

Determination of the Separation in Colloid Probe Atomic Force Microscopy of Deformable Bodies

Graeme Gillies, Clive A. Prestidge, and Phil Attard*

Ian Wark Research Institute, University of South Australia,
Mawson Lakes, South Australia 5095, Australia

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The main difficulty with atomic force microscopy (AFM) measurements on deformable systems is that there is no sharp transition between contact and noncontact because deformation occurs prior to contact due to the extended range of surface forces. This means that the zero of separation cannot be determined in the same way as for rigid bodies. In this paper, we report a rigorous method for determining the separation.

In the literature, one can identify six methods that have been used in an attempt to resolve the problem. First, the piezo drive distance is used as an abscissa and all separations are reported as relative to an arbitrary zero.^{1,2} This approach simply ignores the problem. Second, the deformation is modeled as a Hookean spring and the zero of separation is taken to be the point at which the linear compliance line reaches zero force.^{3–5} This approach is only valid if the surfaces come into intimate contact in the constant compliance region. In the case of bubbles and droplets, often a liquid film remains between the surfaces and the zero is displaced by the thickness of the film, as was originally recognized by Ducker et al.³ Third, a related method assumes the zero to be where deformed surfaces in contact have zero force.^{6–8} Because this occurs due to the balance of van der Waal's attraction and steric repulsions, the amount of flattening can be substantial, and errors arise from ignoring it. Fourth, the zero of separation is taken to be the separation corresponding to the maximum force.^{9–11} This approach also ignores the flattening of the deformable bodies and can be in serious error for compliant bodies. Fifth, the zero of separation is taken to occur at the point of the first measurable force.¹¹ This is appropriate for contact forces of zero range but is evidently incorrect for forces of extended range. For the case of van der Waal's forces, Burnham et al.¹² define contact as the position where a repulsion is first detectable, which they took to be signified by a change in curvature of the force. A related method fixes the zero of relative separation at an arbitrary small force,¹³ which allows

comparison of data with the same force law but not if the forces are of different magnitude or type. Sixth, Mulvaney et al.¹⁴ fit the nonlinear Poisson–Boltzmann equation for rigid bodies by adjusting both the zero of the experimental separation and the surface potential. The problem with this approach is that it ignores the deformation at small separations, which is where the linear and the nonlinear Poisson–Boltzmann equations differ, and at large separations an arbitrary change in surface potential can be compensated by a change in separation. In other words, one cannot determine unique values for the potential and the zero of separation simultaneously.

The method we propose here uses the linear Poisson–Boltzmann equation for rigid bodies at large separations to establish the zero of experimental separation. The rationale for the method is that even soft bodies behave as if they were rigid for weak enough forces. The method requires that the surface potential be independently measured (e.g., by electrophoresis). However, beyond this restriction, it is generally applicable to AFM measurements of charged deformable particles.

The renormalized linear Poisson–Boltzmann equation is

$$F = 64\pi\epsilon_0\epsilon_r R(k_B T/q)^2 \gamma_1 \gamma_2 \kappa e^{-\kappa h}$$

Here, F is the force between a flat substrate and a sphere of radius R , ϵ_0 is the permittivity of free space, ϵ_r is the relative dielectric constant of the aqueous medium, k_B is Boltzmann's constant, T is the absolute temperature, q is the ionic charge, κ is the Debye length of the electrolyte, and h is the separation. The renormalized potential is

$$\gamma = \tanh(q\psi/4k_B T)$$

where ψ is the surface potential. The separation that appears here is that between the two surface charges. The experimental data are shifted horizontally to coincide with this force law at large separations.

Figure 1 illustrates the method for a soft solid cross-linked PDMS particle (for details, see ref 17). The zero of separation has been established by shifting the force vs distance data to coincide with the linear Poisson–Boltzmann theory for rigid bodies. From the decay length of the data, 9.6 nm, it can be seen that the particle does indeed behave as a rigid body at large separations. We used the measured ζ -potentials^{15,16} in calculating the Poisson–Boltzmann curve, which allows the zero to be established unambiguously. We have renormalized the potentials to the nonlinear Poisson–Boltzmann asymptote.¹⁸ We have also performed elastic deformation calculations^{19,20} using the renormalized force law. It can

* To whom correspondence should be addressed at phil.attard@unisa.edu.au.

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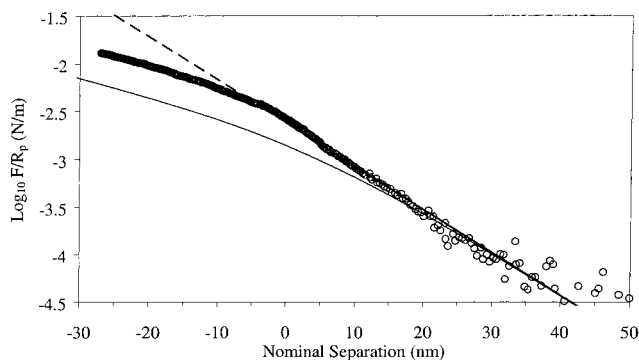


Figure 1. AFM measurements¹⁷ of the force (F) between a silica sphere ($R_1 = 5 \mu\text{m}$) and a soft PDMS particle ($R_2 = 0.5 \mu\text{m}$) in 1 mM KNO_3 at pH 9.3, normalized by ($R_p^{-1} = R_1^{-1} + R_2^{-1}$). The bold line is the rigid body renormalized linear Poisson–Boltzmann result using the measured ζ -potentials, $\psi_1 = -70 \text{ mV}$ ¹⁵ and $\psi_2 = -46 \text{ mV}$ ¹⁶ (shown dashed past contact). The solid curve is the calculated force for an elastic body with a Young's modulus of 1 MPa.^{19,20}

been that these also go over to the rigid body result at large separations, which confirms that the procedure is exact. (There is no arbitrary zero in the theoretical calculations.) Negative nominal separations correspond to interpenetration of undeformed bodies; the actual separation is always positive. Both the elastic theory and the experimental data deviate from the linear Poisson–Boltzmann law at higher loads as deformation becomes important. Using a Young's modulus of 1 MPa, the elastic theory overestimates the extent of the deformation but shows the same qualitative behavior as the experiment. We shall show in a more detailed study that viscoelastic effects and steric interactions are important in this PDMS particle system.¹⁷

Figure 2 shows a representative selection of data from AFM measurements on a sodium dodecyl sulfate (SDS)-stabilized oil drop in 0.01 mM of SDS.¹³ Again, at large separations, the slope of the force data coincides with the Debye length and the zero of separation has been

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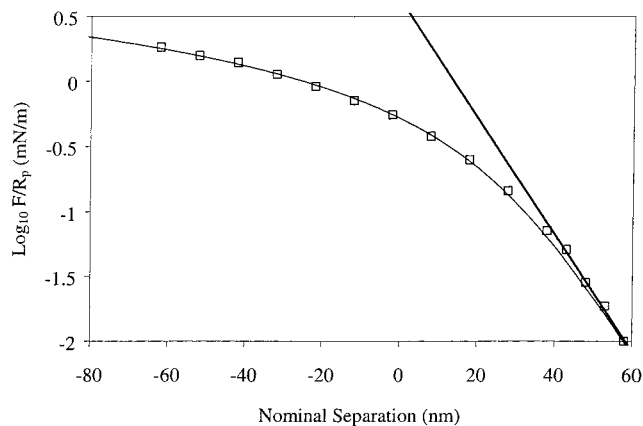


Figure 2. AFM measurements of the force between a silica sphere ($R_1 = 3 \mu\text{m}$) and an *n*-decane oil droplet ($R_2 = 0.25 \mu\text{m}$) in 1 mM NaNO_3 in the presence of 10^{-5} M SDS.¹³ The bold line is the linear rigid body Poisson–Boltzmann result using the measured ζ -potentials, $\psi_1 = -70 \text{ mV}$ ¹⁵ and $\psi_2 = -100 \text{ mV}$,²¹ and the curve is a theoretical calculation that treats the interface as an effective spring.²² The error in the experimental data is comparable to the size of the symbols.

established by shifting the separation to agree with the renormalized linear Poisson–Boltzmann equation using the measured ζ -potentials for silica¹⁵ (-70 mV) and SDS-stabilized *n*-decane²¹ (-100 mV). Furthermore, at higher loads, the data increase less rapidly than the rigid body result, in agreement with a theory that treats the interface as a simple spring.²²

In summary, we have presented a general procedure for determining the zero of separation in AFM measurements of deformable particles. The method consists of shifting the data to coincide with the known rigid body interaction at large separations where the force is weak and the deformation is negligible. The technique is generally applicable to double-layer interactions where the surface potential has been independently measured.

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