

Floating particles which should sink

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Floating particles which should sink are held up by capillary forces at the line of contact of the three phases on the particle surface. The hanging depth between the contact line and the highest point on the meniscus depends on whether the meniscus attaches to the particle on a smooth face with a uniquely determined normal or at a corner or edge where the normal is undefined. Here we show that the hanging depth is determined by the position of the contact line on a floating sphere when the contact angle is fixed by the Young-Dupré law and by the value of the contact angle which changes with the weight of the particle when the contact line is pinned at a sharp edge.

Floating particles with sharp edges

It is well known, but not well understood that liquid-air-solid interfaces tend to locate on sharp edges and corners; heavy objects with sharp edges can be suspended in a free surface (1, 2). Here we show that a heavier-than-liquid cylinder with flat ends sinks to a stable floating position in which the sharp edge is attached to the interface (figure 1). The weight of the cylinder can be changed by inserting ball bearings in a cone cavity centrally cut in the top of the cylinder. The cylinder will float in this manner even as the weight is increased with the caveat that the contact angle adjusts as the weight is added in such a way as to increase the vertical component of the interfacial force. The contact angle at the sharp edge is determined by a static force balance. At a sharp edge the contact line rather than the contact angle is fixed.

Vertical force balance

The weight mg of a heavy particle in equilibrium is balanced by a capillary force F_c and net pressure force F_p satisfying

$$F_c + F_p = mg. \quad (1)$$

If the particle is a cylinder of radius R and height h with a flat top, hanging from its edge as in figure 1, then $F_c = 2\pi R\sigma \sin\alpha$, where σ is the surface tension and $F_p = (P_0 - P_a)\pi R^2$, where $P_0 = P_a + \rho_l g(h + H_\infty)$ and (1) may be written as

$$2\pi R\sigma \sin \alpha + \rho_l gV + \pi R^2 H_\infty \rho_l g = mg, \quad (2)$$

where $V = \pi R^2 h$ is the volume of the cylinder.

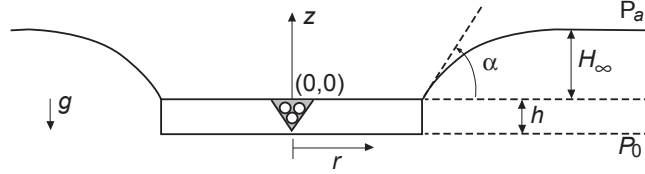


Figure 1. Heavier than liquid cylinder hanging from a sharp edge. The capillary force is given by $F_c = 2\pi R\sigma \sin \alpha$, where σ is the interfacial tension. The meniscus is $z = H(r)$; $H(\infty) = H_\infty$ is the highest value of z on the meniscus. P_a is air pressure and P_0 is the pressure at the bottom of the cylinder $z = -h$. both hydrophobic and hydrophilic cylinders may float in this manner; a glass sphere will not float on water but a glass cylinder with a sharp edge will float.

If the particle is a sphere of radius R , on which the contact angle is prescribed, as shown in figure 2, then the capillary force is given by $F_c = 2\pi R \sin \theta_c \sigma \sin \alpha$, where θ_c gives the position of the contact line (see figure 2). The pressure force can be obtained by integrating the pressure over the sphere surface:

$$\begin{aligned} F_p &= \int_0^{\theta_c} p \cdot \cos \theta \cdot (2\pi R \sin \theta) R d\theta \\ &= \rho_l g \pi R^3 \left(\frac{2}{3} - \cos \theta_c + \frac{1}{3} \cos^3 \theta_c \right) + \rho_l g H_\infty \pi R^2 \sin^2 \theta_c \end{aligned}$$

and (1) may be written as

$$2\pi R \sin \theta_c \sigma \sin \alpha + \rho_l g \pi R^3 \left(\frac{2}{3} - \cos \theta_c + \frac{1}{3} \cos^3 \theta_c \right) + \rho_l g H_\infty \pi R^2 \sin^2 \theta_c = mg. \quad (3)$$

Equation (3) may be written as

$$\sin \theta_c \sin \alpha = \left[mg - \rho_l g \pi R^3 \left(\frac{2}{3} - \cos \theta_c + \frac{1}{3} \cos^3 \theta_c \right) - \rho_l g H_\infty \pi R^2 \sin^2 \theta_c \right] / (2\pi R \sigma).$$

The left side of the equation above, consequently, the right side, lies in the range $-1 \leq \sin\theta_c \sin\alpha \leq 1$. It can be inferred from the equation that large and heavy particles must sink.

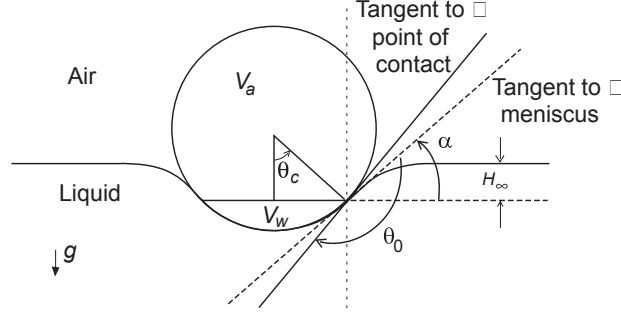


Figure 2. (3,4,5) Heavier than liquid hydrophobic sphere hanging on the contact line at θ_c . The angle α is fixed by the Young-Dupr e law. θ_c is determined by the force balance (3). θ_c is the contact angle.

The vertical force balance for a heavier than liquid particle floating at the interface can be written as an Archimedes' principle generalizing (2) and (3):

$$F_c + \rho_l g V_w + \rho_l g H_\infty A = mg \quad (4)$$

where V_w is the volume of the particle immersed in the liquid and A is the area of the ring of contact. In the sphere case, $V_w = \pi R^3 \left(\frac{2}{3} - \cos\theta_c + \frac{1}{3} \cos^3\theta_c \right)$ and $A = \pi R^2 \sin^2\theta_c$; in the cylinder case, $V_w = \pi R^2 h$ and $A = \pi R^2$. The particle is buoyed up by the weight of liquid displaced by the part of the particle immersed in the liquid and the liquid cylinder $H_\infty A$ above the contact ring.

The shape of the interface $z = H(r)$ is determined by the balance between the pressure drop $\rho g [H(r) - H_\infty]$ across the interface and the surface tension σ times surface curvature. In cylindrical coordinates this is expressed as

$$\rho g [H(r) - H_\infty] = \frac{\sigma}{r} \left[\frac{r H'(r)}{\sqrt{1 + H'(r)^2}} \right]' \quad (5)$$

For the cylinder, $r = 0$ and $z = 0$ are the axis and upper surface of the cylinder, respectively; For the sphere, $r = 0$ and $z = 0$ are the vertical axis through the sphere center

and the plane of the contact ring, respectively. Equation (5) is to be solved together with the condition that the interface is flat far from the particle

$$\lim_{r \rightarrow \infty} \{rH'(r), H(r)\} = \{0, H_\infty\}, \quad (6)$$

The condition to be prescribed at the contact line is different for the cylinder, where the position of the contact line at the sharp edge is known and the contact angle must be determined, and the sphere where the contact angle is prescribed by the Young-Dupré law and the position of the contact line must be determined. For the cylinder, the force balance (2) may be written as

$$2\pi R\sigma \frac{H'(R)}{\sqrt{1+H'(R)^2}} + \rho_l g \pi R^2 h + \rho_l g \pi R^2 H_\infty = mg. \quad (7)$$

The solution of (5), (6) and (7) gives $H(r)$, and the unknown contact angle is then determined from the equation

$$H'(R) = \tan \alpha. \quad (8)$$

For the sphere, the boundary condition at the contact line is (3) with

$$\sin \alpha = H'(R \sin \theta_c) / \sqrt{1+H'(R \sin \theta_c)^2}, \quad (9)$$

which relates the angle α prescribed by the Young-Dupré law to $H(r)$. The solution of (5), (6) and (3) with $\sin \alpha$ in (3) expressed in (9) gives the solutions of $H(r)$ and θ_c .

For the cylinder, the values of α and H_∞ can be determined as functionals of the solution $z = H(r)$ using (2) together with

$$\rho g \int_R^\infty [H_\infty - H(r)] r dr = \sigma R \sin \alpha \quad (10)$$

which follows from (5) and (6). For example, if $H(r)$ were the circular arc $H = H_\infty \sin \zeta$, $0 \leq \zeta \leq \pi/2$, $r = R + H_\infty(1 - \cos \zeta)$, (10) would become

$$\frac{\sigma R}{\rho g} \sin \alpha = \int_R^\infty [H_\infty - H(r)] r dr = \int_0^{\pi/2} H_\infty^2 (1 - \sin \theta) (R + H_\infty [1 - \cos \theta]) \sin \theta d\theta = 0.2146 R H_\infty^2 + 0.0479 H_\infty^3.$$

Together with (2), this determines α and H_∞ .

For the sphere, the values of θ_c and H_∞ can be determined as functionals of the solution $z = H(r)$. The counterpart of (10) for the sphere is

$$\rho g \int_{R \sin \theta_c}^{\infty} [H_\infty - H(r)] r dr = \sigma R \sin \theta_c \sin \alpha. \quad (11)$$

If $H(r)$ were the circular arc, (11) would become

$$\frac{\sigma}{\rho g} R \sin \theta_c \sin \alpha = 0.2146 R \sin \theta_c H_\infty^2 + 0.0479 H_\infty^3.$$

Together with (3), this determines θ_c and H_∞ .

Experiments:

We used a 3.38 g Teflon cylinder with a cone cut in the center. 0.25 g steel beads were put in the cone to change the weight. The radius, height and volume of the cylinder are [1.27 cm, 0.495 cm, 2.51 cc]. The angle α and the depression height H_∞ are measured using a video camera. Measurements are taken at several azimuthal positions and the average values of α and H_∞ are recorded. Inserting the measured parameters into the force balance equation (2), we can compute the residual

$$e = mg - 2\pi R \sigma \sin \alpha - V \rho_l g - \rho_l g H_\infty \pi R^2 \quad (12)$$

which exhibits the accuracy of our experiments. The surface tension σ is 46 dyn/cm. The experimental data for five weights are listed in table 1.

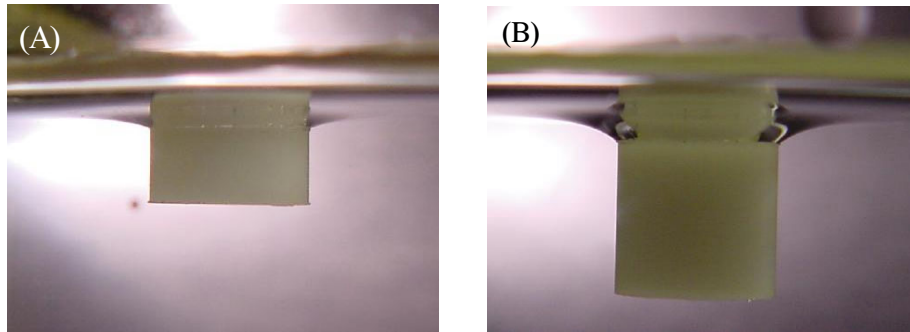


Figure 3. Two photos of floating Teflon cylinders of density $\rho_s = 1.4$ g/cc held at the contact line in water of density $\rho_f = 1$ g/cc. Both cylinders have a diameter of 0.8 cm; the height from the bottom of the cylinder to the contact line is 0.4 cm in (A) and 0.8 cm in (B). The contact angle in (B) is larger than that in (A) in order to satisfy the

force balance. The image of the cylinder projecting above the contact line is a reflection in the surface of the water.

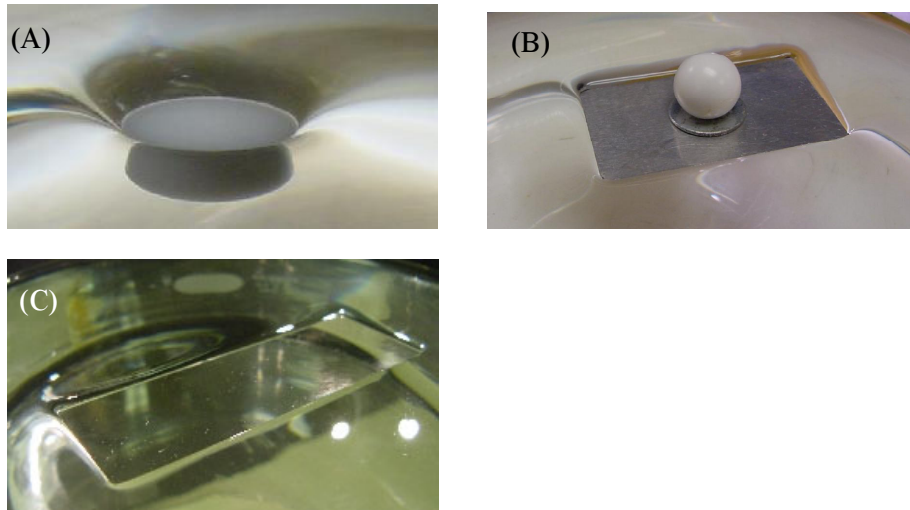


Figure 4. (A) The meniscus for a Teflon cylinder of density $\rho_s = 1.4 \text{ g/cc}$ hanging from a flat edge in water. (B) An aluminum plate can float in water hanging from the sharp edge; when weighted by a Teflon ball, the plate still floats but the hanging depth increases. (C) A floating glass plate is held at the sharp edge in water. Note that spheres of aluminum and glass will sink in water, provided that the spheres are not so small that the surface tension will dominate the buoyant weight.

Table 1 shows that the contact angle at the sharp edge increases when the weight of the particle is increased. There exists a maximum weight that can be held in this manner, beyond which the particle will sink. We did experiments to determine the critical contact angle corresponding to this maximum weight. The 3.38 g Teflon cylinder with a cone cut in the center was used. We did not use ball bearings to change the weight, instead, we used a needle to impose an external vertical force on the cylinder (see figure 5.A). We pushed the needle down very slowly, so that the contact angle increased smoothly until the cylinder sank. A video camera was used to record the whole process and we determined the critical contact angle using the video replay. We found that the contact angle increased up to 90° while the contact line was pinned at the sharp edge (see figure 5.B); when the needle was pushed further down, the contact line moved away from the sharp edge to the flat top of the cylinder and sank instantaneously. We conclude that the

critical contact angle corresponding the maximum weight which could be held at the sharp edge is 90° .

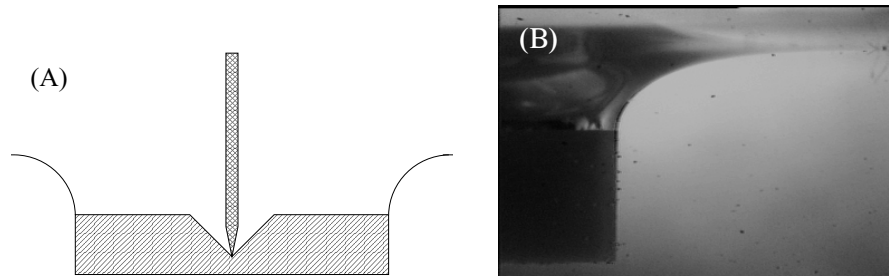


Figure 5. (A) A cartoon for the experiment determining the critical contact angle at the sharp edge. (B) A photo from the video showing that the contact angle reaches 90° at a moment just before the cylinder sinks. The square, solid black part in the photo is the cylinder and the bright part is water.

Capillary attraction

The deformation of the air-liquid interface due to trapped small heavy particles (or to floating lighter-than liquid particles) gives rise to lateral capillary forces which are attractive for particles of like wettability and lead to clusters (6,7,8). The particles self assemble. A second heavier-than liquid floating particle will fall into the depression created by the first. In addition, the rise or fall of the meniscus between particles lead to unbalanced capillary forces which are attractive for particles of like wettability. An unbalanced capillary force can also arise from the rotation of a particle on the when the contact angle is fixed. Gifford and Scriven (8) note that “casual observation ... show that floating needles and many other sorts of particles do indeed come together with astonishing acceleration. The unsteady flow fields that are generated challenge analysis by both experiments and theory. They will have to be understood before the common place ‘capillary attraction’ can be more than a mere label, so far as processes are concerned.”

To address the challenge of describing and understanding the dynamics of clustering and self assembly of particles due to capillary, Singh and Joseph (9) have put up a numerical package which treat the problem by direct numerical simulation. The method is as exact as numerical methods allow; in particular the changing shape of the meniscus

and the hydrodynamic forces which move particles are computed and not modeled. The same two cases enter into the dynamic simulations that control the hanging depth of particles in the static case; the dynamic simulations look at motions of smooth particles, in which the contact angle is maintained at the equilibrium value and the contact line moves on the particles; or at particles, with sharp edges to which the meniscus is always pinned as the particles move and the contact angles change.

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$m(\text{gram})$	3.38	3.63	3.88	4.13	4.38
α (degree)	28.4	37.8	43.0	51.7	71.1
$H_\infty(\text{cm})$	0.130	0.176	0.206	0.255	0.302
$2\pi R\sigma \sin\alpha/mg(\%)$	5.27	6.31	6.58	7.11	8.08
$\rho_1 g H_\infty \pi R^2/mg(\%)$	19.44	24.54	26.94	31.34	34.98
$ e /mg(\%)$	1.03	0.01	1.8	0.77	0.36

Table 1. Quantities entering into the force balance equation (2). The residual e computed by (12) exhibits the accuracy of our experiment.