Current Opinion in Colloid & Interface Science 20 (2015) 19–23

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Depletion forces due to image charges near dielectric discontinuities

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ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form 1 December 2014
Accepted 1 December 2014
Available online 13 December 2014

Keywords:
Depletion force
Dielectric
Electrolyte
Colloids

ABSTRACT

The depletion force is an effective inter-particle attractive interaction that is entropically driven by the exclusion of co-solvent molecules. For large co-solvents, such as polymers, the exclusion is primarily driven by excluded volume interactions. However, the exclusion of co-solvents, such as electrolytes, can be caused by other mechanisms. In this review, we summarize the literature on inter-particle depletion forces that arise from repulsive image-charge forces between low-dielectric particles and electrolytes. In particular, we emphasize the results from a variational perturbation theory for describing the salting-out behavior observed in moderately concentrated salt solutions. The theory predicts an unscreened force with a range given by the Bjerrum length and a magnitude proportional to the osmotic pressure of the salt solution. The force becomes significant at the same salt concentration where salting-out behavior is typically observed.

1. Introduction

The depletion force was originally used to describe the attraction between colloidal particles induced by the addition of small polymer molecules [1]. In this case, the force is driven by polymer exclusion from the colloidal particles. The excluded volume of the colloids restricts the space available to the polymer molecules. The net exclusion volume decreases as colloids approach each other, giving rise to a net inter-colloid attractive force, with a range and magnitude determined by the polymer size and the polymer osmotic pressure, respectively.

Excluded volume interactions are one mechanism that gives rise to an effective inter-colloid depletion force. However, any situation where co-solvents (e.g., polymers) are driven from the surface of a colloidal particle can lead to an entropically driven attraction between the colloids.

In this work, we review and discuss the depletion of ions from a dielectric interface due to image-charge interactions.

This depletion of ions leads to an effective attraction between larger colloidal particles. We discuss the similarities and differences between depletion forces driven by image-charge forces and by excluded volume interactions.

2. Image-charge interactions

2.1. Planar interfaces

Consider a planar interface located at $z = 0$ which separates two mediums with dielectric constants equal to ε' and ε as shown schematically in Fig. 1. The medium to the left corresponds to a particle, which is inaccessible to electrolytes. The right side is referred to as the solvent and contains electrolytes (co-solvent). A point charge with magnitude q located a distance d from the interface will induce a surface charge due to the difference in polarizabilities between the two media. For an isolated planar interface, the potential of the induced surface charge is identical to that of a point charge of magnitude $q' = \Delta q$, where $\Delta = (\varepsilon - \varepsilon')/(\varepsilon + \varepsilon')$, located at $z = -d$, in the absence of the dielectric discontinuity [2]. The interaction energy $u(\mathbf{r})$ of the ion with the induced surface charge is

$$\beta u(\mathbf{r}) = \frac{\Delta l_B}{2z}, \qquad (1)$$

where $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the absolute temperature of the system, and $l_B = \beta q^2/\varepsilon$ is the Bjerrum length. If q is the elementary charge, then $l_B \approx 7$ Å for water at 25 °C.

There is an effective ion-interface attraction when the dielectric constant of the particle is higher than that of the solvent (i.e. $\varepsilon' > \varepsilon$). Conversely, if the dielectric constant of the particle is lower (i.e. $\varepsilon' < \varepsilon$), then the ion is repelled from the interface. The strength of the interaction varies as the square of the ion valency but is independent of the sign of the ion charge. The image force causes a layer of ion depletion about the interface, defined by a depletion length of roughly $l = \Delta l_B/2$, the distance at which the image-charge interaction is of order $k_B T$.

2.2. Spherical geometries

The strength of the image-charge interaction depends on the geometry of the dielectric interface. As an illustrative example, consider a single sphere with a dielectric constant ε' embedded in a solvent of

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http://dx.doi.org/10.1016/j.cocis.2014.12.001
1359-0294/

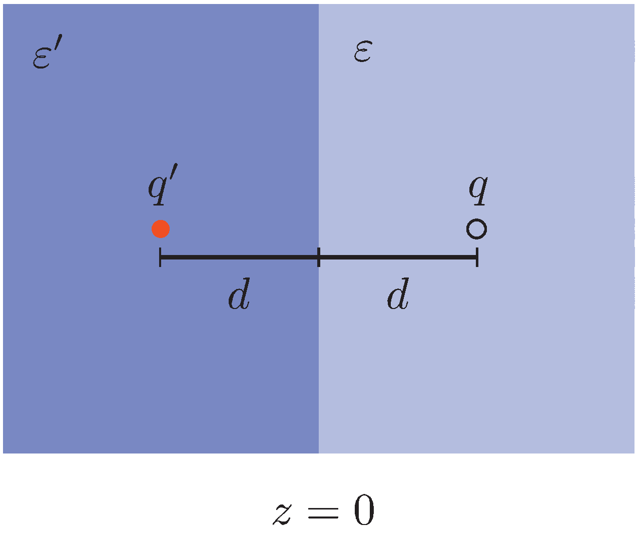

Fig. 1. Schematic diagram of a point charge near a planar dielectric interface.

dielectric constant ε. The presence of charge induces a surface charge on the dielectric interface.

For a point charge located a distance r from the center of the dielectric sphere, the potential generated by the induced surface charge can be represented by the sum of a point charge of magnitude $q_K = \Delta q(R/r)$ located at a distance $r_K = R^2/r$ from the center of the sphere and a line charge stretching from the center of the sphere to r_K with a linear charge density [3–6]

$$\lambda_K(x) = -\Delta q \zeta \left(\frac{r_K}{x}\right)^{1-\zeta} \tag{2}$$

where x is the distance from the center of the sphere, $\eta = \varepsilon'/\varepsilon$, and $\zeta = (1+\eta)^{-1}$.

In the limit that $\varepsilon' \gg \varepsilon$ or $\varepsilon' \ll \varepsilon$, the expressions for the Green's function and ion self energy can be written in closed form [3,4,6].

The self energy in this case is exactly given by

$$\beta u(\mathbf{r}) = \frac{l_B}{R}\left[\frac{R^2}{r^2-R^2} + \ln\left(1-R^2/r^2\right)\right]. \tag{3}$$

The image-charge interaction approaches that of a plane when the distance from the point charge to the surface is much less than the sphere radius. In general, the image-charge interaction for the dielectric sphere is weaker than that for the plane.

When a point charge is inside a sphere of dielectric constant ε that is surrounded by a medium of dielectric constant ε', the image charge can again be represented as a point charge and a line charge. The point charge has magnitude $q_K = \Delta qR/r$ and is located at a distance $r_K = R^2/r$ from the center of the sphere. The line charge stretches from the point r_K outside the sphere to infinity and has a linear charge density given by Eq. (2).

2.3. Other geometries

For other more complex geometries, the potential generated by the induced charge cannot be easily represented in terms of simple image charge distributions. The key quantity in these electrostatic problems is the Green's function $G(\mathbf{r}, \mathbf{r}')$ of the Poisson Eq. (2)

$$-\frac{1}{4\pi}\nabla\cdot[\varepsilon(\mathbf{r})\nabla G(\mathbf{r},\mathbf{r}')] = \delta^d(\mathbf{r}-\mathbf{r}'), \tag{4}$$

where $\delta^d(\mathbf{r} - \mathbf{r}')$ is the d-dimensional Dirac delta function.

The Green's function gives the electric potential of a point charge under a given set of boundary conditions. The potential generated by a general charge distribution $Q(r)$ is given by

$$\phi(\mathbf{r}) = \int d\mathbf{r}' G(\mathbf{r},\mathbf{r}')Q(\mathbf{r}). \tag{5}$$

The Green's function can be represented as

$$G(\mathbf{r},\mathbf{r}') = G_{\text{free}}(\mathbf{r},\mathbf{r}') + \delta G(\mathbf{r},\mathbf{r}') \tag{6}$$

where $G_{\text{free}}(\mathbf{r}, \mathbf{r}') = (\varepsilon|\mathbf{r} - \mathbf{r}'|)^{-1}$ is the Green's function in the absence of any dielectric bodies, and $\delta G(\mathbf{r}, \mathbf{r}')$ represents the influence of any dielectric bodies in the system.

Although analytical expressions do exist for general geometries, most require intensive computation, and, consequently, have limited value to direct simulations of systems containing electrolytes. The key challenge in the simulation and theoretical analysis of problems near dielectric interfaces is the development of new analytical expressions or algorithms for rapidly calculating the Green's function. Recently, several computational algorithms have been developed that efficiently evaluate the electrostatic interaction for arbitrary distributions of the dielectric constant [7–11].

For collections of spheres, a fairly efficient quadrature method to integrate the image-charge interactions has been proposed [12,13]. In order to account for the dispersion interaction, however, further work is required to numerically evaluate the determinant of the Green's function.

3. Electrolytes near dielectric bodies

3.1. Ion depletion

For a symmetric electrolyte solution near a neutral dielectric surface, the average cation charge density will be identical to the average anion charge density. As a consequence, there will be no charge separation, and the system will be everywhere neutral *on average*.

Within mean field theories, the ion density profiles are considered only in an average manner, and, consequently, there will be no repulsion of ions from a low-dielectric interface. Thus, one has to go beyond mean field theories, such as the Poisson–Boltzmann theory, and allow for fluctuations in ion densities to account for ion depletion.

In early theoretical approaches [14,15], the image-charge interaction was included explicitly by using an additional one-body interaction. More recent theories account for correlations between ions, as well as between ions and the dielectric interface, using various methods, such as the self-consistent Born–Green–Yvon equation [16–18], the hypernetted-chain approximation [19,20], loop expansions [21–23], variational perturbation theory [24,25], and strong coupling expansions [26], among many others. These correlations lead to deviations from the mean ion profiles.

Applying these approaches to describe the behavior of small colloids such as proteins or spherical micelles requires determining the effect of curvature on the interfacial behavior. This has been taken into account using a variational perturbation theory.

Fig. 2 shows the ion density profile, as calculated using variational perturbation theory [24], around a sphere of radius R and dielectric constant ε' immersed in a symmetric electrolyte (the co-solvent) dissolved in a solvent with dielectric constant ε, where $\varepsilon' \ll \varepsilon$. The electrolyte concentration is such that the bulk screening length is $\kappa^{-1} = 10 l_B$. The effect of curvature on the density profiles of a symmetric electrolyte about a spherical interface are shown in Fig. 2. For this calculation, the ratio of dielectric constants for the spherical particle over the solvent is taken as $\varepsilon'/\varepsilon \ll 1$ [24].

The repulsive image-charge interactions lead to depletion of ions from the dielectric interface of roughly a distance of $l_B/2$, in the case of the planar geometry; this distance is approximately independent of