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LETTER TO THE EDITOR

Electrical and mechanical contact between rough gold surfaces in air

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Abstract. An original coupling of electrical and mechanical measurements is reported; it concerns the phenomena arising from the interaction between two very close macroscopic electrodes, one a sphere and the other a plane, studied in air. The current–distance and current–voltage curves clearly attest to a tunnelling transfer mechanism, and prove to be in very good agreement with theoretical predictions taking into account the roughness of surfaces. Both electrical and mechanical interpretations coherently indicate the existence of an intermediate substance in the interface, plausibly condensed water with the addition of organic contaminant(s).

The recent increase in availability of very reliable piezo-transducers, which can be used to achieve tiny displacements, has given rise over the last few years to the development of various devices that allow one to control the extremely close approach of two solids, and to carry out, using this facility, electrical or mechanical measurements relating to their interaction. A firm distinction must be made, however, between instruments in which one of the interacting bodies may be regarded as an atomically sharp tip, and equipment where macroscopic solids with surfaces as smooth as possible are preferred. The former have become far more readily available since the introduction of the use of the scanning tunnelling microscope in this field by Binnig and Rohrer [1–4], whereas the latter came to the fore with the introduction of the 'precursor' force apparatus of Tabor and Israelachvili [5–7]. We present in this letter the original coupling of certain electrical and mechanical measurements recently achieved on a sphere/plane device using an instrument from the second category.

The particular experimental unit used for this study has already been described in the literature [8–11]. Although predominantly devoted to mechanical investigations (e.g. of interfacial forces and rheological properties of a liquid between two solids), its features enable one to perform certain electrical measurements simultaneously by simply using metal or plated bodies [10]. The general principle of the system is that a macroscopic spherical body can be moved near to and away from a planar one via a thermal expansion frame and a vibrating piezoelectric crystal. A feedback loop allows one to control the quasi-static operation resulting from use of the thermal device

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with a resolution of about 0.15 Å in the relative displacement h of the solids; the constant speed h thus obtained varies between 0.2 and 10 Å s^{-1}.The piezo-element may superimpose on the linear motion a small sinusoidal component intended to determine the dynamic behaviour of the sphere/plane interactions. The plane specimen is supported by a double-cantilever spring preventing the 'quasi-contact' region from rolling and shearing. A first capacitive sensor measures the elastic deformation of the cantilever and thus the force transmitted to the plane; a second one is designed to measure the relative displacement h between the two solids. The electrodes used for the experiments were a silicon plane and a fused conosilicate glass sphere of radius $R = 3.5$ mm, both covered by sputtering with a 400 Å cobalt sticking layer and a 600 Å gold terminal coating. A STM examination of such surfaces shows irregular connected clusters producing a gently bumpy corrugation similar to the 'blackberry' roughness already observed on comparable Au films [12], with peak-to-valley heights of 50–60 Å and a mean distance between adjacent bumps of about 500 Å [13]. After a basic positioning of the gold solids in ambient air, some P_2O_5 was introduced in the apparatus chamber to dry its atmosphere.

The problematic question of an origin for the absolute displacement of solids requires careful clarification. This is dealt with by making preliminary measurements of the sphere/plane capacitor variations as a function of h for large separation distances (> 200 Å). In fact, theoretical calculations prove that the capacitor values C_s and C_r, respectively relative to smooth and rough electrodes, have derivatives with respect to the reference distance H between ideally smooth and infinitely rigid solids that are nearly the same:

$$\frac{\partial C_r}{\partial H} \approx \frac{\partial C_s}{\partial H} \underset{H/R \ll 1}{\sim} -\frac{2\pi\epsilon_0 R}{H} \qquad (1)$$

as long as H is greater than four to five times the peak-to-valley amplitude of roughness [14–15]. As in such conditions H and h only differ by an unknown but constant offset, an extrapolated point such as

$$\left(\frac{\partial C}{\partial h}(h)\right)^{-1} = 0 \qquad (2)$$

corresponds to the natural zero relative to the separation H. The origin so chosen has the advantage of still having a meaning whatever happens throughout the close approach of solids (e.g. deformation, adhesion). Conversely, as long as such problematic phenomena do not occur, the distance H is simply the true separation of the smooth surfaces. In practice, the capacitor measurement involves an oscillator at a frequency around 4.5 MHz with an amplitude limited to 200 mV RMS. The superimposition of a tiny mechanical vibration (frequency 38 Hz, amplitude 1 Å RMS) on the quasi-static linear motion of the sphere ($\dot{h} = 1$ Å s^{-1}) allows one to obtain the derivative $\partial C/\partial h$ from synchronized demodulation.

The four characteristics shown in figure 1 concern the most significant measurements (three mechanical and one electrical) simultaneously carried out on the sphere/plane device during an approach phase. The sphere motion consists of a linear displacement such as $\dot{h} = 0.5$ Å s^{-1}, combined with a tiny sinusoidal vibration of amplitude 0.25 Å RMS at the frequency of 38 Hz. The parameters displayed are the quasi-static force $F(H)$ acting between the two solids, the real and imaginary parts of

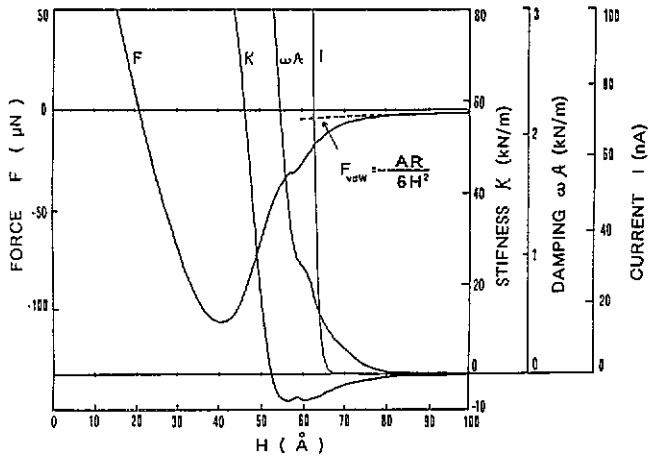

Figure 1. Plot of the main mechanical and electrical parameters simultaneously measured on the sphere/plane device during an approach phase: the quasi-static force F acting between the two solids; the dynamic stiffness $\mathcal{K}$ and damping $\omega\mathcal{A}$ of the interface; and the current I resulting from a small direct bias. A precise description of the experimental conditions and a careful definition of the abscissa parameter H are given in the text.

the 'mechanical transfer function' of the interface, i.e. its stiffness $\mathcal{K}(H)$ and damping $\omega\mathcal{A}(H)$ ($\omega = 238.76$ rad s^{-1}), and lastly the current $I(H)$ resulting from a direct bias V_{app} of 2 mV (this low value induces a negligible electrostatic attractive force). This set of curves shows that, during the approach of solids, certain distinct sequential steps occur, which can be briefly analysed as follows.

(i) For $H > 85$ Å, the damping $\omega\mathcal{A}$ and the current I prove to be too small to be measured. The quasi-static force $F(H)$ is attractive and follows the van der Waals law

$$F_{VDW}(H) = -AR/6H^2. \tag{3}$$

The value of $(2.8 \pm 0.2) \times 10^{-19}$ J found for the Hamaker constant A can be regarded as quite acceptable [16].

(ii) For 85 Å $> H >$ 55 Å, the decrease of H brings about a revealing increase of the damping function $\omega\mathcal{A}(H)$, while the quasi-static force $F(H)$ progressively deviates from the van der Waals law (3). Both of these observations attest to there being a liquid substance in the interface: the former shows a purely viscous behaviour that is more pronounced than would be expected for air damping, whereas the latter indicates an excess of the attractive force that it seems reasonable to attribute to the wetting force of a liquid meniscus. Considering how briefly the gold electrodes were exposed to the air before the experiment, a plausible hypothesis is that the capillary condensation of the water molecules was firmly attached to the metal surfaces, and was probably mixed with some organic contaminants (e.g. hydrocarbons). Together with the above mechanical observations, it may be noticed that a considerable increase of the current $I(H)$ commences at $H \approx 68$ Å.

(iii) For 55 Å $> H >$ 40 Å, the stiffness function $\mathcal{K}(H)$ shows a significant increase, while the force $F(H)$ keeps on becoming more attractive. This stage corresponds to the progressive appearance of the 'pushing-apart' force due to the presence of some or many asperities. The current measurement is saturated.

(iv) For $H = 40$ Å, the quasi-static force reaches its highest attractive intensity. Smaller values of H correspond thus to a global deformation of the solids. A rough evaluation of the radius ρ of the area of contact for ideally smooth surfaces according to the Derjaguin–Müller–Toporov theory [17] gives $\rho \approx 10$ μm. As the density of bumps inferred from the STM observations of the surfaces is around 400 μm^{-2} [13], it can be assumed that a large number of asperities actually touch, and therefore that the contact is elastically deformed. For $H = 21$ Å, the fact that $F = 0$ indicates the transient compensation of the adhesive effect and the total deformation of the contact region.

For completeness, we must add that the measurements of $F(H)$, $\mathcal{K}(H)$, $\omega\mathcal{A}(H)$ and $I(H)$ were continued throughout the corresponding pull-off phase (carried out under similar experimental conditions). Any reference to these results has been, however, intentionally omitted in this letter, because they bring to light a few unusual observations which require, in our opinion, further investigation to elucidate them. For instance, the highly viscoelastic behaviour noticed for the interfacial medium (with $\mathcal{K} > 5\omega\mathcal{A}$), suggests, among other possibilities, that many gold microparticles, appearing as a result of surface separation, could have added to the previous meniscus. It is anticipated that future STM examinations of the surfaces involved at the close of the experiment, not performed in the present case, will provide a basis for confirming—or otherwise—the local degradation of coating(s).

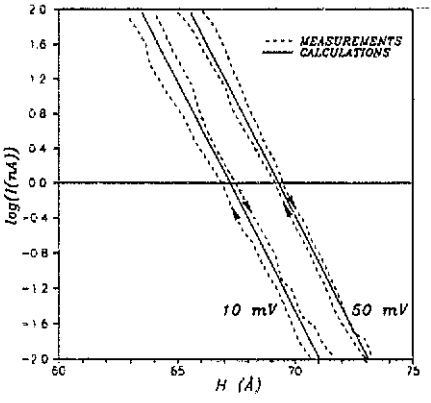

Figure 2. Plot of the current versus distance characteristics quasi-statically measured between the gold sphere and plane for small direct voltages (broken lines), and corresponding theoretical curves calculated from (5) by taking into account the combined local topography of conductors (full lines). The fitting is all the more convincing since the roughness parameters considered in the model are very similar to the real ones observed by scanning tunnelling microscopy.

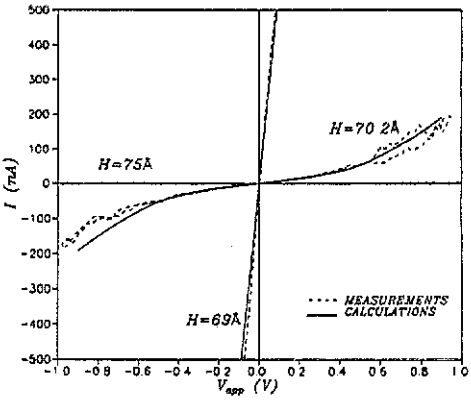

Figure 3. Plot of the current versus voltage characteristics obtained for three values of the sphere–plane separation H (broken lines), and corresponding theoretical curves (full lines).

More thorough investigations focused on the electrical transport phenomenon previously brought to light (stage (ii)), and carried out before any effective contact between surfaces has occurred, are reported on the figures 2 and 3 as broken lines.

Figure 2 shows some current versus distance characteristics measured for low direct biases V_{app} of 10 mV and 50 mV. The arrows indicate the inward and outward motion of the sphere, occurring at a constant speed $\dot{h} = 0.5$ Å s^{-1} (quasi-static operating). In view of the considerable variations of the current, $\log(I)$ is plotted instead of I. The linear trend of the curves thus obtained conveys a law of the form

$$I(H, V_{app}) = I_0(V_{app})\exp(-H/H_0) \tag{4}$$

which is a well-known typical feature of tunnel transport [18,19]. The experimental value found for H_0 is 0.87 Å. Three current versus voltage characteristics obtained for $H = 69$ Å, 70.2 Å and 75 Å are presented in figure 3. The displayed behaviour also proves to be attributable to tunnelling, with an ohmic region at low voltages and a very strong dependence on H.

The fitting of the different current characteristics to calculated curves requires to resolve the difficult theoretical problem of tunnelling between two macroscopic rough conductors. The question has been recently treated by two of us (FH, LB) in the restrictive case of small local slopes on the 'active' areas of both surfaces (i.e. the tops of facing dominant bumps) [14,20]. The current can thus be conveniently expressed through an integral of the form

$$I = \int J_t(\zeta)\frac{\partial S}{\partial \zeta}(\zeta)\, d\zeta \tag{5}$$

in which $J_t(\zeta)$ denotes the current density function, and $\partial S/\partial \zeta$, the distribution of local distances ζ between electrodes, conveys at once their nominal shape and their roughness. As the surfaces involved fulfil the slope limitation, fitting can be attempted using this equation.

The determination carried out for the physical component $J_t(\zeta)$ is based on some standard hypotheses: (i) an exclusively elastic tunnelling process, (ii) a free-electron model for conductors, and (iii) a homogeneous inter-electrode medium simply described through its electron affinity and permittivity [18,19,21,22]. Direct numerical computation avoids the necessity of resorting to debatable approximations such as the WKB one [23]. The unknown physical parameters reduce then to an 'effective work function' Φ_{eff} of the electrodes and an 'effective permittivity' ϵ_{eff} in the insulating region. As regards the topographic contribution $\partial S/\partial \zeta$, the choice of a periodic 'crossed-sinusoidal model' for roughness gives in the situation considered a good compromise between realism and simplicity. An appropriate choice of the 'peak-to-valley height' $2a$ and the 'wavelength' λ of this ideal corrugation may sometimes represent a quite complicated problem. If, however, the rough estimate of λ looks small enough for many bumps to be involved in the process—as is the case here—only the adjustment of a turns out to be significant [24]. In practice, the value of λ was set to 500 Å following STM observations; then, self-consistent calculations quickly led to an optimal set of values for Φ_{eff}, ϵ_{eff} and a, taking into consideration their specific influence upon, respectively, the slope $-1/H_0 \ln(10)$ of the $\log(I)$–H curves, the general shape of I–V_{app} curves and the current magnitude for given H and V_{app}. The best agreement was found in that way, taking $\Phi_{eff} = 1.27$ eV, $\epsilon_{eff} = 8\epsilon_0$ and $a = 29$ Å (full curves in figure 2 and figure 3). The value obtained for Φ_{eff} proves to be coherent with the barrier height deduced from the approximate law Φ_B (eV) $\approx (\partial \ln(I)/\partial H)^2$ (H is in Å) [25,26], since $(1/0.87)^2 \approx 1.32$. The similarity of the calculated and measured roughness amplitudes is also noticeable.

The discrepancy between the values of Φ_{eff} and ϵ_{eff} thus determined and the expected values relative to an ideal gold/air/gold structure ($\Phi_{Au} \approx 5$ eV, $\epsilon_{air} \approx \epsilon_0$) confirms the existence of an intermediate substance in the interface, also attested to by mechanical measurements. As the permittivity $\epsilon \approx 2\epsilon_0$ appropriate to the potentially involved hydrocarbons is not at all suitable for fitting the experimental I–V_{app} curves, it seems to us that a plausible interpretation is that water molecules are gathering close to gold surfaces—i.e. in the restricted range of electron image forces—while organic contaminants mainly lie in the meniscus core. The unintentional condensation of water around surface contact sites has been recognized for a long time [16]. It has been extensively demonstrated, furthermore, that the gathering of dipolar water molecules on a metal surface, in mono- or multilayer form, may substantially reduce the electron work function [27,28]. Lastly, the direct influence of the relative humidity on the behaviour of metal/metal electric contacts has been demonstrated experimentally [29]. As regards the dielectric properties, the extremely short traversal time estimated for tunnelling electrons (about 10^{-15} s [30,31]), leads us to consider, for a rough approximation of ϵ_{eff} the high-frequency permittivity of liquid water. Its value, around $6\epsilon_0$ [32,33], is fairly close to that obtained, $8\epsilon_0$.

To conclude, this letter illustrates the novel possibility of performing simultaneously accurate coupled measurements concerning electrical and mechanical interactions between two macroscopic metal bodies. Tunnelling transport is clearly brought to the fore in a gold sphere/plane 'quasi-contact' situation, and the proposed modelling for current determination convincingly fits the experimental data. The twofold approach adopted coherently reveals the existence of an intermediate substance between conductors, plausibly interpreted in terms of a condensed water micromeniscus with the addition of some organic contaminants. We believe that this work opens up a promising route to further investigations in the field of electric contacts interfaces.

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