On the Adhesion Force between Deformable Solids

The mechanics of the adhesion of curved elastic bodies is in dispute, as evidenced by some recent articles and exchanges in this journal (1, 2). According to the theory of Derjaguin *et al.* (henceforth the DMT theory, Ref. (1)) curved elastic bodies in contact under an external compressive force undergo a Hertzian-type deformation. On reversing the external force the bodies should come apart when the area of contact has fallen to zero, i.e., at the point where the surfaces assume their undistorted shape, and the pull-off (adhesive) force F when this occurs is given by

$$F = 4\pi R\gamma, \qquad [1]$$

where R is the radius of curvature of the surfaces ($1/R = 1/R_1 + 1/R_2$ for two spheres) and γ is their surface energy. According to the theory of Johnson *et al.* (henceforth the JKR theory, Ref. (3)) the shape of the bodies is always non-Hertzian, pull-off occurs spontaneously at a finite contact radius, and the pull-off force is

$$F = 3\pi R\gamma, \qquad [2]$$

though Tabor (2) has argued that a value intermediate between [1] and [2] may be more realistic.

Regarding the shapes of elastic bodies in contact Tabor (2) and Israelachvili (4) have shown that the JKR theory provides a better description of the macroscopic deformation of surfaces in contact, and just before pull-off. In particular, we found that pull-off occurs spontaneously when the contact radius has fallen to 0.58 ± 0.04 of the value under zero external force (cf. the very similar result obtained for bare mica surfaces (4)). These values compare well with the theoretical value of $(1/4)^{1/3} = 0.63$ predicted by the JKR theory. Figure 1A shows the FECO fringe pattern for two surfaces under an external compressive force in the absence of adhesion, and Fig. 1B the fringe pattern for the two surfaces in strong adhesive contact. It is clear that the shapes of the surfaces are different: in the former (nonadhesive) configuration the surfaces bifurcate smoothly at the periphery of the contact zone (Hertzian-like), while in the latter (adhesive) configuration they bifurcate very sharply (JKR-like), though as pointed out by Tabor (2) the microscopic shape in the immediate vicinity of bifurcation may be smooth while optically unresolvable.

Thus it appears that the major issue that remains unresolved is that concerning the pull-off force, which has so far not been directly measured between surfaces of a priori known surface energies. We have measured the pull-off forces between crossed-cylindrical surfaces of molecularly smooth mica each coated with an adsorbed monolayer of either calcium stearate (CaSt) or hexadecyltrimethylammonium bromide (CTAB). CaSt monolayers were deposited by retraction from a 10^{-4} M $CaCO_3$ solution at pH 8.4, piston pressure 16 dyn/cm. The CaSt monolayers had a thickness of 25 Å, as expected (5, 6). CTAB monolayers were deposited by retraction from an 8×10^{-4} M CTAB solution in water. These monolayers had a thickness of 18 Å, also as expected (7). Pull-off forces F and radii of curvature R ($\approx$1 cm) were measured as previously described (8). The monolayer surfaces were thoroughly dried before use and all experiments were performed in an atmosphere of air or dry N_2 at 21°C (no differences in the results were observed). Table I shows the values obtained for the surface energies of the CaSt and CTAB surfaces as deduced from the measured pull-off forces according to Eqs. [1] and [2]. Since the CaSt monolayer is close packed, exposing only $-CH_3$ groups at the surface, a value for γ in the range 22–24 erg/cm^2 is expected (9). In contrast, the trimethylammonium head group of CTAB

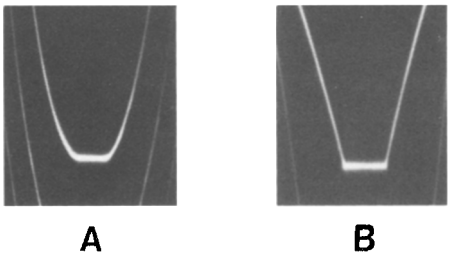

FIG. 1. Fringe pattern for two curved mica surfaces (A) in compressive contact in water in the absence of adhesion, and (B) in adhesive contact in air. The shapes of the fringes accurately reflect the macroscopic shapes of the surfaces after noting that the vertical magnification is about 10^4 times the horizontal magnification (6). In both cases the diameter of the contact zone is about 50 μm (seen as the flat horizontal parts of the fringes).

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TABLE I

Surface Energy Values

Surface	Exposed surface groups	γ (erg/cm^2) from measured pull-off force F	
		Eq. [1] $\gamma = F/4\pi R$	Eq. [2] $\gamma = F/3\pi R$
CaSt	$-CH_3$	23.3 ± 1.0	31.0 ± 1.5
CTAB	$-CH_3$ and $-CH_2$	26.6 ± 1.5	35.5 ± 2.0

has a large cross-sectional area which leads to the exposure of both $-CH_2$ and $-CH_3$ groups to the outside; consequently, a value for γ intermediate between 23 and 31 erg/cm^2 is expected (9). From Table I it is clear that Eq. [1] gives the correct pull-off force when calculated in terms of known surface energies. Equation [2] does not.

We conclude that the DMT theory predicts the correct value for the pull-off (adhesive) force even though the macroscopic geometry of the contact zone is better described by the JKR theory.

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