

# Nanoparticle Charge in Fluid from Atomic Force Microscopy Forces within the Nonlinear Poisson-Boltzmann Equation

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## Abstract

We consider the problem of measuring the electric charge of nanoparticles immersed in a fluid electrolyte. We develop a mathematical framework based on the solution of the nonlinear Poisson-Boltzmann equation to obtain interaction forces between nanoparticles immersed in a fluid electrolyte and an Atomic Force Microscopy micro spherical probe. This force-separation information is shown explicitly to depend on the charge of the nanoparticle. This method overcomes the statistical nature of extant methods and renders a charge value for an individual single nanoparticle.

## Keywords

Nonlinear Differential Equations, Poisson-Boltzmann equation, Atomic Force Microscopy, Colloidal Interaction, Debye Length

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## 1. Introduction

We consider the problem of measuring charge of nanoparticles in electrolytes from experimental forces; specifically forces obtained with Atomic Force Microscopy (AFM) fitted with microsphere tips. Due to the presence of the electrolyte, tip and nanoparticles become charged as dictated by pH and the electric double layer. Electric double layers have been considered at length since the end of the XIX century and new developments are still unfolding today. The quantification of charge at the solid surface presents particular challenges. Here we derive mathematical expressions and propose experimental methods that help in the understanding of surface charges in solid in electrolytes. This mathematical framework considers a charged micron size AFM spherical tip [1] [2] interacting with a charged nanoparticle, both embedded in an electrolyte. We solve the non-

linear Poisson-Boltzmann equation and then, using that information we find the interaction force between the AFM tip and the nanoparticle. This force will be shown to be a function of the surface charges at both objects. Then, based on the force obtained, we propose an experimental procedure to measure the charge on the nanoparticle.

Measurement of surface charge on particles is routinely done using Titration and Zeta-Potential methods. Although titration goes back at least to the beginning of the XVIII century, it was not until the full theory of titration developed by Bjerrum in the 1920s that the methods could be used and related to micron size particle charge [3]. Today, potentiometric titration is used to measure charge of particles by comparing the equilibrium-pH vs titrant-concentration curve for electrolytes, first with, and then without the target particles [4]. The difference in titrant (acid or base) concentration at constant equilibrium pH is proportional to the sought charge. Zeta-potential methods are more recent, and a beginning of a microscopic understanding began with a classical paper [5] requiring computational modeling to understand the region electrostatically bound and the charged region removed by drag under electro kinetics. A complete understanding of the Zeta-potential method at the nanoscale is still under development [6]. In its canonical version, Zeta-potential establishes the potential at the slip plane, which in turn is related to the charge at the surface of the particle of interest [7]. One permanent problem with this technique is that the slip plane is vaguely defined, which translates into an imprecise value of the charge at the surface.

These techniques, titration and zeta-potential, are the workhorses of charge measurements for particles in the micron range size and below. Yet, they are fundamentally limited in that they provide charge values for ensembles of nominally equally prepared particles. With the progress of nanoscience in the last 20 years, it has become necessary to measure charge on individual nanoparticles, for example viruses and proteins. While, as previously explained, a full quantitative measurement is lacking, charge measurements and theoretical computations are made routinely [8] [9]. Here we study the electrostatic interaction of the nanoparticle and microsphere inside an electrolytic aqueous solution to provide a better quantitative method to obtain the charge on the nanoparticle. After solving the nonlinear Poisson-Boltzmann equation, we proceed to derive the force of interaction between AFM tip and nanoparticle. We also propose a quantitative method for experimentally measuring the nanoparticle charge.

## 2. Approach

The particles of interest in this problem are more than a thousand times larger than the ions in solution. Under this condition, effective medium theories for the electrolyte solution are appropriate. Thus, in principle one could compute the total energy of interaction between the two particles within the context of the Poisson-Boltzmann Equation (PBE). However, this direct approach is blocked

by the fact that the PBE is amenable of analytical full solutions only in the simplest of cases. Indeed, the full analytical solution to the PBE is known for a flat wall in contact with an electrolyte [10]. Already for an electrolyte sandwiched between two walls the solution becomes cumbersome [11]. Barring the many extant numerical solutions to PBE [12] [13] [14] [15], a simple and illuminating approximate approach, valid for low voltages, is to linearize PBE in which case analytical solutions for spherical and cylindrical surface boundaries have also been achieved. However, the linearized solutions break down, besides for the obvious mathematical reasons, because for large boundary surface charges, a large amount of screening happens close to the surface, within distances shorter than the Debye's length. Given this physics, and the previously mentioned mathematical limitations we propose the solution of this problem, that is, to compute the interaction force between the microsphere and the nanoparticle by following the subsequent approach. To give context we first review the situation of an electrolyte bounded by a single flat wall. This will serve to establish notation and bring in the standard relevant parameters: Debye's and Bjerrum's lengths. Most importantly we will write down an explicit expression for the *effective charge* that the corresponding linear problem must use to agree with the full nonlinear PBE solution. With this information at hand we subsequently find the electrostatic potential for an electrolyte slab between two planes within the linearized PBE but using the correct effective charge, which solves the nonlinear PB problem. By integrating in this slab, we furthermore obtain the interaction energy as a function of the plane/plane separation. To lay in context the next step, we recall that this energy-vs-separation curve was used by Derjagun to obtain the force-separation curve between two spheres [16]. However, Derjagun's formula works for spheres large compared to the Debye's length, a condition not satisfied by the nanoparticle. An extension to Derjagun's formula exists that works even when one of the particles is small [17]. We use that expression to finally obtain the desired force-separation between the microsphere and the nanoparticle.

In short, we first solve the linear Poisson-Boltzmann equation between to planes with prescribed charge boundary conditions. These charges are effective charges to account for the non-linearity of the Poisson-Boltzmann equation. With this solution we obtain both the charge density and the electrostatic potential between the planes. These in turn are used to obtain the total free energy stored in the system. This plane-plane energy versus separation is then used to obtain the energy between the nano-particle and the AFM tip/sensor. Finally the integral of the energy versus separation curve provides the force versus separation between the nanoparticle and the AFM tip/sensor.

### 3. Effective Charge Density

The one-dimensional non-linear Poisson-Boltzmann equation in a 1-1 electrolyte is [18],

$$\frac{d^2\psi(z)}{dz^2} = \frac{2\rho_0}{\epsilon} \sinh\left(\frac{q\psi}{k_B T}\right) \tag{1}$$

where  $\psi(z)$  is the electrostatic potential and  $z$  the spatial coordinate in the electrolyte,  $\rho_0$  is the absolute magnitude of the bulk anion and cation charge densities,  $\epsilon$  is the permittivity of the medium,  $q$  the elementary charge,  $k_B$  Boltzmann's constant and  $T$  the absolute temperature. To introduce a natural length  $\ell$  of the electrolyte before any solid surface is introduced, it is possible to write the bulk charge densities in terms of  $q$  and the volume it must occupy to have the correct density,

$$\rho_0 = \frac{q}{\ell^3} \tag{2}$$

In other words,  $\ell$  can be interpreted as a putative measure of the bulk density  $\rho_0$ . This length, which is independent of the interface, is convenient because it serves as a comparison for the Debye's and Bjerrum's lengths that will appear below.

Using the Debye's inverse length definition [19],  $k_D^2 = \frac{2\rho_0 q}{\epsilon k_B T}$ , the dimensionless electric potential  $\phi = \frac{q\psi}{k_B T}$ , and introducing the dimensionless length  $\xi = \frac{z}{\ell}$ , and  $\kappa = k_D \ell$ , Equation (1) becomes,

$$\frac{d^2\phi(\xi)}{d\xi^2} = \kappa^2 \sinh(\phi(\xi)) \tag{3}$$

The boundary conditions are

$$\begin{cases} \lim_{z \rightarrow \infty} \psi(z) = 0 \\ \left[ \frac{d\psi}{dz} \right]_{z=0} = -\frac{\sigma}{\epsilon} \end{cases} \tag{4}$$

where  $\sigma$  is the charge density at the surface. Now defining the dimensionless charge  $\Gamma = \frac{4\pi}{\kappa} \frac{\lambda_B}{\ell} \frac{\sigma \ell^2}{q}$ , with the Bjerrum length [20]  $\lambda_B = \frac{q^2}{4\pi\epsilon k_B T}$ , Equation (4) is

$$\begin{cases} \lim_{\xi \rightarrow \infty} \phi(\xi) = 0 \\ \left[ \frac{d\phi}{d\xi} \right]_{\xi=0} = -\kappa\Gamma \end{cases} \tag{5}$$

The exact solution to Equation (3) with boundary conditions (5) is known [21] to be

$$\phi(\xi) = 2 \log \frac{1 + \beta e^{-\kappa\xi}}{1 - \beta e^{-\kappa\xi}} \tag{6a}$$

With

$$\beta = \frac{\sqrt{4 + \Gamma^2} - 2}{\Gamma} \tag{6b}$$

That Equation (6) is a solution can be checked by direct substitution of Equation (6) into (5) and (3).

If one looks far from the surface so that  $\xi$  is large,  $e^{-\kappa\xi}$  is small and the solution is

$$\phi(\xi) \approx 4 \frac{\sqrt{4 + \Gamma^2} - 2}{\Gamma} e^{-\kappa\xi} \quad (7)$$

Equation (7) is the solution for distances  $\xi > \kappa^{-1}$ . On the other hand, one could consider the linearized PB right from Equation (3), valid when  $\phi$  is small, which should be consistent with (7). The linearized PB is

$$\frac{d^2\phi(\xi)}{d\xi^2} = \kappa^2\phi(\xi) \quad (8)$$

The solution to this equation with boundary conditions (5) is

$$\phi(\xi) = \Gamma_{eff} e^{-\kappa\xi} \quad (9)$$

where we wrote  $\Gamma_{eff}$  instead of merely  $\Gamma$  because the linear problem does not necessarily capture properly what happens close to the surface where the potential could be large. The resolution of this ignorance is encapsulated by the introduction of the *effective charge density*  $\Gamma_{eff}$ .

Thus in working with the linear problems but with renormalized charges

$$\Gamma_{eff} = 4 \frac{\sqrt{4 + \Gamma^2} - 2}{\Gamma} \quad (10)$$

we are able to solve the problem analytically while allowing for the possibility of large charge densities at the solid surfaces.

#### 4. Electrolyte between Two Planes

Two planes, at  $\xi = 0$  and  $\xi = \xi_h$  and with effective charges  $\Gamma_{eff}^1$  and  $\Gamma_{eff}^2$ , enclose and electrolyte. Thus we have Equation (8) plus the boundary conditions

$$\begin{cases} \left[ \frac{d\phi}{d\xi} \right]_{\xi=0} = -\kappa\Gamma_{eff}^1 \\ \left[ \frac{d\phi}{d\xi} \right]_{\xi=\xi_h} = \kappa\Gamma_{eff}^2 \end{cases} \quad (11)$$

With solution

$$\phi(\xi) = C_1 \sinh(\kappa\xi) + C_2 \cosh(\kappa\xi) \quad (12a)$$

$$C_1 = -\Gamma_{eff}^1 \quad (12b)$$

$$C_2 = \frac{\Gamma_{eff}^2 + \Gamma_{eff}^1 \cosh(\kappa\xi_h)}{\sinh(\kappa\xi_h)} \quad (12c)$$

The parameter  $\xi_h$ , defined as  $h/\ell$ , contains the plates separation  $h$ . This distance will be allowed to vary below, to enquire into its influence on the energy of the system.

## 5. Electrostatic Energy of the Two-Plane System

The free energy stored in the two-plane system  $U_{pp}$ , which in turn is available for work, is the energy required to charge both plates,

$$U_{pp}(h) = \frac{A}{2} \left\{ \sigma_1 [\psi_h(z=0) - \psi_{h \rightarrow \infty}(z=0)] + \sigma_2 [\psi_h(z=h) - \psi_{h \rightarrow \infty}(z=h)] \right\} \quad (13)$$

where  $A$  is the area of each plane and  $h$  their separation. In this construction, the energy is calculated with respect to having initially both plates at infinity.

By using the variables defined before and substituting in (12),

$$U_{pp} = \frac{A}{8\pi} \frac{k_B T k_D}{\lambda_B} \frac{\left( (\Gamma_{eff}^1)^2 + (\Gamma_{eff}^2)^2 \right) e^{-k_D h} + 2\Gamma_{eff}^1 \Gamma_{eff}^2}{\sinh(k_D h)} \quad (14)$$

## 6. Electrostatic Nanoparticle-AFM Force

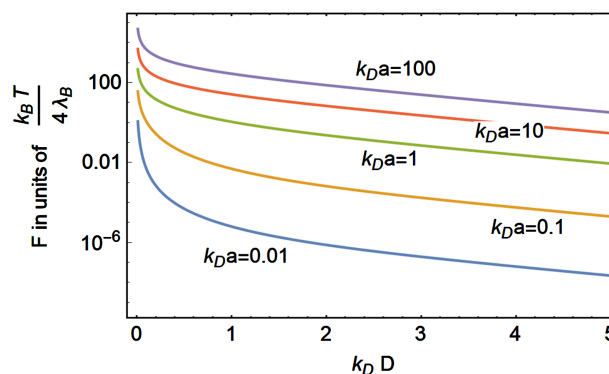
To find the sought nanoparticle-AFM force, Equation (14) *per unit area* is integrated in  $h$  according to Equation (13) in reference [17]. Consider a nanosphere of radius  $a$ , at a closest approach distance  $D$  from the AFM. There are three terms,

$$F_1 = \frac{k_B T k_D a}{4\lambda_B} \frac{\left( (\Gamma_{eff}^1)^2 + (\Gamma_{eff}^2)^2 \right) e^{-k_D D} + 2\Gamma_{eff}^1 \Gamma_{eff}^2}{\sinh(k_D D)} \quad (15a)$$

$$F_2 = \frac{k_B T k_D a}{4\lambda_B} \frac{\left( (\Gamma_{eff}^1)^2 + (\Gamma_{eff}^2)^2 \right) e^{-k_D D} e^{-2k_D a} + 2\Gamma_{eff}^1 \Gamma_{eff}^2}{\sinh(k_D D + 2k_D a)} \quad (15b)$$

$$F_3 = -\frac{k_B T}{4\lambda_B} \left\{ \left( (\Gamma_{eff}^1)^2 + (\Gamma_{eff}^2)^2 \right) \left[ \log \left( \frac{\sinh(k_D D + 2k_D a)}{\sinh(k_D D)} \right) - 2k_D a \right] + 2\Gamma_{eff}^1 \Gamma_{eff}^2 \log \left( \frac{\tanh \left( \frac{k_D D}{2} + k_D a \right)}{\tanh \left( \frac{k_D D}{2} \right)} \right) \right\} \quad (15c)$$

And the total nanosphere-microsphere force is  $F_1 + F_2 + F_3$ . **Figure 1** shows the dependence of the total force on separation (and Debye length) between the nanoparticle and the AFM. This is done for nanoparticles of different radii (or solutions with different Debye screening). In all instances the force decays with separation and eventually decays exponentially at large distances. The graphs were produced by taking the charge on the AFM to be 20% larger than the charge on the nanoparticle. This choice is an estimate assuming the nanoparticle to be a tobacco mosaic virus [22], the AFM tip to be a 1  $\mu\text{m}$  diameter silica microsphere [23] [24] and the system held at a pH of 7.5, in a  $5 \times 10^{-6}$  M electrolyte concentration.



**Figure 1.** Total force between a nanoparticle and the Atomic Force Microscopy sensor. For these plots, the charge at the surface of the tip was taken to be 20% larger than the charge on the nanoparticle as explained in the text. As the radius  $a$  of the nanoparticle increases, also does the force; for large separations  $D$ , regardless of  $a$ , the force always decays exponentially.

## 7. Conclusion

The measurement of charge on nanoparticles is an ongoing program that aims to overcome the restrictions posed by Titration and Zeta Potential approaches. In both cases the methods measure charge over an ensemble of particles, and in the second case there are still foundational questions to answer. Here we analyze and predict the forces of interaction between an AFM microsphere tip and a nanoparticle. Under typical electrolyte conditions, the microsphere and the nanoparticle are charged and one is interested in finding the charge on the nanoparticle from the measured force. This measurement addresses the charge content of an individual nanoparticle. This is especially relevant since for a large number of applications, for example drug delivery via virus capsids, it is relevant to know the true charge in the nanoparticle rather than a probability distribution. The main result of this paper is the set of Equation (15) that can be used to measure the charge on the nanoparticle if the known charge on the AFM microsphere is known. This last charge is usually found in the literature for typical silica microspheres. If one needed to use novel microsphere tips, they would need to be characterized before using Equation (15). However, using the theory in this paper that characterization can be achieved by measuring first the interaction force between two microspheres. In this case, the charge density on both objects is the same at all pHs.

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