

On the shape and size of liquid droplets on flat solid surfaces

Abstract

This article introduces two dimensionless positive geometric parameters that characterize the shape of a liquid droplet on a flat solid surface, which formed by the surface tension. The first parameter, “shape coefficient” K , is defined by the ratio of volume to surface and is always >3 (3 is the space dimension). The second parameter, “holding limit” κ_0 , is defined by the fraction of osculating surface and K and is <1 . The ratio of the surface tension energy of a droplet attached to a substrate in zero gravity to the energy of the same droplet floating in zero gravity is presented through these parameters as $1-(K-3)(\kappa_0-\kappa)/3(1-\kappa_0)$, where the material parameter κ (which appears in the Young equation $\kappa=\cos\theta$) indicates the decrease in liquid surface tension by the solid substrate. The relative energy of the surface tension, K and κ_0 , are explicitly expressed for a droplet of an elliptical rounded segment (ERS) shape through its eccentricity e , relative height χ , and relative rounding radius η . It is shown that the Young equation is a self-consistent (i.e., leading to $\eta=0$) minimum condition of the energy only in the spherical ($e=0$) case. The rounding, either inner or outer, is specified by the legs of a triangle with zero angles and the median as a slope line. The main result obtained is the proof that the outer rounded ERS weighty droplets with inflection points, due to weight and hydrostatic forces, cannot exist if their radii larger than 2-4 capillary length. This proscription is absent in zero gravity.

Keywords: Droplet, Elliptic rounded segment, Zero gravity, Weight droplet maximal size

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Introduction

Determining the shape of a liquid droplet on a solid surface is a part of capillarity theory—one of the most remote backstreets of general physics. The capillarity belongs to the theory of liquids, which is not as advanced as the molecular theory of gases or solids. Therefore, turning to droplets, we are unable to start with a microscopic picture and should use the same phenomenological approach as the one created more than two to three centuries ago.^{1,2} A similar technique prevails in modern theoretical investigations of liquid droplets and has attracted much attention in recent years due to the growing number of experimental works and technical applications [see, e.g., papers,³⁻⁶ monographs,^{7,8} textbooks]^{9,10} The number of cross-references in this field is in the order of tens. This paper does not overstep the limits of the aforementioned ideas, but attempts to avoid using models where droplets have cusp points similar to the border points of spherical or elliptical segments.³⁻⁵ Let us consider a model droplet shape to be an elliptical rounded segment (ERS) that touches the substrate smoothly with a zero-contact angle (see Figure 1). This model permits finding the limit size of a weighty droplet and presenting the droplet energy in zero gravity solely through the universal geometric parameters of its shape. Among other things, we will try to demonstrate (as in, e.g., Ref.)⁹ that basic college-level analytical geometry course is sufficient to solve problems of real physical interest if one is willing to perform cumbersome but simple calculations.

Shape coefficient

The droplet shape is determined by its weight, surface tension, viscosity, etc. The ratio of the surface area of a sphere to its volume is $S/V = 4\pi R^2 / (4\pi R^3/3) = 3/R$. The “shape coefficient 3” is extracted as

$$K = (3 / 4\pi)^{1/3} \frac{S}{V^{2/3}} \quad (1)$$

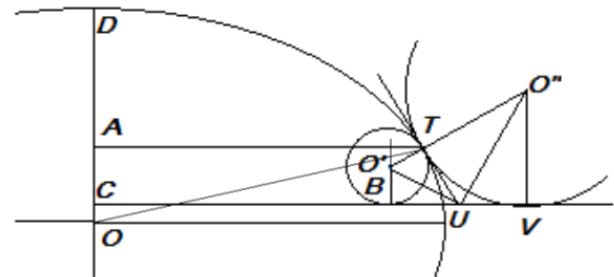


Figure 1 The droplet is formed by rotation of the plane figure $DTBCD$ around vertical axes OD for inner touching and by rotation of figure $DTVCD$ for outer touching. The rounding parts are created by rotation of the round legs TB and TV , respectively, of the triangle BTU with the zero angles. Its median TU is simultaneously a slope line.

This formula can be applied to any geometrical body. The coefficient for sphere $K=3$ coincides with the dimensionality of our space. A similar formula for a sphere in n -dimensional Euclidean space $K=(n/\omega)^{1/n}S/V^{(n-1)/n}$ confirms interpretation “3” as a space dimension (here ω is the solid angle similar to 4π). The shape coefficient for all other space figures is higher. For example, in a cube $K=6(3/4\pi)^{1/3}=3.7221$. The minimal value of K for a cylinder with $V=\pi\chi R^3$ and $S=2\pi(1+\chi)R^2$, $\chi=h/R$ is $K=6^{1/3}(1+\chi)/\chi^{2/3}=3(3/2)^{1/3}=3.4341$ since the fraction $(1+\chi)/\chi^{2/3}$ is minimal for $\chi=2$. The result is lower than that for a cube. The shape coefficient of semi-sphere is, obviously, $K=3\cdot 3/16^{1/3}=3.5717$.

It is now clear why the floating droplets have a spherical shape in zero gravity: their surface tension energy (and surface itself) should be minimal for a fixed volume. For the same reason, when two drops touch, they stick together: their common surface diminishes by the size of the joint parts.

Elliptical rounded segment

After considering the aforementioned examples, we can attend to the main object of our calculations: the ERS (Figure 1).

This body is formed by revolving the two arcs DT of an ellipse and TB of a circle around the vertical axes CD , smoothly joining in point T . The circle arc adheres to the straight-line BC in B , which rotates as well. Cusps, which are unnatural for a liquid, are not present. The droplet consists of the elliptical cap DTA and the round "bowl" TBC with a flat bottom BC .

The equations of the cap are: $x = a \cos u, y = c \sin u$, x is the horizontal coordinate axes CV , y is the vertical coordinate axes CD , C is the coordinate origin, and $u=t$ corresponds to point T . Further, $a=OU$ is the length of big ellipse semiaxes, $c=OD$ is the length of the small one,

$$\text{one, } AT = x, AD = h = c - y, \sin t = \frac{y}{c} = 1 - \frac{h}{c} \equiv \xi, \text{tg } \alpha = \frac{x}{y} = \frac{a \text{ctgt}}{c} \quad (3)$$

and the eccentricity is $e = \sqrt{a^2 - c^2} / a$. The angle $\angle TOD = \alpha$ for the spherical droplet ($a=c$) is equal to the slope angle $\angle TUB = \theta$, but this is not true of the elliptical cap.

$$\text{tg } \theta = \frac{dy}{dx} = \frac{c \text{ctgt}}{a} = \frac{\sqrt{(1-e^2)(1-\xi^2)}}{\xi}, \cos \theta = \frac{\xi}{\sqrt{g(1-e^2)}}, \sin \theta = \frac{\sqrt{1-\xi^2}}{\sqrt{g}}, g = 1 + \frac{(e\xi)^2}{1-e^2} \quad (3)$$

The volume of the ellipsoid cap is

$$V = \pi \int_y^c x^2 dy = \pi c a^2 \int_t^{\pi/2} d \cos u (1 - \sin^2 u) = \pi c a^2 (1 - \xi - \dots + \dots \xi^3) = \frac{\pi c^3 (1 - \xi)^2 (2 + \xi)}{3(1 - e^2)} \quad (4)$$

Finding the lateral surface area is slightly longer:

$$S = 2\pi \int_y^c x dl = \pi a \int_t^{\pi/2} d \cos u \sqrt{a^2 \sin^2 u + c^2 \cos^2 u} =$$

$$\pi a \int_t^{\pi/2} d (\sin u) \sqrt{(a^2 - c^2) \sin^2 u + c^2} = \frac{2\pi a c}{f} \int_{\text{fsnt}}^f d v \sqrt{1 + v^2} = \frac{\pi a c}{f} (v \sqrt{1 + v^2} + \ln(v + \sqrt{1 + v^2})) \Big|_{f_2}^f$$

$$\pi a c \left(\sqrt{1 + f^2} - \xi \sqrt{1 + f^2 \xi^2} + \frac{1}{f} \ln \frac{f + \sqrt{1 + f^2}}{\xi f + \sqrt{1 + f^2 \xi^2}} \right) \text{ where}$$

$$f = \frac{\sqrt{a^2 - c^2}}{c} = \frac{e}{\sqrt{1 - e^2}} \quad (\text{The same coefficient appeared in})$$

Eq. (6) from Ref.3 under the improper name: "eccentricity"). Now the volume, lateral and bottom surface area, and shape coefficient are expressed through dimensionless parameters: $V = \pi c^3 \tau / 3$, $S = \pi c^2 \rho$, $\pi a^2 \cos^2 t = \pi c^2 (1 - \xi^2) / (1 - e^2)$.

$$\tau = \frac{(1 - \xi)^2 (2 + \xi)}{1 - e^2}, \rho = \frac{1 - \xi \sqrt{g(1 - e^2)}}{1 - e^2} + \frac{1}{e} \ln \frac{1 + e}{\xi e + \sqrt{g(1 - e^2)}}, K = 3 \left(\rho + \frac{1 - \xi^2}{1 - e^2} \right) / (2\tau)^{2/3} \quad (5)$$

If $a=c$ parameter $\tau = (1 - \xi)^2 (2 + \xi)$ gives the volume of spherical segment, and the second (logarithmic) term of ρ as well as the first one turns into $1 - \xi$ since $1/e \cdot \ln(1 + e - e\xi) \rightarrow 1 - \xi$. Both terms of ρ are even functions of e ; K of spheroid, which follows from Eq. (5) if $\xi = -1$,

$$K_{\text{sph}} = 3 \left(\frac{1}{2(1 - e^2)^{5/3}} + \frac{\ln(1 + e) - \ln(1 - e)}{4e(1 - e^2)^{2/3}} \right) \approx \frac{3}{2(1 - e^2)^{5/3}} \left(\frac{1}{1 - e} + \frac{1}{1 - e^2} \right) > 3$$

The volume V' and the lateral surface area S' of the bowl TBC require integration over the circle arc BT . Its center O' is the intersection of perpendicular $O'O''$ to the tangent in point T with the bisectrix TU of the angle $\theta = \angle TUB$ between the tangent and the

horizontal bottom line CU . The angle between $O'O''$ and height BO'

$$\text{in point } B \text{ is } \theta. \text{ Then } V' = \pi r \int_0^{\pi - \theta} x^2 \sin \phi d\phi, S' = 2\pi \int_0^{\pi - \theta} (r' + r \sin \phi) r d\phi$$

where $x = r' + r \sin \phi, y = r - r \cos \phi, \phi$ is a variable angle between the height and radius of arc $BT, r'^2 = CB = AT - r \sin \theta = a \cos t - r \sin \theta = c \sqrt{(1 - \xi^2) - \eta \sin \theta} / \sqrt{(1 - e^2)}, r = a \eta$.

$$V' = \pi r \int_0^{\pi - \theta} (r' + r \sin \phi)^2 \sin \phi d\phi = \pi r^2 [r^2 (1 + \cos \theta) + r r' (\pi - \alpha + \frac{1}{2} \sin 2\theta) + r^2 (\dots + \cos \theta - \theta \cos^3 \theta)],$$

$$S' = 2\pi \int_0^{\pi - \theta} (r' + r \sin \phi) r d\phi = 2\pi r r' (\pi - \theta) + 2\pi r^2 (\cos \theta + 1) \quad (6)$$

should be added to the cap data (5), which gives $\pi c^3 (\tau + \omega) / 3$ for the total volume, $\pi c^2 (\rho + \psi)$ for the lateral surface, $\pi r'^2 = \pi c^2$

$$\frac{1 - \xi^2}{1 - e^2} \left(1 - \frac{\eta}{\sqrt{g}} \right)^2 = \pi c^2 \frac{1 - \xi^2}{1 - e^2} \zeta^2 \text{ for the bottom area, shape}$$

coefficient K , and for holding limit κ_0 (see below) of

ERS:

$$\omega c^3 = 3r^2 r' (\pi - \theta + \sin \theta \cos \theta) + 3r r'^2 (1 + \cos \theta) + r^3 (2 + 3 \cos \theta - \cos^3 \theta), \psi c^2 = 2r (r' (\pi - \theta) + r (1 + \cos \theta)),$$

$$\omega c^3 = 3r^2 r' (\pi - \theta + \sin \theta \cos \theta) + 3r r'^2 (1 + \cos \theta) + r^3 (2 + 3 \cos \theta - \cos^3 \theta), \psi c^2 = 2r (r' (\pi - \theta) + r (1 + \cos \theta)),$$

$$r = \eta c, r' = \frac{c \sqrt{1 - \xi^2}}{\sqrt{1 - e^2}} \left(1 - \frac{\eta}{\sqrt{g}} \right) = \frac{c \zeta \sqrt{1 - \xi^2}}{\sqrt{1 - e^2}}, K = 3 \left(\rho + \psi + \frac{1 - \xi^2}{1 - e^2} \zeta^2 \right) / (2(\omega + \tau))^{2/3},$$

$$\kappa_0 = \frac{((2(\omega + \tau))^{2/3} - \rho - \psi)(1 - e^2)}{\zeta^2 (1 - \xi^2)} \quad (7)$$

The center of outer rounding circle O'' is the intersection of perpendicular $O'T$ continuation with perpendicular UO'' to the bisectrix UO' of $\angle TUB = \theta$. The triangles $O'TU$ and $O''TU$ are similar. The radius $O'T = r$ in the smaller one is adjacent to angle $\theta/2$ while the radius $O''T = \tilde{r}$ in the bigger one confronts the same angle. Therefore, $\tilde{r} = r \text{ctg}^2 \theta / 2 = c \eta \text{ctg}^2 \theta$. The corresponding values for outer rounding are distinguished by a caret. In particular, the radius of the bottom appears as $\tilde{r}' = a \cos t + \tilde{r} \sin \theta$, with x and y in integrals as $\tilde{r}' - \tilde{r} \sin \phi, \tilde{r} - \tilde{r} \cos \phi$, respectively, where ϕ corresponds now to the arc of bigger circle, etc. The final result differs from Eq. (7) mainly by covering of r, r' and supplying η by the factor $f = \text{ctg}^2 \theta / 2$.

$$\omega' c^3 = 3\tilde{r}'^2 (1 - \cos \theta) - 3\tilde{r}' \tilde{r} (\theta - \sin \theta \cos \theta) + \tilde{r}^3 (2 - 3 \cos \theta + \cos^3 \theta), \psi' c^2 = 2\tilde{r}' \tilde{r} \theta - 2\tilde{r}^2 (1 - \cos \theta),$$

$$\tilde{r} = a \eta f, \tilde{r}' = \frac{\sqrt{1 - \xi^2}}{\sqrt{1 - e^2}} \zeta_+, K = 3 \left(\rho + \psi + \tilde{r}'^2 / c^2 \right) / (2(\tau + \omega'))^{2/3}, \kappa_0 = \frac{(2(\omega' + \tau))^{2/3} - \rho - \psi}{\tilde{r}'^2 / c^2}, \zeta_+ = 1 + \frac{\eta f}{\sqrt{g}} \quad (8)$$

Thus, the parameters of ERS, ξ, η, e , determine the droplet shape: K characterizes how close it is to a sphere, i.e., how perfect the shape is, the relative height $\chi = 1 - \xi$ sets the size of the flood area, the eccentricity e measures how flattened the droplet is, and the relative rounding radius η defines the smoothness of droplet-to-substrate bond.

Droplet in zero gravity

According to Young,² it is usually accepted that three forces are applied to each point of the border line between the liquid droplet and solid substrate along the tangents to intersection lines of normal plane and the surfaces separating solid and gas (sg), solid and liquid (sl), and liquid and gas (lg). The equilibrium of these forces leads to the equation $(\gamma_{\text{sg}} - \gamma_{\text{sl}}) / \gamma = \kappa \cos \theta$, where γ -s are coefficients of the surface tension, and θ is the contact angle between solid and liquid. The material parameter κ is specific for these gas-liquid-solid. In fact, it indicates how much the coefficient of the surface tension of a particular liquid

is diminished following contact with the solid surface. If $|\kappa| > 1$, it cannot be equal to cosine. Such situation is usually interpreted either as absolute wetting by this liquid (if $\kappa < 0$) i.e., the homogenous covering of the solid surface without concentrating in droplets or (if $\kappa > 0$) as total separation of droplets from the solid surface.

A more detailed picture can be obtained by considering droplet energy. The energy of a spherical droplet floating in zero gravity is $E_0 = 4\gamma\pi R^2$. In fact, it depends on the droplet volume: $E_0 = \gamma\sqrt[3]{\pi(6V)^2}$. Let us compare the energy of the attached deformed droplet $E_A = \gamma S + \gamma\kappa S_c$ with that of the floating droplet. For ERS, S is the lateral surface area $\pi c^2(\rho + \psi)$ and S_c is the area where the substrate and droplet touch each other, i.e., the bottom area $S_c = \pi r^2 = \pi c^2 \frac{1 - \xi^2}{1 - e^2} \zeta^2$.

Considering the volume of the droplet $\pi c^3(\tau + \omega)/3$ and Eq. (7) allows to present E_A/E_0 as $\kappa\zeta^2(1 - \xi^2)/(1 - e^2)[2(\tau + \omega)]^{2/3} + (\rho + \psi)/[2(\tau + \omega)]^{2/3} \equiv \kappa u + Q$, while ratios, u , Q , determine geometric parameters $K = 3(u + Q)$ and $\kappa_0 = (1 - u)/Q$. The last equations can be solved: $Q = (K - 3)/3(1 - \kappa_0)$, $u = 1 - \kappa_0(K - 3)/3(1 - \kappa_0)$. Thus, we finally arrive at

$$E = E_A/E_0 = 1 - \frac{(K - 3)(\kappa_0 - \kappa)}{3(1 - \kappa_0)} = 1 - Q(\kappa_0 - \kappa), \quad E_0 = \gamma(\pi(6V)^2)^{1/3}, \quad Q = \frac{K - 3}{3(1 - \kappa_0)}. \quad (9)$$

This equation is valid independently of the model of droplet used. Only the values of K and κ_0 depend on the shape of the droplet. The condition of concretion of the drop $E_A < E_0$ is reduced to

$$\kappa \leq \kappa_0, \quad \kappa_0 \equiv 1 - \frac{S}{S_n} \left(1 - \frac{3}{K} \right), \quad (10)$$

Now the term ‘‘holding limit’’ for κ_0 is justified. If the substrate reduces the surface tension insufficiently to make it lower than κ_0 concretion is impossible. Therefore, $\kappa_0 < 1$ is a universal geometrical characteristic of a liquid body as K is. The holding limit achieves 1 only for spherical droplet: $K = 3$. When a spherical droplet touches a substrate, it is still spherical since the limit of Q for $K \rightarrow 3$, $\kappa_0 \rightarrow 1$ is zero in ERS. The experimental data on the Young parameter κ are rather scanty.^{3,5} The wetting degree can be characterized by the difference $\kappa_0 - \kappa$, and $w_0 = 1 - \kappa_0$ can be treated as the whole ‘‘stock’’ of wetting of the given shape droplet, and Eq. (9) may be interpreted as $(E_A - E_0)/E_0 = (K - 3)/3 \cdot (w_0 - w)/w_0$, $w = 1 - \kappa$. The relative height $\chi = 1 - \xi$ determines the ‘‘flooding power’’ of the droplet. This picture is illustrated by calculations shown in Table 1.

The first third of Table 1 describes the elliptic segment without rounding. The low droplets ($\chi < 1$) have an unfavorable shape coefficient, weak holding limit, and are not attachable to a substrate as $E > 1$. Only the droplets of the second kind (with the height $\chi > 1$) attach (strongly for $\chi = 1.4$). The next two thirds of the Table 1 contain data for ERS with $\eta = 0.2$. Rounding makes the droplet attachable in most cases (with a single exception). The second kind droplets do not need rounding at all (already the sphere ‘‘overhangs’’ itself if $\chi > 1$). Outer rounding clearly demonstrates that the first kind droplets with inflection of their surface do not congregate, but those with $\chi > 1$ become energetically competitive with inner rounded and spherical droplets (especially with $\chi = 1.6$). This has far-reaching consequences for heavy droplets, which we consider below.

The first column, which describes spherical segments, reveals a connection between Eq. (9) and the Young equation $\kappa = \cos\theta$. It is understood from Figure 1 and Eq. (3), the angle θ is independent of η ; there are only three values of $\cos\theta$ in each row (and only one, 0, for $\chi = 1$). Neither of these coincides with $\kappa = 0.3$. At the same time, the first column shows that $\cos\theta = \xi (= 1 - \chi)$. The equality $\kappa = \xi$ leads to the satisfaction of the Young equation, and, therefore, is the minimum

condition for E in Eq. (9). Indeed, if we complement the first column by the additional row with $\chi = 1.3$ we obtain the deeper than 0.8971 minimum $E = 0.8956$ and $\cos\theta = -0.3$. This minimum is independent of η . In the other words, the spherical segment does not require rounding. However, if by some reason, e.g., the weight, the droplet shape should be flattened: $e > 0$, rounding deepens the minimum.

Influence of weight

Droplet weight is applied perpendicular to the plane of substrate; it presses down the droplet body and affects its spherical shape. The droplet energy now includes the potential energy of the Archimedean force, acting on the droplet in atmosphere.

$$E_p = g(d_k - d_c) \pi \left[\int_{y(B)}^{y(T)} yx^2 dy + \int_{y(T)}^{y(D)} yx^2 dy \right] \quad (11)$$

The volume integral includes two contributions: of the bowl from point B to point T and of the elliptic cap from T to D (Figure 1). The angle ϕ varies along the arc of rounding circle BT , the variable u runs along the elliptic arc DT . Here $g(d_k - d_c) = \gamma/l^2$, $l = \sqrt{[\gamma/g(d_k - d_c)]}$ is the capillary length of the droplet liquid in air. The capillary length enters the Jurin-Borelli formula [1] $h = l^2 \cos\theta/r$ for the height of lifted liquid in a capillary tube of radius r ; proposed centuries ago.

The integral of elliptic cap is

$$\int_{y(T)}^{y(D)} yx^2 dy = \int_{\tau}^{\pi/2} c \sin u a^2 \cos^2 u c \cos u du = a^2 c^2 \int_{\tau}^{\pi/2} (-dv) v^3 = \frac{c^4(1 - \xi^2)^2}{4(1 - e^2)}, \quad (12)$$

and of the bowl in the used notation (7)-

$$\int_0^{\pi-\theta} yx^2 dy = \int_0^{\pi-\theta} r(1 - \cos\phi)(r' + r\sin\phi)^2 r\sin\phi d\phi = \frac{c^4\eta\omega}{3\sqrt{1 - e^2}} + \frac{c^4(1 - \xi^2)^2(4\zeta - \zeta^4 - 3)}{12(1 - e^2)^2} \quad (13)$$

It can be simplified to sum of $c^4\eta\omega/3(1 - e^2)^{1/2}$ and $-\int_0^{\pi-\theta} r\cos\phi(r' + r\sin\phi)^2 r\sin\phi d\phi$ appeared in Eq.(6). The first part was

simplified by variable change $\phi \rightarrow z = \sin\phi$ and notation $\frac{r'\sqrt{1 - e^2}}{c} = \zeta\sqrt{1 - \xi^2}$

by; $\lambda: -\int_0^{\sin\theta} (\lambda + \eta z^2) z dz = -\frac{c^4\eta^2}{(1 - e^2)^2} \left(\frac{\lambda \sin\theta}{2} + \frac{2\zeta \sin^3\theta}{3} + \frac{\eta \sin^4\theta}{4} \right) = -\frac{c^4\eta^2(1 - \xi^2)^2}{12g(1 - e^2)^2} \left(6\zeta^2 \frac{\zeta\eta}{\sqrt{g}} + 3\frac{\eta^2}{g} \right) =$

$-\frac{c^4\eta^2(1 - \xi^2)^2}{12g(1 - e^2)^2} (6\zeta^2 + 8\zeta(1 - \zeta) + 3(1 - \zeta)^2) = \frac{c^4(1 - \xi^2)^2(4\zeta - 3 - \zeta^4)}{12(1 - e^2)^2}$; this result is

shown in Eq. (13). Adding Eq. (12) to Eq. (13), and inserting τ from Eq. (5) we find the potential energy

$$E_p = \frac{\pi\gamma c^4}{l^2} \left[\frac{\eta(\omega + \tau)}{3\sqrt{1 - e^2}} + \frac{(1 - \xi^2)^2(4\zeta - \zeta^4 - 3)}{12(1 - e^2)^2} + \frac{(1 - \xi^2)^2}{4(1 - e^2)} \frac{\eta(1 - \xi)^2(2 + \xi)}{3(1 - e^2)^{3/2}} \right] \quad (14)$$

It is convenient to use the same energy scale factor $E_0 = \gamma(\pi(6V)^2)^{1/3}$ in Eq.(14) as in Eq. (9). It looks for ERS as $E_0 = \gamma\pi c^2(2(\omega + \tau))^{2/3} = \gamma\pi c^2\zeta^2(1 - \xi^2)/Q(1 - e^2)$. Therefore, $\gamma\pi c^2 = E_0 Q(1 - e^2)/\zeta^2(1 - \xi^2)$. On the other hand, $E_0/\pi\gamma l^2 = D^2$, D is the diameter of a spherical droplet floating in zero gravity in units of l , of equal volume with

ERS. Then $(c/l)^2 = D^2 Q(1 - e^2)/\zeta^2(1 - \xi^2)$, $\pi\gamma c^2 \frac{c^2}{l^2} = E_0 \frac{D^2 Q^2(1 - e^2)^2}{\zeta^4(1 - \xi^2)^2}$, and

$$E_p/E_0 = \frac{D^2 Q^2(1 - e^2)^2}{\zeta^4(1 - \xi^2)^2} \left[\frac{\eta\zeta^3(1 - \xi^2)^{3/2}}{6Q^{3/2}(1 - e^2)} + \frac{(1 - \xi^2)^2(4\zeta - \zeta^4 - 3)}{12(1 - e^2)^2} + \frac{(1 - \xi^2)^2}{4(1 - e^2)} \frac{\eta(1 - \xi)^2(2 + \xi)}{3(1 - e^2)^{3/2}} \right]. \quad (15)$$

It has been taken into account simultaneously that $2(\omega + \tau) = \zeta^3(1 - \xi^2)^{3/2}/Q^{3/2}(1 - e^2)^{3/2}$. Similar further transformations allow to cast the total energy of a droplet (including E_A (9)) in the form

$$E = \frac{E_{ERS}}{E_0} = D^2 \left[\frac{1-\zeta}{6\zeta} \sqrt{\frac{Q_+}{1-\zeta^2}} + Q_+^2 \left(\frac{1}{3\zeta^3} - \frac{1}{12} \frac{e^2}{4\zeta^4} - \frac{(1-\zeta)(2+\zeta)\sqrt{g(1-e^2)}}{3\zeta^4(1+\zeta)^2} \right) \right] + 1 - Q_+(\kappa_0 - \kappa), \zeta = 1 - \frac{\eta}{\sqrt{g}} \quad (16)$$

Rounding presents itself in Eq. (16) only through parameter ζ , which equals 1 if rounding is absent. The result (16) can be transferred onto outer rounding in the same way as Eq. (8) was obtained from Eq. (7). The main changes in Eq. (13) stems from the requirement $\eta \rightarrow f/\eta$ and some opposite signs:

$$\int_{y^{(r)}}^{y^{(D)}} y x^2 dy = \frac{c^4 \eta f u}{3\sqrt{1-e^2}} + \frac{c^4 (\zeta_+ - 1)^2 (1-\xi^2)^2 (4\zeta_+^2 - 2\zeta_+ - 3)}{12(1-e^2)^2} + c^4 \frac{(1-\xi^2)^2}{4(1-e^2)}, \zeta_+ = 1 + \frac{f/\eta}{\sqrt{g}} \quad (17)$$

After insertion Eq. (17) into the formula for energy, we conclude

$$E_+ = \frac{E_{ERS}}{E_0} = D^2 \left[\frac{(1-\zeta_+)}{6\zeta_+} \sqrt{\frac{Q_+}{1-\zeta_+^2}} + Q_+^2 \left(\frac{(\zeta_+ - 1)^2 (4\zeta_+^2 - 2\zeta_+ - 3)}{12\zeta_+^4} + \frac{1-e^2}{4\zeta_+^4} - \frac{(1-\zeta_+)\sqrt{g(1-e^2)}(2+\xi)}{3\zeta_+^4(1+\xi)^2} \right) \right] \quad (18)$$

The subscript “+” reminds about outer rounding, which enters also through ζ_+ , Q_+ , and κ_+ :

$$Q_+ = \frac{\zeta_+^2 (1-\xi^2)}{(1-e^2)(2(\tau+\omega))^{2/3}}, \kappa_+ = \frac{((2(\omega'+\tau))^{2/3} - \rho - \psi)(1-e^2)}{\zeta_+^2 (1-\xi^2)} \quad (19)$$

Both Eq. (16) and (18) are simplified significantly when rounding is absent and lead to the identical result

$$E_0 = \frac{E_{ERS}}{E_0} |_{\eta=0} = D^2 Q_0^2 \frac{1-e^2}{4} + 1 + Q_0(\kappa - \kappa_0), Q_0 = \frac{1-\xi^2}{(1-e^2)(2\tau)^{2/3}}, \kappa_0 = \frac{(2\tau)^{2/3} - \rho}{1-\xi^2} \quad (20)$$

Unlike the case of zero gravity the relative energy becomes size-dependent being linear function of the square of “effective diameter” D (which is the same as “bond number” B)³ of the droplet, while in zero gravity attachment depends only on the nature of liquid and substrate. The weight also allows the droplet to stay on the substrate in an unstable state (which does not correspond to the energy minimum over e, ζ, η).

Example calculations of weighty droplet parameters (16, 18) are shown in Table 2. The peculiarities noted in Table 1 are present in Table 2 as well: inner rounding diminishes the energy of the first kind droplets for any e , but does not lead to attachment of droplets lower than half of ellipse. The energy minimum over the eccentricity appears for the further increase of height ($\chi > 1$). For example, the minimum $E = 0.9245$ becomes absolute for $e=0.6, B=2, \eta=0, \chi=1.6$. The minimum for droplets with smaller weights ($B=0.25$) returns to the lower heights ($\chi=1.4$) as in zero gravity. As a result of the fluttering caused by the droplet weight, the energy is reduced, and the minimum moves from spherical ($e=0$) to elliptic ($e=0.4$) shape as in Refs.^{3,4}

Table 1 Relative energy, shape coefficient, and holding limit of ERS

Parameters	e/x	$\kappa=0.3, \eta=0$			$\kappa=0.3, \eta=0.2, \text{inner rounding}$			$\kappa=0.3, \eta=0.2, \text{outer rounding}$		
		0,0	0,4	0,6	0,0	0,4	0,6	0,0	0,4	0,6
E	0.4	11,214	1.1614	1.2329	0.9898	0.997	1.0088	1.5461	1.611	1.7266
K		4.8835	5.0946	5.4617	3.4956	3.5308	3.5863	6.8484	7.173	7.7387
κ_0		0.1322	0.0895	0.0226	0.3401	0.3114	0.2669	-0.219	-0.249	-0.2962
cos θ		0.6	0.6333	0.6839	0.6	0.6333	0.6839	0.6	0.633	0.6839
E	0.6	1.0083	1.0339	1.0813	0.9675	0.9749	0.9876	1.262	1.297	1.36
K		4.25	4.4	4.6655	3.4342	3.4728	3.5358	5.4176	5.609	5.9389
κ_0		0.2857	0.2452	0.1799	0.4283	0.3962	0.3456	-0.0373	-0.064	-0.1067
cos θ		0.4	0.4299	0.4789	0.4	0.4299	0.4789	0.4	0.43	0.4789
E	1	0.9128	0.921	0.9391	0.9363	0.9406	0.95	1.0208	1.028	1.0427
K		3.5717	3.6462	3.7845	3.2624	3.2961	3.3596	4.0562	4.122	4.2364
κ_0		0.5198	0.4879	0.4322	0.5951	0.5631	0.5046	0.2561	0.243	0.219
E	1.4	0.8974	0.8971	0.901	0.932	0.932	0.9363	0.9434	0.941	0.9405
K		3.2108	3.2409	3.305	3.1102	3.1307	3.1793	3.4048	3.422	3.4631
κ_0		0.7155	0.6933	0.6453	0.7545	0.7267	0.6613	0.5068	0.507	0.4947
cos θ		-0.4	-0.4299	-0.479	-0.4	-0.4299	-0.4789	-0.4	-0.43	-0.4789

Outer rounding lowers the energy of the second type droplets even more effectively than inner rounding does of the first type droplets. The shape coefficient for outer rounding becomes close to 3, and even the order of minima can change (see the third row from the bottom in Table 2 – 0.9547 vs. 0.9460). Significantly larger droplets amplify this effect. This effect could be the reason for the nonexistence of big weighty droplets while large masses of liquid can attach to substrate in zero gravity. A nonrounded droplet with an effective diameter of five capillary length ($B=25$) and $\chi=1.4$ is strongly flattened: $E=1.2568$ ($e=0.4$) as compared to the spherical segment ($E=1.2787$) while outer rounded ERS ($\eta=0.2$) energy is noticeably lower ($E=1.2403$) than both and inner rounded with the same η ($E=1.2641$). At the same time, as demonstrated in Table 1, a droplet of the same shape and geometrical parameters is attachable in zero gravity independently of its size ($E=0.942$).

The point T of coalescence of the ellipse and circle in Figure 1, if touching is outer, is an inflection point of the rotating profile DTV forming the second type droplet. The outer circle has a smaller radius than the inner one for the second type droplet that gives the shape shown in Figure 2. This shape for large enough height χ (when point A is close to the end of small ellipse axes) is reminiscent of a mushroom with a thin stipe and big pileus. It is difficult to imagine someone standing under the round dirigible (“flying bowel”) and having atop its liquid floor (but not in zero gravity!). However, from the viewpoint of capillarity theory, this is quite possible as demonstrated by the above-mentioned example. Indeed, almost a perfect sphere is above and a widening pedestal weakens the surface tension that guarantees the smallest surface tension energy. Common sense prevails if we remember the Pascal law. The hydrostatic pressure of all droplet weight through a narrow stipe is transferred onto wide pedestal, and the construction will burst as a barrel in Pascal times and cover the substrate with a uniform liquid layer without any droplets. All this means is that the following proposition is entitled to existence.

If the minimum of the second type droplet energy belongs to the outer-rounded ERS, the droplet channel off the substrate and does not exist as a droplet. To be self-consistent, this proposition, being valid for a droplet of some size, should be simultaneously valid for all bigger droplets. Then it remains to find the size of the first droplet. Table 3 answers this question and demonstrates the self-consistency of the hypothesis.

Table Continued...

Parameters	e/x	$\kappa=0.3, \eta=0$			$\kappa=0.3, \eta=0.2, \text{inner rounding}$			$\kappa=0.3, \eta=0.2, \text{outer rounding}$		
		0,0	0,4	0,6	0,0	0,4	0,6	0,0	0,4	0,6
E	1,6	0.9124	0.9105	0.9123	0.9426	0.9412	0.9435	0.9391	0.935	0.9342
K		3.0988	3.1148	3.1565	3.0535	3.0666	3.1041	3.2049	3.212	3.2391
κ_0		0.8088	0.7903	0.7389	0.8342	0.8083	0.7336	0.6301	0.634	0.6167
cos θ		-0.6	-0.6333	-0.684	-0.6	-0.6333	-0.6839	-0.6	(-0.6839

Table 2 Relative energy, shape coefficient, and holding limit of an ERS weighty droplet

Parameters	e/x	B=2, $\kappa=0.3, \eta=0.$			B=2, $\kappa=0.3, \eta=0.2, \text{inner rounding}$			B=2, $\kappa=0.3, \eta=0.2, \text{outer rounding}$		
		0,0	0,4	0,6	0,0	0,4	0,6	0,0	0,4	0,6
E	0.4	1.3831	1.4084	1.4584	1.0925	1.0905	1.0904	1.5376	1.5927	1.6992
K		4.8835	5.0946	5.4617	3.4956	3.5308	3.5863	6.8484	7.173	7.7387
κ_0		0.1322	0.0895	0.0226	0.3409	0.3114	0.2669	-0.219	-0.2489	-0.2962
E	0.6	1.1785	1.1944	1.228	1.0605	1.0599	1.062	1.2876	1.3096	1.3529
K		4.25	4.4	4.6548	3.4342	3.4728	3.5358	5.4176	5.6087	5.9389
κ_0		0.2857	0.2452	0.1799	0.4283	0.3962	0.3456	-0.0373	-0.0637	-0.1067
E	1	0.9915	0.9953	1.007	0.9976	0.9977	1.0017	1.0656	1.0676	1.0743
K		3.5717	3.6462	3.7845	3.2624	3.2961	3.3596	4.0562	4.1222	4.2364
κ_0		0.5198	0.4879	0.4322	0.5951	0.5631	0.5046	0.2561	0.2431	0.219
E	1.4	0.9279	0.9258	0.9273	0.9621	0.9586	0.9605	0.969	0.9648	0.9622
K		3.2108	3.2409	3.305	3.1102	3.1307	3.1793	3.4048	3.4221	3.4613
κ_0		0.7155	0.6933	0.6453	0.7545	0.7267	0.6613	0.5068	0.5073	0.4947
E	1.6	0.9272	0.9245	0.9251	0.957	0.9547	0.9559	0.9527	0.9483	0.946
K		3.0988	3.1148	3.1565	3.0535	3.0666	3.1041	3.2049	3.2119	3.2391
κ_0		0.8088	0.7903	0.7389	0.8342	0.8083	0.7336	0.6301	0.6344	0.6167

Table 3 Influence of rounding on energy levels sequence and size of droplets

R	$\eta, \kappa; e, \chi$	0	0.7071	1	1.3038	2.1331	2.8107	6
E_0	0.2, 0.3;	0.8971	0.9258	0.9546	0.9949	1.1589	1.3518	2.9692
E	0.4, 1.4	0.932	0.9586	0.9851	1.0223	1.1737	1.3517	2.8447
E+		0.9408	0.9648	0.9887	1.0223	1.1589	1.3194	2.666
R		0	0.7071	1	1.1292	1.9774	3.9147	6
E_0	0.4, 0.3;	0.8971	0.9258	0.9546	0.9704	1.1221	1.7791	2.9692
E	0.4, 1.4	0.9606	0.9873	1.014	1.0287	1.1694	1.7791	2.8833
E+		0.9835	1.0012	1.0189	1.0287	1.1221	1.5269	2.2599
R		0	0.7071	1	1.4318	2.1529	2.7568	6
E_0	0.2, 0.3;	0.8971	0.9272	0.9573	1.0205	1.176	1.3545	3.0635
E	0.2, 1.4	0.9318	0.9596	0.9874	1.0458	1.1896	1.3545	2.934
E+		0.9427	0.9678	0.993	1.0459	1.176	1.3253	2.7555
R		0	0.7071	1	2.7386	3.3875	5.9582	6
E_0	0.2, 0.3;	0.9154	0.9245	0.9385	1.1203	1.2314	1.9032	1.9172
E	0.4, 1.6	0.9412	0.9547	0.9685	1.1444	1.2522	1.9033	1.9168
E+		0.9354	0.9483	0.9612	1.1289	1.2314	1.8511	1.864

The sequence of droplet energy levels for parameter typical values, given in the second column, are presented in Table 3 in the following order: first E_0 (without rounding), then E (with internal rounding), and then E_+ (with external rounding). The radius R of an equal ERS volume sphere determines the weight contribution into the total droplet energy. The third column describes a situation in zero gravity with the initial level sequence E_0 -E- E_+ , which means that rounding is unnecessary. The same situation continues to hold for small droplets with R of order one capillary length ($R=\sqrt{2}/2$ and 1) in the weight presence. The next three columns demonstrate that sequence of levels changes with growing R from E_0 -E- E_+ to E_0 - E_+ -E, then to E_+ - E_0 -E. The unrounded droplet becomes the highest at the final step: E_+ -E- E_0 . The last column shows that the final order does not change with further increase of the droplet size. Thus, the bold numbers in the seventh column can be treated as the limit size of weighty droplets, which our calculation predicts. Figure 2. The outer rounded second type droplet. The values of 2-4 capillary length do not contradict common sense.

However, nothing prevents the existence of much bigger droplets in zero gravity.

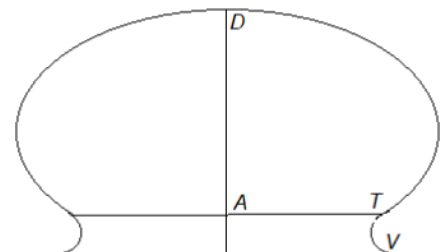


Figure 2 The outer rounded second type droplet.

Conclusion

It is demonstrated in Sec. 3 that in zero gravity the attachment energy is determined by universal geometrical parameters of the droplet

and does not depend on its size—only on the material parameters of the droplet liquid and substrate. The minimum of energy belongs to droplets higher than the semi-sphere. The energy of weighty droplets strongly depends on their size, and gravity destroys them if their size exceeds 2-4 capillary length as calculations of elliptic outer-rounded segment shape droplets prove.

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Conflicts of interest

The authors state that there is no conflict of interest.

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