

4xx Mem 6 - Van der Waals and electrostatic interactions

Lecture Mem 5 examined the distribution of mobile counterions around a single charged plate. We now extend our analysis to consider two rigid plates experiencing:

- the van der Waals force between electrically neutral materials
- the electrostatic force between charged objects.

van der Waals forces

What is often labeled the van der Waals force between neutral atoms or molecules arises from a number of effects, including:

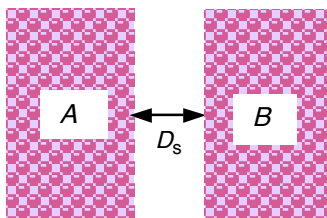
- the attractive interaction between electric dipole moments (Keesom)
- the attraction between permanent electric dipoles and induced dipoles in a neighboring molecule (Debye)
- the attraction between fluctuating dipole moments created by instantaneous movement of the electrons in an atom (London),

The potential energy associated with each of these angle-averaged contributions is proportional to r^{-6} , so they are often collectively written as

$$V_{\text{mol}}(r) = -C_{\text{vdw}}r^{-6}, \quad (1)$$

where r is the separation between molecules and C_{vdw} is a constant. The subscript *mol* indicates that Eq. (1) applies to molecules. The complete van der Waals potential between molecules also includes a short-range repulsive term proportional to $+r^{-12}$.

The interaction energy between aggregates such as sheets and spheres can be obtained by integrating the molecular potential V_{mol} . Of interest for the cell boundary is the interaction energy per unit area between two rigid slabs separated by a distance D_s ,



For a molecular potential energy of the form $V_{\text{mol}}(r) = -C_{\text{vdw}}/r^n$ under the assumption of pairwise addition of forces, the energy per unit area on one slab (*B*) due to its interaction with the other (*A*) is (from Prob. 9.19, MoC2)

$$V_{\text{slab}}(D_s)/A = -2\pi\rho^2C_{\text{vdw}} / (n-2)(n-3)(n-4)D_s^{n-4}, \quad (2)$$

where ρ is the molecular density of the medium (i.e., the number of molecules per unit volume). The slabs are much thicker than the gap between them, and they extend to infinity in directions parallel to the gap. Substituting $n = 6$ of the van der Waals interaction into Eq. (2) gives

$$V_{\text{slab}}(D_s)/A = -\pi\rho^2C_{\text{vdw}} / 12D_s^2. \quad (3)$$

Other geometries possess different V_{slab} for the same V_{mol} :

- thin sheet interacting with a semi-infinite slab: $V_{\text{slab}}(D_s)/A = -\pi C_{\text{vdw}} \rho^2 d_{\text{sh}} / 6D_s^3$,
- two thin, rigid sheets $V_{\text{slab}}(D_s)/A = -\pi C_{\text{vdw}} \rho^2 d_{\text{sh}}^2 / 2D_s^4$.

where D_s is the thickness of the sheet. Comparing Eq. (3) with these two results shows that the energy density decreases faster with distance as the sheets become thinner.

If the materials A and B are dissimilar, then ρ^2 in Eq. (2) is replaced by the product of their densities $\rho_A \rho_B$. The combination $\pi^2 C_{\text{vdw}} \rho_A \rho_B$ is defined as the Hamaker constant, having a value of about 10^{-19} J or $25k_B T$ for many condensed phases interacting across a vacuum. The presence of a medium between the plates reduces the van der Waals energy density, although the reduction is not completely exponential in distance,

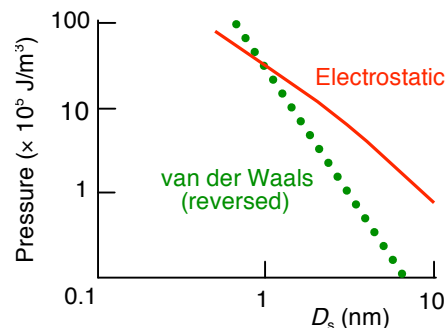
The van der Waals interaction between plates results in a pressure P , which can be obtained from the change in the energy density per unit area $V(D_s)/A$ by

$$P = -d(V(D_s)/A) / dD_s, \quad (4)$$

where $P < 0$ corresponds to attraction. As applied to Eq. (3), this yields

$$P = -\pi \rho^2 C_{\text{vdw}} / 6D_s^3, \quad (5)$$

for two slabs; the attractive pressure decreases more rapidly than this for sheets whose thickness is much less than their separation. To estimate the importance of the van der Waals interaction between bilayers, we consider two blocks of hydrocarbons, which we represent as aggregates of methyl groups with $C_{\text{vdw}} \sim 0.5 \times 10^{-77} \text{ J}\cdot\text{m}^6$ and $\rho = 3.3 \times 10^{28} \text{ m}^{-3}$ (from Table 11.1 of Israelachvili, 1991). With these values, the pressure from Eq. (5) is the dotted line in the figure:

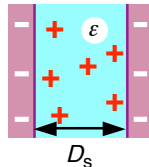


Charged plates with counterions

As a first step towards understanding the forces between charged membranes, we calculate the electric field \mathbf{E} between two rigid charged plates in the absence of positive counterions. The plates, which extend to infinity, are separated by a distance D_s ; they carry a charge density of σ_s and are immersed in a medium with permittivity ϵ ,

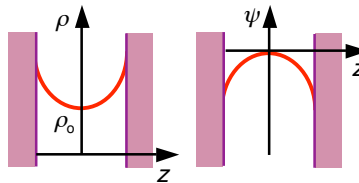
which equals the product of the dielectric constant and ϵ_0 , the permittivity of free space. As described in Lec. Mem 5, the magnitude of the electric field E from *one* plate is $E = \sigma_s/2\epsilon$. For two parallel plates of the same charge density, *including the sign*, E vanishes between the plates and is equal to σ_s/ϵ outside the plates. That is, the fields from each plate cancel because they point in opposite directions between the plates.

Now, let us introduce some (positive) counterions into the space between the plates



If a single positive ion were placed between the plates, it would experience no net force because $E = 0$. However, a group of positive ions, initially spread throughout the space between the plates, would be driven towards the plates by their mutual repulsion. At finite temperature, the ions have thermal energy, allowing them to wander away from the plates and into the medium. This cloud of counterions at the plate is referred to as the electric double layer.

Our next step is to obtain the potential $\psi(z)$ in Eq. (5) of Lec. Mem 5. The mirror symmetry of the system means that the potential and charge distribution must be symmetric about the midplane ($z = 0$), where we choose $\psi(0) = 0$. The counterion density has a minimum and the potential has an extremum (depending on its sign) at the midplane: $d\rho/dz = 0$ and $d\psi/dz = 0$:



Imposing the condition of overall electrical neutrality means that the integral of the counterion charge density $\rho_{ch} = q\rho$ from $z = 0$ to $z = D_s/2$ must equal σ_s in magnitude:

$$\sigma_s = -q \int_0^{D_s/2} \rho \, dz, \tag{6}$$

where the minus sign arises because σ_s and $q\rho$ have opposite signs. Poisson's equation [Eq. (3) of Mem 5], can be used to replace $q\rho$ by $-\epsilon\nabla^2\psi$, which is equal to $-\epsilon d^2\psi/dz^2$ because the function depends only on coordinate z . The integral in Eq. (6) is thus

$$(-1)^2 \epsilon \int_0^{D_s/2} (d^2\psi/dz^2) \, dz = +\epsilon (d\psi/dz)_{D_s/2}, \tag{7}$$

where we have used the condition $(d\psi/dz)_0 = 0$ imposed by symmetry. Combined, Eqs. (6) and (7) yield

$$(d\psi/dz)_{D_s/2} = \sigma_s/\epsilon, \tag{8}$$

which includes the correct signs. Being equal to $|(d\psi/dz)_{D_s/2}|$ from $\mathbf{E} = -\nabla\psi$ the magnitude of the electric field at the plate is $|\sigma_s|/\epsilon$.

Armed with an expression for $(d\psi/dz)_{D_s/2}$, we can determine $\psi(z)$ from the Poisson-Boltzmann equation which, in its one-dimensional form, reads

$$d^2\psi/dz^2 = - (q\rho_o/\epsilon) \exp(-q\psi/k_B T). \quad (9)$$

We replace $\psi(z)$ by the dimensionless function

$$\Psi(z) = q\psi(z) / k_B T, \quad (10)$$

so that Eq. (9) becomes

$$d^2\Psi/dz^2 = - (q^2\rho_o/\epsilon k_B T) \exp(-\Psi) = - 2K^2 \exp(-\Psi), \quad (11)$$

where

$$K^2 = q^2\rho_o / (2\epsilon k_B T) = 2\pi\ell_B\rho_o, \quad (12)$$

and where ℓ_B is the Bjerrum length $q^2 / 4\pi\epsilon k_B T$. Eq. (11) has the solution

$$\Psi(z) = \ln(\cos^2[Kz]), \quad (13)$$

as can be verified by first demonstrating

$$d\Psi/dz = -2K \tan(Kz), \quad (14)$$

from which it follows that

$$d^2\Psi/dz^2 = -2K^2 / \cos^2(Kz). \quad (15)$$

The boundary condition $(d\Psi/dz)_{D_s/2} = q\sigma_s/\epsilon k_B T$ from Eq. (8) fixes the value for K from Eq. (14):

$$-2K \tan(KD_s/2) = q\sigma_s/\epsilon k_B T. \quad (16)$$

Note that $1/K$ has the units of $[length]$. The solution for $\Psi(z)$ in Eq. (13) vanishes at $z=0$ and becomes negative for $|z| > 0$, as expected for negatively charged plates.

Expressing Eq. (13) as $\exp[\Psi(z)] = \cos^2(Kz)$ permits the counterion density profile to be extracted easily from Eq. (4) of Lec. Mem 5, namely

$$\rho(z) = \rho_o / \cos^2(Kz) = \rho_o + \rho_o \tan^2(Kz), \quad (17)$$

where the second equality follows from the trigonometric identity $1 + \tan^2\theta = 1/\cos^2\theta$. From Eq. (16), the value of $\tan^2(KD_s/2)$ at the plate is $[q\sigma_s/(2\epsilon k_B T)]^2/K^2$, which simplifies to just $\sigma_s^2/(2\rho_o\epsilon k_B T)$ when Eq. (12) is used for the definition of K^2 . Thus, the counterion density at the plate obeys the particularly simple expression

$$\rho(D_s/2) = \rho_o + \sigma_s^2/(2\epsilon k_B T). \quad (18)$$

In other words, the number density of counterions is lowest at $z = 0$, from which it rises

to $\rho(D_s/2)$ at the plates. From Eq. (18), the smallest value of $\rho(D_s/2)$ is $\sigma_s^2/(2\epsilon k_B T)$ for a given charge density σ_s . For instance, the magnitude of σ_s could be as large as 0.3 C/m² for one charge per lipid in a bilayer, yielding $\rho(D_s/2) = 1.6 \times 10^{28} \text{ m}^{-3} = 26 \text{ M}$ for water with $\epsilon = 80\epsilon_0$. Eq. (18) demonstrates that the counterion density at the plates declines with increasing temperature, as entropy encourages the counterions to explore new territory away from the plate boundaries.

The pressure P between charged plates in the absence of salts has the appealing form (see Section 12.7 of Israelachvili, 1991)

$$P = \rho_0 k_B T = 2\epsilon K^2 (k_B T / q)^2, \quad (19)$$

where the second equality follows from Eq. (12). Except that ρ_0 is the density of ions at the midplane, the first equality in this expression looks like the ideal gas law. Under what conditions do the counterions fill the gap between the plates and physically behave like a gas? The ions should spread away from the plates when the surface charge density is small, or the temperature is large. In this limit, K is small according to the right-hand side of Eq. (16), which then can be solved to yield

$$K^2 = -q\sigma_s / \epsilon k_B T D_s. \quad (20)$$

Using $\rho_0 = 2\epsilon k_B T K^2 / q^2$ from Eq. (12), this region of K corresponds to

$$\rho_0 = -2\sigma_s / q D_s, \quad (21)$$

which is just the density expected if the counterions are spread evenly across the gap. The same expression for ρ_0 applies at small gap width, where the product $K D_s$ in Eq. (16) is proportional to $\sqrt{D_s}$. Under these conditions (large T ; small σ_s or D_s), the system has the same pressure as an ideal gas of counterions

$$P = -2\sigma_s k_B T / q D_s, \quad \text{(electrostatics, ideal gas limit)} \quad (22)$$

which is inversely proportional to D_s . As usual, σ_s and q have opposite signs, making $P > 0$ and repulsive.

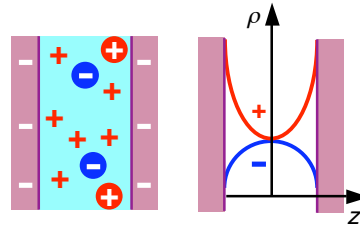
If the charges are more concentrated at the plates, Eq. (16) is easy enough to solve numerically. At large separations, the electrostatic interaction is approximately

$$P = \pi k_B T / 2\ell_B D_s^2, \quad \text{(electrostatics, large } D_s, \text{ no screening)} \quad (23)$$

The figure on p. 2 shows a sample calculation for $\sigma_s = -0.1 \text{ C/m}^2$ in water. The figure demonstrates that the repulsive electrostatic pressure *without screening* dominates the attractive van der Waals pressure for $D_s \geq 1 \text{ nm}$ as it must: the electrostatic pressure decays like $1/D_s^2$ while the van der Waals declines more rapidly as $1/D_s^3$.

Charged plates in an electrolyte

The electrostatic pressure between two plates separated by an electrolyte solution may be considerably less than that predicted by Eq. (23). The ion content of the medium for this case is:



For negatively charged plates, the density of positively charged ions is elevated near the plates while the negatively charged ions are suppressed. The presence of the bulk ions requires a modification of Eq. (19) for the electrostatic pressure between plates (Section 12.17 of Israelachvili (1991)). For a monovalent electrolyte of positive and negative ions, the pressure is

$$P = 4\rho_s k_B T \sinh^2(\Psi_m/2). \quad (24)$$

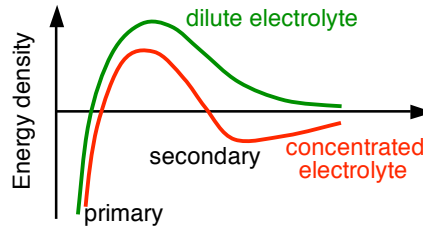
As expected, the pressure goes to zero as the potential vanishes. If Ψ_m is small, and can be regarded as a sum of independent contributions from each plate, the pressure becomes

$$P = (2\sigma_s^2/\epsilon) \cdot \exp(-D_s/\ell_D), \quad (\text{screened electrostatics, small } \psi_0) \quad (25)$$

after eliminating ρ_s . We see from Eq. (25) that the presence of the electrolyte screens the interaction and suppresses the repulsive pressure: the power-law decay in Eqs. (22) and (23) becomes an exponential decay in an electrolyte, with a characteristic length scale ℓ_D , the Debye screening length.

Combined interactions

Given the negative charge on phosphatidylserine, the force between lipid bilayers may include both electrostatic and van der Waals components. At short distances, the van der Waals contribution dominates because of its stronger power-law dependence on $1/D_s$. At longer distances, the electrostatic interaction dominates if the electrolyte is dilute, resulting in a large Debye length. This is shown as the upper curve of the figure below. However, in a concentrated electrolyte with a small Debye length, the electrostatic interaction is rapidly extinguished with increasing distance, opening up the possibility that the electrostatic interaction is important only at intermediate separation, as illustrated by the lower curve:



In this situation, there are two minima in the potential energy density: a global (primary) minimum at short distance and a local (secondary) minimum at intermediate distance. The combined electrostatic and van der Waals interaction, and its dependence on electrolyte concentration, forms the basis for the DLVO theory of colloids (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). If the temperature is low enough, a system may become trapped in the secondary minimum, the thermal fluctuations in its energy being insufficient to carry it into the global minimum on a reasonable time frame. Thus, individual colloidal particles may be stabilized in an electrolyte, rather than adhere to each other at close contact.