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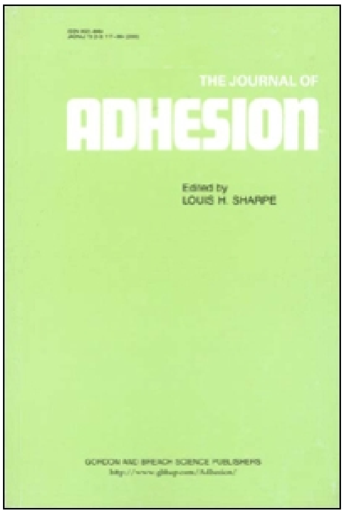

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# Adhesion of Small Spherical Particles to Substrates Immersed in Liquids

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The force required to start small, untreated or siliconized glass spheres rolling on an inclined copper-coated glass surface was determined in water and biphenyl melt. The results establish there are van der Waals attractions between the spheres and substrate. Hamaker coefficients of the studied systems were calculated.

## 1. INTRODUCTION

The main forces responsible for the adhesion of small particles, suspended in a liquid, to a solid surface will normally be van der Waals forces and electrostatic forces. The actual strength of the adhesive bond may also depend on substrate and particle roughness, particle size and shape, the nature of the particle, surface contact area and surface contamination.[1] In the presence of a liquid, the net van der Waals forces may be repulsive.[2] In the case of a spherical particle (1) of radius $R$, suspended in a liquid (3), and separated from a plane solid (2) by a distance $d$, the van der Waals force can be calculated approximately from the relation due to Hamaker:[3]

$$F = \frac{A_{132} R}{6d^2} \tag{1}$$

where $A_{132}$ is the effective Hamaker coefficient of the system. When this coefficient is positive, the force is attractive, and when it is negative, there is a repulsive force.

The techniques available for measurement of adhesion between particles and planar surfaces include the inclined plane,[4] centrifuge methods,[5] aerodynamic or hydrodynamic methods[4,6] and a gravimetric method.[1] While the centrifuge method is particularly suited for submicron particles, the best method for large spherical particles (greater than 2 μm in diameter) is the inclined plane.

Particle adhesion to various substrates is of interest for practical as well as theoretical reasons.[1,5] Our particular interest in particle adhesion to flat surfaces stems from our investigations of particle behaviour at solidification fronts.[2,7–9] In these experiments, particles are embedded in the melt of a suitable matrix and solidification is induced in a horizontal direction, *i.e.*, with a more-or-less vertical solidification front. As these particles may either settle to the bottom of the cell or else float to the top, friction of the particles at either bottom or top of the cell may become a problem.

The freezing-front experiments provided indirect evidence[7] that for particles less than approximately 100 μm in diameter, friction with the cell floor is unimportant. But as particle size increases, friction can produce adverse effects. We describe and discuss here an experiment in which friction between particles and substrates is studied as a function of particle size and material properties.

## 2. EXPERIMENTAL

The particles used are siliconized and untreated glass spheres ranging in size from 135 μm to 190 μm. As a test of the apparatus and procedure, water was first used with large glass spheres, 4.5 mm in diameter. The substrates are smooth copper surfaces, produced by vapour deposition in high vacuum onto clean microscope glass slides. Water and biphenyl melt were used as matrix liquids. Untreated glass spheres were cleaned with chromic acid and rinsed with toluene. Siliconized glass spheres were prepared as follows: after cleaning, the glass beads were heated in silicone oil to approximately 150°C for $2\frac{1}{2}$ hours, and allowed to cool to room temperature while still in the oil. The silicone oil was decanted, and the glass spheres rinsed in toluene to wash off excess silicone oil not bonded to the glass.

Experiments were carried with both sets of particles in water at room temperature (21 ± 2°C), and in biphenyl melt maintained between 77 and 83°C, *i.e.*, approximately 10°C above the melting point.

The inclined plane technique was chosen since it is ideal for large particle sizes, above 2 μm in diameter. The experimental set-up is schematically given in Figure 1. Briefly it consists of a glass trough (100 × 100 × 50 mm inner dimensions) which can be electrically heated from below. The temperature

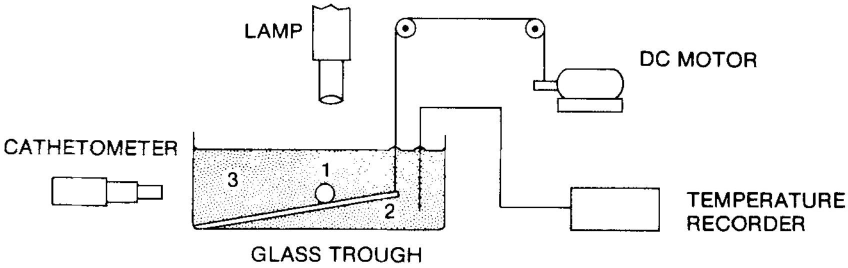

FIGURE 1 Schematic of the experimental set up. A particle 1 is positioned on a substrate 2, immersed in the liquid 3.

inside the trough was monitored with a thermocouple and a recorder. A cathetometer positioned in front of the trough was used to record the size and vertical position of a particle positioned on a marked point on the surface of the copper-coated glass slide (75 × 25 × 1 mm). A lamp at the rear of the trough provided illumination. A silk fibre connected to the rotor of a d.c. motor *via* pulleys permitted one end of the copper-coated glass slide to be raised while the other end was pivoted at the inner edge of the trough until, at an angle of inclination $\phi$, particles started to roll down the slide. The motor speed was adjusted to provide a slow and steady speed of 0.078 cm/min, and the particle was continuously observed through the telescope of the cathetometer. The glass trough was filled two-thirds with the liquid, then the glass spheres were deposited singly with tweezers at predetermined points on the copper surface. The sizes and initial positions of the particles were measured with the cathetometer which could be read to better than $\pm 2 \times 10^{-4}$ cm. As one end of the copper-coated glass slide was raised slowly, the angle of inclination $\phi$ at which rolling of the glass particles occurred was determined by noting the final position of the particle. The angle $\phi$ was calculated from the expression $\sin \phi = h/L$ where $h$ is the vertical distance through which the particle was lifted before rolling down and $L$ is the distance of the particle from the pivot measured on the surface of the copper-coated glass slide.

## 3. RESULTS

The angles of inclination at which sliding or rolling of the glass spheres occurred in water and in biphenyl melts are listed in Tables I and II respectively.

In the four cases, the general trend is an increase of the angle of inclination at which rolling occurs, with decreasing particle size. Scatter in these data may be due to irregularities in the shape of the glass spheres and imperfections of the substrate.

TABLE I

Angles for which rolling occurs for water as test liquid, for siliconed and untreated glass spheres

| Particle diameter | | Untreated glass beads | | Siliconed glass beads | |
|---|---|---|---|---|---|
| *D* (cm) | *L* (cm) | *h* (cm) | $\sin\phi = h/L$ | *h* (cm) | $\sin\phi = h/L$ |
| 0.4500 | 3 | 0.3300 | 0.1100 | 0.1095 | 0.0365 |
| 0.4500 | 3 | 0.2732 | 0.0911 | 0.1580 | 0.0527 |
| 0.4500 | 3 | 0.2160 | 0.0720 | 0.1620 | 0.0540 |
| 0.4500 | 3 | 0.2725 | 0.0908 | — | |
| 0.4500 | 4 | 0.3320 | 0.0830 | 0.1592 | 0.0398 |
| 0.4500 | 4 | 0.4200 | 0.1050 | 0.2100 | 0.0525 |
| 0.4500 | 4 | | — | 0.2200 | 0.0550 |
| 0.4500 | 5 | 0.4328 | 0.0866 | 0.2352 | 0.0470 |
| 0.4500 | 5 | 0.4520 | 0.0904 | 0.2435 | 0.0487 |
| 0.4500 | 5 | 0.4730 | 0.0946 | 0.2388 | 0.0478 |
| 0.0190 | 3 | 0.5128 | 0.1709 | — | |
| 0.0190 | 3 | 0.5933 | 0.1978 | | — |
| 0.0182 | 3 | — | | 0.2801 | 0.0934 |
| 0.0182 | 3 | — | | 0.3055 | 0.1018 |
| 0.0180 | 3 | — | — | 0.2474 | 0.0825 |
| 0.0180 | 3 | — | — | 0.3071 | 0.1024 |
| 0.0170 | 3 | | | 0.2311 | 0.0770 |
| 0.0170 | 3 | — | | 0.2474 | 0.0825 |
| 0.0167 | 3 | — | | 0.3935 | 0.1312 |
| 0.0165 | 3 | 0.5780 | 0.1927 | | — |
| 0.0160 | 3 | — | — | 0.3750 | 0.1250 |
| 0.0160 | 3 | — | | 0.4230 | 0.1410 |
| 0.0155 | 3 | 0.8075 | 0.2692 | 0.4230 | 0.1410 |
| 0.0155 | 3 | | — | 0.4275 | 0.1425 |
| 0.0150 | 3 | 0.6250 | 0.2083 | 0.4200 | 0.1400 |
| 0.0150 | 3 | 0.4765 | 0.1588 | 0.4230 | 0.1410 |
| 0.0150 | 3 | 0.5428 | 0.1809 | — | |
| 0.0150 | 3 | 0.7348 | 0.2449 | | |
| 0.0135 | 3 | 0.8230 | 0.2743 | 0.5476 | 0.1825 |

The angle of inclination was smaller for siliconized glass spheres than for untreated glass spheres in the same liquid, and was smaller in biphenyl than in water for the same type of particles.

## 4. DISCUSSION

Let us denote the apparent weight of the particle in the liquid by $F_0$.

$$F_0 = \tfrac{4}{3}\pi R^3(\rho_1 - \rho_2)g \qquad (2)$$

where

$R$: particle radius,
$g$: acceleration due to gravity,
$\rho_1, \rho_2$: particle and liquid densities, respectively.

TABLE II

Angles for which rolling occurs for biphenyl melt as the test liquid, for siliconed and untreated glass spheres

| Particle diameter | | Untreated glass beads | | Siliconed glass beads | |
|---|---|---|---|---|---|
| $D$ (cm) | $L$ (cm) | $h$ (cm) | $\sin\phi = h/L$ | $h$ (cm) | $\sin\phi = h/L$ |
| 0.0190 | 3 | 0.3900 | 0.1300 | 0.2660 | 0.0887 |
| 0.0182 | 3 | 0.4320 | 0.1440 | 0.2660 | 0.0887 |
| 0.0182 | 3 | 0.3785 | 0.1262 | 0.2380 | 0.0793 |
| 0.0170 | 3 | 0.4175 | 0.1392 | 0.2660 | 0.0887 |
| 0.0170 | 3 | 0.5315 | 0.1772 | — | — |
| 0.0160 | 3 | 0.5315 | 0.1772 | 0.3260 | 0.1087 |
| 0.0160 | 3 | 0.4175 | 0.1392 | 0.2120 | 0.0707 |
| 0.0160 | 3 | 0.3900 | 0.1300 | — | — |
| 0.0160 | 3 | 0.5325 | 0.1775 | — | — |
| 0.0150 | 3 | 0.5315 | 0.1772 | 0.3300 | 0.1100 |
| 0.0140 | 3 | 0.5685 | 0.1895 | 0.4360 | 0.1453 |
| 0.0130 | 3 | — | — | 0.4360 | 0.1453 |

For an angle of inclination $\alpha$ of the plane substrate, the forces acting on the particle are:

—a force normal to the substrate, $F_N$:

$$F_N = F_0 \cos\alpha + F_A \tag{3}$$

$F_A$ being the force of adhesion between the substrate and the particle;

—a force parallel to the substrate, $F_T$

$$F_T = F_0 \sin\alpha \tag{4}$$

Rolling will start when the tangential force $F_T$ becomes equal to the static rolling friction force $F_F$. This happens when $\alpha = \phi$. Then:

$$F_T = F_F = F_0 \sin\phi$$

and we can write the coefficient of rolling friction as the ratio of the friction force to the normal force:

$$\mu = \frac{F_F}{F_N} = \frac{F_0 \sin\phi}{F_0 \cos\phi + F_A} \tag{5}$$

$\mu$ is a static friction coefficient because it is related to the friction force which has to be overcome in order to initiate the movement. A result known as Amontons' law[10] in the field of tribology states that the static friction coefficient is independent of the normal force between the rubbing bodies. Except in some very special cases (breakage of surface sublayers, or softening of the materials due to friction heating) this law is usually satisfied over a wide range of load values. It is also well known that the friction coefficient is strongly dependent on the nature of the materials and environment. We shall therefore assume that the friction coefficient is constant for each set of experiments but has different values for the four systems studied.

Let us express sin $\phi$ from Eq. (5):

$$\sin\phi = \mu\cos\phi + \mu\frac{F_A}{F_0} \tag{6}$$

In our experiments sin $\phi$ is smaller than 0.25. Then cos $\phi$ is greater than $\sqrt{1-0.25^2} = 0.97$. As $\mu$ is a constant for each set of experiments and as $0.97 < \cos\phi < 1$, the quantity $\mu\cos\phi$ will be almost constant. Variations of sin $\phi$ will then depend on variations of the quantity $\frac{F_A}{F_0}$. The relation between $F_0$ and $R$ is given by Eq. (2). $F_A$ is the sum of electrostatic and van der Waals forces. If electrostatic effects are negligible, $F_A$ can be expressed by Eq. (1). In this case (6) becomes:

$$\sin\phi = \mu\cos\phi + \mu\frac{A_{132}R}{6d^2\frac{4}{3}\pi R^3(\rho_1-\rho_2)g} \tag{7}$$

When van der Waals forces are attractive, there is contact between particle and substrate and $d$ has a constant minimal value $d_0$ which is the distance between the outermost centers of polarization of two nearest atoms belonging to the two solids. The value $d_0 = 2$Å is a good approximation, as discussed in Ref. (2). Then, from (7):

$$\sin\phi = A + \frac{B}{R^2} \tag{8}$$

where $A$ and $B$ are constants.

It is interesting to plot our results in the form $\sin\phi = f\left(\frac{1}{R^2}\right)$. This has been done in Figure 2 for water systems and in Figure 3 for biphenyl systems. Each data point represents an average of several values. In spite of the scatter of the experimental results, the best fits for the experimental points are straight lines, which verify Eq. (8) and validate the assumption that electrostatic effects were negligible in our systems. The straight lines drawn on Figures 2 and 3 were obtained by linear regression. The positive slope of these lines shows van der Waals forces are attractive and the particles will touch the solid substrate. This justifies the use of $d_0$, the minimal distance between the particle and the substrate, instead of the variable distance $d$, used in Eq. (7).

Using $d_0 = 2$Å we calculated the friction coefficients and the Hamaker coefficients of our four systems: friction coefficients are obtained from the intercept of the straight lines with the vertical axis, Hamaker coefficients from

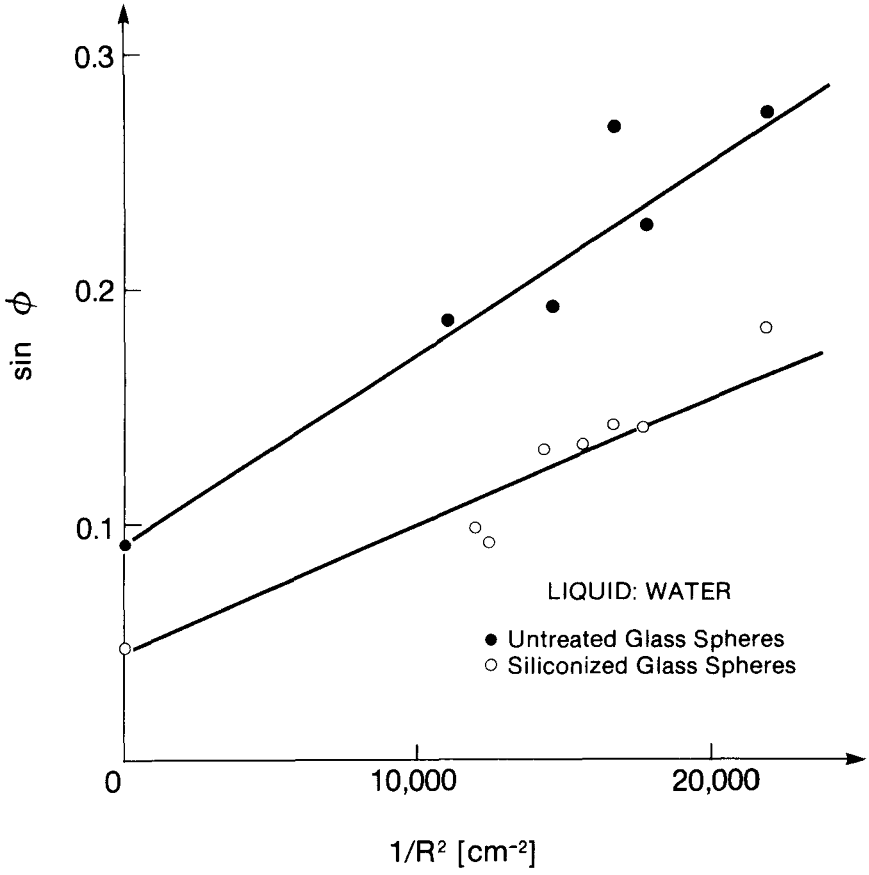

FIGURE 2 The dependence of the angle of inclination $\phi$, at which rolling occurs on the radius $R$ of the particle, for untreated and siliconized glass spheres in water. The straight lines $\sin\phi = A + \frac{B}{R^2}$ are obtained by linear regression.

the slope $m$ of the straight lines by using the relation:

$$A_{132} = m\frac{8\pi\, d_0^2(\rho_1-\rho_2)g}{\mu} \tag{9}$$

and taking the density of glass spheres as $\rho_1 = 2.5$ g/ml, that of biphenyl at 80°C as $\rho_2 = 0.992$ g/ml. Values of the static friction coefficient $\mu$, and the Hamaker coefficient $A_{132}$ are given in Table III for the four systems studied. All friction coefficients are between 0.015 and 0.091 which is quite reasonable, and in both liquids siliconized spheres give lower values than glass spheres;

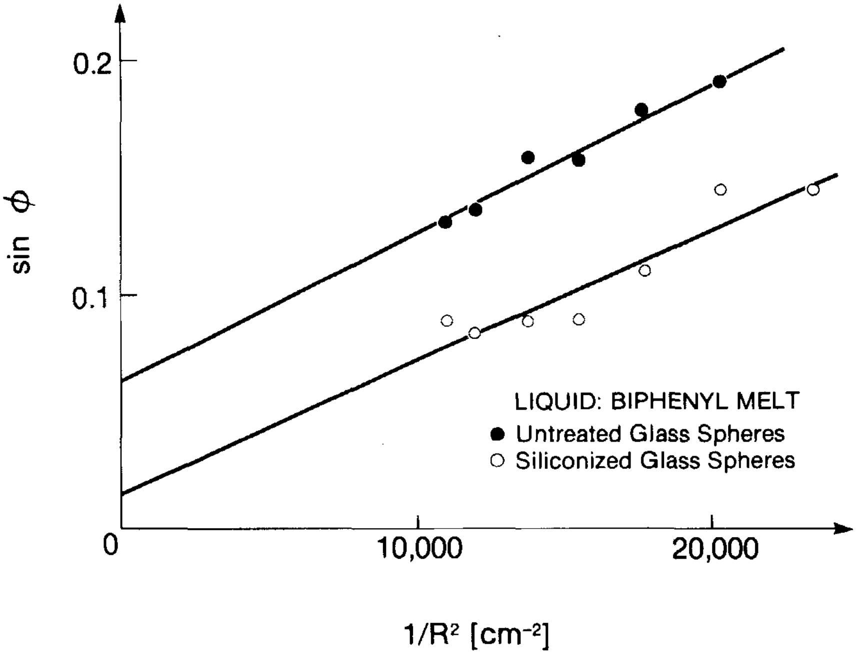

FIGURE 3 The dependence of the angle of inclination $\phi$, at which rolling occurs on the radius $R$ of the particle for untreated and siliconized glass spheres in biphenyl melt. The straight lines $\sin \phi = A + \frac{B}{R^2}$ are obtained by linear regression.

TABLE III

Static friction coefficient $\mu$, slope $m$ of the straight line obtained by linear regression, correlation coefficients weighted over the number of data points, and Hamaker coefficient $A_{132}$, for the four systems studied

| System | Friction coefficient $\mu$ | Slope $m$ of the straight line (cm$^2$) | Correlation coefficient | Hamaker Coefficient $A_{132}$ (erg/cm$^2$) |
|---|---|---|---|---|
| Copper–water–untreated glass | 0.091 | $8.15\ 10^{-6}$ | 0.98 | $1.33\ 10^{-15}$ |
| Copper–water–siliconized glass | 0.046 | $5.39\ 10^{-6}$ | 0.98 | $1.75\ 10^{-15}$ |
| Copper–biphenyl melt-untreated glass | 0.063 | $6.23\ 10^{-6}$ | 0.96 | $1.48\ 10^{-15}$ |
| Copper–biphenyl melt-siliconized glass | 0.015 | $5.55\ 10^{-6}$ | 0.92 | $5.48\ 10^{-15}$ |

this agrees with the fact that silicone monolayers are good boundary lubricants.

Hamaker coefficients are between 1.33 $10^{-15}$ and 5.48 $10^{-15}$ erg/cm$^2$. They fall in the range of usual values for Hamaker coefficients (between $10^{-15}$ and $10^{-13}$ erg/cm$^2$) and correspond to rather weak interactions.

For biphenyl systems, results are not very accurate, since small differences of the slopes of the straight lines yield significant variations in the friction coefficients and thus in the Hamaker coefficients. For water, the experimental points for the large glass spheres were also plotted and lead to a more accurate determination of the friction and Hamaker coefficients.

It is to be noted that for a system with a negative Hamaker coefficient, one would expect a straight line of negative slope in the representation $\sin \phi = f\left(\frac{1}{R^2}\right)$. Such a line would cut the horizontal axis for a value $\frac{1}{R_0^2}$. Spheres of radius smaller than $R_0$ would not adhere to the substrate but roll off under the slightest external force. For such situations the distance of separation $d$ from the substrate would be greater than $d_0$. The value of $d$ would be that giving a repulsive van der Waals force equal to the apparent weight of the particle.

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