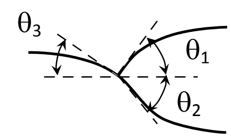
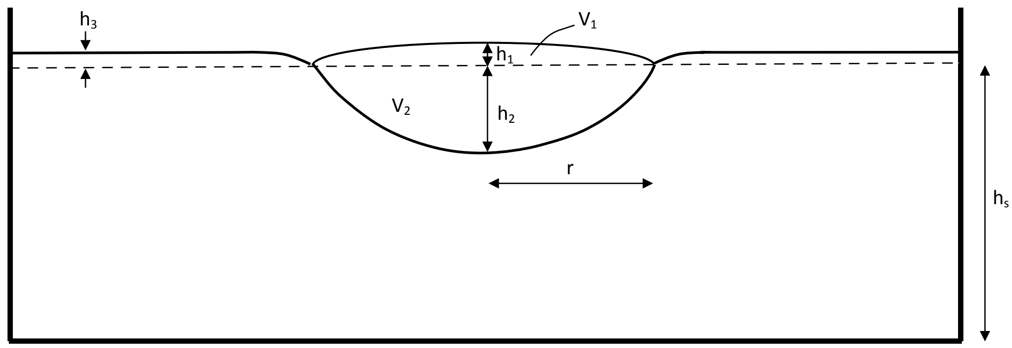
Electronic Supplementary Material (ESI) for Soft Matter.

Estimation of substrate thickness reduction due to evaporation during a single test

It is important to ensure that during the lens lifetime the thickness of the substrate does not change noticeably; this is particularly important for thin substrates. We have measured the evaporation rate of ethanol from the Petri dish with all the substrate thicknesses considered in this study (7, 5, 3, 2, 1 and 0.5 mm) for a length of time of 5 minutes which is way more than what we took to perform an experiment depositing a single lens; the measured values of ethanol evaporation rate range between 1.47 10^{-7} and 1.72 10^{-7} kg/s. We also estimated the FC-72 lifetime (faster evaporating lenses of this study) from the IR measurements; the lens lifetime ranges from 2.86 to 14.08 s for substrate thickness varying between 7 to 0.5 mm, respectively. Therefore, we estimated that the relative change of substrate thickness ($\Delta h_s/h_s$) ranges from 0.003% to 0.5% for substrate thickness varying between 7 and 0.5 mm, respectively. Therefore, we can reasonably assume that the ethanol substrate thickness remains practically constant during the duration of the experiments.

Calculations of the FC-72 lens thickness on ethanol substrate





We will introduce now a similar analysis developed by Phan [19] to estimate the FC-72 lens thickness and how much it sinks inside the ethanol substrate. The floating condition for the lens Phan [19] requires that:

$$g[\rho_l V_l + \rho_a V_a = \rho_s (V_a + V_l)] \quad (1)$$

This relationship says that the weight of the lens ($V_l = V_1 + V_2$) and the air pocket above the lens (V_a) is the same as that of the displaced substrate volume of same value as the combined lens and air pocket (this is the buoyancy term). The density of air is almost 3 order of magnitude less the ones of ethanol and especially FC-72, therefore the second term on the left-hand side of Equ. (1) can be neglected.

Phan [19] also shows that the relationships between the lens contact angles are:

$$\theta_1 + \theta_2 = \pi - arc\, cos\left(\frac{\gamma_l^2 + \gamma_{sl}^2 - \gamma_s^2}{2\gamma_l\gamma_s}\right) \qquad (2)$$

$$\theta_1 + \theta_3 = arc\, cos\left(\frac{\gamma_s^2 + \gamma_l^2 - \gamma_{sl}^2}{2\gamma_s\gamma_l}\right) \qquad (3)$$

In Equ. (2-3) the angles are measured from the horizontal line passing from the contact line and the lens to air interface (θ_1), the FC-72 to ethanol interface (θ_2), and the ethanol to air interface outside the lens (θ_3). θ_1+θ_2 is the total internal angle of the lens. When we evaluate these angles with the surface and interfacial tensions values reported in Table 3 below for a temperature of 10 ^{0}C, we get: $\theta_1 + \theta_2 = 56.7\ ^0$ and $\theta_1 + \theta_3 = 5.2^0$. Because $\theta_1 + \theta_3$ is so small, we can reasonably assume that most of the lens penetrates the ethanol interface and disregard the part of the lens volume (V_1) which remains in air above the contact line. If we do so, in the same spirit as Phan [19], we get the following volume for the lens (considered as a spherical cap) inside the ethanol substrate (using an initial value of 1.5 mm for the lens radius (r)):

$$V_2 = \frac{\pi}{6}\left(\frac{1-\cos\theta_2}{\tan\theta_2}\right)r^3\left[3 + \left(\frac{1-\cos\theta_2}{\tan\theta_2}\right)^2\right] \cong 1.64\ \mu L \qquad (4)$$

The height of the lens below the contact line can be calculated as $h_1 = r\left(\frac{1-\cos\theta_2}{\tan\theta_2}\right) = 0.454\ mm$; the capillary length between lens and substrate liquids is estimated to be just over 1 mm, therefore the spherical cap approximation is reasonable. As we deposited lenses of around 2 μL, the remaining volume ($V_1 = V_l - V_2 = 0.36$ μL) is that of the lens above the contact line. Applying a formula similar to Equ. (4) but for V_1 we can get a height of the lens above the contact line of $h_2 \cong 49\ \mu m$ which is one order of magnitude less than h_1. Using the relations of a spherical cap, we calculate now the radius (R) of the sphere of the circular cap with height h_1, $R = \frac{r^2 + h_1^2}{2\ h_1^2} \cong 23\ mm$ and from this the angle $\theta_1 \cong 3.7^0$, which is rather small as previously assumed. Knowing how much the FC-72 lens penetrates the ethanol substrate is important because when we vary the substrate thickness then the lens bottom interface is going to "feel" the presence of the solid dish bottom and probably interfere with it.

The lens floats on the substrate not only because of the buoyancy forces, but also because of the resultant contribution of the surface tension forces at the contact line around the lens perimeter. If we take the same force balance of Phan et al. [1] and modify it by introducing the resultant of the surface and interface tensions, we get:

$$F = g\left[\rho_l V_l + \rho_a\left(\pi r^2 h_3 - V_1\right) - \rho_s\left(\pi r^2 h_3 - V_2\right)\right] - Z \qquad (5)$$

Of the terms in square bracket, the first is the weight of the lens, the second is the weight of the air pocket above the lens, the third is due to buoyancy and it is the weight of the displaced ethanol volume. Z is the vertical component of the resultant of the surface and interfacial tensions at the lens contact line. In our case, both θ_1 and θ_3 are small and therefore the only contribution to Z is the interfacial tension between lens and substrate. Additionally, because the ratio of Petri dish to lens diameter is more than 18, a lens that is completely immersed in the substrate would raise the substrate level outside of it or less than $h_3 \approx 0.8\ \mu m$ (assuming that the ellipsoidal FC-72 lens volume displaces a hollow ethanol cylinder of equal volume bounded between the Petri dish diameter and the lens diameter). For the FC-72 lens of 2 μL the first three terms of Equ. (5) give approximately 1.7 10^{-5} N. Z can be estimated as: $Z = \gamma_{sl} 2 \pi r \cos(\frac{\pi}{2} - \theta_2) \approx 8\ 10^{-5}\ N$, therefore the FC-72 lens would float despite much heavier than ethanol. If in Equ. (5) we impose $F = 0$, then we can estimate the maximum radius and volume of the FC-72 lens supported by the ethanol substrate to be, respectively:

$$r = \sqrt{\frac{6 \sin\left(\frac{\pi}{2} - \theta_2\right)^3}{g\left[1 - \cos\left(\frac{\pi}{2} - \theta_2\right)\right]^2\left[2 + \cos\left(\frac{\pi}{2} - \theta_2\right)\right]} \frac{\gamma_{sl} \cos\left(\frac{\pi}{2} - \theta_2\right)}{(\rho_l - \rho_s)}} \approx 3.3\ mm$$

;

$$V_l \approx V_2 = \frac{2 \pi r \gamma_{sl} \cos\left(\frac{\pi}{2} - \theta_2\right)}{g\ (\rho_l - \rho_s)} \approx 20\ \mu L$$

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References

(1) Phan C.M., Allen B., Peters L.B., Le T.N., Tade M.O. Can water float on oil?, Langmuir 28, 4609-4613 (2012).