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Getting in shape: Molten wax drop deformation and solidification at an immiscible liquid interface

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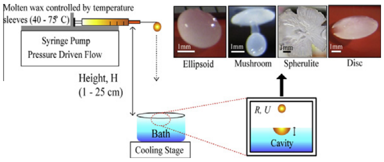
GRAPHICAL ABSTRACT



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ABSTRACT

The controlled production of non-spherical shaped particles is important for many applications such as food processing, consumer goods, adsorbents, drug delivery, and optical sensing. In this paper, we investigated the deformation and simultaneous solidification of millimeter size molten wax drops as they impacted an immiscible liquid interface of higher density. By varying initial temperature and viscoelasticity of the molten drop, drop size, impact velocity, viscosity and temperature of the bath fluid, and the interfacial tension between the molten wax and bath fluid, spherical molten wax drops impinged on a cooling water bath and were arrested into non-spherical solidified particles in the form of ellipsoid, mushroom, disc, and flake-like shapes. We constructed cursory phase diagrams for the various particle shapes generated over a range of Weber, Capillary, Reynolds, and Stefan numbers, governed by the interfacial, inertial, viscous, and thermal effects. We solved a simplified heat transfer problem to estimate the time required to initiate the solidification at the interface of a spherical molten wax droplet and cooling aqueous bath after impact. By correlating this time with the molten wax drop deformation history captured from high speed imaging experiments, we elucidate the delicate balance of interfacial, inertial, viscous, and thermal forces that determine the final morphology of wax particles.

1. Introduction

Non-spherical shaped particles provide great potential for applications in biotechnology [1], cosmetics [2], hierarchically structured materials [3], and pharmaceuticals [4]. When compared with spherical particles, non-spherical particles can offer unique properties such as high packing density [5], large surface areas, enhanced material properties, and anisotropic responses to external electric and magnetic fields [6–8]. For example, the intrinsic shear viscosity of suspensions containing non-spherical shaped particles is dependent on the orientation of the non-spherical particle [9]. Extensive research has been reported on the synthesis of non-spherical polymeric particles using microfluidics and self-assembly processes, with sizes ranging from microns to millimeters [10–14]. However, the particle morphology each method can produce is quite limited, accompanied by the requirement of specialized equipment. Recently, non-spherical particle synthesis was realized by impinging and deforming liquid drops on liquid

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substrates by combining microfluidics and subsequent drop impact and cross linking process in a bulk medium [15,16]. This method is simple, low cost, applicable to both Newtonian and non-Newtonian fluids, and potentially scalable to many industrial applications [17–20]. In addition, liquid drop impact and subsequent deformation on surfaces is of fundamental importance due to its application in a wealth of areas including inkjet printing [21,22], food processing, spray coating in the consumer goods and pharmaceutical industries [23,24], delivery of drugs and agrochemicals, optical sensing, soil erosion from rains [25], and turbine wear.

The materials used for synthesizing non-spherical particles include polymers, gels, foams, wax, and biological materials. In this work, we focus on wax based materials because they are versatile in nature and have been used in dentistry [26], consumer goods [27], food processing [28], and drug delivery fields [29]. Disc and spherical shaped wax particles have been fabricated by research groups recently via electrospray emulsification in a mixture of ethanol and water, and ultrasonic atomization respectively [30,31]. The impact of molten metal or paraffin wax drops on a solid surface has been reported to lead to irregular film, cylinder or disc formation upon subsequent solidification [32–37]. Analytical studies have also been performed to understand the effect of processing conditions on the droplet impact dynamics on a solid surface [32,38]. Previous research mainly focused on liquid bath media whose density was the same or lower than the impacting liquid drops [18,30]. However, to the best of our knowledge, the impact and solidification of molten liquid drops in a liquid medium of higher density has not been studied thoroughly. The interfacial dynamics associated with impinging molten drops on liquid surfaces and the simultaneous solidification is complex and not understood in detail. Moreover, a moving phase interface provides more freedom during the deformation and solidification of the molten drop when compared with a solid surface, possibly leading to a wider range of particle morphologies.

Motivated by both fundamental and application driven needs to make non-spherical particles, the objective of this work is to controllably generate millimeter size non-spherical wax particles produced by the deformation and solidification of molten wax drops in an immiscible cooling liquid of higher density. In Section 2, we provide a brief review of existing work on liquid drops impacting on either a solid or a liquid medium. In Section 3, we describe the experimental procedure. In Section 4 we cover experimental results and discussions. A simplified heat transfer model was solved to estimate the time required to initiate the solidification at the interface of a spherical molten wax droplet and cooling aqueous bath after impact. Section 5 provides the conclusion and perspectives.

2. Background

Many studies have been performed on the deformation of liquid drops upon impact on either solid or liquid surfaces with isothermal conditions, which have been covered extensively in reviews by Rein [39] and Yarin [40]. When a liquid drop impacts a solid substrate, the drop may deposit into a thin disc, disintegrate into secondary drops, or recede and possibly rebound and bounce [17]. The impact of a liquid drop on a liquid pool can yield more complicated flow dynamics and outcomes, which may broadly be classified into three categories: coalescence, splashing, or bouncing off the surface [39,41–43], see schematics in Fig. 1. The result of the liquid–liquid impact depends on the material properties of the drop and the bath fluid which the drop traverses before impact, and impact velocity.

In the case of coalescence the drop disappears quickly in the target liquid. A small crater is formed but otherwise the impacted surface is hardly disturbed and no secondary droplets are produced. This event is usually connected with the formation of a vortex ring below the surface [44]. In the case of splashing the liquid surface is greatly disturbed and may lead to the formation of a jet that rises out of the center of the crater formed after impact, above the original surface of the target liquid. This rising liquid column is known as the Worthington jet [45,46]. A crown with dissipative waves at the liquid surface may form during splashing depending on the impact velocity and the viscosity of both fluids [47]. Right after impact a cavity is formed whose shape is dependent on the impact velocity and material properties of the liquid drop.

The impact energy is a key factor in determining the properties of the phenomena associated with splashing. The occurrence of splashing is also dependent on the viscosity of the drop and bath fluids. Bouncing and coalescence occur only at lower impact velocities [48]. Entrainment of air bubbles during impact may occur under certain conditions during coalescence and splashing [49,50]. The result of the impact is also related to the miscibility between the drop and bath fluids. Drops impinging on a miscible liquid can entrain air bubbles and eventually coalesce with the target pool [51–54]. Drops impinging on immiscible liquids can form lens-shaped structures or retain a metastable spherical configuration above the free surface of the bath liquid [55,56].

This work aims to examine the deformation and solidification of millimeter size, molten wax drops upon impact at an immiscible liquid interface of higher density that produces non-spherical wax particles. We study a model wax system described previously by Pawar et al. [57]. Dimensionless numbers (i.e., the Weber, Reynolds, Capillary, and Stefan numbers) can be used to classify the behavior during the impact, which compare the relative importance of inertial, viscous, interfacial, and thermal forces. These parameters are defined as follows.

$$We = \frac{\rho_w U_o^2 (2R)}{\sigma_{w/f}} = \frac{\text{Inertial Force}}{\text{Interfacial Force}}, \tag{2.1}$$

$$Ca = \frac{\mu_f U_o}{\sigma_{w/f}} = \frac{\text{Viscous Force}}{\text{Interfacial Force}}, \tag{2.2}$$

$$Re = \frac{\rho_f U_o (2R)}{\mu_f} = \frac{\text{Inertial Force}}{\text{Viscous Force}}, \tag{2.3}$$

$$St = \frac{C_p \Delta T}{L_w} = \frac{\text{Sensible Heat}}{\text{Latent Heat}}. \tag{2.4}$$

Here $\rho_w, R, U_o, \sigma_{w/f}, \mu_f, \rho_f, C_P, \Delta T, L_w$ denote the density and radius of molten wax drop, impact velocity, interfacial tension between molten wax and the bath liquid, viscosity of the bath, density and specific heat of the bath, temperature difference between the bath and molten wax, and latent heat of wax respectively. The subscript f denotes the bath liquid property while w denotes wax property. Cursory phase diagrams using the dimensionless numbers will be produced with the objective of elucidating the relationship between the final morphology of the wax particles and the initial process conditions.

3. Experiments and methods

3.1. Materials

Vaseline, hexadecane, glycerol and sodium dodecyl sulfate (SDS) were purchased from Sigma–Aldrich (St. Louis, MO) and used without further processing. Deionized water was used for preparing the bath fluids. BD plastic syringes of 1 ml volume, 26 and 18 gauge sub-Q Luer Lock needles and syringe pumps from Harvard Apparatus were used for extruding molten wax drops. The wax