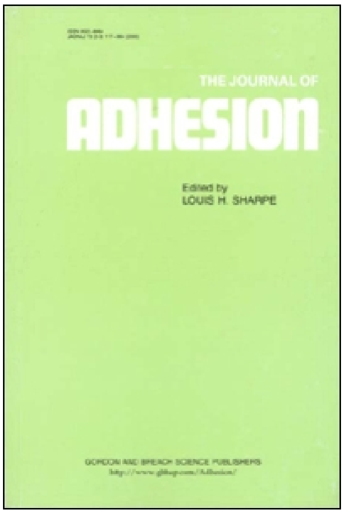

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# Attractive Forces Between Micron-Sized Particles: A Patch Charge Model

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To clarify the role of interparticle attraction in engineering situations that involve the handling of powders, three promising new approaches have recently been described. In this review we outline (i) the use of proximal-probe technology to measure forces acting on an individual particle directly, (ii) the modelling of types of force that depend on interactions between dipole layers or "patch charges" arising from inhomogeneities in work function, (iii) the role of deformation associated with adhesive forces.

KEY WORDS powder; interparticle force; force curve; dipole-dipole interaction; patch field; patch charge; atomic force microscope; AFM.

## INTRODUCTION

Many would agree that we understand in broad terms how interparticle forces contribute to the engineering properties of powders. Unfortunately, this knowledge does not always have much predictive power. Let us briefly consider a few examples, taken largely from the book edited by Briscoe and Adams,[1] of powder properties which depend to a greater or lesser extent upon these forces:

### Strength of Particulate Assemblies: Aggregation and Agglomerate Breakdown

Often, agglomerates of particles are easier to handle than the individual particles themselves. These agglomerates or clusters must be strong enough to withstand handling, but may be required to break up at the end of a processing operation;

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### Mixing and Segregation

The cohesion of powders may usefully be quantified through measurements of Hausner ratio (of aerated to tapped bulk density). However, interpretation depends upon the statistics of a large number of interactions between particles of different size, shape, and surface condition. This disadvantage could be avoided with the help of direct measurement of interparticle forces;

### Particle-surface Interactions: Wall Friction

The adhesion of fine particles to surfaces is of vital importance to the paint industry, in xerography, pharmaceuticals and many other areas. As pointed out elsewhere[40], wall friction and the bulk mechanical behavior of granular materials, in general, have traditionally been measured as "bulk" properties using macroscopic shear test equipment—the role of single particle properties has, by comparison, received relatively little attention;

### Fluidisation

Fluidisation behaviour, in particular the criteria for the transitions between one type of flow and another, involves interparticle forces and their magnitude relative to other relevant forces such as fluid drag;

### Xerography; Electrostatic Powder Coating

Within a range of chemical engineering processes, problems exist through lack of data on spatial variations in surface potential, charge, and other electrical parameters, over the surface of a particulate material.

In fact, much of the difficulty of analysing the effects of interparticle forces in engineering situations (friction and flow of actual powders) arises through the unavoidable complications of having multiple contacts between asperities (microprotrusions) on the two surfaces involved. With the advent of proximal probe technology, controlled experiments on single-area contacts between a surface and an asperity are now possible. This offers a real chance of isolating the different effects of quantities that vary from place to place on the surface, rather than having to rely on a statistical average over many individual contacts.

The parent "proximal-probe" technique is the scanning force microscope, or "AFM" (atomic force microscope). It is now possible to obtain data on the magnitude of the intermolecular attractive forces that act between a solid surface and a test probe, and how these forces vary with separation, as well as information on how the reaction forces produce elastic or plastic deformation, and on real area of contact. Such data are useful in two ways:

(a) they can provide a relatively quick and easy "fingerprint" that is extremely sensitive even to sub-monolayer traces of contamination,

(b) if a reliable model can be found, the data may be matched with theory to give a full interpretation, and values of nanomechanical and adhesive properties of surfaces and films may be derived.

The graph of attractive and repulsive force as a function of separation constitutes a force curve. Much of this article takes the form of a review, and will mention recent work elsewhere involving force curve data obtained with actual particles, although much of the relevant research so far emphasises work with model materials not in powder form. Of particular interest are surface-*electrical* properties, and we briefly review their role in determining interparticle forces, together with proximal-probe techniques for studying them. We end with a discussion of some of our own force curve data which provide evidence of a hitherto-neglected type of long-range interaction, the *patch charge* force. Where appropriate, we summarise the relevant contact mechanics theory.

## FORCE CURVE MEASUREMENTS USING ACTUAL PARTICLES: WORK ELSEWHERE

The first use of the force curve technique to measure colloidal interactions directly was performed by Ducker *et al*[2]. They studied the force between a single silica sphere interacting with a planar silica surface immersed in an aqueous sodium chloride solution. The results were in broad agreement with the DLVO theory (Derjaguin–Landau–Verwey–Overbeek)[15] at long range, although at very short distances there were deviations that may be attributed to hydration forces or roughness effects.

Rimai *et al.*[3] have reviewed their work on how surface forces deform micron-sized particles, as determined by scanning electron microscopy. In collaboration with Schaefer *et al.*[4] they used a micromanipulator and UV-sensitive cement, or simply the action of heat alone, to attach polystyrene spheres to commercially-available silicon nitride AFM cantilevers. They measured the force curves for the interaction between the particle and a p-type silicon substrate. They then estimated the work of adhesion by deriving a value of "work of removal", obtained by integrating the force applied during unloading and dividing by calculated contact area. This work did not correspond to expected values of work of adhesion (discrepancy of more than one order of magnitude): the authors attribute this discrepancy to either temporal effects or to roughness. Rimai *et al.*[3] discuss evidence that, even in the absence of plastic or viscoelastic response, the placing and removal of a particle onto and from a surface may not be a reversible process, owing to the relatively short-range nature of surface forces. The pull-off force required to detach the particle was found to increase significantly with the maximum load applied, as expected on the basis of plastically-induced changes in sample geometry: as we mention later in this article, there was evidence that the surface forces contributed to this plastic deformation.

Mizes and colleagues[5] have examined the interaction between particles and surfaces by a similar technique, the particles being a silicon nitride "pseudoparticle" consisting of a microscopic pyramid (as grown onto the end of the AFM cantilever by the manufacturer) and latex, and also divinylbenzene and glass,[6] and the opposing surfaces polycarbonate, gold, or aluminium. The general form of their force curves is similar to that described by Rimai *et al.*: to date, detailed modelling has not yet been described. They describe also an interesting development in which the pull-off force measured at different points on a sample surface is used to determine the contrast on a "spatial map of adhesion", with a resolution of up to 6 nm. They claim that it will thereby be possible to identify different constituents on a surface according to their different "stickinesses". Mizes[7] has also shown how, for particles attached to a given substrate, the roughness of the substrate can often lead to undesirable variations in particle-substrate adhesion. For example, his spatial adhesion maps confirm that when a particle sits on a ridge of the substrate surface, the adhesion is less than is otherwise the case.

It is worth noting that a part of each curve presented in the work so far discussed tends to be missing, as a result of "cantilever jump" when the measured force gradient exceeded the cantilever spring constant. Accordingly, as in the example discussed later, it is often worth using a relatively stiff cantilever, even at the cost of a lower signal-to-noise ratio.

## SURFACE-ELECTRICAL PARAMETERS AND FORCES

Recent adaptations of the AFM have been successfully used to study surface-electrical variables as follows:

1. *Kelvin force probe microscopy*[8,38] to measure contact potentials, and the distribution of any dielectric material over the surface;
2. *Scanning capacitance microscopy*[39] to measure dielectric properties and impurity dopant distribution;
3. *Surface potentiometry*[9,10];
4. *Charge detection microscopy*[11,12] to look at charge distribution and to measure amounts as small as two or three electron charges;
5. *Scanning damping microscopy*[13] to look at variations in local electrical conductivity;
6. *Chemical potential gradient microscopy.*[14]

It is likely that measurements of this type will be extended to the study of particle-particle interactions to an increasing extent. For a long time it was thought that, as regards the adhesion of particles to solid surfaces, electrostatic effects were dominant under special conditions only, for example in the presence of an applied electric field (electrostatic precipitation, particle collection, xerography, powder coating, fibre filtration, electrophotography). Recently, as we shall see, it has become clear that *even when no field is applied, and with conducting powders as well as non-conductors,* a full description of contact forces requires an understanding of the role of various primary surface-electrical parameters such as surface charge distribution and variations in strength of dipole layers. These, in turn, affect local values of work function (as affected by microscopic contact processes such as charge accumulation, and by variations in the micro-topography and cleanliness of the surface):

### Dipole Layers that Contribute to the Value of Electronic Work Function

A key parameter is the electronic *work function*, $\phi$, representing the difference in energy between the vacuum and bulk Fermi levels. The most important *reasons* for work function variations across a given surface include *spreading* (the spillingout, into the vacuum, of electrons from the solid in consequence of their kinetic energy. This results in a dipole layer that is negative in the outward (vacuum) direction); *smoothing* (of electron charge density in the directions lying within the surface, leading to a dipole layer that is *positive* in the outward direction, and a small reduction in work function which is greater in the case of any surface that corresponds to a high-index crystallographic plane); and *adsorption* (for example of gaseous materials onto the surface, which can give rise to either an increase or a decrease in the work function according to the electronegativity of the adsorbate). We will see that forces between dipole layers that arise from adsorbed material can, in principle, give rise to powerful long-range forces that may be either attractive or repulsive.

## Van der Waals Forces Between Macroscopic Bodies

The van der Waals interaction is often assumed to be the dominant type of long-range force in many situations. Israelachvili[15] describes, for example, how the term van der Waals force includes the Keesom "orientation" interaction between rotating permanent dipoles, the Debye "induction" contribution, and the normally dominant "dispersion" force involving dipole-dipole interactions between non-polar molecules. He emphasizes an important distinction. The properties of gases and condensed phases, apart from ionic crystals, are determined mainly by the strength of the operative forces at, or close to, molecular contact. However, when we sum the relevant pair potentials in order to calculate the interaction between two *macroscopic* particles, the result proves to be still appreciable at long range (separations of up to 100 nm or more). Given the shapes of two bodies in contact, it is possible to integrate the appropriate potentials or forces, so that, for example, the omnipresent van der Waals force varies as the inverse square of the separation in the case of sphere-against-flat geometry.

Let us consider how the van der Waals interaction is affected by *adsorbed layers of a dielectric material*, as discussed by Burnham *et al*[16]. The applicable value of the Hamaker constant will depend upon the permittivity of the adsorbed layers involved. Israelachvili and Tabor[17] have analyzed the behaviour of two surface, each covered with a thin layer (thickness $t$) of oxide or chemisorbed material, $j$, that has a relative permittivity $\varepsilon_j$, that differs from the bulk value, and whose effect will dominante at a separation $D < t$. Thus, there is no longer a simple power law for the force $F(D)$; the Hamaker constant will in effect vary with $D$, and the Hamaker constants needed in expressions for force and for potential energy will themselves be different functions of $D$. Furthermore, at small $D$, $F(D)$ can become much less than predicted by a simple van der Waals model, and may even be negative in certain cases where the value of $\varepsilon$ for the bulk medium is varied[18]. In a simple situation where dry gas, $k$, separates two identical solids, $i$, that are both coated with layer, $j$, the Hamaker constant is given by

$$H = H_{jkj} - \frac{2H_{ijk}}{1 + (\frac{t}{D})^3} + \frac{H_{iji}}{1 + (\frac{2t}{D})^3} \tag{1}$$

(Here, expressions such as $H_{123}$ represent the value of $H$ that would apply for the force between materials 1 and 3 separated by medium 2). Thus, for reasonably small values of $t/D$, we have $H=(H_{jkj}-2H_{ijk}+H_{iji})+(H_{ijk}-H_{iji})6t/D$. As shown in equation 11.21 of Ref. 15, the first term is equal to $H_{iki}$, so that the value of $H$, instead of being $H_{iki}$ is reduced by an amount

$$|\Delta H|=(H_{ijk}-H_{iji})\frac{6t}{D} \tag{2}$$

As with the case $k$ = vacuum, in practice $H_{ijk}$ will be negative (Ref. 15, equation 11.13). Thus, $\Delta H$ does represent a reduction in $H$ at small $D$, so that $F(D)$ in effect moves through a family of $1/D^2$ curves, the net result being a force that is longer-ranged than a simple van der Waals force.

### Forces Between Layers of Fixed Permanent Dipoles

The possibility of another type of force will arise if we consider near-surface layers of dipoles of moment $\mu_1$ and $\mu_2$ on the two solids, at volume densities $\rho_1$ and $\rho_2$, these parameters, together with the layer thickness $t$. Elsewhere[16] we have derived expressions for the force as a function of separation, $F(D)$, for two alternative geometries (but for special dipole configurations only). Note that, in principle, the layer could represent either adsorbed material or a near-surface region of the solid itself, having properties different from those of the bulk. For the sphere-sphere geometry, the rather complex equation reduces to the following simple expression in the limit of $D<t$ ($k_i$ terms are constants):

for $D<t$:

$$F(D)=-k_1t^2/D \tag{3}$$

For $t<D\ll R$:

$$F(D)=k_4t/D \tag{4}$$

So far, all these expressions assume that the dipoles are "fixed", *i.e. not free to rotate* (a different relation, with lower force at small $D$, would be expected if the dipoles were allowed to rotate to some extent as the two surfaces approach). This model could readily explain the large differences in maximum force observed for different pairs of solids. Relevant experimental evidence is scanty, although Thomas *et al.*[38] have shown how tightly-bound monolayers of polar molecules can shift the work function of a gold surface. For certain values of dipole moment and relative orientation, one might expect to measure a repulsive interaction, which so far has not been seen experimentally.

Of course, for particles in aqueous solution there exists, in general, a repulsive electrostatic force characterised by a double-layer-induced interfacial free energy (DLVO theory).

## Patch Charges

Surface patch charge arises due to different values of the work function on a material's inequivalent surface regions[19]. The regions can be inequivalent due to surface preparation, to the uneven distribution of adsorbates, to crystallographic orientation, or to variations in local geometry. If one takes an electron out of one face of a sample with work function, $\phi_A$, and puts it back *via* another face with work function, $\phi_B(\phi_A \neq \phi_B)$, the energy $-e(\phi_A - \phi_B)$ is not conserved. To conserve energy, the two faces must be at different electrostatic potentials $V_A$ and $V_B$, such that $V_B - V_A = \phi_A - \phi_B$. The surface charge density must change from region to region. (Of course, for an electrically neutral sample the total charge difference over the entire sample must remain zero). This phenomenon is known as the patch field effect. It has long been recognized that patch fields significantly affect electron trajectories in field emission microscopy; of course, except for a perfectly insulating body, Gauss's law implies that such a field will lead to the appearance of charges at the surface, which we have termed *patch charges*. Until recently, however, the force between such charges lying on two different bodies has not been discussed.

The size of the distributed patch charge may vary between patches with radii of a few nanometres (as observed with faceted tips in field emission microscopy) to the entire side of a crystal if it is a perfectly prepared flat surface. The method of images is used[20] to model the force, $F$, between a spherical tip and a flat sample each with its own initial surface charge, and each with an image charge due to the presence of the other dielectric body. The result, in the limit of separation, $D$, less than the depth of the patch charge below the tip surface, with this in turn being less than the tip radius, is

$$4\pi\varepsilon_0|F| = -k_1Q_t^2(1-k_2D) + k_3Q_tQ_s(k_4 - k_5D). \tag{5}$$

where the constants $k_1 \cdots k_5$ are functions of tip radius, location of patch charges $Q_t$ and $Q_s$, and material permittivities ($\varepsilon$) only. Note that the $-Q_t^2$ term is always attractive. Higher order multipolar images were not taken into account in this approximate calculation, and will be significant especially at small separations: this point has been discussed by Hartmann[18].

This effect is not limited to good conductors, although it may be seen[20] that, as the permittivity of the sample approaches that of the intervening medium, the force goes to zero. The definition of work function of an insulator is problematic because there are no electrons at the Fermi level, but it could be thought of as the energy difference per electron between the vacuum level just outside the surface and the highest occupied state inside the surface[19,18]. The only additional complication is that charge redistribution takes a finite amount of time.

## Surface-electrical Measurements on Individual Particles

Activity in the area of force measurement on individual particles in aqueous solution is expanding rapidly[2,21-25]. Such work gives valuable information on the role of electrical double layers in removing the attractive primary maximum in the force curve[23], and allowing values of non-retarded Hamaker constant to be derived[26].

Direct force curve measurements may, likewise, be used in connection with attempts to separate the complex inter-related factors that characterise the role of electrostatic interactions in the adhesion of dry particles. This was the approach adopted by Mizes[6], who used a commercial AFM slightly modified so that it was possible to apply an electric field to the particle, attached directly to the AFM cantilever as before.

Mizes' measurements confirm the conclusions of Hays and Wayman[27], who used a strong electric field instead of a cantilever to detach a particle from a surface, the strong electrostatic force being the result of particle charge. Recently, Hays[28] has described evidence that when irregularly-shaped toner particles have been tribologically charged by mixing with larger carrier beads, the toner adhesion tends to vary with the charge, rather than with the square of the charge as would be expected. His analysis explains the reason: the charge is concentrated into widely-separated "charge patches" (not to be confused with patch charges, see above), and the electrostatic adhesion of a single particle can vary widely according to the ratio of contact area to patch area. This basic detachment phenomenon has recently been analysed by Tombs and Jones[29] and by Tombs[30], who consider how the image force between a dielectric particle and a ground plane will relax if an ohmic surface layer is present.

## EVIDENCE FOR LONG-RANGE FORCES ARISING FROM WORK FUNCTION INHOMOGENEITIES

Our own exploratory work in this area has concentrated on two points in particular: 1. the use of cantilevers (force transducer components) that are stiff enough to allow the whole of the force curve to be plotted, in order to obtain reliable hysteresis data (this is at the cost of some reduction in sensitivity). If a highly-compliant cantilever is used, the well-known lever jump phenomenon means that some of the curve is lost; 2. more detailed analysis of the data in terms of the relevant contact mechanics, as discussed later. Like others using an atomic force microscope in non-scanning mode, we measure the force between a cantilever-mounted tip and the sample surface, as a function of relative tip-sample position. In principle, the resulting plot, referred to as a force curve, contains information about i) the magnitude and functional dependence of long-range attractive and adhesive forces, ii) the point of tip-sample contact, iii) the tip sample contact area, and iv) the elastic modulus and plasticity of thin and thick films.

Figure 1 shows typical data for a nylon surface brought into contact with a platinum/iridium wire tip used to simulate a particle of metal debris in a reproducible manner (any desired tip material could in priciple be used: several groups have successfully used individual powder particles in experiments of this kind). The *attractive region* (A) of the curve extends over several tens of nanometres: matching this region to a suitable model (tip geometry, long-range interactions) is not a simple matter. *Contact* may be defined as the point where repulsion is first detectable, as shown by a change from negative to positive curvature (B). A *transition or deformation region* extends from contact, through the *pull-on force* (C) or maximum negative load

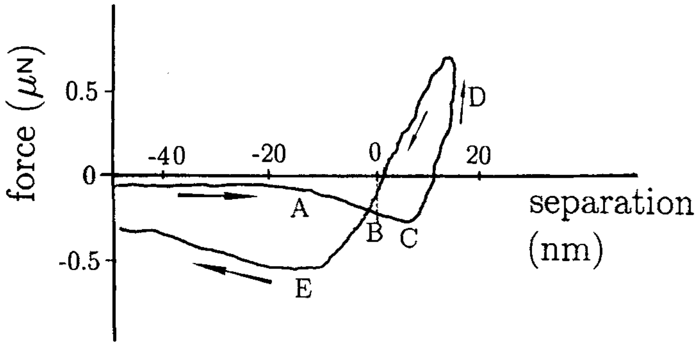

FIGURE 1 Force spectroscopy (force curve for nylon/Pt-Ir "particle"): **A**, long-range attraction; **B**, contact; **C**, pull-on; **D**, Hertzian (or bulk plastic) deformation; **E**, pull-off.

during loading, to some point where attraction becomes negligible in comparison with the positive applied load. At higher loads (D) we have *Hertzian* behaviour, provided that there is no bulk plastic deformation. On unloading, some hysteresis is almost always seen, the *pull-off force* (E) or *adhesion* being greater than the pull-on force.

Elsewhere[16] we have discussed in more detail the general form of a force curve, in particular (a) the definition of contact, (b) models for long-range force interactions (surface layers, fixed dipoles, patch charges), (c) emphasised the differences in adhesion shown by different tip-sample combinations, and (d) discussed reasons for the variations in pull-off force as a function of the maximum load applied. We used samples of highly-oriented pyrolytic graphite, crystalline diamond and polycrystalline nickel surfaces, and diamond and gold tips, and measurements were done in a glove box under dry nitrogen.

## The Long-range Attractive Region of the Force Curve

In this article we concentrate upon the rather surprising result, found also by other workers, that the van der Waals force law (in experiments with sharp tips, of radius of curvature less than, say, 300 nm as used in force microscopy) does not appear to account for the observed long-range attraction. In principle, this should be the most straightforward part of the force curve to interpret, since deformation of the samples should be insignificant and contact (repulsive) forces absent. For a typical diamond-diamond or diamond-graphite force curve, a separation of as much as 10 nm is needed for the force to fall to half its maximum (pull-on) value (see Fig. 2). Such long-range behaviour is seen for a wide variety of pairs of solids; other examples for diamond-graphite and gold-nickel are described in Ref. 16. The range of the interaction may vary according to the choice of materials and the details of surface preparation.

In our earlier paper[16] we ruled out various alternative models for the observed long-range attraction, after considering them at some length. To summarise, magnetic forces play only a minor role except when the particle itself, rather than the flat surface, is ferromagnetic; capacitance forces and forces due to discrete electronic charges, on the basis of any reasonable specimen geometry, are predicted to be either much too small or too short-range; the characteristic force curve discontinuities associated with capillary forces were not seen; and, for van der Waals forces, as found by others,[37] to obtain the best fit for various pairs of solids using sphere-on-flat model geometry, it is necessary to postulate an unreasonably large value of $H R$, where $R$ is the radius of the sphere and $H$ is the Hamaker constant. Even then, the fit is very poor, the prediction being too short-range. Similarly, theoretical van der Waals curves for alternative geometries have been tried, none of which give a good match. Morever, the more complicated geometries, implying a larger number of geometrical variables (pimple radius, etc.), would tend to give a much larger scatter in the data than is normally observed. This failure is puzzling, in that microscopic experiments with smooth mica surfaces[15] give data that scale correctly with $R$ and $D$, under conditions where $D \ll R$. In our work, the very small forces ($\approx 1$ nN) detectable *at large values of* $D$($\approx 4$ nm) for the diamond/graphite interaction, for example, agree to within an order of magnitude with a simple van der Waals expression based on the values $H \approx 10^{-19}$ J, R $\approx 300$ nm. However, the fit to van der Waals models is unsatisfactory, and thus we were thus led to consider more complex types of long-range interaction which depend on a change in material properties of the near-surface region, giving increased attraction at small separations.

Considering the role of *surface layers of dielectric material*, on the basis of reasonable values of $t$ and of the constant term in Eq. (1), we found[16] that, once again, a good fit requires a value of $R$ an order of magnitude greater than that measured by SEM. In addition, the observed low level of scatter in the data is hard to reconcile with the random variations in layer thickness that might be expected (the predictions of the model are very sensitive to the value of $t$). We, therefore, have not pursued this model further. The above model based on interactions between *fixed permanent dipoles* does not fit the data very well, but the required slow variation with distance is found. Although this model readily explains the large difference in maximum force observed for different pairs of solids, some doubts remain. For certain values of dipole moment and relative orientation, one might expect to measure a repulsive interaction, which so far has not been seen under the conditions of our experiments.

Finally, the *patch charge* model gives the most promising explanation and the best fit to the data[16]: as shown in Figure 2, we fitted our experimental data for a diamond tip and a graphite surface, for example, to the equation given in the figure caption (to which Eq. (5) is an approximation), using the values $Q_t = 2.4 \times 10^{-16}$ C, $BQ_s/Z = 2 \times 10^{-15}$ C, $A = 10$ nm, $B = 50$ nm, $\varepsilon_1 = 5.5$, $\varepsilon_2 = \infty$, and $\varepsilon_3 = 1$, where $A$, $B$ and $Z$ are dimensions. The above value of $Q_t$, distributed over an area of 300 nm radius, yields a charge density of $10^{-5}$ electrons/Å$^2$, the value for the sample being $10^{-6}$ electrons Å$^2$ (presumably for highly-oriented pyrolytic graphite, any work function inhomogeneities arise mainly from the presence of adsorbates or surface defects. For example, an adsorbate patch much larger than the tip radius would give rise to a field that is essentially uniform over the gap between tip and flat surface). Patch charge densities are very small by comparison with the charge density of the surface double layer itself.

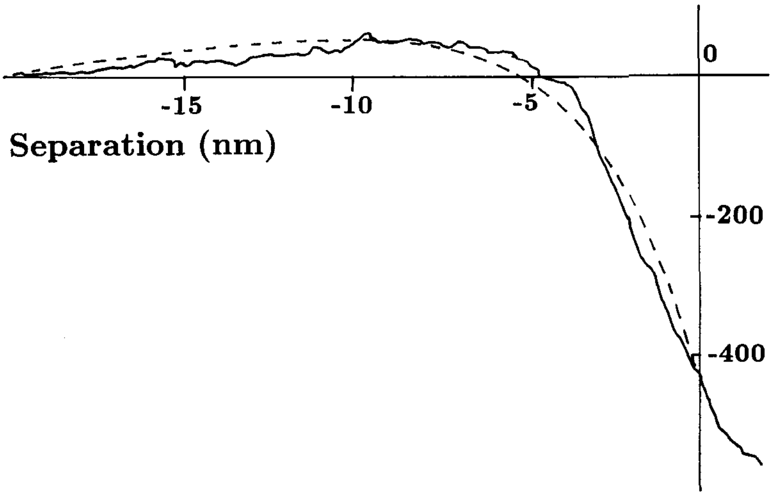

FIGURE 2 Long-range attraction for the diamond/graphite interaction. The continuous line shows experimental data; dashes represent the patch charge equation[20]

$$4\pi\varepsilon_3\varepsilon_0|F| = -\frac{Q_t^2}{4(D+A)^2}\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right) + \frac{BQ_tQ_s}{Z(2D+A+B)^2}\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right). \qquad (8)$$

where $Q_t$ represents the charge on the tip, $D$ is the tip-sample separation, A represents the position of $Q_t$ within the tip, $Q_s$ represents the charge on the surface of the sample, $B$ is the effective radius of curvature of the tip, and $Z$ is the position of $Q_s$, respectively. The relative permittivities $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon_3$ correspond to the tip, sample and intervening medium.

The patch charge theory explains in particular why the dependence of the detected force on distance is much longer ranged than predicted for van der Waals forces. In addition, this model accounts for the following effects:

(a) we have observed a fivefold change in pull-on force for alumina when coated with a monolayer of stearic acid, over an order of magnitude change for diamond/diamond according to whether the sample surface had been terminated by hydrogen of fluorine atoms. The patch charge hypothesis is fully consistent with these observations, in that work function, and hence patch charge density, is known to be very sensitive to adsorbates and to details of surface preparation;

(b) at intermediate separation, we occasionally detected a slight *repulsion*, as expected for two like patch charges. Then, as the tip and sample approach, the charge/image charge attraction becomes dominant. Neither van der Waals forces in air or vaccum, nor forces due to contact potential differences, are ever repulsive;

(c) When one studies the force between surfaces of low curvature, a parallel plate model for the surface charge interaction is appropriate. The force is then independent of $D$, so that the patch charge effect is not noticed: van der Waals forces dominate, as extensively verified in experiments with the "surface force apparatus"[17]. The interaction in experiments with particles (or fine tips) is much longer ranged. This discrepancy can now be explained in terms of the patch charge model. A force microscope, with a highly curved tip, retains the sensitivity to $D$.

## CONTACT MECHANICS: DEFORMATION ASSOCIATED WITH ADHESIVE FORCES

Once the forces involved have been identified, it would seem logical to model the *contact region* of the force curve, in which long-range and short-range forces overlap, and thereby to derive values of elastic modulus, contact area and adhesion energy. However, we first have to take account of the deformation that these forces produce. Here, in interpreting experimental data there are various pitfalls to be avoided, including, for example, the assumption that the deformation produced by an attractive force is the same as what would be produced by externally-applied load of equal vaule; or the assumption that deformations arising from more than one simultaneously-acting force are additive. This raises the whole subject of contact mechanics. Adhesion and deformation are interdependent, and one consequence is that the effective force of attraction between two solids is, in general, *not* the same as the pull-off force required to separate them. Force example, the observed pull-off force will often depend upon both short-range and long-range forces: but if, say, the long-range contribution is increased (by the application of an electric field, for example), then, owing to deformation, the contact area just before pull-off is also greater, and the short-range contribution will increase also. Thus, the pull-off force is not determined by simple addition of long-range and short-range components. There is also the complication that the attractive force can give rise to plastic as well as elastic increases in the area of contact.

The fracture mechanics treatment of adhesion[31] and the role of surface forces in deformation and friction[32] have recently been reviewed, and we next discuss various general points that result from these analyses, some of which are perhaps surprising at first sight:

1. *The force of attraction is not proportional to the contact area,* since its value is determined by a Griffith fracture criterion. If $w$ is the Dupré energy of adhesion, equal to $\gamma_1 + \gamma_2 - \gamma_{12}$ (where $\gamma_1$ and $\gamma_2$ are the surface energies and $\gamma_{12}$ the interfacial energy), $K$ is the effective elastic modulus, and $a$ is the radius of the contact region, then the stress intensity factor is proportional to $(wK)^{1/2}$, the stresses involved vary as $(wK/a)^{1/2}$, and the force of attraction, $\Pi$, is proportional to stress × area or to $(wKa^3)^{1/2}$;

2. *Attractive forces produce an increase in elastic contact area. The smaller the radius of curvature, the more important are the adhesive forces in comparison with a given external load.* To calculate $a$, we can show[33] that its value in the presence of surface forces is equal to the calculated value that would result from an external load of $P + 2\Pi$ (not $P + \Pi$!) in the absence of surface forces:

$$P + 2\Pi = Ka^3/R \tag{6}$$

If we use the result summarised by point (1) to eliminate $\Pi$ from equation (6), we obtain the rather complex "JKRS" expression for $a$ that Johnson *et al.*[34] first derived by minimising the sum of the surface, elastic and potential energies involved.*

We thus see that the increase in elastic contact area produced by attractive forces is *not* the same as what would be produced by an externally-applied load of equal value: the deformations arising from the externally-applied load and from the force of attraction do not just add together, as is shown by the JKRS equation.* Surface forces give increased deformation, which in turn leads to an increase in surface force.

If these are large enough, it is clear that *surface forces alone can induce plastic deformation, even in the absence of an externally-applied load* ("adhesion-induced plastic deformation"). The increase in contact area produced by attractive forces need not remain elastic. This follows from a simple consideration of the size effect involved. Whereas $\Pi$ varies as $a^{3/2}$, the force *required* to initiate plastic deformation tends to vary as the area, i.e. as $a^2$. Thus, at small enough values of $a$, the former will exceed the latter. The relevant equations for initiation of plastic deformation, and for full plasticity, are derived elsewhere[35], and it is possible to construct adhesion maps, showing what should happen as regards adhesion-induced plastic deformation in the special case of zero load, for different values of $w$ and $R$. Rimai and colleagues, as described in the papers mentioned earlier[3,36], found that the deformation of the particle (measured as displacement) varied linearly with the applied load, in accordance with the relevant adhesion-induced plastic deformation formula[35]. They have shown also that, by using an electron microscope to measure the deformation of an individual particle, it is possible to establish the nature of this deformation (elastic, plastic, etc.) *at equilibrium*, without the need to measure forces directly. In particular, they measure how the contact radius scales with the radius of the particle itself: the power-law dependence that is found is compared with that predicted by the different contact mechanics models. Often the result is close to the value predicted by the adhesion-induced plastic deformation formula and, in some cases, a meniscus is seen to surround the particle[36], further indicating the presence of a tensile interaction at the contact periphery. Sometimes a depression or crater next to the meniscus suggests that the stresses induced by surface forces are inducing viscoelastic flow of material up the side of the particle. In such cases, the macroscopic theory mentioned does not adequately predict the behaviour of the system, and the authors attribute such behaviour to viscoelastic effects, with the additional possibility of non-linear elasticity arising from the large surface-force-induced stresses acting on the materials. There is also evidence that the surface forces may induce creep of either particle or substrate, leading to time-dependent variation of contact area (and of the consequent force that would be needed to remove the particle from the substrate). This is evidenced by a bridging or "creeping-up" of the substrate, in such a way as to link two particles together eventually - in cases where the contact radius is so large as to approach the particle radius in value, it appears that the particle may be almost completely, or even wholly, embedded in the substrate material.

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* The relevant equation is: $a^3 = \frac{PR^*}{K}\left[1 + \frac{3\pi w R^*}{P} + \left(2 \times \frac{3\pi w R^*}{P} + \left[\frac{3\pi w R^*}{P}\right]^2\right)^{1/2}\right]$

Burnham *et al.*[16] discuss how the model for the long-range attraction may be combined with the fracture-mechanics-based equations to interpret the *transition region* of the force curve. In the case of a diamond tip and a flat graphite sample, the effective modulus, $K$, was first determined from the slope of the curve at higher loads, and was found to be 4.7 GPa. This is in the range of 3.5 to 28 GPa for the modulus of carbon and industrial graphites. The work of adhesion, $w$, was then determined from the fit in the transition region, and was found to be 0.3 $J/m^2$. This is slightly greater than works of adhesion from van der Waals interactions[15]. The work of adhesion calculated by integrating the patch charge force equation is 0.7 $J/m^2$, a little more than a factor of two different[16].

### Patch Charge Attraction Between Individual Particles: a Speculative Suggestion

We end with an order of magnitude estimate of how patch charge forces could dominate the adhesion of sub-micron sized particles.

Take, for example, two spherical particles of equal radius, $R$, each with two patches differing in work function by $\Delta\phi$ volts (Fig. 3). Each particle will act as a dipole of moment, $p = 4\pi\varepsilon_0 R^2 \Delta\phi$. If they are a distance $r$ apart, the force between the dipoles varies with orientation but has a maximum value of

$$3p^2/(\pi\varepsilon_0 r^4) = 48\pi\varepsilon_0 (R/r)^4 (\Delta\phi)^2. \qquad (7)$$

If the particles are in contact ($r = 2R$), then the force of attraction is independent of radius, and for $\Delta\phi = 1$ volt, has a value of *ca.* 0.04 nN, which is large compared, for example, to the weight of a micron-sized particle. If this idea proves to be confirmed, it would have significant implications for the agglomeration behaviour of ultrafine powders.

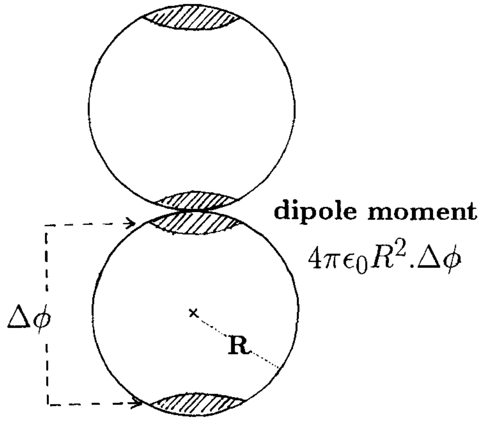

FIGURE 3 Patch charges on two spherical particles, giving rise to electrostatic dipole-dipole attraction.

## CONCLUSIONS

Experiments performed at the individual particle level, using AFM technology and often involving actual rather than model particles, so far give promising indications that macroscopic concepts such as adhesion energy or plasticity provide a valid basis for interpretating force curves.

One model, in particular, explains the unexpected fact that at long ranges, van der Waals attraction predicts too rapid a variation of force with separation: instead, we invoke an electrostatic force that results from the appearance of patch charges whenever these exist fluctuations in work function over the particle surface. An order of magnitude calculation suggests that a situation could easily arise where the patch charge force dominates the interaction between two particles in contact.

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