



HAL
open science

The role of Laplace pressure in the maximal weight of pendant drops

Laure Lecacheux, Abdelkrim Sadoudi, Agnès Duri-Bechemilh, Véronique Planchot, Thierry Ruiz

► **To cite this version:**

Laure Lecacheux, Abdelkrim Sadoudi, Agnès Duri-Bechemilh, Véronique Planchot, Thierry Ruiz. The role of Laplace pressure in the maximal weight of pendant drops. *Journal of Colloid and Interface Science*, 2022, 606, pp.920-928. 10.1016/j.jcis.2021.08.047 . hal-03345528

HAL Id: hal-03345528

<https://hal.inrae.fr/hal-03345528v1>

Submitted on 16 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 **The role of Laplace pressure in the maximal weight of pendant drops**

2

3 Laure Lecacheux^{1,2}, Abdelkrim Sadoudi², Agnès Duri², Véronique Planchot², Thierry Ruiz^{1*}

4

5 ¹ UMR QualiSud, Univ. Montpellier, CIRAD, Montpellier SupAgro, Univ. Avignon, Univ. La
6 Réunion – 15 avenue Charles Flahault, 34093, Montpellier cedex 5, France.

7 ² UMR IATE 1208 INRAE/Montpellier SupAgro/Univ. Montpellier – 2 Place Pierre Viala,
8 34060 Montpellier cedex 1, France.

9

10 * corresponding author

11 Email. thierry.ruiz@umontpellier.fr

12

13 **Abstract.**

14

15 *Hypothesis*

16 The value of the maximal weight of a pendant drop formed at the end of a syringe needle is
17 lower than the intensity of the corresponding capillary force. The balance of the external
18 forces applied to the maximal pendant drop must be completed by the overpressure generated
19 by the piston of the syringe. Inside the drop, the Laplace pressure corresponds to this
20 overpressure.

21

22 *Experiments*

23 Pendant drops are made with three liquids and five different needle diameters. The influence
24 of Laplace pressure on the maximal weight is experimentally highlighted by modulating the

25 drop curvatures thanks to glass beads placed at the apex of the pendant drop. Their maximal
26 weight and curvatures are measured by image analysis.

27

28 *Findings*

29 Experiments confirm that the balance of external forces must be completed by the force acting
30 on the syringe piston. The overpressure on the piston has an impact on the drops via the
31 Laplace pressure. A master curve between the mean curvature and the maximal volume of the
32 pendant drops is observed. This result allows to validate an expression of the maximal weight
33 which integrates the Laplace pressure. This work contributes to a better understanding of the
34 maximal pendant drop properties and beyond, of the capillary phenomenon.

35

36 **Keywords.** Pendant drop; Maximal drop weight; Capillary force; Laplace pressure;
37 Curvature; Image analysis.

38

39 **Nomenclature**

40

41 *Abbreviations*

42

43 b (glass) bead

44 d drop

45 e external

46 eq equilibrium

47 i internal

48 l liquid

49 n needle

50	p	piston
51	*	loaded drop
52		
53	<i>Symbols</i>	
54		
55	B_o	Bond number [-]
56	$2H$	mean curvature [m^{-1}]
57	D_n	Diameter of the needle [m]
58	\vec{F}_p	force increment applied by the piston on the pendant drop [N]
59	\vec{F}_c	capillary force at the wetted perimeter [N]
60	g	gravity acceleration [$m.s^{-2}$]
61	H_l	height of liquid column in the syringe [m]
62	L_n	needle length [m]
63	M_b	mass of a glass bead [kg]
64	M_d	maximal mass of a pendant drop [kg]
65	M_d^*	maximal mass of a loaded pendant drop [kg]
66	M_l^*	mass of the liquid in a loaded pendant drop [kg]
67	P_n	pressure at the end of the needle [Pa]
68	P_p	pressures at the piston [Pa]
69	Q	feeding volume flow rate [$m^3.s^{-1}$]
70	Re	Reynolds number [-]
71	R_1	radial curvature radius [m]
72	R_2	axial curvature radius [m]
73	\vec{v}_d	barycentric velocity of the drop [$m.s^{-1}$]
74	V_d	maximal volume of a single pendant drop [m^3]

75	V_d^*	maximal volume of a loaded pendant drop [m ³]
76	\vec{z}	vertical position from the bottom of the needle [m]
77	γ	surface tension of the liquid [N.m ⁻¹]
78	ΔP_L	Laplace pressure [Pa]
79	ΔP_n	overpressure within the fluid at the end of the needle [Pa]
80	ΔP_p	overpressure at the piston [Pa]
81	$\Delta P_{p \rightarrow n}$	pressure drop in the syringe [Pa]
82	Δz	incremental displacement of the piston lowering [Pa]
83	η	viscosity of the liquid [Pa.s]
84	θ	wetting angle [rad]
85	κ^{-1}	capillary length [m]
86	ρ_l	true density of the liquid [kg.m ⁻³]
87	ρ_b	true density of the glass [kg.m ⁻³]
88	Ω_s	internal section of the syringe [m ²]

89

90 **1. Introduction**

91

92 Pendant drops at the end of a syringe capillary, are easily made objects that have a regularity
93 of size and shape, offering the possibility to use them in multiple applications. They can be
94 used as micromanipulators to capture small objects by capillary interaction thanks to the
95 formation of a liquid-bridge at their apex [1,2]. These same capillary interactions are also
96 used to structure assemblies of colloidal or granular particles. Liquid marbles are other
97 applications that implement these surface interactions with colloids [3,4,5]. Drops are also
98 used for agglomeration or granulation unit operations [6,7]. The drop properties (in particular
99 their size and volume), which interact with powder to associate them into agglomerated

100 structures [8,9], require a precise control in order to best master the associative processes
101 [10,11]. Because the small drop volume is circumscribed by surface tension, it can also be
102 directly used as a millireactor where various chemical reactions can be performed [12,13].
103 The pendant drop of a colloidal suspension or a macromolecular solution constitutes a
104 reactional volume in which a "stoichiometric forcing" can occur as the volume decreases by
105 evaporation [14]. In spray-drying, specific reactions are achievable and the control of the
106 structural mechanisms to which they lead, requires the mastering of the evolution of the drop
107 volume which can be studied in a pendant configuration [15]. Pendant drops are also
108 employed to determine the surface tension of a liquid [16,17,18], from the analysis of the
109 shape of a pendant drop in equilibrium and matching its contouring curve to a mathematical
110 solution of the Young-Laplace equation. This inverse method allows to identify the surface
111 tension value which represents the fitting factor.

112 There is a second method, called the drop weight method [19], which is based on the
113 comparison between the weight of a falling drop (measured) and its theoretical value
114 estimated from Tate's law [20]. The surface tension is the adjustment parameter that allows to
115 fit these two values. Tate's law relates the maximum weight of a pendant drop to the capillary
116 force that holds the drop in equilibrium at the end of a syringe needle, just before it falls off.
117 Since only part of the pendant drop falls off, leaving a residual fraction on the needle, it is
118 necessary to correct the weight of an "ideal drop" given by Tate's law by a correction factor.
119 Among the most widely used works for this purpose, that of Harkins and Brown [21]
120 proposes values of the correction factor tabulated on a chart. But the exact calculation of the
121 maximum weight just before its detachment would ensure even greater precision.

122

123 The aim of this work is to determine the maximal weight of a pendant drop at the end of a
124 syringe needle by experimental investigations and theoretical developments. We propose to

125 define a consistent expression of the maximum weight of a pendant drop. No particular
126 application of this result will be favored. Experimental results related to the measurement of
127 the maximal weight of drops performed with three liquids of different known surface tensions
128 and five different needle sizes, are presented. These experiments are carried out at small Bond
129 numbers of the needle in order to achieve the same drop shape (piriform). We observe that the
130 weight of the pendant drop is not equal to the capillary force which ensures the drop/needle
131 connection. This gap is attributed to the lack of a force in the balance of external forces
132 applied to the drop. In order to reveal the importance of this missing force, mechanical stress
133 tests are performed by adding a calibrated glass bead at the apex of the drop, without
134 changing the intensity of the capillary force. Beads of increasing mass induce a variation of
135 the mean curvature directly associated with a variation of the maximal weight of the drops
136 following a master curve. The repercussion of these variations on the Laplace pressure
137 generates a force which completes the force balance. To demonstrate mathematically this
138 important point, a physical reasoning, based on the fluid mechanics, is developed. These
139 results allow us to introduce the Laplace pressure in the mathematical model which predicts
140 the maximal weight of a pendant drop.

141

142 **2. Experimental procedure**

143

144 **2.1. Prototype description**

145

146 A prototype, presented in Figure 1, was designed to study the formation of a pendant drop at
147 the end of a capillary until its maximal volume, just before its detachment. It consists of a PPT
148 syringe composed of a body of an internal section $\Omega_S = 61 \text{ mm}^2$, a piston and a tapered tip
149 allowing the adaptation of a straight cut steel needle (Doseurope) of section Ω_{ni} . Five

150 different needle sizes were used. Their external diameter D_{ne} is: 0.23, 0.5, 0.8, 1.26 and 1.80
151 mm and their internal diameter D_{ni} is respectively: 0.11, 0.26, 0.51, 0.84 and 1.37 mm. In
152 order to ensure a constant flow rate of liquid ($Q \sim 0.097$ to $0.387 \text{ mm}^3 \cdot \text{s}^{-1}$), a syringe pump
153 driven by a stepper motor (MicroLYNX, M-1410-0.75D) is used to provide a vertical
154 displacement according to \vec{z} . This flow rate gives a velocity intensity in the needle comprised
155 between 0.26 and $5 \text{ mm} \cdot \text{s}^{-1}$. For each test, the laminar flow inside the needle is achieved with
156 a Reynolds number comprised between 18×10^{-3} (Triacetin with the largest needle) and
157 5.6×10^{-1} (water with the smallest needle). The evolution of the pendant drop formation until
158 its maximal volume is filmed using a USB microscope (DinoLite®) placed in front of the
159 needle with an acquisition rate of $25 \text{ images} \cdot \text{sec}^{-1}$. A LED backlight system is also used to
160 enhance the contrast.

161

162 The prototype is placed on an insulated support to avoid any vibration and is isolated in a
163 plexiglass chamber to minimize any contamination. All the tests are performed in quintuples,
164 at a controlled temperature of $25.0 \pm 0.2 \text{ }^\circ\text{C}$, and a relative humidity of $40 \pm 16 \%$. The total
165 duration of formation of a drop is between 1 and 2 minutes which allows to neglect the
166 evaporation phenomena [22].

167

168 **2.2. Characteristics of liquids**

169

170 Pure water, Tween® 80 (Sigma-Aldrich) diluted at $2 \times 10^{-3} \text{ g/L}$, and Triacetin® (C2 99.0%,
171 Sigma-Aldrich) are the three considered liquids. The surface tension, γ , measured using a
172 tensiometer Kruss K100 (Kruss, Germany) according to the Wilhelmy plate, is equal to
173 $71.83 \pm 0.59 \text{ mN} \cdot \text{m}^{-1}$ for water, $43.74 \pm 0.09 \text{ mN} \cdot \text{m}^{-1}$ for Tween 80, and $34.55 \pm 0.25 \text{ mN} \cdot \text{m}^{-1}$ for
174 Triacetin. The density, ρ_l , obtained thanks to DSA 5000M sonodensimeter (Anton Paar,

175 France), corresponds to 0.997 ± 0.001 g.cm⁻³ for water and Tween 80, and 1.152 ± 0.001 g.cm⁻³
176 for Triacetin. The viscosity, η , determined using a rheometer Physica MCR 301 equipped
177 with a double gap mobile (Anton Paar, Austria), has the value of 1.005 ± 0.005 mPa.s for
178 water, 1.010 ± 0.012 mPa.s for Tween 80, and 23.021 ± 0.001 mPa.s for Triacetin. All
179 measurements were performed in triplicate at 25°C.

180

181 These three liquids are distinguished by the capillary length: $\kappa^{-1} = \sqrt{\gamma/\rho_l g}$, sufficiently
182 contrasted (2.71 mm for water, 2.11 mm for Tween 80 and 1.83 mm for Triacetin) to show
183 differences in the geometric characteristics of the drops. For each tested configuration, the
184 Bond number of the drop: $B_{od} = (R_1/\kappa^{-1})^2 < 1$ (Fig. 2) and the Bond number of the needle:
185 $B_{on} = (D_{ne}/2\kappa^{-1})^2 < B_{od}$, ensure a piriform geometry of the drops.

186

187 **2.3. Description of the mechanical test**

188

189 This mechanical test, adapted from the works of Li et al. [23] and Neeson et al. [24], consists
190 in loading with a calibrated particle of known mass a pendant drop obtained from a needle of
191 a given diameter. Then the maximal weight of the loaded drop just before its detachment is
192 measured. In order to highlight the role of Laplace pressure on the weight of a pendant drop,
193 this test allows to modulate the main curvatures of the drop (see video).

194

195 The aim of this test is to achieve conditions that ensure invariance of the capillary force at the
196 drop/needle wetted perimeter while modulating Laplace pressure within the drop. When the
197 drop reaches a stage of development corresponding to about 30% of its maximum volume, the
198 glass bead is then approached to its apex. At its contact, the drop exerts a capillary traction
199 that captures the bead and keeps it in suspension in a position that respects the global

200 axisymmetry (Fig. 2). The hydrodynamic flow conditions in the syringe allow a quasi-
201 stationary evolution of the growth of the loaded drop. The shape of the drop, and in particular
202 its main curvatures, adapt to the resultant external forces applied to it [24]. Six spherical glass
203 beads (density of 2.501 g.cm^{-3}) of different masses (0.62, 1.48, 2.55, 4.52, 8.38 and 12.03 mg)
204 are used. The Bond numbers of the glass beads are less than 1, which ensures their capillary
205 capture by the pendant drop.

206

207 The operating conditions are identical to those used during the formation of a single pendant
208 drop and the evolution of the loaded drops is also captured by the USB microscope (Fig. 1).

209

210 **2.4. Determination of drop characteristics**

211

212 An image analysis method was developed to determine the maximum pendant drop volume
213 and the two radii of curvature. Technical details are given in the Supplementary Materials file.

214

215 *Maximal volume.* Each drop is filmed (from 1 to 2 min at 25 fps) during its entire
216 development and all the images are extracted (from 1500 to 3000) then analyzed to precisely
217 determine the maximum volume of each pendant drop. The linear progression of the volume
218 of the drop, due to the constant flow, makes it possible to locate the maximal volume reached
219 with an error less than 0.01 %. The maximum weight is then calculated from the
220 determination of the volume.

221

222 *Radius of curvature, main curvature and Laplace pressure.* The image, corresponding to the
223 limit stage of drop development, is used to determine the curvature radii. The curvature radius
224 R_1 , is determined at the level of the maximum diameter in the horizontal plane. The curvature

225 radius R_2 , is located in the vertical plane, and corresponds to the radius of the circle being
226 superimposed with the drop curve [18]. The main curvature of the drop is then deduced from
227 these measurements according to its standard definition in 3D space, $2H = \frac{1}{R_1} + \frac{1}{R_2}$. The
228 Laplace pressure in the drop is then calculated according to its definition [25]: $\Delta P_L = \gamma 2H$.
229 This procedure is used for single and loaded drops.

230

231 **3. Results and discussion**

232

233 **3.1. Maximal weight of a pendant drop**

234

235 Pendant drops are formed at the end of needle of a syringe using a stationary flow rate of the
236 liquid, Q , ensured by a force \vec{F}_p applied on the piston. The maximal mass reached by the drop,
237 M_d , is calculated from the measurement of the volume. The laminar regime ensures the
238 stability of the drop formation and we verify that neither the value of the flow nor the height
239 of liquid (H_l) between the surface of the piston and the lowest part of needle, does not change
240 the maximal mass of the drop (see Supplementary Materials file). This point implies that the
241 hydrostatic pressure does not affect the maximal weight of a pendant drop generated by a
242 syringe.

243 In these conditions, the balance of the external forces applied to a pendant drop takes into
244 account only three actions (the weight, the capillary force exerted at the triple line and inertia
245 [25]), and can be written as follow:

246

$$247 \quad M_d \vec{g} + \vec{F}_c = M_d \frac{d\vec{v}_d}{dt} \approx \vec{0} \quad (1)$$

248

249 where the inertial force is negligible when a steady state is imposed (a constant flow rate
250 implies that the barycentric velocity of the drop inertia center, \vec{v}_d , remains constant). The
251 projection of this vectorial equation on the horizontal axis cancels out, while on the vertical
252 axis we find that the weight must be compensated by the projection of the capillary force on
253 \vec{z} . Assuming that the intensity of the capillary force is equal to [25]: $F_c = \pi D_{ne} \gamma \cos(\theta)$, for
254 each tested condition, the wetting angle θ at the drop connection on the outer perimeter of the
255 needle is checked. It is always close to 0° and does not impact the value of the capillary force,
256 as already observed by Nazari et al. [26]. With this definition, the maximal weight of the
257 pendant drop is given by:

258

$$259 \quad M_d g = \gamma \pi D_{ne} \quad (2)$$

260

261 This expression is well known as the Tate's law [20, 27], and the maximal weight defined by
262 Equation (2) is classically called the weight of the "ideal drop". We remind that this
263 maximum weight is the weight of a pendant drop still attached to its needle and not the weight
264 of a detached drop. By plotting the measurements of the maximum drop weight as a function
265 of the corresponding capillary force for each tested case, it can be clearly observed in Figure
266 3a that Equation (2) is not verified. The capillary force is systematically higher than the
267 weight, and this gap is about $35.0\% \pm 1.2\%$ on average. Surprising as it may seem, we are not
268 aware of any experimental data in the scientific literature on the weight of pendant drops. All
269 the numerous works deal with detached drops with all the precautions on the validity of Tate's
270 law. Lee et al. [28] pointed out that the force balance used to define the weight of the "ideal
271 drop" does not include a compressive force in the upper plane of the drop. This balance needs
272 to be redefined [29,30]. Therefore, such a gap implies to consider again the balance of
273 external efforts applied to a pendant drop [30] taking into account the repercussion of the

274 force increment applied on the piston, \vec{F}_p , called the Laplace force, on the pendant drop. A
275 drop generated by a syringe is only developed by the action of a force increment on the
276 piston. This force is oriented in the same direction as the weight and is transmitted until the
277 top surface of the drop: $\pi D_{ni}^2/4$, via an overpressure throughout the liquid column. We can
278 show that this overpressure corresponds to the Laplace pressure in the pendant drop. The
279 expression of the external force balance becomes:

280

$$281 \quad M_d \vec{g} + \vec{F}_p + \vec{F}_c \approx \vec{0} \quad (3)$$

282

283 Under all these hypotheses and by introducing the definition of the Laplace pressure in the
284 external force balance exerted on the pendant drop, Equation (3) can be written as:

$$285 \quad M_d g = \gamma \pi D_{ne} - \Delta P_L \pi D_{ni}^2 / 4 \quad (4)$$

286

287 This equation involves the internal D_{ni} , and external D_{ne} diameters of the needle. From
288 Laplace's pressure measurements, we verify in Figure 3b that the maximal weight of a
289 pendant drop is then well described by Equation (3).

290

291 We propose in the following section an experiment at the drop level in order to highlight the
292 role of the Laplace pressure and the trend with which it acts on the maximal weight drop. The
293 implication of Laplace pressure in the balance of external forces applied to a pendant drop has
294 already been suggested by Garandet et al. [29]. However, our approach highlights the non-
295 contribution of hydrostatic pressure, contrary to the equation presented by Garandet et al.
296 [29]. We also provide an explanation of the origin of this involved Laplace force and a
297 justification by establishing a model under well-identified hypotheses.

298

299 3.2. Drop loading to highlight the Laplace pressure

300

301 The drop keeps held to the needle by the capillary force at its triple line which equilibrates the
302 weight added to the force applied on the piston transmitted to the drop via the pressure in the
303 liquid column. The test consists of keeping the capillary force constant (constant needle
304 diameter and constant surface tension of the liquid) and varying the drop weight by
305 distributing it between the liquid and a glass bead placed at the apex. Whatever its weight, the
306 presence of a glass bead does not modify the intensity of the capillary force exerted on the
307 pendant drop due to the fact that: (i) the wetted perimeter is unchanged, (ii) the contact angle
308 value just before drop detachment has been systematically measured by image analysis (Fig.
309 4) and remains unchanged: $\theta \approx 0^\circ$, and (iii) the liquid surface tension is not modified (the
310 beads are carefully cleaned beforehand). Thus, the force balance (Eq. 4) is satisfied for the
311 maximal total weight of the loaded drop: $M_d^*g = M_b g + M_l^*g$, where M_l^*g is the liquid
312 weight and $M_b g$ is the glass bead weight. The weight of the bead has an impact on the shape
313 of the drop (Fig. 4) and therefore on the Laplace pressure inside the drop. The drop loading
314 with a glass bead constitutes therefore a reliable mechanical test with a fixed capillary force.

315

316 For each liquid, increasing loads with calibrated glass beads were realised for all pendant
317 drops obtained with the five needles. Figures 5 presents an illustration of the maximal weight
318 of the loaded pendant drops, as a function of the bead mass. Whatever the needle diameter
319 and the liquid, the maximal weight of the loaded drops is not constant but decreases with the
320 increase of the bead mass. In all cases, $M_d g > M_d^*g$ and so, the hypothesis of the capillary
321 force, only opposed to the weight of the maximal pendant drop in the external force balance,
322 is invalidated by the imposed conditions in these experiments.

323

324 This result indicates that at constant capillary force, if the maximum weight of a pendant drop
325 decreases with increasing loads, then the Laplace pressure should increase to ensure the
326 external force balance (Eq. 4).

327

328 In order to determine the Laplace pressure in the drop, the mean curvature is measured. For a
329 given needle, as the particle mass increases, a loaded drop adopts an increasingly elongated
330 shape (Fig. 4). The axisymmetry being satisfied, the quantitative analysis of the main
331 curvatures (Fig. 2) shows that the increasing mechanical solicitation induces an elongation of
332 the axial radius of curvature (vertical plane), R_2 , and simultaneously a narrowing of the radial
333 radius of curvature (horizontal plane), R_1 (Fig. 6a). For each liquid and each needle, the radii
334 of curvature of the loaded drops are resized by those of the unloaded drops made with the
335 same needle: R_1^*/R_1 and R_2^*/R_2 . The antagonistic variation of the two radii of curvature
336 systematically leads to an increase of the mean curvature defined by: $2H^* = \frac{1}{R_1^*} + \frac{1}{R_2^*}$, for all
337 loaded pendant drops.

338

339 Figure 6b shows that $2H^*/2H$ ratio increases linearly with the solid mass fraction and is
340 superimposed on a single curve for all experiments.

341

342 For each tested liquid and needle, experiments show that loading induces a decrease of the
343 maximal weight of the pendant drops (Fig. 5) and an increase of the Laplace pressure (Fig. 7).
344 This point represents an experimental validation of the influence of the Laplace pressure in
345 the weight of a pendant drop. The expression of the external force balance given by Equation
346 (3) seems more correct than Equation (1).

347

348 Because of the glass and liquid incompressibility, the volumes of unloaded drops and loaded
349 drops are respectively given by: $V_d = M_d/\rho_l$, and $V_d^* = M_l^*/\rho_l + M_b/\rho_b$. For all maximal
350 drops (loaded and unloaded), a well-defined relationship is shown between the mean
351 curvature and the volume of a maximal pendant drop (Fig. 8). This power law dependence
352 between these geometrical quantities constitutes a master curve for the maximal pendant
353 drops. When unloaded maximal pendant drops are quasi-spherical, which is the case for very
354 small drops, $R_1 \approx R_2 \approx R$, the curvature follows a power law with the volume: $2H \sim V_d^{-\frac{1}{3}}$.
355 Such a trend is experimentally obtained as shown in Figure 8a.

356 Regardless of the mechanical loading, for each liquid and according to the variation of the
357 mean curvature, Laplace pressure decreases with the maximal weight of the pendant drops
358 (Fig. 8b). The surface tension value discriminates Laplace pressure levels within drops made
359 of different liquids. At equal density, the mixture of water and Tween 80 has a lower surface
360 tension than water, so the Laplace pressure is lower.

361

362

363 **3.3. Demonstration of maximal pendant drop weight expression**

364

365 For a pendant drop generated at the end of a syringe needle, the external force balance (Eq. 3)
366 includes (Fig. 9): (i) the weight of the drop: $M_d \vec{g}$, (ii) the force increment applied on the
367 piston that propagates until the drop via the internal section of the needle ($\pi D_{ni}^2/4$): \vec{F}_p , and
368 (iii) the capillary force at the wetted perimeter (here the outer perimeter of the needle): \vec{F}_c . The
369 rigorous demonstration that the intensity of the force \vec{F}_p is related to the Laplace pressure is
370 not so obvious. The intensity F_p exerted on a pendant drop can be written as a function of the
371 overpressure at the piston (ΔP_n) within the fluid at the end of the needle: $F_p = \Delta P_n \pi D_{ni}^2/4$

372 (the force exerted on the piston equals: $\Delta P_p \Omega_s$). The overpressure ΔP_n can be calculated from
 373 the momentum balance of the flowing fluid between the piston and the end of the needle.
 374 Assuming that the liquid is incompressible and the flow in a steady-state, Bernouilli's
 375 equation gives:

376

$$377 \quad P_p + \rho_l g(H_l - \Delta z) + \frac{1}{2} \rho_l \frac{Q^2}{\Omega_s^2} = P_n + \frac{1}{2} \rho_l \frac{Q^2}{\Omega_{ni}^2} + \Delta P_{p \rightarrow n} \quad (5)$$

378

379 with Δz , the displacement corresponding to the piston lowering, P_p and P_n respectively the
 380 pressures in the liquid at the piston interface and at the end of the needle, and $\Delta P_{p \rightarrow n}$ the drop
 381 pressure between the piston and the end of the needle. During all the pendant drop formation,
 382 the ratio $\Delta z/H_l$ remains below 1 %. The term contributions related to the kinetic energy:

383 $\frac{1}{2} \rho_l Q^2 / \Omega_s^2$ and: $\frac{\frac{1}{2} \rho_l Q^2}{\Omega_{ni}^2}$, take values of the order of magnitude of 10^{-4} Pa at most and are

384 therefore negligible. Due to the large gap between the internal sections of the syringe and the
 385 needle ($\Omega_{ni}/\Omega_s \approx 0.025$ at most), the pressure drop in the body of the syringe is negligible
 386 compared to the one in the needle. The flow occurs in laminar regime so, we assume that the

387 pressure drop is given by Hagen-Poiseuille formula: $\Delta P_{p \rightarrow n} = \frac{128 \eta L_n Q}{\pi D_{ni}^4}$, with η the viscosity of

388 the liquid and L_n the length of the needle. With these value ranges of the parameters, this
 389 pressure drop does not exceed $\sim 10^2$ Pa in the worst case (Triacetin with the smallest needle)

390 and ~ 10 Pa for all other conditions. Therefore, the viscous dissipation can be neglected
 391 compared to the other pressure values ($\sim 10^5$ Pa). Under these considerations, the balance (Eq.

392 5) can be reduced to the hydrostatic part:

393

$$394 \quad P_n \approx P_p + \rho_l g H_l \quad (6)$$

395

396 As the liquid was initially drawn into the syringe by the application of a vacuum, the
 397 condition of hydrostatic equilibrium that precedes the application of the overpressure to the
 398 piston can be written as: $P_n^{eq} = P_p^{eq} + \rho_l g H_l$, where P_n^{eq} and P_p^{eq} are the pressures at
 399 equilibrium after the entrance of the liquid. When the pendant drop is generated, the
 400 overpressure applied to the piston is given by: $\Delta P_p = P_p - P_p^{eq}$, and is transmitted to the end of
 401 the needle by: $\Delta P_n = P_n - P_n^{eq}$. The momentum balance (Eq. 6) leads to the conclusion that
 402 $\Delta P_p \approx \Delta P_n$. In quasi-static conditions, the overpressure applied to the piston is transmitted to
 403 the drop. We find that hydrostatic pressure no longer plays a role on the drop weight, as
 404 experimentally verified (see Supplementary materials file).

405 For the studied configuration and the implemented process conditions, we verified that the
 406 stationary kinetics of the drop growth can be assimilated to a succession of equilibrium states
 407 ($1.8 \times 10^{-2} \leq R_e \leq 5.6 \times 10^{-1}$). Under this hypothesis of local quasi-static state, we consider that
 408 the expression of the overpressure within the drop can be given by the Laplace-Young
 409 relation. Consequently, $\Delta P_n = \Delta P_L$ and so the ‘‘Laplace force’’ is given by: $F_p = \Delta P_L \pi D_{ni}^2 / 4$.
 410 Under all these hypotheses, the expression of the maximal weight of a pendant drop at the end
 411 of a syringe needle is consistent with Equation (4). By noting the ‘‘ideal drop’’ weight: $M_T g =$
 412 $\gamma \pi D_{ne}$, equation (Eq. 7) provides a correction to Tate's law in the case of a pendant drop
 413 generated by a syringe, that is expressed as follows:

$$414$$

$$415 \quad M_d g = M_T g - \Delta P_L \pi D_{ni}^2 / 4 \quad (7)$$

$$416$$

417 Figure 3b shows the set of experimental results that validates Eq. 7. Figure 9 illustrates more
 418 intuitively the meaning of Eq. 7: the maximum weight of the pendant drop is equal to the
 419 capillary force exerted at the end of the needle, from which must be subtracted the force
 420 coming from the pressure increment applied to the piston and which imposes the value of the

421 Laplace pressure within the drop. We provide a justification of Eq. 7 by establishing this
422 model under well-identified hypotheses and mathematical developments and it differs from
423 that one suggested by Garandet et al. [29].

424

425 **Conclusion**

426

427 This work contributes to the characterization of the weight of pendant drops. It experimentally
428 and mathematically demonstrates the influence of the Laplace pressure on the maximum
429 weight of a pendant drop. The involved physical phenomena in the equilibrium of a pendant
430 drop are well known. However, the writing of the balance of the applied external forces to the
431 pendant drop associated with the rigorous demonstrations of (i) the non-influence of the
432 hydrostatic pressure (which appears in the equation of Garandet et al. [29]) and (ii) the
433 equality of the overpressure exerted on the piston with the Laplace pressure, lead to an
434 original equation (Eq. 7) providing a correction to the well-known Tate's law. Tate's law [20],
435 based on the theoretical balance of applied external forces to a drop, is usually used to
436 theoretically calculate this weight. Despite numerous criticisms [28-30], to the best of our
437 knowledge, no experimental measurements relating to the validation of Tate's law are
438 reported in the scientific literature. Our work thus constitutes a new basis of reflection
439 associated with experimental data in order to elucidate the factors that determine the weight of
440 a pendant drop.

441 We have carried out the weight measurement of maximal pendant drops at the end of a
442 syringe needle of different sizes for three liquids of contrasting capillary lengths. The results
443 show a gap with the capillary force alone. These experimental results invalidate Tate's law
444 under the employed conditions. This difference, highlighted with three liquids, is corrected by
445 taking into account the exerted force on the piston in the applied external force balance to a

446 pendant drop. This force can be related to the Laplace pressure within the drop. A mechanical
447 loading experiment, with imposed capillary force adapted from the works of Li et al. [23] and
448 Neeson et al. [24], is proposed in order to highlight the role of Laplace pressure in the
449 mathematical expression of the maximal weight.

450 The principle of the mechanical loading with a bead attached to the drop apex, allows to
451 modulate its main curvature and therefore the Laplace pressure. The results show that the
452 mean curvature increases with the mechanical loading according to a master curve which is
453 independent of the liquid characteristics and the needle size. If they are extended to a larger
454 number of liquids, they would provide the basis for a remarkable universality. For each
455 unloaded pendant drop, the curvature is a decreasing function of the drop volume. The
456 relationship between Laplace pressure and the applied force on the piston is mathematically
457 established. An analytical expression of the maximal weight of a pendant drop is deduced.
458 The model, which considers the weight equal to the capillary force, is then revisited and
459 replaced by a new model that explicitly incorporates the Laplace pressure. It is experimentally
460 validated for each tested case.

461

462 Our approach can be extended to determine the liquid-solid adhesion work using centrifugal
463 adhesion balance [31, 32]. For this, one needs to replace the piston motion with the increase
464 of the effective gravity performed with centrifugal device. It could be also used to define with
465 high precision the volume that constitutes a pendant drop, especially in the context of
466 downsizing technologies [33]. The better knowledge of the maximum weight of a pendant
467 drop could participate to the improvement of particle coating techniques as used for marbles
468 [4,5]. In the pharmaceutical field, this work could have repercussions on the precision of
469 active drugs formulation distributed as drop (eye drops, perfusion, oral solution in drops...).

470 Finally, Tate's law is mainly used to characterize the weight of detached drops [19, 21, 27].
471 The work of Harkins and Brown [21] shows that the ratio of the volume of a detached drop to
472 the volume predicted by Tate's law, varies according to a unique characteristic curve as a
473 function of the capillary radius scaled by the cube root of the detached drop volume. What
474 happens to this relationship if we now consider the real maximum weight of a pendant drop
475 and not the one given by Tate's law? This last point, which constitutes our future work, will
476 bring a new representation of the weight of the drops that fall from a capillary.

477

478 **CRedit authorship contribution statement**

479 Laure Lecacheux: Conceptualization, Investigation, Methodology, Validation, Visualization,
480 Writing - original draft & editing. Abdelkrim Sadoudi: Conceptualization, Methodology,
481 Validation, Visualization, Writing - original draft. Agnès Duri: Investigation, Validation,
482 Supervision, Writing - review & editing. Véronique Planchot: Formal analysis, Project
483 administration, Resources, review & editing. Thierry Ruiz: Formal analysis, Validation,
484 Methodology, Project administration, Resources, Supervision, Writing - original draft &
485 editing.

486

487 **Acknowledgments**

488 The authors thank the project DEFI Blé Dur (2016-2022), that has received funding from
489 Programme d'investissement d'avenir (PIA), and the French Région Occitanie for their
490 financial supports.

491

492

493

494

495 **References**

496

- 497 [1] K.J. Obata, T. Motokado, S. Saito, K. Takahashi, A scheme for micro-manipulation
498 based on capillary force, *Journal of Fluid Mechanics* 49 (2004) 113-121.
- 499 [2] P. Lambert, A. Delchambre, A study of capillary forces as a gripping principle,
500 *Assembly Automation* 25(4) (2005) 275-283.
- 501 [3] P. Aussillous, D. Quéré, Liquid marbles, *Nature* 411 (2001) 924-927.
- 502 [4] E. Bormashenko, New insights into liquid marbles, *Soft Matter*, 8 (2012) 11018.
- 503 [5] G. McHale, M.I. Newton, Liquid marbles: topical context within soft matter and recent
504 progress, *Soft Matter* 11 (2015) 2530.
- 505 [6] H.N. Emady, D. Kayrak-Talay, W.C. Schwerin, J.D. Litster, Granule formation
506 mechanisms and morphology from single drop impact on powder beds, *Powder*
507 *Technology* 212 (2011) 69-79.
- 508 [7] D. Rossetti, X. Pepin, S.J.R. Simons, Rupture energy and wetting behavior of pendular
509 liquid bridges in relation to the spherical agglomeration process, *Journal of Colloid and*
510 *Interface Science* 261 (2003) 161-169.
- 511 [8] K.P. Hapgood, J.D. Litster, S.R. Biggs, T. Howes, Drop penetration into porous powder
512 beds, *Journal of Colloid and Interface Science* 253 (2002) 353-366.
- 513 [9] B. Bellocq, B. Cuq, T. Ruiz, A. Duri, K. Cronin, D. Ring, Impact of fluidized bed
514 granulation on structure and functional properties of the agglomerates based on the
515 durum wheat semolina, *Innovative Food Science and Emerging Technologies* 45 (2018)
516 73-83.
- 517 [10] S.M. Iveson, J.D. Litster, K. Hapgood, B.J. Ennis, Nucleation, growth and breakage
518 phenomena in agitated wet granulation processes: a review, *Powder Technology* 117
519 (2001) 3-39.

- 520 [11] S. Mandato, E. Rondet, G. Delaplace, A. Barkouti, L. Galet, P. Accart, T. Ruiz, B. Cuq,
521 Liquids' atomization with two different nozzles: Modelling of the effects of some
522 processing and formulation conditions by dimensional analysis, *Powder Technology*
523 224 (2013) 323-330.
- 524 [12] R. Abdelaziz, D. Disci-Zayed, M.K. Hedayati, J.H. Pohls, A.U. Zillohu, B. Erkartal,
525 V.S.K. Chakravadhanula, V. Duppel, L. Kienle, M. Elbahri, Green chemistry and
526 nanofabrication in a levitated Leidenfrost drop, *Nature Communications* 4 (2013) 2400.
- 527 [13] G.A. El-Nagar, O. Delikaya, I. Lauermann, C. Roth, Platinum nanostructure tailoring
528 for fuel cell applications using levitated water droplets as green chemical reactors, *ACS*
529 *Applied Materials & Interfaces* 11(25) (2019) 22398-22407.
- 530 [14] C. Boissiere, D. Grosso, A. Chaumonot, L. Nicole, C. Sanchez, Aerosol Route to
531 Functional Nanostructured Inorganic and Hybrid Porous Materials, *Advanced Materials*
532 23 (2011) 599-623.
- 533 [15] C. Sadek, H. Tabuteau, P. Schuck, Y. Fallourd, N. Pradeau, C. LeFloch-Fouéré, R.
534 Jeantet, Shape, shell, and vacuole formation during the drying of a single concentrated
535 whey protein droplet, *Langmuir* 29 (2013) 15606-15613.
- 536 [16] R. Gunde, A. Kumar, S. Lehnert-Batar, R. Mäder, E.J. Windhab, Measurement of the
537 surface and interfacial tension from maximum volume of a pendant drop, *Journal of*
538 *Colloid and Interface Science* 244 (2001) 113-122.
- 539 [17] A.T. Morita, D.J. Carastan, N.R. Demarquette, Influence of drop volume on surface
540 tension evaluated using the pendant drop method, *Colloid and Polymer Science* 280
541 (2002) 857-864.
- 542 [18] J.D. Berry, M.J. Neeson, R.R. Dagastine, D.Y.C. Chan, R.F. Tabor, Measurement of
543 surface and interfacial tension using pendant drop tensiometry, *Journal of Colloid and*
544 *Interface Science* 454 (2015) 226-237.

- 545 [19] O.E. Yildirim, Q. Xu, O.A. Basaran, Analysis of the drop weight method, *Physics of*
546 *Fluids* 17 (2005) 062107.
- 547 [20] T. Tate, On the magnitude of a drop of liquid formed under different circumstances,
548 *Philosophical Magazine* 27 (1864) 176-180.
- 549 [21] W.D. Harkins, F.E. Brown, The determination of surface tension and the weight of
550 falling drops: The surface tension of water and benzene by the capillary height method,
551 *Journal of the American Chemical Society* 41 (1919) 499-524.
- 552 [22] E. Portuguez, A. Alzina, P. Michaud, M. Oudjedi, A. Smith, Evolution of a Water
553 Pendant Droplet: Effect of Temperature and Relative Humidity, *Natural Science* 9
554 (2017) 1-20.
- 555 [23] C. Li, J.A. Simmons, M. Moradiafrapoli, J.O. Marston, Direct visualization of particle
556 attachment to a pendant drop, *Soft Matter* 13 (2017) 1444.
- 557 [24] M.J. Neeson, D.Y.C. Chan, R.F. Tabor, Compound pendant drop tensiometry for
558 interfacial tension measurement at zero bond number, *Langmuir* 30 (2014) 15388-
559 15391.
- 560 [25] P.G. de Gennes, F. Brochard-Wyart, D. Quéré, *Capillarity and wetting phenomena:*
561 *drops, bubbles, pearls, waves*, Springer-Verlag New York Inc. (2013).
- 562 [26] A. Nazari, A.Z. Derakhshi, A. Nazari, B. Firoozabadi, Drop formation from a capillary
563 tube: Comparison of different bulk fluid on Newtonian drops and formation of
564 Newtonian and non-Newtonian drops in air using image processing, *International*
565 *Journal of Heat and Mass Transfer* 124 (2018) 912-919.
- 566 [27] M.C. Wilkinson, Extended use of, and comments on, the drop-weight (drop-volume)
567 technique for the determination of surface and interfacial tensions, *J Journal of Colloid*
568 *and Interface Science* 40 (1972) 14.

- 569 [28] B-B. Lee, P. Ravindra, E-S. Chan, A critical review: Surface and interfacial tension
570 measurement by the drop weight method, *Chemical Engineering Communications*
571 195(8) (2008) 889-924.
- 572 [29] J.-P. Garandet, B. Vinet, P.O. Gros, Considerations on the pendant drop method: a new
573 look at Tate's law and Harkins' correction factor, *Journal of Colloid and Interface*
574 *Science* 165(2) (1994) 351-354.
- 575 [30] A. Kumar, M.R. Gunjan, R. Raj, On the validity of force balance models for predicting
576 gravity-induced detachment of pendant drops and bubbles, *Physics of Fluids* 32 (2020)
577 101703.
- 578 [31] R. Tadmor, R. Das, S. Gulec, J. Liu, H.E. N'guessan, M. Shah, P.S. Wasnik, and Sakshi
579 B. Yadav, Solid-Liquid Work of Adhesion, *Langmuir* 33 (2017) 3594.
- 580 [32] S. Yadav, S. Gulec, R. Tadmor, I. Lian, A Novel Technique Enables Quantifying the
581 Molecular Interaction of Solvents with Biological Tissues, *Scientific Reports* 9 (2019)
582 9319.
- 583 [33] O.A. Basaran, Small-scale free surface flows with breakup: drop formation and
584 emerging applications, *AIChE Journal* 48(9) (2002) 1842-1848.
- 585

Figure 1. Scheme of the experimental prototype for pendant drop generation and contouring acquisition of the maximal pendant drop.

Figure 2. Illustration of the curvature radii measurement for a single pendant drop (left) and a loaded pendant drop with a glass bead (right).

Figure 3. (a) Capillary force as a function of the maximal drop weight (Eq. 2) for all experiments, (b) capillary force minored by the “Laplace force” versus maximal drop weight (Eq. 4) for all experiments. The order of the error magnitude is about 10^{-4} mN. The dashed line is a guideline.

Figure 4. Illustration of the drop loading with a glass bead at constant capillary force. The images correspond to pendant water drops just before their detachment and formed with a same needle of diameter ($D_{ne} = 1.80$ mm) and an increasing load.

Figure 5. Maximal mass of loaded pendant drops as a function of bead mass for Water (circle), Tween 80 (square) and Triacetin (triangle). For each liquid only results, obtained for needles of external diameters equal to 1.26 (empty symbols) and 1.80 mm (blank symbols), are shown. The dashed lines are a guideline. Full results are available in the Supplementary Materials file.

Figure 6. Variation of the loaded pendant drop curvatures as a function of the solid mass fraction for all experiments: (a) dimensionless curvature radii, (b) dimensionless mean curvature. The dashed lines are a guideline.

Figure 7. Laplace pressure within the maximal pendant drops as a function of the particle mass for (a) Water, (b) Tween 80, (c) Triacetin and different external diameters of the needle ($D_{ne} = 0.23, 0.50, 0.80, 1.26$ and 1.80 mm). The order of the diameters is respected for each figure. The dashed lines are a guideline.

Figure 8. (a) Variation of the mean curvature as a function of the maximum pendant drop volume ($R^2 = 0.9736$) for all liquids and needles used (Log-Log representation), (b) Laplace pressure within the maximal pendant drops as a function of its weight.

Figure 9. Scheme of the external forces applied to a maximal pendant drop generated by a syringe.

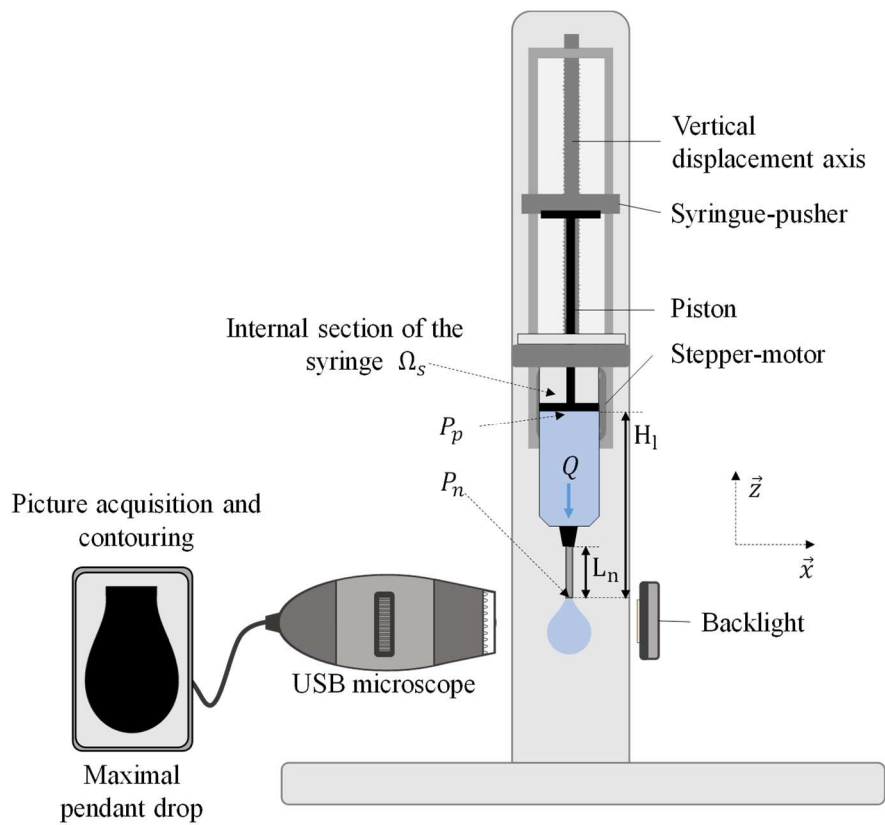


Figure 1. Scheme of the experimental prototype for pendant drop generation and contouring acquisition of the maximal pendant drop.

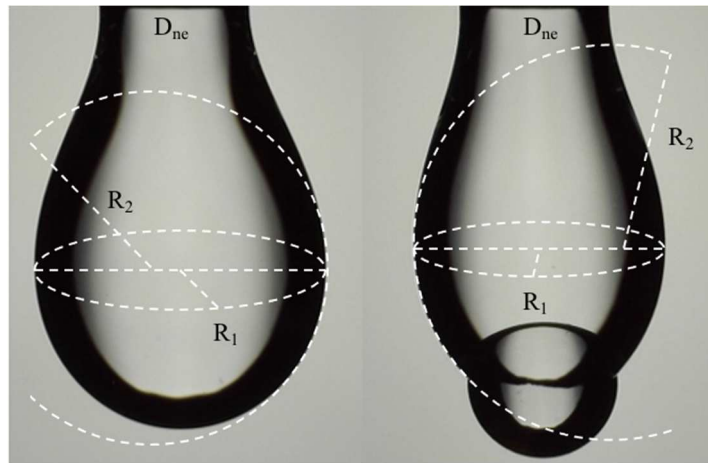


Figure 2. Illustration of the curvature radii measurement for a single pendant drop (left) and a loaded pendant drop with a glass bead (right).

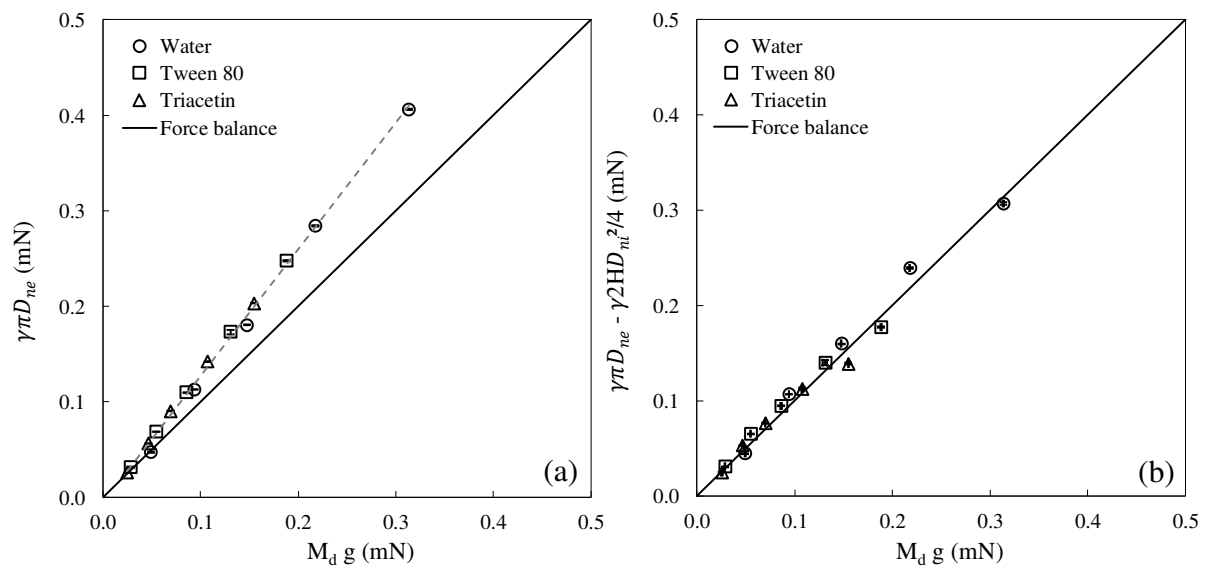


Figure 3. (a) Capillary force as a function of the maximal drop weight (Eq. 2) for all experiments, (b) capillary force minored by the “Laplace force” versus maximal drop weight (Eq. 4) for all experiments. The order of the error magnitude is about 10^{-4} mN. The dashed line is a guideline.

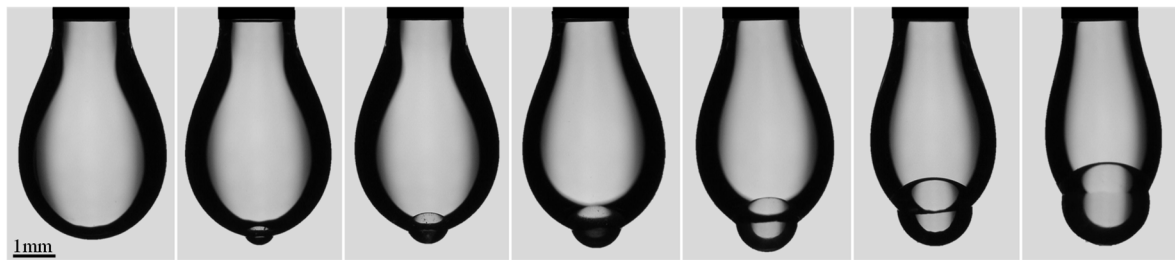


Figure 4. Illustration of the drop loading with a glass bead at constant capillary force. The images correspond to pendant water drops just before their detachment and formed with a same needle of diameter ($D_{ne} = 1.80$ mm) and an increasing load.

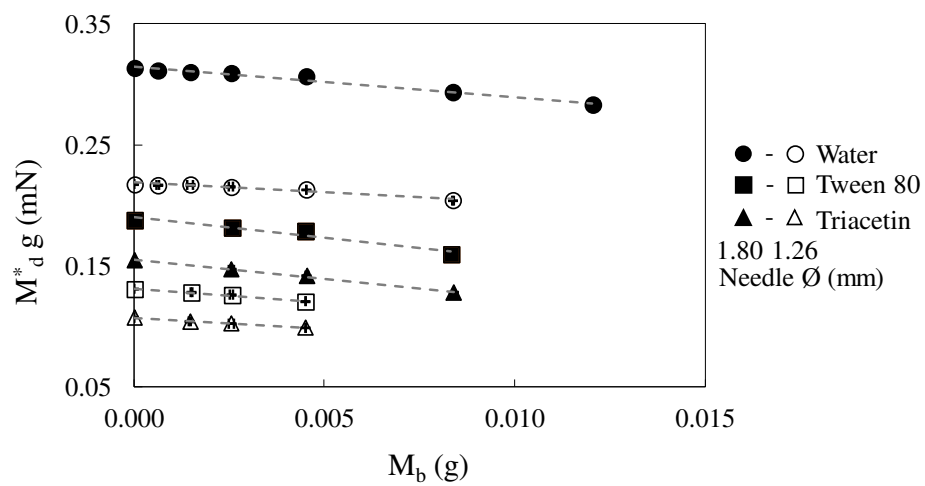


Figure 5. Maximal mass of loaded pendant drops as a function of bead mass for Water (circle), Tween 80 (square) and Triacetin (triangle). For each liquid only results, obtained for needles of external diameters equal to 1.26 (empty symbols) and 1.80 mm (black symbols), are shown. The dashed lines are a guideline. Full results are available in the Supplementary Materials file.

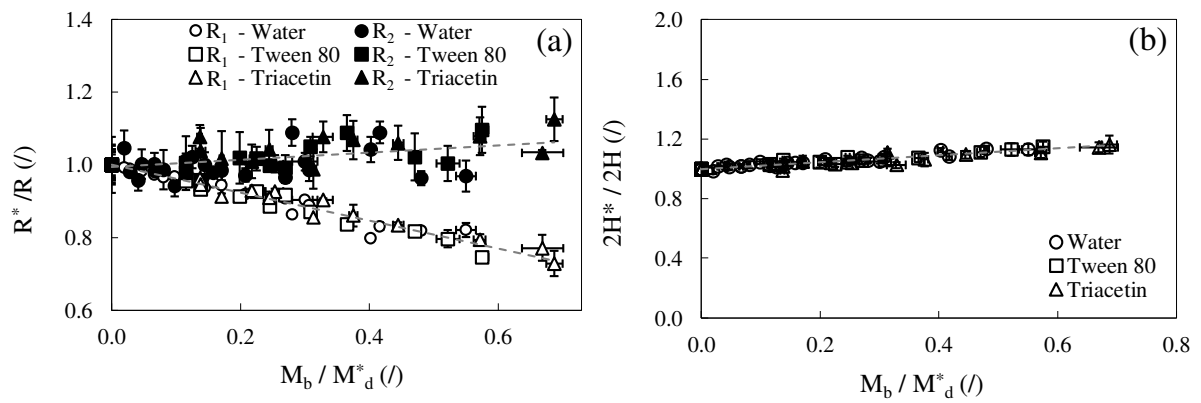


Figure 6. Variation of the loaded pendant drop curvatures as a function of the solid mass fraction for all experiments: (a) dimensionless curvature radii, (b) dimensionless mean curvature. The dashed lines are a guideline.

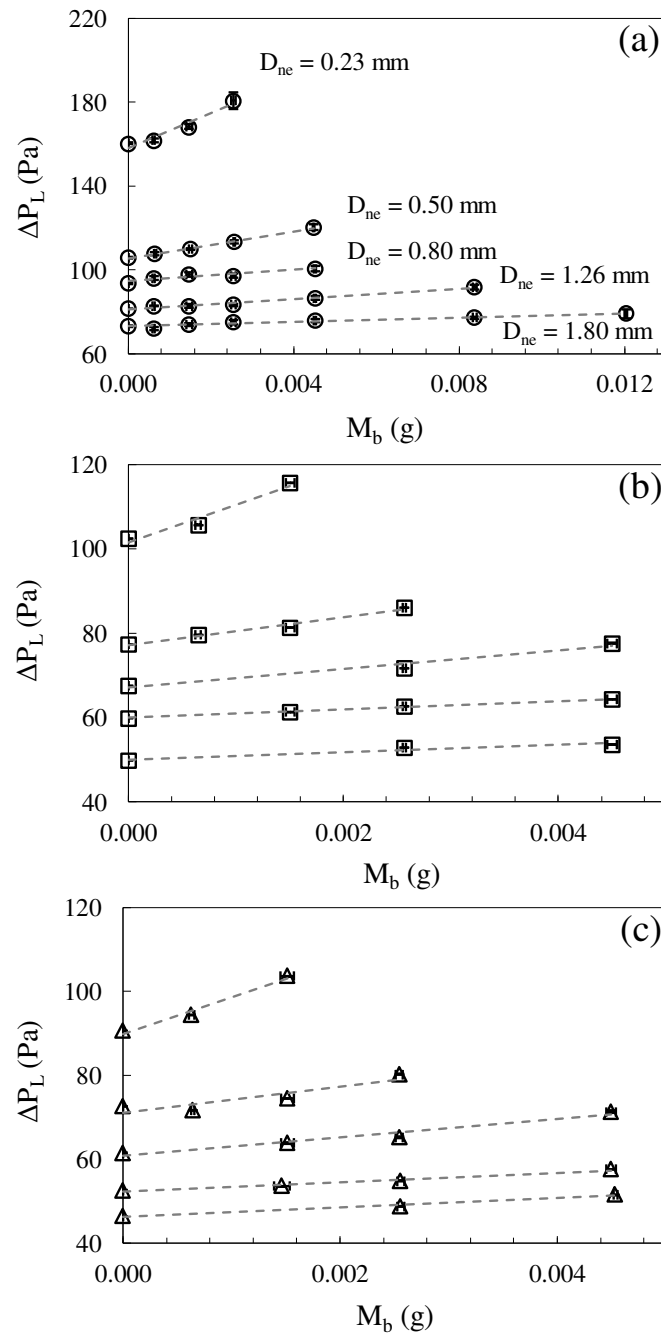


Figure 7. Laplace pressure within the maximal pendant drops as a function of the particle mass for (a) Water, (b) Tween 80, (c) Triacetin and different external diameters of the needle ($D_{ne} = 0.23, 0.50, 0.80, 1.26$ and 1.80 mm). The order of the diameters is respected for each figure. The dashed lines are a guideline.

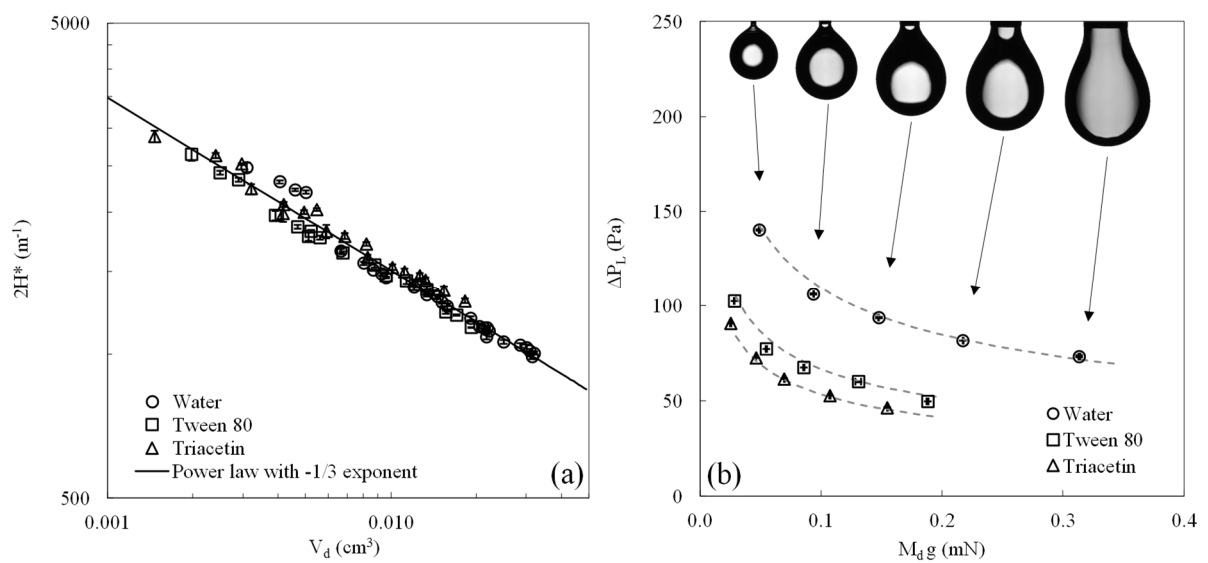


Figure 8. (a) Variation of the mean curvature as a function of the maximum pendant drop volume ($R^2 = 0.9736$) for all liquids and needles used (Log-Log representation), (b) Laplace pressure within the maximal pendant drops as a function of its weight.

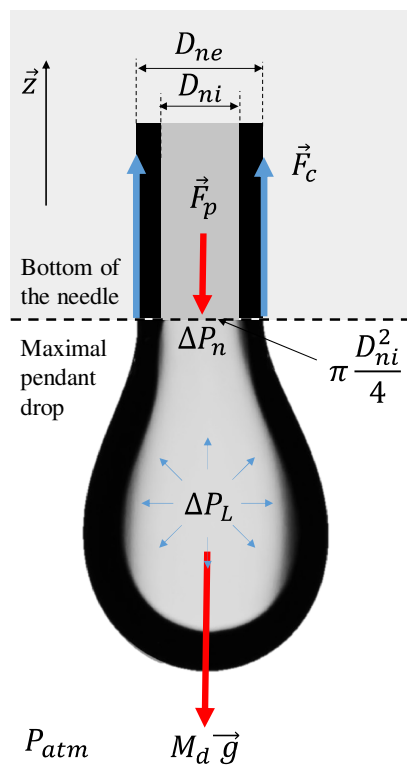


Figure 9. Scheme of the external forces applied to a maximal pendant drop generated by a syringe.

Laplace force + Weight = Capillary force

