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Double emulsion in a compound droplet

D. Terwagne[a,*], T. Gilet[b], N. Vandewalle[a], S. Dorbolo[a]

[a] GRASP, Physics Department B5a, University of Liège, Allée du Six Aout 17, B-4000 Liège, Belgium
[b] Department of Mathematics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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ABSTRACT

A compound drop is made of a millimetric water drop encapsulated in an oil shell. They are obtained by merging one drop of each component (water and oil). Afterwards, they are laid on a high viscosity oil bath which is vertically vibrated. When the forcing acceleration is higher than a given threshold Γ_{th}, compound drops can bounce on the surface. We show that above a second threshold $\Gamma_e > \Gamma_{th}$ some oil contained in the shell enters in the inner water droplet forming a stable double emulsion.

1. Introduction

Compound droplets are very fascinating systems. They are made of two immiscible liquids, called liquid #1 and liquid #2. This object is constituted by two interfaces: air–liquid #1 and liquid #1–liquid #2. The impacts of such drops on a hot solid surface have been studied [1,2] showing new behaviours. Emulsified compound droplets impacting on solid surface have been also characterized in [3].

The bouncing droplets on a vertically shaken liquid bath have been largely investigated since the pioneer works by Couder et al. [4–6]. The principle is to avoid the coalescence with the bath by regenerating the interstitial air film located in between the droplet and the bath. First, the substrate on which the droplet bounces has to be a clean liquid. Dust particles on a liquid or asperities on a solid surface provoke the air film collapse. The bouncing occurs when the maximum vertical acceleration of the bath exceeds a threshold Γ_{th} that depends on the forcing frequency and on the physical parameters of the droplet (surface tension, viscosity and size) [7].

The nature of the liquid used for the droplet is an important parameter. Indeed, considering a bath of very viscous silicone oil (>1 Pa s), the oil viscosity of the droplet must be lower than 1 Pa s. In the same way, a pure water droplet does bounce on high viscosity silicone oil bath. On the other hand, it is difficult to observe a water droplet bouncing on a water bath: surfactant must be added in order to decrease the influence of the hydrogen bonds.

In this paper, we investigate a water droplet that is covered by a thin layer of oil. The phenomenon is presented in an award video of the gallery of nonlinear images hosted by the Group on Nonlinear and Statistical Physics of the APS [8]. This kind of compound droplet is able to bounce at the surface of a high viscous bath. We consider low viscosity droplets on a high viscosity bath which leads to highly deformed droplets and negligible bath deformations. The present paper experimentally explores when it is possible to generate an emulsion in the droplet by adding some surfactant in the water droplet. In so doing, the interface tension between the water droplet and the oil is very low. That allows high deformation of the oil/water interface.

2. Experimental set-up

A circular container of 10 cm of diameter and 2 cm of height is filled with silicone oil (Dow Corning 200) of 1 Pa s viscosity. The container is then vertically shaken by an electromagnetic shaker (Gear & Watson 20). This container is submitted to a vertical oscillating acceleration $\gamma = \gamma_m \cos(2\pi f t)$ where γ_m is the amplitude, f the forcing frequency, and t the time. In the following the control parameter of the system is the adimensional forcing acceleration: $\Gamma = \gamma_m / g$ where g is the gravity acceleration.

A compound drop is composed by two liquids: water + surfactant and silicone oil. We added to the distilled water drop the anionic surfactant, sodium dodecyl sulphate (SDS), in a concentration of 10 times the critical micelle concentration. The silicone oil (Dow Corning 200) composing the compound drop has a viscosity η equal to 1.275×10^{-3} Pa s, surface tension $\sigma = 16.8$ mN m^{-1} and density $\rho = 850$ kg m^{-3}. The surface tension at the interface surfactant water/oil was measured by an optical goniometer CAM200 (KSV Instruments) using the pendant drop method. The interface tension $\sigma_{w/o}$ is found to be 8.6 ± 0.2 mN m^{-1}.

* Corresponding author.
E-mail address: D.Terwagne@ulg.ac.be (D. Terwagne).

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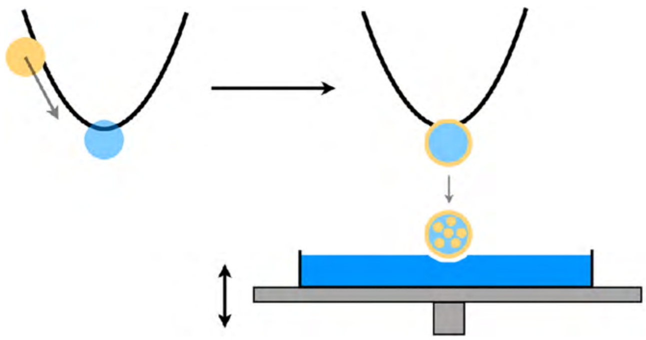

Fig. 1. Two syringes (not represented) are used to generate the compound drops. A thin copper wire makes a link between both needles. One of the syringe injects a water droplet along the wire. Afterwards, the second syringe creates an oil droplet that coats the water droplet. The obtained compound drop is too heavy to be sustained by the wire and falls on the oscillating liquid surface.

The compound drop is produced using two syringes connected by a thin copper wire (Fig. 1). First, the surfactant water drop is generated using one of the syringe (in light blue in Fig. 1) (for interpretation of the references to color in this sentence, the reader is referred to the web version of the article), the water drop slides along the wire and stops at the lower point of the loop. Afterwards, an oil drop is released from the second syringe on the wire (in yellow in Fig. 1). This droplet slides on it and encapsulates the water drop. This object, too heavy to be sustained by the wire, falls on the oscillating liquid surface of the container. When the droplet detaches from the wire, the droplet has roughly a spherical shape. The free fall height is about 5 mm and the first impact is just sufficient to allow the droplet to bounce on the surface. In doing so, deformations at impact are not sufficient to affect the structure of the compound droplet and the bouncing mechanism.

The motion of the bouncing drop can be observed and recorded using a fast video camera (IDT motion, 1000 fps). Four different compound droplets have been tested, their compositions are shown in Table 1. Each fluid component comes from two droplets moving from each side of the wire. In order to change the droplet size of each component, we changed the syringes needles. The volume of each pure component droplet has been first measured: one or two droplets are made on the wire till detachment, then the pure component droplet size is measured during free fall. The volume of liquid remaining on the wire after droplet detachment is pretty small (<5% of the initial compound droplet volume on the wire). When the compound droplet detaches from the wire, some oil from the shell only is let on it. The estimation of the error made on the compound drop volume is estimated to 5% at worst. The adimensional acceleration Γ is tuned for frequencies between 25 and 130 Hz.

Table 1
Composition and size of the four tested compound drops. The third and fourth columns give the volume of the water drop and of the oil drop composing the compound drop. The error is roughly 5% in absolute value.

Symbols	Compound drop radius	SDS water volume	Oil volume
□, ▼	0.80 mm	1.10 μL	1.05 μL
♦	0.83 mm	1.75 μL	0.68 μL
▲	0.94 mm	1.42 μL	2.10 μL
●	1.00 mm	2.99 μL	1.15 μL

3. Experimental results

The frequency being fixed, the amplitude of oscillation is increased. At each amplitude step, a compound droplet is dropped on the oil bath. For low accelerations, the compound droplet coalesces with the bath. Above a given threshold Γ_{th} that depends on the frequency, the compound droplet bounces on the oil bath exactly as described in previous works for pure bouncing droplets [4,9]. At large accelerations, some oil from the shell can enter into the water droplet forming a double emulsion. The double emulsion is characterized by oil droplets in a surfactant water phase surrounded by an oil shell. An example of this later phenomenon is

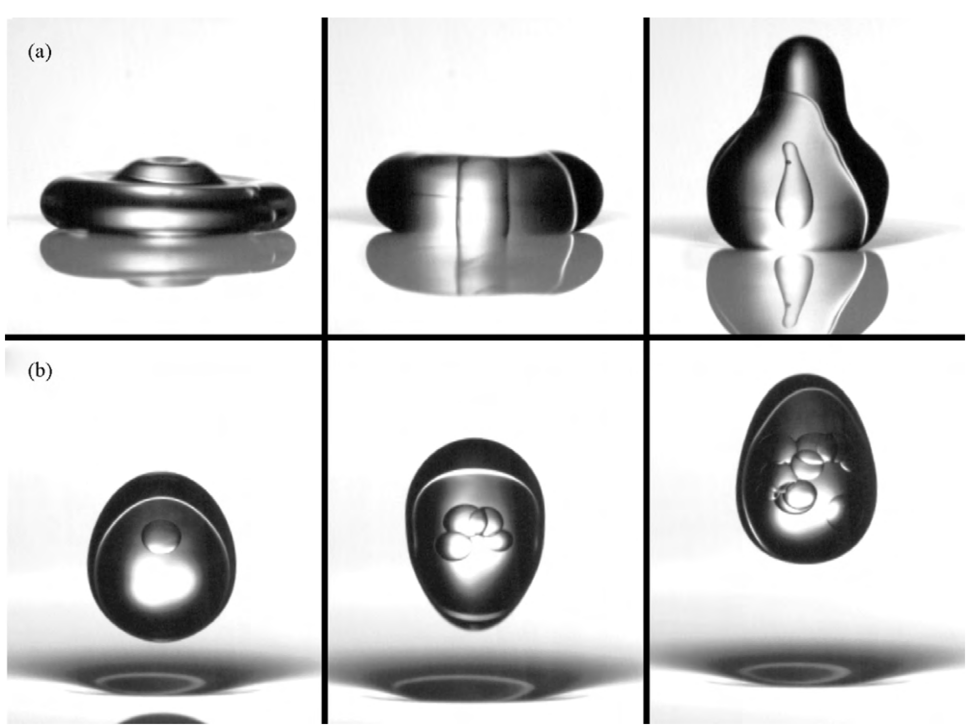

Fig. 2. A compound drop is made on a liquid surface that is oscillating sinusoidally at 50 Hz with an acceleration $\Gamma > \Gamma_e$. (a) Creation of an oil droplet coming from the shell during a single bounce. (b) Bounce after bounce, tiny oil droplets are injected in the inner water droplet. The three snapshots represent the same compound drop after 3, 20 and 49 bounces.

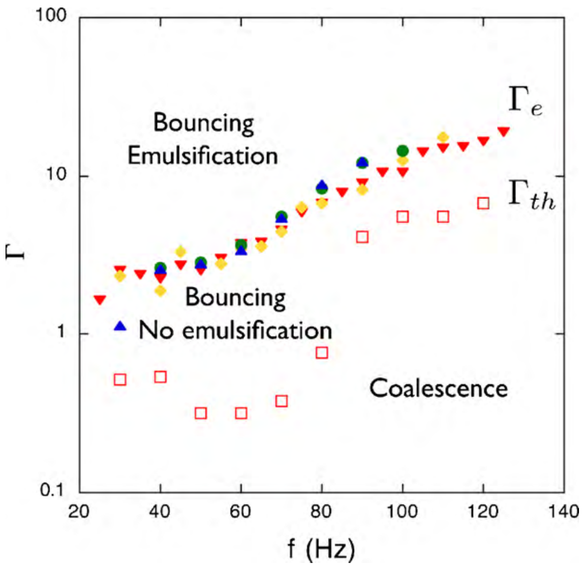

Fig. 3. Bouncing threshold acceleration Γ_{th} (□) and emulsion threshold acceleration Γ_e (▼, ♦, ▲, ●) as a function of the oscillation frequency f for the four tested compound drops represented in Table 1.

displayed in Fig. 2: a large compound drop of 0.94 mm of radius (see ▲ symbol in Table 1) is dropped on a liquid surface oscillating sinusoidally at 50 Hz with an acceleration equals to $\Gamma = 4.4$. The three upper snapshots (Fig. 2a) represent the formation of the first oil droplet in the inner water drop during the impact. We can observe that the oil droplets originates from the top of the oil shell. The three snapshots below (Fig. 2b) represent, respectively, the drop after 3, 20 and 49 bounces.

In the studied range of frequencies (25–130 Hz), at the forcing amplitude threshold Γ_{th}, the drop deformation is accurately modeled by the spherical harmonic function Y_2^0 [9,10], this axisymmetric mode is simply a succession of oblate and prolate shapes. At any higher acceleration, the double emulsion is initiated as other large deformation modes appear. At the impact, capillary waves are generated at the bottom of the drop and propagate along the surface of the drop [11]. They converge at the top and deform the drop. That leads to the formation of an oil drop coming from the shell in the water core (see Fig. 2a). To start emulsification in the drop, capillary waves have to deform enough the shape of the drop. That occurs above an impact speed threshold [2]. The emulsion threshold can be correlated with a relative impact speed threshold.

The influences of the compound droplets radii and the oscillating frequency on the emulsion apparition have been tested. We may think that when the compound droplet is too small, capillary waves cannot deform enough the droplet. On the other hand, when the compound drop is very large, it cannot bounce on the surface. Therefore, there exists a range of radii for which bouncing and mixing can be observed. We test compound drops of different sizes in this size range (see Table 1). For each size of compound drop, we measured the emulsion acceleration Γ_e in function of the frequency f. The results are presented, in Fig. 3, on a (Γ, f) phase diagram. The emulsion threshold $\Gamma_e(f)$ (▼, ♦, ▲, ●) of the four tested compound drop sizes and the bouncing threshold curve $\Gamma_{th}(f)$ (□) of the compound drop of 0.80 mm of radius are presented on a same phase diagram. The Γ_e is not found to be much influenced by the size variation of the studied droplet. We do not observe any drop size dependence for the emulsification threshold.

Finally, it is interesting to note that when we decrease the forcing acceleration to the region where the compound drop only bounces, the emulsion is stabilized. Actually, as fluids are maintained in motion, the droplet coalescence is prevented. It is also possible to set in motion the emulsified droplet by adjusting the frequency and the amplitude to excite a specific mode of deformation called "roller mode" (see a complete study of the deformation modes in open access Ref. [10]).

4. Conclusion

We show that it is possible to generate a double emulsion inside a compound drop (oil + surfactant water) when it is laid on a vibrating high viscous oil bath. Above a certain threshold the compound droplet bounces. Above another threshold, oil droplets from the shell enter into the water droplet forming a double emulsion. This emulsion can then be stabilised by adjusting the forcing acceleration Γ to an intermediate value between Γ_{th} and Γ_e.

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