

An Extension of Delayed Coalescence at a Liquid-Liquid Boundary to a Liquid-Solid Boundary

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ABSTRACT

We present the results of an experimental study of solid drop submersion in the presence of an initial temperature difference ΔT between a solid drop of ice and a bath of deionized water. We characterize experimentally the dependence of the residence time before submersion as ΔT . Delayed submersion does not appear to manifest as delayed coalescence does with fluids at the same timescale in an array of common temperature ranges.

I. INTRODUCTION

It has been well documented, experimentally as well as with anecdotal instances in everyday life like pouring cool milk into hot coffee, that when a liquid drop falls onto a bath of a miscible liquid, it often takes time for that drop to coalesce. The evidence suggests that this is due to the formation of a thin lubricating air layer between the drop and bath that must drain to a critical thickness before coalescence is initiated by inter-molecular forces [1]. Coalescence has been studied extensively and the influence of relevant physical quantities (fluid density ρ , surface tension σ , viscosity μ , surface charges, etc.) has been characterized [2–4], leading to a classification of different regimes [5].

More recently, an illuminating study from MIT [6] has shown that all these physical quantities can be unified into effects caused by the impact of a temperature gradient on surface tension. This study demonstrates that above a critical temperature difference, coalescence is prevented by Marangoni stresses driving convective flows inside the drops and bath that assist in creating the in-between lubrication pressure. However, previous studies, including the one from MIT, have limited their residence time results (denoted τ_r here on out) to liquid-liquid surfaces and in turn a more limited range of temperatures and states which have precluded edge-cases. Here, we focus on how the curated theoretical model shown in the MIT paper breaks down upon a phase change of the liquid drop to a solid drop even when initial temperature difference ΔT_0 are nearly identical or far greater than those achieved in the MIT paper. In §2, we provide experimental evidence for a breakdown in the model between τ_r and ΔT_0 . In §3, we attempt to find a theoretical temperature difference at which an effect similar to that produced in the MIT paper could occur for a solid drop. We also rationalize our observations through mathematical consideration of the lack of advection flows in the drop that leads to its inability to form convection currents.

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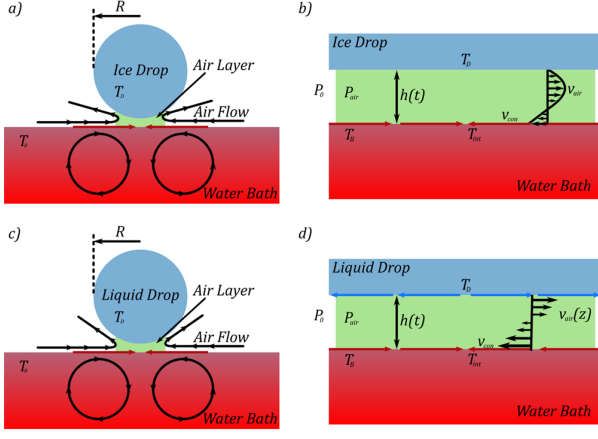


FIG. 1: Schematic of flows surrounding the falling of the solid drop a) and b), comparing it to a schematic of flows on the liquid drop.

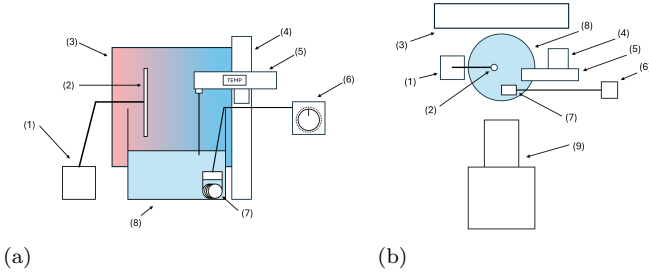


FIG. 2: Apparatus used to carry out investigation; (a) being of the view from the position of the camera; (b) being the bird's-eye view of the experimental setup. With the components labelled as follows (1) stand and arm holding the pipette in position, (2) pipette used to hold the drops, (3) back-light with colour filter, (4) thermometer stand, (5) thermometer, (6) variable power-supply, (7) heating element, (8) beaker with water, (9) high-speed camera.

II. EXPERIMENTATION

Consider a frozen drop of DI saline solution of initial temperature T_d approaching a bath of liquid DI water of varying temperatures T_b . The drop is released at a distance from the surface of the bath such that its initial velocity is negligible and it remains a solid. Due to the lack of convection current within the drop, it is subject to no Marangoni stresses, thus a high ΔT is maintained. The temperature of the water bath was chosen to be 3 distinct temperatures ranging from $T_1 \simeq 25^\circ\text{C}$ (room temperature), $T_2 \simeq 50^\circ\text{C}$, and $T_3 \simeq 80^\circ\text{C}$. These temperatures through experimentation were determined to be sufficiently distinct from one another. Three drops tested for each temperature.

A. Materials and Methods

Fig. 2(a) shows a schematic of our experimental setup. The bath consists of a pool of deionized (DI) water in a standard 500 mL borosilicate glass beaker, with a radius of 5 cm and a height of 12 cm. To control the bath's temperature, we used an immersion heater (Lewis N. Clark), allowing for precise temperature control via a variac. The temperature of the bath (T_b) and that of the drop (T_d) were monitored with a hand-held thermometer equipped with a K-type thermocouple. Drops were dispensed from a pipette centered above the bath, released from a height of one drop radius. The drops, both liquid and solid, were dispensed by releasing the pipette suction, allowing them to fall naturally with gravity to minimize velocity effects.

Drops were created by thoroughly mixing 200 μL of NaCl solution into 500 mL of DI water, then adding 10 drops of red food coloring. NaCl was added to increase the solution's density, as standard ice is less dense than liquid water. Drops were formed by pipetting 20 μL onto a hydrophobic polystyrene petri dish, creating a semi-circular ellipsoid with a diameter of 6 mm. To form the pipetted liquid drops into solids, the petri dish they rested in was placed into a standard food storage freezer and wrapped in tin-foil to prevent melting during transportation. Using geometrical and lubrication approximations, the difference between the experimental drops and a proper droplet shape can be considered negligible.

A high-speed camera, mounted on a 3-axis positioning stage, recorded each experiment at 2000 fps. Fig. 2(b) shows a digital video frame of a drop floating on the bath prior to submersion. The residence time τ_r was measured from drop detachment to submersion. The onset of submersion was determined to be the first moment at which the drop no longer had any part of its geometry above the surface. The error margin for residence time was about 1 ms, making it negligible compared to the variability between successive measurements.

III. THEORETICAL FORMULATION

A. Dynamics of the lubrication layer

Our analysis relies on a series of simplifying assumptions based on the lubrication approximation. We begin with defining h_0 as the height at which the drop is once it is directly above the surface of the bath, some time after the drop has been dispensed. Assuming $h_0 \ll R$ and $\text{Re}(h_0/R) \ll 1$ (where $\text{Re} = \rho_a U h_0 / \mu_a$) we can invoke the lubrication approximation, and we simplify the contact area of the drop where lubrication effects are occurring to be a cylindrical disk with height $h(t)$ and radius $a \simeq R$.

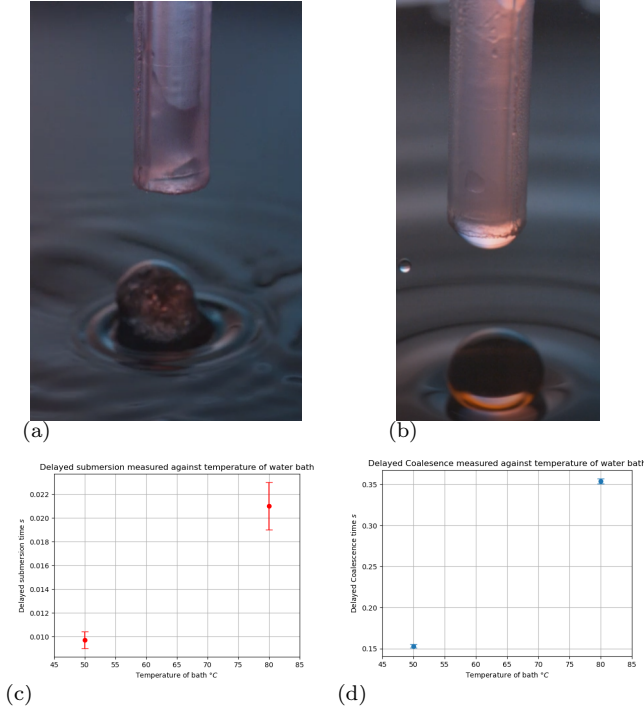


FIG. 3: (a)(b) Solid (a) and liquid (b) drop. (c)(d) Plots showing the delays at measured temperatures of the liquid bath, with (c) showing the submersion delay of the solid drop at varying temperature, and (d) showing the coalescence delay at varying temperatures. A measurement was also taken when the bath was at room temperature but was not included as no noticeable delay occurred.

The Navier-Stokes equation is thus simplified to:

$$0 \simeq -\frac{\partial p}{\partial r} + \mu_a \frac{\partial^2 u}{\partial z^2}, \quad 0 \simeq -\frac{\partial p}{\partial z} \quad (1)$$

where u denote the radial velocity, and p the pressure field inside the contact region.

Since $\mu_w \ll \mu_a$, the no-slip boundary condition applies, and we can assume

$$u(0) = v_{\text{conv}}, \quad u(h(t)) = 0 \quad (2)$$

where $h(t)$ is the width of the lubrication layer at time t . Noticing that $\partial^2 p / (\partial z \partial r) = 0$, direct integration with boundary conditions gives the velocity profile

$$u(z) = \frac{1}{2\mu} \frac{\partial p}{\partial r} (z^2 - h(t)z) + v_{\text{conv}} \left(1 - \frac{z}{h(t)}\right) \quad (3)$$

The volume flux of the ring with radius r is given by

$$Q(r, t) = \int_0^{h(t)} u(r, z, t) 2\pi r dz = \frac{\pi r}{6\mu_a} \frac{\partial p}{\partial r} h^3 + \pi r v_{\text{conv}} h$$

The conservation of mass gives $\pi r^2 \dot{h} = -Q(r, t)$, from which we can get the pressure gradient:

$$\frac{\partial p}{\partial r} = \frac{6\mu_a (r\dot{h} - v_{\text{conv}}h)}{h^3} \quad (4)$$

Assuming the boundary condition $p(a) = p_0$, the atmospheric pressure, we can solve the pressure field

$$p(r) = p_0 + \frac{3\mu_a \dot{h}}{h^3} (r^2 - a^2) + \frac{6\mu_a v_{\text{conv}}}{h^2} (r - a) \quad (5)$$

Assuming a quasistatic process, where the solid drop is completely supported by the air pressure, we have the force balance (write m as the mass of the drop)

$$mg = \int_0^a (p(r) - p_0) 2\pi r dr \quad (6)$$

which gives rise to a differential equation for height:

$$-\frac{3\pi\mu_a a^4 \dot{h}}{2h^3} - \frac{2\pi\mu_a a^3 v_{\text{conv}}}{h^2} = mg \quad (7)$$

Recognizing that this differential equation is a simple force balance between the pressure contained in the lubrication layer and the drop we can make simplifying assumptions to determine the needed temperature difference ΔT to sustain our drop. In order to obtain this we realize that the height of the lubrication layer must not be changing so $\dot{h} = 0$. The only other term which is not a known constant is h which simply must be much less than a for the lubrication approximation to hold. This allows us to approximate h to be on the order of $h_c = 10^{-5}$ m. Based on this, we can first determine a value for v_{conv} the convection current needed to sustain this force balance and then find a ΔT that it can occur. First we solve for v_{conv} :

$$v_{\text{conv}} = \frac{-mgh^2}{2\pi\mu_a a^3} \quad (8)$$

Simplifying, and realizing that v_{conv} is negative because it is the flow directed into the center so it is the absolute value that we are interested in we get:

$$|v_{\text{conv}}| = \frac{2\rho_{\text{ice}}gh^2}{3\mu_a} \simeq 2.6 \times 10^{-2} \text{ m/s} \quad (9)$$

To achieve a ΔT we turn to dimensional analysis to relate the temperature difference needed to form a convection current in the bath large enough to create v_{conv} . To do this, we consider the Rayleigh number, which determines when convection is likely to occur. The Rayleigh number is defined as:

$$\text{Ra} = \frac{g\rho_w\beta\Delta Th_c^3}{\nu_w\alpha_w} \quad (10)$$

where $g = 9.8 \text{ m/s}^2$, $\rho_w = 1.0 \times 10^3 \text{ kg/m}^3$, $\beta = 2.07 \times 10^{-4} \text{ K}^{-1}$ is the thermal expansion coefficients, $\nu_w = 1.0 \text{ cSt}$ is the kinematic viscosity of water. Second, we find a dimensionless quantity which relates the velocity of flow to thermal effects, defined by

$$\Pi_2 = \frac{v_{\text{conv}} h_c}{\alpha_w} \quad (11)$$

We receive $\Pi_2 \simeq 1.86$ after plugging in the data.

Finally, to remedy the orders of magnitude scale difference between the drop and the bath we construct a dimensionless number composed of this recognize that the characteristic length of the bath $L_1 = 10^{-2}$ m and $L_2 = 3 \times 10^{-3}$ m

$$\Pi_3 = \frac{L_1}{L_2} \simeq 3.33 \quad (12)$$

Consider the relation $\text{Ra} \sim \Pi_2 \Pi_3$. Isolating ΔT in our Rayleigh formulation:

$$\Delta T \sim \Pi_2 \Pi_3 \frac{\nu_w \alpha_w}{g \rho_w \beta h_c^3} \simeq 155^\circ \text{C} \quad (13)$$

Which is the estimated required temperature difference to create a stable and effective convection currents inside the bath at the desired v_{conv} .

This makes physical sense considering the temperature difference a small drop would need to impart on a comparatively large body of water to create the convection current necessary to support the drop.

B. Liquid-film mechanism for the absence of thermal delay

In the study [6], an advection-diffusion model was considered for the case of liquid drop, which asserts that before homogenization within the drop, the circulation dominates the process and keep the temperature difference to be a constant. This may not happen to a solid drop. In fact, it's highly probable that the solid drop facilitates the thermal exchange and homogenization in the lubrication region and significantly decreases the delay time.

After further inspection of the submersion process, we find that before approaching the bath, the solid drop is actually surrounded by a thin film of melted water which, without noticeable advection inside the solid drop, has direct heat exchange with the liquid bath. That thin liquid film may quickly destroy the lubrication layer and shorten the delay time (see Fig. 4).

Let's assume the lubrication region Ω to be a cylinder with radius a and height h . The heat diffusion is governed by the following heat equation

$$\frac{\partial T}{\partial t} = \alpha_a \nabla^2 T$$

with some mixed-type boundary conditions.

If we assume an axial-symmetric temperature distribution, the Laplacian is written as

$$\nabla^2 = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) + \frac{\partial^2}{\partial z^2}$$

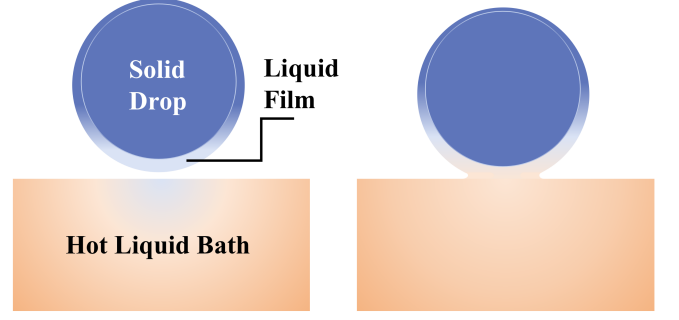


FIG. 4: The liquid film outside the solid drop is quickly heated. Without an effective advection-diffusion mechanism, the film quickly breaks down the lubrication layer and attaches to the liquid bath, sending the remaining solid part into the water.

If we change $r^* = r/a$, $z^* = z/h_c$, $T^* = T/T_b$ (where T_b is the initial temperature of the bath), $t^* = t/t_c$ for some characteristic timescale t_c , we get the non-dimensionalized equation

$$\frac{T_b}{t_c} \frac{\partial T^*}{\partial t^*} = \frac{\alpha_a T_b}{a^2} \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial T^*}{\partial r^*} \right) + \frac{T_b \alpha_a}{h_c^2} \frac{\partial^2 T^*}{\partial z^{*2}}$$

Since $h_c \ll a$, the characteristic timescale should be $t_c = h_c^2/\alpha_a$. The parabolic-type diffusion is characterized by an exponential decay:

$$\frac{T}{T_b} \sim \phi_1(r, z) e^{-\lambda_1(\Omega^*) t/t_c}$$

where $\lambda_1(\Omega^*)$ is the first nonzero eigenvalue of the scaled Laplacian $(\nabla^2)^*$ in the nondimensionalized region Ω^* with the given boundary conditions, and $\phi_1(r, z)$ is the associated eigenmode of the thermal distribution. With our nondimensionalization scheme, these two quantities can all be regarded as of order $\mathcal{O}(1)$. Using the estimate $1 - e^{-x} \sim x$ for x small, we finally get

$$\tau_d \sim \frac{h_c^2}{\alpha_a} \frac{\Delta T_c}{T_b}$$

where ΔT_c is the characteristic scale of temperature change. Choosing $\Delta T_c = 80^\circ \text{C}$ and plugging in the data, we get $\tau_d \simeq 1.22 \times 10^{-6}$ s.

In the absence of convective currents in the bath, the lubrication layer is simply solved by

$$\begin{aligned} h(t) &= \left(\frac{1}{h_0^2} + \frac{4mg}{3\pi\mu_a a^4} t \right)^{-1/2} \\ &= \frac{h_0}{\sqrt{1 + (t/\tau_s)^2}} \end{aligned} \quad (14)$$

where $h_0 \simeq h_c$ is the initial width of the layer, and $\tau_s = 3\pi\mu_a a/(4mgh_0^2) \simeq 0.031$ s is the timescale for the classical lubrication squeezing.

Since $\tau_d \ll \tau_s$, the thermal homogenization in the contact region would dominate at first, resulting in the breakdown of the lubrication layer. After that, the delay of submersion is completely characterized by the classical lubrication squeezing problem solved by (14), and the residence time τ_r is measured by the classical timescale ($\tau_r \sim \tau_s \sim 10^{-2}$ s). This corresponds well with the experimental data.

IV. CONCLUSION

Based on the observed experimental effects and theoretical calculations, we conclude that Marangoni stresses do not appear to have the same significant effect on delaying the submersion of a solid in the temperature regimes tested as it would for a liquid. Section II B shows that the submersion delays in solid samples are minimal as compared to the delays in liquid coalescence. However, a slight delay does appear with increasing temperature, as Fig. 3(c) illustrates. It is important to note however, that other factors might contribute to the delay, and the theoretical basis suggests that these effects would become significant only at much higher temperatures ($\Delta T \simeq 155^\circ\text{C}$) than those tested experimentally.

Some factors that may have lead to the observed small delay in the solid drops is the melting of the drop on the descent to the bath. Due to the high temperature difference and delays in the dropping process, it would be possible for a film of liquid to condense on the solid drops creating a layer in which advection is negligible. Also as observed, this effect would be very small as full convection currents would not be able to form in this regime.

In terms of seeing a lack of delay akin to that of a liquid drop the most significant factor is the lack of advection-diffusion process inside the drop, which maintains a constant temperature difference and stabilizes the convection flow inside the bath. These findings highlight the greater importance of Marangoni stresses within the drop compared to the surface stresses in the liquid bath.

For future investigations into the Marangoni flow mechanism, it would be useful to use a liquid with a higher surface tension than water, as this would make the effects more apparent due to greater resistance. A liquid with a far higher boiling temperature than water

could also be beneficial, allowing for a larger temperature gradient without the phase transition effects that would be experienced by water at the theoretically determined large ΔT . Ideally, the solid drop used would be a chilled bead of equal to the density to the bath liquid which is unable to melt. Other avenues of experimentation, with similar albeit distinct implications would be trying to exploit phase changes like those found in the Leidenfrost effect, where instead of air velocity, vapor pressure is able to create a layer between a liquid and solid boundary creating a somewhat similar effect of a lubrication layer.

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