

DLVO interaction

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Introduction

This document considers some aspects of a general description of colloids interactions known as *DLVO theory*, based on the names of the scholars involved in its development: Derjaguin, Landau, Vervey and Overbeek. We have seen that virtually all surfaces are subject to van der Waals interactions, which are attractive and can be captured by means of the Hamaker constant A . Moreover, in the case of charged surfaces also electrostatic interactions play a key role and for similarly-charged surfaces they are repulsive in nature. Due to the universality of van der Waals interactions, a proper theoretical framework should take also these attractions into account. This is the basis of the DLVO theory, which brings these two contributions together. The DLVO theory has been shown to successfully describe quantitatively the force measured when putting planar surfaces in proximity of each other, although with various caveats to be considered.

Here, we are mainly interested in DLVO to rationalize the aggregation of *colloids*, which are generally defined as macroparticles of sizes ranging from units of nanometers up to several microns. Within this category, one can include for instance globular proteins and giant lipid vesicles. In order to describe the interaction between two colloids, we focus on the case of two identical spherical particles with Hamaker constant A , radius R and surface charge density $-\sigma e_0^2$. The solution contains salt with bulk concentration ρ_∞ , corresponding to a Debye length $l_D = 1/\sqrt{8\pi\rho_\infty l_B}$, with $l_B \simeq 0.7$ nm being the Bjerrum length.

General features of DLVO

Joining the contributions coming from Van der Waals and electrostatic interactions, we can write for the interaction free energy

$$F_{\text{DLVO}}(D) = -\frac{AR}{12D} + \frac{1}{2}RZe^{-\frac{D}{l_D}}. \quad (1)$$

This free energy can be used to describe the interaction between two colloids. For instance, the distance will be distributed according to $D^2 e^{-F_{\text{DLVO}}(D)/(k_B T)}$, where the factor D^2 comes

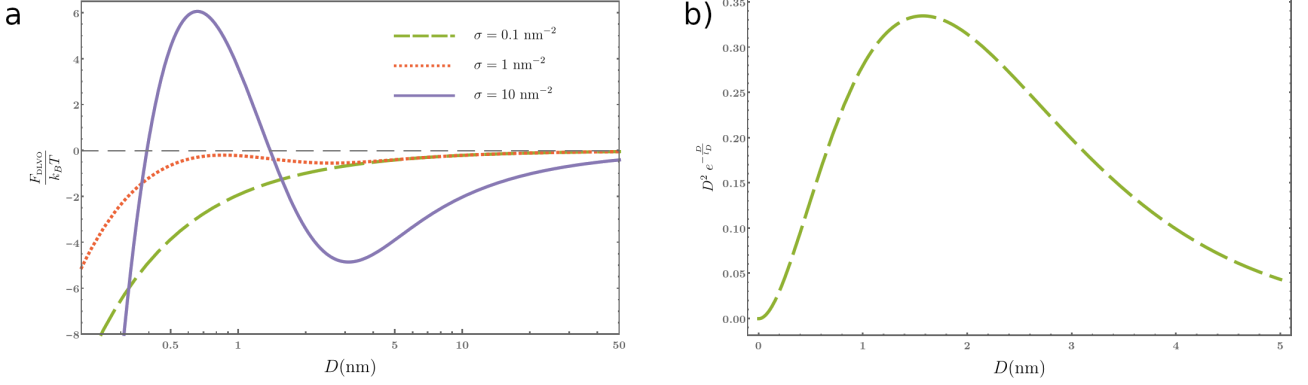


Figure 1: a) Plots of DLVO interaction free energy for different choices of σ at fixed values of the other variables. b) Plot of the function $D^2 e^{-D/l_D}$.

from the volume element in polar coordinates. In Fig.1a, we plot some representative examples of $F_{\text{DLVO}}(D)$ corresponding to $A = 10^{-19}$ J, $\rho_\infty = 150$ mM, $R = 1$ nm and different values of σ , which enables exploring the features of the DLVO interaction as a function of the relative strength between electrostatic repulsion and Van der Waals attraction. First of all, as a general feature the attractive part decreases according to a power law, while the repulsion decays exponentially. Therefore, at large D the attraction dominates and the interaction goes to zero from below. At small D , the attractive term diverges, while the repulsion goes to a finite value. Also in this case, the attraction dominates and $F_{\text{DLVO}}(D)$ goes to $-\infty$. Between these two limits, there are two possible behaviors: either the interaction free energy increases monotonically (as in the case of the green dashed curve in Fig.1a) or it shows peaks and valleys (red dotted curve and purple continuous curve). In order to understand under which conditions these features appear, we note that a stationary point satisfies the equation $dF_{\text{DLVO}}/dD = 0$, i.e.

$$\frac{AR}{12D^2} - \frac{RZ}{2l_D} e^{-\frac{D}{l_D}} = 0 \Rightarrow e^{-\frac{D}{l_D}} D^2 = \frac{Al_D}{6Z}. \quad (2)$$

The left-hand side of the previous formula is shown in Fig.1b, while the right-hand side is independent of D , i.e. it corresponds to a horizontal straight line. Since the function $e^{-D/l_D} D^2$ ranges between 0 and a peak located at a certain D_p , the previous equation has solutions if and only if $e^{-D_p/l_D} D_p^2 \geq Al_D/(6Z)$. The value of D_p is easily found by minimizing the derivative of $e^{-D/l_D} D^2$, yielding $D_p = 2l_D$. Hence, the condition for the presence of peaks and valleys in Fig.1a is

$$e^{-\frac{2l_D}{l_D}} (2l_D)^2 \geq \frac{Al_D}{6Z} \Rightarrow \frac{Ae^2}{24l_D Z} \leq 1. \quad (3)$$

Since Z increases with σ , we conclude that a non-monotonous behavior appears only when the electrostatics is strong enough. This makes sense, since the van der Waals attraction dominates both for $D \rightarrow 0$ and for $D \rightarrow \infty$, so that for weak electrostatics one simply finds that the system

collapses to $D = 0$, i.e. the two spheres stick irreversibly with each other. The infinite well located at $D = 0$ is called the *primary minimum* of the DLVO interaction. In contrast, if σ is large enough, a peak and a valley appear¹, which provides a non-trivial physical picture. Indeed, although the thermodynamically-stable state corresponds to the primary minimum at $D = 0$, there is now a *secondary minimum* at a finite D separated from the global minimum by a free-energy barrier. If one considers as a starting state two spheres at sufficiently large separation (which is then out of thermodynamic equilibrium), in order for the system to reach $D = 0$ it needs to cross the barrier. The system will be thus found for a certain time around the secondary minimum, which thus provides a *metastable state*. The timescale at which the equilibrium ($D = 0$) is reached is set by the free-energy barrier. If the barrier is large enough, this time can be so large that for all practical purposes one can consider the secondary minimum as being *kinetically stable*.

The special role of proteins

In Eq.(1) the size R of the sphere appears linearly in both terms, i.e. $F_{\text{DLVO}} \propto R$. This means that all the various features characterizing the free-energy profile will be scaled accordingly. In Fig.2 we plot the dependence on R of the free-energy barrier ΔF , defined as the difference between the values of F_{DLVO} at the peak and at the secondary minimum (see inset). As expected, the barrier increases linearly with size. As mentioned above, the time τ needed for thermal fluctuations to overcome a barrier increases with the height. Particularly, it can be estimated that $\tau(\Delta F) \simeq \tau_0 e^{\Delta F/(k_B T)}$, where τ_0 depends on the microscopic details of the colloidal particles and of the solvent, such as the drag coefficient, the viscosity, etc. Therefore, the time needed for reaching the primary minimum grows exponentially with ΔF , hence there is an exponential dependence also on the size R of the particles! This implies that large particles will spend relatively long times beyond the peak and, in some cases, they will never cross it.

This analysis highlights a special role for the smallest colloids, whose size ranges in the units of nanometers². For such colloids, the free-energy barrier is of the order of a few $k_B T$, meaning that thermal fluctuations alone can trigger the transition to the primary minimum, i.e. irreversible sticking of the colloids. When putting a bunch of such particles in a solution, one will therefore observe in a reasonable time that they *aggregate* into clusters. An excellent example of small colloids are globular proteins, which have size of a few nanometers and are indeed prone to aggregation when put into a solution. The DLVO is thus a powerful tool to give a microscopic mechanism capable of explaining the experimental observations. Another good confirmation of the theory comes from electrostatics itself. Indeed, as we show in Fig.2, stronger

¹Only two intersections with a horizontal line can be found in Fig.1b, which correspond to a maximum and a minimum.

²This is a practical limit imposed by the derivation of the two contributions to the DLVO interaction, since one needs that the size R is large with respect to the length scales characterizing the electrostatics, e.g. l_D . For typical experimental setups, l_D ranges between 0.1 and 3 nm, so that for an object to be considered within the DLVO framework some nanometers of size are a must.

electrostatics (corresponding to smaller ionic strength) leads to larger free-energy barriers. This makes sense, since it is the presence of electrostatics that originates the barrier in the first place, as seen in Fig.1a. Therefore, one expects that aggregation can be triggered or prevented by a suitable change in the salt content of the solution, which is actually observed experimentally.

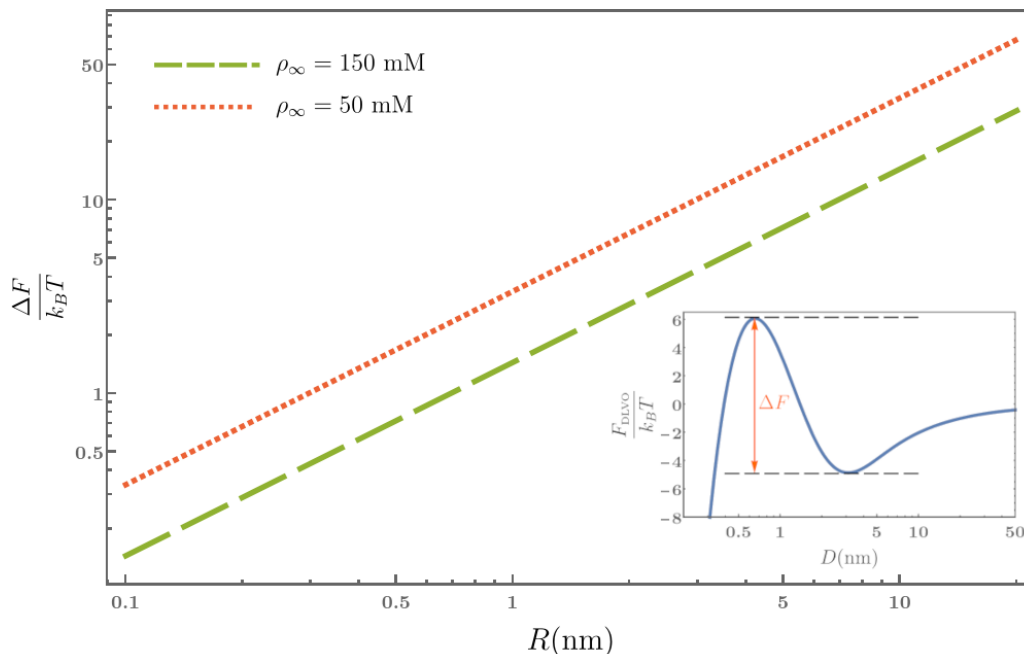
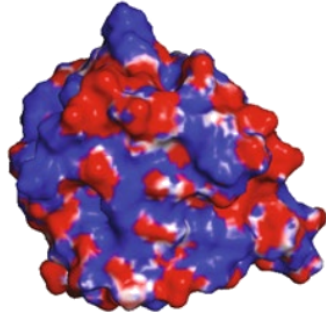


Figure 2: Dependence of the free energy barrier ΔF on the size R of the colloidal particles for different values of the ionic strength. In the inset a graphical definition of ΔF is shown.

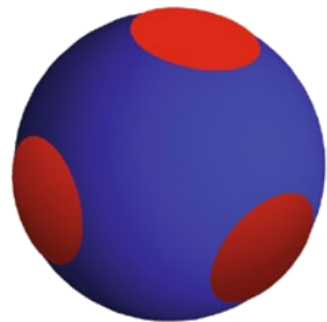
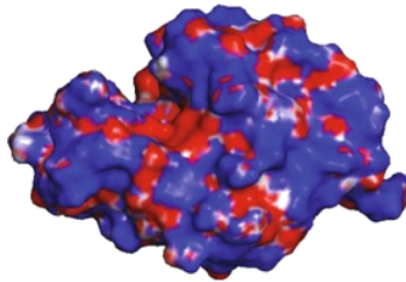
Beyond DLVO

Proteins are extremely complex objects. Although for a protein with a net charge one does expect that both Van der Waals and electrostatic interactions are present, the DLVO framework is too simplistic to capture quantitatively the behavior of protein solutions. For instance, ascribing a protein to a uniformly-charged surface is a very strong assumption, since proteins are actually *zwitterionic*, i.e. they present patches with charges of both signs on their surfaces, as depicted in Fig.3. Moreover, there are other kinds of short-range interactions to be accounted for, e.g. the formation of hydrogen bonds. Based on this, it is expected that proteins will stick together only at suitable relative orientations, so that for instance a negative patch on a protein faces a positive spot on another one. In order to capture this kind of features, more complex models have been introduced in the literature. Particularly, *patchy colloids* are theoretical descriptions where each particle presents particular spots at certain positions (see Fig.3), so

β -lactoglobulin



Lysozyme



Patchy
colloid

Figure 3: Charge distribution of the proteins β -lactoglobulin and lysozyme (top), with red and blue indicating negatively- and positively-charged regions, respectively. In the bottom a schematic picture of a patchy colloid is reported. Reprinted from S. Assenza and R. Mezzenga, “Soft condensed matter physics of foods and macronutrients”, *Nature Rev. Phys.* **1**:551 (2019).

that the particle-particle interaction does not depend only on the distance but also on the orientation.

Further reading

- J. N. Israelachvili, “Intermolecular and Surface Forces”, 3rd Ed., Academic Press (2011), Chapter 14