

Feature article:

How do they stick together? The statics and dynamics of interfaces

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ABSTRACT

The understanding of interfaces between unlike solids is recognized as important both from the traditional static perspective ('What is the work of adhesion?') and dynamically (e.g. 'Can one predict friction and wear?'). These questions have also broadened to cover interfacial control, for instance effects on carrier transport and epitaxial relations. We address these issues by atomic-scale modelling, using mainly molecular dynamics combined with self-consistent chemistry. First we shall contrast the systems where chemical bonding is a key component (such as polyimide-metal) with those where the chemistry primarily determines which interface controls adhesion (such as oxide-metal). Second, we shall comment on the other roles of electrons: charge transfer, polarization, and dispersion forces. Third, we shall discuss the interactions which determine friction and wear in atomic force microscopy and indicate how these can be related to macroscopic tribological behaviour.

§1. INTRODUCTION

Sticking things together is commonplace in everyday life. Yet understanding what is involved and controlling it, raises substantial scientific issues. These issues become both more difficult and more significant when surfaces are in relative motion, not least because an amount equivalent to more than 1% of the UK gross domestic profit is wasted through avoidable wear and friction. The issues can be addressed under three broad questions. Firstly, what holds two materials in place or why do they stick at all? The standard answers usually assert 'van der Waals forces', or 'chemical bonding', both answers being generally misleading even when not false. Secondly, when two materials stick together, how much work must be done to separate them? Here it is often true that the work needed vastly exceeds the energy gain from van der Waals forces or chemical bonds. The issues of adhesion raised by these two questions will be addressed in §2. The third question is: what happens when two surfaces remain in contact whilst in relative motion, that is the problems of friction and wear? Here some of the understanding is discussed in §3.

These questions raise still further questions. Is chemistry involved, at all, or is the effect physical? Here, of course, a distinction has to be defined too, but it is normal to regard Coulomb interactions, short-range repulsions and van der Waals forces as

physical, as distinct from, say, the undoubtedly chemical covalent bonds of many semiconductors or glasses. In fact, the main effect of chemical reaction at an interface is to change the interface which one should consider: the reaction of a metal M with an oxide AO to give a complex oxide (M, A)O means that there are two interfaces (M with (M, A)O, and AO with (M, A) O), and it is one of these two new interfaces that will decide the effective adhesion of oxide to metal. Are surface texture and roughness involved? For friction and wear, the asperities are a crucial part of the behaviour. Categorizing the roughness is central to predicting friction, as well as to other properties such as electric breakdown and perhaps contact charging.

What makes the new developments in the theory particularly interesting is that they can be linked to new classes of experiment, and especially to data from the atomic force and frictional force microscopes. Historically, the practical researcher would have measured adhesion by the cotton-bud test (see whether it wipes off with cottonwool on a wooden stick) or the Scotch tape test (put sticky tape down and see whether the layer stays there when the tape is pulled off). The possibility of quantitative local measurements opens up a rich variety of processes and allows tests of old hypotheses as well as new ideas. However, the link between atomistic studies of adhesion and macroscopic tribology is not as simple as is often suggested. Later we shall argue that the microscopic and the macroscopic should be linked via a mesoscopic stage, for which the roughness statistics are central. Yet the link exists, and the science of tribology is emerging in parallel with the existing technology.

§2. TYPES OF ADHESION

We survey here a range of interfaces and identify some of their special features. For the first cases, we shall be concerned with the interfacial energy which might be measured, for instance, from the contact angle for a liquid metal drop on a substrate. Thus the interfacial energy might be that of a non-reactive metal (Au or perhaps Cu) on an oxide or carbide. Other cases can have reactive additions, such Ti, an important additive in practice, but the scientific issues are clearest for non-reactive systems.

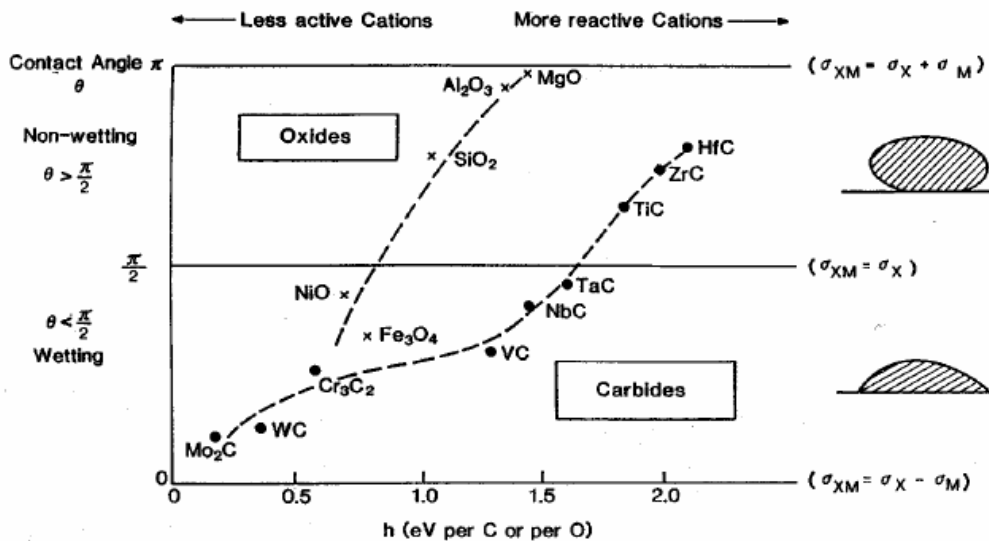
2.1. *The van der Waals interaction*

The van der Waals (dispersion) interaction is a dynamic dipole-dipole interaction; a fluctuating dipole in one medium interacts with the dipole it induces in the other. The interfacial energies can be estimated in two related ways. One uses interatomic potentials in a primitive way; it is a real-space approach, which too often uses the inverse sixth power of distance, which is really only appropriate at distances for which the interaction is largely negligible. The alternative is to use the frequency-dependent dielectric function for the two media. In simple cases, analytic expressions can be obtained for both the free surface energies and the interfacial energy in terms of the plasmon energies and bandgaps of the two media (Barrera and Duke 1976). These results can be rewritten to predict the wetting angle (Stoneham 1982) so as to link theory and experiment. Comparisons for liquid Cu on a series of carbides and oxides (fig. 1) lead to interestingly different conclusions.

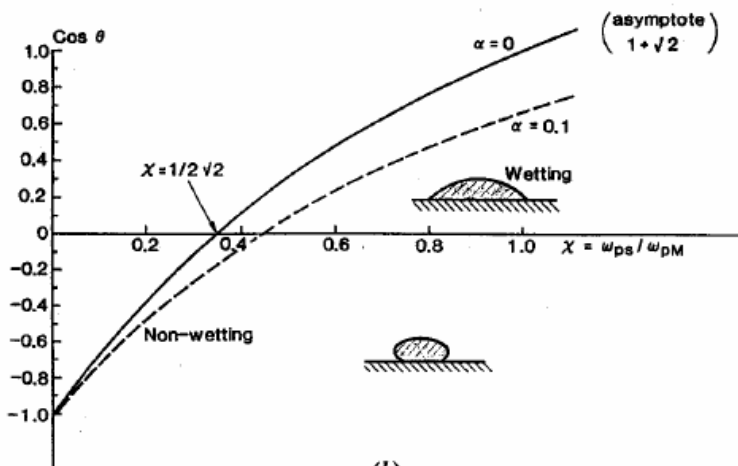
2.2. *Trends for the carbides*

Ramqvist (1965) measured wetting angles for Cu on a series of transition-metal carbides. These carbides are metals, albeit with poor conductivity, and so their band gaps will be zero; they are also often non-stoichiometric. There is a complication, in that the plasmon energies are not known for these carbides, but there is reason to expect

Fig. 1



(a)



(b)

(a) Wetting of various oxides and carbides by liquid Cu (see Stoneham and Tasker (1989) for details). Despite the apparent similarities, the oxides constitute two separate groups, unlike the reasonably continuous trend for the carbides. (b) Theory of the wetting angle for a liquid metal M on a substrate S as a function of their relative plasma frequencies (a measure of their relative electron densities). (After Stoneham *et al.* (1992).)

a simple relation between the plasmon energy of a carbide and that of the metal which forms the carbide (e.g. between the plasma frequencies of V and VC). What Ramqvist observed was that the wetting angle correlated with the enthalpy of formation of the carbide. Indeed Stoneham and Tasker (1989), reploting the data in terms of h , the enthalpy of formation per C atom in the carbide, showed that there is a smooth relation between the systems with small h (Mo, W, Cr, etc., which are wetted by Cu) and those with large h (Hf, Zr, Ti, etc., which are not wetted).

The explanation (Stoneham, Duffy, Harding and Tasker 1993) appears to be that dispersion forces do dominate. The correlation with enthalpy of formation arises because h depends on the electron density of the carbide, as does the plasmon energy

(the physicist would remark that the energy to insert a carbon atom into an electron gas depends largely on the density at the point at which it is placed; even for carbides, where the admixture of transition-metal d orbitals and C s and p orbitals can be complex, the electron density still appears to be a useful link between properties). One consequence is that the dependence of wetting angle on carbon concentration or on alloying the metal (e.g. HfC with WC) can be predicted by relatively simple arguments.

2.3. Trends for oxides

A remarkably similar plot to that for carbides is found for the wetting angle for Cu on oxides against enthalpy of formation per O atom. Yet it proves that the explanation is quite different. There is no agreement with van der Waals theory for the systematics of the observed wetting angles (Stoneham 1982). The oxides actually form two distinct classes. For those which have low refractive indices (and which, *inter alia* tend to be highly stoichiometric; MgO, alumina and thoria are examples), wetting does not occur; for those with high refractive indices (and for which non-stoichiometry or other disorder is common; NiO, chromia and urania are examples), wetting is seen.

What is happening is that electrostatic interactions are dominant. It is obvious that the image interaction (interaction of a charge with the static polarization that it induces in a metal) affects the motion of a test charge near an interface between two media. In the converse effect, the fixed ionic charges in the oxide affect the energy to separate two media with different dielectric constants. For stoichiometric oxides, the balance between the attractive image interaction and the short-range repulsion is fairly close; however, charged defects in the oxide enhance the metal-ionic oxide interaction because the attractive image term is larger (Stoneham and Tasker 1985, 1988). Clearly the adhesion here is due neither to 'bonding' nor to dispersion forces.

This simple electrostatic argument leads to several implications. Some are unrelated to adhesion and concern the stability of particular charge states in the oxide near to its surfaces. Thus one might expect high nominal charge states near to the metal, and this is indeed observed; when Fe or Ni are oxidized, the layers closest to the metal appear to be O rich rather than metal rich. There is also an interesting consequence that carriers close to the Si-oxide interface may be self-trapped (they are not in bulk quartz, although the energy differences are close) and responsible for electrical noise associated with carrier transfer between Si and its oxide (Stoneham 1991). Other consequences relate to the fact that interfacial energies affect wetting angles and the morphology of drops or blobs of material on a surface. Thus the way that water spreads as thermal oxide grows on silicon appears to be associated with surface charges on the outside of the oxide. Strong metal-support interaction in catalysis by metal particles on oxide substrates correlates systematically with precisely the differences in the oxide's tendency to be non-stoichiometric noted in the wetting behaviour; presumably the strong metal-support interaction is associated with changes in metal morphology during the processing or operation of the catalyst (Stoneham 1982). However, a third consequence is the opportunity to control adhesion by manipulating the charges of near-surface species. Certainly a substantial number of observations have been reported, using mainly irradiation; contact charging (Horn and Smith 1992) and electrostatic writing (Sauernbach and Terris 1992) are other examples. Some effects (especially for metal-to-metal contact) are clearly associated more with surface contamination and its modification or removal; others, especially for polymers (to which we shall turn) involve either free-radical generation or altered cross-linking. Other effects, such as radiation-enhanced adhesion for oxides, appear to be consistent

with the role of image charges generated by radiation. This gives the possibility for controlling adhesion, either by generating charged defects or by redistributing electronic charge over traps by optical or other excitation. It would be of great interest to check this explanation properly with the atomic force microscopy (AFM) methods now available.

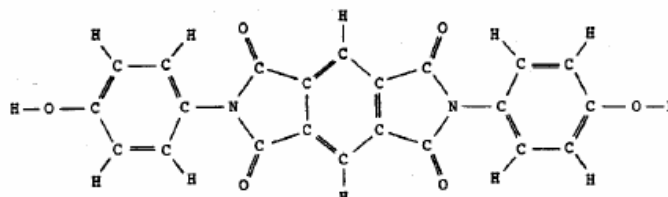
2.4. Trends for metal–polyimide interfaces

The polyimides are a versatile class of polymers, exhibiting good dielectric behaviour and strong adhesion to relatively high temperatures. They are widely used in microelectronics and are a standard coating for glass fibres which are to be embedded in a matrix. In the microelectronic applications especially, the adhesion of polyimide to metals, and the converse process of depositing metals on polyimide, are of some importance. It is natural to assume that there is a chemical interaction between the polymer and the metal, but this is not the whole story for, as de Gennes (1990) and others have stressed, the energy needed to remove the polymer from the metal is several orders of magnitude larger than that associated with breaking bonds between the outer metal atoms and the polymer itself. Likewise, it is tempting to interpret the changes in core-level spectra in terms of bonding-induced shifts only at polyimide sites close to the deposited metal atom site. One point to emerge from our calculations (Ramos, Stoneham and Sutton 1993) is that the metal can induce changes in charge distribution at several atomic distances away, so that reinterpretation of the sites and nature of bonding is needed.

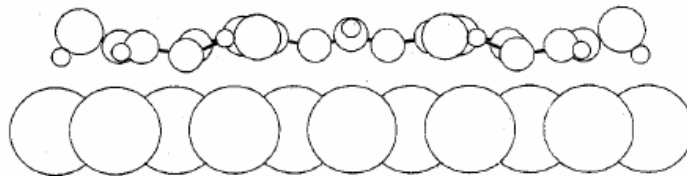
The calculations that we have done concern polyimide interacting with four metals: Al (on which we have concentrated), Cu, Ni and Cr. This can be done by relatively standard methods of quantum chemistry, namely the semiempirical complete-neglect-of-differential-overlap method, but with two generalizations. One is self-consistent molecular dynamics, using analytical forces (Wallace 1989, Wallace *et al.* 1991a, b). The other is a reparametrization of the third-row transition-metal elements to concentrate on energy prediction (and so using small-molecule data from experiment as a basis) rather than on reproducing Hartree–Fock calculations. The self-consistent molecular dynamics are essential, for the molecule distorts in a complex way which has a significant effect on the adhesion (fig. 2).

The results are as follows. Firstly, the adhesion is strong. This is consistent with experiment, and also with de Gennes' explanation of the large energy needed to remove a polymer; the work done is within the polymer itself, where one must break many weak interactions in pulling polymer chains through the tangle of other chains, and the metal–polymer link need only be strong enough to survive. Experiment (Pappas and Cuomo 1991) confirms that the join tends to fail within the polymer, and not at the polymer–metal interface. The values that we predict are consistent with this picture, for all metals are predicted to bond strongly. Secondly, our calculations for radicals as well as simple polyimide molecules are consistent with the adhesion enhancements observed when chemical etching, ultraviolet irradiation or plasma treatments are used. Thirdly, whilst we are in no doubt that chemical interactions are significant, the actual charge transfer between polyimide and metal is small. The changes in charge distribution that do occur are largely within the polyimide molecule itself. We also remark that the same theoretical approach, using self-consistent molecular dynamics, appears to predict well the electrical contacts between metal electrodes and conducting polymers (Ramos 1992). It is therefore a means to model such phenomena as organic electroluminescent devices.

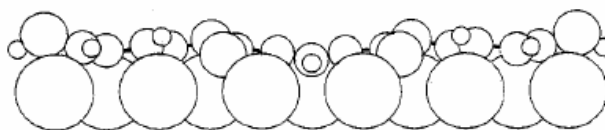
Fig. 2



PMDA-ODA polyimide



Polyimide/Al(100)



Polyimide/Ni(100)

Distortion of polyimide molecules on Al and Ni, calculated by self-consistent molecular dynamics (Ramos *et al.* 1992): PMDA-ODA, Here there is chemical bonding, although there is little net charge transfer. The work of adhesion is determined more by the weaker cross-links within the polymer than by the strong bonding directly between polymer and metal. The predicted (reversible) bonding is actually somewhat greater for Al than for Ni, even though the molecule sits further from the Al surface.

2.5. Atomic force microscopy

It is well known that the work of adhesion (to remove, say, a metal from a ceramic) far exceeds the gain in energy when (in a fictional ideal experiment) the metal is first placed in contact with the ceramic. The energy of plastic deformation is substantial. Only for the most brittle solids, for example, do cleavage energies give a good guide to surface energies. As noted above, the work of adhesion of polymer and metal can be determined primarily by the breaking of weak links within the polymer itself. Indeed, with ingenious design (as with some of the new self-sealing polymer bags), adhesion can be achieved with no bonding at all, simply by exploiting the friction between interfaces pushed together. If the standard work-of-adhesion data are a poor guide to interface energies, even when properly interpreted (Kendall 1971, 1978), can the atomic force microscope do better?

Certainly the atomic force microscope offers the potential for highly local measurements that are clean and well defined. Certainly too, its sensitivity and mode of operation introduce (or make visible) new effects (Ramos *et al.* 1990, 1993). One is the dramatic deformation of a tip as it comes close to a substrate (Sutton and Pethica 1990). This can be understood from continuum arguments, as well as demonstrated by

atomistic models and observed by experiment. The key issue is the relative size of the surface rigidity (essentially the vertical displacement per unit force) and the second derivative of the attractive interaction between tip and substrate; this interaction is attractive at the separations of interest, before the short-range repulsions take over at contact. The rigidity S in continuum models is given by an elastic constant multiplied by a length, the length being the geometric mean of the atomic force microscope tip radius and a length related to the tip-to-substrate spacing without deformation or to a characteristic length of the interaction. For reasonable interactions and tip radii (say 2 nm) the critical spacing at which instability occurs is 0.1–0.5 nm. This instability affects the resolution, other capabilities and interpretation of scanning tunnelling microscopy and AFM images at very small spacings; it also determined in part the size of electrical contact created by the resulting tip and substrate link.

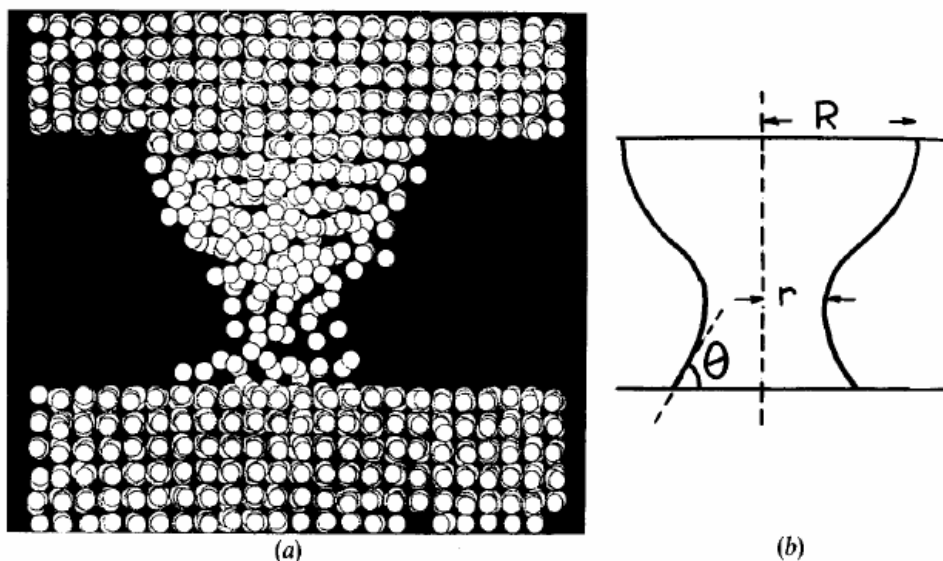
Another striking result emerges when the tip is pulled from the substrate (Sutton, Pethica, Rafii-Tabar and Nieminen 1992). We may define the force of adhesion (for a given separation of the tip holder from the substrate) as the tensile force needed to pull the tip off the substrate. Then the force of adhesion is strongly influenced by the deformation of the tip as it comes away from the substrate. Remarkably, the force of adhesion is always *reduced* by a layer of different material on the substrate surface, even when the interlayer has bonds stronger than those in the tip or the substrate, and irrespective of whether or not wetting occurs between the tip and the interlayer. What happens is that the interlayer reduces the radius of the neck during pull-off, and this reduces the maximum tensile force that can be sustained (the failure, obviously, takes place at the weakest point, and not in the strongly bonded regions). This is consistent with point-contact measurements for a W tip on Ni in ultra-high vacuum (Pashley, Pethica and Tabor 1984). A simple 'liquid-drop' model describes what is happening (fig. 3). The important region of the tip deforms at roughly constant volume; its profile is determined by the interfacial energies. However, unlike the standard description, fracture does not take place at the interface between tip and substrate: the interface energies affect the necking-down process (and hence the maximum neck radius) rather than the interfacial energy for some fixed area of contact and fixed tip surface energy. These ideas lead to possible reinterpretations of embrittlement.

A further important feature of the atomic force microscope is that the tips can be regarded as idealizations of the asperities, which are the 'hills' on rough surfaces at which contact will occur. It can therefore be a model system for studies of mechanisms of friction and wear.

§3. FRICTION AND WEAR: ADHESION AND RELATIVE MOTION

In friction, there are two especially important issues. One is the force to start the relative motion of two surfaces in contact, which is described by the coefficient of static friction. The other is the force needed to keep two interfaces in relative motion, where the coefficient of dynamical friction is the key quantity. We shall concentrate on the dynamical case. Thus we want to predict the rate at which energy is dissipated in the relative motion, and to predict this as a function of the parameters which might control it: surface roughness, properties of surface layers and lubricants, and the elastic or anelastic properties of the substrate. We shall also want to know about the wear at the interface, and how the surface degrades during rubbing and the consequent evolution of the coefficient of friction. Some of the recently developed dry lubricant coatings for space vehicles (Roberts and Price 1989) do have incredibly good friction (coefficients as low as 0.01–0.02) and wear (up to a million cycles on a coating a few microns thick). The

Fig. 3



(a) Molecular dynamics model (Sutton *et al.* 1992) for a Pb tip necking down as it is removed from a Pb substrate. Note the disorder in the lower part. (b) Liquid-drop model (Sutton *et al.* 1992). The radius and contact angle at the top (tip end) are constrained. At the lower (substrate) end the contact angle is fixed by the interfacial energies. The shape, and hence the neck radius, can be calculated; analytic bounds can be put on the force of adhesion, which is a maximum when the lower radius and contact angle are equal to the upper values.

reliability of such lubricants is especially important too, given the cost of each space vehicle launched, and it is remarkable that no failures of these lubricants have occurred.

3.1. Friction: length scales and mechanisms

The mechanisms of friction normally given are relatively few in number (Bowden and Tabor 1950, 1973). One involves adhesion; surfaces adhere, and then work is done in separating them. Another is ploughing, in which one surface pulls away small amounts of the other. A third is anelasticity; the assumption that energy is dissipated by dislocation motion and plastic deformation in the media. There is even a small elastic contribution (Stoneham and Harker 1982) because the asperities of one surface generate time-dependent forces (and hence generate sound waves) in the other medium. The atomic force microscope allows the possibility of being more precise about the mechanism (Landman, Luedtke, Burnham and Cohen 1990, Landman 1992a, Niemenen, Sutton and Pethica 1992a, b, Ramos 1992, Sutton *et al.* 1992), but the link to macroscopic tribology is not usually identified, nor clear. There is an intermediate layer of 'mesoscopic modelling' to bring the atomistic studies into useful juxtaposition with full-scale studies. The point (to which we return later) is that the surface roughness (which will usually be characterized statistically) is not recognized in studies on an atomic scale and yet is central to what is observed macroscopically.

3.2. Friction on a mesoscopic scale

We follow here the arguments of Ogilvy (1991, 1992a, b) and Roberts, Williams and Ogilvy (1992). This work involves two main steps. The first is the characterization of the rough surfaces and their contact. This is done by calculating a number of realizations of

each surface, with r.m.s. height and correlation length (characterizing the point-to-point height variations) corresponding to experiment. Obviously, the elastic (or plastic) response must be calculated at each contact point, that is one has to solve the static problem in which the asperities support the applied load. There is a natural generalization when one surface moves relative to the other. The second step is to assume some law of friction at the asperity (i.e. specifically for the asperity, and not averaging over the whole macroscopic area of the surface). There are several possibilities here; suffice it to say that it is in these laws of friction that the AFM data and its interpretation can be crucial.

What emerges is this. Firstly, it proves possible to rationalize much of the experimental data. The observed (macroscopic) friction coefficients are predicted rather well for their dependence on roughness (scale length as well as r.m.s. height) and on the elastic constants of the substrate (e.g. ceramic as opposed to steel) on which the solid lubricant is deposited. Secondly, other observables, such as wear and the dependence of friction on load, are predicted satisfactorily. Thirdly, there is information about the spread of friction values. Just because the roughness is describable statistically, there will be patches of lower friction and patches of higher friction, and the variations to be expected in experiments can be modelled too. Finally, it is clear that this approach provides a framework for the exploitation of AFM data.

3.3. Friction on an atomic scale

3.3.1. Atomistic studies of lubrication

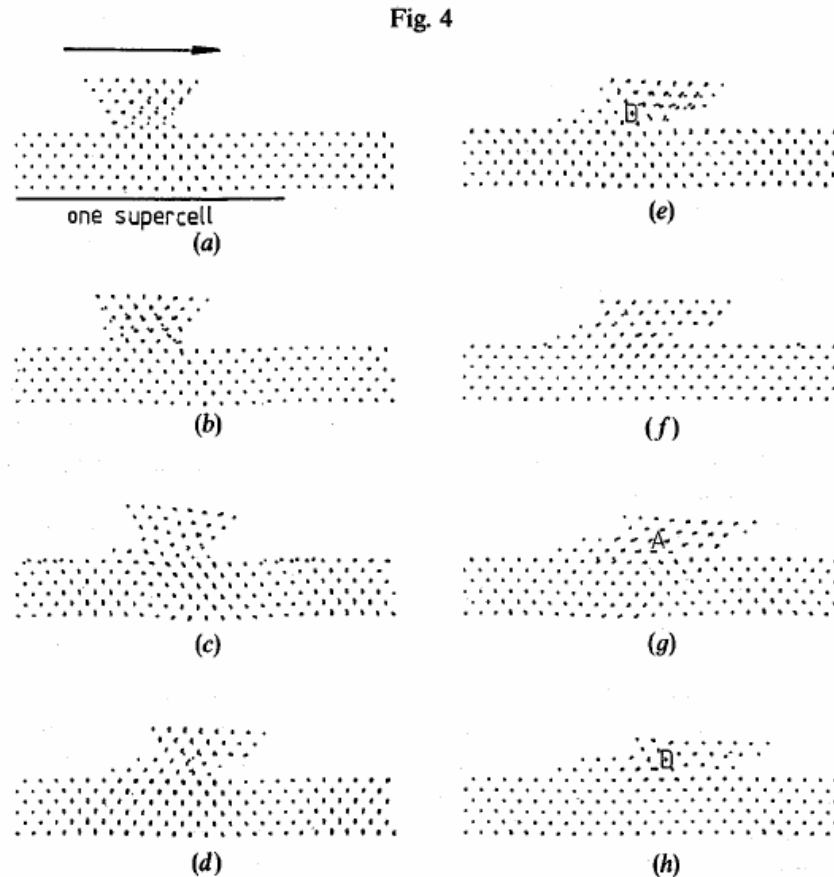
Atomic-scale modelling in the atomic force microscope has been carried out by several groups, with different emphasis. The calculations of Landmann *et al.* (1990) and Landmann (1992a, b) show some of the key features of lubrication by chemically inert organic molecules. One striking feature concerns the way that the lubricant molecules organize themselves in the narrow confines between tip and substrate, so that the frictional force varies in an oscillatory way with the separation of tip and surface. This class of behaviour is widespread (for example Henderson (1988)) applying too to hydration forces. Harrison, Brenner, White and Colton (1991) show the pronounced effects of adsorbed species, considering the interactions between (111) diamond surfaces both with and without a layer of H; here the formation of a connecting C-C link between the two surfaces leads to significant surface and subsurface damage. There are interesting similarities and differences between the effects of these adsorbed species and the effects on wear discussed below of one or two layers of low-shear-strength material on the substrate.

3.3.2. Junction growth and wear

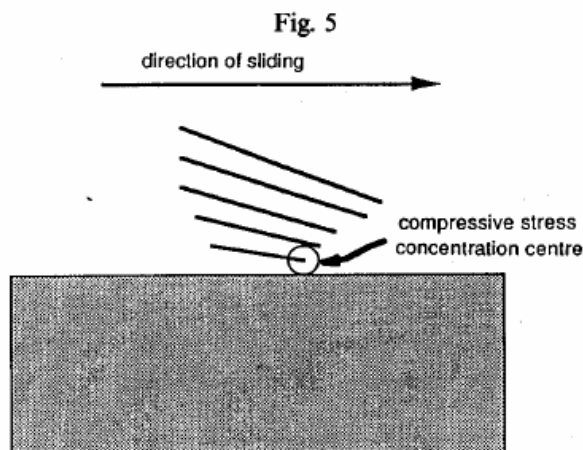
The motion of an atomic force microscope tip over an unlubricated substrate is both an experiment in force microscopy and a simulation of the standard situation in tribology, where an asperity on one surface moves over another surface with which it makes contact. Nieminen *et al.* (1992a, b) have modelled this situation, showing the ways in which deformation of the tip occurs, and hence the processes and micro-mechanics of wear. Their model exploited molecular dynamics, with interactions via a Morse potential fitted to Cu; after equilibration, the system was kept at a low temperature by rescaling the velocities of substrate atoms several layers below the interface to keep them at 11 K. Periodic boundary conditions were used; while this meant that an array of many tips was considered, these were arranged in a way that avoided interactions between them (of course, in real friction experiments, there will

always be many asperities, and indeed the periodic array could be modelled mesoscopically too in linking atomistic and macroscopic experiments). The velocity of motion of the tip was about 100 ms^{-1} , which is large compared with traditional experiments, but well below the crucial velocity of sound. The several figures show snapshots of atomic positions, frictional force and the temperature of the contact region. The temperature depends partly on specific shear processes and also on a balance between the work done by the frictional force and cooling processes.

Figure 4 shows snapshots of events as the tip moves over the substrate along a $[110]$ direction; the normal to the substrate is $[001]$. A stacking fault is introduced at the contact because of the way in which the periodicity is built in; this can be removed only by eliminating one of the substrate layers under the combined effects of sliding and the compressive load. As the displacement coincides with a specific tip-substrate relationship, the upper three layers of the tip slide over the lower two layers. This releases potential energy; the temperature rises and the frictional force falls. The potential energy rises again as the shear stress deforms both the tip and the substrate, since the tip



Friction and wear under compressive load. (a) A five-layer tip with a stacking fault at the contact is considered. (b) The upper layers of the tip slide over the others. (c) Tip rotation results. (d) An overhang develops which is ameliorated by rapid migration of atoms into the overhang, relieving the concentrated compressional stress and extending the first layer of the tip. (e) The second and third layers of the tip merge to eliminate the stacking fault. (g) Further sliding and diffusion processes reduce the tip to three layers of larger area. D indicates a dislocation in (e) and (h) and A identifies the centre of compression in (g).



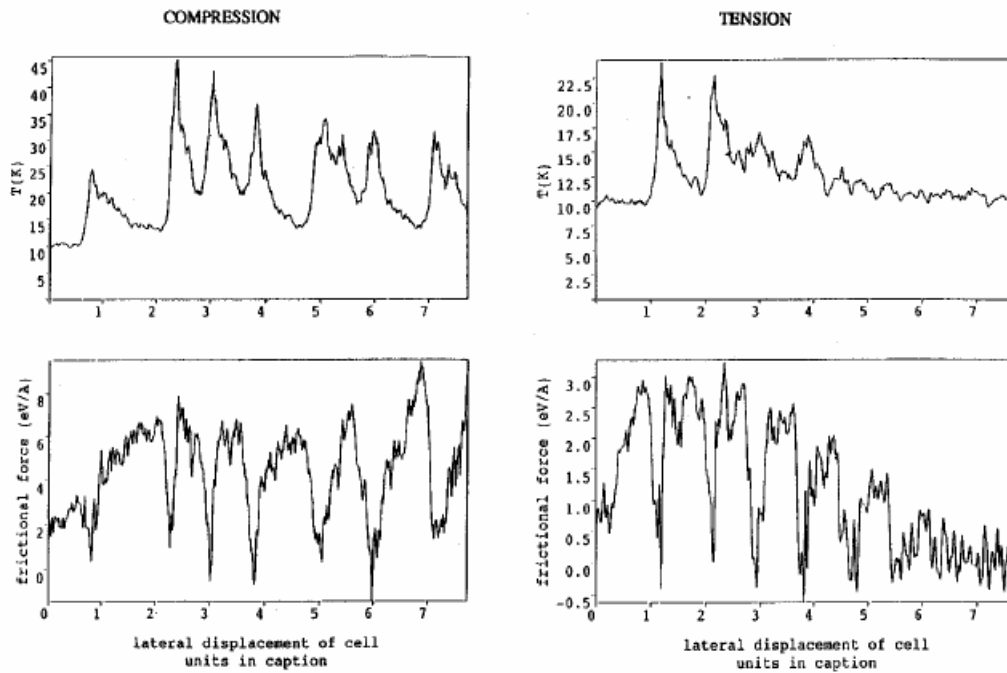
The bending of the tip under sliding shear stress. This schematic diagram corresponds to fig. 4 (c), shown enlarged below.

sticks to the substrate. The substrate distorts elastically into a sinusoidal form. The tip deforms in a more important way; the tip rotates so that the front is compressed and the rear is lifted off the substrate. (shown schematically in fig. 5). As the process continues, there are changes in the nature of the surface over which sliding occurs within the tip, so that the extrema of frictional force and temperature (fig. 6) are not regular. The shear and diffusional processes in fig. 4 transform the tip from five to three layers by what can be described as the climb of two successive edge dislocations. The high stress concentration and small distances involved mean that climb is rapid even at low temperatures.

The combined effect of compressive stress and sliding force is to increase the static area of contact, similar to the junction growth discussed by Tabor (1959). However, where as Tabor deduced an associated increase in frictional force, this is not the case here, where sliding occurs mainly within the tip. The area over which sliding occurs does not change much, and there is no simple relation between the static area of contact between tip and slab and the magnitudes of the maxima in frictional force.

Under tensile load (fig. 7) the tip lengthens to eliminate the stacking fault found for compression. Again, sliding starts between the first and second layers of the tip. The area of dynamic contact decreases and eventually pulls away. Even so, the tip leaves some atoms behind on the substrate. However, the structural changes within the tip are less dramatic than under compression, so that the stick-slip events in the frictional force (fig. 6) are more regular under tensile stress. Clearly frictional forces should persist

Fig. 6



Frictional force and local temperature variations corresponding to fig. 4 (compressive load) and fig. 7 (tensile load). The structural changes are less substantial under tension; so the stick-slip events are more regular in time. The temperature is defined solely in terms of the kinetic energy; so the frictional force can rise as the potential energy is increasing, without an increase in temperature readily related to the rate of doing work.

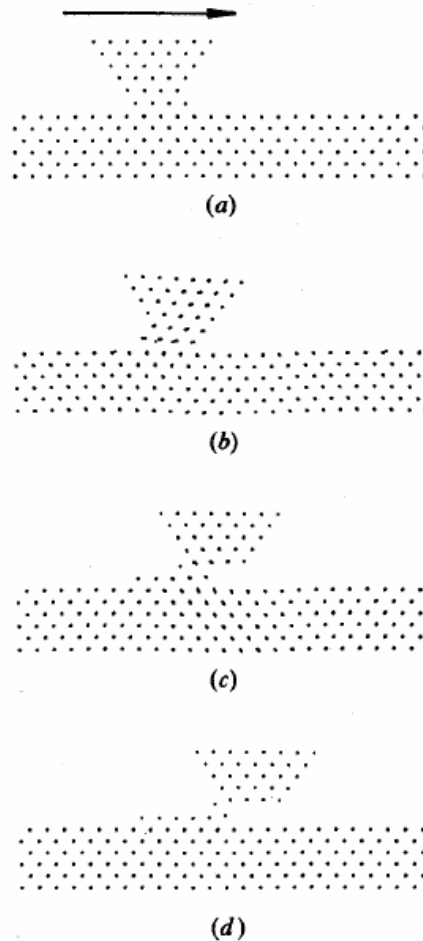
under tensile loads which are insufficient to overcome the adhesion between the interfaces.

When there is a layer of lubricant (for instance if the substrate is covered with a film of one or two layers of atoms with low shear strength), then sliding can take place between tip and substrate (Niemenen *et al.* 1992b). If there is a single layer of lubricant atoms, the rotation of the tip is reduced, the compressive stress concentrated at the front of the tip is less, and wear does not take place but, with two layers, the tip can penetrate the film, so that some wear of the tip will occur when sliding starts. Since the general rule is that wear occurs through sliding within the tip, rather than at the tip-substrate interface, the three requirements for wear avoidance are firstly that the shear strength of the tip-film interface is less than the shear strength of the tip, secondly the shear strength of the tip-film interface is less than the shear strength of the underlying substrate and thirdly that the film strength in compression is sufficient to prevent the tip from penetrating the film.

3.3.3. Lubrication chemistry

All the current modelling has used interatomic potentials of varying sophistication. Yet there are situations for which that is insufficient. A good example is when chemical reactions occur, as undoubtedly they do during wear; indeed, there is evidence from AFM that oxidation is partly responsible for the degradation of molybdenum disulphide (Kim, Hiang and Lieker 1991). Likewise, the wear of diamond by diamond is reduced when there is moisture present (Field *et al.* 1992), although there is evidence of

Fig. 7

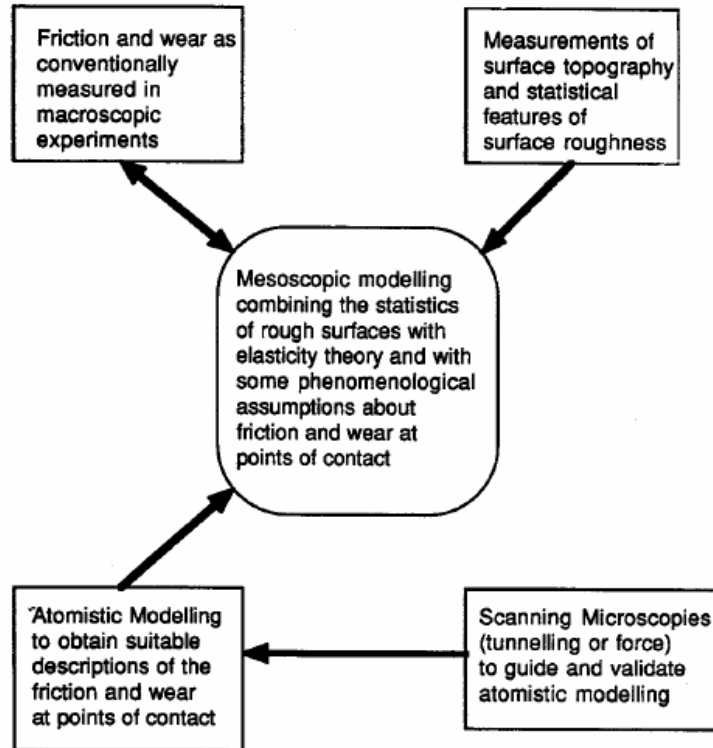


Friction and wear under tensile load. Note that the first layer of the tip remains in epitaxial contact with the substrate, even though strained. (c) The applied tensile load overcomes adhesive interatomic forces at the overhang. Despite the tensile force, tip atoms remain on the substrate after separation.

friction increasing with moisture for diamond-like carbon (Enke 1989). It proves possible to extend calculations of friction (Ramos 1992) to the chemistry of wear, the two components being conventional molecular dynamics and the CHEMOS code (Wallace 1989, Wallace *et al.* 1991a, b) for self-consistent chemistry and molecular dynamics for the central group of a few tens of atoms where reactions occur.

One interesting use of this approach is for a different situation in which standard potentials fail, namely for the conducting polymers such as *trans*-polyacetylene (*t*-PA), where the bonding pattern is in a continual state of flux. As an example, one can compare the lubrication by *t*-PA with that by a more conventional lubricant, such as polytetrafluoroethylene (PTFE). What emerges is that *t*-PA appears to have a low but distinctly higher coefficient of friction. It is tempting to suggest that this is because *t*-PA, unlike PTFE, can support soliton motion, and that this might allow other channels for energy dissipation.

Fig. 8



Friction on macroscopic, mesoscopic and microscopic (atomistic) scales. The mesoscopic regime must be included if rational links between atomistic and technological scales are to be made.

§4. CONCLUSIONS

Interfaces, especially those between unlike media, raise many issues: surface chemistry, atomic processes and dynamics, and other aspects of solid-state science. Our paper concentrates on the adhesion of interfaces, both those simply in static contact and those in relative motion. We have aimed to identify the common themes from a range of studies, mainly atomistic modelling. One such theme is the link between macroscopic behaviour and experiment and theory on an atomic scale (fig. 8). Here, especially for friction and wear, the important messages are both the need to involve mesoscopic modelling (and so to take account of statistical roughness, for instance) and the variety of insight which the atomistic studies give, indicating new types of behaviour within asperities under stress. Another theme is the way that Coulomb forces and, not just 'bonding' or dispersion forces, can dominate in adhesion. Indeed, in some cases (notably metal-ionic systems) this means that adhesion can be controlled to some degree by controlling charged defect populations and the distribution of carriers over near-surface traps. Perhaps the most important concept is the idea of an atomic force microscope tip as an active probe in the study of surface processes, and not merely a passive observer, but a source of local fields or stress which can probe the response of small regions (perhaps ultimately individual molecules) in real space.

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