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Sessile drops in weightlessness: an ideal playground for challenging Young's equation

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ABSTRACT

Sessile drop creation in weightlessness is critical for designing scientific instruments for space applications and for manipulating organic or biological liquids, such as whole human blood or DNA drops. It requires perfect control of injection, spreading, and wetting; however, the simple act of creating a drop on a substrate is more complex than it appears. A new macroscopic model is derived to better understand this related behavior. We find that, for a given set of substrate, liquid, and surrounding gas properties, when the ratio of surface free energies to contact line free energy is on the macroscopic scale, the macroscopic contact angle can vary at static equilibrium over a broad volume range. It can increase or decrease against volume depending on the sign of this ratio up to an asymptotic value. Consequently, our model aims to explore configurations that challenge the faithful representativity of the classical Young's equation and extends the present understanding of wetting.

1 Introduction

2 A sessile drop is a liquid drop deposited on a solid substrate and surrounded by a gaseous environment. Sessile drops are
3 ubiquitous all around us, either in natural environment (raindrops on a surface), or in industrial processes in which liquids
4 intervene. For scientific purposes, they can be processed by injecting liquid through a small hole in the substrate, as shown in
Figure 1. The underlying scientific question is, given a set of solid-liquid-gas material properties and injected volume, what is

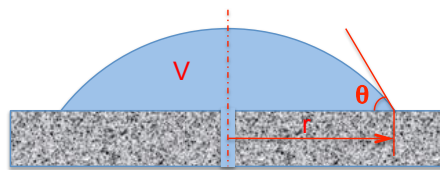


Figure 1. Sketch of sessile drop injected from below through a sub-millimetric hole in the substrate.

5 the macroscopic size and shape of the resulting sessile drop?

6 The first answer to this question is provided by the classical Young's equation¹, Eq. (1), which was formulated roughly two
centuries ago. Nevertheless, it remains an undisputed reference for the determination of macroscopic contact angles, denoted
by θ (cf. Figure 1), according to its famous relationship:

$$\sigma_{sg} - \sigma_{sl} = \sigma_{lg} \cos\theta \quad (1)$$

7 where σ_{sg} , σ_{sl} , and σ_{lg} are the interface free surface energies, and the subscripts s , l , and g represent a solid, liquid, and
8 gas, respectively. The effectiveness of Young's equation lies in its ability to translate subtle and complex molecular-scale
9 physico-chemical interactions near material interfaces to the macroscopic scale in a simple manner. However, as Young's
10 equation is assumed to be general, it remains unclear why neither the contact line free energy nor gravity forms a part of
11 the macroscopic contact angle relationship in this equation. One possible answer is that in most classical cases, these two

12 parameters are negligible with respect to the surface free energies, inducing only second-order deviations as compared with the
13 leading mechanisms. However, from a scientific standpoint, the question is whether there are configurations for which these
14 two contributions could lead to non-negligible effects.

15 Indeed, several experiments have shown some influence of volume on the macroscopic contact angle under Earth's
16 gravitational conditions²⁻⁷. These experiments show that a volume dependence exists for macroscopic sessile drops on Earth
17 for several sets of liquid/substrate/surrounding gas (water on PTFE in air, alkanes on Teflon in air, etc.), provided that the sessile
18 drop size remains below its capillary length. Above the latter, self-adaption of the local interface curvature to the hydrostatic
19 pressure is the dominant contact line mechanism. Hence, the static macroscopic contact angle becomes independent of the drop
20 volume. To explain the influence of volume on macroscopic contact angle, Boruvka and Neumann⁸ introduced the concept
21 of line tension associated with the triple line (first introduced by Gibbs more than a century and a half ago) and suggested a
22 modified version of Young's equation to account for it^{4,6,7}. However, no definitive consensus has emerged regarding a physical
23 understanding of the translation of events from the microscopic to the macroscopic scale^{9,10}, but a recent and sounding review
24 provides many inputs that enables to make its own view on this tentacular line tension topic¹¹.

25 Thus, revisiting a way to determine the macroscopic contact angle of sessile drops in a manner different from the well-
26 established one could either be tremendously risky at the worst or very ambitious at best. However, this is the goal of the
27 present study in order to explore configurations that challenge the faithful representativity of the classical Young's equation.

28 Indeed, a second possibility or alternate approach is to determine the macroscopic contact angle of sessile drops following
29 the pioneering work of Laplace¹², who, unlike Young, considered a macroscopic mechanistic approach. This resulted in
30 the famous Young-Laplace equation that governs the shape of any interface separating non-miscible fluids, as it relates the
31 capillary pressure to the liquid-gas surface tension and mean interface curvature. Unfortunately, this governing equation
32 is a highly nonlinear differential equation that has no analytical solution in its most general form. However, in the case of
33 axisymmetric sessile drops, Bashforth and Adams¹³ were the first to provide very accurate numerical solutions by means of
34 high-order Taylor series expansions, which agreed well with the best experimental results available at that time. Based on
35 this pioneering numerical work, numerous improvements have been achieved to enhance the capabilities and accuracy of the
36 original calculation methods¹⁴. Notably, minimizing the total free energy of a sessile drop enables the recovery of both the
37 Young-Laplace equation and Young's equation for the contact angle in completely independent ways¹⁵. However, most existing
38 numerical methods for axisymmetric sessile drops¹⁶⁻¹⁹ assume knowledge of at least two geometrical quantities from among
39 sessile drop volume, height, or wetted radius. Only when this information is available can these methods be used to determine
40 the static contact angle for a given set of material properties or to deduce some of the latter when all geometrical quantities are
41 known through experiments.

42 To the best of the authors' knowledge, no such influence of volume on macroscopic contact angle has been reported yet in
43 weightlessness. Therefore, the present study focuses on the potential influence of contact line tension on macroscopic contact
44 angle and on providing a better design for future experiments on weightless sessile drops. Therefore, geometrical data on
45 sessile drops are not assumed to be a prerequisite and one seeks for the complementary approach with respect to classical one.
46 Furthermore, it is assumed that the set of material properties is known, along with one of the geometrical target quantities of the
47 sessile drop, either its volume, height, or wetted radius. Then, all other related geometrical quantities to be determined (static
48 macroscopic contact angle, etc.) are predicted. In addition, some more generic, albeit related questions are addressed: What are
49 the equilibrium sizes and macroscopic shape of a weightless sessile drop of a prescribed volume for a given set of properties of
50 liquid, substrate, and surrounding gas materials? How do the related geometrical quantities, such as static macroscopic contact
51 angle, drop wetted radius, and height evolve with respect to sessile drop volume? How does the bulk pressure in the sessile
52 drop evolve in turn?

53 **Results**

54 **Exploring the parameter space**

55 As the proposed model is proven to be capable of reproducing the volume dependence of the macroscopic contact angle (see
56 the Methods section for all notations), the parameter space in weightlessness is explored. For conciseness, the focus is on
57 the main feature of the model through parametric studies that investigate the influence of the three leading parameters, i.e.,
58 sessile drop volume \mathcal{V} , surface free energy ratio \mathcal{S} , and the sign of the contact line tension σ_{slg} . These parametric studies were
59 performed by solving Eqs. (7) for the macroscopic contact angle in the range $]0, \pi[$ using the Mathematica software²⁰. Once the
60 macroscopic contact angle is computed, the three related geometrical quantities of interest—drop wetted radius, height, and
61 sphere radius—can be explicitly obtained using Eq. 6(a-c).

62 ***Influence of volume for given sets of liquid-solid-gas properties***

63 Let us first consider the influence of the sessile drop volume on its shape for various values of \mathcal{S} and both signs of contact
64 line tension σ_{slg} . The resulting macroscopic contact angle is plotted against all dimensionless geometrical quantities (\mathcal{L} , h ,

65 r , and R) in Figure 2, for $\mathcal{S} = 0, \pm 1/3, \pm 2/3, \pm 0.99$, cf. figure caption, and $l_\sigma = \pm 10^{-3} \mathcal{S}$, except for the case of $\mathcal{S} = 0$,
 66 where l_σ is set to $\pm 10^{-3}$. Solid (dashed) lines represent the positive (negative) values of the \mathcal{S}/l_σ ratio. First, the limit angle
 67 associated with this macroscopic model, denoted as θ_{lim} in Eq. (9), always tends to $\frac{\pi}{2}[1 - \text{sign}(\sigma_{slg})]$, regardless of the sign
 68 of \mathcal{S} . This suggests that when the length l_σ is commensurable at the macroscopic scale, it dictates the limit behavior when
 69 the drop size reaches its lowest macroscopic limit. Moving slightly away from singularity, the macroscopic contact angle
 70 is now well-defined and continuously increases (decreases) with the sessile drop size, depending on whether σ_{slg} is positive
 71 (negative), up to its asymptotic limit, $\theta_\infty = \arccos \mathcal{S}$. Thus, a crossover between hydrophobic (non-wetting) and hydrophilic
 72 (wetting) behaviors or vice-versa only occurs if the \mathcal{S}/l_σ ratio is negative. Furthermore, the asymmetry with respect to $\pi/2$ of
 73 the trigonometric functions in Eq. (7) induces a strong asymmetry in the macroscopic contact angle for low drop sizes. The
 74 macroscopic contact angle varies monotonically with the dimensionless drop size \mathcal{L} , height h , and wetted radius r , as shown in
 75 Figure 2(a-c). However, it exhibits a non-monotonic behavior with respect to the sphere radius for positive l_σ (see Figure 2(d)).
 76 Finally, as can be observed from Figure 2, the chosen definition of the reference length is optimal. It enables the depiction of
 77 the full picture in the smallest span range of the drop size, as compared with other dimensionless quantities, h , r , or R , which
 78 would require at least one more decade. Furthermore, one can notice that the widely used plot of macroscopic contact angle
 79 versus wetted radius, Figure 2(c), does not contain the lowest asymptotic limits fairly reproduced in Figure 2(a). On the other
 80 hand, Figure 2(d) interestingly indicates that positive l_σ always leads to the existence of a minimal sphere radius, whose value
 81 depends on \mathcal{S} . Above this minimum, any given sphere radius admits two macroscopic contact angles, as the relationship
 between these two related quantities is multi-valued.

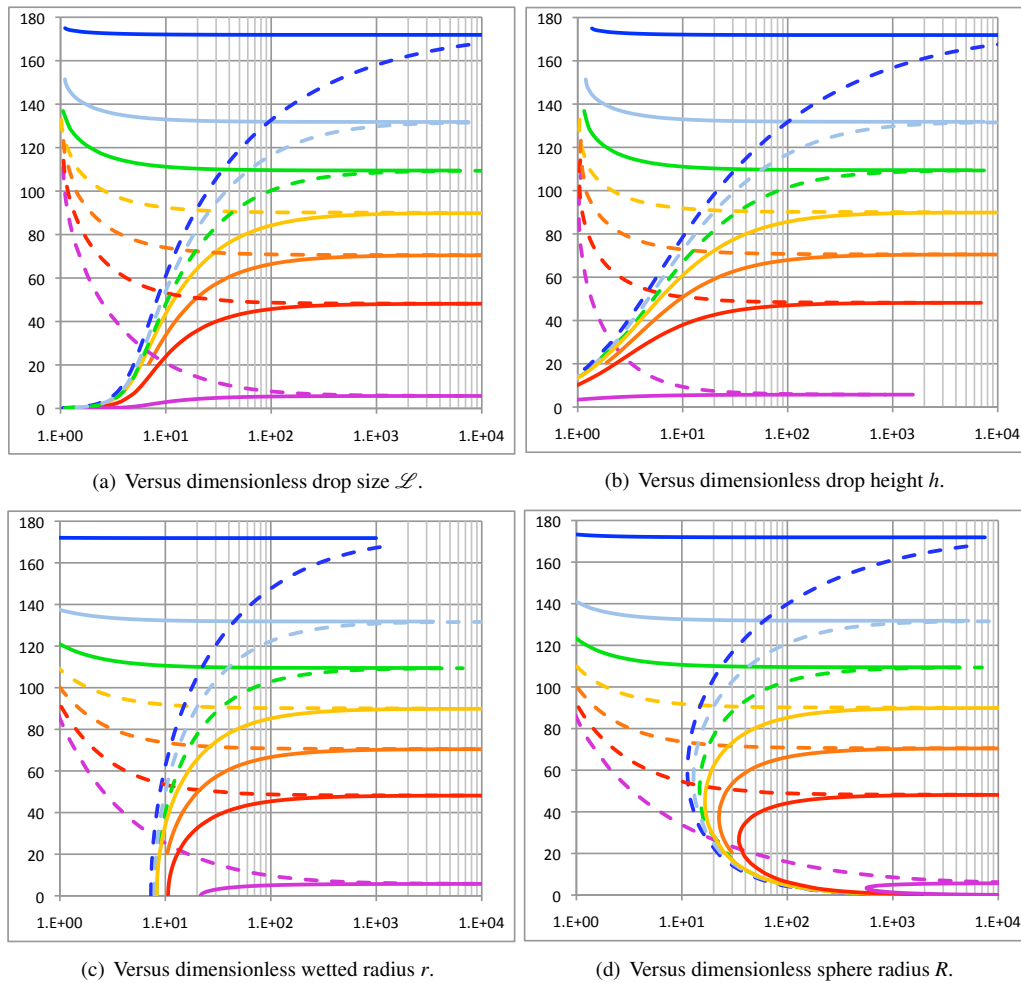


Figure 2. Macroscopic contact angle versus dimensionless geometrical quantities (\mathcal{L} , h , r and R), for $\mathcal{S} = -0.99$ (blue),
 $-2/3$ (cyan), $-1/3$ (green), 0 (yellow), $1/3$ (orange), $2/3$ (red) and 0.99 (magenta). The solid (dashed) lines represent the
 plots of positive (negative) \mathcal{S}/l_σ .

82
 83 The definition of \mathcal{W}_θ is derived from the closely related behavior of the relative variation in the macroscopic contact

84 angle over its span range, defined as $\vartheta = \frac{\theta - \theta_{\infty}}{\theta_{lim} - \theta_{\infty}}$. The latter is plotted against the dimensionless drop size in Figure 3(a) and
 85 emphasizes the asymmetry between the positive and negative values of the \mathcal{S}/l_{σ} ratio. Furthermore, this log–log scale plot
 86 clearly indicates that there are three distinctive regions with specific behaviors. The first is at the upper-left corner of the
 87 plot, where curves asymptote either the ordinate axis for negative l_{σ} or the unity horizontal line for positive one. Therefore,
 88 it is a connecting region to θ_{lim} , which spreads over very different drop size ranges, depending on θ_{lim} . In the opposite plot
 89 corner, in the region of the largest drop sizes, the final asymptotic $1/\mathcal{L}$ behavior occurs. Between these two extreme regions
 90 lies the transition region, whose extension strongly depends on the \mathcal{S}/l_{σ} ratio. These specific behaviors enable us to derive
 91 related functions, f_{co} , f_{pa} , defined in Eq. (10c–10d), which are at the core of the proposed definition of \mathcal{W}_{θ} . To appreciate how
 92 representative is the proposed model, the computed macroscopic contact angle θ is plotted against the proposed dimensionless
 93 number \mathcal{W}_{θ} in Figure 3(b) for all considered volumes, \mathcal{S} and l_{σ} values. The collapse of data in this plot indicates that \mathcal{W}_{θ}
 94 accurately represents the macroscopic contact angle dependence on sessile drop volume and material properties of the system,
 and it is actually able to characterize it.

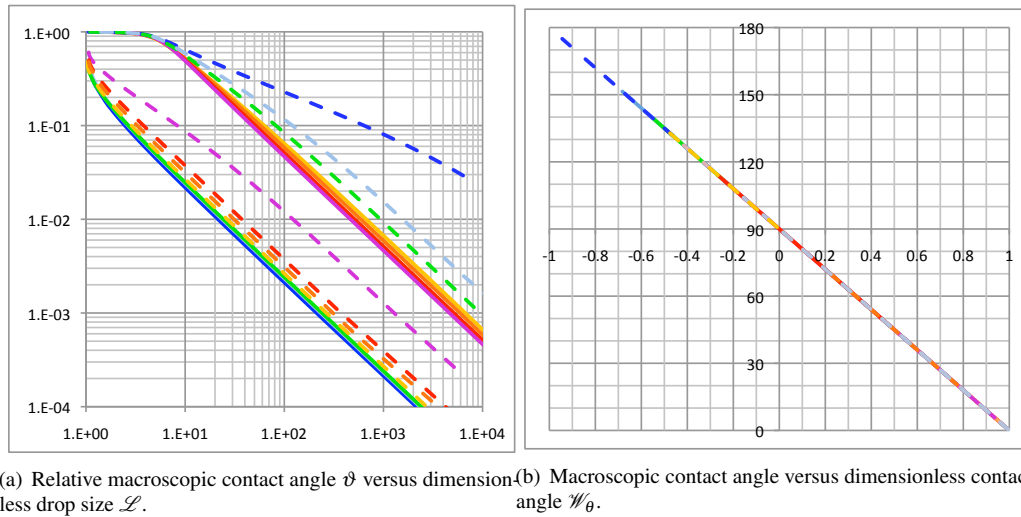


Figure 3. Macroscopic contact angle versus (a) dimensionless drop size \mathcal{L} and (b) dimensionless contact angle \mathcal{W}_{θ} , for $\mathcal{S} = -0.99$ (blue), $-2/3$ (cyan), $-1/3$ (green), 0 (yellow), $1/3$ (orange), $2/3$ (red) and 0.99 (magenta). The solid (dashed) lines represent the plots for positive (negative) \mathcal{S}/l_{σ} .

95 The plots in Figure 4 display how the various dimensionless geometrical quantities related to the spherical cap model
 96 (wetted radius, height and spherical cap radius) evolve both with respect to the dimensionless drop size and to the proposed
 97 dimensionless number \mathcal{W}_{θ} . The dimensionless sessile drop radius (wetted radius, r) is plotted against the dimensionless drop
 98 size \mathcal{L} in Figure 4(a) and against the dimensionless contact angle \mathcal{W}_{θ} in Figure 4(b). For positive l_{σ} , contact line tension
 99 induces wetting; thus, it starts with an asymptotic value that is approximately one order of magnitude greater than the smallest
 100 drop size. Its initial slope is horizontal with respect to both the dimensionless drop size and the contact angle. Then, it evolves
 101 in the transition region in a quasi-logarithmic manner and reaches the region of its asymptotic linear behavior. The higher the
 102 value of \mathcal{S} , the higher the wetted radius at a given drop size. In contrast, for negative l_{σ} , the dimensionless drop radius evolves
 103 linearly with drop size above the transition region. The plot of sessile drop radius against the dimensionless contact angle \mathcal{W}_{θ}
 104 expands this underlying behavior, as shown in Figure 4(b).
 105

106 The dimensionless height of the sessile drop (h) is plotted against the dimensionless drop size \mathcal{L} in Figure 4(c) and
 107 dimensionless contact angle \mathcal{W}_{θ} in Figure 4(d). The height clearly exhibits symmetric behavior compared with the drop wetted
 108 radius with respect to the sign of the contact line tension l_{σ} . Indeed, positive values of the latter induce wetting, which translates
 109 into greater spreading and consequently a smaller drop height at a given drop size. Thus, the higher the \mathcal{S}/l_{σ} ratio, the smaller
 110 the sessile drop height for a given sessile drop size.

111 Finally, the dimensionless sphere radius (R) is another geometric quantity of interest, as it determines the sessile drop bulk
 112 pressure for a given liquid–gas surface tension, as per the Young–Laplace equation. It is plotted against the dimensionless drop
 113 size \mathcal{L} in Figure 4(e) and dimensionless contact angle \mathcal{W}_{θ} in Figure 4(f). Unlike the dimensionless drop radius and height,
 114 the dimensionless sphere radius exhibits a peculiar behavior for positive l_{σ} . It exhibits a minimum value that increases with
 115 \mathcal{S} . Therefore, since the capillary pressure evolves as $1/R$, this minimum value is associated with an extreme bulk pressure in
 116 the sessile drop, which is of practical interest to design weightless experiments. Conversely, for negative l_{σ} , the sphere radius

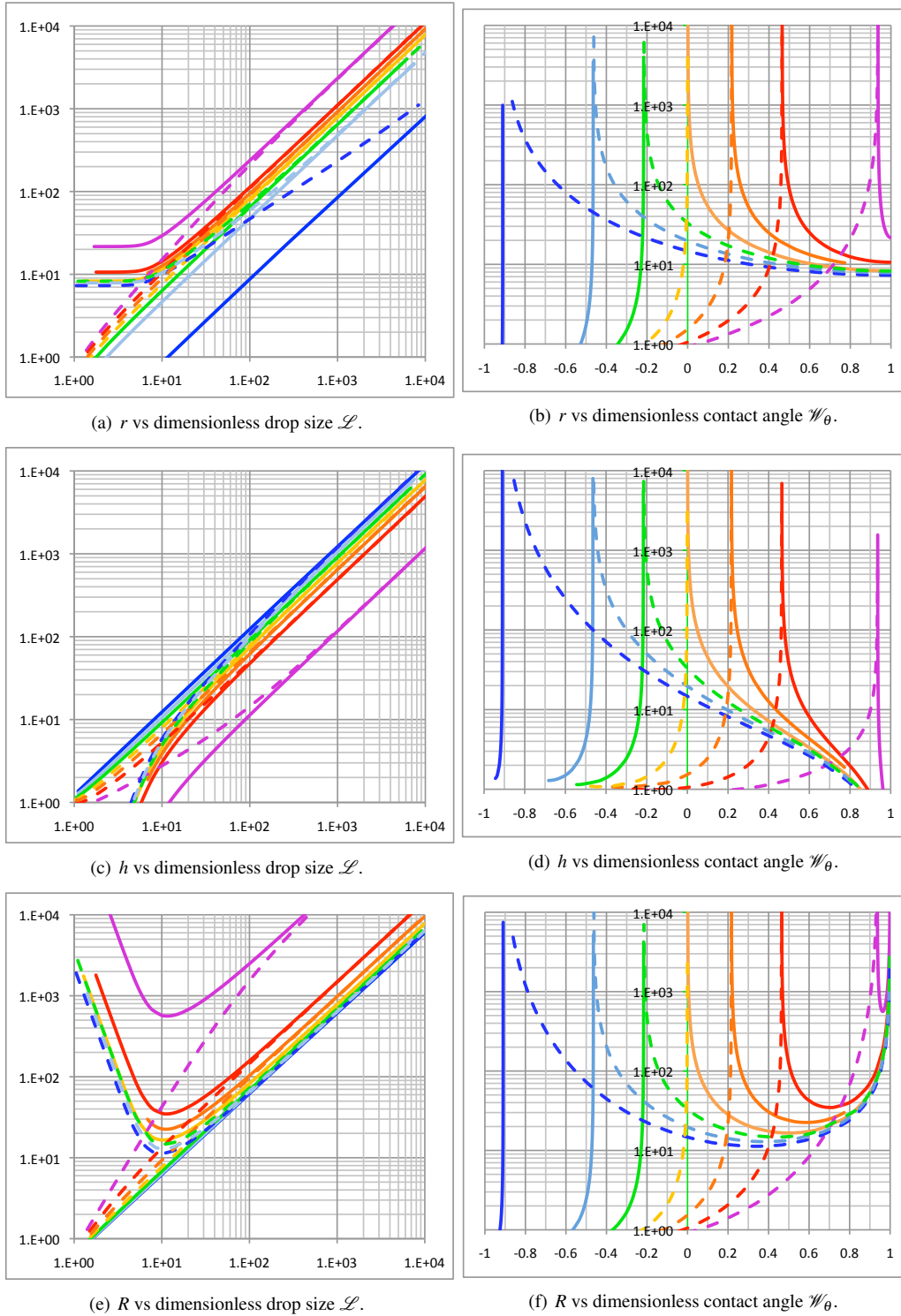


Figure 4. Plots of related sessile drop dimensionless quantities: (a-b) wetted radius, (c-d) drop height, (e-f) sphere radius, for $\mathcal{S} = -0.99$ (blue), $-2/3$ (cyan), $-1/3$ (green), 0 (yellow), $1/3$ (orange), $2/3$ (red) and 0.99 (magenta). The solid (dashed) lines represent the plots for positive (negative) \mathcal{S}/l_σ .

117 continuously increases with decreasing drop size.

118 Some sessile drop shapes are shown in Figure 5 in the axisymmetric (r, z) frame for several sample volumes, six values of
 119 \mathcal{S} , and a negative \mathcal{S}/l_σ ratio. These shapes clearly display a continuous evolution of the static macroscopic contact angle
 120 with respect to \mathcal{S} and sessile drop volume. The latter is small (few degrees) owing to the limited volume range that can be
 distinctively represented in the same figure; however, it is perceptible.

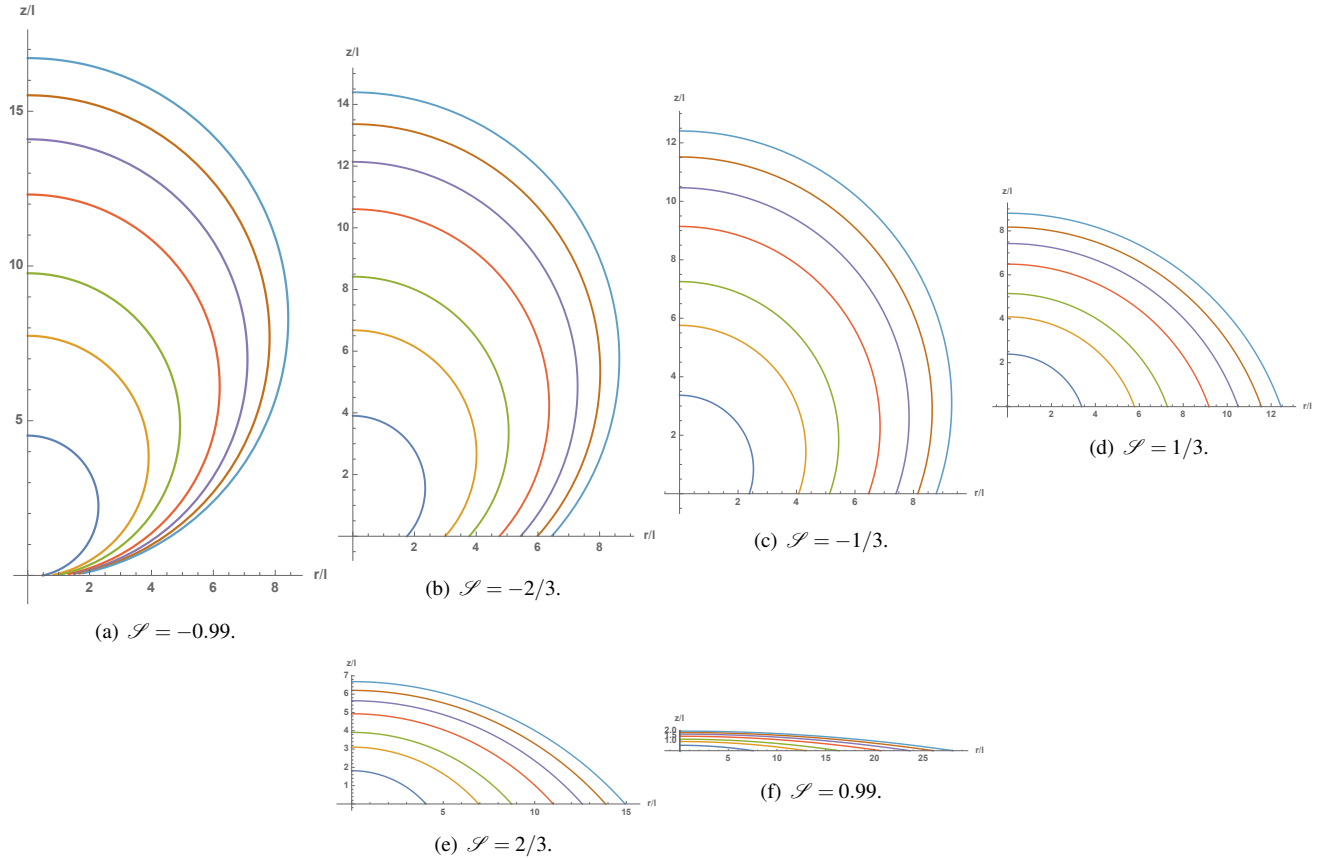


Figure 5. Influence of sessile drop volume on its shape in the small to medium range ($\mathcal{V} = 5$ (dark blue), 25 (brown), 50 (purple), 100 (orange), 150 (green), 200 (yellow) and 250 (light blue)) for six values of \mathcal{S} and negative \mathcal{S}/l_σ .

121

122 **Influence of material properties for given drop volume**

123 The sessile drop shapes of four given volumes ($\mathcal{V} = 10, 10^2, 10^3,$ and 10^4) are plotted in Figure 6 for seven values of \mathcal{S} (in the
 124 range $\mathcal{S} \in [-0.99, 0.99]$, with six uniform increments). For the considered drop volumes, which are greater than those for
 125 which line tension dominates alone, the influence of volume on the macroscopic contact angle is stronger for negative values of
 126 \mathcal{S} than for positive ones. Therefore, in this case, the higher the sessile drop volume, the stronger the influence of \mathcal{S} on its
 127 shape.

128 **Discussion**

129 A new macroscopic mechanical model was derived to compute the shape of weightless sessile drops in static equilibrium.
 130 Our initial motivation was to understand more clearly the repeatability issues encountered while creating sessile drops in
 131 weightlessness by injecting liquid through a small hole in a substrate^{21,22}. The derived model is based on the classical
 132 Young–Laplace equation, Eq.(4), supplemented with a constitutive relationship for the pressure difference across the liquid–gas
 133 interface, Eq. (5). Assuming a flat, smooth, and homogeneous solid substrate, the model considers both the surface densities
 134 of the free energy at the solid–liquid and liquid–gas interfaces, along with the line density of energy along the contact line.
 135 The \pm sign in Eq. (5) accounts for the contact angle hysteresis associated with an advancing or receding contact line. First,
 136 the resulting governing equation, Eq. (7), clearly indicates that the volume affects the macroscopic contact angle only when
 137 $(\sigma_{sg} - \sigma_{sl})/\sigma_{slg}$, the ratio of the difference in the substrate surface tensions to the contact line one, is commensurable on the
 138 macroscopic scale.

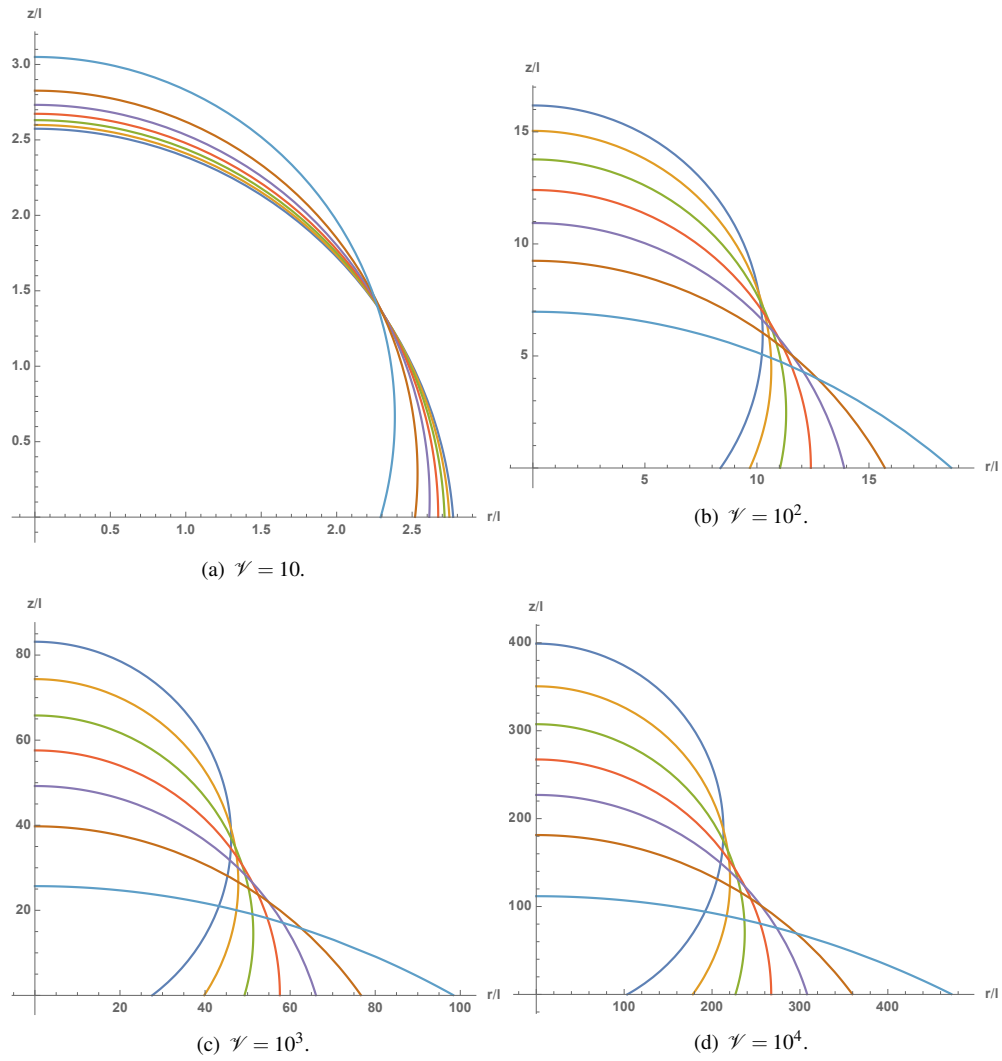


Figure 6. Influence of \mathcal{S} on sessile drop shape for four volumes and seven values of \mathcal{S} , ranging from -0.99 (dark blue) to 0.99 (light blue), separated by six equidistant steps.

The volume dependence of the macroscopic contact angle results from the solution of the derived governing equation, Eq.(7). Indeed, unlike in Boruvka and Neumann's line tension model^{4,6-8}, no a priori explicit dependence of the macroscopic contact angle on the drop radius was introduced in the proposed model. Therefore, the main outcome of the present mechanistic macroscopic model is that neither the classical Young's equation¹ nor the modified Young's equation proposed by Boruvka and Neumann⁸ are appropriate for determining the macroscopic contact angle of weightless sessile drops. The evidence of this assertion is contained in Eq. 2, which is the governing equation for the macroscopic contact angle derived from our weightless model with respect to the drop wetted radius r (instead of drop volume V , that results in Eq. (7)). It reads:

$$(2 - 3 \cos \theta + \cos^3 \theta) + \sin^2 \theta \left(\mathcal{S} + \frac{2 \sigma_{slg}}{r \sigma_{lg}} - 1 - \tan^2 \left(\frac{\theta}{2} \right) \right) = 0 \quad (2)$$

139 Interestingly, this governing equation expressed in drop wetted radius, Eq. 2, evidences that in weightlessness the macroscopic
 140 contact angle does not evolve as simply as in the $1/r$ Boruvka and Neumann's model, but in much more subtle highly
 141 nonlinear way. Indeed, upon approaching the very small drop volumes for which line tension dominates, the obtained behavior
 142 significantly deviates from the $1/r$ slope because of the highly non-linear trigonometric functions involved in the spherical
 143 cap model. These latter dominate the sessile drop shape at the lower limits of macroscopic volumes, as depicted in Figures 2
 144 and 3(a).

145 Furthermore, the proposed model reproduces the influence of volume on the macroscopic contact angle of a sessile drop,
 146 which has been reported in several ground experimental studies^{2,3,6}. Interestingly, in weightlessness, the influence of volume
 147 on the macroscopic contact angle exists over a much wider range of drop size, as no capillary length exists, unlike under Earth's
 148 gravity conditions. Indeed, unlike in the latter, it is not obscured by any hydrostatic pressure effect on the local interface
 149 curvature, as no capillary length exists in weightlessness. This enabled us to perform extended parametric studies on volume
 150 size effects. The proposed macroscopic model has a lower bound volume at which only line tension dictates the limit behavior,
 151 hydrophobicity (hydrophilicity), depending on whether its sign is negative (positive). Indeed, when the drop size reaches the
 152 lowest macroscopic limit, the related macroscopic contact angle approaches its limit value, $\theta_{lim} = \frac{\pi}{2} [1 - \text{sign}(\sigma_{slg})]$, regardless
 153 of the sign of \mathcal{S} . No lower sessile drop volume can be considered, as the present macroscopic model reaches its limit of
 154 physical representativity. At this lower limit, the driving mechanisms that act at microscopic scales, such as meniscus curvature,
 155 are not accounted for. Upon increasing the drop volume from this lower bound, the macroscopic contact angle continuously
 156 evolves with respect to the drop volume toward its asymptotic infinite value, $\theta_{\infty} = \arccos \mathcal{S}$. Notably, this infinite limit value
 157 coincides exactly with that from the classical Young's equation, Eq. (1), although the latter is not involved in the present model.
 158 Therefore, the volume dependence of the macroscopic contact angle is maximum for negative values of $(\sigma_{sg} - \sigma_{sl})/\sigma_{slg}$ and
 159 increases with the magnitude of $|\mathcal{S}|$. Furthermore, a crossover between hydrophobic (non-wetting) and hydrophilic (wetting)
 160 behaviors or vice versa always occurs for a specific sessile drop volume, $\mathcal{V}_{co} = 1/|\mathcal{S}|^3$, when $(\sigma_{sg} - \sigma_{sl})/\sigma_{slg}$ is negative, i.e.,
 161 when the line tension and surface tension act in opposite directions.

162 Furthermore, the macroscopic contact angle can vary at static equilibrium over a broad volume range and it can increase or
 163 decrease against volume depending on the sign of the surface to line ratio of free energies until it reaches its asymptotic value.
 164 Finally, the injection pressure is not a relevant control parameter for creating in a well-controlled way sessile drops of a target
 165 volume by injecting liquid through a small hole in the substrate. Indeed, the injection pressure evolves in a strongly non-linear
 166 manner with sessile drop volume: it continuously decreases against drop volume for negative \mathcal{S}/l_{σ} cases, whereas conversely,
 167 it first increases and then decreases (please refer to Figure 4(e)). Thus, feedback control systems based on pressure only are
 168 likely to be unstable, so the authors recommend enslaving the injection mass flow rate to drop volume instead of drop pressure.
 169 Actually, a constant injection pressure would result in a continuously accelerating injection flow rate, which makes inertia terms
 170 to become more and more prevalent, and prevent to achieve at the end of the injection stage a sessile drop of prescribed target
 171 volume. Moreover, since it exists some macroscopic contact angle hysteresis from advancing and receding contact line modes,
 172 getting back from an oversized drop to an accurate target volume becomes even much trickier.

173 Future research must focus on experiments in weightlessness on sessile drops for much larger volume ranges than those that
 174 exist under Earth's gravity conditions. Indeed, the present weightless model clearly indicates that the macroscopic contact
 175 angle asymptotically converges towards the value of the Young's equation in the limit of large volumes. So, in this limit
 176 weightless experiments can provide reference data for the surface tension values (σ_{sg} , σ_{ls} , and σ_{lg}), which are crucial for
 177 accurate predictive modelling. Then, considering on the other hand the lower volume range, one can evaluate in turn the line
 178 tension value σ_{slg} , enabling us to assess the validity of the volume dependence of the macroscopic contact angle. Finally, one
 179 can check the model predictions on limit volumes for both hydrophilic and hydrophobic cases. If such experiments confirm the
 180 predictions of the proposed model, they will potentially have an impact on the current physical understanding of sessile drops,
 181 even under Earth gravity conditions. If the sessile drop volume influences the macroscopic contact angle in weightlessness,
 182 it should also have the same effect under Earth gravity. However, this is somehow blurred or screened by the self-adaption
 183 of the local interface curvature to the hydro-static pressure, which becomes the dominant contact line mechanism as soon as

184 the drop size exceeds some fraction of its capillary length. Therefore, the authors believe that the present weightless model
 185 could nevertheless predict some representative results either in micro-gravity or Earth gravity conditions, provided the relative
 186 perturbation induced by the hydro-static pressure with respect to capillary one does not exceed few percent (below 10%),
 187 according to a first order perturbation technique. Hence, the validity of the classical Young's equation¹ for the macroscopic
 188 contact angle is affected to some extent by the volume dependence previously reported in ground experiments^{2,4-7}.

189 Methods

190 A new model

191 Let us consider the static mechanical equilibrium of a weightless sessile drop of a given volume and with a fixed set of
 192 properties for the liquid, substrate, and surrounding gas. To prevent unnecessary modeling complexity and related issues, the
 193 solid substrate is assumed to be flat, smooth, and homogeneous. To create this sessile drop by injecting liquid through a small
 194 hole in the substrate (monotonously advancing contact line), the supplied injection pressure should overcome the free energies
 195 associated with the curved liquid–gas interface, wetting a certain amount of substrate area at the liquid–solid interface, and the
 196 advancing contact line, respectively.

197 Governing equations

Assuming a sufficiently slow injection flow rate, such that inertia and viscous dissipation terms are negligible with respect to the surface and line free energies, the mechanical work associated with liquid injection for a sessile drop of volume V is:

$$\int_V [p_i(v) - p_e] dv = \int_{A_{lg}} \sigma_{lg} da + \int_{A_{sl}} (\sigma_{sl} - \sigma_{sg}) da + \int_{L_{slg}} \sigma_{slg} dl \quad (3)$$

198 where p_i and p_e are the liquid drop bulk pressure and surrounding gas pressure, respectively; σ_{lg} , σ_{sg} , and σ_{sl} are the liquid–gas,
 199 solid–gas, and liquid–solid surface densities of the surface free energy, respectively; and A_{lg} and A_{sl} are the liquid–gas and
 200 solid–liquid interface areas, respectively. Finally, σ_{slg} is the line density of the three-phase zone free energy associated with the
 201 macroscopic contact line, defined as the perimeter of the wetted surface, L_{slg} .

202 To proceed in this weightless static mechanical equilibrium, it is noteworthy that the bulk pressure in the liquid drop
 203 and surrounding gas pressure are both constant, so their difference behaves accordingly; this results in a constant curvature
 204 of the liquid–gas interface. Consequently, the weightless sessile drops are spherical caps. This geometrical feature and its
 205 associated trigonometric relationships are crucial for deriving any analytical expression that relates the mechanical equilibrium
 206 to quantities associated with the macroscopic shape of the sessile drop in a closed form: volume (V), wetted radius (r), height
 207 (h) and static macroscopic contact angle (θ).

A static equilibrium results in a normal and tangential macroscopic force balance at the solid–liquid and liquid–gas interfaces, respectively. Its normal component to the substrate leads to the Young–Laplace equation:

$$p_i - p_e = 2\sigma_{lg} \frac{\sin \theta}{r} = \frac{2\sigma_{lg}}{R} \quad (4)$$

208 where R is the radius of the resulting spherical cap.

To derive a well-posed governing equation, a constitutive relationship was introduced for the bulk pressure of weightless sessile drop. Therefore, assume that any difference in chemical potential between the liquid, solid substrate, and surrounding gas produces adhesive or repulsive forces at the molecular scale acting along their respective solid–liquid, liquid–gas, and three-phase zone. Then, these forces can translate into pressure in the bulk of the liquid drop. Assuming thermodynamic equilibrium, both the surface and line densities of free energy become constant, enabling the formal integration of Eq. (3). Then, dividing the integrated equation by the consistent drop volume leads to the proposed local constitutive relationship for the bulk pressure:

$$p_i - p_e = \frac{\sigma_{lg} \pi (r^2 + h^2) + (\sigma_{sl} - \sigma_{sg}) \pi r^2 \pm \sigma_{slg} 2\pi r}{V_{ci}} \quad (5)$$

where the \pm in front of the contact line free energy (σ_{slg}) is associated with the contact angle hysteresis, with a positive (negative) sign for an advancing (receding) contact line. Moreover, the consistent volume integration is such that the final governing equation satisfies the surface-to-volume ratio for any spherical cap, that is, $V_{ci} = 3V/2$. Equating the bulk pressure differences from Eq. (4) and Eq. (5) and replacing R , r , and h with their respective trigonometric relationships defined in

Eq. (6),

$$R = \left[\frac{3V}{\pi(2 - 3\cos\theta + \cos^3\theta)} \right]^{1/3} \quad (6a)$$

$$\frac{h}{r} = \tan(\theta/2) \quad (6b)$$

$$r = \left[\frac{6V}{\pi \tan(\frac{\theta}{2}) [3 + \tan^2(\frac{\theta}{2})]} \right]^{1/3} \quad (6c)$$

the following governing equation for the weightless macroscopic contact angle θ of the advancing contact line is finally obtained:

$$\begin{aligned} & \left[(2 - 3\cos\theta + \cos^3\theta)^{\frac{1}{3}} \left(\tan\left(\frac{\theta}{2}\right) \left[3 + \tan^2\left(\frac{\theta}{2}\right) \right] \right)^{\frac{2}{3}} - 2^{\frac{2}{3}} \left(1 + \tan^2\left(\frac{\theta}{2}\right) - \mathcal{S} \right) \right] \mathcal{V}^{\frac{1}{3}} \\ & + \left(\tan\left(\frac{\theta}{2}\right) \left[3 + \tan^2\left(\frac{\theta}{2}\right) \right] \right)^{\frac{1}{3}} = 0 \end{aligned} \quad (7)$$

\mathcal{S} and \mathcal{V} are two dimensionless numbers that determine the macroscopic contact angle in weightlessness. They are related to the physical parameters of the problem, as follows:

$$\mathcal{S} = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}} \quad (8a)$$

$$\mathcal{V} = \frac{V}{l_{ref}^3} \quad (8b)$$

$$l_{ref} = \left(\frac{16\pi}{3} \right)^{\frac{1}{3}} |l_\sigma| \quad (8c)$$

where $l_\sigma = \frac{\sigma_{slg}}{\sigma_{lg}}$ and l_{ref} are the physical reference lengths of the weightless sessile drop. However, another scale associated with the volume of the derived macroscopic model can also be defined:

$$l_{mac} = \lim_{\theta \rightarrow \theta_{lim}} V^{\frac{1}{3}}, \text{ with } \theta_{lim} = 0^+ \text{ if } \sigma_{slg} > 0, \text{ otherwise } \theta_{lim} = \pi^- \quad (9)$$

209 According to this definition, the minimal macroscopic length l_{mac} is the size of the weightless sessile drop above which a
210 macroscopic contact angle can be determined using Eq. (7). Conversely, below l_{mac} , we expect the presented macroscopic
211 model to be irrelevant.

The expression of Eq. (7) is dimensionless, which reveals the direct influence of the $\mathcal{S}\mathcal{V}^{\frac{1}{3}}$ product on the macroscopic contact angle. Therefore, this is a key component in the definition of a dimensionless number, which quantifies the static macroscopic contact angle of a weightless sessile drop. The first method introduced herein is defined as follows:

$$\mathcal{W}_\theta = \left[\frac{2}{\pi} \arccos \mathcal{S} + \text{sign}(\sigma_{slg}) - 1 \right] [(1-s)f_{co} + sf_{pa}] + \text{sign}(\sigma_{slg}) \quad (10a)$$

$$s = [1 + \tanh(a\mathcal{L} + b)] / 2 \quad (10b)$$

$$f_{co} = \exp\left(-\left[\frac{\mathcal{L}-1}{c}\right]^d\right) \quad (10c)$$

$$f_{pa} = \frac{e}{f\mathcal{L} + g} + \frac{1}{\mathcal{L}} \quad (10d)$$

$$\mathcal{L} = V^{\frac{1}{3}} / l_{mac} \quad (10e)$$

212 The proposed definition of \mathcal{W}_θ , Eq.(10a), is tailored to lie within $[-1, 1]$ and to indicate the hydrophobic, neutral, or hydrophilic
213 behavior of the weightless sessile drop for negative, null, or positive values, respectively. Moreover, it represents the signed
214 dimensionless distance to cross-over behavior. To meet all these requirements, we introduce a sigmoid function, defined as
215 s in Eq.(10b), which is built on the hyperbolic tangent for generating a smooth transition between the contrasting behaviors
216 encountered at the limit angle and away from it. \mathcal{L} is the dimensionless drop length for characterizing the macroscopic

217 contact angle in weightlessness. f_{co} and f_{pa} , account for the specific behaviors encountered over the entire variation range. f_{co}
 218 connects to the limit angle θ_{lim} at $\mathcal{L} = 1$, and f_{pa} enables the transition from this connecting region to the asymptotic region
 219 of hyperbolic $1/\mathcal{L}$ behavior. All constants (a, b, c, d, e, f , and g) depend on \mathcal{S} , l_σ , and $\text{sign}(\sigma_{slg})$, which are the physical
 220 parameters of the problem.

221 **Model validation using published experimental data**

222 Before discussing the proposed model, it is important to validate it using existing experimental results. Unfortunately, to
 223 the best of the authors' knowledge, none of the published experimental results on weightlessness include any quantifiable
 224 dependence of the macroscopic contact angle on volume. Therefore, the results obtained using the proposed model are plotted
 in Figure 7 against the experimental data obtained considering Earth's gravity conditions.

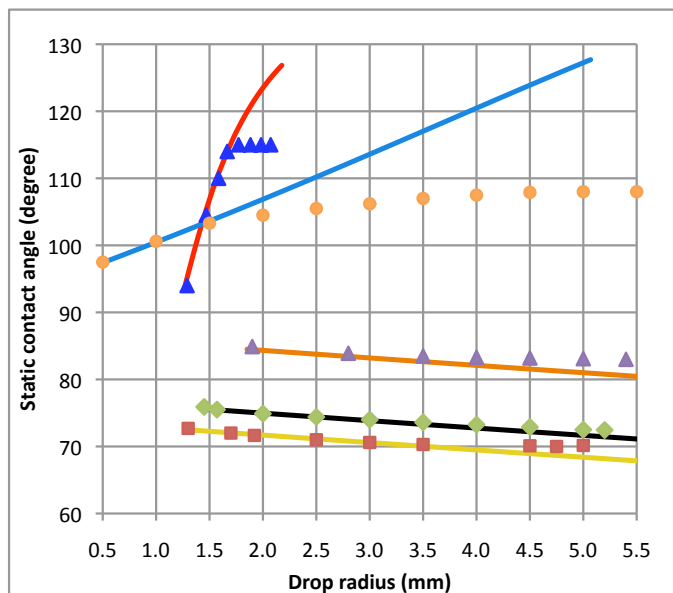


Figure 7. Comparison of proposed model with published experimental data. Legend: blue triangles – Herzberg and Marian² (table 1), orange solid line – present model ($\mathcal{S} = -0.96$ and $l_\sigma = 0.25\text{ mm}$); orange dots – Ponter and Yekta-Fard³ (figure 4), blue solid line – present model ($\mathcal{S} = -0.77$ and $l_\sigma = 0.035\text{ mm}$); purple triangles – Li and Neumann⁶ (figure 3, lower plot), orange solid line – present model ($\mathcal{S} = 0.26$ and $l_\sigma = -0.015\text{ mm}$); green diamonds – Li and Neumann⁶ (figure 3, middle plot), black solid line – present model ($\mathcal{S} = 0.42$ and $l_\sigma = -0.015\text{ mm}$); red squares – Li and Neumann⁶ (figure 3, top plot), yellow solid line – present model ($\mathcal{S} = 0.47$ and $l_\sigma = -0.015\text{ mm}$).

225 Although a broad range of fluids, substrates, and surrounding gases are involved in the five selected experimental results^{2,3,6},
 226 fitting the \mathcal{S} and l_σ parameters of the proposed model to the lower drop size experimental points in each of the considered
 227 cases enables us to determine the influence of volume on the macroscopic contact angle satisfactorily. Interestingly, the results
 228 of the proposed weightlessness model deviate from those of Earth gravity experiments as soon as the drop size reaches some
 229 fraction of its capillary length (water / air fluids: $\lambda_c \approx 2.6\text{ mm}$, ethylene glycol / air fluids: $\lambda_c \approx 2.0\text{ mm}$, respectively). This
 230 occurs because the influence of volume no longer exists under gravity conditions, whereas it persists in weightlessness. A
 231 sharp departure is observed for the most hydrophobic case of water on a polyethylene substrate² for a drop radius exceeding
 232 $r = 1.7\text{ mm}$ (drop volume from Table 1 in Herzberg and Marian² translated into drop radius, as shown in Eq. (6c)). Moreover,
 233 this case is that of highest slope among the five considered cases ($\mathcal{S} = -0.96$). For the second hydrophobic case of water
 234 on Polytetrafluoroethylene (PTFE), a milder deviation occurs between the present model and experimental results from Ponter
 235 and Yekta-Fard³ above a comparable radius of $r > 1.7\text{ mm}$. For both hydrophobic cases considered here, fairly consistent l_σ
 236 have been introduced to fit experimental results from Herzberg and Marian² and Ponter and Yekta-Fard³, $l_\sigma = 0.25\text{ mm}$ and
 237 0.035 mm , respectively. On the other hand, for the three hydrophilic cases, either for Dodecane on FC-721 substrate and Zonyl
 238 FSC one, or Ethylene Glycol on DDOAB substrate⁶, only a slight volume dependence of the macroscopic contact angle is
 239 observed, which results in a minute slope for the three cases. This explains why only minor deviations can be observed for
 240 drop radii beyond $r = 4\text{ mm}$, cf. Figure 7. Moreover, very small l_σ have been introduced to fit the experimental values from⁶
 241 comparatively to those introduced for the two hydrophobic cases, a same $l_\sigma = -0.015\text{ mm}$ in the three cases.
 242

243 Data availability

244 The data that support the findings of this study are available from <https://doi.org/10.5281/zenodo.4382265>

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250 Author contributions statement

251 M. M. derived the governing equations and produced the results. All authors contributed to their analyzes and wrote the
252 manuscript.

253 Competing interests

254 The authors declare no competing interests.

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293 Figure legends

294 Figure 1: Sketch of sessile drop injected from below through a sub-millimetric hole in the substrate.

295 Figure 2: Macroscopic contact angle versus dimensionless geometrical quantities (\mathcal{L} , h , r and R), for $\mathcal{S} = -0.99$ (blue),
 296 $-2/3$ (cyan), $-1/3$ (green), 0 (yellow), $1/3$ (orange), $2/3$ (red) and 0.99 (magenta). The solid (dashed) lines represent the
 297 plots of positive (negative) \mathcal{S}/l_σ .

298 Figure 3: Macroscopic contact angle versus (a) dimensionless drop size \mathcal{L} and (b) dimensionless contact angle \mathcal{W}_θ , for
 299 $\mathcal{S} = -0.99$ (blue), $-2/3$ (cyan), $-1/3$ (green), 0 (yellow), $1/3$ (orange), $2/3$ (red) and 0.99 (magenta). The solid (dashed)
 300 lines represent the plots for positive (negative) \mathcal{S}/l_σ .

301 Figure 4: Plots of related sessile drop dimensionless quantities: (a-b) wetted radius, (c-d) drop height, (e-f) sphere radius,
 302 for $\mathcal{S} = -0.99$ (blue), $-2/3$ (cyan), $-1/3$ (green), 0 (yellow), $1/3$ (orange), $2/3$ (red) and 0.99 (magenta). The solid (dashed)
 303 lines represent the plots for positive (negative) \mathcal{S}/l_σ .

304 Figure 5: Influence of sessile drop volume on its shape in the small to medium range ($\mathcal{V} = 5$ (dark blue), 25 (brown), 50
 305 (purple), 100 (orange), 150 (green), 200 (yellow) and 250 (light blue)) for six values of \mathcal{S} and negative \mathcal{S}/l_σ .

306 Figure 6: Influence of \mathcal{S} on sessile drop shape for four volumes and seven values of \mathcal{S} , ranging from -0.99 (dark blue) to
 307 0.99 (light blue), separated by six equidistant steps.

308 Figure 7: Comparison of proposed model with published experimental data. Legend: blue triangles – Herzberg and Marian²
 309 (table 1), orange solid line – present model ($\mathcal{S} = -0.96$ and $l_\sigma = 0.25\text{ mm}$); orange dots – Ponter and Yekta-Fard³ (figure 4),
 310 blue solid line – present model ($\mathcal{S} = -0.77$ and $l_\sigma = 0.035\text{ mm}$); purple triangles – Li and Neumann⁶ (figure 3, lower plot),
 311 orange solid line – present model ($\mathcal{S} = 0.26$ and $l_\sigma = -0.015\text{ mm}$); green diamonds – Li and Neumann⁶ (figure 3, middle
 312 plot), black solid line – present model ($\mathcal{S} = 0.42$ and $l_\sigma = -0.015\text{ mm}$); red squares – Li and Neumann⁶ (figure 3, top plot),
 313 yellow solid line – present model ($\mathcal{S} = 0.47$ and $l_\sigma = -0.015\text{ mm}$).