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Contact electrification and the work of adhesion

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Abstract – We present a general theory for the contribution from contact electrification to the work necessary to separate two solid bodies. The theory depends on the surface charge density correlation function $\langle \sigma(\mathbf{x})\sigma(\mathbf{0})\rangle$ which we deduce from Kelvin Force Microscopy (KFM) maps of the surface electrostatic potential. For silicon rubber (polydimethylsiloxane, PDMS) we discuss in detail the relative importance of the different contributions to the observed work of adhesion.

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When two solid objects are removed after adhesional or frictional contact, they will in general remain charged [1–5]. At the macroscopic level charging usually manifests itself as spark discharging upon contact with a third (conducting) body, or as an adhesive force. The long-range electrostatic force resulting from charging is important in many technological processes such as photocopying, laser printing, electrostatic separation methods, and sliding-triboelectric nanogenerators based on in-plane charge separation [6]. Contact charging is also the origin of unwanted effects such as electric shocks, explosions or damage of electronic equipments.

Contact electrication is one of the oldest areas of scientific study, originating more than 2500 years ago when Thales of Miletus carried out experiments showing that rubbing amber against wool leads to electrostatic charging [7]. In spite of its historical nature and practical importance, there are many not-well-understood problems related to contact electrification, such as the role of surface roughness [8–10], surface migration [11] and contact de-electrification [12].

The influence of contact electrification on adhesion has been studied in the pioneering work by Derjaguin et al. [13,14] and by Roberts [15]. These studies, and most later studies, have assumed that removing the contact between two bodies results in the bodies having uniform surface charge distributions of opposite sign. However, a very recent work [16–18] has shown that the bodies in general have surface charge distributions which vary rapidly in space (on the sub-micrometer scale) between positive and negative values, and that the net charge on each object is

much smaller (sometimes by a factor of ~ 1000) than would result by integrating the absolute value of the fluctuating charge distribution over the surface area of a body.

Contact electrification occurs even between solids made from the same material [16]. This has been demonstrated for silicon rubber (PDMS). If two rubber sheets in adhesive contact (contact area A) are separated, they obtain net charges $\pm Q$ of opposite sign. However, as discussed above, each surface has surface charge distributions fluctuating rapidly between positive and negative values, with magnitudes much higher than the average surface charge densities $\pm Q/A$. The net charge scales with the contact surface area as $Q \sim A^{1/2}$, as expected based on a picture where the net charge results from randomly adding positively and negatively charged domains (with individual area ΔA) on the surface area A: when $N = A/\Delta A \gg 1$, we expect from statistical mechanics that the net charge on the surface A is proportional to $N^{1/2}$ as observed [16]. Note that in the thermodynamic limit, $A \to \infty$, the net surface charge density Q/A = 0.

In this letter we will present an accurate calculation of the contribution from contact electrification to the work of adhesion to separate two solids. The same problem has been addressed in a less accurate approach by Brörmann et al. [19]. They assumed that the charged domains formed a mosaic pattern of squares, where each nearby square has charge of opposite sign but of equal magnitude. To this problem they applied an approximate procedure [1] (see also [20,21]) to obtain the contribution to the work of adhesion from charging. In this letter we will present a general theory, where the surface charge distribution $\sigma(\mathbf{x})$

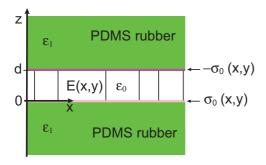


Fig. 1: (Colour on-line) After separation the bottom solid has the surface charge distribution $\sigma_0(\mathbf{x})$ and the top solid the surface charge distribution $-\sigma_0(\mathbf{x})$, *i.e.*, the charge distribution on one surface is the negative of that of the other surface.

is characterized by the density-density correlation function $\langle \sigma(\mathbf{x})\sigma(\mathbf{0})\rangle$, the power spectrum of which can be deduced directly from Kelvin Force Microscopy (KFM) potential maps. We find that for polymers the contact electrification may contribute only with a small amount to the observed work of adhesion. However, more KFM measurements at smaller tip-substrate separation are necessary to confirm the conclusion presented below.

We will calculate the force between the two charged solids when the surfaces are separated by the distance d, see fig. 1. The lower surface has the surface charge density $\sigma_0(\mathbf{x})$, where $\mathbf{x}=(x,y)$ is the in-plane coordinate, and the upper surface the surface charge density $-\sigma_0(\mathbf{x})$, *i.e.*, the charge distribution on one surface is the negative of that of the other surface. We write the electric field as $\mathbf{E}=-\nabla\phi$ so that the electric potential ϕ satisfies $\nabla^2\phi=0$ everywhere except for z=0 and z=d. We write

$$\sigma_0(\mathbf{x}) = \int d^2 q \ \sigma_0(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{x}}.$$

The electrostatic stress tensor:

$$\sigma_{ij} = \frac{1}{4\pi} \left(E_i E_j - \frac{1}{2} \mathbf{E}^2 \delta_{ij} \right).$$

Here we are interested in the zz-component:

$$\sigma_{zz} = \frac{1}{8\pi} \left(E_z^2 - \mathbf{E}_{\parallel}^2 \right). \tag{1}$$

In the space between the surfaces the electric potential:

$$\phi = \int d^2q \left[\phi_0(\mathbf{q}) e^{-qz} + \phi_1(\mathbf{q}) e^{qz} \right] e^{i\mathbf{q} \cdot \mathbf{x}},$$

where $\mathbf{q} = (q_x, q_y)$ and $\mathbf{x} = (x, y)$ are 2D vectors. Thus, for z = 0:

$$E_z = \int d^2 q \ q \left[\phi_0(\mathbf{q}) - \phi_1(\mathbf{q})\right] e^{i\mathbf{q}\cdot\mathbf{x}}$$
 (2)

and

$$\mathbf{E}_{\parallel} = \int d^2 q(-i\mathbf{q}) \left[\phi_0(\mathbf{q}) + \phi_1(\mathbf{q})\right] e^{i\mathbf{q} \cdot \mathbf{x}}.$$
 (3)

Using (1), (2) and (3) gives:

$$\int d^2x \, \sigma_{zz} = 2\pi \text{Re} \int d^2q \, q^2 \phi_0(\mathbf{q}) \phi_1^*(\mathbf{q}). \tag{4}$$

We now calculate $\phi_0(\mathbf{q})$ and $\phi_1(\mathbf{q})$. We write the electric potential $\phi(\mathbf{q}, z)$ as:

$$\begin{split} \phi &= \phi_0 e^{-qz} + \phi_1 e^{qz}, & \text{for } 0 < z < d, \\ \phi &= \phi_2 e^{qz}, & \text{for } z < 0, \\ \phi &= \phi_3 e^{-q(z-d)}, & \text{for } z > d. \end{split}$$

Since ϕ must be continuous for z = 0 and z = d we get:

$$\phi_0 + \phi_1 = \phi_2, \tag{5}$$

$$\phi_0 e^{-qd} + \phi_1 e^{qd} = \phi_3. \tag{6}$$

Let ϵ_0 and ϵ_1 be the dielectric function of the region between the bodies (0 < z < d) and in the bodies (z < 0) and z > d, respectively. In our application the space between the bodies is filled with non-polar gas and $\epsilon_0 \approx 1$. From the boundary conditions $\epsilon_0 E_z(0^+) - \epsilon_1 E_z(-0^+) = 4\pi\sigma_0$ and $\epsilon_1 E_z(d+0^+) - \epsilon_0 E_z(d-0^+) = -4\pi\sigma_0$, and using (5) and (6), we get:

$$\phi_0 + g\phi_1 = \frac{2\pi}{q}\sigma,$$
$$g\phi_0 e^{-qd} + \phi_1 e^{qd} = -\frac{2\pi}{q}\sigma,$$

where $\sigma = \sigma_0 2/(\epsilon_1 + \epsilon_0)$ and $g = (\epsilon_1 - \epsilon_0)/(\epsilon_1 + \epsilon_0)$. Solving these equations gives:

$$\phi_0 = \frac{2\pi}{q} \frac{\sigma}{1 + ge^{-qd}}, \qquad \phi_1 = e^{-qd}\phi_0.$$

Using these equations in (4) gives:

$$\langle F_z \rangle = \int d^2 x \langle \sigma_{zz} \rangle = (2\pi)^3 \int d^2 q \langle |\sigma(\mathbf{q})|^2 \rangle \frac{e^{-qd}}{(1 + ge^{-qd})^2},$$
(7)

where we have performed an ensemble average denoted by $\langle ... \rangle$.

Consider the correlation function:

$$\langle |\sigma(\mathbf{q})|^2 \rangle = \frac{1}{(2\pi)^4} \int d^2x d^2x' \langle \sigma(\mathbf{x})\sigma(\mathbf{x}') \rangle e^{i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')}.$$

Assuming that the statistical properties of the surface charge distribution are translational invariant, we get:

$$\langle \sigma(\mathbf{x})\sigma(\mathbf{x}')\rangle = \langle \sigma(\mathbf{x} - \mathbf{x}')\sigma(\mathbf{0})\rangle$$

and

$$\langle |\sigma(\mathbf{q})|^2 \rangle = \frac{A_0}{(2\pi)^4} \int d^2x \langle \sigma(\mathbf{x})\sigma(\mathbf{0}) \rangle e^{i\mathbf{q}\cdot\mathbf{x}},$$

where A_0 is the surface area. If $\bar{\sigma} = \langle \sigma(\mathbf{x}) \rangle$ denotes the average surface charge density, then we define the charge density power spectrum:

$$C_{\sigma\sigma}(\mathbf{q}) = \frac{1}{(2\pi)^2} \int d^2x \langle [\sigma(\mathbf{x}) - \bar{\sigma}][\sigma(\mathbf{0}) - \bar{\sigma}] \rangle e^{i\mathbf{q}\cdot\mathbf{x}}.$$
 (8)

Using this definition, we get:

$$\langle |\sigma(\mathbf{q})|^2 \rangle = \frac{A_0}{(2\pi)^2} \left[C_{\sigma\sigma}(\mathbf{q}) + \bar{\sigma}^2 \delta(\mathbf{q}) \right].$$
 (9)

Substituting (9) in (7) gives:

$$\langle F_z \rangle = 2\pi A_0 \bar{\sigma}^2 + 2\pi A_0 \int d^2 q \ C_{\sigma\sigma}(\mathbf{q}) \frac{e^{-qd}}{(1 + ge^{-qd})^2}.$$

We expect the statistical properties of the surface charge distribution to be isotropic which imply that $C_{\sigma\sigma}(\mathbf{q})$ only depends on the magnitude $q = |\mathbf{q}|$. This gives:

$$\langle F_z(d) \rangle = 2\pi A_0 \bar{\sigma}^2 + (2\pi)^2 A_0 \int dq \ q C_{\sigma\sigma}(q) \frac{e^{-qd}}{(1 + ge^{-qd})^2}.$$

The first term in this expression is the attraction between the surfaces due to the (average) uniform component of the charge distribution which, as expected, is independent of the separation between the surfaces (similar to a parallel condenser). The second term is the contribution from the fluctuating components of the surface charge distribution. The contribution to the work of adhesion from the surface charge is given by:

$$U = \int_0^d dz \langle F_z(z) \rangle = 2\pi A_0 \bar{\sigma}^2 d$$

+ $(2\pi)^2 A_0 \int_0^\infty dq \ q C_{\sigma\sigma}(q) \int_0^d dz \frac{e^{-qz}}{(1 + qe^{-qz})^2}.$ (10)

For an infinite system, the first term in U increases without limit as the surfaces are separated. For bodies of finite size the expression given above for the contribution from the net charging is of course only valid for separations smaller than the linear size of the bodies (i.e. d < L, where $A_0 = L^2$), and the interaction energy will decay like $\sim 1/d$ for large separation. Thus, for a finite-sized system the contribution to the normalized work U/A_0 to separate the solids, from the first term in U, will be of order $\sim \bar{\sigma}^2 L$, with a prefactor which depends on the actual shape of the bodies. Note that in the thermodynamic limit $L \to \infty$, since $\bar{\sigma} \sim 1/L$ this contribution to U/A_0 will actually vanish. Roberts (see ref. [15]) has argued that the first term in (10) gives a negligible contribution to the work of adhesion also for finite-sized objects. Here we take a more pragmatic approach and we will not include this term in the work of adhesion, in particular since it depends on the shape of the bodies, and also because experimentally it is easy to measure the work to separate the solids to such small distance that the first term in (10) is completely negligible, see ref. [22]. The contribution to the work of adhesion from the second term in (10) (for $d \to \infty$) is:

$$w_{\rm ch} = \frac{U}{A_0} = \frac{(2\pi)^2}{1+q} \int_0^\infty dq \ C_{\sigma\sigma}(q).$$
 (11)

Note that the integral:

$$\int d^2 q \ C_{\sigma\sigma}(\mathbf{q}) = \langle [\sigma(\mathbf{x}) - \bar{\sigma}]^2 \rangle = \langle \Delta \sigma^2 \rangle$$
 (12)

is the mean of the square of the fluctuating surface charge distribution. Using this equation, we can write:

$$w_{\rm ch} = \frac{2\pi}{1+g} \frac{\langle \Delta \sigma^2 \rangle}{\langle q \rangle},\tag{13}$$

where

$$\langle q \rangle = \frac{\int_0^\infty dq \ q C_{\sigma\sigma}(q)}{\int_0^\infty dq \ C_{\sigma\sigma}(q)}.$$
 (14)

The study above is for the limiting case where the surfaces separate so fast that no decay in the surface charge distribution takes place before the separation is so large as to give a negligible interaction force. Experiments [17] have shown that the charge distribution decay with increasing time as $\exp(-t/\tau)$, where the relaxation time $\tau \approx 10^3$ s depends on the atmospheric condition (e.g., humidity and concentration of ions in the surrounding gas). Taking into account the decay in the surface charge distribution, and assuming z = vt (where v is the normal separation velocity) we need to replace the integral over z in (10) with:

$$f(q,v) = \int_0^\infty dz \frac{e^{-qz}e^{-2t/\tau}}{(1+ge^{-qz})^2} = \int_0^\infty dz \frac{e^{-(qz+2z/v\tau)}}{(1+ge^{-qz})^2}$$

and (11) becomes

$$w_{\rm ch} = (2\pi)^2 \int_0^\infty \mathrm{d}q \ q C_{\sigma\sigma}(q) f(q, v). \tag{15}$$

In the limit $v \to \infty$ we have $f \to 1/[q(1+g)]$ and in this limit (15) reduces to (13). In the opposite limit of very small surface separation velocity, $f \to v\tau/[2(1+g)^2]$ and in this limit:

$$w_{\rm ch} = \frac{(2\pi)^2 v\tau}{2(1+q)^2} \int_0^\infty \mathrm{d}q \ q C_{\sigma\sigma}(q) = \frac{\pi v\tau \langle \Delta \sigma^2 \rangle}{(1+q)^2}. \tag{16}$$

Note that this expression is of the form (13) with $1/\langle q \rangle$ replaced by $v\tau/[2(1+g)]$. Since typically $\tau \approx 10^3 \,\mathrm{s}$ and $(1+g) \approx 1$ and $\langle q \rangle \approx q_1 \approx 10^9 \,\mathrm{m}^{-1}$ (where q_1 is defined below) we get $v_c = 2(1+g)/(\langle q \rangle \tau) \approx 10^{-12} \,\mathrm{m/s}$. In most applications we expect the separation velocity in the vicinity of the crack tip $v \gg v_c$, and in this case the limiting equation (13) holds accurately. Note, however, that the separation velocity v may be much smaller than the crack tip velocity.

In the KFM measurement the local potential at some fixed distance d above the surface is measured, rather than the surface charge density. From the measured data the potential power spectrum:

$$C_{\phi\phi}(\mathbf{q}) = \frac{1}{(2\pi)^2} \int d^2x \langle [\phi(\mathbf{x}) - \bar{\phi}] [\phi(\mathbf{0}) - \bar{\phi}] \rangle e^{i\mathbf{q}\cdot\mathbf{x}}$$

can be directly obtained. However, we can relate the potential to the charge density:

$$\phi(\mathbf{q}) = \frac{2\pi}{q} \sigma(\mathbf{q}) e^{-qd}.$$

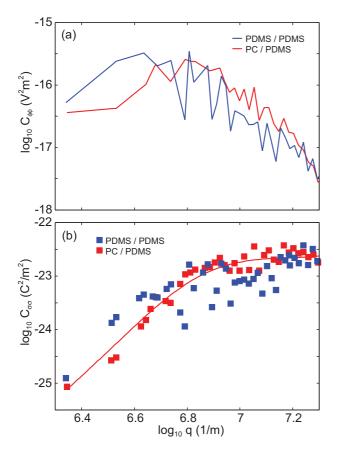


Fig. 2: (Colour on-line) (a) The voltage power spectrum $C_{\phi\phi}$ and (b) the surface charge density power spectrum $C_{\sigma\sigma}$ as a function of the wave vector. The results have been calculated from the measured (KFM) voltage maps for PDMS/PDMS (blue) and PDMS/polycarbonate (PC) (red) [17].

Thus:

$$C_{\sigma\sigma}(\mathbf{q}) = \frac{q^2}{(2\pi)^2} C_{\phi\phi}(\mathbf{q}) e^{2qd}.$$
 (17)

The results presented above is in Gaussian units. To obtain (17) in SI units we must multiply the right-hand side with $(4\pi\epsilon_0)^2$, where $\epsilon_0 = 8.8542 \times 10^{-12} \,\mathrm{C~V^{-1}~m^{-1}}$. Thus:

$$C_{\sigma\sigma}(\mathbf{q}) = 4\epsilon_0^2 q^2 C_{\phi\phi}(\mathbf{q}) e^{2qd}.$$
 (18)

To get (11) in SI units we must multiply the right-hand side by $(4\pi\epsilon_0)^{-1}$:

$$w_{\rm ch} = \frac{\pi}{2\epsilon_0(1+g)} \int_0^\infty \mathrm{d}q \ C_{\sigma\sigma}(q). \tag{19}$$

We now analyze experimental data involving elastically soft solids with smooth surfaces, where the initial contact between the solids is complete due to the adhesion between the solids. In ref. [17] several such systems where studied and here we focus on PDMS rubber against PDMS. After breaking the adhesive contact between two sheets of PDMS (which involves interfacial crack propagation) the electrostatic potential a distance d above one of the surfaces was probed using KFM measurements. From the

measured potential map we have calculated the potential power spectrum $C_{\phi\phi}(q)$ and then from (18) the charge density power spectrum $C_{\sigma\sigma}(q)$. The measurements where done at the tip-substrate separation $d \approx 10^{-7} \,\mathrm{m}$, and since the electric potential from a surface charge density distribution with the wave vector q decay as $\exp(-qd)$ with the distance d from the surface, the KFM is effectively limited to probing the surface charge distribution with wave vector q < 1/d. In fig. 2 we show both power spectra for $q < 2 \times 10^7 \,\mathrm{m}^{-1}$. Note that the charge density power spectrum appears to saturate for a large wave vector, say $q > q_0$, with $q_0 \approx 10^7 \,\mathrm{m}^{-1}$. This result follows if, as expected, the process of creating surface charges is uncorrelated in space at short length scales. In that case $\langle \sigma(\mathbf{x})\sigma(\mathbf{0})\rangle \sim \delta(\mathbf{x})$ and using (8) this gives $C_{\sigma\sigma}(\mathbf{q}) = \text{const.}$ The fact that $C_{\sigma\sigma}(\mathbf{q})$ decays for decreasing q for $q < q_0 \approx 10^7 \,\mathrm{m}^{-1}$ implies that at some length scale $\lambda_0 = 2\pi/q_0 \approx 0.6 \,\mu\mathrm{m}$ the charge distribution becomes correlated. The physical reason for this may relate to inhomogeneities on the PDMS surface, e.g., due to filler particles (see below).

We assume that the charge density power spectrum saturates for $q > q_0$ at $C_{\sigma\sigma}^0 \approx 2.2 \times 10^{-23} \, \mathrm{C}^2/\mathrm{m}^2$ (see fig. 2(b)). The assumption that the process of creating surface charges is uncorrelated in space at short length scales gives $C_{\sigma\sigma}^0 = (2\pi)^{-2}e^2n$, where $n = 1/\lambda_1^2$ is the number of elementary charges ($\pm e$) per unit surface area. Thus we obtain $n = 3.4 \times 10^{16} \, \mathrm{m}^{-2}$ and $\lambda_1 \approx 6 \, \mathrm{nm}$ and $q_1 = 2\pi/\lambda_1 \approx 10^9 \, \mathrm{m}^{-1}$. The charge density $\langle |\sigma| \rangle = ne \approx 0.5 \, \mu \mathrm{C/cm}^2$ is similar to what was estimated by Baytekin $et \ al. \ [17]$. Using (12) we get the mean square charge fluctuation $\langle \Delta \sigma^2 \rangle \approx \pi q_1^2 C_{\sigma\sigma}^0 \approx 7 \times 10^{-5} \, \mathrm{C}^2/\mathrm{m}^4$ or the rms charge fluctuation $\approx 1 \, \mu \mathrm{C/cm}^2$, which, as expected, is similar to ne.

From (19) we get $w_{\rm ch} \approx (q_1 - q_0) C_{\sigma\sigma}^0 / \epsilon_0$, where we have used that $\pi/[2(1+g)] \approx 1$. The large wave vector cut-off q_1 is of order $2\pi/\lambda_1$, where λ_1 is of order the average separation between the surface charges (which we assume to be point charges of magnitude $\pm e$, where e is the electron charge). Since $q_0 \ll q_1 \approx 10^9 \, {\rm m}^{-1}$ we get $w_{\rm ch} \approx q_1 C_{\sigma\sigma}^0 / \epsilon_0 \approx 0.002 \, {\rm J/m^2}$. This value is smaller than the measured work of adhesion during adiabatic (very slow) separation of the surfaces where [22] $w \approx 0.05 \, {\rm J/m^2}$.

The calculation above does not include the interaction between the charges when the surface separation is smaller than ~ 1 nm. However, this contribution cannot be accurately estimated without an accurate knowledge of the exact location and spatial extent of the localized charges, and probably also requires a knowledge about how the charge separation processes occur, e.g., does it involve electron tunneling at some finite surface separation?

The analysis above is based on the assumption that the surface charge density power spectrum saturates at a value $C_{\sigma\sigma}^0 \approx 2.2 \times 10^{-23} \, \mathrm{C^2/m^2}$ for large wave vectors. This hypothesis should be tested by performing KFM measurements to smaller tip-substrate separations. The number of surface charges per unit area, n, which determines the

cut-off q_1 in the study above, may also be probed by surface reaction experiments, such as bleaching experiments reported in ref. [18].

Sylgard 184, which was used in [17], is intrinsically a heterogeneous polymer with siliceous fillers [23]. Even though the filler is partially modified by organic groups, it imparts non-negligible polarity of the polymer as evidenced from the high contact angle hysteresis ($\sim 20^{\circ}-40^{\circ}$) of water on this polymer as compared to that $(\sim 5^{\circ})$ on a pure PDMS matrix. X-ray photoelectron spectroscopy [24] also shows that the silicon (Si2p) peak of the silica is 1 eV higher than that of the surrounding matrix, thus suggesting that the electron affinity of the silica-rich region is likely different from the surrounding matrix. So, when two surfaces of sylgard 184 are brought close to each other, electrons may be transferred from one type of domain to another, which may show up as heterogeneous patches when the surfaces are separated. If the binding energy of the Si2p peak is an indicator, the PDMS matrix is more electron rich than the silica-rich region. The breaking of the siloxane bond requires very large force and is unlikely to contribute to charging [24–26]. Silica almost always has silanol (SiOH) groups. The silanol groups may form very weak hydrogen bond with the oxygen of polydimethylsiloxane. If that happens some charge transfer may occur during the separation of the surfaces, which will show up as heterogeneous charge after the two surfaces are separated. This idea may be tested experimentally by performing KFM experiments using a clean PDMS network that does not have silica fillers.

At low crack-tip velocities, where the viscoelastic energy dissipation at the crack tip, and other non-equilibrium effects, are negligible (see ref. [22]), the work of adhesion is usually assumed to result from the Van der Waals interaction between the surfaces at the interface. The study above indicate indeed that the contributions from contact electrification gives only a small fraction ($\sim 4\%$) of the observed work of adhesion.

To summarize, we have derived a general expression for the contribution to the work of adhesion from contact electrification, and we have shown that for PDMS (and probably for polymers in general) the contact electrification gives only a small fraction of the observed work of adhesion. More KFM measurements at smaller tip-substrate separation are necessary to confirm this conclusion.

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