Particle Transport, Deposition and Removal

Particle-Substrate Interactions: Microscopic Aspects of Adhesion

Don Rimai
NexPress Solutions LLC.
Rochester, NY 14653-6402
donald_rimai@nexpress.com

Outline

- Importance of Particle Adhesion
- History of Particle Adhesion
- Method of measurement of Adhesion
- Adhesion Induced Deformation
- JKR and non-JKR Theory
- Role of Electrostatic Forces
- Conclusions

References

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Importance of Particle Adhesion

Technologically important

A. Semiconductor fabrication

B. Electrophotography

C. Pharmaceuticals

D. Paint

E. Agriculture

F. Aeronautics and space

G. Etc.

Importance of Particle Adhesion

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.

Particle Adhesion

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

Particle Adhesion

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

History

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- Hertz (circa 1890): Proposed that a rigid indenter, 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

$$a^3 = \frac{3(1-\nu^2)RP}{4E}$$

- 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.

History

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- 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

$$A = \pi^2 n_P n_S \lambda$$

The load *P* is then given by

$$P = \frac{A\ R}{6\ z_0^2}$$

History

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

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

History

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- 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.

History

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- 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.

History

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- 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.

History

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- 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.

Methods of Measuring Particle Adhesion

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1. Centrifugation
   - A. Better on large (R>20 μm)
   - B. Slow
   - C. Well established technique
   - D. Minimal interactions
   - E. Good statistics

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Methods of Measuring Particle Adhesion

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2. Electrostatic Detachment
   - A. Medium to large particles (R>5 μm)
   - B. Interaction with electric field
   - C. Good statistics
3. Hydrodynamic Detachment
   - A. Small particles (R<0.5 μm)
   - B. Good statistics
   - C. Introduces a fluid

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Methods of Measuring Particle Adhesion

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4. Atomic Force Techniques
   - A. Measures attractive as well as removal force
   - B. Can exert precise loads on particles
   - C. Short and variable time scales
   - D. Can distinguish force mechanisms
   - E. Poor statistics

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Methods of Measuring Particle Adhesion

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5. Contact Area Technique
   - A. Good statistics
   - B. Forces not directly measured.
   - C. Equilibrium measurement
   - D. Need spherical particles
   - E. Wide range of particle sizes

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Methods of Measuring Particle Adhesion

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6. Nanoindentor

- A. Easy to interpret measurements
- B. Readily repeatable
- C. Simulation of particle adhesion rather than actual measurement.

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Methods of Measuring Particle Adhesion

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7. Israelachvili Surface Force Apparatus

- A. Uses crossed cylinders rather than particles
- B. Cylinders can be coated with materials of interest
- C. Simulation of particle adhesion

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Examples of Adhesion-Induced Deformations

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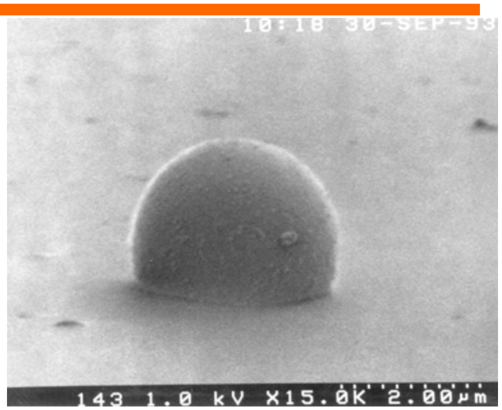

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Examples of Adhesion-Induced Deformations

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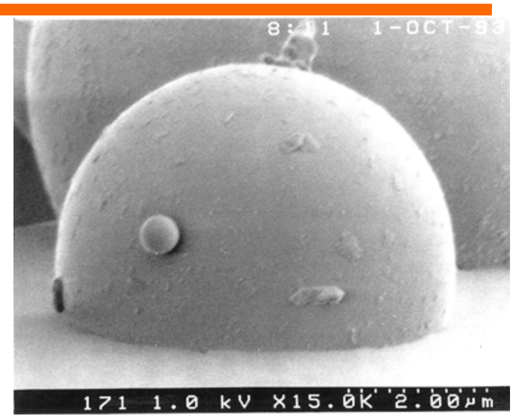

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Examples of Adhesion-Induced Deformations

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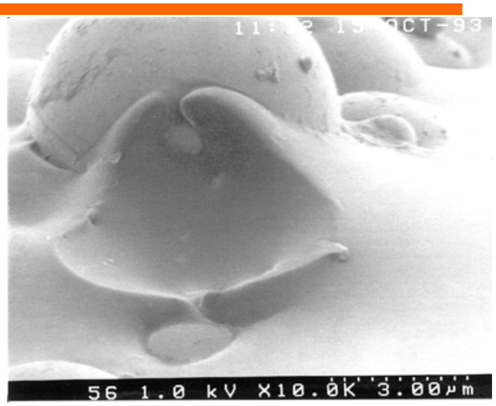

Examples of Adhesion-Induced Deformations

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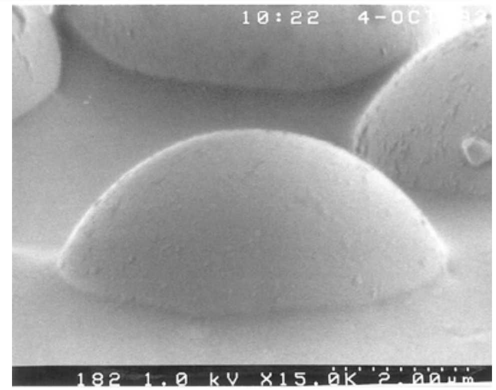

Examples of Adhesion-Induced Deformations

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JKR Theory

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There is a total energy U_T of a system, where

$$U_T = U_E + U_M + U_S$$

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 = $w_A \pi a^2$

JKR Theory

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The JKR equation is given by:

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

Fundamental Assumptions of the JKR Theory

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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.**

Examples of Adhesion-Induced Deformations Quintessential JKR Systems

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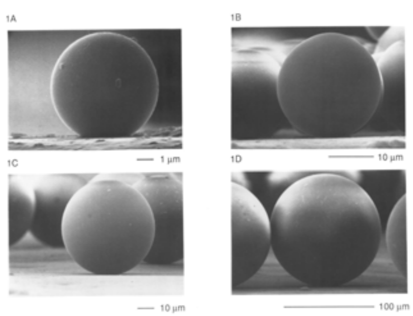
High elastic modulus spherical particles on elastomeric substrates.

Polystyrene on Polyurethane



Examples of Adhesion-Induced Deformations Quintessential JKR Systems

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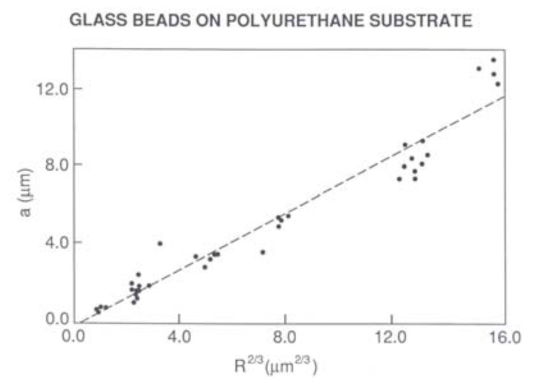

Non-JKR Systems

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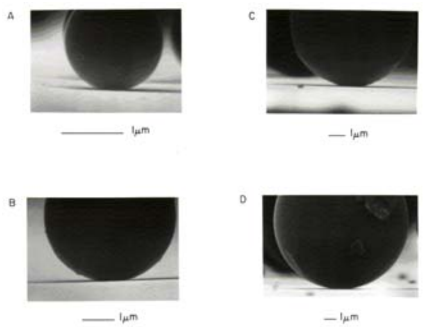
Polystyrene particles on a silicon wafer



Non-JKR Systems

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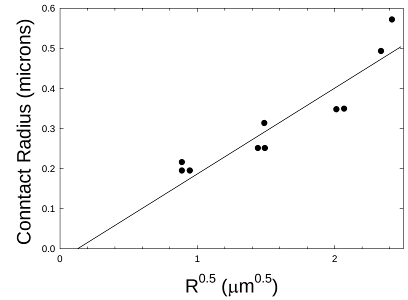

Role of Electrostatics in Particle Adhesion

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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.

Role of Electrostatics in Particle Adhesion

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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.

Role of Electrostatics in Particle Adhesion

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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).

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Role of Electrostatics in Particle Adhesion

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- **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?**

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Role of Electrostatics Interactions in Particle Adhesion

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Consider a spherical toner particle of radius

R = 6 μm and q/m = 15 μC/g.

$\Rightarrow q = 1.4 \times 10^{-14}$ C.

$\Rightarrow \sigma = 3 \times 10^{-5}$ C/m^2.

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Forces Acting on Particle

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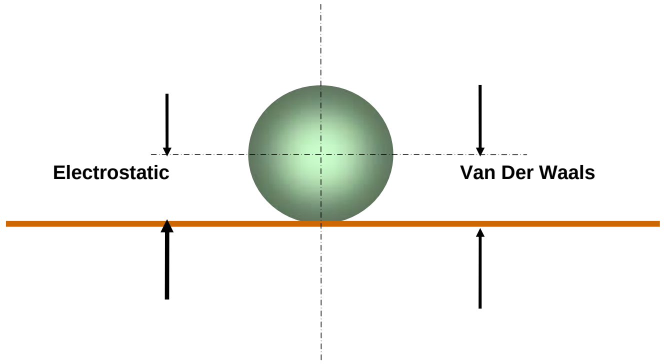

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Image Force

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For a single, dielectric, spherical particle with a uniform charge distribution

$$F_{Im} = \frac{1}{4\pi\varepsilon_0}\left(\frac{q}{2R}\right)^2 = \frac{1}{4\pi\varepsilon_0}\left(\frac{4\pi R^2 \sigma}{2R}\right)^2$$

$$F_{Im} = \frac{1}{4\pi\varepsilon_0}\left(4\pi^2 R^2 \sigma^2\right) = \frac{\pi R^2 \sigma^2}{\varepsilon_0}$$

$$F_{Im} = 12 \text{ nN}$$

van der Waals Force

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van der Waals Attraction:

$$F_{VW} = \frac{A R}{6 z_0^2}$$

$$F_{VW} = 625 \text{ nN}$$

van der Waals Force = Image Force

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Define R_{crit} by $F_{VW} = F_{Im}$

$$R_{crit} = \frac{A\varepsilon_0}{6\pi z_0^2 \sigma^2}$$

If: $A = 10^{-19}$ J $z_0 = 4$ Å

$\Rightarrow R_{crit} = 0.5$ mm

For $R < R_{crit}$: van der Waals dominated

For $R > R_{crit}$: electrostatic dominated

However: Both forces contribute to adhesion.

Toner Transfer Experiments

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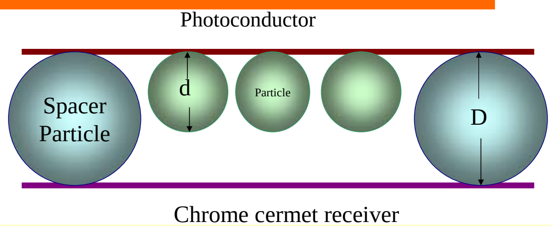

Schematic illustration of experimental setup. The larger toner particles fix the size of the air gap while the applied electric field cause the smaller particle to transfer from the photoconductor (top) to the receiver (bottom).

Adhesion Force Measurement

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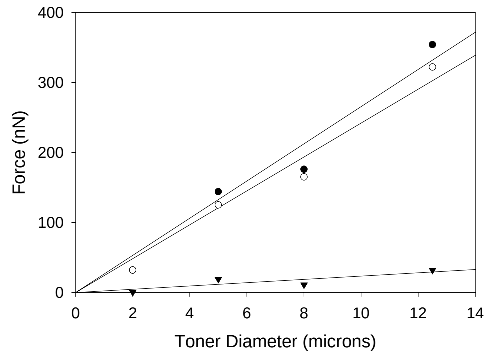

Adhesion Force Measurement

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- **Thus far, it would appear that the JKR contact mechanics assumption is valid.**
- **However, if electrostatic forces become more significant, long-range interactions would have to be taken into account.**

What can make electrostatic interactions more significant?

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$$R_{crit} = \frac{A\varepsilon_0}{6\pi z_0^2 \sigma^2}$$

What can make electrostatic interactions more significant?

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Increase the size of the particle. Electrostatic forces as R^2 whereas van der Waals forces vary linearly with R.

Increase the surface-charge density. The critical radius varies as $1/\sigma^2$.

Decrease the surface energy/Hamaker constant. Examples include coating a surface with Teflon or zinc stearate.

What can make electrostatic interactions more significant?

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Add asperities to the particle. **These serve as physical separations that reduce adhesion (Tabor and Fuller (Proc. R. Soc. Lond. A 345, 327 (1975); Schaefer et al. J. Adhesion Sci. Technol. 9, 1049 (1995))**

Add neighboring particles having a similar charge. **(Goel and Spencer, in *Adhesion Science and Technology Part B*, L. H. Lee (ed.)).**

What can make electrostatic interactions more significant?

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Localize charge to specific areas on surface of the particle rather than uniformly distributing it – the so-called "charged patch model." (D.A. Hays, in *Fundamentals of Adhesion and Interfaces*, D. S. Rimai, L. P. DeMejo, and K. L. Mittal (eds.))

Neighboring Particle Charge Effect

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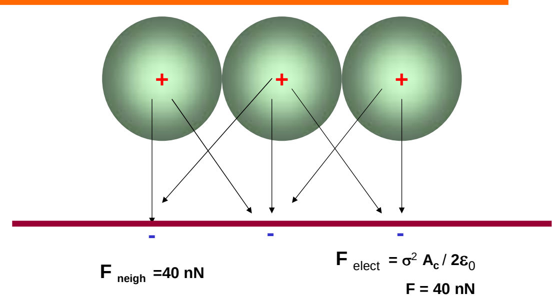

Neighbor Forces Acting on Particle

Charged-Patch Model

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Assume that the particle charge is localized to a discreet section of the particle

Electrostatic contribution to attractive force F_E is given by

$$F_E = \frac{\sigma^2 A_C}{2\,\varepsilon_0}$$

A_C is the contact area

σ is the charge density

Estimate of Fvw

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Note: These particles are irregularly-shaped

No silica: Particle radius = 4μm

W_A = 0.05 J/m², q/m = 37 ± 3 μC/g, ρ = 1.2 g/cm³

From JKR theory:

$$F_S = \frac{3}{2} w_A \pi R = 943 \text{ nN}$$

Measured value: F_S = 970 nN

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Estimate of Fvw

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2% Silica: Assume JKR contact radius = 196 nm

r_{silica} = 30 nm, ρ_{silica} = 1.75 g/cm³.

⇒have about 10 silica particles within the contact zone.

Approximate JKR removal force by

$$F_S' = n \frac{3}{2} w_A \pi r = 39 \text{ nN}$$

Measured: F_S' = 70 nN

Estimate of Fim

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$$F_{Im} = \alpha \frac{q^2}{4\pi \varepsilon_0 (2R)^2}$$

⇒ F_{Im} = 20 – 40 nN

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Estimate of Fe

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Patch charge density limited by dielectric strength of air.

⇒ $F_E \approx$ 30 nN

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Key Feature

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- If the particle has sufficient irregularity, van der Waals forces, electrostatic image forces, and charged-patch forces all predict about the same size force, which is comparable to experimentally determined detachment force.

Conclusions

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- For small, spherical particles, adhesion appears to be dominated by van der Waals interactions.
- As the particles become bigger or more irregular, electrostatics become more important.
- van der Waals interactions can be reduced, even for small, spherical particles, to the point where electrostatic forces can become dominant.

Conclusions

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- The electric charge contribution increases with increasing charge and the presence of neighboring particles.
- These results hold for macroscopic systems as well as microscopic ones.
- Electrostatic interactions are long-range.
- JKR theory should be extended to allow for long-range interactions

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Thank you!

Questions?