0 to \( \pi/2 \), so using spherical coordinates we obtain

\[
n_o = n_b \int_0^{\pi/2} \sin \theta \, d\theta = n_b
\]

giving

![Fig. 2.27](Image)

Hard rod at a (hard) wall (left) and confined between two walls (right)
This result could have been written down at once as the infinitely thin rods behave ideally. Between two confining walls separated by a distance $h < L$ the second wall prevents contact configurations with the first wall for distances $x \geq h/2$. Hence

$$n_i = n_b \int_{\delta_{h/2}}^{\pi/2} \sin \theta \, d\theta = n_b \frac{h}{L} \quad 0 \leq h \leq L$$

$$= n_b \quad h > L$$

From this result (plotted in Fig. 2.28) it follows using (2.76) that

$$P_i = n_b kT \frac{h}{L} \quad 0 \leq h \leq L$$

$$= n_b kT \quad h > L \quad (2.98)$$

By combining (2.97) and (2.98) we obtain for the force

$$K(h) = P_i - P_o$$

$$= -n_b kT \left[ 1 - h/L \right] \quad 0 \leq h \leq L$$

$$= 0 \quad h > L \quad (2.99)$$

Integration of the force (2.99) yields the interaction potential per unit area $W(h)$ between the plates

$$W(h) = -\frac{1}{2} n_b kT \frac{(L - h)^2}{L} \quad 0 \leq h \leq L$$

$$= 0 \quad h > L \quad (2.100)$$
This result was first obtained by Asakura and Oosawa [55] (see also Auvray [57]). Mao et al. [58, 59] considered the depletion interaction due to long thin rods with a finite diameter $D$. Then the system is no longer ideal and the interaction potential contains higher order terms in $n_b$. Like in the case of hard spheres the interactions between the rods themselves and with the wall results in the accumulation of rods at the wall which in turn leads to a repulsive contribution to the depletion interaction. For details we refer to the papers by Mao et al. [58, 59].

### 2.4.1.2 Interaction Potential Between Two Flat Plates from the Extended Gibbs Equation

The concentration profile of the rods near a wall also follows by considering the allowed angles. For a rod at a distance $x<L/2$ from a single wall the angles ranging from $\theta_s$ (defined by (2.96)) to $\pi/2$ are allowed (see Fig. 2.27).

Hence

$$n(x) = n_b \int_{\theta_s}^{\pi/2} \sin \theta \, d\theta = n_b \frac{x}{L/2}. \quad (2.101)$$

(see Figs. 2.27 and 2.28). This provides an adsorbed amount at one wall

$$\Gamma_{\text{single wall}} = \int_0^{L/2} [n(x) - n_b] \, dx = -n_b L/4,$$

and thus

$$\Gamma(\infty) = 2\Gamma_{\text{single wall}} = -n_b L/2. \quad (2.102)$$

For two confining walls separated by a distance $h<L$

$$n(x) = \begin{cases} n_b \frac{x}{L/2} & 0 \leq x \leq h/2 \\ n_b \frac{h - x}{L/2} & h/2 \leq x \leq h \end{cases} \quad (2.103)$$

(see Fig. 2.29). Hence

$$\Gamma(h) = \int_0^h [n(x) - n_b] \, dx = n_b \left[ \frac{h^2}{2L} - h \right] \quad 0 \leq h \leq L$$

$$= -n_b \frac{L}{2} \quad h > L \quad (2.104)$$
Consequently,

\[ \Gamma(h) - \Gamma(\infty) = n_b \left( \frac{L - h}{2L} \right)^2 0 \leq h \leq L \]

\[ = 0 \quad h > L \quad (2.105) \]

Substituting (2.105) in (2.13) and carrying out the integration, taking account that \( \mu = kT \ln n_b \) (ideal behaviour) immediately results in the interaction potential (2.100). For the calculation and simulation of concentration profiles at walls of rods of finite thickness and the evaluation of the resulting depletion interaction to higher orders of \( n_b \), we refer to Mao et al. [60].

### 2.4.2 Interaction Between Two (Big) Colloidal Spheres Using the Derjaguin Approximation

Using the Derjaguin approximation (2.27) we obtain the interaction between two big spheres with radius \( R \gg L \) by integration

\[ W_s(h) = \pi R \int_h^L W(h')dh' . \]

Using (2.100) for the interaction potential per unit area in the above integration we obtain

\[ W_s(h) = -n_b kT \pi R \frac{(L - h)^3}{6L} . \quad (2.106) \]
This expression for the interaction potential is also valid to order \( n_b \) for long thin rods with a finite diameter \( D \) and we can then write (2.106) in the form

\[
W_s(h) = -\frac{2}{3} kT \phi \frac{R L}{D D} \left( 1 - \frac{h}{L} \right)^3, \quad (2.107)
\]

where

\[
\phi = n_b \frac{\pi}{4} L D^2 \quad (2.108)
\]

is the volume fraction of the rods. Comparing this expression for the depletion interaction between two big spheres with that for small spheres as depletant (2.94) for low \( \phi \) reveals that the factor \( L/D \), which usually is significantly larger than unity, is an important difference. Take as an example \( R = 1 \mu m, L = 200 \text{ nm} \) and \( D = 10 \text{ nm} \). Then the factor

\[
\frac{R L}{D D} = 2000,
\]

which implies that for a volume fraction of rods as low as 0.1% the depletion interaction will already be of order \( kT \). For small colloidal spheres with \( \sigma = 10 \text{ nm} \) this would require a volume fraction of about 1%.

The higher order terms calculated by Mao et al. [59], result, as in the case of small spheres as a depletion agent, in a repulsive barrier in the depletion interaction.

### 2.5 Depletion Interaction Due to Thin Colloidal Disks

Thin colloidal disks provide another example of an anisometric colloidal particle as an efficient depletion agent. This problem was first considered by Piech and Walz [61]. At the end of this section, where we compare spheres, rods and disks as depletion agents, we will see that the disk is intermediate in efficiency to induce depletion attraction between spheres and rods. Here we consider disks of diameter \( D \) and thickness \( L \), see Fig. 2.30. Notice that for the simplest case, i.e., infinitely thin hard disks, the excluded volume of the disks with respect to each other is non-zero and only in limit of the concentration going to zero will the disks behave thermodynamically ideal. We restrict ourselves to this limiting case.

#### 2.5.1 Depletion Interaction Between Two Flat Plates

##### 2.5.1.1 Interaction Potential Between Two Flat Plates from the Force Method

We again use (2.75) as the starting point for the calculation of the force. To make contact with the wall, the distance of the center of the disks from the wall should
be smaller than $D/2$. At a distance from the wall $x < D/2$ the angle between the normal of the disk and the normal of the wall that leads to contact is now given by

$$\theta_x = \arcsin \left( \frac{x}{D/2} \right).$$

(2.109) (see Fig. 2.30). Outside the confining walls $x$ runs from 0 to $D/2$. The contact density $n_o$ follows as

$$n_o = n_b \int_0^{\pi/2} \sin \theta \, d\theta = n_b$$

and hence (2.76)

$$P_o = n_b kT.$$

Between two confining walls separated by a distance $h < D$ the second wall prevents contact configurations with the first wall for distances $x \geq h/2$. Hence

$$n_i = n_b \int_0^{\theta_{h/2}} \sin \theta \, d\theta = n_b \left[ 1 - \sqrt{1 - (h/D)^2} \right] \quad 0 \leq h \leq D$$

$$= n_b \quad h > D$$

and hence

$$P_i = n_b kT \left[ 1 - \sqrt{1 - (h/D)^2} \right] \quad 0 \leq h \leq D$$

$$= n_b kT \quad h > D$$
This leads to the following expression for the force between the plates

\[ K(h) = P_I - P_o \]

\[ = -n_b kT \sqrt{1 - (h/D)^2} \quad 0 \leq h \leq D \]

\[ = 0 \quad \text{for} \quad h > D \] \hspace{1cm} (2.110)

Integration of the force (2.110) yields the interaction potential per unit area \( W(h) \) between the plates

\[ W(h) = -n_b kT \frac{D}{2} \left[ \frac{\pi}{2} - \frac{h}{D} \sqrt{1 - \left( \frac{h}{D} \right)^2} - \arcsin \left( \frac{h}{D} \right) \right]. \] \hspace{1cm} (2.111)

**Exercise**

Derive the interaction potential (2.111) from the force (2.110).

### 2.5.1.2 Interaction Potential Between Two Flat Plates from the Extended Gibbs Equation

The concentration profile of the disks near a wall also follows by considering the allowed angles [57]. For a disk at a distance \( x < D/2 \) from a single wall the angles ranging from 0 to \( \theta_x \) (defined by (2.109)) are allowed (see Fig. 2.30).

Hence

\[ n(x) = n_b \int_0^{\theta_x} \sin \theta \, d\theta = n_b \left[ 1 - \sqrt{1 - \left( \frac{x}{D/2} \right)^2} \right] \] \hspace{1cm} (2.112)
Fig. 2.32 Density profile of hard platelets between two walls for $h = 4D/5$

(see Fig. 2.31). Hence

$$\Gamma_{\text{single wall}} = \int_0^{D/2} [n(x) - n_b] \, dx = -n_b \frac{\pi}{8},$$

and thus

$$\Gamma(\infty) = 2\Gamma_{\text{single wall}} = -n_b \frac{\pi}{4}. \quad (2.113)$$

For two confining walls separated by a distance $h < D$

$$n(x) = n_b \left[ 1 - \sqrt{1 - \left( \frac{x}{D/2} \right)^2} \right] \quad 0 \leq x \leq \frac{h}{2}$$

$$= n_b \left[ 1 - \sqrt{1 - \left( \frac{h-x}{D/2} \right)^2} \right] \quad \frac{h}{2} \leq x \leq h \quad (2.114)$$

(see Fig. 2.32). Hence

$$\Gamma(h) = \int_0^h [n(x) - n_b] \, dx$$

$$= -n_b \frac{D}{2} \left[ \left( \frac{h}{D} \right) \sqrt{1 - \left( \frac{h}{D} \right)^2} + \frac{1}{2} \arcsin \left( \frac{h}{D} \right) \right] \quad 0 \leq h \leq D$$

$$= -n_b \frac{\pi}{4} \quad h > D \quad (2.115)$$
Combining (2.113) and (2.115) we obtain for $0 \leq h \leq D$

$$\Gamma(h) - \Gamma(\infty) = nb \frac{D}{2} \left[ \frac{\pi}{2} - \left( \frac{h}{D} \right) \sqrt{1 - \left( \frac{h}{D} \right)^2} - \arcsin \left( \frac{h}{D} \right) \right]. \quad (2.116)$$

Substituting (2.116) in (2.13) and carrying out the integration with $\mu = kT \ln nb$ once again yields the interaction potential (2.111).

### 2.5.2 Interaction Between Two (Big) Colloidal Spheres

**Using the Derjaguin Approximation**

Using the Derjaguin approximation (2.27) we obtain the interaction between two big spheres with radius $R \gg D$ by integration

$$W_s(h) = \pi R \int_h^D W(h') dh'.$$

Using (2.111) for the interaction potential per unit area in the above integration we obtain

$$W_s(h) = -nbkT \frac{\pi}{3} R D^2 \times \left[ -\frac{3}{4} \pi \frac{h}{D} + \frac{3}{2} \frac{h}{D} \arcsin \left( \frac{h}{D} \right) + \left( 1 + \frac{1}{2} \left( \frac{h}{D} \right)^2 \right) \sqrt{1 - \left( \frac{h}{D} \right)^2} \right]. \quad (2.117)$$

This result obtained for infinitely thin disks will presumably also be valid for disks with finite thickness $L$ to lowest order in $nb$ (although such a calculation has not been carried out) and we can then write (2.117) in the form

$$W_s(h) = -\frac{4}{3} kT \phi \frac{R}{L} \times \left[ -\frac{3}{4} \pi \frac{h}{D} + \frac{3}{2} \frac{h}{D} \arcsin \left( \frac{h}{D} \right) + \left( 1 + \frac{1}{2} \left( \frac{h}{D} \right)^2 \right) \sqrt{1 - \left( \frac{h}{D} \right)^2} \right], \quad (2.118)$$

where

$$\phi = nb(\pi/4) LD^2. \quad (2.119)$$
For thin disks $L$ is small so $R = L$ is large. Assume $R = 1 \mu m$, $D = 200 \text{ nm}$ and $L = 1 \text{ nm}$ then $R/L = 1000$ implies that for volume fractions $\phi$ of the disks of 0.1% the depletion interaction is already of the order $kT$.

Comparison of the depletion potentials due to spheres (2.94), rods (2.107), disks (2.117) and ideal polymers (2.58) reveals that to lowest order in the depletant density they all have the general form

\begin{equation}
W_s(h) = -n_b kT R C \ell^2 f \left( \frac{h}{\ell} \right),
\end{equation}

where $\ell$ is the characteristic length scale of the depletion agent, the prefactor $C$ determines the depth of the potential and the function $f$ sets the distance dependence normalized such that $f(0) = 1$ and $f(1) = 0$. This is summarized in Table 2.1.

Because for the ideal chain result higher-order $h/R_g$ terms are not available the $f(1) = 0$ limit can not be accessed. In Fig. 2.33 we present the functions $f$ for ideal chains (small $h$), spheres, rods and plates. It is clear that the dependence on the interparticle separation $f(h/\ell)$ is similar for greatly different depletants. The results for depletion interaction between big spheres discussed here are based on the Derjaguin approximation valid for $R \gg \ell$ ($\ell = \sigma, L, D$ for spheres, rods and disks).

### Table 2.1 Characteristic parameters for $C, \ell$ and $f$ in (2.120)

<table>
<thead>
<tr>
<th>Depletion agent</th>
<th>$C$</th>
<th>$\ell$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>$\pi/2$</td>
<td>$\sigma$</td>
<td>$(1 - h/\ell)^2$</td>
</tr>
<tr>
<td>Rod</td>
<td>$\pi/6$</td>
<td>$L$</td>
<td>$(1 - h/\ell)^3$</td>
</tr>
<tr>
<td>Disk</td>
<td>$\pi/3$</td>
<td>$D$</td>
<td>$\frac{3}{4} (\frac{h}{\ell}) \text{arcsin} (\frac{h}{\ell}) - \frac{3}{4} (\frac{h}{\ell}) + \left( 1 + \frac{1}{2} (\frac{h}{\ell})^2 \right) \sqrt{1 - (\frac{h}{\ell})^2}$</td>
</tr>
<tr>
<td>Ideal polymer</td>
<td>$\pi/2$</td>
<td>$R_g \sqrt{8 \ln 2}$</td>
<td>$\left( 1 - \frac{8}{\pi \ln^2 (h/\ell)} + (h/\ell)^2 + \cdots \right)$</td>
</tr>
</tbody>
</table>

For thin disks $L$ is small so $R/L$ is large. Assume $R = 1 \mu m$, $D = 200 \text{ nm}$ and $L = 1 \text{ nm}$ then $R/L = 1000$ implies that for volume fractions $\phi$ of the disks of 0.1% the depletion interaction is already of the order $kT$. In Fig. 2.33 we present the functions $f$ for ideal chains (dotted), rods (dashed-dotted), spheres (solid) and ideal chains (dashed), see Table 2.1.
In [62] an analysis of the accuracy of the Derjaguin approximation for depletion potentials is presented. From this analysis it follows that the depletion potential of large spheres due to small spheres is underestimated by the Derjaguin approximation, is surprisingly accurate for disks and is overestimated for rod-like depletion agents. A statistical mechanical analysis of the Derjaguin approximation applied to depletion interactions in colloidal fluids is presented by Henderson [63].

2.6 Measurements of Depletion Interactions

In this section we summarize experimental methods that enable measuring (depletion) interaction potentials between particles [64]. We distinguish pair interactions (Sects. 2.6.1–2.6.3) and many-body interactions (Sect. 2.6.4). The latter can be measured indirectly using scattering techniques or microscopy, whereas for pair interactions direct methods are available. Common instruments for investigating such pair interactions are the surface force apparatus (SFA) [65], optical tweezers [66, 67], atomic force microscopy (AFM) [68], and total internal reflection microscopy (TIRM) [69, 70].

The SFA was the first method allowing to measure forces between particles. It was developed by Tabor and Winterton [71] for two cylindrical surfaces in air or vacuum. An upgrade of the apparatus enabling measurements in liquids was constructed by Israelachvili and Adams [72, 73]. An advantage of SFA is the high spatial resolution of 0.1 nm when using molecularly smooth mica sheets; SFA is mainly used for model surfaces. Unfortunately, the force resolution is small ($O(10^{-8} \text{N})$) and the contact area between the surfaces needs to be very large ($O(1 \text{m}^2)$). Overall, it turned out SFA is less suitable for measuring depletion forces and therefore we restrict ourselves here to AFM, TIRM and optical tweezers and briefly introduce these techniques below. A few arbitrarily chosen experimental examples of potentials in the presence of depletants are given as illustrations.

The effective pair interactions measured with these techniques are the direct pair interactions between two colloidal particles plus the interactions mediated by the depletants. In practice depletants are polydisperse, for which there are sometimes theoretical results available. For the interaction potential between hard spheres we quote references for the depletion interaction in the presence of polydisperse penetrable hard spheres [74], polydisperse ideal chains [75], polydisperse hard spheres [76] and polydisperse thin rods [77].

2.6.1 Atomic Force Microscopy

The atomic force microscope (AFM) was designed for high-resolution surface topography analysis. The basic measuring principle is sketched in Fig. 2.34. A sample is scanned by a sharp tip attached to a sensitive cantilever spring via a
piezo electric positioner. Forces on the tip lead to spring deflection, which is detected optically [78]. Topographic images of the sample are obtained by plotting the deflection of the cantilever as a function of the sample position. Alternatively, a feedback loop can be used to fix the spring deflection, and response of the piezoelectric positioner generates the image [68]. The pair interactions between a colloidal sphere and a surface by free depletants can be studied with a colloidal probe particle attached to the cantilever tip [79].

Interactions between a spherical colloid and a wall can be measured by bringing probe and substrate together and monitoring the cantilever deflection as a function of the interparticle distance. The photodetector voltage versus piezo position curve can be converted into a force–distance curve. The force acting on the cantilever follows from the deflection of the cantilever and its known spring constant. The zero force is defined by the deflection of the cantilever as the colloidal probe is far from the surface of the substrate. To obtain the force–distance dependence on an absolute scale the zero distance, i.e., where the colloid touches the wall, has to be determined. Commonly, the zero distance is obtained from the force curve itself and not through an independent method [68].

In practice, the position where the motion of the probe complies with the piezo movement defines the point of zero distance. Force–distance curves recorded with AFM depend on the specific geometry of the probe and the surface. Usually, the interaction is displayed as the force divided by the radius of the colloid, $R$, in units $N/m$. The Derjaguin approximation relates this quantity to the interaction potential per unit area between equivalent flat surfaces at given separation distance, see (2.29).
Since AFM is widely used for imaging, the technology is well-developed. Due to its high lateral resolution of ~1 nm small samples can be used and material inhomogeneities can be mapped and imaged. The small contact areas (~10 nm²) reduce the probability of experimental artifacts due to surface contamination and roughness [68]. The high spatial resolution capability makes AFM a complementary approach to the SFA which has been used to measure interfacial forces between proximal surfaces over areas on the order of ~1 µm². Moreover, the force resolution of AFM is better than that of the SFA.

The determination of the zero separation distance using AFM remains a complicated issue in some cases. This makes it often difficult to fully quantify depletion interactions. The force sensitivity is limited as compared to TIRM. This makes AFM only suitable for measuring strong depletion forces.

In Fig. 2.35 we show the measured force oscillating between a silicon wafer and a silica sphere (radius $R = 2.2 \mu m$) attached to a cantilever spring in the presence of Ludox silica spheres with a radius of 11 nm [80]. The volume fraction of the Ludox spheres was 1.5%. The effective volume fraction is much larger due to repulsive double layer interactions.

![Fig. 2.35](image)

2.6.2 Total Internal Reflection Microscopy

The interaction potentials between a single particle and a wall can be obtained using evanescent field scattering in total internal reflection microscopy (TIRM) [69, 70]. The fluctuations of the separation distance resulting from thermal motion can be directly detected from the scattered intensity. In a typical TIRM set-up a laser beam is directed via a prism to the glass/solution interface as sketched in Fig. 2.36, with an incident angle that is chosen such that total reflection occurs. The electric field of the laser beam penetrates the interface causing an
Fig. 2.36 Sketch of a TIRM set-up. Whenever the incident angle is larger than the critical angle the incident beam is totally reflected at the glass–fluid interface and an evanescent wave penetrates into the fluid. A colloidal particle located close to the surface will scatter light from the evanescent wave, which is collected by a photomultiplier and provides the probability density of separation distances between the particle and the wall. A CCD camera is used to image the field of view.

An evanescent wave, the amplitude of which decays exponentially along the normal to the interface. A single colloidal sphere in the field of gravity, interacting with this evanescent wave, will scatter light depending on its position \( h \) as [81]

\[
I_s(h) = I(h = 0) \exp[-h/\varrho],
\]

where \( \varrho \) is the penetration depth of the evanescent wave.

**Exercise**

Why does the scattered intensity due to a colloid decrease with increasing distance from the surface?

A photomultiplier is used to monitor the time dependence of the scattered intensity, with a resolution in the millisecond range. A sufficient number of data points allows to convert a histogram of intensities to the probability density distribution of the intensity. Through (2.121) the intensity histogram can be converted a probability density distribution (pdf) of separation distances. Using Boltzmann’s law \( \ln[pdf(h)] - U(h)/kT \), this pdf provides the potential energy \( U(h) \). Usually, a charged sphere is used with a size of the order of a \( \mu \)m. The solvent often is an aqueous salt solution. In this way double layer repulsion between particle and like-charged surface counterbalances gravity, enabling the particle to fluctuate near the wall. From \( U(h) \) the bare pair depletion potential can be found by subtraction of double layer repulsion and gravity.

An optical trap can be set up to prevent the colloidal particle from moving out of the microscope’s observation area. For this purpose a second laser beam has to
be focused directly at the particle. It is recommended to use \( p \)-polarized light and a penetration depth below 150 nm.

Major advantages of TIRM relative to AFM and SFA for studying depletion potentials are its outstanding force sensitivity and its non-invasive nature. With TIRM it is possible to investigate the interactions of a single, freely moving, Brownian particle. This method enables measurements of forces as small as \( 10^{-14} \text{N} \). The reason for this high sensitivity is the use of a molecular gauge for energy (\( kT \)) instead of a mechanical gauge for the force determined by a spring constant, as it is used in AFM and SFA [70].

TIRM is less suited for measuring strong depletion potentials. When the repulsion between the particle and the wall is bigger than 5 \( kT \) the pdf for finding the particle in this range becomes virtually zero. Therefore, the error in determining \( pdf(h) \) becomes very large. If the attraction between the sphere and the wall becomes too strong, the intensity histogram becomes narrower than the range set by the electronic noise of the photomultiplier [70].

An example of a pair potential measured using TIRM is given in Fig. 2.37. The data are measured wall-sphere potentials between a flat silica surface and a polystyrene sphere (\( R = 1.85 \mu m \)) mediated by polydisperse boehmite rods (0.09 vol%) with averaged length of 200 nm. Redrawn from Helden et al. [82].

![Fig. 2.37 Interaction potential between a flat silica surface and a polystyrene sphere \((R = 1.85 \mu m)\) mediated by polydisperse boehmite rods (0.09 vol%) with averaged length of 200 nm. Redrawn from Helden et al. [82]](image)

2.6.3 Optical Tweezers

Around 1970 it was found that laser radiation forces can be used to trap and manipulate small dielectric particles [83]. A laser beam can push a particle towards the centre of the beam, provided the particle has a higher refractive index than the surrounding medium. Thus, optical tweezers allow to pick up and manipulate
colloidal particles; experts nowadays can even spell your name with a single optical tweezer and colloidal particles. This technique found a broad application in biology as well as in colloid science [84, 85]. Figure 2.38 illustrates a typical optical tweezer arrangement. The laser beam is tightly focused using the microscope objective lens, which also gives the possibility to image trapped particles with a camera. Optical tweezers can be configured using multiple beams to trap many particles simultaneously. This can be implemented in the following manner. Firstly, a single beam is used to rapidly scan two or more trap positions. Next, the beam is split at an early stage in the optical circuit to produce two separate light paths which are then recombined before entering the microscope. Finally, computer-generated holograms are used to generate multiple beams simultaneously.

Boltzmann’s law is used to find the interaction potential between the trapped particles using the measured probability density as a function of separation distance. Position detection results either from particle tracking using video microscopy or back focal plane interferometry [67]. Accurate video microscopy requires the acquisition of bright field or fluorescent images from the microscope [86]. Particle centre separations can then be determined with a sub-pixel resolution through image-processing operations [86]. A spatial resolution of $\sim 10 \text{ nm}$ can be achieved. Back focal plane interferometry enables reducing the spatial resolution to $\sim 1 \text{ nm}$.

A major advantage of optical tweezers is that the detected forces range between $10^{-13}$ and $10^{-10} \text{ N}$. Like TIRM, optical tweezers enable studying colloidal interactions in a non-invasive manner. Complementary to TIRM it enables to measure the interaction potentials between two colloidal particles, whereas TIRM and AFM

---

**Fig. 2.38** Sketch of a simple optical tweezers arrangement. The microscope objective lens enables the tight focusing of the laser beam and imaging of trapped particles.
are restricted to wall-particle potentials. The main problems that can arise when making measurements with optical tweezers is that the results are susceptible to misinterpretations due to image processing problems [87, 88].

The pair interaction measured using optical tweezers between two silica spheres in the presence of rather monodisperse, non-adsorbing DNA chains [89] is plotted in Fig. 2.39. Data are given for three DNA concentrations beyond the coil overlap concentration indicated in the plot.

2.6.4 Scattering and Microscopy

One of the manifestations of depletion effects in a colloidal dispersion is that its fluid structure is affected by the presence of non-adsorbing depletants (for instance polymer chains). This is reflected in the radial distribution function $g(r)$; the local concentration of particle centers from a distance $r$ to a fixed particle center. Statistical mechanics links $g(r)$ to the potential of mean force $W_{mf}$ [90],

$$W_{mf}(r) = -kT \ln g(r). \quad (2.122)$$

For a dilute colloidal dispersion, $g(r) = \exp[-W(r)/kT]$, where $W(r)$ is the pair interaction. The quantity $g(r)$ can be measured using confocal laser scanning microscopy. This method allows to perform quantitative three-dimensional real space measurements of the positions of the (fluorescently labeled) colloidal particles. Analysis of the positions of the particles yields $g(r)$. This means that confocal microscopy enables to indirectly measure both the potential of mean force and (using a dilute dispersion) the pair interaction in a mixture of colloids and depletants. Royall et al. [91] have performed such a study in a colloid–polymer mixture with free polymers as depletants.
Scattering techniques allow to measure the structure factor $S(Q)$ as a function of the wave vector $Q$ of colloidal dispersions defined as

$$Q = \frac{4\pi}{\lambda_m} \sin\left(\frac{\theta_s}{2}\right).$$

Here $\lambda_m$ is the wavelength of radiation through the medium and $\theta_s$ the scattering angle. Statistical mechanics relates the structure factor $S(Q)$ to the radial distribution function $g(r)$ [92]:

$$S(Q) = 1 + \frac{\phi}{\nu_0} \int_0^\infty 4\pi r^2 [g(r) - 1] \frac{\sin Qr}{Qr} dr.$$  \hspace{1cm} (2.124)

Hence, via (2.122), (2.124) reveals $S(Q)$ contains the potential of mean force in the long wavelength limit ($Q \to 0$).

In the case of a colloid plus depletant mixture in which the depletant is made ‘invisible’ by contrast matching, the scattered intensity $I(Q)$ reads

$$I(Q) \sim \phi P(Q) S(Q),$$

where $P(Q)$ is the particle scattering form factor. The proportionality constant is the squared particle scattering amplitude. The structure factor then follows from (2.125) as

$$S(Q) = \frac{I(Q)}{I_0(Q)} \frac{\phi_0}{\phi},$$

where $\phi_0$ is the volume fraction of and $I_0(Q)$ is the scattered intensity in a very dilute dispersion. Here the fact was used that $S(Q)$ equals unity in a very dilute dispersion.

Following an early light scattering study of De Hek and Vrij [93], Ye et al. [94] made a small-angle neutron scattering (SANS) study on mixtures of CaCO$_3$ particles, stabilized with alkylbenzene sulfonate, plus polyethylene propylene (PEP) copolymers with $R_g = 8.3$ nm. Here $R = 4.8$ nm so $q = 2.1$. SANS allows contrast matching as to independently measure the structure factors of the free polymers or the colloids, see [95, 96] for a theoretical analysis. Further SANS is much less sensitive to multiple scattering problems as encountered in light scattering.

In Fig. 2.40 a few representative measured structure factors $S(Q)$ of colloidal spheres at a colloid volume fraction $\phi = 0.086$ are plotted at a few PEP concentrations. Clearly, the measured structure factor increases upon adding more free polymer at $Q < 0.2$ nm$^{-1}$, corresponding to an increase of the attraction between the colloids. This increase of $S(Q)$ at small $Q$ has been found also in a few other studies [97–99]. Mutch et al. [99] showed it is possible to rescale structure factors at high $q$ (relatively large polymers) to obtain a universal $S(Q)$ behaviour.

PRISM [100, 101] would be quite useful in quantifying these experimental data. Static and dynamic light scattering can be used also on colloid–polymer mixtures.
to quantify the spinodal, defined at $1/S(Q \to 0) \equiv 0$ using extrapolation \cite{97}. When the attraction becomes very strong the structure factor diverges at small $Q$ and the dispersion starts to decompose. This demixing will be considered in Sect. 4.5.

**Exercise**

Why does $1/S(Q \to 0) \equiv 0$ correspond to the spinodal? Hint: check (1.30)

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