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LETTER TO THE EDITOR

Size-dependent adhesion of nanoparticles on rough substrates

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Abstract

When the size of particles varies over the *entire* realm of nanotechnology, we find that surface forces can change by orders of magnitude depending on how surface interactions are influenced by the irregular fluctuations of rough surfaces at *all* length scales from atoms to microns. The length scales and roughness exponent define the distribution of asperities at points of contact and the adhesion that is maintained by van der Waals forces and contact deformation via asperities.

The dominating forces of adhesion between solid particles and solid surfaces consist of van der Waals, electrostatic and deformational forces [1–5]. For particles less than 1 μm, the long-range electrostatic forces are no longer as important as van der Waals forces, which have their origin from electrodynamics fluctuations [6] and define surface energies of molecularly smooth surfaces.

The adhesion of nanoparticles is vast in scope encompassing the physics of surfaces and interfaces, polymers, microelectronics, adsorption, tribology, and impinges on modern biology and biomedical applications [7, 8]. Roughness is a real-world problem, and it has completely different effects on wetting and adhesion of solids. Wetting of non-planar substrates has shown that roughness enhances the critical surface energy [9], but roughness reduces the adhesion between elastic solids [10]. It becomes apparent that the surface energy alone cannot account for the adhesion of contacting solids. The roughness-induced real asperity contact and deformation are going to influence the intensity of adhesion. The interplay between the tackiness and surface roughness of soft solids at the micron scale was illustrated [11] and the adhesion of a rough surface in contact with a rigid flat surface was demonstrated [12]. Using a multiscale model, we would like to describe the nanoscale particle-roughness phenomena coupled with their dependence on surface energy and bulk deformation in this letter. The strong coupling between the particle size, local surface roughness, surface energy and elastic constant of contacting materials are going to be shown as the reasons for very large variations in nanoparticle adhesion.

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Fractals present a natural language for describing the scaling behaviour of roughness on *all* length scales. Since surface forces are short-ranged, the length scales are expected to play important roles. The height of a rough surface can be represented by the function $h(\vec{r})$, where $\vec{r}$ is the position vector on an appropriate reference plane. Self-affine fractals are invariant under an anisotropic dilation [13–15]. This means that there exists an exponent α ($\leqslant 1$) such that the transformation

$$\vec{r} \to m\vec{r}, \qquad z \to m^{\alpha} z \tag{1}$$

leaves the surface statistically invariant with the scaling factor m assumed to be $0 < m < 1$. The roughness exponent is related to the fractal dimension by $d_f = d - \alpha$, where d is the spatial dimension and $2 \leqslant d_f < 3$ with $d = 3$. In addition to α, two length scales are needed to characterize self-affine fractals: the root mean square fluctuations σ (standard deviation) normal to the surface and the correlation length ξ parallel to the surface. α defines the scaling properties of surface and measures the roughness in short range ($<\xi$). A large value of α ($>1/2$) corresponds to a smooth short-ranged surface profile, a smaller α ($<1/2$) corresponds to rougher local variation of a surface structure, and $\alpha = 1/2$ represents the Gaussian surface [16, 17].

The change of the height correlation function with distance follows a power law $\langle[\Delta h(r)]^2\rangle \sim r^{2\alpha}$ for $r \ll \xi$ and $\langle[\Delta h(r)]^2\rangle = \sigma^2$ for $r \gg \xi$. The local radius of curvature of asperities averaged over the range of ξ is $\xi^2/2\sigma$ which goes to infinity with $\sigma \to 0$ or $\xi \to \infty$ for a flat surface [18]. The effective radius of curvature (ρ) of a spherical particle with radius R in contact with a rough substrate becomes $\rho = 1/(1/R + 2\sigma/\xi^2)$. The displacement w at the point of asperity relates to ρ and the radius of contact area a by $w = a^2/\rho$. Including the effect of surface energy in the analysis of the Hertzian-contact deformation [19] and using equation (19) in [4], we obtain a normalized nonlinear force–displacement relation:

$$f = (w/\varepsilon)^{3/2} - 2(w/\varepsilon)^{3/4} \qquad \text{for } w/\varepsilon \geqslant 1 \tag{2}$$

and $f = -1$ for $w/\varepsilon < 1$. The maximum extension at the tip of asperities above the undeformed height before separation occurs at $\varepsilon = (3F_0/4E')^{2/3}\rho^{-1/3} > 0$, where $F_0 = (3/2)\pi\gamma\rho$ and γ is the work of adhesion. The effective elastic constant of the particle–substrate is $E' = 1/[(1-\nu_p^2)/E_p + (1-\nu_s^2)/E_s]$, where E is Young's modulus, ν is Poisson's ratio and the subscripts p and s refer to particle and substrate, respectively. It turns out that ε is equal to the separation of contacting reference planes. The first term on the right-hand side of equation (2) is due to the bulk contribution related to the elastic contact and the second term is due to the surface contribution related to the surface energy. A question may arise as to whether the localized contact is likely to be elastic or plastic deformation. Since the ratio of elastic constant to hardness for most materials, such as polymers, are larger than 10, the asperity contacts are much more likely to be elastic for $\sigma/\rho < 25$, which covers the present case in accordance with a criterion of the plasticity index [20].

Following the general description of self-affine fractals, we also obtain a causal probability distribution of asperity heights:

$$\psi(z) = \frac{1}{\sigma\alpha^{1-\alpha}\Gamma(\alpha)} \exp[-\alpha(z/\sigma)^{1/\alpha}], \qquad 0 < \alpha \leqslant 1 \tag{3}$$

where Γ is the gamma function. When $\alpha = 1/2$, we get the familiar Gaussian distribution. The exponential distribution is the case of $\alpha = 1$. Adhesion is maintained between a few asperities by van der Waals forces and contact deformation depending on the symmetrical distribution of asperity height. The relative particle adhesion can, in general, be written as

$$F/F_0 = -\int_0^{\infty} f\left(\left|\frac{z-\varepsilon}{\varepsilon}\right|\right)\psi(z)\,\mathrm{d}z. \tag{4}$$

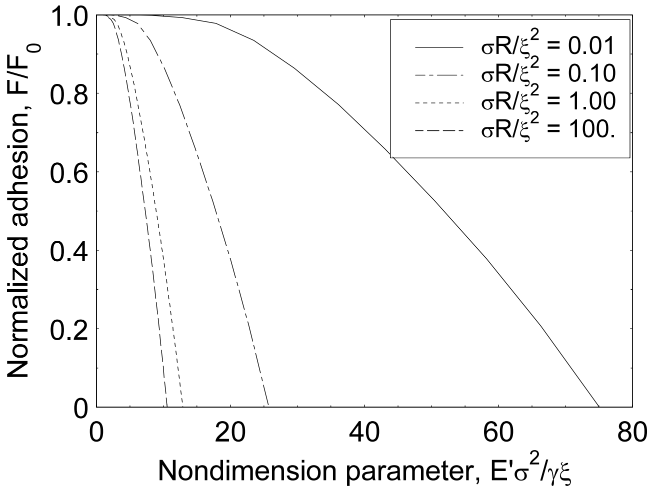

Figure 1. The particle adhesion is calculated from equation (4) as a function of two non-dimensional parameters: $E'\sigma^2/\gamma\xi$ and $\sigma R/\xi^2$. The roughness exponent of the substrate is chosen to be $\alpha = 0.7$. The elastic constant and surface energy is scaled with the standard deviation σ and correlation length ξ of a rough surface. The domain of adhesion increases as the relative length scale $\sigma R/\xi^2$ decreases for finer particles and/or smoother substrates. The curve with $\sigma R/\xi^2 = 100$ is approaching the case of a rough surface in contact with a flat surface.

where $z - \varepsilon = w$ is the displacement. The pull-off force under tension immediately after the contact formation under compression is going to be determined by the above equation. Equations (2)–(4) serve as the basis for multiscale predictions of particle adhesion on rough substrates over all length scales.

The strength of particle adhesion is shown in figure 1 as a function of the particle radius (R), the microstructure of rough substrate (α, σ, ξ), the surface energy (γ) and the effective elastic constant (E'), which are grouped into two non-dimensional parameters. The bulk and surface properties are linked by $E'\sigma^2/\gamma\xi(\equiv\beta)$ and the relative length scales of the particle size and substrate roughness by $\sigma R/\xi^2$. All curves in figure 1 collapse at $F = F_0$ when β becomes smaller depending on the value of $\sigma R/\xi^2$. In the case of $\alpha = 1/2$ and $R \to \infty$ [10], small β was related to the situation that the indentation is of the order of the roughness amplitude σ. This was also interpreted as the fraction of the surface area that is truly in contact. Figure 2 predicts the combined effects of the exponent α and parameter β for relatively smaller particles and smoother substrates. More than an order of magnitude decrease in the adhesion can be expected for a given β as α increases from 0.3 to 1.0 for different deposited or polymeric thin films [13–15]. These two figures reveal that a smaller particle, smoother short-range surface texture, higher surface energy and softer contacting materials result in stronger particle adhesion. Detaching particles from substrates is important to many technological applications and is related to the adhesion failure by setting $F = 0$ in equation (3). We obtain the master detachment curves between the critical bulk-surface property β_c and the relative particle-roughness $\sigma R/\xi^2$ in figure 3. The detachment transition in the vicinity of $\sigma R/\xi^2 = 1$ is shown that suggests the importance of the relative length scales to the short-ranged surface interactions. Figure 4 shows how orders of magnitude change in the size of particle, in the local roughness of substrate and in the rigidity of the contacting solids are closely intertwined in the mechanism of adhesion failure.

Based on fundamental principles, we find that the system sizes ranging from atomic dimensions up to micron scale have a very strong influence on nanoparticle adhesion. Our

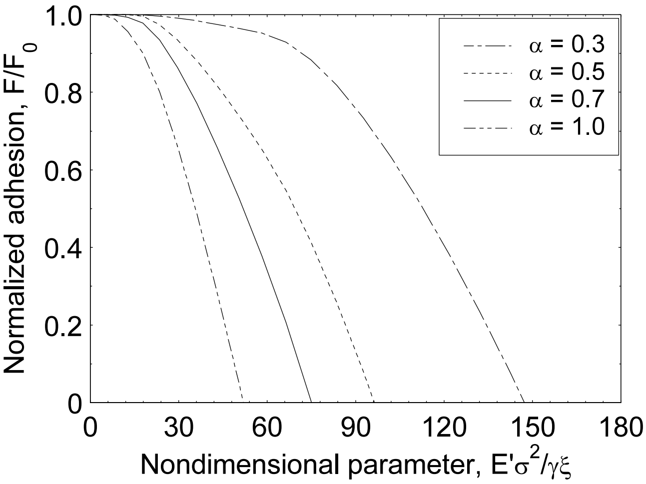

Figure 2. The strong effect of the roughness exponent α on the normalized adhesion is plotted against the non-dimensional parameter $E'\sigma^2/\gamma\xi$ in the case of $\sigma R/\xi^2 = 0.01$. Considering $E'\sigma^2/\gamma\xi = 75$, we see an order of magnitude decrease in the adhesion as α increases from 0.3 to 0.7, which represents the change in local surface structure from a rougher to a smoother texture.

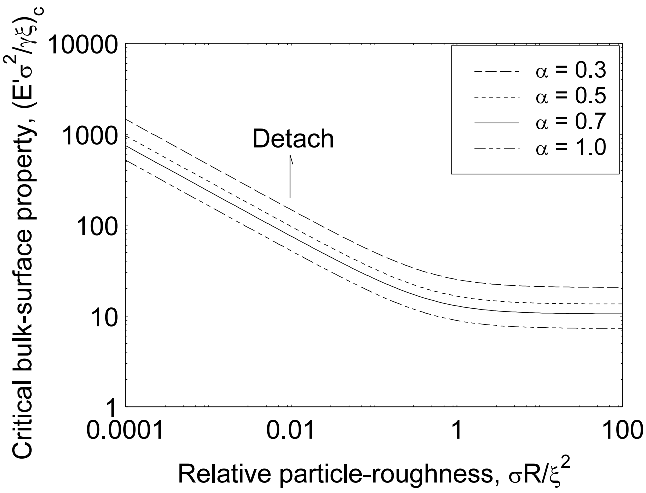

Figure 3. Criteria for the detachment of particles from substrates: the scaling relations between the critical parameter $(E'\sigma^2/\gamma\xi)_c$ and the relative length scale $\sigma R/\xi^2$ are obtained for different values of α.

investigation helps us to gain a quantitative understanding of the dependence of particle adhesion on the size of the particle, on the structure of the self-affine fractal surface, on surface energy and on bulk deformability. A scaling relation between the critical bulk-surface properties and the relative particle size–substrate roughness is obtained to describe the detachment of particles from substrates. These new findings are important to many technological and biomedical applications like image transfer and formation, thin-film technology, drug-delivery systems and the possible health risks of nanoparticles that may accumulate in the body. The importance of the relative length scales of particle and roughness to the short-ranged interactions is also revealed by the presence of the detachment transition.

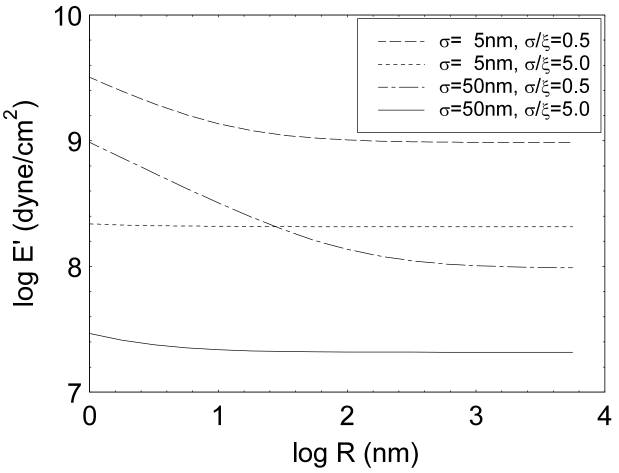

Figure 4. Dependence of the critical elastic constant during detachment on the particle size that varies over the entire length scales of nanotechnology. We choose $\alpha = 0.7$, $\gamma = 20$ erg cm^{-2} and different surface structures of the substrate. In the case of a 10 nm particle, an almost two orders of magnitude increase in the effective elastic constant of the particle–substrate from $E' = 2.19 \times 10^7$ to 1.83×10^9 dyn cm^{-2} is needed to separate particle from substrate when the short-range surface texture is smoothed by an order of magnitude in both σ and σ/ξ.

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