

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

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1	The role of Laplace pressure in the maximal weight of pendant drops
2	
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4	
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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

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

28	Findir	lgs				
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	Laplac	ce 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	1	liquid				
49	n	needle				

50	р	piston
51	*	loaded drop
52		
53	Symbo	ols
54		
55	Bo	Bond number [-]
56	2 <i>H</i>	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 colum 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	R _e	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	ź	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	$\Delta P_{p \to n}$	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	$ ho_l$	true density of the liquid [kg.m ⁻³]
87	$ ho_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. Since only part of the pendant drop falls off, leaving a residual fraction on the needle, it is 117 necessary to correct the weight of an "ideal drop" given by Tate's law by a correction factor. 118 119 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 theorical 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 connection. This gap is attributed to the lack of a force in the balance of external forces 131 132 applied to the drop. In order to reveal the importance of this missing force, mechanical stress tests are performed by adding a calibrated glass bead at the apex of the drop, without 133 134 changing the intensity of the capillary force. Beads of increasing mass induce a variation of the mean curvature directly associated with a variation of the maximal weight of the drops 135 following a master curve. The repercussion of these variations on the Laplace pressure 136 137 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.

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142 **2.** Experimental procedure

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144 **2.1. Prototype description**

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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

different needle sizes were used. Their external diameter D_{ne} is: 0.23, 0.5, 0.8, 1.26 and 1.80 150 151 mm and their internal diameter D_{ni} is respectively: 0.11, 0.26, 0.51, 0.84 and 1.37 mm. In order to ensure a constant flow rate of liquid ($Q \sim 0.097$ to 0.387 mm³.s⁻¹), a syringe pump 152 153 driven by a stepper motor (MicroLYNX, M-1410-0.75D) is used to provide a vertical displacement according to \vec{z} . This flow rate gives a velocity intensity in the needle comprised 154 between 0.26 and 5 mm.s⁻¹. For each test, the laminar flow inside the needle is achieved with 155 a Reynolds number comprised between 18×10⁻³ (Triacetin with the largest needle) and 156 5.6×10^{-1} (water with the smallest needle). The evolution of the pendant drop formation until 157 158 its maximal volume is filmed using a USB microscope (DinoLite®) placed in front of the needle with an acquisition rate of 25 images.sec⁻¹. A LED backlight system is also used to 159 160 enhance the contrast.

161

The prototype is placed on an insulated support to avoid any vibration and is isolated in a plexiglass chamber to minimize any contamination. All the tests are performed in quintuples, at a controlled temperature of 25.0 ± 0.2 °C, and a relative humidity of 40 ± 16 %. The total duration of formation of a drop is between 1 and 2 minutes which allows to neglect the evaporation phenomena [22].

167

168 **2.2.** Characteristics of liquids

169

Pure water, Tween® 80 (Sigma-Aldrich) diluted at 2×10^{-3} g/L, and Triacetin® (C2 99.0%, Sigma-Aldrich) are the three considered liquids. The surface tension, γ , measured using a tensiometer Kruss K100 (Kruss, Germany) according to the Wilhelmy plate, is equal to 71.83±0.59 mN.m⁻¹ for water, 43.74±0.09 mN.m⁻¹ for Tween 80, and 34.55±0.25 mN.m⁻¹ for 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

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

194

The aim of this test is to achieve conditions that ensure invariance of the capillary force at the drop/needle wetted perimeter while modulating Laplace pressure within the drop. When the drop reaches a stage of development corresponding to about 30% of its maximum volume, the glass bead is then approached to its apex. At its contact, the drop exerts a capillary traction that captures the bead and keeps it in suspension in a position that respects the global axisymmetry (Fig. 2). The hydrodynamic flow conditions in the syringe allow a quasistationary evolution of the growth of the loaded drop. The shape of the drop, and in particular
its main curvatures, adapt to the resultant external forces applied to it [24]. Six spherical glass
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)
are used. The Bond numbers of the glass beads are less than 1, which ensures their capillary
capture by the pendant drop.

206

The operating conditions are identical to those used during the formation of a single pendantdrop 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

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

Maximal volume. Each drop is filmed (from 1 to 2 min at 25 fps) during its entire development and all the images are extracted (from 1500 to 3000) then analyzed to precisely determine the maximum volume of each pendant drop. The linear progression of the volume of the drop, due to the constant flow, makes it possible to locate the maximal volume reached with an error less than 0.01 %. The maximum weight is then calculated from the 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 radius R_2 , is located in the vertical plane, and corresponds to the radius of the circle being superimposed with the drop curve [18]. The main curvature of the drop is then deduced from these measurements according to its standard definition in 3D space, $2H = \frac{1}{R_1} + \frac{1}{R_2}$. The Laplace pressure in the drop is then calculated according to its definition [25]: $\Delta P_L = \gamma 2H$. 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

Pendant drops are formed at the end of needle of a syringe using a stationary flow rate of the 235 liquid, Q, ensured by a force \vec{F}_p applied on the piston. The maximal mass reached by the drop, 236 M_d , is calculated from the measurement of the volume. The laminar regime ensures the 237 stability of the drop formation and we verify that neither the value of the flow nor the height 238 239 of liquid (H_1) 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.

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

246

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

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

258

259
$$M_d g = \gamma \pi D_{ne} \tag{2}$$

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 3a that Equation (2) is not verified. The capillary force is systematically higher than the 266 267 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 to be redefined [29,30]. Therefore, such a gap implies to consider again the balance of 272 273 external efforts applied to a pendant drop [30] taking into account the repercussion of the

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

280

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

282

283 Under all these hypotheses and by introducing the definition of the Laplace pressure in the284 external force balance exerted on the pendant drop, Equation (3) can be written as:

$$M_d g = \gamma \pi D_{ne} - \Delta P_L \pi D_{ni}^2 / 4 \tag{4}$$

286

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

290

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

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. 4) and remains unchanged: $\theta \approx 0^{\circ}$, and (*iii*) the liquid surface tension is not modified (the 309 310 beads are carefully cleaned beforehand). Thus, the force balance (Eq. 4) is satisfied for the maximal total weight of the loaded drop: $M_d^*g = M_bg + M_l^*g$, where M_l^*g is the liquid 311 312 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

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

This result indicates that at constant capillary force, if the maximum weight of a pendant drop decreases with increasing loads, then the Laplace pressure should increase to ensure the 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 shape (Fig. 4). The axisymmetry being satisfied, the quantitative analysis of the main 330 331 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 same needle: R_1^*/R_1 and R_2^*/R_2 . The antagonistic variation of the two radii of curvature 335 systematically leads to an increase of the mean curvature defined by; $2H^* = \frac{1}{R_1^*} + \frac{1}{R_2^*}$, for all 336 337 loaded pendant drops.

338

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

341

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

348 Because of the glass and liquid incompressibility, the volumes of unloaded drops and loaded 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 349 drops (loaded and unloaded), a well-defined relationship is shown between the mean 350 351 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 drops. When unloaded maximal pendant drops are quasi-spherical, which is the case for very 353 small drops, $R_1 \approx R_2 \approx R$, the curvature follows a power law with the volume: $2H \sim V_d^{-\frac{1}{3}}$. 354 355 Such a trend is experimentally obtained as shown in Figure 8a.

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

- 361
- 362

363 3.3. Demonstration of maximal pendant drop weight expression

364

For a pendant drop generated at the end of a syringe needle, the external force balance (Eq. 3) includes (Fig. 9): (*i*) the weight of the drop: $M_d \vec{g}$, (*ii*) the force increment applied on the piston that propagates until the drop via the internal section of the needle $(\pi D_{ni}^2/4)$: $\vec{F_p}$, and (*iii*) the capillary force at the wetted perimeter (here the outer perimeter of the needle): $\vec{F_c}$. The rigorous demonstration that the intensity of the force $\vec{F_p}$ is related to the Laplace pressure is not so obvious. The intensity F_p exerted on a pendant drop can be written as a function of the 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
$$P_{p} + \rho_{l}g(H_{l} - \Delta z) + \frac{1}{2}\rho_{l}\frac{Q^{2}}{\Omega_{s}^{2}} = P_{n} + \frac{1}{2}\rho_{l}\frac{Q^{2}}{\Omega_{nl}^{2}} + \Delta P_{p \to n}$$
(5)

378

with Δz , the displacement corresponding to the piston lowering, P_p and P_n respectively the 379 pressures in the liquid at the piston interface and at the end of the needle, and $\Delta P_{p \to n}$ the drop 380 pressure between the piston and the end of the needle. During all the pendant drop formation, 381 the ratio $\Delta z/H_l$ remains below 1 %. The term contributions related to the kinetic energy: 382 $\frac{1}{2}\rho_l Q^2/\Omega_s^2$ and: $\frac{\frac{1}{2}\rho_l Q^2}{\Omega_{ri}^2}$, take values of the order of magnitude of 10⁻⁴ Pa at most and are 383 therefore negligible. Due to the large gap between the internal sections of the syringe and the 384 needle ($\Omega_{ni}/\Omega_s \approx 0.025$ at most), the pressure drop in the body of the syringe is negligible 385 compared to the one in the needle. The flow occurs in laminar regime so, we assume that the 386 pressure drop is given by Hagen-Poiseuille formula: $\Delta P_{p \to n} = \frac{128 \eta L_n Q}{\pi D_{ni}^4}$, with η the viscosity of 387 the liquid and L_n the length of the needle. With these value ranges of the parameters, this 388 pressure drop does not exceed $\sim 10^2$ Pa in the worst case (Triacetin with the smallest needle) 389 390 and ~ 10 Pa for all other conditions. Therefore, the viscous dissipation can be neglected compared to the other pressure values ($\sim 10^5$ Pa). Under these considerations, the balance (Eq. 391 392 5) can be reduced to the hydrostatic part:

393

$$P_n \approx P_p + \rho_l g H_l \tag{6}$$

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 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 398 399 equilibrium after the entrance of the liquid. When the pendant drop is generated, the overpressure applied to the piston is given by: $\Delta P_p = P_p - P_p^{eq}$, and is transmitted to the end of 400 the needle by: $\Delta P_n = P_n - P_n^{eq}$. The momentum balance (Eq. 6) leads to the conclusion that 401 $\Delta P_p \approx \Delta P_n$. In quasi-static conditions, the overpressure applied to the piston is transmitted to 402 the drop. We find that hydrostatic pressure no longer plays a role on the drop weight, as 403 404 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 $(1.8 \times 10^{-2} \le R_e \le 5.6 \times 10^{-1})$. Under this hypothesis of local quasi-static state, we consider that 407 the expression of the overpressure within the drop can be given by the Laplace-Young 408 relation. Consequently, $\Delta P_n = \Delta P_L$ and so the "Laplace force" is given by: $F_p = \Delta P_L \pi D_{ni}^2/4$. 409 410 Under all these hypotheses, the expression of the maximal weight of a pendant drop at the end of a syringe needle is consistent with Equation (4). By noting the "ideal drop" weight: $M_T g =$ 411 $\gamma \pi D_{ne}$, equation (Eq. 7) provides a correction to Tate's law in the case of a pendant drop 412 413 generated by a syringe, that is expressed as follows:

414

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

416

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

(7)

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.

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

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

Our approach can be extended to determine the liquid-solid adhesion work using centrifugal 462 463 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 downsizing technologies [33]. The better knowledge of the maximum weight of a pendant 466 467 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...).

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

CRediT authorship contribution statement

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

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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 (blanck 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 $(D_{ne} = 0.23, 0.50, 0.80, 1.26 \text{ and } 1.80 \text{ mm})$. 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.



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Laplace force + Weight = Capillary force

