Adhesion and Friction Forces between Spherical Micrometer-Sized Particles

Lars-Oliver Heim and Jürgen Blum*
Astrophysikalisches Institut und Universitäts-Sternwarte, Friedrich-Schiller-Universität Jena, Schillergäßchen 3, 07745 Jena, Germany

Markus Preuss and Hans-Jürgen Butt
Institut für Physikalische Chemie, Johannes-Gutenberg-Universität Mainz, 55099 Mainz, Germany
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An experimental setup, based on the principles of atomic force microscopy (AFM), was used to measure directly the adhesion and rolling-friction forces between individual silica microspheres of radii between 0.5 and 2.5 μm. It showed that the linear dependence of the pull-off force on the particle radius is still valid for micron-sized particles. Rolling-friction forces between silica microspheres were measured for the first time by combining AFM methods and optical microscopy: They are $\sim$100 times lower than the corresponding adhesion forces.

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Adhesion and friction forces between small particles are important for a variety of natural phenomena and industrial processes. Examples are the aggregation and dispersal of powders and colloidal dispersions, and the flow properties of granular materials. Our particular interest was raised by the lack of knowledge on cosmic dust aggregation as a first step in planet formation. Depending on the adhesion forces, friction forces, and impact velocities, collisions between dust aggregates in the preplanetary nebula result in the formation of fluffy fractal structures, of compact aggregates, or in fragmentation [1].

In order to understand and predict the aggregation of small particles, the vertical and tangential forces between two particles in contact need to be known. When two particles in vacuum or in a gaseous environment come close, they usually experience attractive forces such as the van der Waals force. Once in contact, they are inevitably deformed due to their finite elasticity. Contact between two solid spheres is usually described by the model of Johnson, Kendall, and Roberts (JKR) [2] or by the model of Derjaguin, Muller, and Toporov (DMT) [3]. Both models are based on an earlier analysis by Hertz, who considered two elastic bodies in contact under an external load but ignored attractive interparticle forces [4]. In the JKR approach, the effective steady-state pressure in the contact circle is assumed to be the superposition of elastic Hertzian pressure and of attractive surface forces which act only over the contact area. As a result, a tensile force is necessary to separate the adhering particles. This pull-off force between two spherical particles is given by

$$F_{\mathrm{JKR}} = 3\pi R\gamma\,. \tag{1}$$

Here γ is the effective solid surface energy and R is the reduced radius of curvature of the two surfaces, $R = R_1R_2/(R_1 + R_2)$, with R_1 and R_2 being the individual particle radii.

DMT published an alternative theory which also accounts for noncontact forces in the vicinity of the contact area. It predicts a slightly higher pull-off force of

$$F_{\mathrm{DMT}} = 4\pi R\gamma\,. \tag{2}$$

In the JKR and DMT models, the separation force between two spherical particles is independent of the elastic material properties but is a linear function of the particle size and the surface energy. It turned out that both models are limiting cases of a more general description [5]. The JKR model is appropriate for large, soft bodies with high surface energies. For small, hard solid particles with low surface energy, the DMT model should be applied [6,7]. For silica (SiO_2) microspheres considered in this paper, the DMT model is expected to give more realistic adhesion values.

The main results of JKR theory have been verified experimentally for relatively soft materials and surfaces with large radii [8–11]. For particles with $R < 0.1$ mm, experimental results are rather limited. Rimai *et al.* [12] found that the contact radii for soft ($E \approx 10^6$ N/m^2) and small ($3\ \mu\mathrm{m} \leq R \leq 100\ \mu\mathrm{m}$) bodies do not depend on R as predicted by theory. Adhesion forces between particles and planar surfaces have been measured with the centrifugal method [13–16]. A significant part of the knowledge about the behavior of powders stems from such experiments, which are, however, restricted to particles larger than 5 μm. Otherwise, the centrifugal force is not strong enough to detach the adhering particles from the surface.

Enachescu *et al.* [17] verified the relation between contact area and load predicted by DMT theory with an atomic force microscope (AFM). Using electrically conducting tips and assuming that the conductance is proportional to the contact area, they found reasonable agreement between measured and calculated results. With the invention of the atomic force microscope [18] the interaction between individual small particles could for the first time be measured repeatedly and in detail [19–21]. Still, to our knowledge, the only systematic study

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of the size dependence of adhesion forces is the one of Ando and Ino, who measured forces between flat tips and submicron-sized asperities [22]. As predicted by the JKR and DMT models, they found a linear increase of the adhesion by increasing the size of the asperity. One objective of this paper is to experimentally verify the linear relation between the adhesion force and radius for small and hard particles. This is particularly important for most industrial powders and aerosols which consist of small grains. In addition, for irregular particles the asperities which form the actual contact usually have small contact radii.

For our experiments we chose spherical silica (SiO_2) particles with particle radii between 0.5 and 2.5 μm (Bangs Inc., Carmel, California, USA) because silicates are among the most abundant cosmic substances. To measure the adhesion force between two solid particles, silica microspheres were glued with epoxy heat resin (Epikote 1004, Shell) to a microscopy slide and to the ends of AFM cantilevers (Digital Instruments, Santa Barbara, California, USA, V-shaped, made of silicon nitride, 190 μm long, 0.6 μm thick) (see inset in Fig. 1). Spring constants of cantilevers were determined by measuring their resonance frequency before and after adding small end masses [23] as described previously [24].

All experiments were done in a specially developed setup (for details, see Ref. [24]). To obtain the force acting between two particles, the cantilever deflection was measured and multiplied with the spring constant. The deflection of the cantilever was determined by the change in position of a laser spot reflected off the free end onto a position sensitive device (United Detectors, UK, active area 30×5 mm^2). The advantage of a position sensitive device over the usually used split photodiode is the significantly larger dynamic range which also keeps a high sensitivity [25].

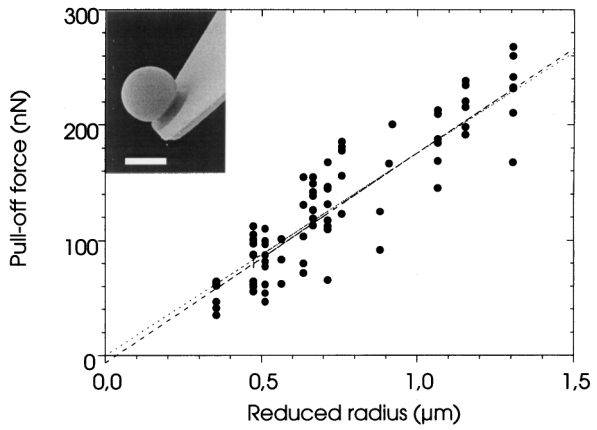

FIG. 1. Pull-off force versus reduced particle radius obtained from direct force measurements between silica microspheres. Each data point (solid circles) is an average value from seven adhesion measurements obtained with one pair of microspheres. The dashed line represents the best linear regression fit and gives a pull-off force of -6 nN at vanishing particle radius. The best linear fit to the data points through the origin of the diagram has a slope of 0.176 N/m (dotted line). The inset shows a SEM image of a silica microsphere glued to the end of an AFM cantilever. The scale bar indicates 3 μm.

Cantilevers were fixed to a movable cantilever holder. The experimental procedure was started by positioning the particle on the cantilever a few μm above a particle on the glass slide. Positioning was done with a micrometer stage under optical control (precision 0.5 μm) by the use of two microscopes with long-distance lenses which were mounted mutually perpendicular. Then, the particle on the glass slide was moved towards the other particle using a 15 μm range piezoelectric translator (Queensgate, DPT-CS, England) until contact was established. The translator stage was equipped with integrated capacitance position sensors with an accuracy of 1 nm. After contact had been established, the glass slide-particle unit was moved away from the cantilever-particle unit. At the point of separation, the pull-off force was determined. Complete force curves were usually taken in 20 s time intervals. This leads to typical relative velocities between the particles of 0.5 μm/s which we regard as quasistatic. The position of the sample and the deflection of the cantilever were recorded with a digital oscilloscope (12-bit effective resolution). All experiments were done at room temperature. After the experiments, the particle radii were measured using a scanning electron microscope (SEM).

Figure 1 shows our measured adhesion forces versus reduced particle radii. A regression analysis showed that, within the experimental errors, the adhesion force increases linearly by increasing reduced radius R. Extrapolating to zero radius, a linear fit gives a negligible force of (-6 ± 6) nN (dashed line in Fig. 1). In this respect, the results agree with predictions of the DMT and JKR models. Hence, continuum theories are still applicable although adhesion-induced particle deformations are of the order of interatomic distances only [26]. The adhesion force does not depend on the previously applied load (0–600 nN), ambient air pressure (10^2–10^5 Pa), or humidity (10%–40%). Hence, the capillary force due to a condensed meniscus of water is negligible at such low humidity, as was observed before [15,27]. From our measured normalized adhesion force of $F/R = [0.176 \pm 0.004(\text{stat}) \pm 0.026(\text{syst})]$ N/m (dotted line in Fig. 1), a surface energy of $\gamma = [0.0186 \pm 0.0004(\text{stat}) \pm 0.0028(\text{syst})]$ J/m^2 is calculated with the JKR model and $\gamma = [0.0140 \pm 0.0003(\text{stat}) \pm 0.0021(\text{syst})]$ J/m^2 with the DMT model. Here, the statistical error is the uncertainty of the slope of the dotted line in Fig. 1. The systematic error is due to the uncertainty of determining the spring constants of the cantilevers. The values of the surface energy are slightly lower than $\gamma = 0.025$ J/m^2 which has been determined from the elastic behavior of a silica powder [28] or $\gamma = 0.040$ J/m^2 as measured by a modified surface force apparatus [29]. Although the proportionality between

adhesion force and particle radius was verified, we cannot explain the low surface energy obtained.

Results from repeated adhesion measurements with one pair of particles were highly reproducible and showed a standard deviation of only 4%. In contrast, results obtained with different pairs of particles having identical reduced radii varied considerably more and showed standard deviations from the mean value of 25% which possibly indicates the presence of small-scale surface heterogeneity.

Surface roughness is known to decrease the adhesion force [30]. To get information about the surface roughness of the contact zones, we imaged silica microspheres with an AFM using oxide-sharpened AFM tips (Olympus Ltd., Tokyo) for high resolution. The roughness (root mean square deviation from the ideal sphere) was $(0,13 \pm 0,01)$ nm, measured over an area of 50×50 nm^2, which is comparable to the contact area [26]. The roughness value is considerably lower than the expected deformation δ, so that roughness effects should be negligible.

In addition to adhesion, friction forces influence the aggregation, dispersal, and flow behavior of powders and the processes occurring in collisions between particles. Based on the JKR theory, Dominik and Tielens have developed an expression for the friction forces in transversal particle-particle contacts [31]. It turns out that the sliding-friction forces between spherical surfaces exceed the rolling-friction forces by many orders of magnitude so that, in collisions between particle aggregates, restructuring will be caused by rolling of the constituents whenever the impact energy is sufficiently large. For the rolling-friction force between two spherical particles, Dominik and Tielens derived

$$F_r = 6\pi\gamma\xi\,. \tag{3}$$

Here, ξ is the critical rolling displacement, which is the distance a sphere may roll on top of the other before irreversible rearrangement in the contact zone occurs. In general, ξ should depend on the particle size. A lower limit for ξ is given by the mean distance between neighboring atoms in the material so that $\xi \geq 0.2$ nm. The maximum value for ξ is given by the radius of the contact area a_0 between the two adhering particles. For $R_1 = R_2 = 1$ μm and $\gamma = 0.014$ J/m^2, this sets an upper limit at $\xi \leq 14$ nm [26] so that we expect a rolling-friction force between 5×10^{-11} and 4×10^{-9} N. To our knowledge, rolling-friction forces between spherical microparticles have not been determined experimentally. However, the stick-slip behavior of rolling motion has been recently investigated for carbon nanotubes [19].

In order to measure rolling-friction forces directly, we produced chainlike structures of 5 to 20 microspheres and tested their resistance to a forced motion on one end of the chain while the other end was fixed to a tipless AFM cantilever [Fig. 2(a)]. Chainlike structures were produced from aggregate precursors [32] [Fig. 2(b)] by pulling on an aggregate with the AFM tip until a chain was formed. Monodisperse silica spheres of 0.95 μm radius (hence $R = 0.475$ μm) were used. We investigated a sample of 11 different particle chains on which we applied a forced up-and-down motion through the piezoelectric translator. The frequency of the piezoelectric-crystal motion was kept constant at 0.1 or 1 Hz with peak-to-peak amplitudes of 4 or 8 μm. For these experiments, the high-resolution long-distance microscope was additionally equipped with a video camera which allowed us to observe structural changes in the chains. Figure 2(c) shows an example from a measurement cycle which encompasses a total of 500 images. Each of the snapshots in Fig. 2(c) was taken roughly 2.5 s after the previous image shown, thus representing a full measurement cycle, starting from maximum stretching on the left side. A movie of the particle chain oscillation under external forced motion is also available [33].

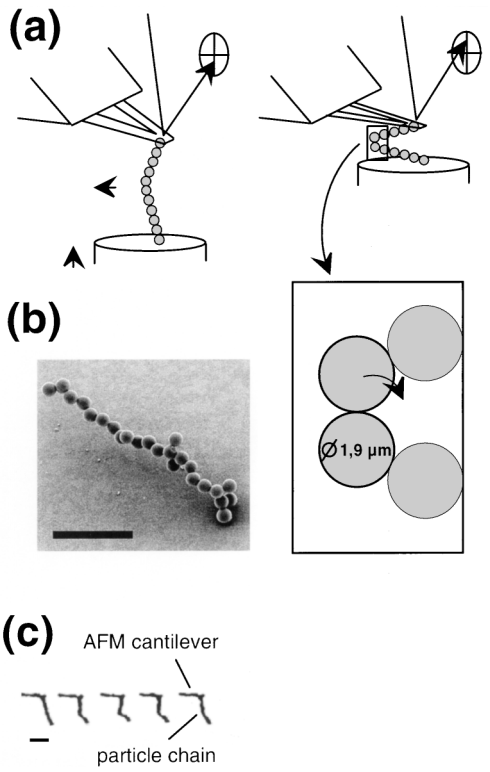

FIG. 2. Principles of rolling-friction force measurements with particle chains (a). SEM image of a typical microsphere aggregate precursor (b). Sequence of optical microscope images taken every 2.5 s during one bending-and-stretching cycle of a microsphere chain (c). The forced up-and-down motion of the lower end of the aggregate stems from a piezoelectric stage which is not visible in the images. The scale bars in (b) and (c) indicate 10 μm.

We calculated F_r from the measured force at the position of maximum angular restructuring of the particle chains, taking into account each individual geometric arrangement (lever arm) as imaged by long-distance microscopy.

In total, we sampled 122 force-displacement cycles for the different particle chains, oscillation amplitudes, and frequencies mentioned above. We get $F_r = [8.5 \pm 0.3(\text{stat}) \pm 1.3(\text{syst})] \times 10^{-10}$ N for the mean rolling-friction force. The statistical error is the uncertainty of the mean value calculated from the results of all 122 force cycles. Peak-to-peak variations of individual force measurements were as much as a factor 3. The systematic error is due to the uncertainty of determining the spring constants of the cantilevers.

Using the theory of Dominik and Tielens [31] with $\gamma = 0.014$ J/m^2, a critical displacement $\xi = 3.2$ nm is calculated. This is larger than the minimum displacement of 0.2 nm anticipated by Dominik and Tielens. It is, however, not unrealistic since it is still much smaller than the calculated contact radius. Hence, the critical displacement is of the order of ten interatomic distances rather than one.

In conclusion, with a novel approach we verified the proportionality between adhesion force and particle radius as predicted by DMT theory for microspheres with radii between 0.5 and 2.5 μm. Rolling-friction forces between the same microspheres were measured to be $\sim$0.01 of the corresponding pull-off forces. This is 1 order of magnitude larger than previously estimated.

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*To whom correspondence should be addressed.
Present address: Space Science Division, Naval Research Laboratory, 4555 Overlook Av. SW, Washington, D.C. 20375-5320.
Email address: jblum@ssd5.nrl.navy.mil

[1] S. J. Weidenschilling and J. N. Cuzzi, in *Protostars and Planets III*, edited by D. C. Black and M. S. Matthews (University of Arizona Press, Tucson, 1993), p. 1031.
[2] K. L. Johnson, K. Kendall, and A. D. Roberts, Proc. R. Soc. London A **324**, 301 (1971).
[3] B. V. Derjaguin, V. M. Muller, and Y. P. Toporov, J. Colloid Interface Sci. **53**, 314 (1975).
[4] H. Hertz, J. Reine Angewandte Mathematik **92**, 156 (1882).
[5] D. Maugis, J. Colloid Interface Sci. **150**, 243 (1992).
[6] D. Tabor, J. Colloid Interface Sci. **58**, 2 (1977).
[7] V. M. Muller, V. S. Yushchenko, and B. V. Derjaguin, J. Colloid Interface Sci. **92**, 92 (1983).
[8] R. G. Horn, J. N. Israelachvili, and F. Pribac, J. Colloid Interface Sci. **115**, 480 (1987).
[9] M. K. Chaudhury and G. M. Whitesides, Science **255**, 1230 (1992).
[10] H. J. Christenson, Langmuir **12**, 1404 (1996).
[11] B. J. Briscoe, K. K. Liu, and D. R. Williams, J. Colloid Interface Sci. **200**, 256 (1998).
[12] D. S. Rimai, L. P. DeMejo, W. B. Vreeland, and R. C. Bowen, Langmuir **10**, 4361 (1994).
[13] R. I. Larsen, Ind. Hygiene J. **19**, 265 (1958).
[14] M. C. Kordecki and C. Orr, Arch. Environ. Health **1**, 1 (1960).
[15] M. Corn, in *Aerosol Science*, edited by C. N. Davies (Academic Press, New York, 1966), pp. 359–392.
[16] F. Podczeck and J. M. Newton, J. Pharm. Sci. **84**, 1067 (1995).
[17] M. Enachescu, R. J. A. van den Oetelar, R. W. Carpick, D. F. Ogletree, C. F. J. Flipse, and M. Salmeron, Phys. Rev. Lett. **81**, 1877 (1998).
[18] G. Binnig, C. F. Quate, and C. Gerber, Phys. Rev. Lett. **56**, 930 (1986).
[19] M. R. Falve *et al.*, Nature (London) **397**, 236 (1999).
[20] W. A. Ducker, T. J. Senden, and R. M. Pashley, Nature (London) **353**, 239 (1991).
[21] H.-J. Butt, Biophys. J. **60**, 1438 (1991).
[22] Y. Ando and J. Ino, Wear **216**, 115 (1998).
[23] J. P. Cleveland, S. Manne, D. Bocek, and P. K. Hansma, Rev. Sci. Instrum. **64**, 403 (1993).
[24] M. Preuss and H.-J. Butt, Langmuir **14**, 3164 (1998).
[25] M. Pierce, J. Stuart, A. Pungor, P. Dryden, and V. Hlady, Langmuir **10**, 3217 (1994).
[26] The contact radius under zero load for two spheres of identical material is $a_0 = [18\pi\gamma R^2(1-\nu^2)/E]^{1/3}$, where E is the Young modulus and ν is the Poisson ratio of the particle material. The deformation of the particles due to their mutual attraction, $\delta = (1/3)(a_0^2/R)$, is comparable to interatomic distances. [The calculation of the contact radius and the deformation is based on JKR theory; more precise calculations [see D. Maugis, Langmuir **11**, 679 (1995)] showed that for $\delta m \approx (2RE/3\pi\gamma_S)^{1/3} > 10$ the JKR theory can be applied to calculate a_0 and δ, although the adhesion force is estimated too low.] With $E = 7.3 \times 10^{10}$ N/m^2 and $\nu = 0.17$ for silica [S. Spinner, J. Am. Ceram. Soc. **45**, 394 (1962)], $R = 1$ μm and a typical surface energy of $\gamma = 0.025$ J/m^2 [K. Kendall, N. M. Alford, and J. D. Birchall, Nature (London) **325**, 794 (1987)], a contact radius of $a_0 = 27$ nm and an equilibrium particle deformation of $\delta = 0.24$ nm is derived.
[27] F. Podczeck, J. M. Newton, and M. B. James, J. Colloid Interface Sci. **187**, 484 (1997).
[28] K. Kendall, N. M. Alford, and J. D. Birchall, Nature (London) **352**, 794 (1987).
[29] R. G. Horn, D. T. Smith, and W. Haller, Chem. Phys. Lett. **162**, 404 (1989).
[30] K. N. G. Fuller and D. Tabor, Proc. R. Soc. London A **345**, 327 (1975).
[31] C. Dominik and A. G. G. M. Tielens, Philos. Mag. A **72**, 783 (1995).
[32] For the method of fluffy aggregate production, see J. Blum, G. Wurm, T. Poppe, and L.-O. Heim, in *Laboratory Astrophysics and Space Research*, Astrophysics and Space Science Library Vol. 236, edited by P. Ehrenfreund, C. Krafft, H. Kochan, and V. Pirronello (Kluwer, Dordrecht, 1999), pp. 399–423.
[33] See http://www.astro.uni-jena.de/Users/heim/heim.html