Adhesion between weakly rough beads

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Cohesion effects are of prime importance in powders and granular media, and they are strongly affected by the roughness of the grain surface. We report measurements of the adhesion force between surfaces of Pyrex having a nanometric roughness, with a surface force apparatus. The two surfaces are immersed in liquid *n*-dodecane. The adhesion force measured is much smaller than expected in the case of smooth surfaces. We find that the adhesion force depends on the maximal load that has been applied on the surfaces, but does not depend on the time during which they have been in contact. We propose a model of plastic deformation of the small asperities in a macroscopic Hertz contact which is in good agreement with the experimental data.

Recently, there has been growing interest in the effects of cohesion in granular media. There are many industrial processes and environmental situations involving cohesive granular media, and they are encountered as well in geophysics problems, in soil mechanics, and in the industrial processing of powders. In the field of soil mechanics, cohesive effects are usually taken into account at the macroscopic scale by a stability criterion relating the normal and tangential components τ and σ of the stress tensor in the medium [1]:

$$\tau < c + \sigma \tan \phi, \tag{1}$$

where $\tan \phi$ is the internal static friction coefficient of the granular medium, and c is some cohesive stress. This cohesive stress is purely phenomenological, and there is little understanding of how it relates to "microscopic" properties of the contact between grains. One reason for this is that adhesion phenomena are usually studied with smooth and clean surfaces, whereas adhesion of real surfaces is strongly dependent on their roughness. Cohesion effects are, however, very important in granular matter made of small grains, and lead to effects such as clumping and fracture.

It is usually considered that cohesion effects are very important in humid granular media, because of the capillary forces exerted by small liquid bridges that form at the contacts between grains. Some recent experimental work has aimed at quantifying the effect of a very small volume of liquid in a granular medium on its maximum stability angle [2–4]. An attempt to connect the "microscopic" cohesion force to the macroscopic cohesion stress was proposed by Halsey and Levine [5] who studied the cohesive stress due to small liquid bridges between the beads in a granular medium. They showed that surface roughness is the key parameter determining the importance of the capillary cohesion

force between grains. They also emphasized the size effects induced by cohesion: in the case of a granular heap for instance, Eq. (1) predicts that failure occurs at the bottom of the heap for a critical angle of the free surface depending on its height h [5]: $\tan \theta_m = \tan \phi (1 + c/\rho g h \cos \theta_m)$, with ρ the mass density of the granular material and g the gravity intensity. Therefore, if c is a constant independent of the normal stress, cohesion effects should vanish at large size. This effect, however, was not observed in experiments in humid granular media. More generally, the specific dependence of the cohesive stress on σ has to be known to discuss size dependences in avalanche processes.

In this work we address the problem of solid-solid adhesion forces between rough surfaces. We study Pyrex surfaces of nanometric roughness immersed in liquid dodecane, in order to prevent any capillary adhesion. We use a surface force apparatus (SFA) to measure the "pull-off" force, i.e., the maximum value of the adhesion force obtained just before the surfaces are pulled apart. Our main result is that, in contrast to the case of smooth surfaces, the value of the adhesion force is not solely determined by the surfaces themselves, but depends on the maximum normal load F_{max} that has been applied on the surfaces before pulling them apart. We find that F_{adh} scales as $F_{max}^{1/3}$. We interpret this result with a model of plastic deformation of the asperities. This result could have some important consequences for the macroscopic properties of granular media because it leads to a cohesive stress that depends on the normal stress in the sandpile. Such a dependency is not generally taken into account in modeling granular media. The importance of solid-solid cohesion forces could also explain some recent results on submarine avalanches [6].

Our system consists of a plane and a sphere of radius $R = 1.8 \pm 0.1$ mm, both of fire-polished Pyrex. The surfaces are first rinsed in an ultrasonic bath and then placed in a flame. The typical roughness of the surfaces prepared using this procedure was measured with an atomic force microscope (AFM) (Fig. 1). According to the measurements, the rms roughness of the surfaces on a 10×10 μm^2 scan is less than 5 Å. The peak to peak roughness of the surfaces, which is the

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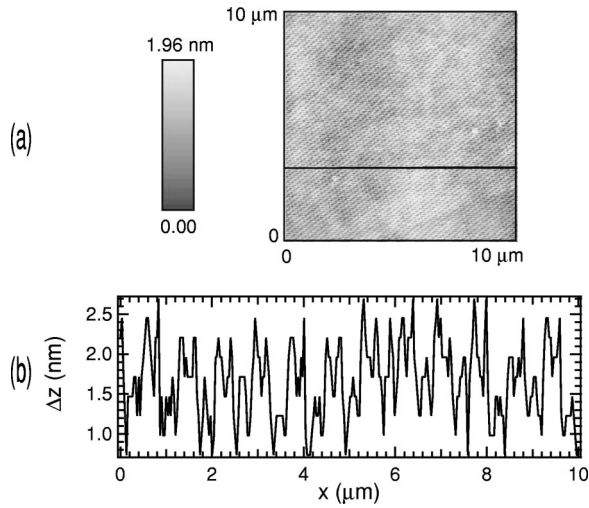
FIG. 1. (a) Image of a plane of Pyrex obtained with an AFM. This shows the very small rugosity of the surfaces responsible for the weak adhesion observed between the sphere and the plane. (b) Height profile of a Pyrex surface measured on the black line in (a).

FIG. 2. The interaction force F between the surfaces as a function of the relative surface displacement h. The sign of the force is chosen so that a repulsive force is positive. The arrows indicate the direction of the relative motion of the surfaces. F_{max} is the maximum force applied. The adhesion force F_{adh} is the pull-off force, i.e., the opposite of the minimum force measured, just before the surfaces jump apart.

significant quantity for quantifying the asperities, is 10 Å. The surfaces are mounted on the SFA described in [7]. This SFA consists of two double-spring cantilevers, allowing motion of the surfaces in the direction normal to the plane only. The displacement of the plane is measured by a Nomarsky interferometer, with a resolution of 0.1 Å. It is proportional to the force F acting on the plane; the stiffness of the cantilever supporting the plane is $k=2000$ N/m. The cantilever supporting the sphere can be moved in the direction normal to the plane with a piezolectric element. The relative displacement of the surfaces is measured with a capacitive sensor, with a resolution of 1 Å. The whole system is placed in a chamber in the presence of a desiccator (P_2O_5). A drop of n-dodecane is put between the surfaces. The drop is large enough that we can neglect the variation of the capillary force when the surfaces undergo a relative motion of the order of a few micrometers.

An experimental run consists of the following: the surfaces being initially located 50–100 nm apart, the sphere is moved toward the plane at constant velocity (1 nm s^{-1}) beyond mechanical contact. Figure 2 shows the force F between the surfaces as a function of the relative displacement x. When the surfaces reach mechanical contact, a repulsive force is measured due to the elastic repulsion of the two solids. The repulsive force increases until a value F_{max}. We then stop the relative motion of the surfaces, which are kept under the constant load F_{max} during a waiting time t_w. At this point, the relative motion of the surface is reversed at the same velocity. The force exhibits a small hysteresis and goes through a minimum whose amplitude is the pull-off force F_{adh}.

Figure 3 shows the evolution of the adhesion force F_{adh} between the surfaces as a function of the waiting time t_w for a value of the normal load $F_{max}=225\pm5$ μN, which is of the order of magnitude of the weight of the sphere. The first important result is that the adhesion force measured is three orders of magnitude smaller than expected for smooth ideal
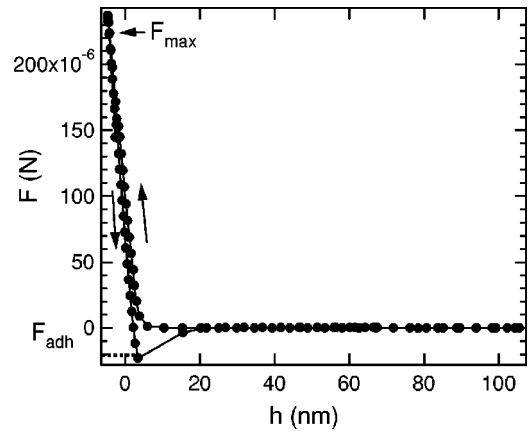
surfaces. The adhesion force between two ideal spheres has been calculated in the case of an elastic contact [8–10]:

$$F_{S\text{-}S}=f\pi\gamma R \tag{2}$$

with R the sphere radius, γ the solid/interstitial medium surface tension ($\gamma=\gamma_{SG}$ if the spheres are in a gas atmosphere, and $\gamma=\gamma_{SL}$ if they are immersed in a liquid), and f a numerical factor between 1.5 and 2. The lower value $f=1.5$ corresponds to the Johnson-Kendall-Roberts (JKR) calculation [8] and is obtained when the attractive forces are strong enough to deform the sphere surfaces. The higher value $f=2$ corresponds to the Derjaguin-Muller-Toporov (DMT) calculation [9], and is reached in the opposite limit of weak attraction
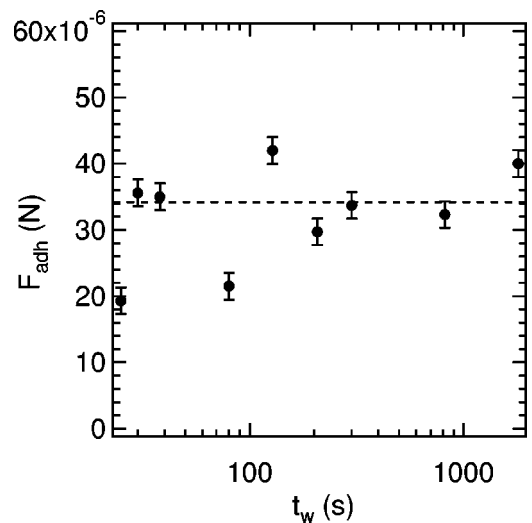

FIG. 3. The pull-off force F_{adh} of the surfaces as a function of the time t_w during which they have been in contact. During this time the value of the normal load is $F_{max}=225\pm5$ μN. The dashed line is the mean value of the adhesion force for this load.
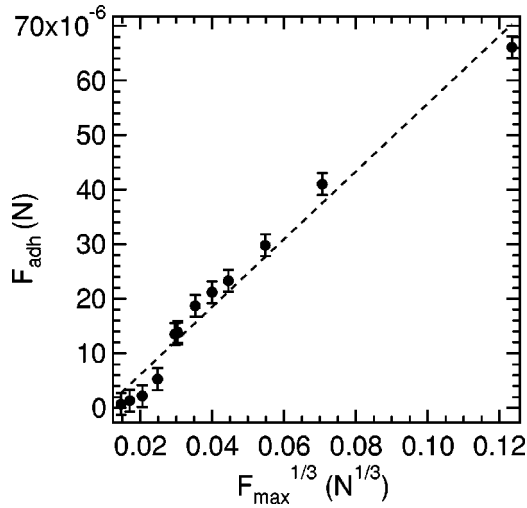
FIG. 4. Evolution of the adhesion force as a function of the maximum load force $F_{\max}$ to the power 1/3. The dashed line represents the best linear fit of the data.

and rigid solids. The JKR formula is usually used for adhesion in vacuum or in a dry gas, whereas the DMT expression is used in a liquid medium, since γ_{SL} is usually smaller than γ_{SG}. The JKR-DMT transition has been solved theoretically and studied experimentally with atomically smooth mica surfaces by Maugis and Gautier-Manuel [10].

In our system a crude approximation to estimate the Pyrex-dodecane surface tension is [11] $\gamma_{SL} = (\sqrt{\gamma_L} - \sqrt{\gamma_S})^2$ where $\gamma_L = 26$ mJ m^{-2} is the dodecane surface tension and γ_S the pyrex surface tension in vacuum. A typical value of γ_S for a ceramiclike Pyrex is $\gamma_S \approx 1$ J m^{-2}. This leads to $\gamma_{SL} \approx 0.7$ J m^{-2}. Therefore the adhesion force between a smooth sphere and plane in dodecane should lie between 12 mN and 16 mN (in the case of a contact between a sphere and a plane, the limiting values for f are 3 and 4). Therefore the nanometric roughness of our surfaces significantly screens the solid-solid interactions [12].

We have studied the dependency of the adhesion force on the time t_w during which the surfaces are held in contact, and on the maximum normal load applied to the contact $F_{\max}$. We find that the adhesion force does not depend significantly on t_w (Fig. 3). However, it depends significantly on $F_{\max}$ (Fig. 4). Since the contact time t_w is not an important parameter, the maximum load has been reached at a constant sphere velocity, and not in a constant time. The dependency observed is a scaling law $F_{adh} \propto F_{\max}^{1/3}$. Clearly this result is not compatible with the theoretical predictions for smooth surfaces. It is not compatible either with a purely elastic contact, since the surfaces keep the memory of the maximum load that has been applied to them at the point where they pull apart. This shows the occurrence of some plastic deformation in the contact.

Bowden and Tabor suggested that, in a contact between solid surfaces that are not atomically smooth, the plastic deformation of asperities should induce an adhesion force which depends on the normal force [13]. Their idea is that rough surfaces are in molecular contact only at the tips of their asperities, and because of the short range of attractive interactions only this molecular contact of area A_r contributes to the adhesion force. On the other hand, this area A_r depends on the normal load that has been applied on the surfaces, because of the plastic deformation of the tips of the asperities:

$$A_r = F_{\max}/H, \tag{3}$$

where H is the hardness of the solid material.

We use here the analysis of Bowden and Tabor to propose an expression for the adhesion force between rough curved surfaces. As long as the maximum load $F_{\max}$ does not exceed the elastic limit of the bulk of the solids, the overall deformation of the surfaces remains elastic, with stresses and strains in the bulk being given by Hertz's classical analysis. The area of this elastic contact region between the solids is

$$A_{app} = \pi a_H^2 = \pi \left[\frac{F_{\max} R}{E^*} \right]^{2/3} \tag{4}$$

with $E^* = 2E/3(1-\nu^2)$, E and ν being the Young modulus and Poisson ratio of the solid material. Inside this contact region, the surfaces are in contact only at the tips of their asperities. We assume that outside those solid-solid junctions the solid-solid interactions are negligible. The surface free energy gained in applying the load is then $\gamma_{SL} A_r$. We now assume that the number of such solid-solid junctions is large. Then, everything happens as if the surfaces were smooth with an effective surface tension

$$\gamma_{\text{eff}}^* = \gamma_{SL} \frac{A_r}{A_{app}}. \tag{5}$$

Using Eq. (2),

$$F_{adh} = 4 \gamma_{SL} R^{1/3} E^{*2/3} F_{\max}^{1/3}/H. \tag{6}$$

We have assumed here that the DMT model is valid ($f=4$) since the glass surface is a hard surface and the adhesion through dodecane is weak.

This expression gives a dependency of the adhesion on the power 1/3 of the maximum normal load, which is in good agreement with our experimental results. Indeed, the hypothesis of a large number of solid-solid junctions should be realized in our system since the roughness is weak. With a value of $H=6$ GPa for the Pyrex hardness [14], and assuming a typical area of 9 nm^2 for a solid-solid junction, the number of junctions under the load $F_{\max}=225$ μN is 4500. Using Eq. (6), one can estimate the value of the Pyrex-dodecane surface tension from the prefactor of the $F_{\max}^{1/3}$ dependency of F_{adh} observed in the experiments. With $R = 1.8$ mm, $E=60$ GPa, and $\nu=0.3$ one finds $\gamma_{SL} = 0.430$ mN/m, which is the order of magnitude expected for the Pyrex/dodecane surface tension.

In this paper, we have experimentally studied the adhesion force between two moderately rough surfaces of Pyrex immersed in a liquid, with an original surface force apparatus. We have shown that a roughness of 1 nm is enough for the adhesion force to decrease to a small fraction of its theoretical value for ideally smooth surfaces. In this system we

have not found any dependency of the adhesion force on the time during which the surfaces have been in contact, for times ranging from some seconds to 1 h. This means that the creep of the asperities in contact is negligible on those time scales. The main result of this study is that the adhesion force increases as the power 1/3 of the maximal load applied to the surfaces. We find that this effect can be explained with a crude model of plastic deformation of the tips of the asperities in contact, in good quantitative agreement with the data. An important feature of this model is that the adhesion force does not depend on the detailed shape of the roughness. Such a law for the adhesion of real contacts could be interesting for a better understanding of adhesion effects in powders or granular media. With such an adhesion law between two surfaces, we can estimate the effective surface tension between two glass beads of 200 μm diameter immersed in dodecane at the bottom of a pile. If the height of the pile is 10 cm, then Eq. (6) leads to an effective surface tension of a few mJ m^{-2}. This should lead to measurable effects in the mechanics of granular materials. Therefore it would be important to test this adhesion law with roughnesses of various sizes. Another important question is the role of the layer of liquid trapped between the asperities of the surfaces. Further work is in progress to understand these effects.

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