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Particle-Substrate Interactions: Microscopic Aspects of Adhesion

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(Edited for course presentation by G. Ahmadi)

Part 1

Importance of Particle Adhesion

1. Technologically important

   A. Semiconductor fabrication
   B. Electrophotography
   C. Pharmaceuticals
   D. Paint
   E. Agriculture
   F. Aeronautics and space
   G. Etc.

2. Fundamentally important

   A. Avoids confounding interactions (gravity, applied loads, etc.
   B. Allows thermodynamic parameters such as work of adhesion to be determined.
   C. Allows present understanding of adhesion to be tested.

Summary of Key Points

- Particles are attracted to substrates (or other particles) via certain types of interactions. These interactions create stresses between the materials. These stresses, in turn, create strains that may be large or small, elastic or plastic.

- Only by understands both the interactions and the mechanical response of the materials to these interactions can adhesion be understood.

- The JKR model is the underlying theory on which most of our present understanding of adhesion is based.

- This presentation will focus on particle adhesion. However, just as the JKR theory describes adhesion between macroscopic bodies, the concepts presented can be readily generalized to other situations.

History

Hertz (circa 1890): Proposed that a rigid indentor, acting under a compressive load P, would cause a deformation of radius *a* in a substrate having a Young's modulus E and a Poisson ratio ν given by

$$a^3 = \frac{3\left(1-\nu^2\right)R}{4E}P \tag{1}$$

1930s: Derjaguin and Bradley independently proposed the concept of adhesion-induced deformations between particles and substrates. Derjaguin assumed that the adhesion-induced contact radius can be calculated from Hertzian theory.

1937: Hamaker proposes that surface forces were related to the density of atoms in the particle and substrate, n_P and n_S, respectively. Hamaker further proposed that the interaction parameter *A* (commonly referred to as the Hamaker constant) was related to London dispersion forces by

$$A = \pi^2 n_P n_S \lambda \tag{2}$$

The load *P* is then given by

$$P = \frac{AR}{6z_0^2} \tag{3}$$

By combining this result with the Hertzian indenter model, one sees that the Derjaguin model relates the contact radius to the particle radius by

$$a^3 = \frac{A\left(1-\nu^2\right)}{8z_0^2}R^2 \tag{4}$$

1956: Lifshitz proposes a model relating the London dispersion forces (i.e. the major component of van der Waals interactions in most systems) to the generation of electromagnetic waves caused by instantaneous dipole fluctuations. Surface forces are shown to have an effective range, rather than being contact forces.

1967: Krupp proposes adhesion-induced plastic deformations. He proposed that the adhesion-induced stresses between a particle and a substrate could exceed the yield strength of at least one of the contacting materials.

Circa 1969: David Tabor approaches Ken Johnson about a rather perplexing student Tabor has that does not seem to believe Hertz.

1971: The JKR (Johnson, Kendall, and Roberts) theory of adhesion is published. This theory recognized that both tensile and compressive interactions contribute to the total contact radius. JKR model is derived using contact mechanics. It assumes that there are no long-range interactions.

1975: Derjaguin, Muller, and Toporov generalize the original Derjaguin model of adhesion to include tensile interactions. This is the DMT theory.

1977: Tabor highlights differences in assumptions and predictions between JKR and DMT theories. Also shows that, as long as the meniscus height is large compared to the range of surface forces, the JKR assumption of no long-range interactions is valid.

1980: Muller, Yushchenko, and Derjaguin (MYD) propose a general model that purports that both the JKR and DMT theories are subsets of the MYD model. They further divide the universe between small particle, high modulus, low surface energy systems (DMT) and larger particle, lower modulus, higher surface energy (JKR systems).

1984: Maugis and Pollock generalize the JKR theory to include adhesion-induced plastic deformations.

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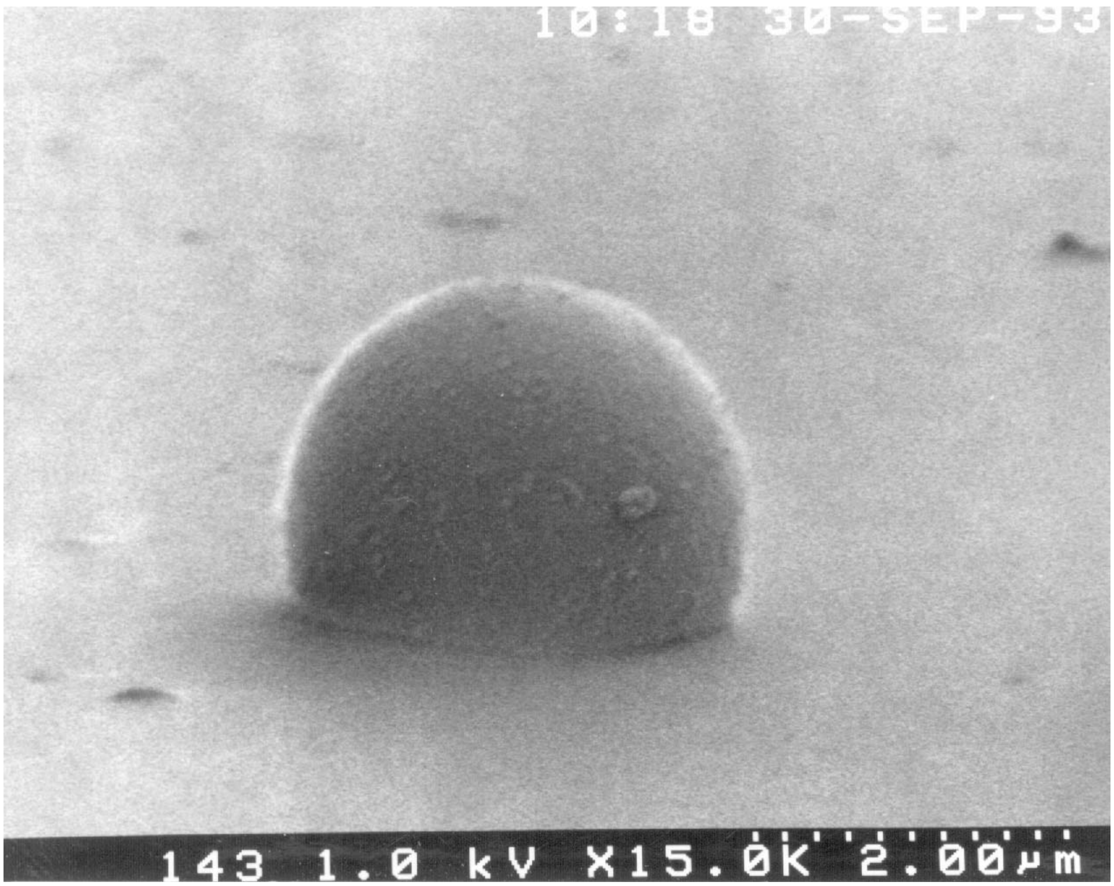
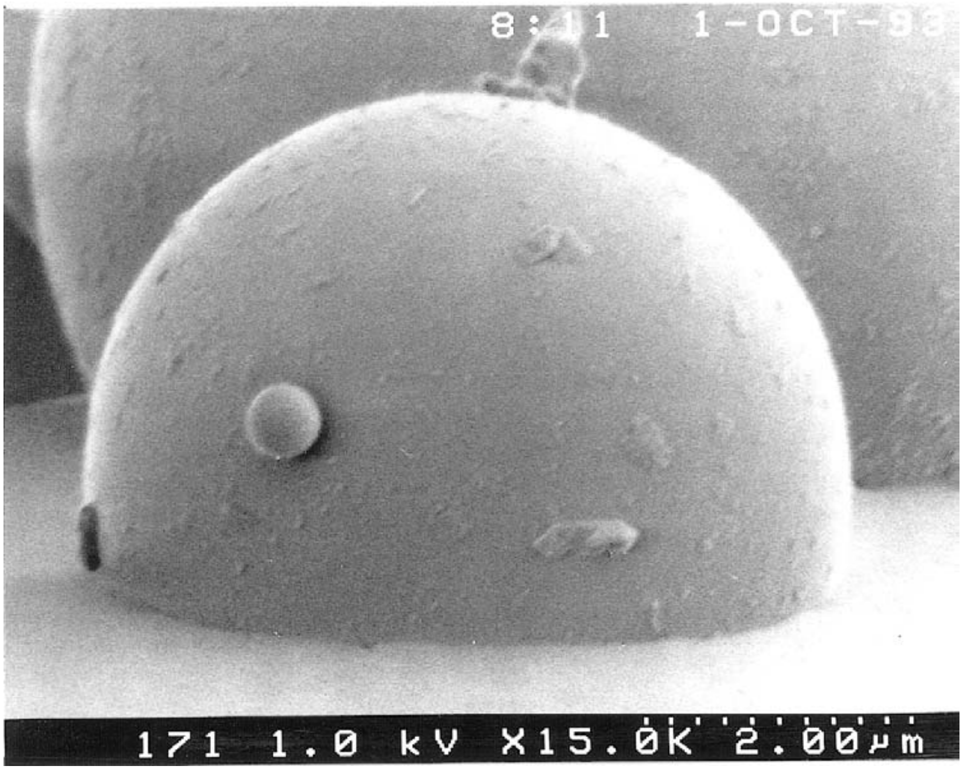
Examples of Adhesion-Induced Deformations

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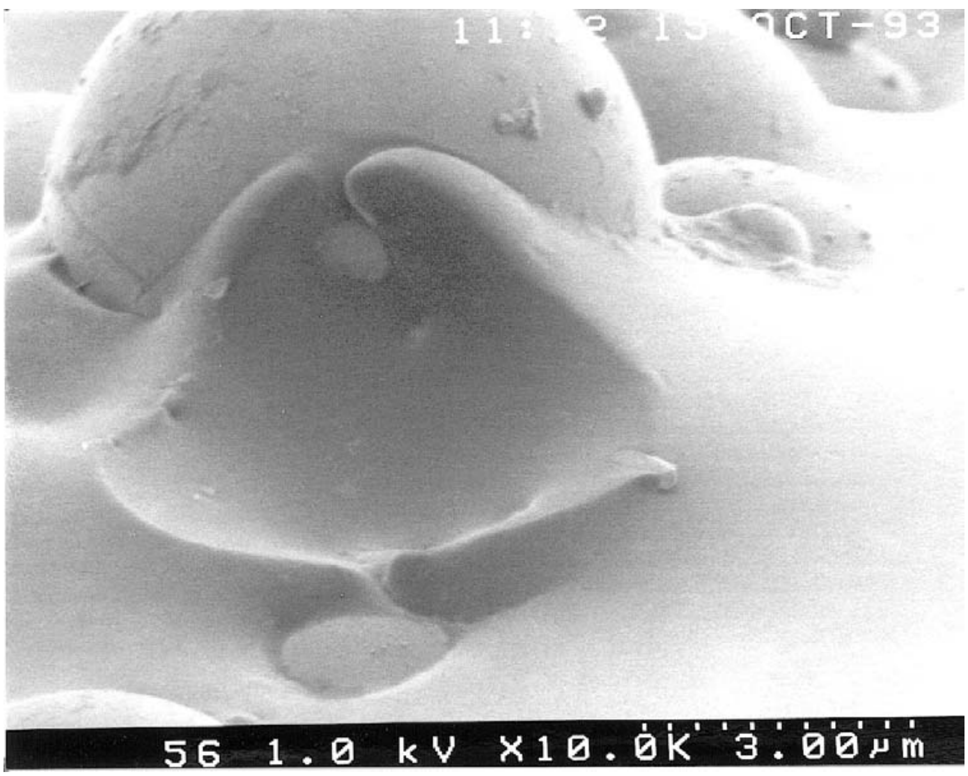
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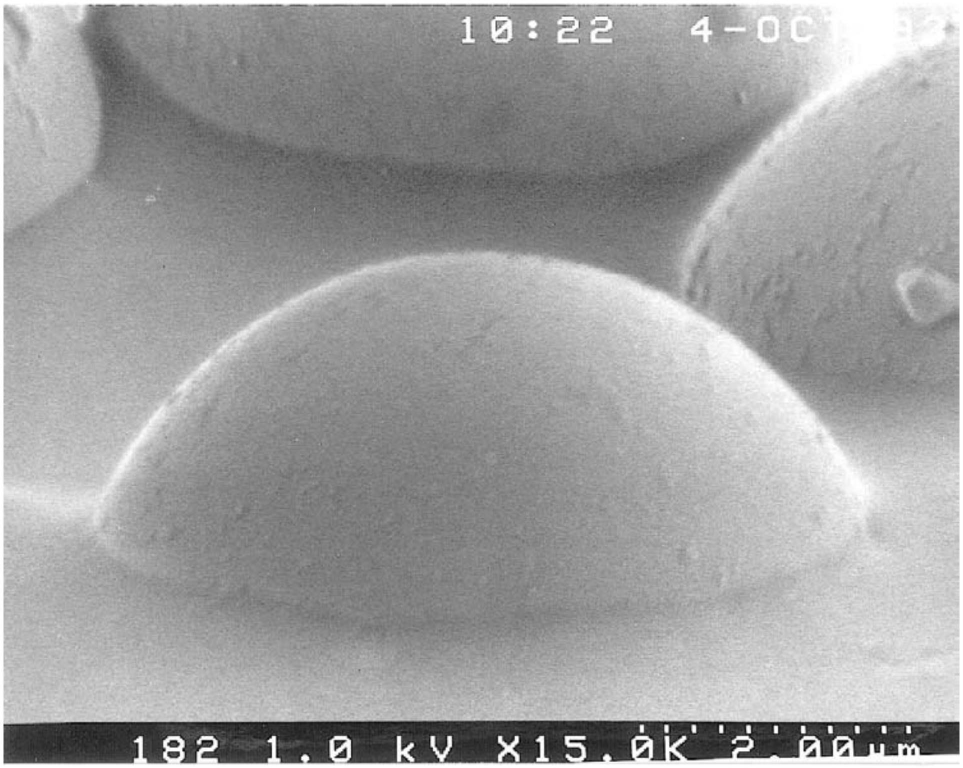
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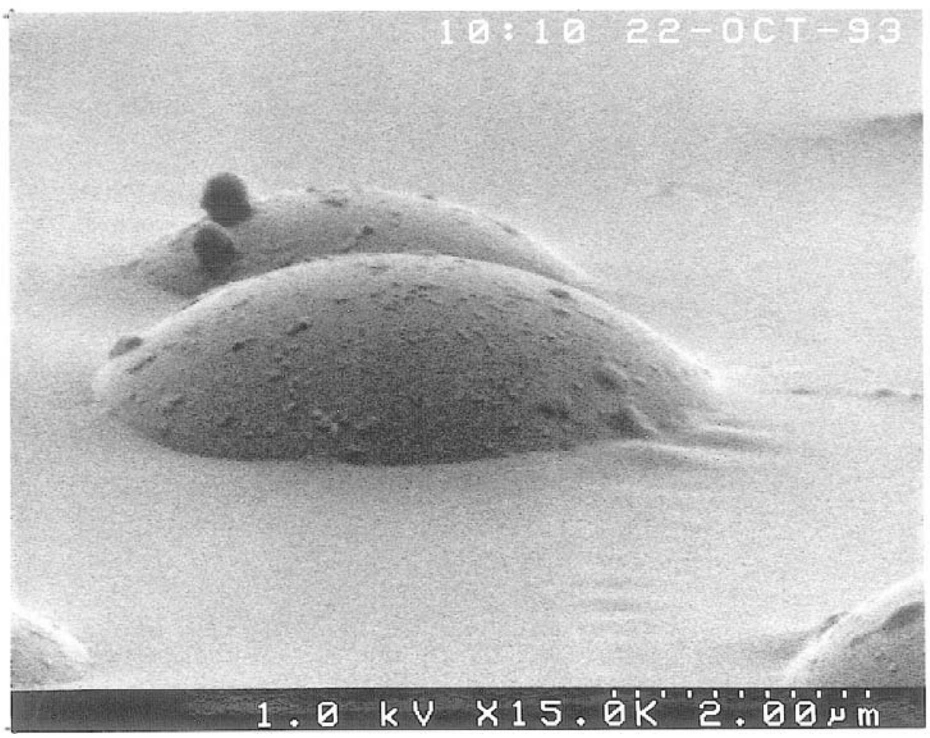
10:10 22-OCT-93
1.0 kV X15.0K 2.00μm

JKR Theory

There is a total energy U_T of a system, where

$$U_T = U_E + U_M + U_S \tag{5}$$

where

U_E is the elastically stored energy

U_M is the mechanical energy associated with the applied load.

U_S is the total surface energy = $w_A \pi a^2$

The JKR equation is given by:

$$a^3 = \frac{R}{K}\left\{P + 3w_A \pi R + \left[6w_A \pi R P + (3w_A \pi R)^2\right]^{1/2}\right\} \tag{6}$$

Fundamental Assumptions of the JKR Theory

1. The deformations are elastic.

2. The contact radius is small compared to the particle radius.

3. All interactions are localized to within the contact region, *i.e.* there are no long-range interactions.

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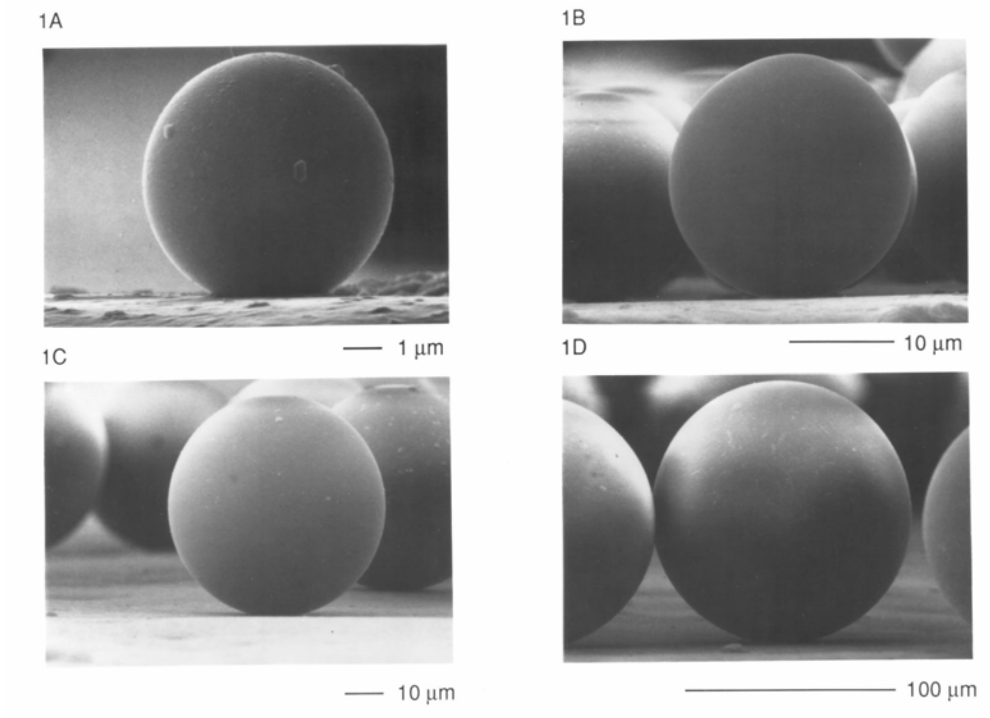
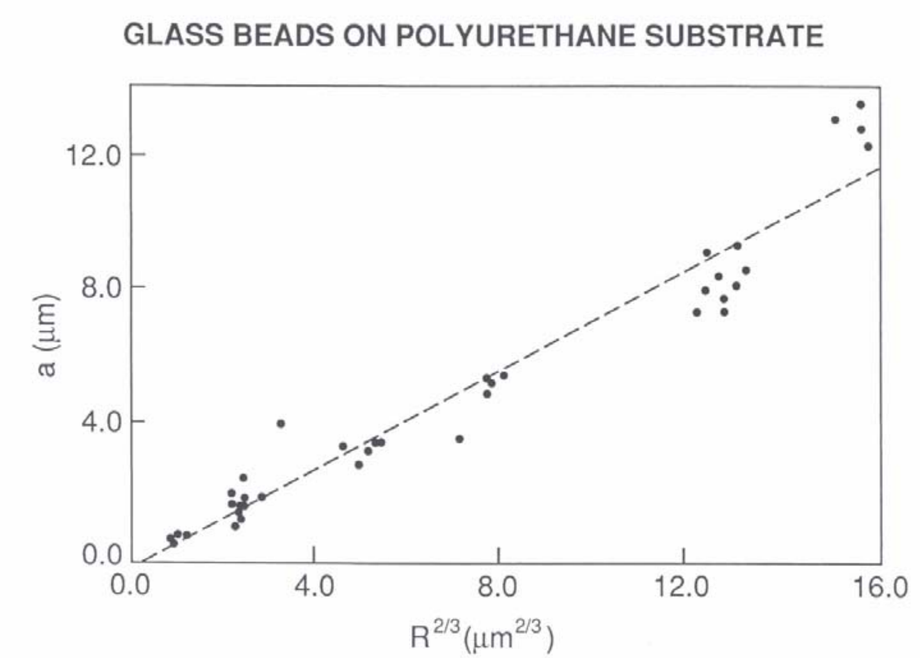
Examples of Adhesion-Induced Deformations
Quintessential JKR Systems

Consider high elastic modulus spherical particles on elastomeric substates.

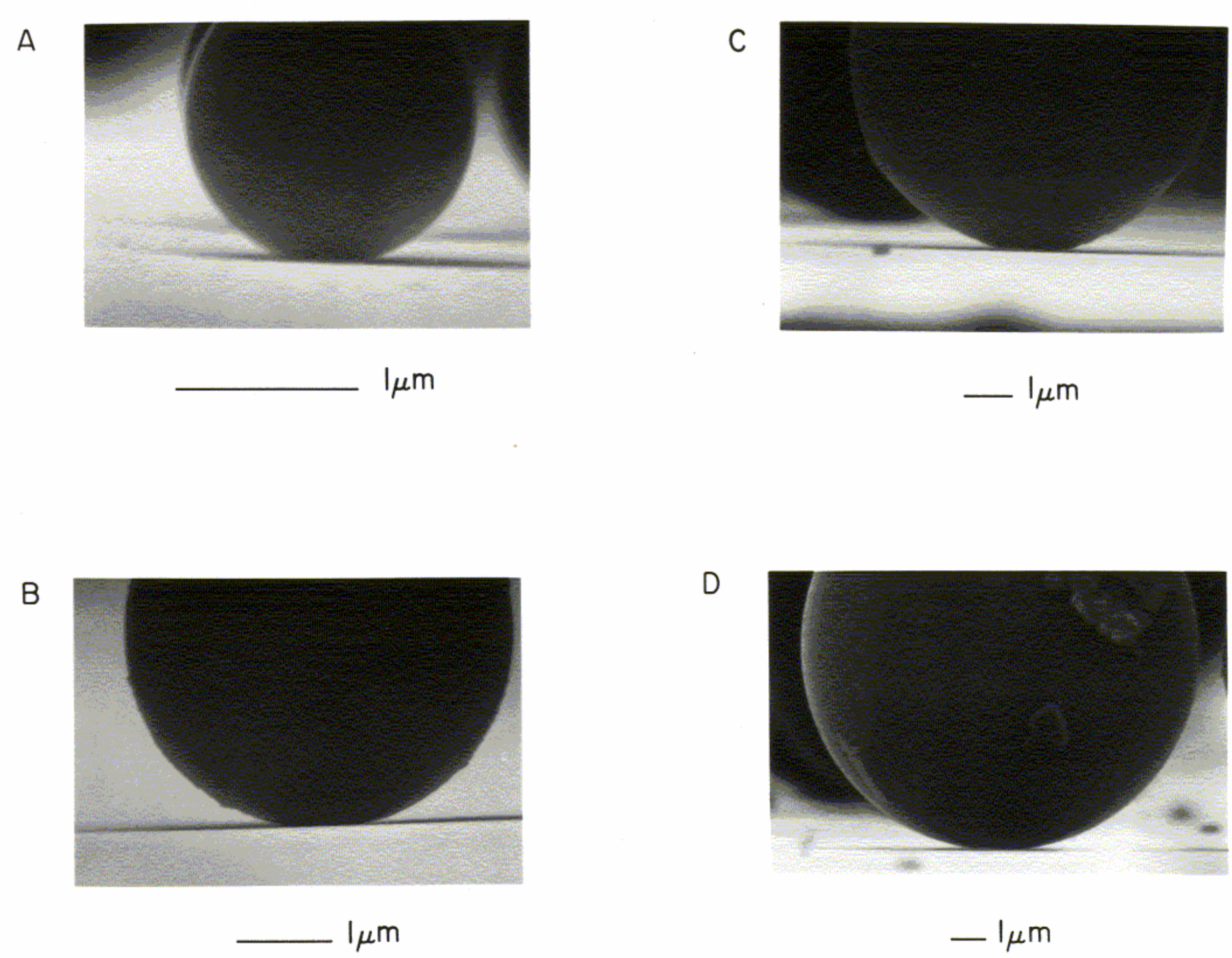
Polystyrene on Polyurethane

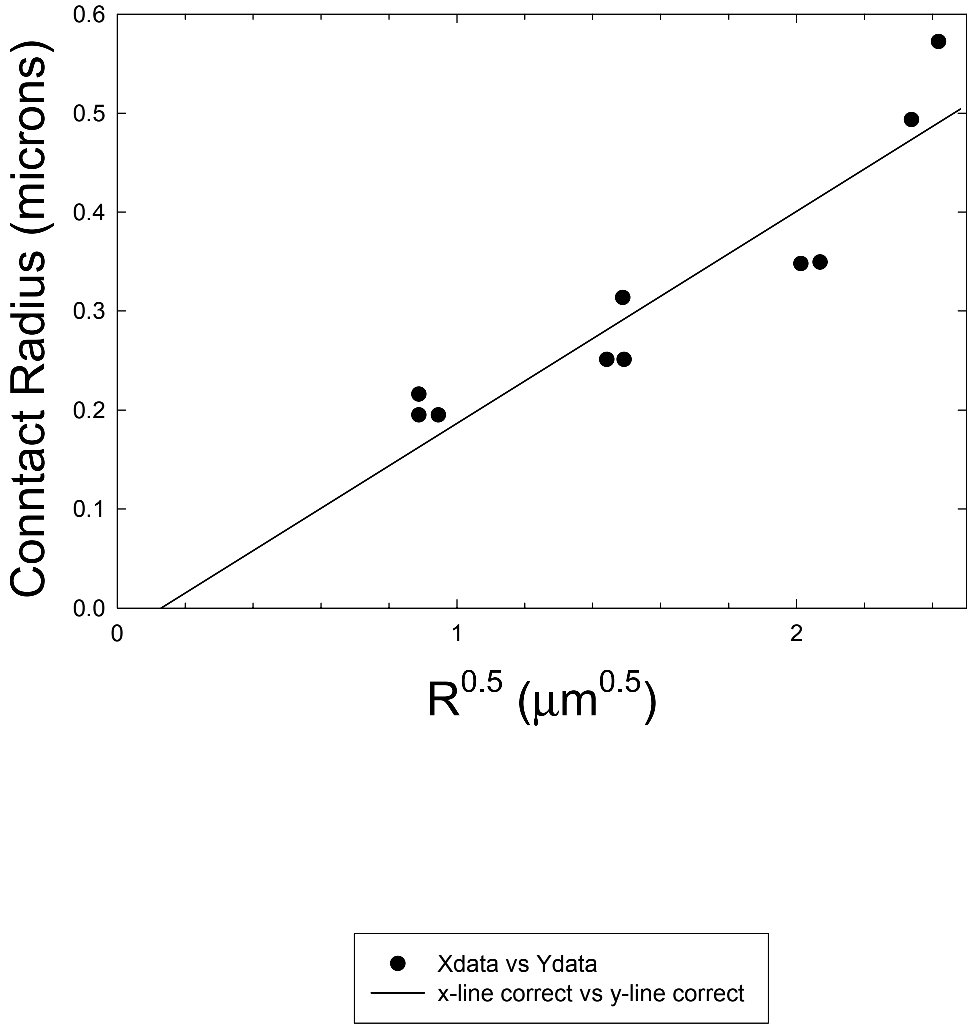



GLASS BEADS ON POLYURETHANE SUBSTRATE
a (μm)
12.0
8.0
4.0
0.0
0.0
4.0
8.0
12.0
16.0
R^2/3(μm^2/3)

Non-JKR Systems

Polystyrene particles on a silicon wafer





Burnham, Colton, and Pollock (Phys. Rev. Lett. **69**, 144 (1992) measured the attractive force between an AFM cantilever tip and a flat graphite surface. They reported that the range of attractive forces was too great to be explained in terms of van der Waals forces.

Horn and Smith (Nature **366**, 442 (1993); Science **256**, 362 (1992); J. Electrostatics **26**, 291 (1991)) reported an increase in detachment force between two flat silica substrates, one of which had been coated with dimethyethoxysilane. The increase in adhesion was associated with a transfer of charge from one material to the other.

Dickinson (see, for example, *Fundamentals of Adhesion and Interfaces*, Rimai, DeMejo, and Mittal (eds.), pp. 179-204 (1995) reported the emission of charged particles generated upon the fracture of a material (fractoemissions).

Points

- Van der Waals forces are electrodynamic and are expected to be short range. Under certain circumstances they may contribute significantly to adhesion.

- There are long-range interactions that contribute to adhesion. These may be due to electrostatic interactions.

- There is evidence that adhesion has long-range contributions. If this is correct, is the JKR theory, which is based on contact mechanics, appropriate?