Particle-Substrate Interactions: Microscopic Aspects of Adhesion

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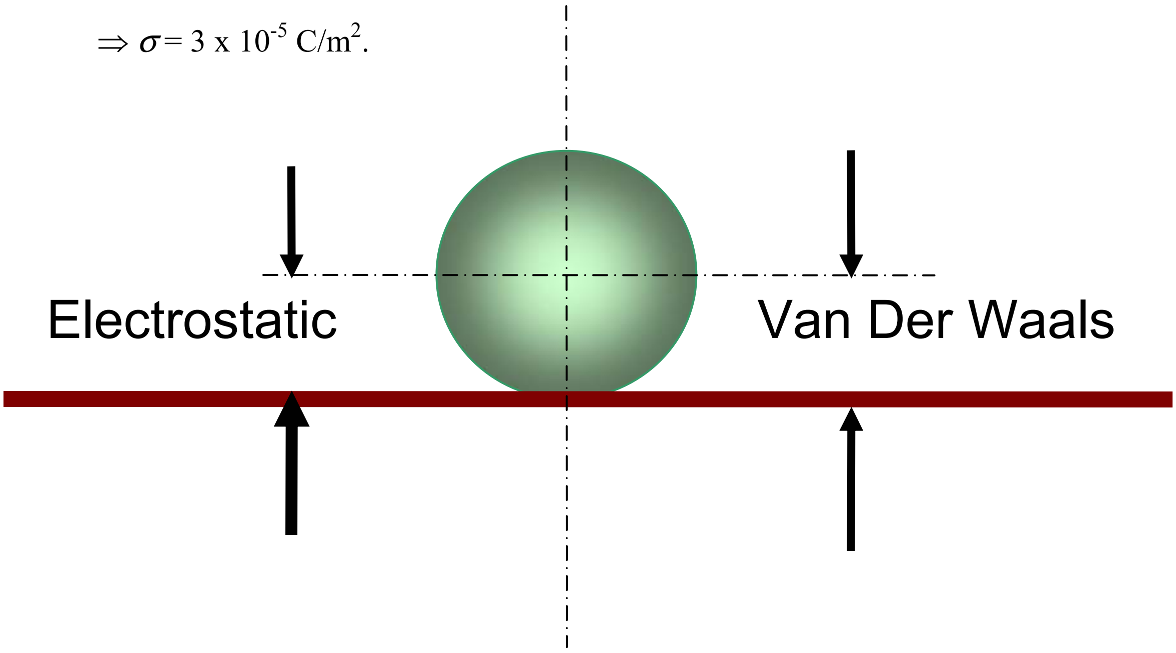
Part 2

Role of Electrostatic Interactions in Particle Adhesion

Consider a spherical toner particle of radius $R = 6$ µm and $q/m = 15$ µC/g.

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

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



Forces Acting on Particle

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

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

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

$F_{Im} = 12$ nN

Van der Waals attraction:

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

$F_{VW} = 625$ nN

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

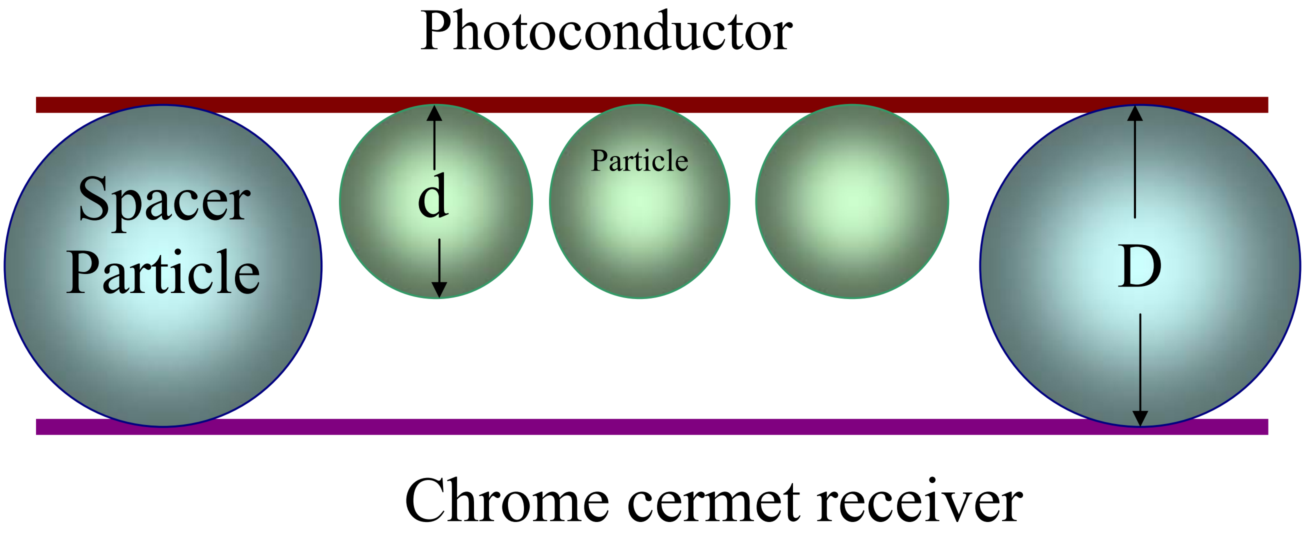
$$R_{crit} = \frac{A\varepsilon_0}{6\pi z_0^2 \sigma^2}$$

If: $A = 10^{-19}$ J $z_0 = 4$ Å

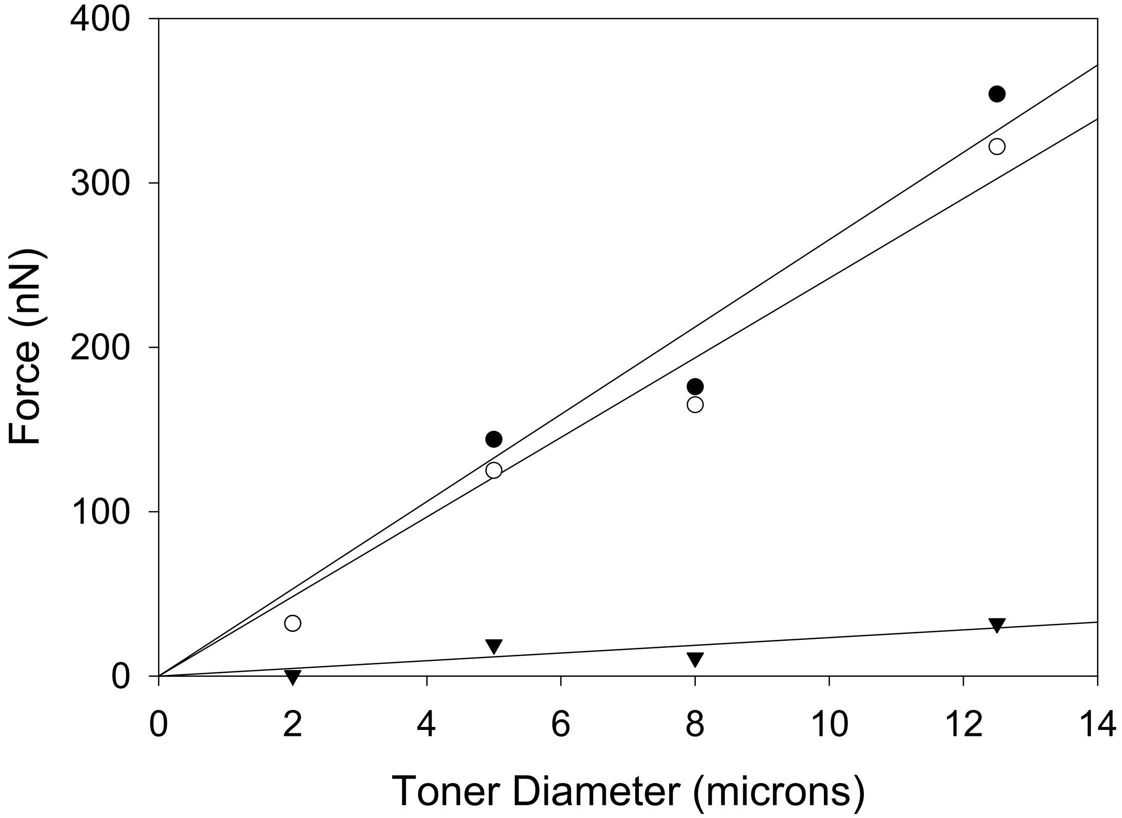
$\Rightarrow R_{crit} = 0.5$ mm

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

However: Both forces contribute to adhesion.



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).



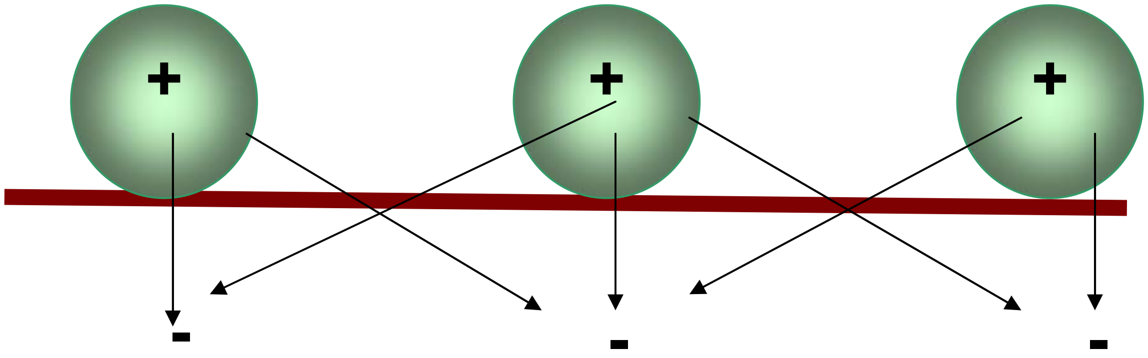
Thus far, it would appear that the JKR contact mechanics assumption is valid.

However, if electrostatic forces become more significant, long-range interactions would have to be taken into account.

What can make electrostatic interactions more significant?

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

1. Increase the size of the particle. Electrostatic forces as R^2 whereas van der Waals forces vary linearly with R.
2. Increase the surface-charge density. The critical radius varies as $1/\sigma^2$.
3. Decrease the surface energy/Hamaker constant. Examples include coating a surface with Teflon or zinc stearate.
4. 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))
5. Add neighboring particles having a similar charge (Goel and Spencer, in *Adhesion Science and Technology Part B*, L. H. Lee (ed.)).
6. 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.))



$F_{neigh} = 40\text{ nN}$

$F_{elect} = \sigma^2 A_c / 2\varepsilon_0$

$F = 40\text{ nN}$

Charged-Patch Model

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 F_{VW}

Note: These particles are irregularly-shaped

<u>No silica</u>:

Particle radius = 4μm
$W_A = 0.05$ J/m^2
$q/m = 37 \pm 3$ μC/g
$\rho = 1.2$ g/cm^3

From JKR theory:

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

Measured value: $F_S = 970$ nN

<u>2% Silica</u>:

Assume JKR contact radius = 196 nm
$r_{silica} = 30$ nm
$\rho_{silica} = 1.75$ g/cm^3.

⇒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 F_{Im}:

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

$\Rightarrow F_{Im} = 20 - 40$ nN

Estimate of F_E:

Patch charge density limited by dielectric strength of air.

$\Rightarrow F_E \approx 30$ nN

Key feature to note: 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

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.

The electric charge contribution increases rapidly 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.

Methods of Measuring Particle Adhesion

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

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

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

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

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

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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