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Adsorption isotherms of charged nanoparticles

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We present theory and simulations which allow us to quantitatively calculate the amount of surface adsorption excess of charged nanoparticles onto a charged surface. The theory is very accurate for weakly charged nanoparticles and can be used at physiological concentrations of salt. We have also developed an efficient simulation algorithm which can be used for dilute suspensions of nanoparticles of any charge, even at very large salt concentrations. With the help of the new simulation method, we are able to efficiently calculate the adsorption isotherms of highly charged nanoparticles in suspensions containing multivalent ions, for which there are no accurate theoretical methods available.

I. Introduction

The interaction between lipid membranes, DNA, electrodes, and other charged surfaces with nanoparticles is of fundamental importance in biochemistry, biophysics, and diagnostic medicine. It is well known that salt can modify significantly the interaction between biomolecules in aqueous suspensions, affecting their stability.^{1–11} The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory¹² attributes the stability of suspensions to the competition between electrostatic and dispersive, van der Waals (vdW), forces. Electrostatic repulsion between colloidal particles prevents them from coming into a close contact at which strong dispersion forces can make the particles stick together, resulting in flocculation and precipitation. The vdW attraction is very short-ranged and is only weakly affected by the presence of an electrolyte. On the other hand, the Coulomb repulsion between like charged particles is strongly susceptible to the presence of the electrolyte, which screens the electrostatic interactions. The DLVO theory provides a qualitative understanding of the stability of colloidal systems in suspensions containing the 1 : 1 electrolyte. The theory, however, is not able to account for either the ionic specificity (Hofmeister effect),^{13–17} like-charge attraction,^{18–21} or the reversal of the electrophoretic mobility often observed in suspensions containing multivalent ions.^{22–24} In this paper, we will explore the interaction between nanoparticles and charged surfaces. Our goal is to quantitatively calculate the adsorption isotherms for dilute

suspensions of nanoparticles in solutions containing large – physiological – concentrations of electrolyte.

When studying Coulomb systems the starting point is often the Poisson–Boltzmann (PB) equation. Indeed, it has been observed that the PB equation can very accurately describe the density profiles of monovalent ions near a charged wall. However, since the PB equation does not take into account either electrostatic correlations or steric repulsion between ions it is bound to fail if used to calculate the adsorption isotherms of charged nanoparticles near a charged wall.²⁵ Nevertheless, we will show that a very simple modification of the PB equation can extend its validity to study an important class of weakly charged nanoparticles, allowing us to quantitatively calculate their adsorption isotherms. For more strongly charged nanoparticles, or if solution contains multivalent ions, we will present a simulation method which allows us to obtain adsorption isotherms at infinite dilution of nanoparticles, which are often of great practical interest.

This paper is organized as follows: in Section II, we introduce a modified PB (mPB) equation which allows us to accurately calculate the density profiles of weakly charged nanoparticles near a charged surface. In Section III we present an efficient Monte Carlo (MC) simulation method which can be used to obtain the adsorption isotherms for very dilute suspensions of nanoparticles at large salt concentrations. In Section IV, we compare the theory with the simulations and discuss suspensions containing multivalent ions. In Section V, conclusions of the present work are presented.

II. Model and theory

Consider a spherical colloidal particle of radius a and charge Z in an electrolyte solution. If Z is not too large, there is no counterion condensation, and the electrostatic potential produced

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by a colloidal particle inside a 1:1 electrolyte solution can be found analytically by solving the linearized PB equation^{25,26}

$$\beta\phi(r) = \lambda_B Z \left(\frac{e^{\kappa_c a}}{1 + \kappa_c a} \right) \frac{e^{-\kappa_c r}}{r}, \quad (1)$$

where r is the distance from the center of the nanoparticle, $\kappa_c = \sqrt{8\pi\lambda_B\rho_s}$ is the bulk inverse Debye length, ρ_s is the salt concentration, $\lambda_B = q^2/\varepsilon k_B T$ is the Bjerrum length, q is the proton charge and ε is the dielectric constant of the medium. We observe that the electrostatic potential in eqn (1) is identical to the potential produced by a point charge of

$$Z_{\text{eff}} = Z \left(\frac{e^{\kappa_c a}}{1 + \kappa_c a} \right). \quad (2)$$

Note that Z_{eff} can be significantly larger than the bare charge Z . The interpretation of this curious result is that if we want to replace a finite sized colloidal particle by a point particle and require that this point particle produces the same electric field at a distance $r \gg a$, the charge of the point particle must be larger than the bare colloidal charge in order to account for the absence of screening inside the colloidal core.^{27,28} This suggests that in the absence of the counterion condensation, the system of weakly charged nanoparticles can be mapped onto a system of point particles with an effective charge given by eqn (2).

The dispersion interactions between nanoparticles and the surface can be taken into account using the Hamaker potential which can be written as¹²

$$U_v(z) = -\frac{A}{6} \left[\left(\frac{\bar{a}}{(z-\bar{a})} + \frac{2\bar{a}}{[4\bar{a} + 2(z-\bar{a})]} \right) + \log \left[\frac{2(z-\bar{a})}{4\bar{a} + 2(z-\bar{a})} \right] \right], \quad (3)$$

where A is the Hamaker constant, set to $1.3 \times 10^{-20} \text{ J}$, $\approx 3.15 k_B T$ corresponding to polystyrene–polystyrene interaction in water at room temperature,²⁹ and $\bar{a} = a - 4 \text{ \AA}$ is the vdW radius of the nanoparticle (radius minus the hydration layer).³⁰ We expect that the pairwise additive approximation on which the Hamaker potential is based will break down at short separations, where we would need to use the Lifshitz theory.³¹ In the present paper we will neglect this non-additive short distance effect.

Now, suppose that we have a dilute suspension of charged nanoparticles inside a 1:1 electrolyte solution. If an oppositely charged surface is introduced into solution some of the particles will become adsorbed to it. The surface adsorption excess can be defined as

$$\Gamma = \int_0^\infty [\rho(z) - \rho(\infty)] dz, \quad (4)$$

where $\rho(z)$ is the number density of nanoparticles at a distance z from the surface and $\rho(\infty) = \rho_B$ is the bulk nanoparticle concentration.

To calculate the surface adsorption excess we need to know the density profile of nanoparticles $\rho(z)$. It is well known that for weakly charged small ions, Poisson–Boltzmann theory is very accurate, however, it fails for large or strongly charged ions.²⁵ On the other hand, from the above argument we

observed that for nanoparticles which are not too strongly charged, the effect of the hardcore can be taken into account by simply renormalizing the colloidal charge. In this sense, we can map weakly charged nanoparticles onto point particles with an effective charge. Since the PB equation works very well for point-like ions, we expect that it will also work reasonably well for our weakly charged nanoparticles which are mapped onto point-like particles with an effective charge.^{11,32} Note that in this formalism, the electrostatic correlations between the nanoparticles and the ions are taken into account through the charge renormalization. A modified PB (mPB) equation for this system can then be written as

$$\begin{aligned} \nabla^2 \phi(z) &= -\frac{4\pi q}{\varepsilon_w} [\sigma + q\rho_+(z) - q\rho_-(z) + Z\rho(z)], \\ \rho(z) &= \rho_B e^{-\beta Z_{\text{eff}}(z)\phi(z) - \beta U_v(z) - \beta U_c(z)}, \\ \rho_+(z) &= \rho_s e^{-\beta q\phi(z)}, \\ \rho_-(z) &= \rho_s e^{\beta q\phi(z)}, \end{aligned} \quad (5)$$

where z is the distance from the charged wall, $\phi(z)$ is the mean electrostatic potential, $\rho(z)$, $\rho_+(z)$, and $\rho_-(z)$ are the density profiles of nanoparticles, cations, and anions, respectively, and ρ_s is the bulk concentration of salt. The hardcore potential $U_c(z)$ prohibits the centers of nanoparticles from coming nearer than a distance a to the surface. The vdW interaction between the nanoparticles and the surface is given by eqn (3). The effective charge which appears in the mPB equation, eqn (5), is calculated using the local density approximation

$$Z_{\text{eff}} = Z \left(\frac{e^{\kappa(z)a}}{1 + \kappa(z)a} \right), \quad (6)$$

where

$$\kappa(z) = \sqrt{4\pi\lambda_B [\rho_+(z) + \rho_-(z)]} \quad (7)$$

is the local inverse Debye length. This is similar to the well known WKB approximation.³³ The Bjerrum length is set to 7.2 \AA , value for water at room temperature. The mPB equation can be solved numerically using the Picard iteration method. To check the accuracy of the mPB equation we compare its predictions with the results of Monte Carlo simulations.

III. Monte Carlo simulations

In order to accurately construct the nanoparticle density profile for dilute suspensions at physiological concentrations of salt a very large simulation cell containing many ions is required. The long range Coulomb force prevents us from using simple periodic boundary conditions, requiring more sophisticated Ewald summation methods which are computationally very expensive. Furthermore the presence of many salt ions results in very low MC acceptance rates, requiring the introduction of clusters³⁴ or inversion moves,³⁵ leading to additional complications. To overcome these difficulties we have developed a new approach for calculating adsorption isotherms of dilute suspensions using MC simulations.

Our algorithm is based on the fundamental observation that the density profile of nanoparticles can be written as

$$\rho(z) = \rho_B e^{-\beta\omega(z)}, \quad (8)$$

where $\omega(z)$ is the potential of mean force. For very dilute suspension of nanoparticles in a solution containing a large amount of salt, the interaction between nanoparticles can be ignored, so that the potential of mean force depends only on the surface charge density and the concentration of electrolyte.

The MC simulations are performed in a box of sides $L_x = L_y = 218 \text{ \AA}$ and $L_z = 5L_x$. The electrolyte is confined in the z direction between $z = 0$ and $z = L = 150 \text{ \AA}$. A charged wall with a uniform surface charge density $\sigma = -0.03 \text{ C m}^{-2}$ is located at $z = 0$. A nanoparticle has charge $Z = 5q$ and effective radius $a = 20 \text{ \AA}$, similar to lysozyme,³⁶ where q is the proton charge, and is placed at position z and $x = 0$ and $y = 0$. We also consider $N_c = \left(\frac{89}{\alpha} - \frac{Z}{\alpha q}\right) / L_x L_y$ counterions of charge αq , where α is the ionic valence. Positive and negative ions from the dissociation of the $\alpha:1$ electrolyte are also present in the system. All ionic species have a radius of 2 \AA . Water is treated as a uniform medium of dielectric constant $\epsilon = 80\epsilon_0$, where ϵ_0 is the dielectric constant of vacuum. The electrostatic interactions are determined by summing over all the periodic replicas of the system using the Ewald summation method, modified for slab geometry.^{37,38} Here we adopt a recently introduced efficient simulation algorithm developed specifically for this geometry.³⁹ The electrostatic energy of a periodically replicated system, containing N charged particles, is

$$U = \sum_{\mathbf{k} \neq 0} \frac{2\pi}{\epsilon_w V |\mathbf{k}|^2} \exp\left[-\frac{|\mathbf{k}|^2}{4\kappa_c^2}\right] [A(\mathbf{k})^2 + B(\mathbf{k})^2] + \frac{2\pi}{\epsilon_w V} [M_z^2 - Q_t G_z] + \frac{1}{2} \sum_{i \neq j}^N q_i q_j \frac{\text{erfc}(\kappa_c |\mathbf{r}_i - \mathbf{r}_j|)}{\epsilon_w |\mathbf{r}_i - \mathbf{r}_j|} - \frac{2\pi}{\epsilon_w} \sum_{i=1}^N \sigma z_i q_i, \quad (9)$$

where

$$\begin{aligned} A(\mathbf{k}) &= \sum_{i=1}^N q_i \cos(\mathbf{k} \cdot \mathbf{r}_i), \\ B(\mathbf{k}) &= -\sum_{i=1}^N q_i \sin(\mathbf{k} \cdot \mathbf{r}_i), \\ M_z &= \sum_{i=1}^N q_i z_i, \\ Q_t &= \sum_{i=1}^N q_i, \\ G_z &= \sum_{i=1}^N q_i (z_i)^2. \end{aligned} \quad (10)$$

The \mathbf{k} -vector is defined as $\mathbf{k} = \left(2\pi \frac{n_x}{L_x}, 2\pi \frac{n_y}{L_y}, 2\pi \frac{n_z}{L_z}\right)$, where n are integers. $V = L_x L_y L_z$ is the volume of the simulation box, $\kappa_c = 4/L_x$ is the dumping parameter of the Ewald summation method, and q_i and \mathbf{r}_i are the charge and the position of particle i , respectively. The MC simulations are performed using the Metropolis algorithm with 10^7 movements to achieve equilibrium and 100 movements per particle to obtain uncorrelated states. The force profiles are obtained using 30 000 uncorrelated states. To achieve convergence of the electrostatic energy we use around 400 \mathbf{k} -vectors.

For a nanoparticle fixed at a distance z from the charged surface, we calculate the ensemble averaged electrostatic and entropic forces acting on the particle. The electrostatic force is given by

$$F_{\text{elec}} = -\left\langle \frac{\partial U}{\partial z} \right\rangle, \quad (11)$$

where U is the electrostatic energy of the system.³⁹

The entropic force is obtained using the approach of Wu *et al.* which requires performing a virtual displacement of the nanoparticle and counting the number of overlaps with the ions of the electrolyte.⁴⁰ It is given by

$$F_{\text{ent}} = \frac{\langle N^c \rangle - \langle N^f \rangle}{\beta \Delta R}, \quad (12)$$

where N^c is the number of virtual overlaps between the colloid and the ions after a small displacement $\Delta R = 0.5 \text{ \AA}$ that brings colloids and plate closer together (superscript c stands for closer) and N^f is the number of overlaps of the colloids and the ions after a displacement ΔR that moves the colloids and the plate farther apart (superscript f stands for farther).

After the force profile is calculated, the potential of mean force is obtained by integration

$$\omega(z) = U_v(z) + \int_z^\infty [F_{\text{elec}}(z') + F_{\text{ent}}(z')] dz'. \quad (13)$$

The great advantage of this method is that the calculation of force is easily parallelized by running it on different CPUs for each z .

IV. Results

In Fig. 1, we plot the density profiles of nanoparticles for different salt concentrations obtained using a numerical solution of eqn (5). The agreement between simulations and theory is excellent. In the same figure, the dashed lines show the density profiles which are obtained if charge renormalization is not taken into account. In this case we see a very strong deviation from the results of MC simulations. The electrostatic and vdW plus hard core potentials are shown in Fig. 2 for a specific set of parameters.

The adsorption isotherms can be calculated by performing the integral in eqn (4). In Fig. 3 we plot the scaled adsorption isotherms, $\bar{\Gamma} = \Gamma/\rho_B$, as a function of salt concentration for various surface charge densities on the wall. We see a very strong dependence of surface adsorption excess on the surface charge density at low salt concentrations. For larger concentrations, Debye screening of electrostatic interactions leads to a much

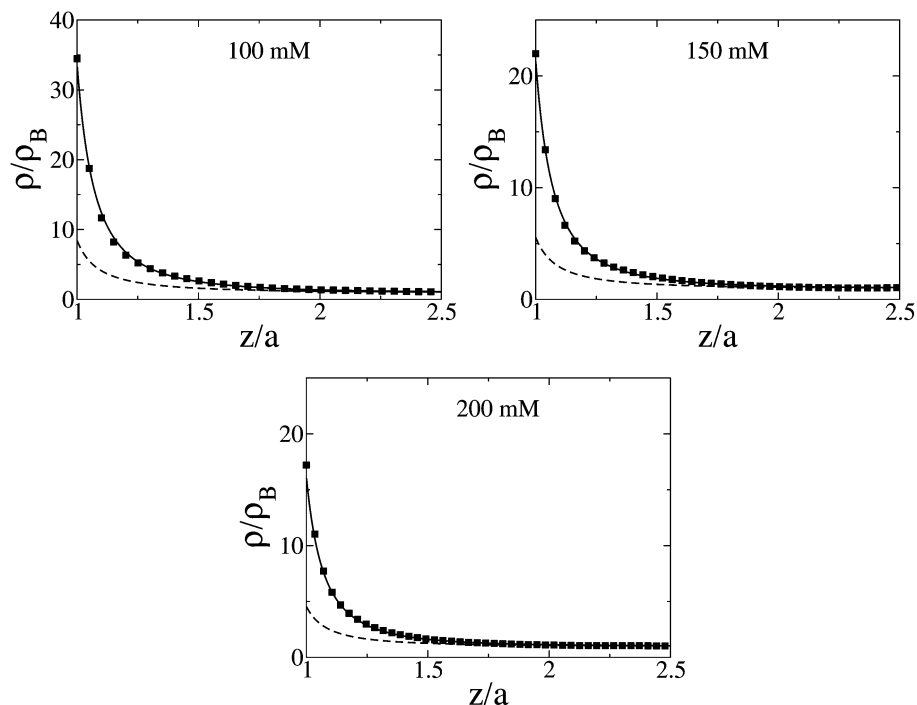


Fig. 1 Density profiles of nanoparticles for salt concentrations of 100, 150 and 200 mM near a charged wall with $\sigma = -0.03 \text{ C m}^{-2}$. Symbols are the results of MC simulations and solid lines are the predictions of the present theory. The dashed lines represent a solution of the PB equation without taking into account charge renormalization. The bare nanoparticle charge is $Z = 5q$ and the radius is $a = 20 \text{ \AA}$.

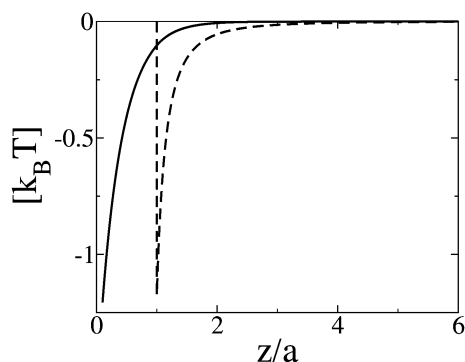


Fig. 2 The scaled electrostatic potential, $\beta q \phi(z)$, is shown by the solid line, and vdW plus hard core potential, $\beta U_v(z) + \beta U_e(z)$, the dashed line. The parameters are the same as Fig. 1 for salt at 150 mM.

weaker dependence of surface adsorption excess on the wall surface charge density.

For dilute colloidal suspensions, counterion condensation becomes important when $Z > 4a(1 + \kappa a)/\lambda_B$.^{25,41} Indeed, when the nanoparticle charge exceeds this limit we see a significant deviation between theory and simulations. Furthermore, in this regime, we find that using more sophisticated theories to account for the counterion condensation and charge renormalization^{42–46} is not sufficient to improve the agreement between theory and simulations. Therefore, in order to calculate the adsorption isotherms of strongly charged nanoparticles, or if suspension contains multivalent ions, we are forced to rely on computer simulations which were discussed in Section III.

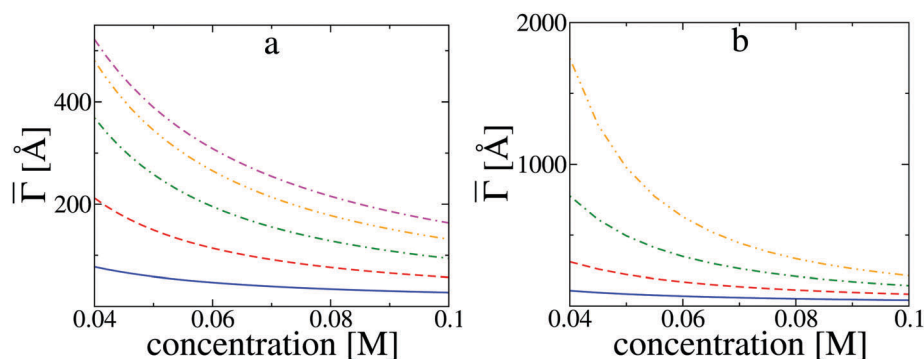


Fig. 3 Surface excess vs. salt concentration calculated using mPB theory. In (a), $Z = 5q$, while the surface charge densities are $\sigma = -0.01, -0.02, -0.03, -0.04$ and -0.05 C m^{-2} , from bottom to top, respectively. In (b), $\sigma = -0.03 \text{ C m}^{-2}$ while the charge on the nanoparticle is $Z = 3q, 5q, 7q$ and $9q$ from below to above, respectively.

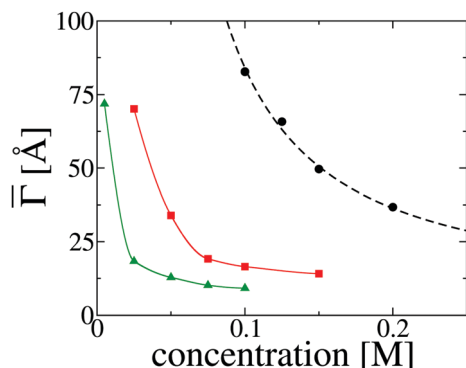


Fig. 4 MC calculations for the rescaled surface excess vs. salt concentration for $Z = 5q$. Circles represent monovalent salt, $\alpha = 1$; squares, divalent counterions, $\alpha = 2$; and triangles, trivalent counterions, $\alpha = 3$. The solid lines are interpolations. The dashed line represents the theory presented in this paper.

In Fig. 4 we present $\bar{\Gamma}$ for a dilute suspension, as a function of the added $\alpha:1$ electrolyte. We see that screening of electrostatic interactions by the electrolyte significantly reduces the nanoparticle adsorption. Furthermore, increasing cation valence, α , dramatically decreases the amount of adsorption, see Fig. 4. The figure also shows that for the 1:1 electrolyte the adsorption isotherm calculated using the mPB equation is in excellent agreement with the results of MC simulations. For more strongly charged nanoparticles, or in the presence of multivalent ions, there are no accurate theoretical methods available and one must rely on MC simulations. For example, in the case of highly charged nanoparticles, we observe more adsorption than that predicted using the modified PB equation, eqn (5). The mechanism of this attraction is both electrostatic and entropic in its origin. The counterions condensed onto nanoparticle are repelled from the charged wall, shifting to the far side of the nanoparticle, leading to enhanced electrostatic and entropic attraction.

V. Conclusions

We have presented a theory which enables us to accurately calculate the density profiles and adsorption isotherms of weakly charged nanoparticles. Both electrostatic and dispersion interactions between the nanoparticles and a charged surface are taken into account. The theory can be used even at large – physiological – concentrations of salt. However it fails for strongly charged nanoparticles and strongly charged surfaces. For such systems we have developed an efficient MC algorithm which can be used to obtain both density profiles and the adsorption isotherms, which are of great practical importance in various applications. The simulations show that the counterion condensation near a strongly charged surface results in a short distance entropic repulsion which is not properly captured by the mPB equation. The strength of this repulsion depends on the surface charge density and salt concentration. For physiological salt concentrations used in the present paper the mPB equation remains accurate for surface charge densities up to

$\sigma = -0.03 \text{ C m}^{-2}$. However for smaller salt concentration, the range of validity of the mPB equation increases. For example, for $\approx 60 \text{ mM}$ salt concentration, we find that the mPB equation remains accurate for surfaces with σ up to -0.06 C m^{-2} . Finally, we note that the simulation approach developed in this paper can be easily applied to solutes of arbitrary shape and can also be extended to explicit solvent models.

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