

## Chapter 2

# Phenomenology of Adhesion: From Macro- to Nano-Systems

*the solid support influences the form and arrangement  
assumed by the moving cells*

Harrison (1914)

Adhesion of macroscopic polymer particles and films has been explained in the previous chapter. The difficulty is to understand adhesion of cells and viruses which are much smaller; from  $\mu\text{m}$  to  $\text{nm}$  in diameter. To overcome this problem of moving from macro- to nano-systems, we have to prepare and measure surfaces with nano-scale perfection.

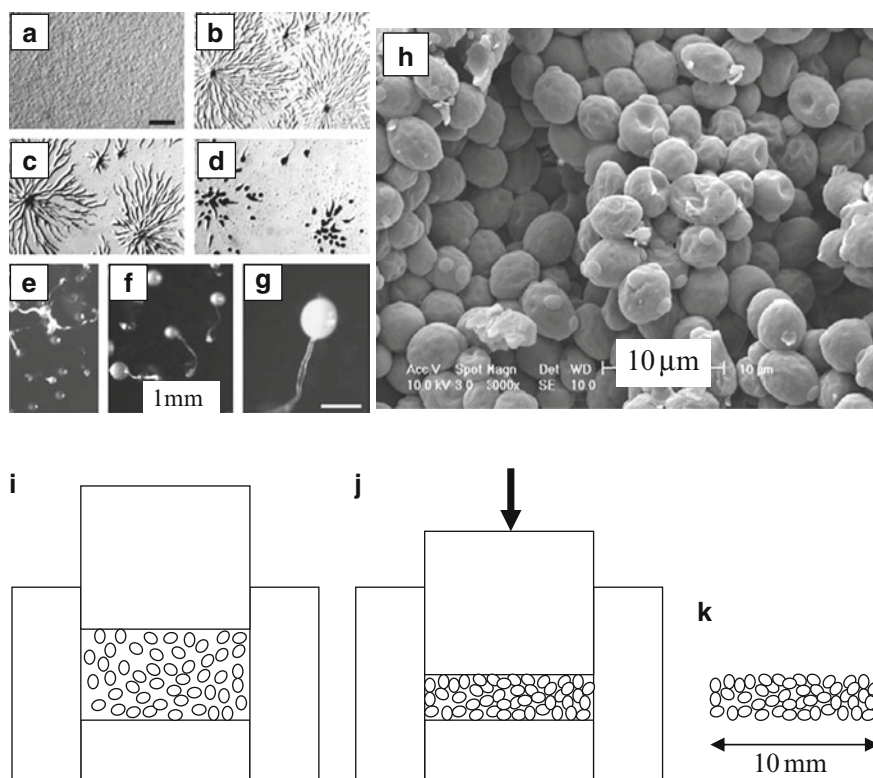
Two hundred years before van der Waals, Isaac Newton was the first person to suggest that two particles brought into close contact should adhere strongly when he wrote ‘two polish’d marbles, ... by immediate contact stick together’.<sup>1</sup> However, the experimental demonstration of this phenomenon for larger spheres was not so readily achieved. Newton reasoned that the imperfection of surfaces was the most important factor inhibiting contact, either through surface roughness or through contamination as described in the previous chapter. Therefore he developed better methods for polishing glass lenses to upgrade their quality. This was the work that brought him recognition in 1671 when he first displayed at the Royal Society his marvellous new reflecting telescope lenses for improved observation of the stars and planets. But Newton only observed adhesion between the smooth glass lenses sporadically. There seemed to be asperities and dust preventing perfect contact.

It turns out that Newton would have been much more successful in proving his ideas on adhesion if he had used the rubbery material which Columbus had brought back from the new world. Such soft material sticks far better than glass. Also, it has become evident that large bodies, like Newton’s glass lenses, are less likely to show adhesion than small ones. If Newton had done his experiments on fine polymer beads or yeast cells, then he would have seen the adhesion he was expecting. The conclusion is that van der Waals adhesion is observed best on small, smooth, soft objects like polymer spheres or biological cells.

## 2.1 Showing the van der Waals Adhesion Force

Our argument is that van der Waals forces attract cells towards each other. Of course, the key question is how cells self-assemble. In other words, how do they forge a suitable contact and then produce close-packed aggregates of cells, as in the slime mould shown in Fig. 2.1a–g, *Dictyostelium Discoideum*,<sup>2</sup> which can exist as a single cell that aggregates into a multicellular organism when food is scarce. The ‘Sultan of Slime’ Prof John Bonner has a movie showing this on his web-site and a book describing his work. The detailed molecular effects at the cell contacts have been described in recent papers but the overall mechanics depending on geometry and elasticity are not normally considered.<sup>2</sup>

It is easy to show that, even when cells do not spontaneously self-assemble, they can adhere strongly. For example, a dispersion of yeast cells (*Saccharomyces cerevisia*) in water when spray-dried forms small spherical aggregates with good



**Fig. 2.1** (a) Slime mould cells growing on no-nutrient agar plate; (b)–(d) starved cells aggregating; (e)–(g) fruiting bodies [<sup>2</sup>]; (h) yeast cells before compaction; (i) loose powder loaded into steel die; (j) powder compressed by die; (k) pellet after release from die (with permission of the Royal Society)

strength (Fig. 2.1h). The individual  $4.5\text{ }\mu\text{m}$  diameter cells can be seen to form extended contact spots with each other about  $1\text{ }\mu\text{m}$  in size, indicating a work of adhesion around  $200\text{ mJm}^{-2}$  from JKR theory.<sup>10</sup>

One gram of yeast cells in the form of spray dried, almost spherical, aggregates was poured into a hard steel pelleting die, as shown in Fig. 2.1i. Electrostatic forces were prevented by the presence of 0.2 g moisture which leaked away any stray electrons.

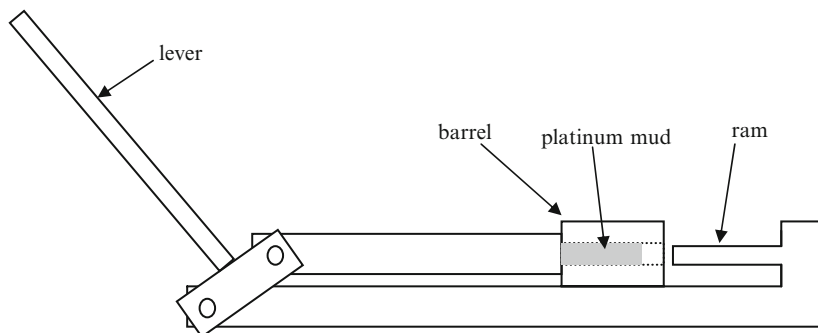
After squeezing the powder with a pressure of 10 MPa, as in Fig. 2.1j, the pellet was ejected from the die in one piece (Fig. 2.1k). The yeast cell particles then stuck together with considerable strength. Of course, the tablet was porous because the yeast cells did not pack together perfectly to exclude all the pores. But where the yeast particles touched each other, the molecules of the cell membranes were in close proximity as a result of the large force which had urged them into molecular contact. Then, the short range van der Waals adhesion forces discussed above pulled the particles strongly together, thereby resisting external stresses and giving substantial adhesion.

By testing the pellet in bending or tension, it is easy to find that the compacted pellet has the properties of a gel. It is viscoelastic and brittle, but not so strong as a dense elastomer which has no pores to weaken it. The adhesion energy was measured by cutting a radial slit into the pellet with an abrasive file and pulling the disc apart with an edge force. From the 1 mN force applied across the 2 mm width of the pellet, the adhesion fracture energy would be  $200\text{ mJm}^{-2}$ , about that expected for van der Waals forces.

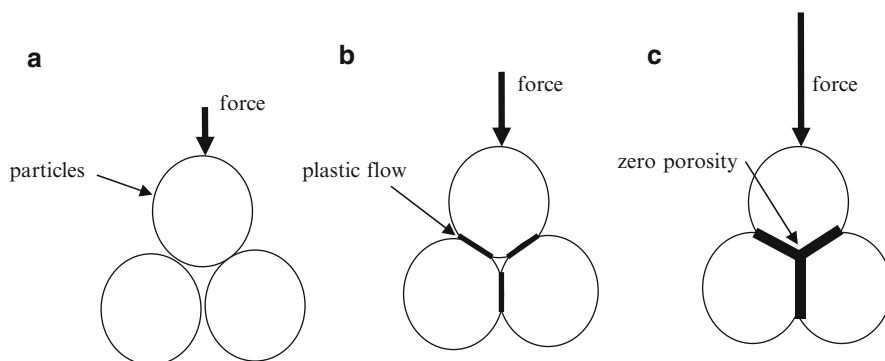
## 2.2 The First Demonstration of Nanoparticle Adhesion

William Hyde Wollaston<sup>3</sup> first described this type of adhesion experiment in 1829. He was interested in making dense and strong wires from platinum and other rare metals such as palladium and osmium which he had just discovered. Platinum is so hard and refractory that it is extremely difficult to work by ordinary melting and casting techniques. Wollaston prepared the platinum in fine particle form by precipitating the metal from an acid solution which had been used to remove impurities. This produced a mixture of water and particles which were cleaned by washing, then dispersed by milling in a wooden mortar and pestle. Wollaston called the mixture ‘mud’ whereas we would now describe this as a nanoparticle dispersion.

The difficulty was converting the fine metal powder into a dense block. To achieve this, Wollaston needed to get the particles sticking together in a dense packing. First he constructed a mechanical press, shown in Fig. 2.2, consisting of a brass cylinder into which fitted an iron piston around 25 mm diameter. The barrel of the cylinder was tapered so that the pellet could be ejected after compaction. After placing the platinum mud in the barrel, then covering it with blotting paper to allow the water to soak out, and greasing the piston with lard, Wollaston pressed on the ram to apply a force of about 30 tonnes weight to the powder mass. This force was sufficient to increase the packing of the fine particles from a loose state of 20%



**Fig. 2.2** Wollaston's press for compacting platinum powder together into an adhering pellet



**Fig. 2.3** Three stages in compaction of plastic particles; (a) low load; (b) higher load causes plastic deformation; (c) higher load removes all pores

packing to a porous pellet near 50% dense. This pellet was ejected in one piece and was 'hard and firm' suggesting that each platinum particle was adhering to its neighbours by van der Waals forces.

Heating of the pellet with burning charcoal was sufficient to remove moisture and organic lubricant. Then the pellet was raised to white heat in a Staffordshire coke furnace. This caused the pellet to contract as the particles sintered together. Pounding the hot pellet with a hammer produced a material which was 99% dense and which produced platinum wire of the 'highest tenacity'.

The adhesion between plastic particles during compaction is even more striking than that between elastic platinum grains. This is readily demonstrated by compressing potassium bromide powder in a steel die, as routinely done for infra red analysis. During the compression of the grains, the pressure at the contact points becomes larger than the yield pressure and consequently the contact spots enlarge until all the porosity has been excluded, as indicated schematically in Fig. 2.3.

On removal from the die, the compacted pellet is seen to be fully transparent and completely dense. The pellet is also very strong, elastic and brittle, comparable to

a piece of solid potassium bromide made by other methods. Thus the conclusion is that the compaction force has brought the grains into molecular contact, generating adhesion. Further force sheared the material close to the contacts, allowing plastic flow to produce more intimate molecular contact until all the particle surfaces adhered strongly.

The lessons we learn from such demonstrations are fourfold; all bodies can be made to adhere together by van der Waals attractions but finer, softer particles stick more easily; force is usually required to overcome friction or repulsive forces and to push the bodies into molecular contact; and deformation, especially plastic or diffusive flow, allows more extensive contact to give maximal adhesion.

### 2.3 Arguments Against van der Waals Adhesion

Sceptics say that the adhesion developed in the above experiments can be explained by other well-known ideas. Four sorts of argument levelled against molecular adhesion phenomena can be listed. There is first the suction argument, which says that the particles are acting as rubber suction pads, and merely sealing around the edges; this is easily shown to be false because the pellets are just as strong in vacuum, where suction pads fall apart. Secondly, there is the mechanical keying argument, which suggests that the particles behave like Velcro, with little hooks and eyes to cause adhesion. This is easily answered because when you look at the surfaces by electron microscopy, the particles are often extremely smooth and shiny. There are no hooks and eyes. Moreover, the smoother particles show stronger adhesion than rough particles. A third argument is that there is some adhesive material, e.g. adhesion molecules, on the particle surfaces acting like a glue to bind the particles together. This is simply disproved by cleaning up the surfaces; the cleaner the particles, the better they stick. In fact adhesives are known to reduce adhesion between particles as we showed in Chapter 1. Finally, a fourth argument is that the particles are oppositely charged, to give electrostatic attractions. This is readily disproved by doing the experiment in the presence of moisture or ionising radiation to leak away the electrons: Adhesion is not affected.

Having dismissed all the plausible yet simplistic theories of adhesion between particles, we can now conclude; adhesion is dominated by van der Waals forces.

### 2.4 Definition of van der Waals Adhesion

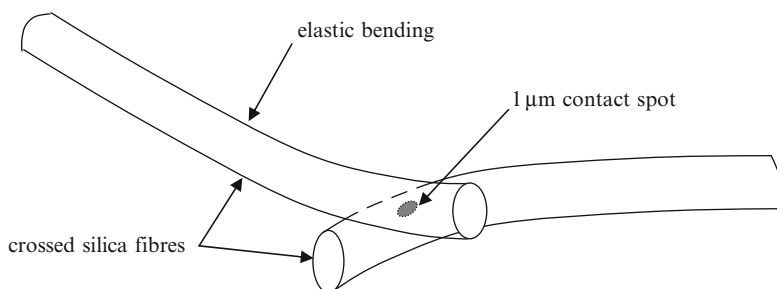
Consider a definition of adhesion which allows it to be distinguished from all the other known forms of attractions between bodies: van der Waals adhesion is the force experienced when bodies make contact at the molecular level, with gaps around 1nm, near molecular dimensions, allowing van der Waals forces to dominate.

This definition raises a number of questions which will be addressed in the following chapters. The obvious question relates to the origins and laws of van der Waals adhesion. How can one measure and interpret such phenomena? Clearly molecular adhesion forces have the same origins as the forces of cohesion which hold the molecules of solids and liquids together. These can be understood in terms of the heats of melting or evaporation, the elastic stiffness or the chemical reactivity of materials, as described later.

These van der Waals forces had been measured for the first time in the 1920s as de Boer, London and others were formulating the basic equations of the instantaneous dipole attractions. Tomlinson in 1928 heated and drew fresh fibres of fused silica to perform adhesion experiments, bringing the crossed fibres together to observe the contact point, which he estimated to have a black spot size less than  $1\text{ }\mu\text{m}$ , and measuring the force of adhesion by elastic deflection of the fibre, as shown in Fig. 2.4. He also formed spherical blobs on the ends of the fibres and tested these in the same way.<sup>4</sup>

Tomlinson was careful to release electric charges by ionising the air, and also made sure that the silica was dry to avoid questions about surface moisture. The best adhesion was observed immediately on cooling from red heat because there was then no roughness or contamination. Also marked damage was seen after adhesion of the surfaces, proving that the forces of adhesion were large enough around the black spot to crack the glass material.

A typical fibre was  $60\text{ }\mu\text{m}$  in diameter, about the same as a human hair, and the adhesion force measured was  $30\text{ }\mu\text{N}$ . This force was readily determined by the  $5\text{ mm}$  deflection of the fibre just before detachment. The interesting feature of the experiment reported by Tomlinson was the sudden attachment of the fibres when contact was approached. The surfaces jumped into contact! He took trouble to apply no force pushing the surfaces together, and concluded that ‘the molecular attractions acting at the instant of geometrical contact are sufficient to draw the fibres together’. The adhesion force seemed to be in proportion to the diameter of the bodies and was related to the energy of adhesion per square metre of interface, the work of adhesion  $W$ .



**Fig. 2.4** Tomlinson's experiment on adhesion of silica fibres

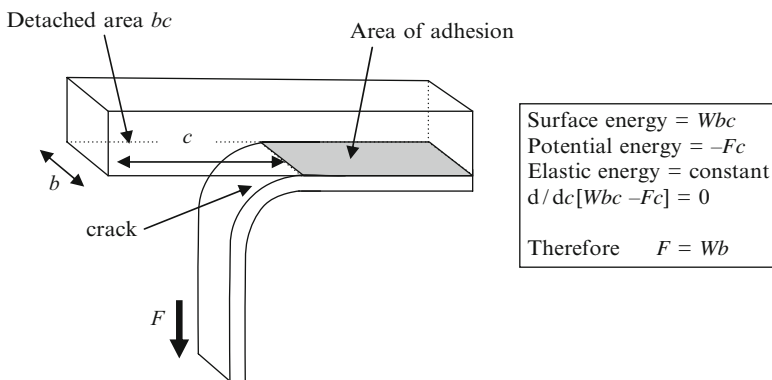
## 2.5 Definition of $W$ , the Work of Adhesion in Peeling

In order to quantify van der Waals forces, it is necessary to take into account the area of contact of the bodies in contact. With spheres this is difficult because the contact spot is often very small and difficult to measure. Therefore it is best to start with an extended uniform contact such as that between a sheet of cellular tissue and a smooth flat acrylic surface. Also van der Waals forces vary rapidly with separation distance, so it is best to deal with the energy of the adhesion process than with the force/distance curves. Therefore we define a work of adhesion  $W$  as the energy to break reversibly  $1 \text{ m}^2$  of contact.  $W$  can then readily be measured by finding the energy needed to separate a known area of contact. The simplest test is that first defined by Rivlin in 1944 to describe paint peeling from a smooth surface.<sup>5</sup> He analysed the test using the energy balance approach described below.

Imagine an elastic film, made of cells for example, peeling under a force  $F$  from a rigid smooth substrate as in Fig. 2.5. A crack can be observed moving at steady speed along the interface by looking through the transparent substrate with reflected light. After a while, the crack has moved a distance  $c$ . The area of interface broken by this crack movement is  $bc$  where  $b$  is the width of the peeling film. Therefore the energy expended to create new surfaces by breaking the van der Waals bonds is  $Wbc$  where  $W$  is the thermodynamic work of adhesion (i.e. the reversible energy required to break one square metre of van der Waals bonds at the interface). The work done by the force is force times distance i.e.  $Fc$  which is all presumed to go into the surface energy  $Wbc$ , because energy must be conserved. Therefore the peel equation is (see box)

$$F = Wb \quad (2.1)$$

Of course there is elastic deformation energy in the bent elastic film, from the time when the force was first hung on the film. But this remains constant during peeling and so does not supply any energy to the surfaces. It is merely a constant energy term which moves along with the crack. Consequently it does not change during



**Fig. 2.5** Energy conservation theory applied to peeling of an elastic film from a transparent substrate

the energy balance. We also assume that there are no stretching or dissipation energy terms as the film is detached.

This theory presumes that the crack can also heal at the same force. In practice, the force has to be slightly reduced for healing to be seen. For the most perfect elastic system, there is a force which can be suspended on the film whereby the crack does not know whether to peel or heal. The crack is essentially in thermodynamic equilibrium in which a slight increase in force will cause separation, and a slight decrease will cause healing. This is the situation to which the peel equation  $F = Wb$  applies.

The peel equation derived by Rivlin above is most interesting because it seems to have no connection with the strength of the interface, that is the stress required to pull the interface apart. The idea that solid materials require a stress or pressure to tear them apart goes back to Galileo and his treatise on the two sciences of mechanics and strength of materials.<sup>6</sup> This has been a remarkably persistent idea which has not been justified by work on many materials. For example, it has been known for many years that glass can fail at a whole range of different stresses depending on the chemistry at the surface. Indeed, that was the whole point of Griffith's original work,<sup>7</sup> to understand why the failure stress of glass can vary so much. Here we reject the concept of a constant fracture stress because it has no place in the equilibrium theory of van der Waals bond breakage adopted in this chapter. Equation 2.1 shows quite clearly that the work of adhesion  $W$  (i.e. the energy of the van der Waals bonds) is the main material property resisting cracks. Only the width of the strip is then relevant to the adhesion force, not the area of contact.

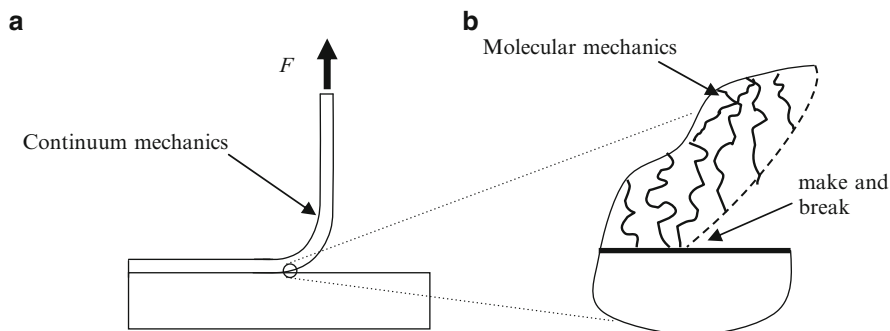
## 2.6 Nature of Bonds in the Equilibrium Theory of Adhesion

The model of adhesion described above is a macroscopic thermodynamic model which satisfies the conservation of energy principle, averaging the behaviour of all the bonds in the system over the large scale sample. The quantity  $W$  is the measurable parameter which assumes that the bodies behave as elastic continua.

But such a continuum theory must fail as we approach molecular dimensions where adhesive failure is actually occurring. In order to reconcile the macroscopic picture with our knowledge of the molecular reality, consider the situation depicted in Fig. 2.6 which shows a film of polymer peeling from a glass surface. This shows that, at large scales (2.6a) we should treat the materials by continuum mechanics, but at the molecular scale (2.6b) we must consider molecular models where adhesion is governed by an interaction potential and by statistical mechanics of a large number of molecular bonds.

Magnifying the crack tip where the separation of molecules is occurring as in Fig. 2.6b shows the polymer molecules making and breaking contact continuously as Brownian motion arises at the molecular level. At macroscopic resolution, the crack seems to be in equilibrium at a particular loading (Fig. 2.6a). There does not seem to be any motion at the crack tip. However, when viewed at the atomistic level the crack tip is seen to be in rapid thermal Brownian motion. The attracted





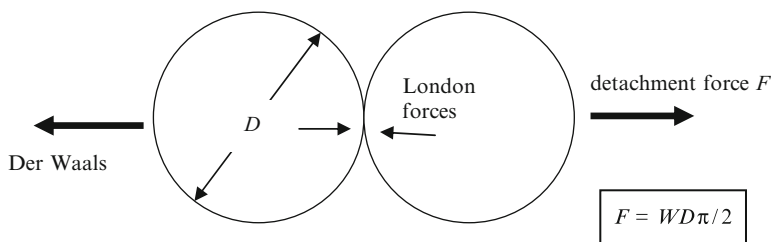
**Fig. 2.6** Schematic picture showing how continuum mechanics applies at large scale (a) but molecular modelling takes over at nanometre scales (b)

molecules form the adhered region to the left of the crack tip, whereas the unattracted molecules lie to the right at the open crack surface. The crack tip is not a static point in this model. It is wandering kinetically from right to left as the molecules spontaneously break and then rebond. Cracking is thus viewed as a reversible van der Waals interaction between molecules at the crack tip. The force applied to open or close the crack is not the cause of interaction, i.e. peeling or healing, at the crack tip. The interaction is happening spontaneously and equally in both directions, causing the crack to open and close spontaneously at the molecular scale. Applying the crack driving force merely shifts the van der Waals equilibrium in one particular direction, either opening or closing the crack.

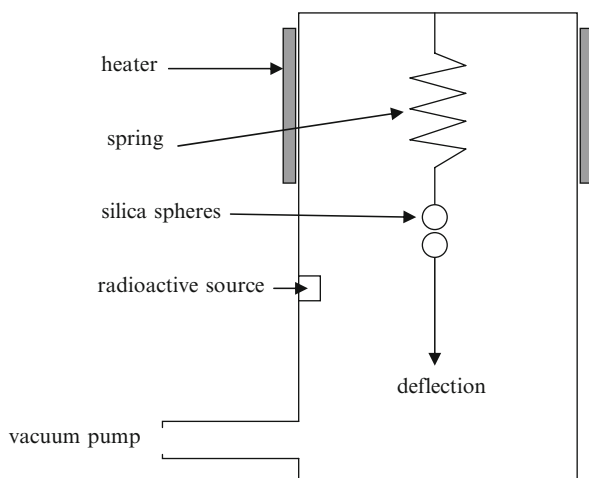
Work of adhesion must be distinguished from surface energy which is often used to describe liquid surface attractions. Surface energy  $\gamma$  (i.e. surface tension) is extremely useful for liquids because many liquid surfaces have no resistance to flow at low rates, and so reach an equilibrium shape which is dominated by surface energy. Thus, surface energy of liquids is readily measured by the deformation of liquid surfaces in surface tension measurements such as Wilhelmy plate or sessile drop.<sup>8</sup> Unfortunately, the surfaces of solids are elastic under ordinary conditions. These elastic forces are so much larger than surface tension that the measurement of solid surface energy has proved very difficult. Certainly, the adhesion of bodies depends on the work of adhesion  $W$  and if the bodies are identical and smooth, we can take  $W=2\gamma$  where  $\gamma$  is the surface energy of the solid as shown by Johnson et al.<sup>10</sup> However, surface energy of solids is seldom enough to overcome elasticity, which is the next major variable to be discussed.

## 2.7 Bradley's Adhesion Rule

Bradley<sup>4</sup> had read Tomlinson's paper and developed an improved method of measuring the adhesion together with a better theory based on London's wave mechanics theory of the van der Waals forces between molecules. By adding up the



**Fig. 2.7** Bradley's theory of attraction between rigid spheres based on London van der Waals forces

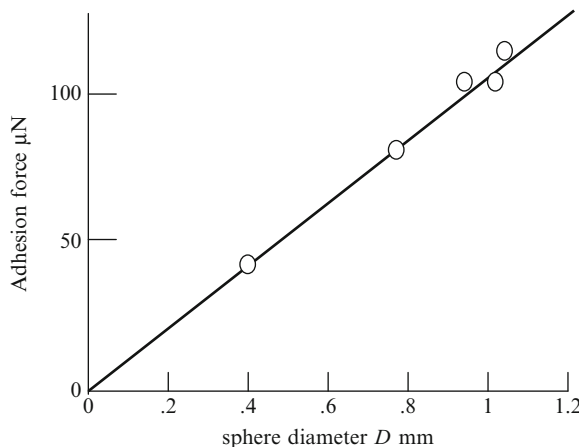


**Fig. 2.8** Schematic of Bradley's apparatus for measuring the adhesion of silica spheres

forces for all the molecules in two rigid spheres, Bradley came to the conclusion that the adhesive force required to separate them should be proportional to the sphere diameter, as shown in Fig. 2.7. He also showed that the force should be proportional to the work of adhesion  $W$  of the spheres, that is the energy required to separate  $1 \text{ m}^2$  of interface reversibly. Thus he produced his famous equation for adhesion of spheres.

Bradley then constructed an apparatus (Fig. 2.8) for measuring the force required to separate two silica spheres from adhesive contact. The rig could be evacuated to remove moisture and other contamination. Heaters were used to bake the glass. A radioactive source ionised the gas to leak away any stray charges. The silica balls were heated to incandescence immediately before the measurements. A deflection was applied to the bottom sphere until it detached from the upper sphere, giving the results shown in Fig. 2.9.

Bradley found that the adhesion remained constant as gas was evacuated, so water was obviously not the cause of the adhesive force. However, the spheres were probably too large to give the molecular contact which Tomlinson had



**Fig. 2.9** Bradley's results for adhesion of silica spheres

observed on his ten times smaller fibres. The force was proportional to diameter which fitted the theory, but the force was several times smaller than expected, and smaller than Tomlinson observed. This problem became evident when Bradley attempted to use sodium borate spheres instead of fused silica. Although adhesion was seen, it was variable and Bradley suggested the surfaces were rough as a result of reaction with water. The conclusion was that these spheres were still too large and insufficiently smooth to obtain reliable van der Waals adhesion.

Another significant issue was the deformation and flattening of the spheres at the point of contact. Newton had stated that this occurred as the spheres were pulled together by adhesion forces. Tomlinson worked out from the well-known Hertz equations of elasticity, described below in 2.9, that the contact spot diameter should be around  $1\text{ }\mu\text{m}$  for the contact of his silica fibres. Bradley took no account of this idea and his theory was based on the assumption of rigid spheres, obviously inapplicable to elastic particles. Derjaguin<sup>9</sup> attempted a solution of this question in 1934 by combining the Hertz and Bradley ideas, but his answer was not quite right. The final solution was obtained in 1971, showing that Bradley's equation requires only slight numerical modification, by about a factor 2, to  $F = WD\pi 3/8$  when elastic deformation is taken into account<sup>10</sup> So elastic stiffness hardly affects adhesion of spheres, and therefore it should not matter whether we stick stiff diamond or compliant bacterial spheres together, we should get the same adhesion force result for the same work of adhesion. This is a surprise because the contact areas are obviously much bigger for the cells than the diamonds. Contact area and adhesion force are not proportional. In fact, the surprising conclusion from these arguments is that the adhesion of particles is in proportion to the particle diameters, not the contact diameters. This result, Bradley's rule, is of outstanding importance because it means that adhesion dominates all other forces at dimensions below  $1\text{ }\mu\text{m}$  particle size.

## 2.8 The Significance of Bradley's Rule

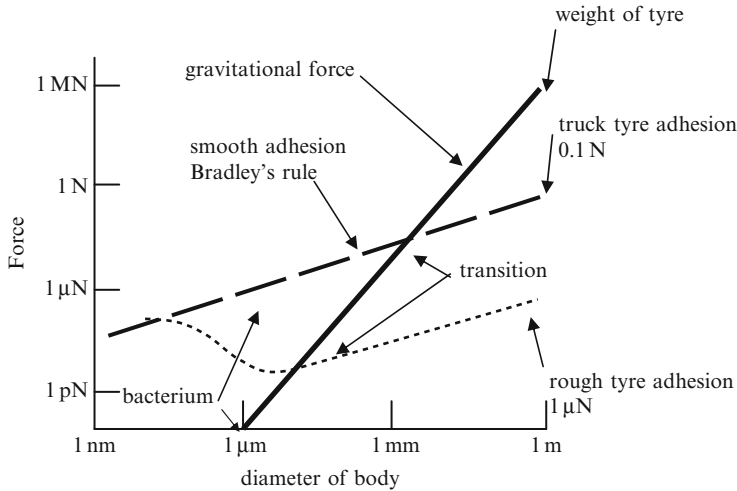
The discovery that solid bodies jump into adhesive contact under the influence of the van der Waals attractions was enormously significant. This experiment was certainly known to Tomlinson<sup>4</sup> in 1928 and was studied both by Obreimoff in 1930 as described in Chapter 1, then by Derjaguin and Abrikossova<sup>15</sup> sometime later. Once you see this phenomenon, you become convinced that molecular adhesion due to van der Waals force exists. When you observe it in different situations; on mica, on glass, on metals, on polymers, then you realise it is a universal observation that applies to all bodies when there are no contaminant molecules or surface roughness to stop the adhesive electromagnetic interaction of the particles.

In a sense, although it came 100 years after Brown, this observation stands with Brownian motion as a critical break-through. Before Brownian motion was seen, engineers thought that matter was continuous and static. Suddenly they were aware that it was molecular and moving, though this molecularity and movement could often be ignored at the macroscopic level because the atoms and the energies were so small. In a similar vein, engineers normally treat objects as non-adhering. Wheels roll and particles flow macroscopically without sticking. But it turns out that this is an illusion brought about by the small values of the work of adhesion, and by Bradley's rule. Bodies should always stick but this depends greatly on size.

Consider the wheel of a truck, which is 1 m in diameter. This does not adhere significantly to the road surface, and can be lifted up without significant sticking. However, applying Bradley's rule that the adhesion force should be the product of the diameter and the work of adhesion, which we know to be about  $0.1 \text{ Jm}^{-2}$ , then the adhesion force should be 0.1 Newton. This is the theoretical prediction shown in Fig. 2.10 on the Bradley's rule line. It is a small force, compared to weight, as can be seen by the logarithmic scales in the diagram.

Compared to the gravity force acting on the truck tyre, this theoretical adhesion force is a million times smaller. But we also know that the tyre is so rough that it does not make perfect molecular contact with the road surface, so the measured adhesion is another million times less, as shown on the dotted curve. Thus it is clear that the adhesion at the engineer's level is much smaller than the weight, and can normally be neglected. Racing car tyres are an exception to this because they are made much smoother to obtain better grip. In this case the adhesion is small but measurable.

The interesting thing about Fig. 2.10 is the way the forces change as the size of the body becomes smaller. The force of gravity falls with the cube of diameter and so drops rapidly for smaller bodies, whereas the adhesion falls more slowly, proportional to diameter. Thus for smooth particles, there is a transition around 1mm diameter, where gravity and adhesion are equal. There is a problem here because this suggests that 1 mm dust particles should cling to the ceiling if they are smooth enough to obey Bradley's rule. Fortunately, the surfaces are rough and so the bottom curve applies and the transition is near  $20 \mu\text{m}$ . Thus, when we are dusting, we tend to find particles which are not 1 mm large but small enough to be just about visible. However, geckoes can use Bradley's rule, and can stick to ceilings by increasing the number of their contact spots as described in Chapter 6.



**Fig. 2.10** Adhesion between bodies of different size, compared to gravity, showing Bradley's rule and the influence of roughness

Consider now a bacterium cell which is  $1\ \mu\text{m}$  in diameter. This now behaves in a completely different way to the truck tyre, as seen in Fig. 2.10. Because of the rapid decline in gravitational force with diameter, the weight of a bacterium is now extremely tiny, below  $1\ \text{pN}$ , less than a single weak chemical bond force. But adhesion according to Bradley's rule has not declined so fast and is around  $1\ \mu\text{N}$  for a smooth bacterium or  $1\ \text{nN}$  for a rough surface contact about the same as a chemical bond. Thus a bacterium in dry conditions will always stick to a surface and cannot behave like a truck tyre which exhibits near zero adhesion. A virus particle is 10–50 times smaller than the bacterium and consequently from Fig. 2.10 will be even more adherent compared to gravitational and fluid forces. Therefore it will be even more subject to van der Waals forces. Of course, the presence of water reduces adhesion considerably, and the addition of surface contamination (e.g. adhesion molecules) drops adhesion still further, even to zero or negative values.

The conclusion from this argument is that Bradley's rule can explain the transition from the clean macroscopic engineering world, where nothing sticks, to the nano-world of the virus where everything sticks.<sup>11</sup> The transition for smooth spheres in clean air is about  $1\ \text{mm}$ , depending on the density. Larger than  $1\ \text{mm}$ , ball bearings roll around and behave as we expect from our common experience. Below this they should stick, as smooth silicone rubber spheres are known to do. However, roughness introduces another dimension into this argument because true molecular contact is not achieved. This shifts the transition down to smaller particles, around  $20\ \mu\text{m}$  in size. Thus there is a grey area of transition where particles can behave in a schizoid way depending on surface roughness, sometimes sticking, sometimes not, between one micrometre and one millimetre in particle size. This is the size range occupied by cells which therefore should be expected to have complex adhesive behaviour. Contamination with water or adhesion molecules will

reduce this still further. We would like to emphasise that this region, where the adhesion force of individual cells is on the same order of magnitude as their gravitational force, is essential for multicellular organisms and therefore the prerequisite for our very own existence. It allows for switching between an adherent and a free state due to small changes in topography or surface chemistry. One could say that no ‘real’ life is possible in the ‘always sticky’ and the ‘never sticky’ regime.

## 2.9 Adhesion of Spheres; Hertz Theory

Although Newton had measured the black spot at the contact of glass spheres, and also seen the black spot expand and contract reversibly as the spheres were pressed together, he did not pursue the relationship between the spot size and the load. Almost 200 years were to elapse before Hertz defined the connection published in two papers of 1881 and 1882.<sup>12</sup> Hertz was a 23 year old assistant to Helmholtz in Berlin when he was stimulated by Newton’s rings and derived the elastic theory of sphere contact in his Christmas vacation in 1880.<sup>13</sup> He found that the spot diameter increased with the cube root of load  $F$ , showed that the elastic modulus  $E$ , Poisson’s ratio  $\nu$  and sphere diameter  $D$  were also important, and verified his equation

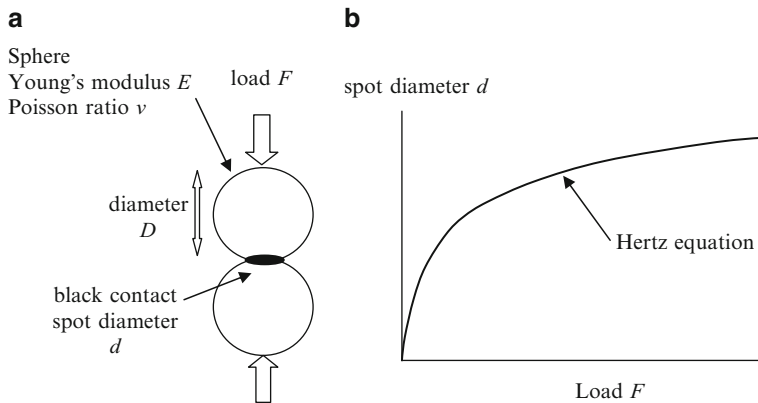
$$d^3 = 3 (1 - \nu^2) F D / E \quad (2.2)$$

which applies to equal spheres, by measuring contact spots for glass and metal spheres, as shown in Fig. 2.11. Hertz was a prodigy; unfortunately he moved onto radio waves rather than studying the influence of adhesion on the sphere contacts. For spheres of different diameters  $D_1$  and  $D_2$  and materials of different elastic constants, the effective diameter  $D = 2 D_1 D_2 / (D_1 + D_2)$  and effective modulus  $E / (1 - \nu^2) = 2 E_1 E_2 / (E_1 + E_2)$  could be substituted into Eq. 2.2, where  $E_1 = E_1 / (1 - \nu_1^2)$  and  $E_2 = E_2 / (1 - \nu_2^2)$ .

The brilliant contribution of Hertz was to understand that the spheres press into each other to give a hemispheric pressure distribution, with maximum pressure  $P$  in the middle, falling as  $P(1 - z^2/d^2)^{1/2}$  to zero pressure at the edge of the contact spot, where  $z$  is the diameter of a circle within the contact spot of diameter  $d$ . He also knew that the centres of the two spheres approached each other because of such pressure by a distance  $\delta = d^2/D$  given by

$$\delta^3 = 9 (1 - \nu^2)^2 F^2 / E^2 D \quad (2.3)$$

All these expressions assumed that no adhesion or friction existed at the contact between the spheres. This was an excellent assumption for large loads such as those experienced in ball bearings, under train wheels, and where car tyres meet a road surface. The experimental measurements then fitted the theory very well. However, when the load was zero, or even tensile, as in the experiments conducted by Bradley<sup>4, 14</sup> in the 1930s on adhering spheres, it was clear that the spheres were still



**Fig. 2.11** (a) Two elastic spheres pressed into contact; (b) increase in spot diameter with load

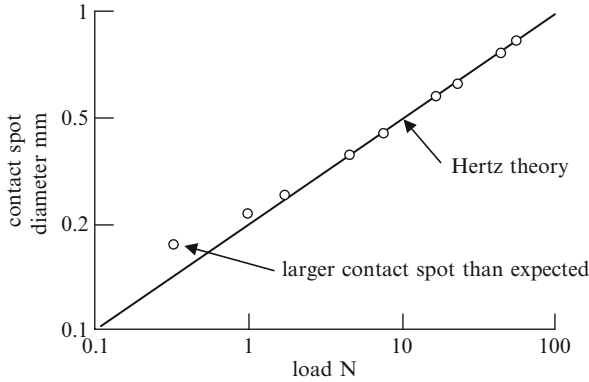
deforming, but now the pressure was generated by the van der Waals attractions and not by the external load. The simplest way to take this into account was to assume that the van der Waals attractions were acting like an external load and to use Eq. 2.1 to describe the results, as Derjaguin did in 1934. His basic thermodynamic argument was correct because it equated the work done by the surface attractions against the work of deformation in the elastic spheres. However, the deformation Derjaguin used was not exactly correct because he did not take into account the effect of surface attractions on the pressure distribution at the contact.

## 2.10 The JKR Contribution

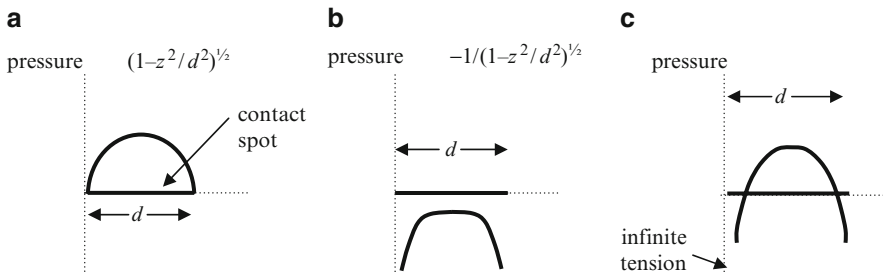
An improved solution to the problem of contact between elastic spheres with surface adhesion was obtained by Johnson, Kendall and Roberts<sup>10</sup> 37 years later. This came about because Roberts<sup>16</sup> and Kendall had both been supervised by Tabor while studying for doctorates in Cambridge, while Johnson had collaborated over many years with Tabor on the contact problems associated with friction and lubrication.<sup>17</sup>

Roberts,<sup>18</sup> while observing the contact of rubber windscreen wiper blades on glass, had noticed that the contact spot was much larger than he expected from Hertz theory under dry conditions, yet approached the Hertz predictions rather precisely when wetted with soapy water. Kendall<sup>19</sup> had been measuring the contact spot size between polymer, glass and metal surfaces using optical and ultrasonic methods, and became convinced that adhesion made the Hertz equation incorrect at low loads because the contact spot was larger than expected, as illustrated in Fig. 2.12.

The problem was to explain such increased values of contact size. Long before these experimental measurements, Johnson<sup>20</sup> had attempted to do this by showing that the pressure distribution within an adhesive contact could be described by adding two simple stress distributions together. However, he was puzzled by the



**Fig. 2.12** Results for contacts between glass surfaces measured optically and by ultrasonics<sup>19</sup>



**Fig. 2.13** (a) Hemispherical compressive stress at Hertzian contact spot; (b) rigid punch tensile stress distribution; (c) resultant pressure distribution obtained by adding (a) and (b)

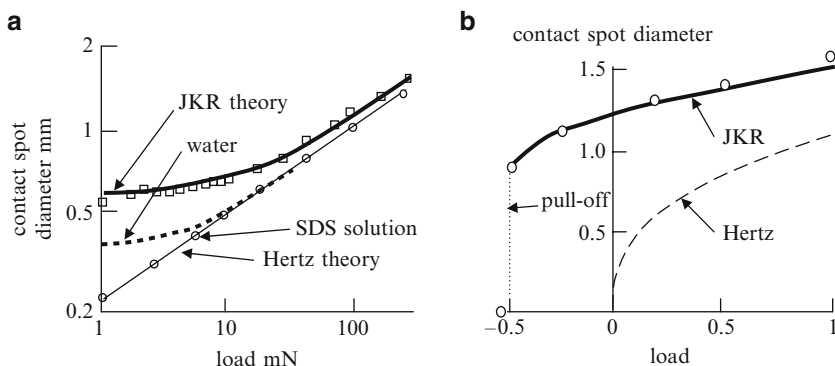
resulting infinite stresses at the edge of the contact which he therefore expected to fail under the high tension. Figure 2.13 shows the way the component stresses add within the contact region.

It became clear in 1970 that the answer lay in applying the method of Eq. 2.5 to Johnson's stress distribution. Johnson did the mathematics to provide the correct equation, the so-called JKR equation, for the elastic contact spot diameter  $d$  of equal spheres, diameter  $D$  and elastic constants  $E$  and  $\nu$ , with short-range work of adhesion  $W$ .

$$d^3 = 3(1 - \nu^2)D \left\{ F + 3\pi WD/4 + \left[ 3\pi WDF/2 + (3\pi WD/4)^2 \right]^{1/2} \right\} / E \quad (2.4)$$

Roberts and Kendall then did more experimental work on rubber/rubber and gelatin/poly(methyl methacrylate) contacts. These results fitted Eq. 2.4 extremely well, as shown in Fig. 2.14, and allowed the work of adhesion to be scaled to the observations. It later turned out that a similar mathematical argument had been produced by Sperling in 1964, but he had found no experimental evidence to support his theory.<sup>21</sup>





**Fig. 2.14** (a) Results for contacts between two rubber spheres measured optically,<sup>10</sup> on log scale; (b) results for gelatin to glass contact plotted on linear scale showing tensile loads

From the contact spot size  $d_0$  at zero load, where

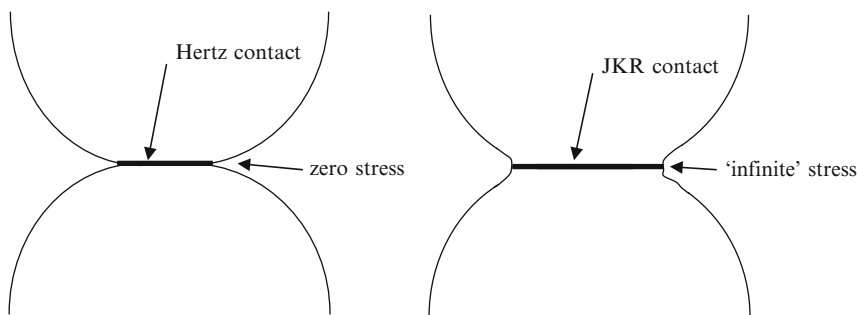
$$d_0^3 = 9\pi W D^2 (1 - \nu^2) / 2E \quad (2.5)$$

the work of adhesion fitting the results for dry rubber contact was  $71 \text{ mJm}^{-2}$  and that for gelatin on poly(methyl methacrylate) was  $105 \text{ mJm}^{-2}$ . When water was present at the rubber contact, the work of adhesion dropped to  $6.8 \text{ mJm}^{-2}$ , and this was consistent with Young's equation for the contact angle of  $66^\circ$  measured for water droplets sitting on the smooth rubber. This was the first time that Young's equation had been verified by direct measurement. When 0.01 M sodium dodecyl sulphate (SDS) solution was the immersion medium, the rubber contact size fitted the Hertz equation down to the lowest loads obtainable, showing that the work of adhesion was less than  $1 \text{ mJm}^{-2}$ . This was consistent with the presence of the surfactant film preventing adhesive contact between the wetted rubber surfaces.

## 2.11 The Nature of Adhesive Contact Between Polymer Spheres

This theory and its supporting experimental evidence changed the conception of adhesive contact considerably (Fig. 2.15). Not only was it evident that van der Waals adhesion could have a considerable effect for small compliant particles and for small loads, where the particles were significantly attached by the adhesive forces, but also the elastic contact was acting as its own measuring device which sensed adhesion. In short, van der Waals adhesion between solids could be measured by observing the size of Newton's black spot, while knowing the elasticity and geometry of the particles. The black contact spot was an adhesion sensor.

The assumption of very short-range molecular force, which acts only within the contact spot, is reasonable for contact sizes larger than a few nanometres, though



**Fig. 2.15** Hertz contact on *left* becomes JKR contact on *right* as adhesion pulls the surfaces together to change the shape of the elastic surfaces

much discussion has continued on this.<sup>22–24</sup> There is then an ‘infinite stress’ at the contact edge, exactly the same kind of stress singularity found in cracking problems, as shown by Griffith. Obviously, such an ‘infinite stress’ cannot exist in reality. Near the crack tip, the molecules must be fluctuating rapidly with Brownian movement and the crack will be making and breaking many times per second. An applied compression force pushes the equilibrium towards more contact, as shown by considering a molecular dynamics model.<sup>22</sup>

On the other hand, when a tensile force is applied to pull the spheres apart, the black contact spot shrinks. An equilibrium contact spot size could be obtained as the load was reduced, but below a certain contact size, equilibrium could no longer be found and the surfaces then came apart rather quickly at a load given by the JKR analysis

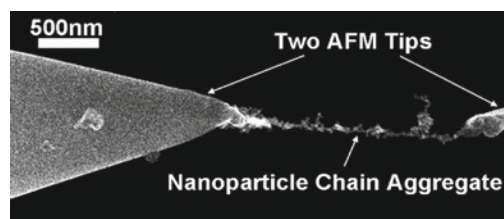
$$F = -3\pi WD/8 \quad (2.6)$$

where  $D$  was the diameter of the equal spheres.

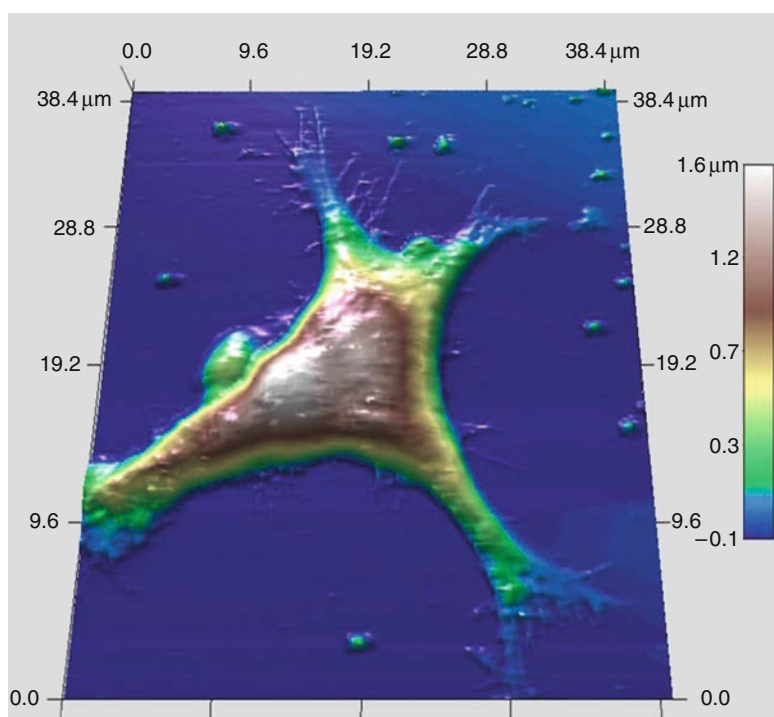
## 2.12 Application to Nanoparticles, Viruses and Cells

These ideas are relevant to both viruses and cells because we can treat living spherical organisms as complex polymer particles. In the same way that nanoparticles can be imaged and probed in contact with each other or adhering onto a surface, cells and viruses can be observed and prodded to understand their behaviour. But, because the cells and viruses are so small compared to the spheres described above, much more sensitive instruments are needed to measure the small forces. Typically, the Atomic Force Microscope (AFM) is required to detect the forces which range down from microNewtons to nanoNewtons.

Figure 2.16 shows an Atomic Force Microscope (AFM) experiment in which a chain aggregate of carbon nanoparticles prepared by evaporation was stretched to test the force of adhesion holding the individual grains together.<sup>25</sup> Clearly, this force depends on the contact spot size between particles and this can be estimated by JKR or Maugis-Dugdale models.<sup>26</sup> JKR analysis has also been applied to manipulation



**Fig. 2.16** A chain aggregate of carbon nanoparticles being stretched between AFM tips<sup>25</sup> with permission



**Fig. 2.17** Human lung fibroblast cell on glass coverslip surface as viewed by AFM (permission by Dr Murphy, Liverpool John Moores University)

of gold nanoparticles on silicon surfaces in order to understand the deformation of the particles, their sliding and pull-off behaviour.<sup>27</sup>

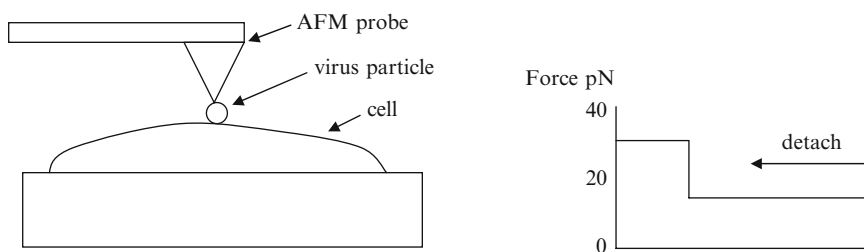
AFM can also be used to image cells using the standard silicon or Si<sub>3</sub>N<sub>4</sub> probes as shown in Fig. 2.17. A human lung cell is shown, illustrating how the cell is pulled down almost flat onto the glass surface. If a virus particle is attached to the silicon tip, then the virus can be brought into contact with the cell and interaction forces measured. Such experiments have been carried out with virus particles, typically spherical virions of HIV.<sup>28</sup> The 100 nm diameter spheres were functionalised and attached to AFM tips, then brought into contact with a living GHOST parental cell, a well-defined cancer cell line.

After the virus particles were coated onto the AFM probe, the experiment was repeated and force curves were generated then interpreted in terms of single molecule interactions. The problem is that the deformations of the virion and the cell were not accounted for. There must be substantial contact between a sphere and a soft essentially flat cell surface and it seems unlikely that only one molecular bond of force 35 pN is formed as suggested by Wirtz et al. Figure 2.18 illustrates the model proposed by the authors. That model did not take into account simple elasticity considerations.

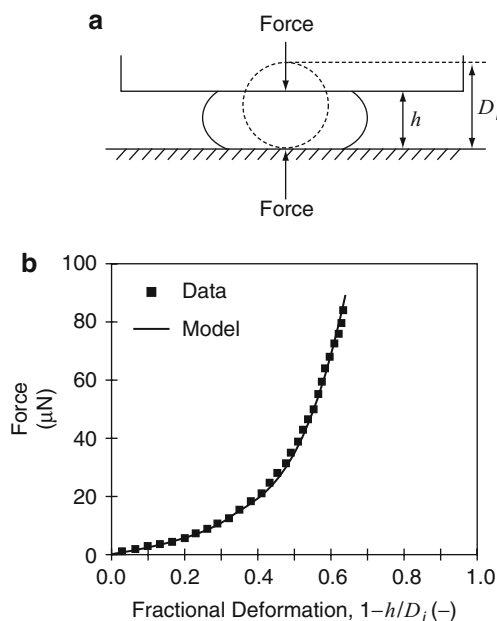
A more interpretable experiment was discussed by Roos et al. in 2007 on the compression of a virus particle against a plane solid surface using an AFM probe.<sup>29</sup> The mechanical properties of the virus particles could be measured by squeezing 40 separate virions and plotting the force deflexion curves, the stiffness was calculated to be 523 pN/nm. The adhesion energy could in principle be extracted from these measurements but this was not done.

By comparison, most force experiments on single cells have focused on the elastic and plastic deformations of the particles. For example, a typical experiment on yeast cells was carried out by Ren, Donald and Zhang in 2008.<sup>30</sup> The cells were imaged in an environmental scanning electron microscope and remained alive for 5 min, during which they could be compressed to understand their mechanical behaviour. Previously,<sup>31</sup> such cells had been probed between glass plates in air in a compression test machine to give the results shown in Fig. 2.18. The cells were not fully elastic and showed substantial time dependent deformation. However a computer model of the cells was found to fit the data. In this example, the adhesion forces were small, especially under water, and were neglected. However, from the contact diameter of 1  $\mu\text{m}$  in air at zero load, and the cell diameter of 4.5  $\mu\text{m}$ , taking the measured elastic modulus as 127 MPa, the work of adhesion between yeast and glass in humid air was calculated from Eq. 2.5 (modified for sphere/flat contact) to be 146  $\text{mJm}^{-2}$ , comparable with that obtained by peeling.

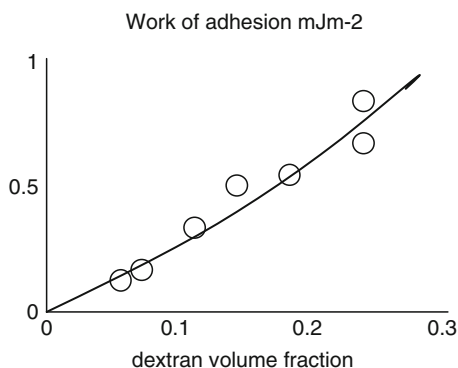
These results were comparable with optical contact black spot measurements on swollen agarose beads<sup>32</sup> and on microcapsules.<sup>33</sup> Work of adhesion down to 0.01  $\text{mJm}^{-2}$  in phosphate buffered saline solution could be measured by these methods to show the effects of osmotic pressure and temperature. It is clear from these results that contamination of the cells with water and surface molecules reduces the adhesion from about 100  $\text{mJm}^{-2}$  in air to much lower values, less than 1  $\text{mJm}^{-2}$ .



**Fig. 2.18** *Left:* AFM probe with virion attached touching cell surface; *right:* result showing typical 30 pN jump on separation of the virion from the cell



**Fig. 2.19** (a) An optic fibre is positioned above a single cell and moved down to compress it, measuring the force. (b) Force versus deformation results fitted the finite element model<sup>31</sup> ignoring adhesion; reprinted with permission



**Fig. 2.20** Work of adhesion for S180 cells increasing with added dextran compared to the theoretical line from depletion theory<sup>34</sup>

Another interesting study of small adhesive forces was carried out by Chu et al. in 2005<sup>34</sup> where the measurement technique was advanced over the standard micropipette methods.<sup>35</sup> S180 cells, which usually do not adhere because of repulsive forces, were brought into contact using micropipettes and the work of adhesion was measured in solutions of dextran at increasing concentrations. Dextran is a non-adsorbing polymer which pushes particles together by the depletion effect, causing small adhesion which could be measured by the JKR method. The results are shown in Fig. 2.20, fitting the depletion theory of de Gennes.

## 2.13 Conclusions

It is evident from this chapter that particles in general adhere by van der Waals forces which can be defined in terms of  $W$  the work of adhesion, taking into account the geometry, elasticity and forces applied in the system. Viruses and cells can be viewed like polymer particles or capsules which can be subjected to the same measurement processes and analysed by conventional theories. Of course, cells are not perfectly smooth, nor spherical, nor elastic but valuable data can be collected in an effort to understand their adhesion behaviour as affected by surface topography and surface chemistry (e.g. adhesion molecules). Dry cells stick best and the effect of water is to reduce the adhesion considerably. Further addition of contaminant molecules gives additional changes in adhesion depending on the charge, the surface adsorption and the size of the molecules. Adhesion molecules reduce adhesion.

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