Deformation and Adhesion of Viscoelastic Particles: Theory and Atomic Force Microscopy

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A summary is given of the authors' recent research on viscoelastic theory and its application to colloid probe atomic force microscopy. A general computational approach for the interaction of viscoelastic colloids interacting with realistic surface forces of extended range is outlined, and the origins of velocity and time dependent effects including hysteresis is discussed. A general method for establishing the zero of separation in atomic force microscopy of deformable bodies is described and utilised in force measurements made on a poly-(dimethylsiloxane) colloid particles. A quantitative analysis of the velocity and load dependence of the hysteresis in the measurements yields the viscoelastic parameters of the colloid.

Keywords: atomic force microscope, adhesion, deformation, elastic, viscoelastic

I. INTRODUCTION

Colloid science is concerned with the properties of dispersions of small particles in a fluid. The rheology and stability of the dispersion, and the rate of aggregation and the nature of the aggregates, are determined by the interactions between the colloid particles, and much attention has been given to predictive theories for these forces and to their quantitative measurement. The nature of the particle surface determines these forces, and there is a close relationship between surface science and colloid science, and between particle interactions with each other and with surfaces. Although most attention has focussed upon rigid solid particles and surfaces, which are the easiest to characterise theoretically and experimentally, there are nevertheless many common systems where deformation cannot be ignored. Examples of deformable colloid particles and surfaces include oil, water, and polymerised emulsion droplets; bubbles, froths, and foams; surfactant aggregates in the form of micelles, vesicles, lamellae, and deposited or assembled monolayers; biological cells, membranes, and biomolecules; polymers and macromolecules; polymer coated particles and surfaces; polymer films, aggregates, rubbers, and gels; and interlayers of glues and adhesives. In fact, even apparently rigid colloid particles deform, not only for large forces, but also in the important case of adhesion, since the stresses in the contact zone are large even in the absence of an applied load or tension.

There are experimental and theoretical challenges to characterising the interactions between deformable particles and surfaces. The most common technique used for direct force measurement is colloid probe atomic force microscopy (AFM)\cite{1,2}. The constant compliance region, which for rigid particles is used both to calibrate the photodiode and to establish the zero of separation, may, for deformable particles, have a particle-dependent slope, or may not exist at all, and new methods need to be developed for the quantitative presentation of force measurements. Further, soft solid particles and fluid droplets are viscoelastic, and careful attention has to be paid to the time- and velocity-dependence of the measured forces, which is rarely necessary for rigid particles. Finally, because so little theoretical work has been done on the interactions of deformable colloids and substrates, there are few quantitative or even qualitative guides to the expected interactions, and it is therefore difficult to distinguish real phenomena from experimental artefacts.

The dearth of theory can be explained by the complications introduced by deformation. For rigid particles the total interaction force is the integral over the interface of the local pressure, which depends upon the local separation, which in turn is determined by the particles' geometry. The latter is fixed and taking it into account gives rise to the Derjaguin approximation, which greatly simplifies the calculation of the interaction. For deformable particles, the local pressure likewise depends upon the local separation, but the latter depends upon the particles' shape, which itself depends upon the local pressure. The self-consistent solution of these poses great challenges, and the problem is exacerbated when the deformation becomes time-dependent.

We have now developed methods for solving these problems and are in a position to obtain detailed quantitative data for the interactions of deformable systems. In this review we give a brief summary of the experimental protocol that we have developed for AFM measurements on these systems, and we outline the theory that we use to model the measurements. A quantitative comparison of the two demonstrates their utility.

II. ELASTIC DEFORMATION

The deformation and adhesion of soft solids have been measured directly in various experiments, ranging from the macroscopic\cite{3-13} to the microscopic with the AFM\cite{14-24}. The JKR apparatus—named after Johnson, Kendall, and Roberts—yields the contact radius and the amount of flattening as a function
of the applied load, and also the adhesion, which is the pull-off force or the maximum tension that can be sustained. The AFM gives the deformation as a function of load, and the adhesion, but do not give directly the surface shape. Its advantage is its ease of use, its molecular resolution, and its electronic data acquisition capability that allows dynamic measurements to be performed.

The theory that describes the deformation of elastic bodies is based upon continuum linear elasticity theory in the semi-infinite half-space approximation.\cite{25}

\[
    u(r) = -\frac{2}{\pi E} \int ds \frac{p(s)}{|r - s|},
\]

(1)

Here the elasticity parameter \( E \) is given in terms of Young's moduli \( E_1 \) and Poisson's ratios \( \nu_1 \) of the two bodies, \( 2/E = (1 - \nu_1^2)/E_1 + (1 - \nu_2^2)/E_2 \), \( r = |s| \) and \( s - |s| \) are the lateral distances from the central axis connecting the centres of the bodies, \( p(s) \) is the local pressure. The quantity on the left-hand side, \( u(r) \), is the total deformation normal to the surfaces at each position. Equation (1) shows how the deformation decays away from the point of application of the local stress, and how the total deformation at any point is the linear superposition of the deformation due to these local pressures.

The deformation relates the local nominal separation between the two bodies, \( h_0(r) \), which would be the separation if the bodies did not deform, to the actual local separation,

\[
    h(r) = h_0(r) - u(r).
\]

(2)

Here the local separation of the undeformed surfaces is \( h_0(r) = h_0 + \tau^2/2R_c \), where \( h_0 \) is the separation on the axis, and where \( R_c^{-1} = R_1^{-1} + R_2^{-1} \) is the effective radius of the interacting bodies; in general each \( R_i \) is related to the principle radius of curvature of each body.\cite{26}

The oldest theories for the elastic deformation of bodies are contact theories in which the local pressure \( p(r) \) is a specified function of radius that when integrated gives \( u(r) = \tau^2/2R_c \), which corresponds to a flat contact region, \( h(r) = 0 \). Hertz theory is applied to repulsive contact, and JKR theory\cite{27} and the theory of Derjaguin, Muller, and Toporov (DMT)\cite{28} are applied to adhesive bodies.

The virtue of contact theories is that they give simple analytic results, but they are unrealistic because the actual interaction forces between surfaces have an extended range. For example, the van der Waals attraction can be measured at 10nm separation, and the electric double layer repulsion can be measured at 100nm separation. It is particularly important to take into account the range of the force when comparing with measurements taken with molecular resolution, as is the case with the AFM. In these cases the local pressure depends upon the local separation,

\[
    p(r) = p(h(r)),
\]

(3)

where \( p(h) \) is the pressure between two infinite planar walls at a separation of \( h \), and is given by the van der Waals or electric double layer force law appropriate for the bodies being analysed. In these so-called soft contact theories, the local separation depends upon the deformation, and Eqs (1-3) must be solved by iteration for each nominal separation \( h_0 \). This can be done, and the elastic deformation and adhesion as a function of load for elastic solids interacting with realistic surface forces of extended range has been characterised.\cite{29-38}

An efficient algorithm for the solution of the non-contact elastic equation has been given by Attard\cite{34, 36} and it is used for the results presented here. The algorithm self-consistently calculates the surface shape of the elastically deformed bodies due to the local pressure, which, in turn, depends upon the local separation of the deformed bodies. In this way one obtains the actual surface shape and the actual pressure profile, whereas contact mechanics assumes simplified forms for both. For the present elastic calculations there was no hysteresis between the loading and unloading cycles. (The hysteresis observed in the original papers\cite{34, 35} for soft adhering bodies has since been attributed to a non-equilibrium viscoelastic effect;\cite{36, 37} see Section III.)

The algorithm has been used to obtain results for van der Waals attractions, electrical double layer repulsions, and oscillatory structural forces.\cite{34-38} The pressure law used for the van der Waals attraction is

\[
    p(h) = \frac{A}{6\pi a^3} \left[ \frac{h_0^{6}}{h^6} - 1 \right],
\]

(4)

where \( A \) is the Hamaker constant, and \( h_0 \) characterises the length scale of the soft-wall repulsion.

Figure 1 shows the shape of adhesive elastic spheres during their interaction for two values of the elasticity parameter that approximately correspond to a rubbery material and to a glass. At the largest separation where the force is negligible the surfaces are undeformed. At separations just larger than contact, the surfaces bulge toward each other under the influence of the extended range of the van der Waals attraction. This effect cannot be accounted for by contact theories, and is more pronounced for the softer material. There is a relatively sudden jump into or out of contact, and the radius of the flattened contact region changes most rapidly in the vicinity of the jump. The edges of the contact region are less pronounced for the harder material, but even for the soft material the edge is not infinitely sharp, as JKR theory assumes.

Figure 2 plots the force against the nominal separation for an adhesive elastic particle, as one would measure in an AFM experiment. Most noticeable is the post-contact soft compliance regime, which has a finite slope and is never really linear. The negative nominal
separations in this regime indicate the amount of flattening of the elastic colloid particle. Prior to contact the attraction is greater than for rigid particles due to the bulge exhibited in the preceding figure. This is clear in the inset, which tests the so-called central deformation approximation (CDA).\[34\] This gives the amount of pre-contact deformation as a function of the actual separation,

\[ u(0) = \frac{A \sqrt{2R}}{8Eh(0)^{3/2}}. \] (5)

From this one may obtain the nominal separation as a function of the actual separation, \( h_0 = h(0) + u(0) \), and the consequent force,

\[ F(h_0) = -\frac{AR}{6h(0)^{3/2}}. \] (6)

It can be seen from the inset to Fig. 2 that this simple analytic approximation is quite accurate in the pre-contact regime.

III. VISCOELASTIC DEFORMATION AND ADHESION

The elastic theory becomes inapplicable as the adhesion or deformability of the bodies is increased, because in this regime viscoelastic effects become important. Experiments clearly show hysteresis and time-dependent effects, such as variability in the pull-off force,\[5, 12, 39\] and, particularly for soft-bodies with large adhesions, hysteresis in the measurements, with the pull-off force depending upon the history of the sample and the details of the loading-unloading cycle,\[19, 40, 41, 42\] Maugeis and Barquins have reviewed adhesion experiments on viscoelastic materials, and they have attempted to interpret these in JKR terms with a somewhat ill-defined time-dependent surface energy.\[13\]

For viscoelastic materials, the elasticity parameter in Eq. (1), which gives the instantaneous response to the pressure, is replaced by the creep compliance function, which gives the response to past pressure changes, and this accounts for the prior history of the sample. Hence the generalisation of the elastic half-space equation involves a time convolution integral,\[43, 44\]

\[ u(r, t) - u(r, t_0) = \int_{t_0}^{t} \frac{dt'}{\pi E(t-t')} \int ds \frac{\phi(h(s, t'))}{|r-s|}. \] (7)

Here \( \phi(h(r, t)) \) is the time rate of change of the local pressure at a distance \( r = |r| \) from the axis and at time \( t \). The bodies are assumed stationary up to time \( t_0 \), and, if interacting or in contact, have at that time fixed deformation corresponding to static elastic equilibrium, \( u(r, t_0) = u_\infty (r) \). This expression is the generalisation to interactions of extended range of the contact mechanics expression used by a number of authors.\[45-48\] In contact mechanics an analytic \( \phi'(r, t) \) is specified, whereas in the present approach \( \phi(h(s, t)) \) is determined self-consistently by the physical force law and the rate of change of separation.

An algorithm has been developed for solving the viscoelastic problem with arbitrary surface forces of extended range when creep compliance function is exponential,\[43\]

\[ \frac{1}{E(t)} = \frac{1}{E_\infty} + \frac{E_\infty - E_0}{E_\infty E_0} e^{-\tau}. \] (8)

Here \( E_0 \) and \( E_\infty \) are the short- and long-time elasticity parameters, respectively, and \( \tau \) is the relaxation time. The algorithm can be generalised to more complex materials with multiple relaxation times.\[43\] The present three-parameter model is perhaps the simplest model of viscoelastic materials, although an alternative three-parameter expression, \( E(t)^{-1} = C_0 + C_1 t^m \), \( 0 < m < 1 \), has also been used to model liquid-like materials.\[47-49\]

With the exponential creep compliance function, differentiation of the deformation yields\[43\]

\[ \dot{u}(r, t) = -\frac{1}{\tau} \left[ u(r, t) - u_\infty (r, t) \right] - \frac{2}{\pi E_\infty} \int ds \frac{\phi(h(s, t))}{|r-s|}. \] (9)

where \( u_\infty \) is the static deformation that would occur in the limit \( t \to \infty \) if the pressure profile were fixed at its current value,

\[ u_\infty (r, t) = -\frac{2}{\pi E_\infty} \int ds \frac{\phi(h(s, t))}{|r-s|}. \] (10)

The rate of change of the pressure is

\[ \dot{\phi}(h(r, t)) = \phi'(h(r, t)) \left[ \dot{u}_0 (t) - \dot{u}(r, t) \right], \] (11)

where \( \dot{u}_0 (t) \) is the specified drive trajectory. Accordingly, Eq. (9) represents a linear integral equation for the rate of change of deformation. It can be solved using the same algorithm that has been developed for the elastic problem.\[34, 36\] It is then a simple matter to solve the differential equation for the deformation by simple time stepping along the trajectory, \( u(r, t + \Delta t) = u(r, t) + \Delta \dot{u}(r, t) \).

The algorithm has been used to obtain results for an electrical double layer repulsion\[43\] and for a van der Waals attraction.\[44\] Figure 3 shows the shape of viscoelastic spheres that interact with the same van der Waals attraction as in Fig. 1. The total time spent on the loading branch is ten times the relaxation time, so that one expects to see viscoelastic effects. There are clear similarities with the elastic spheres of Fig. 1, which correspond to the short- and long-time
viscoelastic limits of the Fig. 3. One can see the undeformed surfaces at the largest separation prior to approach, the bulge prior to contact, the relatively rapid jump into contact, and initially a fast spreading of the flattened contact region, which continues to grow as the bodies are driven further together. At the edges of the contact region there is a noticeable rounding of the surface profiles on the approach branch. Following the reversal of the motion, (unloading), the surfaces become extended as they are pulled apart, and there is a sharper transition between contact and non-contact than on the loading branch. Again it should be noted that even in this case the slopes at the edge of the contact region are not discontinuous as predicted by the JKR theory. Following the turning point, the surfaces appear pinned in contact for a short time before the contact region begins to recede. After the surfaces jump apart they retain a memory of the stretching that occurred during unloading, and over times comparable to the relaxation time the local separation is smaller on the unloading branch out of contact than at the corresponding position upon loading.

The difference in surface shape on loading and unloading gives rise to force hysteresis, Fig. 4. The hysteresis in the force curves for viscoelastic bodies indicates energy dissipation: the energy required to move the surfaces a nominal distance on loading, is not entirely recovered from the system in moving the same distance on unloading. The area of the hysteresis loop therefore measures the amount of energy dissipated during the force measurement, and it increases with increasing drive velocity. The physical origin of the decreased repulsion on the unloading curve is that at a given nominal separation the actual local separation is larger on retraction than upon approach, (because, as Fig. 3 reveals, it takes a finite time for the flattened surfaces to relax), and the local pressure and hence the total repulsion is weaker. At slow speeds the viscoelastic curve tends toward the elastic result of Fig. 2 for the long-time elasticity, $E = E_\infty$, and conversely, at high speeds it tends toward the short-time elastic result, $E = E_0$, (but only on approach). This is precisely what one would expect from the definitions of the short- and long-time elastic parameters.

The minimum in the force curves in Fig. 4 increases with increasing velocity. The absolute value of the minimum, $F^*$, which is the maximum tension sustained by the bodies, is called the adhesion. It can be seen that the adhesion of the viscoelastic bodies is significantly greater than that of elastic bodies, (Fig. 2). This velocity-dependent adhesion is explored in more detail in Fig. 5. As the velocity is decreased, the curves asymptote to the static equilibrium elastic result, calculated from Eq. (1). The JKR elastic prediction, $F^* = 3\gamma R/2$, is not exact, (as a contact approximation it neglects the range of the van der Waals interaction), but it is increasingly accurate as the surface energy is increased, (equivalently, as the elasticity is decreased). As the velocity increases, and the system is given less time to equilibrate, viscoelastic effects become more evident and the adhesion increases. The data in Fig. 5 suggest that at very high speeds the adhesion will be independent of the surface energy.

It was shown in Fig. 2 that the central deformation approximation (CDA) was relatively accurate for elastic particles in the pre-contact situation. An analogous approximation can be made for the viscoelastic case, again replacing the deformation $u(r,t)$ everywhere by its value on the central axis, $u(0,t)$, and results in an analytic differential equation that has been tested for the van der Waals attraction used above,[44] and for an electrical double layer repulsion.[43] The latter has the form

$$p(h) = Pe^{-\eta h},$$

and in this case, the analytic approximation for the central deformation $u(t) \equiv u(0,t)$ is$^{[43]}$

$$\dot{u}(t) = f(t)h_0(t) - [u(t) - u_\infty(t)]/\tau,$$  \(13\)

where $f(t) \equiv \sqrt{8\pi \kappa RF^2/E_0^2 \exp(-\kappa [h_0(t)-u(t)])}$. For a given trajectory $h_0(t)$, the deformation $u(t)$ is readily obtained from the preceding equation for $u(t)$ by simple time-stepping. The force in this approximation is

$$F(t) = 2\pi R\kappa^{-1} Pe^{-\kappa [h_0(t)-u(t)]},$$  \(14\)

which shows that the change in surface shape has little effect on the pre-contact force, whereas the change in separation due to the central deformation is all-important.

Figure 6 tests the CDA for the pre-contact flattening of the particles under their mutual repulsion. The approximation is quantitatively accurate and correctly shows that at a given position $h_0$, the deformation is greater at the slower driving speed. This is because the long-time component of the elasticity, which is softer than the short-time component, has more time to take effect. This means that the force is weaker at slower driving speed because the surface separation of the effectively softer material is greater at a given position (not shown). The inset tests the CDA for the load, and compares a viscoelastic sphere to an undeformable one. At a given position the load is less for the deformable particle that that for a rigid particle because the surface separation between deformed particles is greater than that between undeformed particles. The agreement between the central deformation approximation Eq. (13) and the exact calculations shows the utility of the approximation and confirms that deformation affects the force through the change in separation rather than through any increase in contact area due to flattening. Notice that at large separations the force on the viscoelastic particle equals that on the rigid particle. In this weak force regime the deformation is negligible. This fact can be used to establish the zero of separation in AFM force measurements on deformable systems (see next).
IV. DEFORMATION AND ADHESION MEASUREMENTS

Controlled dynamic measurements with the AFM can be used to study viscoelastic effects and detailed analysis with the theory described above allows the measurement of the material properties of the viscoelastic particle or substrate. The data that are directly obtainable are the force as a function of drive distance for both loading and unloading, and the adhesion. Although there have been a number of previous AFM studies of deformable solid surfaces,[14-24] these have generally not provided a quantitative description of deformation or of time-dependent effects. Such a research program of quantitative AFM measurements and analyses has recently been commenced by us for viscoelastic particles.[60] An emulsion polymerization process is used to make poly(dimethylsiloxane) (PDMS) droplets or particles.[51, 52] The ratio of trimer cross-linking agent to monomer used in the synthesis controls the deformability: 50% trimer yields the solid-like droplets analysed below. The droplets, which range in size from 0.1-1 μm, adhere to a glass slide that is transferred to the AFM. A 7 μm diameter silica colloid probe, which is effectively flat compared to the droplets, is attached to the cantilever; the well-known surface chemistry of the probe enables a quantitative analysis of the measurements. Electrophoresis is used to measure the zeta potential of the droplets.[53] The surface chemistry of the droplets is very similar to that of the silica probe; at pH9.6 the zeta potential of a droplet is -46 mV and that of the silica colloid is -70 mV.

For deformable systems special arrangements have to be made to calibrate the normal sensitivity factor of the force-measuring photodiode because there is either no constant compliance region, or else it has a particle-dependent slope due to the effective spring constant of the deformable substrate or particle. One can perform the vertical calibration by a prior measurement on a hard substrate in the constant compliance regime. We performed this calibration in situ by simply moving away from the droplet and pressing the cantilever against the substrate.[50] If this is not possible, (because either the drop is macroscopic or because a deformable probe is attached to the cantilever), then one can perform the calibration on another cantilever provided that one takes care with the remounting and alignment of the laser beam.[54]

Gillies et al.[50] have given a method for determining the zero of separation when the force between rigid particles with the same surface properties is known, as is generally the case for electric double layer repulsions. As shown in the inset to Fig. 6, the weak forces at large separations cause negligible deformation, and so the zero of nominal separation may be established by simply shifting the measured data horizontally to coincide with the rigid body result in this regime. In practical terms the instrumental factors limit the measurement of weak forces, and whether one has adequate resolution to establish the zero is determined by the ratio of the cantilever spring constant to the deformability of the substrate or particle. Assuming that this regime is accessible, the shift converts the drive distance, which has arbitrary zero, to the nominal separation, which is the separation between undeformed particles.

Figure 7 shows the force measured for a solid-like PDMS droplet.[50] On approach the two negatively charged surfaces display an electric double layer repulsion, followed by a van der Waals jump into contact, and then a soft compliance regime that indicates flattening of the droplet. There is hysteresis on unloading, and it is only after several hundred nanometres of reverse travel that the particle jumps out of contact.

The inset to Fig. 7 shows the data analysis protocol. It can be seen that the measured data has the correct decay length, κ_D = 9.6 nm, at large separations, which confirms that the deformation is negligible. A horizontal shift brings the data into coincidence with the rigid body result and this allows the drive distance to be converted to the nominal separation h₀. The relatively short range of this regime is due to a combination of the large deformability of the PDMS droplet and the stiffness of the cantilever, k = 0.58 N/m, chosen in order to measure large applied loads and as much of the adhesion as possible.

For the rigid body interaction the linear Poisson-Boltzmann law is used, \( F(h₀) = 2πRκ_D^{-1}Pe^{-κ_Dh₀} \), where \( κ_D^{-1} = 9.6 \text{ nm} \) is the Debye screening length, \( h₀ \) is the nominal separation (between rigid particles), and \( R = 0.6 \mu\text{m} \) is the radius of the PDMS droplet. In linear Poisson-Boltzmann theory, the pre-factor in the pressure law, Eq. (12), is given by

\[
P = 2κ₀eᵣκ_D^{-1}(4k_BT/e)^{3/2}γ₁γ₂, \tag{15}
\]

where \( κ₀ = 8.854 \times 10^{-12} \text{ C}^2/\text{J} \text{m} \) is the permittivity of free space, \( eᵣ = 78 \) is the dielectric constant of water, \( q = 1.6 \times 10^{-19} \text{ C} \) is the charge on the monovalent electrolyte ions, \( k_B = 1.38 \times 10^{-23} \text{ J} \text{K}^{-1} \) is Boltzmann's constant, and \( T = 300 \text{ K} \) is the temperature. A renormalised surface potential is used that converts this into the non-linear Poisson-Boltzmann law in the asymptotic regime.[53, 56]

\[
γᵢ = \tanh qψᵢ/4k_BT, \quad i = 1, 2, \tag{16}
\]

with \( ψ₁ = -46 \text{ mV} \) and \( ψ₂ = -70 \text{ mV} \) being the independently measured surface potential.[53]

The inset to Fig. 7 also tests the elastic theories described in §II. The full elastic theory agrees well with the measured data over most of the inward regime shown using a fitted elasticity of \( E = 0.4 \text{ MPa} \). The slight increase in the measured data near the end of the regime, and the fact that the measured data increases beyond the maximum Poisson-Boltzmann force (at \( h₀ = 0 \)), indicates the presence of an additional repulsion, which most likely originates from
steric interactions of polymer chains that extend out from the PDMS surface. For this reason a short-range repulsion, \( P(z_0/h)^6 \), with \( z_0 = 0.5\text{nm} \), has been added to the Poisson-Boltzmann law in these calculations.

As discussed briefly in connection with Eq. (5), the central deformation approximation (CDA) is accurate for the pre-contact deformation. For the present electric double layer repulsion the CDA gives for the deformation on the axis \[ u(0) = -\sqrt{8\pi R/\kappa D} P e^{-\kappa D h(0)} \equiv \omega e^{-\kappa D h(0)}, \tag{17} \]
and the corresponding nominal separation is \( h_0 = h(0) + u(0) \). The resultant force is \( F(h_0) = 2\pi R\kappa D e^{-\kappa D h} \). This elastic CDA agrees well with the measured data up to the maximum Poisson-Boltzmann force, which equals the CDA force at \( h = 0 \). (No steric interactions have been included in the CDA.) The agreement between the approximation and the measurements is good enough to allow an initial estimate of the elasticity parameter and to confirm the role of deformation in the measurements.

The force given by theories and the measurements becomes relatively linear on the logarithmic plot at negative nominal separations, (ie. when driven past undeformed contact). Effectively, the decay length has been renormlised due to the elasticity of the substrate. The CDA decay length in this regime may be obtained from Eq. (17), with the limiting force given by
\[ F(h_0) = 2\pi R\kappa D e^{-\kappa D h}. \tag{18} \]
The decay length is in this regime
\[ \kappa = \frac{\kappa D}{1 + \omega \kappa D}, \tag{19} \]
and the renormlised pressure coefficient is
\[ P' = P e^{-\kappa \omega}. \tag{20} \]
This result is valid in the range \(-\omega < h_0 < \kappa D^{-1} \).

Although the elastic theory fits the inward data in Fig. 7, the hysteresis in the data shows that the PDMS droplet is in reality viscoelastic, and the full theory should be applied. This is done in Fig. 8, which shows measurements on a smaller PDMS droplet. A weaker cantilever has been used here to give greater resolution in the weak force regime (see the inset). This has the additional benefit that the van der Waals jump into contact can be more easily avoided (ie. weaker loads are used here than in Fig. 7) and hence the electric double layer force law can be used in the viscoelastic theory, Eq.(9), without adding a van der Waals component. The data in Fig. 8 show good agreement between theory and experiment for the particular elastic parameters used, with in particular the width of the hysteresis loop and the force maximum correctly given by the theory.

On the outward run in Fig. 8 there is evidence of a weak adhesion. Other measurements (not shown) display evidence for long-range attractions that increase with separation and that appear as discrete steps. These may be attributed to individual bridging polymers, with the flat regions corresponding to the peeling of the polymer from the silica sphere segment by segment, and the regions of increasing force corresponding to the stretching of the individual polymer chains. Such forces between individual bridging polymers have been explored in other AFM measurements. Because these attractions are ignored in the present theoretical calculations there is a limit to the quantitative accuracy of the fits to the experimental data.

Figure 9 compares the measured and predicted force curves when the parameters of the trajectory are changed. In the case of an increase in the maximum applied load, (ie. the particle was driven 50nm further toward the substrate), there is almost quantitative agreement between the theory and the experiment for the increase in the hysteresis and the increase in the load. (Note that the viscoelastic parameters fitted in Fig. 8 were used in the calculations shown here. The only difference between the two figures are the drive trajectories.) The slight increase in the measured data compared to the theory at high loads may be due to the influence of the rigid substrate. The 80nm of deformation that occurs here is not negligible compared to the 300nm radius of the viscoelastic particle, and the viscoelastic half-space model that underlies Eq.(9) may break down for this amount of flattening.

The inset to Fig. 9 explores the dependence of the force law on the speed of the measurement. As predicted, the measured force is greater at a given drive position because of the increased contribution from the short-time elasticity. The theory is quantitatively accurate in predicting this increase on the inward run, but it underestimates the amount of hysteresis when the direction of motion is reversed. It is possible that more refined fitting of the viscoelastic parameters could improve the agreement here. In any case, the data in Figs 7-9 indicate unambiguously that the PDMS droplets deform during the force measurements, and that the deformation is viscoelastic in nature. The theory correctly predicts the qualitative behaviour of the interaction, and may be described as sufficiently quantitative as to allow an estimate of the material properties of the viscoelastic colloid.

V. SUMMARY AND CONCLUSION

Characterising the interaction of viscoelastic particles and substrates now appears feasible despite a number of theoretical and experimental challenges. The theory has to take into account the extended range of realistic surface forces and the effect that this has on the deformation of the particles. Whilst a number of workers \cite{23-33} including one of us, \cite{34-38}
have done this for elastic particles, it is only recently that viscoelastic systems have been treated at the same level of sophistication. The challenge has been to account for the time-dependence of viscoelastic phenomena, which adhesion and deformation measurements show cannot be ignored for soft solids.

The atomic force microscope is ideally suited to carrying out dynamic measurements that can elucidate a variety of time-dependent and non-equilibrium phenomena, but there are likewise experimental issues that are unique to deformable substrates and particles that must be addressed. The calibration of the photodiode must be performed on a rigid substrate and the zero of nominal separation has to be established by comparison with the known rigid body interaction at large separation. For viscoelastic bodies, there is the further obvious requirement that the speed and time scale of the measurement must be controlled.

As has been summarised in this review, the theory described above provides a guide to the phenomena that can be expected in the experimentally accessible regime and helps to distinguish usable data from contamination and artefacts. The examples given demonstrate that the AFM can be used to obtain a qualitative understanding of the interactions of viscoelastic particles, and, in conjunction with the theory described above, it can also yield quantitative values for their material properties.

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Fig. 1. Surface profiles for adhering elastic spheres. The profiles are plotted after every 2nm drive distance from $h_0 = 10\text{nm}$ (top) to $-10\text{nm}$ (bottom). The Hamaker constant is $A = 10^{-19}\text{J}$, with $\varepsilon_0 = 0.5\text{nm}$ and $R = 10\mu\text{m}$. The right hand panel is for $E = 10^{14}\text{N m}^{-2}$, and left hand panel is for the $E = 10^{10}\text{N m}^{-2}$.

Fig. 2. Force for adhering elastic spheres. From left to right in contact the curves are for $E = 10^{9}$, for $E = 10^{10} \text{N m}^{-2}$, and for rigid spheres, respectively, with all other parameters as in the preceding figure. The inset tests the central deformation approximation, Eq. (5), prior to contact, (dotted curves).

Fig. 3. Surface profiles for adhering viscoelastic spheres. The profiles are plotted every millisecond, or every 2nm from $h_0 = 10\text{nm}$ (top) to $-10\text{nm}$ (bottom). The drive speed is $|h_0| = 2\mu\text{m/s}$ and the Hamaker constant is $A = 10^{-19}\text{J}$, with $\varepsilon_0 = 0.5\text{nm}$ and $R = 10\mu\text{m}$. The viscoelastic parameters are $E_0 = 10^{14}\text{N m}^{-2}$, $E_\infty = 10^{9}\text{N m}^{-2}$, and $\tau = 1\text{ms}$. The right hand panel is for loading and the left hand panel is for unloading.

Fig. 4. Force for adhering viscoelastic spheres. From inside to outside the hysteresis loops correspond to driving velocities of $|h_0| = 1$, 2, and 5 $\mu\text{m/s}$, using the viscoelastic parameters of Fig. 3. The crosses represent the static equilibrium elastic result for $E_\infty = 10^{10}\text{N m}^{-2}$, (Fig. 2). Inset. Loading curves in the region near initial contact. The circles represent the static equilibrium elastic result for $E_0 = 10^{10}\text{N m}^{-2}$, and the bold curve is the force for rigid particles.

Fig. 5. Viscoelastic adhesion. The maximum tension (pull-off force) normalised by the JKR elastic adhesion is plotted as a function of the drive velocity.
(logarithmic scale). The parameters are as in Fig. 3, except that the Hamaker constant is \( A = 1, 5 \), and \( 10 \times 10^{-20} \text{J} \), (the surface energy is \( \gamma \equiv A/16\pi = 0.80, 3.98, \) and \( 7.96 \text{mJ/m}^2 \)), for the dotted, dashed, and solid curves, respectively.

**Fig. 6.** Flattening prior to contact for non-adhesive viscoelastic particles.\(^{[43]}\) The symbols represent the exact calculation, and the solid curves are the central deformation approximation, Eq. (13). The viscoelastic and particle parameters are as in Fig. 3, with \( P = 10^7 \text{N m}^{-2} \) and \( \kappa = 1 \text{nm} \) being used in the pressure law, Eq. (12). A constant driving velocity of \( h_0 = 5 \) (upper) and of \( 1 \mu \text{m s}^{-1} \) (lower) is used. The inset shows the corresponding forces normalised by the radius for \( h_0 = 1 \mu \text{m s}^{-1} \), with the bold curve representing the infinitely rigid case (no deformation).

**Fig. 7.** AFM force measurements\(^{[50]}\) between a PDMS droplet (\(-46 \text{mV}, R = 0.6 \mu\text{m}\)) and a silica sphere (\(-70 \text{mV}\)) in 1mM KNO\(_3\) at pH9.8, with triangular drive trajectory, (speed = 1.2 \mu\text{m/s}). The drive distance is with respect to an arbitrary zero, and the flat force extrema arise from photodiode saturation. **Inset.** Force on a logarithmic plot.\(^{[50]}\) The zero of the nominal separation is determined by shifting the data to coincide with the electrical double layer force at large separation calculated using the measured zeta potentials in the renormalised linear Poisson-Boltzmann law for rigid particles, (straight line). The curves are the elastic theory with fitted elasticity \( E = 0.4 \text{MPa} \) and Poisson-Boltzmann law. The truncated curve is the CDA, Eq. (17), and the longer curve is the full elastic theory, Eq. (1), with added short-range, \((1/h^6)\), steric repulsion.

**Fig. 8.** AFM force measurements\(^{[50]}\) as in the preceding figure with an \( R = 0.3 \mu\text{m} \) PDMS droplet at a drive speed \( 1 \mu\text{m/s} \). The curve is the full viscoelastic theory, Eq. (9), using the Poisson-Boltzmann law plus an exponential steric repulsion (decay length 1.5nm) and fitted parameters of \( E_0 = 1.2 \text{MPa} \), \( E_\infty = 0.8 \text{MPa} \), and \( \tau = 0.07 \text{s} \). The zero of nominal separation has been established by shifting the data to coincide with the rigid body result at large separations (inset).

**Fig. 9.** AFM force measurements\(^{[50]}\). The triangles are the data from the preceding figure, the circles are for a 50nm increase in the drive distance, and the crosses (inset) are for a drive speed of 4 \mu\text{m/s}. The curves are the full viscoelastic theory using the parameters fitted in the preceding figure.