Dynamics of aqueous "liquid marbles" in three dimensional biphasic systems

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Abstract

Liquid marbles are defined as hydrophilic liquid droplets that are coated with hydrophobic powdered materials. Till now, the behaviour of liquid marbles has been studied for triphasic systems comprising of the constituent hydrophilic phase, the hydrophobic coating and ambient air. In this article, we report the dynamics of aqueous droplets of varying pH (i.e. acidic, neutral and basic, respectively) moving under the influence of gravity in commonly available mustard oil. We find that the said dynamics could be divided into four parts: (i) formation of hanging aqueous droplets from the top surface of oil, (ii) oblate spheroid droplets moving at constant velocity due to viscous drag, (iii) distant repulsive interactions between two droplets due to "reverse Cheerios effect" and (iv) final impact between the two droplets explained by viscoelastic sliding friction over a compliant surface. This work would be of great interest to researchers working in the domain of interfacial phenomena like oil exploration, biomedical engineering, food technology and towards the realization of droplet-based microfluidic computational platforms for "more than Moore's" paradigm in the domain of unconventional computation.

Keywords: Interfacial phenomena; liquid marbles; reverse Cheerios effect

Introduction

Liquid marbles are defined as liquid droplets (generally hydrophilic) that are covered by hydrophobic powdered solids. These droplets would not spread on the surface and would be

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very easy to move around by application of a little amount of force. Movement of these structures would not have any interference due to the nature of the substrate. The structural integrity of the said “liquid marble” is always intact because the constituent fluid leakage is prevented by the hydrophobic coating. All the above mentioned studies were conducted in triphasic systems: comprising of aqueous droplets in the core, hydrophobic powder as coating to the said droplet and ambient air. Thus, to form liquid marbles, an aqueous drop capped with a hydrophobic material is required **[1, 2]**. There have been several studies pertaining to the triphasic dynamics of liquid marbles **[3-10]**. The most commonly available hydrophilic and hydrophobic materials are water and oil. Dynamics of oil-water interfaces have been well studied for the generation of alternating currents upon application of DC voltage **[11]** and the flattening of the interfacial menisci at extremely alkaline pH **[12]**.

In this article, we report the dynamic behaviour of aqueous droplets acting as liquid marbles in oil environment starting from: (i) formation of small hanging droplets at the top surface of the oil, (ii) secession of the aqueous droplet to form an oblate spheroidal shape, (iii) distant repulsive interaction between two droplets and (iv) physical impact between the two droplets explained by the movement of the deformable viscoelastic water capsules over a compliant surface (in this case, another viscoelastic droplet).

Materials and Methods

5 ml. of commercially available mustard oil was taken in three (03) glass test tubes (diameter: ~ 1.6 cm.). 150 microliters of food grade vinegar, normal drinking water and aqueous solution of food grade baking soda were added to each of the test tubes marked A, N and B, respectively. Vinegar used contained 4% acetic acid **[13]**, 0.1 g baking soda was dissolved in 10 ml of normal drinking water. The baking soda powder contained ~12.29 mEq. sodium bicarbonate (i.e. 59 mEq. in 4.8 g) **[14]**. Vinegar and aqueous solution of baking soda were used as an acid and a base, respectively. The dynamics of sinking aqueous droplets were

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recorded using a Nikon D3400 DSLR camera, at a speed of 60 frames per second (fps). Experimental setup is shown in Fig. 1. The video furnished as supplementary information shows the dynamics at half the actual speed i.e. the video speed is 0.5x.

Fig. 1 (Left panel) Experimental setup showing three test tubes filled with mustard oil & the camera used for the recording. (Right panel) Diameter of the test tube measured to be ~ 1.6 cm.

Results and Discussion

I. Hanging aqueous droplets from the top

At the beginning when the aqueous droplet was put into oil, it formed a hanging droplet at the top surface of the oil in the test tube. The same can be seen in Fig. 2 for the acidic (A), neutral/normal (N) & basic (B) aqueous solutions, respectively.

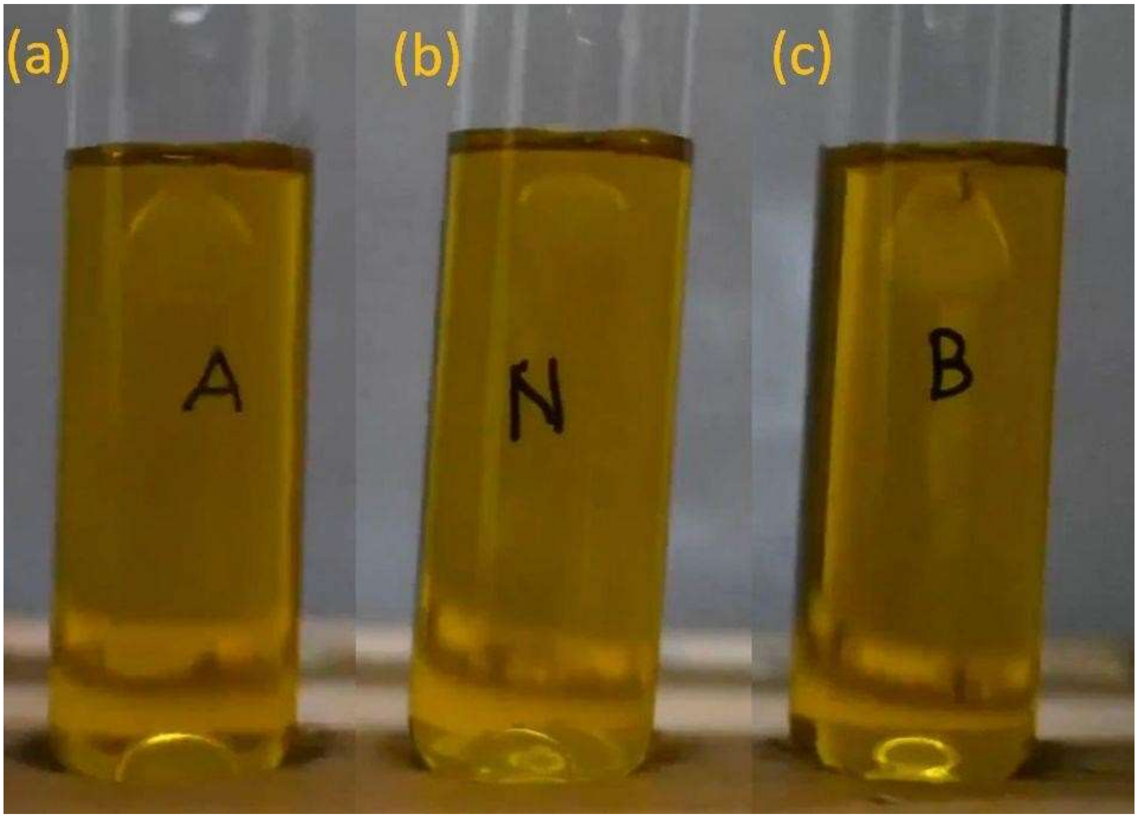

Fig. 2 Hanging aqueous droplets at the top of oil surface seen in the three test tubes, labelled (a) acidic (A), (b) neutral/normal (N) and (c) basic (B).

The droplets hung at the top till they reached a critical volume, when their respective weights were counterbalanced by the buoyant forces & surface tension **[6]**. The schematic diagram depicting the mentioned phenomenon is shown in Fig. 3, as follows:

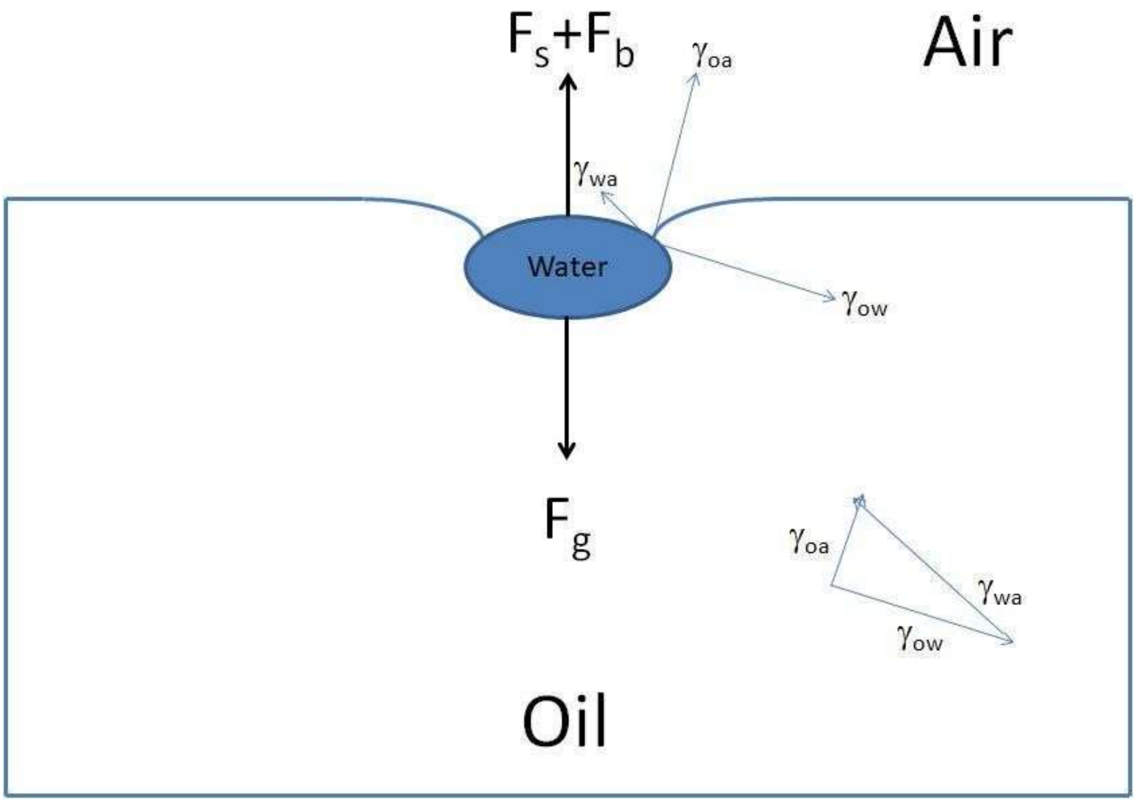

Fig. 3 Schematic diagram showing the hanging aqueous droplets, with their weights (gravitational force, F_g) balanced by the forces of surface tension (F_s) and buoyancy (F_b). The vectorial representation of the surface tension forces is also shown. The triangle in the inset showing the vector addition for surface tension balance is known as a "Neumann triangle" **[6]**.

II. Oblate spheroidal droplet moving in viscous drag

When the volume of the drop hanging from the top exceeds the force balancing limit (i.e. $F_g > F_b + F_s$, where F_g, F_b & F_s are weight, buoyant force and surface tension force, respectively), the aqueous droplet starts to sink into the viscous mustard oil medium. The shape of the droplet during the downward movement appeared to be that of an oblate spheroid. Before we proceed any further with theoretical analyses of the dynamics of aqueous droplets, the approximation of the oblate spheroid into perfect spheres is warranted. For this purpose, we use the concept of sphericity. Sphericity is defined as the measure of how closely an object resembles to a perfect sphere **[15]**, and is defined by the relationship given in equation 1:

$$Sphericity, S = \frac{A_{sphere}}{A_{object}} \tag{1}$$

where, A_{sphere} denotes the surface area of a perfect sphere whose volume is equal to the volume of the object we intend to compute the sphericity of and A_{object} is the surface area of the said object. Sphericity and surface area of an oblate spheroid S_{ob} and A_{ob} are given by equations 2 **[15]** & 3 **[16]**.

$$S_{ob} = \frac{2\alpha^{2/3}}{1 + \frac{\alpha^2}{2\sqrt{1-\alpha^2}} ln\,(\frac{2 - \alpha^2 + 2\sqrt{1-\alpha^2}}{\alpha^2})} \tag{2}$$

$$A_{ob} = \frac{\pi}{\sqrt{1-\alpha^2}} \{2\sqrt{1-\alpha^2} + c^2 ln\,(\frac{1+\sqrt{1-\alpha^2}}{1-\sqrt{1-\alpha^2}})\} \tag{3}$$

where, α (< 1) is the ratio of minor axis to major axis of the spheroid & c is the minor axis of the spheroid. Thus, the radius of the equivalent sphere can be calculated as

$$r_{eq} = \sqrt{\frac{1}{4\pi} S_{ob} \times A_{ob}} \tag{4}$$

Since the droplet appeared to move at a constant velocity, the movement of thus discussed oblate spheroid droplet can be explained by the viscous drag movement due to the viscosity of the oil environment **[17]**. The oil environment is hydrophobic in which the aqueous droplet is sinking, a very important dimensionless parameter called Bond number, B **[18]**, ought to be defined as

$$B = \frac{\rho_e g r_{eq}^2}{\gamma_{ow}} \tag{5}$$

where, ρ_e: effective density of the aqueous droplet, $\rho_{water} - \rho_{oil}$;

r_{eq}: as defined in equation 4;

g: acceleration due to gravity;

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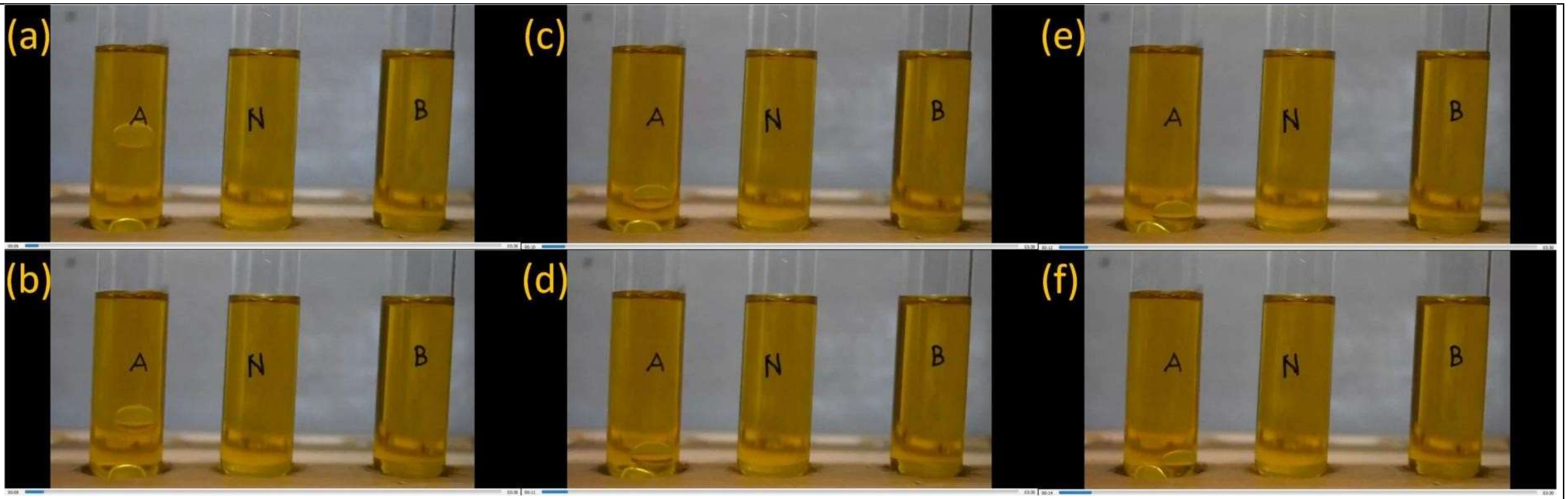
γ_{ow}: surface tension between oil and water;

The Bond number is a measure of the gravitational and surface tension forces acting on the aqueous droplet. It helps us in understanding the shapes and dynamic behaviour of the said droplets.

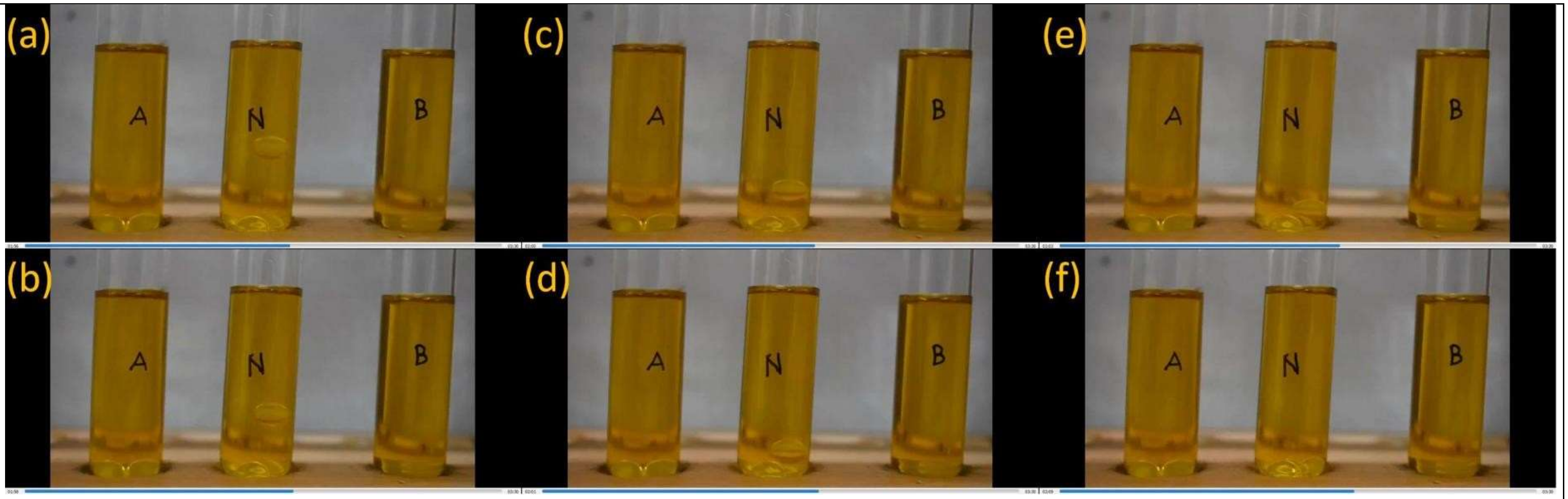
III. Distant repulsive interactions of aqueous droplets

We observed that when one droplet was sitting at the bottom of the test tube and the other one was sinking, the two droplets repelled each other from a distance. This observation was consistent for acidic, neutral and basic solutions, respectively. The said tele-repulsive behaviour has been shown in Fig. 4(i), 4(ii) & 4(iii) as screenshots of the video (shared in the supplementary information).

(i)



(ii)



(iii)

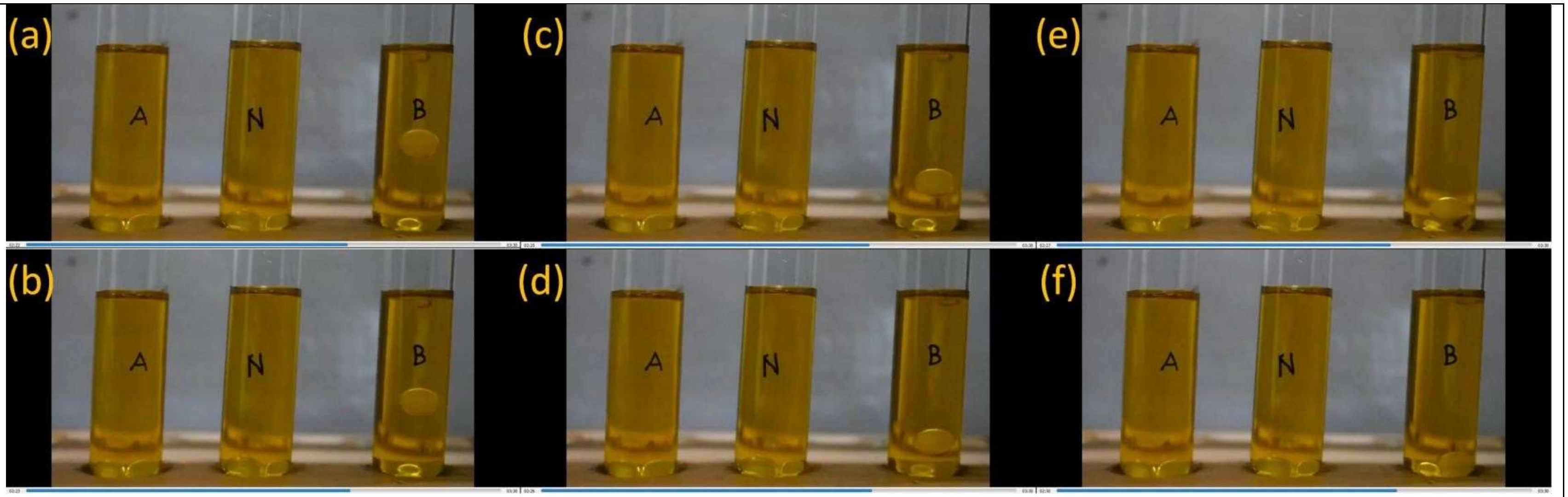


Fig. 4 Screenshots of the dynamic interactions of (i) acidic (A), (ii) neutral (N) and (iii) basic (B) aqueous droplets in mustard oil. For each system, the sequence of events followed the order (a)-(f).

The repulsive interaction between the two droplets (as shown in Fig. 4) could be explained by a well-studied reverse/inverted Cheerios effect **[19, 20]**, in which the force of interaction is given by the relationship given in equation 6.

$$F_c = -2\pi\gamma_{oil} r_{eq} B^{5/2}\Gamma^2 K_l \left(\frac{\delta}{L_{cl}}\right) \tag{6}$$

where, γ_{oil}: surface tension of oil;

r_{eq}: Equivalent radius of the aqueous droplet (as calculated from equation 4);

B: Bond number;

Γ: $\frac{2\rho-1}{3}$; $\rho = \frac{\rho_{droplet}}{\rho_{oil}}$($\rho$: density);

K_l: Modified Bessel's function of first kind;

δ: Instantaneous distance between the droplets;

L_{cl}: capillary length ($= \sqrt{\frac{\gamma_{oil}}{\rho_{oil} \times g}}$) ; g: acceleration due to gravity;

The repulsive behaviour reported here is attributed to the reverse/inverted Cheerios effect only because of the low Reynolds number (i.e. laminar) flow of the droplet, which would not account for the hydrodynamic pushing of the droplet at the bottom. That is why we see that droplets of different pH repel their counterparts with different intensities (video is given in supplementary information); otherwise all of them would have been pushed equally if only a hydrodynamic push were a reason. The other forces acting on the aqueous droplets are gravitational force and viscous drag. Thus, the force balance equation for interacting and sinking droplets in viscous hydrophobic environment is given as follows:

$$6\pi\mu_{oil} r_{eq} \frac{d\delta}{dt} + 2\pi\gamma_{oil} r_{eq} B^{5/2}\Gamma^2 K_l \left(\frac{\delta}{L_{cl}}\right) = (\rho_{water} - \rho_{oil}) \times \frac{4}{3}\pi r_{eq}^3 \times g \tag{7}$$

The first term on the L.H.S. denotes the viscous drag, with μ_{oil} being the dynamic viscosity of oil and $\frac{d\delta}{dt}$ being the instantaneous velocity of the droplet; the second term denotes the repulsive interaction force (reverse/inverted Cheerios effect). These two forces add up together to balance the weight of the sinking droplet (thus preventing it from accelerating i.e. moving at constant velocity).

IV. Physical impact between two aqueous droplets

Final stage of dynamic behaviour of aqueous droplets accounts for impacting & sliding of one viscoelastic droplet over another. Since the two droplets being studied are submerged in a hydrophobic environment, they don't coalesce with each other (as it is evident from the video in the supplementary information) thus resulting in a non-coalescing collision. Such collisions can be well studied with the aid of a dimensionless quantity known as Weber number (We) **[9]**, defined as the ratio of deforming inertial forces (like weight etc.) and (de)stabilizing forces (like electrostatic interactions, surface tension etc.).

$$We = \frac{2 \times r_{eq} \times (\rho_{water} - \rho_{oil})}{\gamma_{ow}} \times (\frac{d\delta}{dt})^2 \quad (8)$$

Here $\frac{d\delta}{dt}$ is expressed at the time of impact. Another parameter that plays a key role in the impact outcome is the offset ratio, which is given by the ratio of the axial distances to the effective diameter of droplets. The offset ratio can be represented as

$$X^* = \frac{x}{2 \times r_{eq}} \quad (9)$$

Post collision, the aqueous droplets were observed to be smoothly sliding over each other (as seen in the video provided in the supplementary information). The same behaviour could well be explained using viscoelastic sliding resistance while droplets move over compliant surfaces, as has been discussed by many eminent researchers.

Conclusions

In this article, we have studied the dynamics of aqueous droplets in a hydrophobic environment moving under the action of gravity. These aqueous droplets have been argued to behave as liquid marbles, as by definition liquid marbles are hydrophilic liquids surrounded by hydrophobic coating that prevents the constituent liquid from leaking and spreading on the surface. We have discussed the dynamics of these droplets by dividing them broadly into four domains: (i) starting from their introduction at the top of oil surface, forming hanging droplets reasoned by Neumann triangles, (ii) formation of oblate spheroids after getting detached from the top due to excess weight of the droplets and moving down under the action of gravity at constant velocity, (iii) distant repulsive interactions between the two aqueous droplets owing to "reverse/inverted Cheerios effect" and (iv) final physical impact of the sinking droplet on the stationary droplet sitting at the bottom of the test tube. This behaviour was explained by the non-coalescing collision followed by viscoelastic sliding friction over a compliant surface. Determination of the phenomenon of sliding can be carried out further by the researchers working in this domain. This work would be of immense interest to scientists and researchers working in the domain of interfacial sciences including oil exploration from water bodies **[21]**, food technology **[22]**, biomedical engineering **[23]** and towards the realization of microfluidic computational platforms for "more than Moore's" paradigms **[24]**.

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