Nanoadhesion between Rough Surfaces

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A model is developed to describe the adhesion between deformable fractal surfaces over the mesoscopic realm that covers the familiar range of interest in nanotechnology from atomic dimensions to microns. This model helps us gain a quantitative understanding of the variation of adhesion with surface energy, with microstructure of rough surfaces, and with bulk deformability. The present analysis goes beyond the Gaussian distribution of asperity heights by investigating the influence of the microstructure of self-affine fractal surfaces. Our calculation reveals that orders of magnitude increase in adhesion are possible as the roughness exponent decreases.

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Developing a sophisticated understanding of adhesion between solid-solid interfaces will help modern technology better design the processes of bonding or debonding that are essential to many applications from adhesives, thin film coating, image formation, to microelectronics. It has been known for a long time that the surface roughness is very important in the determination of the force that is required to separate two materials after they had been brought into contact. The experiment measurement of the debonding forces between two atomically smooth mica surfaces reveals that the adhesion is comparable to the van der Waals force [1], which defines the surface energy. For low-energy solids such as polymers, the surface energy is usually determined by the extrapolated contact angle measurement and is expressed in terms of the critical surface energy to characterize a solid surface [2].

Recent studies of wetting of nonplanar substrates have shown that roughness enhances the critical surface energy [3,4]. On the other hand, roughness reduces the adhesion between elastic solids [5]. It becomes apparent that the surface energy alone cannot account for the adhesion of contacting solids. The roughness-induced real area of contact and bulk deformation are going to influence the intensity of adhesion. Indeed, a recent reported interplay between the tackiness and surface roughness on the micron scale concludes that roughness is tough on stickiness and soft solids are sticky [6,7]. Air bubbles can be trapped inside the surface roughness during the contact formation before a pull-off force is applied. A typical value of the elastic constant for soft materials is in the order of 10^6 dyn/cm^2 [8,9], which may be enough to enhance the real area of contact and deformation to achieve a sufficient level of adhesion.

The present state of theoretical studies of roughness related to adhesion has been limited to the analysis of height fluctuation normal to surface, which is assumed to be Gaussian [5,10]. In view of the crucial importance of roughness on adhesion, we shall go beyond the Gaussian surfaces by investigating the influence of the microstructure of rough surfaces. The use of the fractal concept in the understanding of rough surfaces is increasingly important these days [11]. It is the purpose of this paper to develop a model that describes the solid-solid adhesion between deformable fractal surfaces over the mesoscopic realm. That covers the familiar range of interests in nanotechnology from atomic dimensions to microns [12]. The present model can help us to gain a quantitative understanding of the following issues. Why are soft solids stickier than hard materials when the roughness is on the micron scale? What is the general relationship between the roughness and the rigidity of contacting materials during debonding? How strong is the influence of the surface microstructure on the failure of adhesion?

Adhesion is maintained between a few asperities by van der Waals forces depending on the distribution of asperity height ϕ. When the maximum force that can be sustained by adhesion before separation is F_0, the relative adhesion (or pull-off force) for rough surfaces in contact can be written in the general form,

$$F/F_0 = -\int_{-\infty}^{\infty} f(z - d, \varepsilon)\phi(z)\, dz = -\int_0^{\infty} f\left(\left| \frac{z - d}{\varepsilon} \right|\right)\psi(z)\, dz\,. \quad (1)$$

When ϕ is a symmetrical function, it is often convenient to analyze the problem by using the causal distribution function $\psi = 2\phi$ instead. In Eq. (1), ε is the maximum extension of the tip of an asperity above its undeformed height before separation occurs, and d is the separation of two reference planes of contacting rough surfaces, and it is smaller than the asperity heights. The force of separation under tension immediately after the contact formation under compression is going to be determined by Eq. (1). It has been mentioned in the literature that neither the asperity shape nor the force-displacement relationship f for an individual asperity is generally known. Based on the general description of the microstructure of self-affine fractal surfaces, we plan to present analytical expressions (i) of the asperity shape, (ii) of the nonlinear force-displacement relationship f, and (iii) of the non-Gaussian height probability function ψ. That is beyond the Gaussian distribution

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assumption adopted frequently in the literature. Our objective is to obtain a quantitative understanding of the variation of adhesion with surface energy, with microstructure of rough surfaces, and with bulk deformability.

The height of a continuous rough surface from its smooth reference is represented by the function $h(\vec{r})$, where $\vec{r}$ is the position vector on the reference surface. It is usual to ensure that $\langle h \rangle = 0$, where the angular bracket denotes the average across the surface. Three independent parameters are needed to describe the microstructure of a self-affine fractal surface. The standard deviation σ is the root mean square fluctuation normal to the surface and the correlation length ξ parallel to the surface. In addition to the length scales, the third independent parameter is the roughness exponent α, which defines the scaling properties of the surface and is equal to $\alpha = \frac{1}{2}$ for the Gaussian surfaces. For a given domain size of short-range surface profile, smaller α corresponds to rougher local variation of a surface, and smoother hills and valleys are expected as $\alpha \to 1$ [13].

In terms of the microstructure of a self-affine fractal surface, the change of the height correlation function with distance r has been derived to be [14]

$$\langle [h(\vec{r}_0 + \vec{r}) - h(\vec{r}_0)]^2 \rangle = \sigma^2 \{1 - \exp[-(r/\xi)^{2\alpha}]\} \equiv C(r/\xi), \qquad 0 < \alpha \leq 1 . \quad (2)$$

This equation results in a familiar power law $C \sim r^{2\alpha}$ for $r \ll \xi$, and an asymptotic value $C = \sigma^2$ for $r \gg \xi$ [11]. The shape of asperity peak can be described by

$$g(r/\xi) = 2 \int_0^{r/\xi} \sqrt{C(r')}\, dr' \cong \frac{2\sigma}{(1+\alpha)} \left(\frac{r}{\xi}\right)^{\alpha+1} + \ldots, \qquad r \ll \xi . \quad (3)$$

The presence of two in front of integration is due to the symmetric surface with its the origin at the center of contact. The radius of curvature of spherical asperity R is then determined as

$$\frac{1}{R} = \frac{1}{\xi} \int_0^{\xi} \frac{d^2 g/dr^2}{[1 + (dg/dr)^2]^{3/2}}\, dr \cong \frac{1}{\xi} \int_0^{\xi} \frac{d^2 g}{dr^2}\, dr = \frac{2\sigma}{\xi^2}, \quad (4)$$

where the spatial average is taken over the range of ξ because the two heights become uncorrelated at a distance of the order of ξ in accordance with Eq. (2). As one might expect, $R \to \infty$ for a smooth surface when the standard deviation $\sigma \to 0$ or the correlation length $\xi \to \infty$.

Most of the literature on rough surfaces assumes that the height distributions are Gaussian, which is too restrictive for many important applications. Following the above-mentioned general description of fractal surfaces, we obtain a non-Gaussian probability distribution of asperity heights to be

$$\psi(z) = \psi_0 \exp[-\alpha (z/\sigma)^{1/\alpha}], \qquad 0 < \alpha \leq 1 , \quad (5)$$

where

$$\psi_0 = \left[\sigma \int_0^{\infty} \exp(-\alpha u^{1/\alpha})\, du \right]^{-1} = \frac{1}{\sigma \alpha^{1-\alpha} \Gamma(\alpha)}, \quad (6)$$

where Γ is the gamma function. When $\alpha = \frac{1}{2}$, we get the Gaussian distribution function from the above two equations. The exponential distribution is the case of $\alpha = 1$. The next step is to analyze to bulk deformability related to a single contact. The displacement w at the tip of an asperity relates to the radius of contact area a and the radius of curvature R by $w = a^2/R$. Including the effect of surface energy γ in the analysis of Hertz for contact deformation [15] and using Eq. (19) in [16], we obtain

$$w = (F + 2F_0 + 2\sqrt{F_0 F + F_0^2})^{2/3} R^{-1/3} (4E'/3)^{-2/3}, \quad (7)$$

where $F_0 = (3/2)\pi\gamma R$. More precisely, $\gamma = \gamma_1 + \gamma_2 - \gamma_{12}$ is the work of adhesion where γ_1, γ_2, and γ_{12} are the surface energies of the surface 1, the surface 2, and the interface, respectively. From Eq. (4), the effective radius of curvature of two surfaces in contact is related to their roughness parameters by

$$\frac{1}{R} = \frac{2\sigma_1}{\xi_1^2} + \frac{2\sigma_2}{\xi_2^2} \equiv \frac{2\sigma}{\xi^2}, \quad (8)$$

and the effective elastic constant E' by

$$\frac{1}{E'} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} . \quad (9)$$

Clearly, soft materials dominate the contact deformation when they are in contact with hard materials, and rougher surfaces dominate the contribution to the curvature.

Introducing $f = F/F_0$, $\varepsilon = (3F_0/4E')^{2/3} R^{-1/3} > 0$, Eq. (7) leads to the nonlinear force-displacement relation of a single asperity contact:

$$f = (w/\varepsilon)^{3/2} - 2(w/\varepsilon)^{3/4}. \quad (10)$$

This expression is the new form of Eq. (19) in [16] with our notations. The first term on the right-hand side of Eq. (10) 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. When the displacement in Eq. (10) is chosen to be $w = z - d$ and the height probability density is assumed to be a delta function, Eq. (1) becomes

$$F/F_0 = -f\left(\left| -\frac{d}{\varepsilon} \right| \right) \Rightarrow d = \varepsilon, \quad (11)$$

by looking at Fig. 1. This figure also suggests that $f = -1$ for $w/\varepsilon < 1$, which is consistent with experimental data of a rubber sphere in dry contact with a rubber flat [16].

Combining Eqs. (1), (5), (10), and (11), we finally obtain

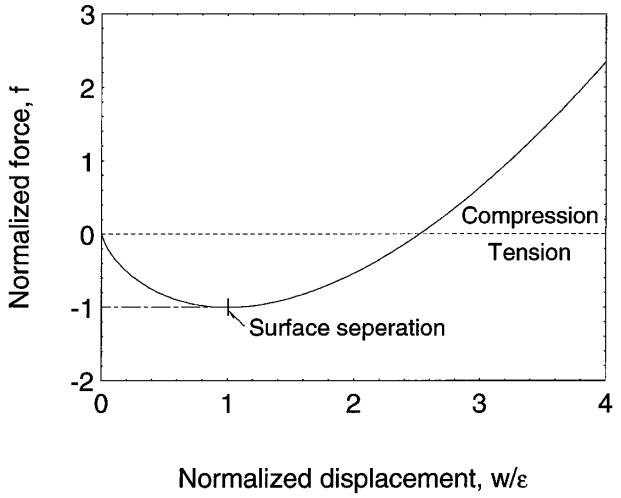

FIG. 1. Nonlinear force-displacement relationship for the contact deformation of a single spherical asperity that includes the effect of surface energy.

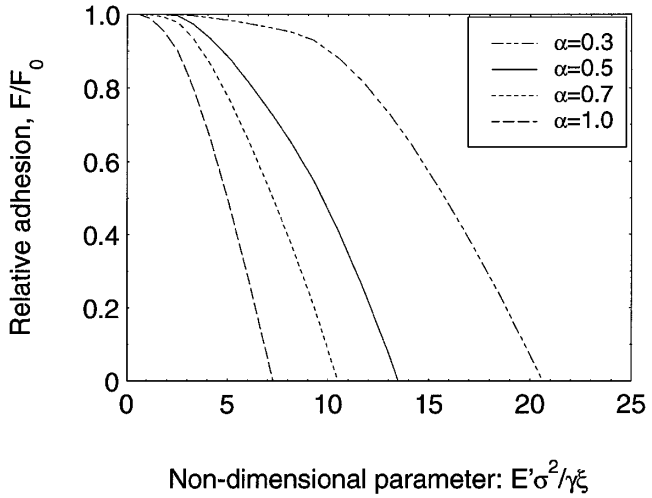

FIG. 2. The strong influence of the roughness exponent α, amplitude σ, and correlation length ξ on the relative adhesion is calculated from Eqs. (12). The surface energy and elastic constant are scaled with the roughness amplitude and correlation length in accordance with Eq. (13).

$$\frac{F}{F_0} = -\frac{1}{\alpha^{1-\alpha}\Gamma(\alpha)} \int_0^\infty f(|\beta s - 1|) \exp(-\alpha s^{1/\alpha})\, ds\,, \tag{12}$$

where the nondimensional parameter,

$$\beta = \frac{\sigma}{\varepsilon} = 2\left(\frac{4E'\sigma^2}{3\pi\gamma\xi}\right)^{2/3} = 0.543\left(\frac{E'\sigma^2}{\gamma\xi}\right)^{2/3}, \tag{13}$$

and the normalized force-displacement relationship,

$$\begin{aligned} f(|\beta s - 1|) &= -1, \qquad \text{for } 0 \le |\beta s - 1| < 1 \\ &= |\beta s - 1|^{3/2} - 2|\beta s - 1|^{3/4}, \\ &\text{for } |\beta s - 1| \ge 1\,. \end{aligned} \tag{14}$$

Equations (12)–(14) are the sought-after equations for quantitative predictions of the adhesion between deformable fractal surfaces. Equation (13) can be related to the Fuller-Tabor (FT) parameter, given by Eq. (17) in [5], which, however, does not contain the roughness amplitude σ and correlation length ξ in its original form. When the radius of curvature of spherical asperity in the FT parameter is replaced by that of Eq. (4), a nondimensional parameter $(E'\sigma^2/\gamma\xi)$ is obtained which links directly to β.

For simplicity, one of the surfaces is assumed to be rigid and flat in seeking the numerical solutions of Eqs. (12)–(14). The strong effect of the microstructure of rough surfaces on the relative adhesion is shown in Fig. 2. All curves in this figure collapse at $F = F_0$, for β below unity was interpreted by FT [5] as the fact that the indentation is of the order of the roughness amplitude σ, and it was further interpreted [17] in terms of the fraction of the surface area that is truly in contact: The fraction goes to unity when the parameter β is below unity. Considering $E'\sigma^2/\gamma\xi = 10$, we see an order of magnitude increase in the adhesion as the roughness exponent α decreases from 0.7 to 0.3, which is known for thin films deposited on substrates [11,13]. Our result compares well with that of Johnson in the case of an exponential distribution of asperity heights (see Fig. 6 in [5]), but differs somewhat from that of FT in the case of a Gaussian distribution. Because $dF/d\beta \to 0$ in the vicinity of $F = 0$, the FT equation cannot provide a solution for the quantitative prediction of adhesion failure to be discussed later. The new features of this Letter are (i) Eq. (5) and its application to Eq. (10) that lead to Eq. (12), and (ii) Fig. 2 that predicts the resulting effects of α with β to be important.

Figure 3 shows that the relevant standard deviation of asperity heights for hard materials such as mica with $E' \sim 10^{10}$ to 10^{11} dyn/cm^2 has to be in the order of nanometer, $\sigma \sim 1$ nm. Soft solids such as rubber have the effective elastic modulus $E' \sim 10^6$ to 10^7 dyn/cm^2. Figure 3 also reveals that the pertinent length scale should be in the order of micron, $\sigma \sim 1\mu$m, that compares well with what has been reported [5–8]. The suction-cup effect induced by air bubble trapping [6] may attribute in part to the reduction in the effective elastic constant [18] and in the roughness exponent. The profile of a bubble-trapping rough surface looks quite like that of a fractal surface with $\alpha = 0.3$ shown in Fig. 8.1 in [12]. In addition, this particular problem may also involve disconnected rupture of bubbles, which is beyond the scope of this Letter.

Both Figs. 2 and 3 have clearly illustrated the strong and sensitive relationships between the relative adhesion, surface roughness, and material rigidity. Equations (7) and (8) give

$$F_0 = \frac{3\pi\gamma\sigma}{4}\left(\frac{\xi}{\sigma}\right)^2. \tag{15}$$

For given γ, α, and σ/ξ, we obtain the ratio of the maximum adhesion forces between soft and hard solids, $F(\text{soft})/F(\text{hard}) \sim 10^3$, from Fig. 3, and Eqs. (12) and

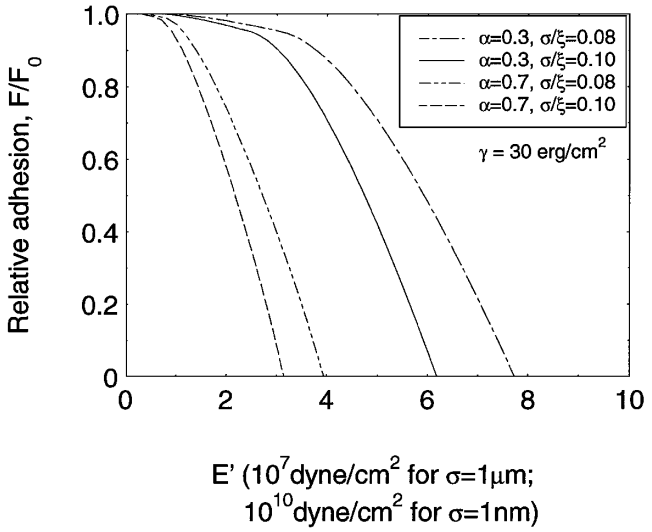

FIG. 3. Relative adhesion is predicted as a function of the elastic constant with different roughness exponent α and ratio of surface fluctuations σ/ξ. The abscissa is shifted by 3 orders of magnitude as the standard deviation σ of asperity height changes from a micron to a nanometer. These curves correspond to either $\sigma = 1$ μm and E' in 10^7 dyn/cm^2 or vice versa.

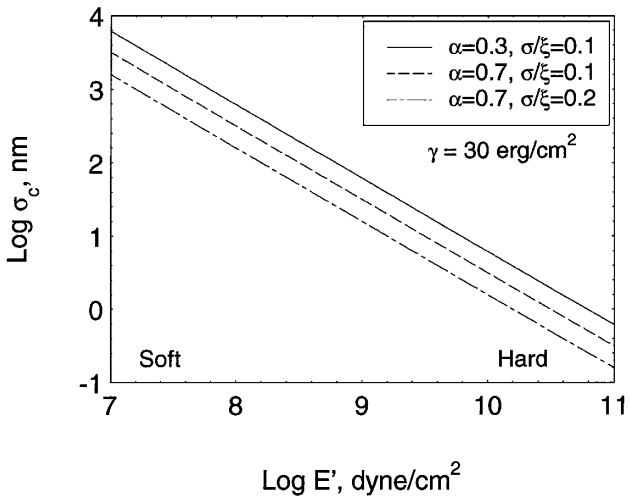

FIG. 4. Dependence of adhesion failure on roughness over the entire mesoscopic scales from microns to atomic dimensions when materials are changed from soft to hard. The relationship between the critical roughness and elastic constant during detachment is predicted as a function of the structure parameters of rough surfaces for a given surface energy.

(15) in the case of $\beta \ll 1$. Under such restrictive conditions, the maximum pull-off forces for soft solids are found to be 3 orders of magnitude higher than the weak van der Waals forces for smoother hard materials [1]. The criterion for adhesion failure is obtained by choosing $F = 0$ on the left-hand side of Eq. (12). The strong influence of the surface microstructure on the relationships between the roughness and rigidity of contacting solids during the adhesion failure is shown in Fig. 4 by solving Eq. (12). In order to maintain good adhesion between hard materials, the length scales of the roughness parameters σ and ξ have to approach atomic dimensions. Of course, the precise value of adhesion may vary over orders of magnitude and is controlled by the above-mentioned surface and bulk properties.

In summary, an integral equation has been derived to predict the strength of adhesion as a function of the surface energy (γ), the microstructure (α, σ, ξ) of fractal surfaces, and the effective elastic constant (E') over the mesoscopic realm. Based on the general description of the microstructure of self-affine fractal surfaces, we obtain the analytical expressions of the asperity shape, of the nonlinear force-displacement relation, and of the non-Gaussian height probability function. All these relations are then integrated into Eq. (12). Its solution reveals that orders of magnitude increase in adhesion are possible as the roughness exponent decreases. A relationship between the critical roughness and material rigidity is also obtained that describes the detachment of contacting surfaces: the roughness length scales reduce from microns to nanometers when materials are changed from soft to hard. The adhesion of soft solids can be several orders of magnitude higher than the van der Waals forces in some cases, and a small variation of roughness in the nanometer scale is sufficient to result in the adhesion failure for hard materials.

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