

Particle Electrostatic Interactions in Liquids

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***Abstract*— We make a formal connection between colloidal particle interactions and Scanning Force Microscopy (SFM). This allows for the interpretation of SFM measurements on the light of the well studied theories of electrostatics in colloids. In this context, we start from an analytical generalization of Derjaguin's approximation that allows for the interpretation of electrostatic SFM measurements in liquids on charged particles as small as tens of nanometers. We show applications to electrostatic measurements in liquids.**

I. INTRODUCTION

Knowledge of the form of force-separation functions in Scanning Force Microscopy (SFM) is necessary to build inversion algorithms to measure the morphology and chemical activity of the sample under study. In vacuum, the tip and the sample can be modeled as a collection of atoms. The total tip-sample force can thus be evaluated from the appropriate atom-atom forces. These elemental forces have been modeled via Morse and 6-12 pair potentials. More sophisticated, quantum N-body approaches have also been used in the past [1, 2]. Nevertheless, a large number of applications occur for tip-sample interactions in aqueous solutions where the elemental atom-atom interactions are screened by ions at the surfaces. In addition, beyond applications in SFM, knowledge of the plane-particle interaction is significant in particle deposition [3], antireflection coating [4], data storage [5] and membrane separation processes [6]. Indeed, since the inception of Colloid Probe Microscopy [7,8], sphere-plane force measurements have become routine in aqueous solutions studies.

Within the DeJarguin-Landau-Verwey-Overbeek (DLVO) theory, the generation of closed-form expression for these colloidal interactions has been hampered by the fact that analytical solutions to the Poisson-Boltzmann equation (PBE) are restricted to planar geometries. Numerical solutions for other geometries do exist, but it is always desirable to have analytical expressions.

To bypass the difficulty of obtaining analytical solutions to PBE curved geometries, a major effort has been placed on constructing a set of reasonable assumptions that,

when taken together with the planar solution to PBE, generate good expressions for the interactions between colloidal particles.

The most celebrated effort in that direction, the Derjaguin approximation, provides an explicit recipe for the calculation of the interaction energy between two spheroidal particles, from the knowledge of the interaction energy between two planes. A detailed study of the limitations of this approach can be found elsewhere [9], however its major restriction is that the radii of curvature of the particles, at closest approach, must be much larger than the interaction length. This condition is not satisfied in many cases of interest. Notably, typical interaction lengths in liquids are 1-10 nm –similar to the radius of curvature of sharp SFM tips. Thus, the Derjaguin approximation is expected not to provide a good tool for the analysis of SFM tip-sample forces.

A more recent approach, the Surface Element Integration (SEI), has been used to obtain colloidal interaction energies [10]. In particular, this method has been shown to be very robust when restricted to plane-particle interactions. This geometry is of intrinsic interest to SFM when studying extended samples, and for the interpretation of calibration procedures.

We begin by recalling a relationship between generic plane-plane interaction energy, and its corresponding plane-sphere force. Then we apply that relationship to obtain closed-form sphere-plane interactions for the van der Waals. We also study a model system based on experimental data and present explicit formulas for forces in that case.

II. RESULTS

We begin from the equation from reference [11]

$$F(D) = 2\pi a[E(D) + E(D + 2a)] - 2\pi \int_D^{D+2a} E(x) dx \quad (1)$$

Equation (1) provides an economical prescription to evaluate the particle-surface force from knowledge of the energy-separation function between two planes. It presents clear advantages to common numerical approaches, in that equation (1) can be directly integrated analytically for many cases of interest. We show explicit applications next.

A. Van der Waals interaction

The van der Waals case has been solved a long time ago [12], and we only report it here as an example of use of equation (1). The plane-plane van der Waals interaction is given by [13]

$$E(h) = -\frac{A_H}{12\pi h^2} \quad (2),$$

where A_H is the effective Hamaker constant.

Substituting equation (2) into (1) provides

$$F(D) = -\frac{A_H}{6} \left[\frac{a}{D^2} + \frac{a}{(D+2a)^2} + \frac{1}{D+2a} - \frac{1}{D} \right] \quad (3)$$

This force comes from the potential

$$U(D) = -\frac{A_H}{6} \left[\frac{a}{D} + \frac{a}{D+2a} + \ln\left(\frac{D}{D+2a}\right) \right] \quad (4),$$

which is in agreement with the usual Hamaker's expression.

B. Analysis of SFM Experiments

Forces between an *SFM* tip and a plane in aqueous solutions have been investigated as a function of pH and ionic concentration [14]. Given that the tip, at its closest approach to the surface, appears spherical, it is reasonable to conjecture that the tip-plane forces can be derived from equation (1). Thus, here, the tip plays the role of a large colloidal particle. In addition, once the tip-surface interaction is found, it can also be used to gain understanding of a colloidal system, in which the colloidal particles interact with the plane.

The plane-plane energy is [14]:

$$E(h) = \frac{2\pi}{\varepsilon_r \varepsilon_0 \kappa} \sigma_1 \sigma_2 e^{-\kappa(h-D_0)} + \frac{B}{72\pi(h-D_0)^8} \quad (5)$$

where σ_1 and σ_2 are the surface charge densities of plane and tip, and B and D_0 are parameters, usually determined experimentally [9].

Given the relevance of equation (5) to *SFM* measurements in liquids, we now use equation (1) to produce a closed-form expression for the force-separation,

$$F(D) = 2\pi a \left[\frac{2\pi\sigma_1\sigma_2}{\varepsilon_r \varepsilon_0 \kappa} \left(e^{-\kappa(D-D_0)} + e^{-\kappa(D+2a-D_0)} \right) + \frac{B}{72\pi} \left(\frac{1}{(D-D_0)^8} + \frac{1}{(D+2a-D_0)^8} \right) \right] + \quad (6)$$

$$2\pi \left[\frac{2\pi\sigma_1\sigma_2}{\varepsilon_r \varepsilon_0 \kappa^2} \left(e^{-\kappa(D+2a-D_0)} - e^{-\kappa(D-D_0)} \right) + \frac{1}{7} \frac{B}{72\pi} \left(\frac{1}{(D+2a-D_0)^7} - \frac{1}{(D-D_0)^7} \right) \right]$$

Figure 1 shows two sets of curves for experimentally relevant situations [14]. The dashed lines correspond to plots of equation 6.

By having available the expression (6) for the force, we can answer theoretical questions. For example, the zero of $F(D)$ in equation (6) (when $\sigma_1\sigma_2 < 0$) corresponds to an accretion region for colloidal particles near the surface. That is, if the solution contained colloids, that region is where a large concentration of the particles would be found. Since no zeros exist for $\sigma_1\sigma_2 > 0$ one expects a homogeneous distribution of the colloidal particles, with the exception of a small depletion layer near the surface due to the dominant repulsion there. This problem is of particular current relevance to understand adsorption and self-assembly of colloidal nanoparticles on surfaces and has been studied both experimentally [15] as well as computationally [16]. In addition, from the closed-form expressions reported in this paper we can al-

so evaluate the gradient of the force at equilibrium, which is related with the effective spring constant of oscillation of particles around equilibrium. This parameter, in conjunction with the knowledge of the viscosity of the liquid, is related with the time scales necessary for the colloidal layer to achieve equilibrium, thus providing a useful tool for colloidal adlayer formation.

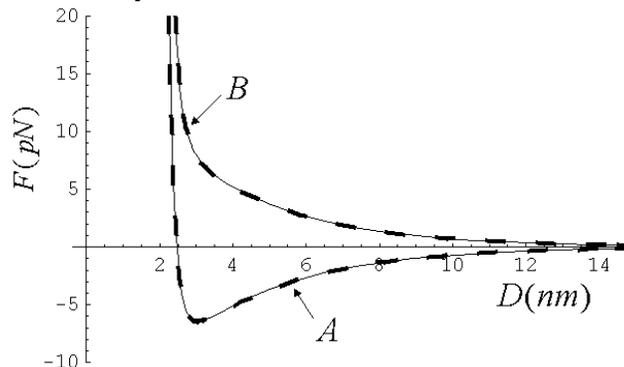


Figure 1. SFM tip-surface force curve for experimental parameters $D_0 = 1\text{nm}$, $a = 7\text{nm}$, $B = 10^{-72}\text{Jm}^6$, $\epsilon_r = 78.5$, $1/\kappa = 3\text{nm}$. A corresponds to $\sigma_1\sigma_2 = -20(\text{pC}/\text{nm})^2$, and B to $\sigma_1\sigma_2 = 20(\text{pC}/\text{nm})^2$. The dashed thick lines are those of this work and the thin continuous lines are experimental [17].

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