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From a Bouncing Compound Drop to a Double Emulsion

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We show that a double emulsion (oil in water in oil) can be created starting from a compound droplet (surfactant solution in oil). The compound drop bounces on a vertically vibrated liquid surface. When the amplitude of the vibration exceeds a threshold value, the oil layer penetrates the water content and leaves a tiny oil droplet within. As this phenomenon occurs at each vigorous impact, the compound drop progressively transforms into a double emulsion. The emulsification threshold, which is observed to depend on the forcing frequency but not on the drop size, is rationalized by investigating the impact of compound drops onto a static liquid surface. The droplet creation occurs when the kinetic energy released at impact is larger than the energy required to deform the compound drop, namely when the Weber number is higher than a given threshold value.

Introduction

Emulsion-producing companies started to be interested in the endless applications offered by double-emulsions, namely emulsions inside emulsions. Droplets of a liquid A are encapsulated in a drop of a liquid B, which is itself surrounded by a third immiscible liquid C (possibly liquid A). The liquid B is mainly used to protect A from C, or to delay the release of A into C. This strategy is useful in the food industry[1] and in pharmaceutics for a prolonged delivery of drugs.[2]

During the past few decades, the production, the complex structure, and the possible metastability of compound drops and double emulsions have concerned scientists. The stability may be extended by the use of surfactant molecules[3,4] or microparticles.[5] The well-defined production of these multiphasic objects is more complicated. Loscertales et al.[6] presented a method to produce micrometer/nanometer compound drops using the action of electro-hydrodynamic forces. Chiu et al. and Chen et al.[7,8] produced compound drops of about 700−1000 μm of outer diameter with a piezoelectric generator and studied their impact on a hot surface. Prunet-Foch et al.[9] investigated the impact of compound drops in simple emulsion on a solid substrate. Traditionally, double emulsions are formed in microchannels[10] or by shear-induced rupturing,[11,12] usually in two emulsification steps. Thus, a first emulsion is created with two immiscible fluids and then this emulsion is again emulsified in a third continuous phase. More recently, some other fabrication processes have been developed in order to generate a relatively well-controlled double emulsion in one step.[13]

In this paper, we propose an experimental method to create a double emulsion, oil in water in oil, starting from a single compound drop (water in oil). The underlying phenomenon has been recently presented in the Gallery of Nonlinear Images.[14−16] The method is based on the repeated impacts and rebounds of the compound drop onto a liquid interface. The smoothness of liquid interfaces prevents coalescence: a thin lubricating air film is maintained in between the drop and the underlying liquid.[17,18] To achieve many successive high-amplitude rebounds, some kinetic energy is supplied to the drop through the vertical vibration of the underlying liquid bath. This energy input balances the viscous dissipation, mainly inside the drop.[19] Sustained bouncing is observed when the amplitude of the forcing vibration exceeds a threshold value that depends on the forcing frequency and the drop properties (surface tension, viscosity, and size among others).[20−22] The spontaneous creation of a double-emulsion is observed for a much larger forcing amplitude, when the bouncing trajectory becomes chaotic.

We first determine experimentally the parameters (forcing and mixture composition) required to produce a double emulsion from a compound drop. To rationalize these observations, we analyze the behavior of a compound drop impacting a static liquid surface. The link between both experiments (static and

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vibrated) is finally made by measuring the trajectory of a bouncing oil drop on a vibrated interface.

Experimental Setup

A container filled with 1000 cSt silicone oil (Dow Corning 200) is vertically vibrated using an electromagnetic shaker. The oscillation is sinusoidal of amplitude A and frequency $f \in [25,130]$ Hz. We define the dimensionless forcing amplitude $\Gamma = 4\pi^2 A f^2/g$. The drop experiences sustained bouncing instead of coalescence when Γ is higher than the bouncing threshold Γ_b.

The initial compound drop results from the merging of a distilled water drop (density $\rho_w = 998$ kg·m^{-3} and kinematic viscosity $\nu_w = 1$ cSt at 20 °C) and a silicone oil (Dow Corning) drop (density $\rho_o = 850$ kg·m^{-3} and kinematic viscosity $\nu_o = 1.5$ cSt at 25 °C). The surface tension of the oil (relative to the air) is $\sigma_{o/a} = 16.8$ mN·m^{-1}. To favor the deformations of the water/oil interface, an anionic surfactant, sodium dodecyl sulfate (SDS), has been added in the water drop, at a concentration 10 times higher than the critical micellar concentration (CMC). The resulting interfacial tension between oil and water is estimated from the natural oscillations of a water drop immersed in oil:[23,24]

$$\sigma_{w/o} = \frac{3\pi m}{8T^2}\left[1+\frac{2\rho_o}{3\rho_w}\right] = 7.1 \pm 1.0 \text{ mN}\cdot\text{m}^{-1} \qquad (1)$$

where m is the mass of the drop and T is the period of its first mode of self-oscillation (spheroid). This estimation is in good agreement with a direct measurement ($\sigma_{w/o} = 8.6 \pm 1.0$ mN·m^{-1}) using the pendant drop method measured with an optical goniometer CAM200 (KSV Instruments).

The compound drop generation device consists of two syringes (one for each liquid) of which the nozzles are connected by a thin copper wire curved downward (see Figure 1).[25] The surfactant solution drop (light blue in Figure 1), created with the first syringe, slides along the wire and stops at the lowest point. Then, the oil drop is released from the second syringe (yellow in Figure 1); it slides down and encapsulates the water drop. The resulting compound drop is sufficiently large to spontaneously detach from the wire; it falls and bounces onto the oscillating liquid surface, approximately 5 mm below. The bouncing motion is recorded at 1000 fps with a fast video camera (IDT-N3).

The volume of both drops is tuned by changing the diameter of the needles and the width of the wire.[25] Five different compositions of millimetric compound drops have been tested (Table 1). To assess the influence of viscosity on the deformations, the Ohnesorge number $Oh = \nu\rho^{1/2}/(\sigma R)^{1/2}$ is estimated from the radius R of the compound drop and the liquid properties of oil and water successively. In any case, this Ohnesorge number is less than 0.01, so the drop deformations are slowly damped. On the other hand, the Ohnesorge number calculated from the properties of the underlying oil bath is about 7, its deformations are therefore quickly and fully damped by viscous effects and they may be neglected.

It is difficult to characterize the inner oil droplets formed during the emulsification process. The high curvature of both air−oil and oil−water interfaces behaves as a lens system that may deeply alter the apparent size and shape of these tiny droplets. For a given composition, the relative size of the inner droplets can be estimated each time they passes through the center of the compound drop.

Results

Emulsification Threshold. At a relatively low forcing amplitude ($\Gamma \simeq 1$), the compound drop is observed to bounce periodically on the vibrated liquid surface, in a similar way to monophasic bouncing drops. The relatively small deformations may be assimilated to the spherical harmonic function Y_2^0.[20,21] For larger forcing, the drop trajectory becomes chaotic.[26] During vigorous impacts, the drop deformation may become so important that a tiny droplet from the oil layer is injected into the water drop. This phenomenon is shown in Figure 2 for a compound drop of total volume 3.52 μL (Δ in Table 1) and forcing parameters $(f,\Gamma) = (50 \text{ Hz}, 4.4)$. According to these snapshots, the drop flattens as soon as it impacts the bath. The resulting capillary waves start propagating from the bottom to the top of the drop.[27] The convergence of these waves at the top locally pushes the oil shell inside the water interface. A pinch-off occurs such that an oil droplet is released in the inner water drop. This mechanism of droplet creation through wave convergence and pinch-off is relatively similar to what was observed in the partial coalescence of low viscosity drops.[28,29] By analogy, we may therefore expect a critical Ohnesorge number above which these waves are damped and the water−oil interface does not pinch off anymore. Each sufficiently strong impact creates an additional oil droplet into the water drop (Figure 3), progressively turning the initial compound drop into a double emulsion. The process stops when the numerous oil droplets inside the water drop start to strongly dampen the capillary waves, therefore preventing an additional pinch off. The large impact velocities might weaken the air film and lead to premature coalescence of the emulsion with the underlying bath. Therefore, as soon as the emulsification is completed, the forcing acceleration can be significantly decreased in such a way that the bouncing becomes smoother and much more stable. Then, the emulsified compound drop can be manipulated, for example, by adjusting the forcing parameters in order to excite the so-called “roller” mode of deformation inducing a drop motion.[21]

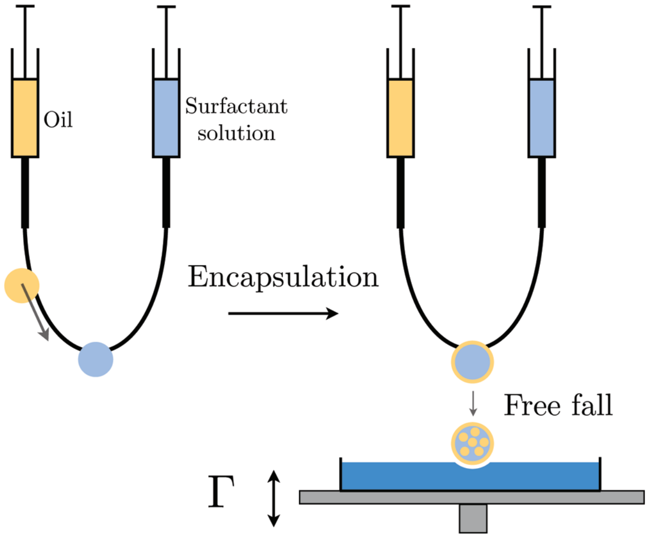

Figure 1. The compound drop is created by using two syringes connected by their ends by a thin copper wire. Both water and oil drops are released from the syringes, they slide on the wire and stop at the lowest point where they eventually merge. The compound drop detaches from the wire and falls onto the oscillating liquid bath.

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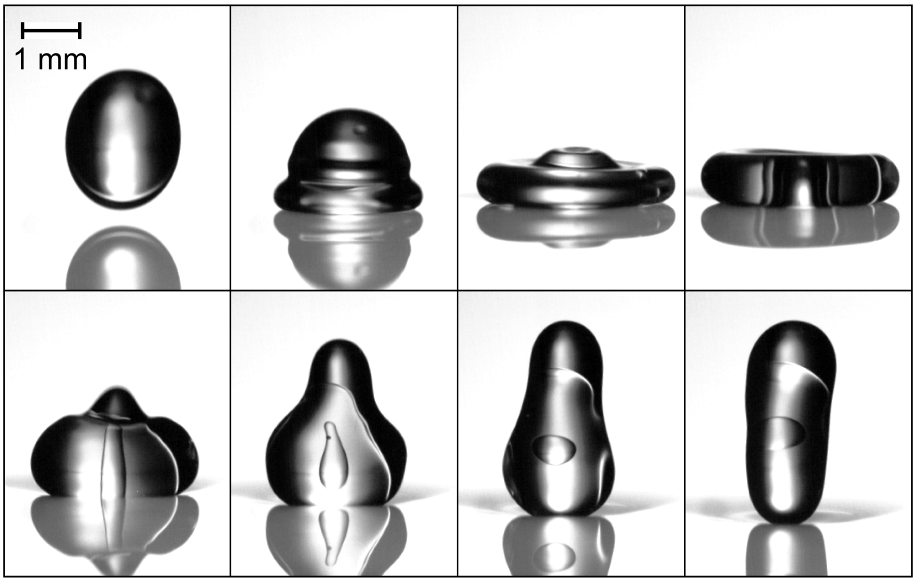

Figure 2. A compound drop (Δ in table Table 1) bounces on a liquid surface vibrated sinusoidally at f = 50 Hz and Γ = 4.4. The convergence of capillary waves on the top of the drop pushes the oil layer inward. The water–oil interface pinches off and a tiny oil droplet is released into the water core.

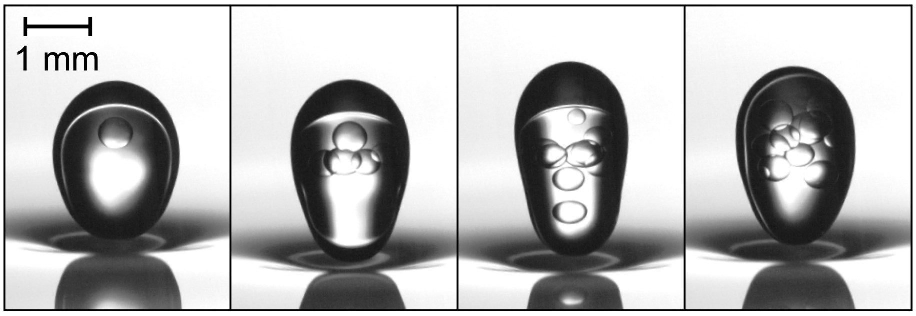

Figure 3. Each time the droplet impacts the bath with a sufficiently high velocity, an additional oil droplet is injected into the inner water drop, progressively creating a double emulsion of oil droplets into a water drop surrounded by an oil shell. The four snapshots represent the same compound drop after 5, 20, 34, and 51 bounces.

Table 1. Composition and Volume of the Different Tested Compound Drops (Five Sizes)[a]

Symbols	$\Omega_w(\mu L)$	$\Omega_o(\mu L)$	$\Omega_{cd}(\mu L)$
⊠ □	1.1	1.05	2.15
◊	1.75	0.68	2.43
▽	1.29	1.29	2.58
△	1.42	2.10	3.52
○	2.99	1.15	4.14

[a] The columns represent the volume of water Ω_w, the volume of oil Ω_o, and the total volume of the compound drop Ω_{cd}, respectively.

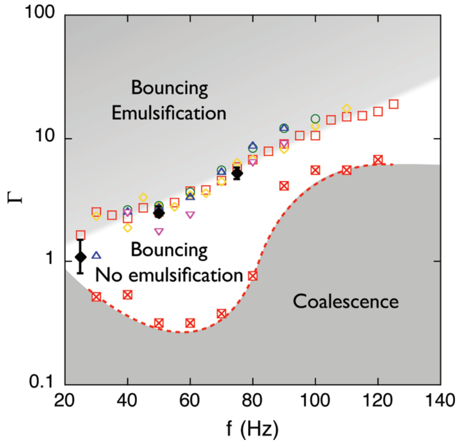

Figure 4. Bouncing threshold acceleration Γ_b (square with x) and emulsion threshold acceleration Γ_e (□, ◊, Δ,○,▽) as a function of the forcing frequency f. Symbols correspond to various sizes of the compound drop, as detailed in Table 1. Black diamonds are explained in Figure 6 (see text).

The emulsification behavior is only observed for high dimensionless forcing acceleration Γ. A second threshold value Γ_e does exist above which pinch-off occurs and the inner droplets are created. To measure this threshold, the forcing amplitude is increased step by step, the frequency being fixed. A compound drop is gently released on the oil bath at each step. Three scenarios are observed: when $\Gamma < \Gamma_b$, the compound drop quickly coalesces with the bath; when $\Gamma_b < \Gamma < \Gamma_e$, the compound drop bounces on the oil bath exactly as a monophasic drop;[17,20] and when $\Gamma > \Gamma_e$, a double emulsion starts forming. Both Γ_b and Γ_e are measured as a function of the forcing frequency, for various drop sizes (Table 1). The emulsion threshold $\Gamma_e(f)$ is reported in Figure 4 for each of the five drop sizes that we have investigated, while the bouncing

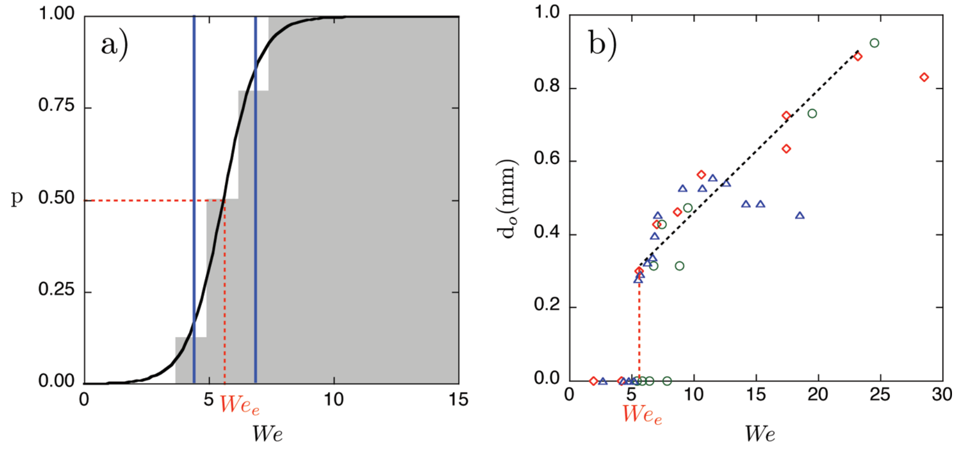

Figure 5. (a) Probability p for encapsulating an oil droplet in the water drop by impact on a static bath, as a function of the Weber number We. The black line is a guide for the eye. The water−oil interface pinches off when We is higher than a critical value $We_e \simeq 5.7 \pm 1.25$. (b) Diameter d_o of the inner oil droplets as a function of We. The dashed lines are guides for the eye. The symbols are the same as those used in Figure 4 and explained in Table 1.

threshold $\Gamma_b(f)$ is only reported for the 2.15 μL drop (square with x symbol in Table 1).

As already noted in previous works,[21] the bouncing threshold for a pure oil drop is dependent on the drop size. Because bouncing is ensured by the deformation of the oil drop, Γ_b only depends on the ratio between the forcing frequency and the natural frequency of the drop deformation. This latter scales as $(\sigma_{o/a}/m)^{1/2}$, where m is the total mass of the compound drop. Conversely, the emulsion threshold Γ_e is not found to be much influenced by the drop size. The corresponding curves in Figure 4 collapse on each other when represented as a function of f. While the volume is doubled from the smallest to the largest drop (and so is the square of the natural frequency), the emulsion threshold remains unchanged. The conclusion is that the drop deformations are too large to be directly affected by the forcing frequency. This latter only influences the emulsion threshold by modifying the height of the jump and consequently the strength of the impact. Nevertheless, it should be noted that emulsification is not possible for very large drops, for which even sustained bouncing is not possible. Indeed, it has been shown[29] that for a given frequency, there is a maximum size of drops that are allowed to bounce without coalescing.

According to both direct observations and the discussion of Figure 4, the deformation of the compound drop plays a key role in the possible formation of a double emulsion. The energy required to deform the drop mainly comes from the kinetic energy released at impact. This energy originates from the relative velocity V_i between the drop and the bath and is transferred into surface energy just after the impact. The calculation of the surface energy must take into account both the water/oil and the oil/air interfaces. The ratio between the kinetic energy and the surface energy of the compound drop is given by the Weber number, as defined by Chiu et al.:[7]

$$We = \left(\frac{6}{\pi}\right)^{1/3} \frac{[\rho_w \Omega_w + \rho_o \Omega_o]}{\sigma_{o/a}(\Omega_o + \Omega_w)^{2/3} + \sigma_{w/o} {\Omega_w}^{2/3}} {V_i}^2 \qquad (2)$$

The impact velocity V_i can be seen as the sum of the free fall velocity V_f of the drop and the velocity of the vibrating bath V_b, that is, $V_i = V_f + V_b$. To fix the ideas, we find it interesting to calculate the maximum expected V_i. The free fall velocity is given by $V_f = (2gh)^{1/2}$, where h is the maximum height reached during the flight, $h = 0$, corresponding to the mean position of the bath. The velocity of the bath V_b varies between $-\Gamma g/(2\pi f)$ and $\Gamma g/(2\pi f)$, the most favorable case for generating an emulsion being $V_b = \Gamma g/(2\pi f)$. For typical values of Γ, $V_b \approx 0.3$ m/s, which is of the same order of magnitude as V_f. This confirms that both velocities must be taken into account in the definition of We.

In the following we will show that in the case of a static bath ($V_b = 0$) V_f is tuned by changing the falling height. There exists a critical value $We = We_e$ above which the double emulsification is triggered. Then, assuming that the same threshold applies in the vibrated case, we will rationalize the emulsification threshold Γ_e observed in Figure 4.

Impact of Compound Drops on a Static Liquid Surface. The influence of the impact velocity V_i (and consequently the We) has been investigated by releasing 60 compound drops (with various compositions, according to Table 1) from different heights onto an oil bath at rest. In Figure 5a, the probability of encapsulating an oil droplet in the water droplet is represented as a function of We. Data are binned in classes of 1.25 of width. The droplet generation is not possible for low We and systematic for high We. A smooth transition is observed in between, where the probability p of emulsification increases with We; a black line is used as a guide for the eye. We define the critical Weber for emulsification We_e as the Weber value for which the probability to create an oil droplet in the water droplet is 50%. We choose to characterize the width of the transition as twice the size of one class, consequently we claim $We_e = 5.7 \pm 1.25$. The various compositions are presented together, as almost no effect of the relative sizes can be evidenced from the experimental data. Nevertheless, we expect that highly different compositions/sizes would lead to a different value of the critical We.

The relative size of the inner oil droplets is measured as a function of We (Figure 5b). Only compound droplets of the same composition (so having the same optical magnification) can be compared together. The diameter of the inner droplets is seen to increase with We. As the kinetic energy at impact is increased, there is more available energy. In particular, more surface energy can be generated by the impact. That process conducts to form larger oil droplets inside the water droplet.

Impact Velocity on a Vibrated Liquid Surface. It is reasonable to assume that the critical Weber number We_e does not depend on the motion of the bath, provided that the relative impact velocity $V_i = V_b + V_f$ is considered in eq 2. Remembering that $V_b = \Gamma g/(2\pi f)$ in the most favorable case, we can say that the

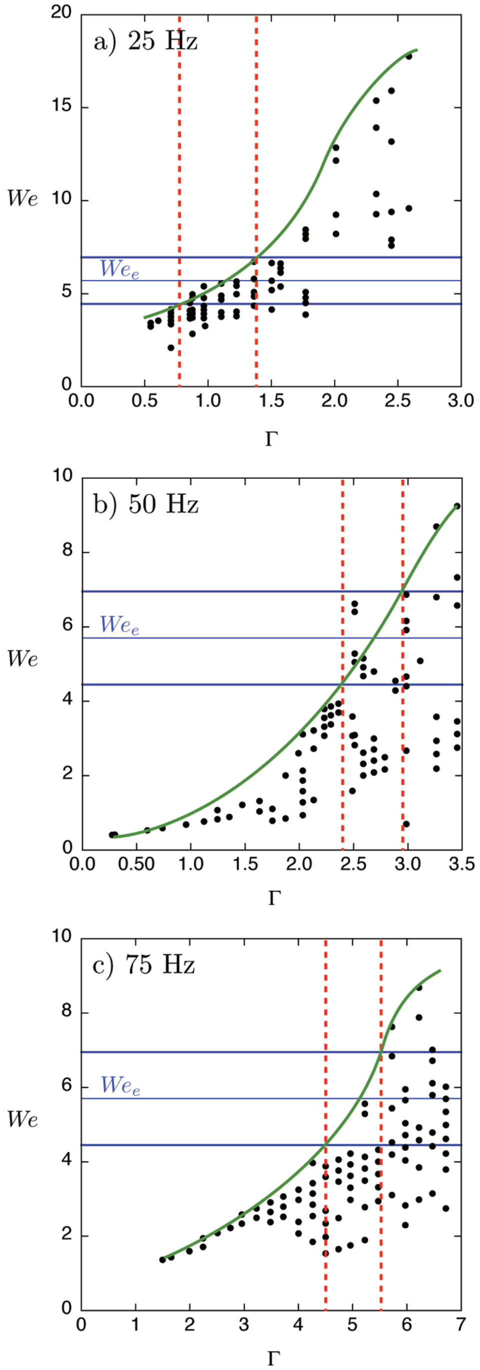

Figure 6. Relative Weber number We of an oil drop ($\nu = 1.5$ cSt, $\Omega_o = 2.15\,\mu$L) impacting the bath vibrated at (a) 25, (b) 50, and (c) 75 Hz, as a function of the forcing amplitude Γ. Compound drops are assumed to experience the same range of We for a given Γ. The emulsification is triggered when We is higher than We_e (range represented by the two horizontal blue lines). The dashed lines indicate the corresponding range of Γ_e.

emulsion threshold Γ_e is the dimensionless forcing acceleration for which the resulting $We = We_e$. Unfortunately, the height of the rebounds h (and so the free fall velocity V_f) also depend on Γ in a nontrivial way, exactly as in the classical bouncing ball problem.[30−32]

To evaluate $h(\Gamma)$, we have recorded the trajectory of a drop being the same size as the compound drops, but made only of oil (kinematic viscosity $\nu = 1.5$ cSt and volume $\Omega_o = 2.15\,\mu$L). Indeed, far above the emulsion threshold the presence of thin oil droplets in the water core induces a dissipation process that modifies the compound droplets trajectory. As we want to determine statistically when the speed of a bouncer is large enough to induce double emulsion, we consider a pure system. Moreover, it has been checked that the compound drop which as not emulsified yet has approximately the same restitution coefficient $\varepsilon = (1 - \Delta We/We)^{1/2} \approx 0.33$ as the pure 1.5 cSt oil drop. Therefore, the nonemulsified bouncing compound drop may adopt the same trajectory as the oil drop for a given set of forcing parameters (f,Γ). The measurement has been made for three forcing frequencies $f = 25$, 50, and 75 Hz. From the measurements of the heights reached by the droplet during the bouncing, the falling speed V_f is calculated and V_i is deduced and injected in the definition of the Weber number We rewritten for a pure oil droplet. It is now defined as

$$We = \left(\frac{6}{\pi}\right)^{1/3} \frac{\rho_o V_i^2 \Omega_o^{1/3}}{\sigma_{o/a}} \qquad (3)$$

It is represented as a function of Γ for f equal to 25, 50, and 75 Hz in Figure 6, each point corresponding to one bounce. The bouncing height h is measured experimentally, then V_f and We are calculated through eq 3. These diagrams (Figure 6) are similar to the bifurcation diagram observed in the elastic bouncing ball problem.[33,34] The important deformations of the drop make the trajectory chaotic,[26] leading to a large range of impact Weber numbers. The envelope curve is drawn (in green) on each diagram and represents the maximum impact Weber number expected for given forcing parameters (f,Γ).

The critical Weber number $We_e = 5.7 \pm 1.25$ measured in the static case defined a range in Figure 6 as indicated by two blue and bold horizontal lines. Their intersection with the envelope curve indicates what is the minimum forcing amplitude Γ_e required for double emulsification. According to Figure 6, the emulsification transition occurs at $\Gamma_e \in [0.7,1.4]$ for $f = 25$ Hz, at $\Gamma_e \in [2.4,2.9]$ for $f = 50$ Hz, and at $\Gamma_e \in [4.5,5.5]$ for $f = 75$ Hz. These values are reported in Figure 4 (black diamonds). Their good agreement with the direct measurements of Γ_e confirms that the relative Weber number at impact is the relevant parameter to rationalize the emulsification threshold.

Conclusion

The experimental work presented in this article shows that double emulsions can be formed from a compound drop (surfactant solution surrounded by an oil layer) permanently bouncing onto a vibrated liquid surface. No contact with a solid part is involved in the emulsification process. Above a given threshold Γ_e in the dimensionless amplitude of the vibration, the oil shell penetrates the water drop and leaves a tiny oil droplet inside. As this phenomenon occurs at each strong impact, a double emulsion (oil in water in oil) is progressively formed. We note that Γ_e depends on the forcing frequency, but surprisingly not so much on the droplet size. The mechanism responsible for the encapsulation is the convergence of capillary waves to the top of the compound droplet.

To rationalize this emulsion threshold, the impact of a compound drop onto a static liquid surface has been investigated.

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The irreversible penetration of the oil shell within the water core is observed above a critical Weber number We_e. We have shown that We_e may be related to Γ_e by considering their bounds of the chaotic trajectory of the bouncing drop.

The influence of viscosity on the emulsification process has been investigated for an oil layer viscosities of 10 and 100cSt. No emulsification has been observed. An analogy can be made with the partial coalescence of a water droplet at a water/oil interface.[35] Partial coalescence occurs when the viscous forces arising in both water and oil are negligible compared to the surface tension forces. This criterion can be expressed by using the Ohnesorge number Oh which compares viscosity force to surface tension. We believe that the emulsification is only possible when both Ohnesorge numbers (respectively based on the viscosity of each fluid) are much smaller than 1.

The bouncing ability of the compound droplet relies on the presence of a thin air film in between the droplet and the bath. Since the relatively large values of Γ required for emulsification might remove the air layer and lead to coalescence with the underlying bath, the forcing amplitude is usually decreased as soon as the emulsion is formed. The emulsified droplet can then be handled on the bath surface by changing the forcing parameters (amplitude and frequency). For example, it can be set into spontaneous motion,[21] or several double emulsions can be merged together.[29] Controlled droplet bouncing may be a promising way to manipulate liquids for microfluidic operations; this study proves that spontaneous emulsification is possible in that context.

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