

Experimental Studies of the Cryogenic Leidenfrost Effect

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Abstract

We study experimentally the Leidenfrost phenomena of liquid droplets levitating above the surface of liquid nitrogen. The drops are supported by the film of nitrogen gas that is evaporated by the heat transferred to the liquid nitrogen from the drops. For small water drops the results are in good agreement with theoretical predictions, though in fitting the theory it was necessary to adjust the Leidenfrost temperature of the drop (the point where it falls through the surface) to a value of 80 K, a reduction from a previous estimate of 126 K. To further test the theory other liquid drops such as ethylene glycol, acetone, and hydrogen peroxide were studied.

Introduction

The film boiling of small drops of liquid on a relatively hot flat surface in air is commonly known as the Leidenfrost Phenomenon or Leidenfrost Effect, after J. G. Leidenfrost who first studied the effect in 1756. The phenomena is responsible for water droplets “dancing” on the surface of an extremely hot frying pan as well as liquid nitrogen (LN) beading up on a relatively hot laboratory or classroom floor [1]. Likewise, as is studied here, the Leidenfrost Effect is responsible for the levitation of small drops of liquid above the relatively cold flat surface of a pool of LN. Consider a droplet of liquid at room temperature dropped onto the surface of a pool of LN. Conduction of heat from the droplet to the LN below causes nitrogen to boil off rapidly. The now gaseous nitrogen exerts an upward viscous force on the droplet and is itself supported by the surface tension force of the LN. The upward forces balance the gravitational force on the droplet and it floats above the surface of the LN below. Since the density of LN of 0.81 g/cc is smaller than that of water or ice, the drop otherwise would have fallen through the surface.

Figure 1 graphically illustrates the phenomena. The droplet sits on a layer of

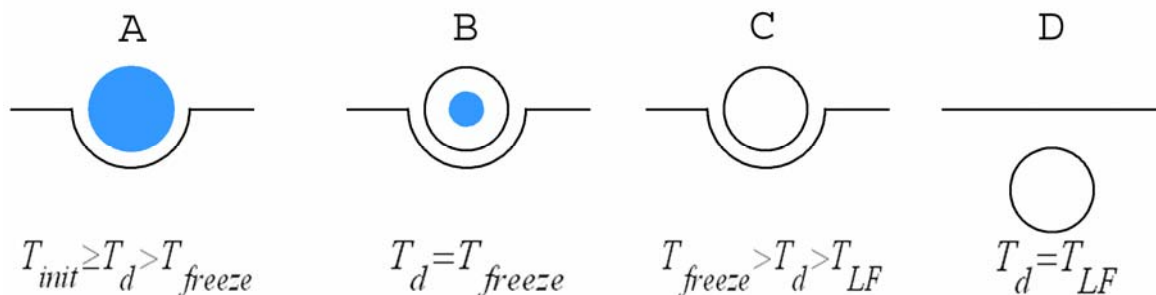


Figure 1. Cartoon illustration of the cryogenic Leidenfrost phenomenon. A shows the droplet levitating as a liquid. In B the latent heat at the freezing temperature is being removed as the drop resides in a state of transition. In C the drop is completely frozen and still levitating as it cools further until reaching T_{LF} in D, at which point levitation stops.

poorly conducting nitrogen vapor above the LN, allowing levitation for a nontrivial time. The drop first cools to its freezing temperature, and then freezes from the outside in until completely solid. The drop cools further until reaching its so called Leidenfrost temperature (T_{LF}), the average temperature of the drop when the outer surface reaches 77K (the temperature of the LN), at which point film boiling ceases and transition-nucleate boiling takes over. The viscous force is then lost and levitation ceases [2].

Theory

A drop floating above the surface of LN has two vertical forces acting on it: gravity and a viscous force. For the drop to levitate these forces must balance, thus the force due to gravity must be equal to the viscous force which includes a contribution from the LN surface tension:

$$W_s = F_v + F_\sigma$$

In this equation,

$$W_s = \frac{4}{3} \pi R^3 \rho_d g$$

$$F_\sigma = 2\pi R\sigma$$

$$F_v = 0.39 \left(\frac{2\eta_v}{\rho_v l} \right) \left(-\frac{\partial m_{LN}}{\partial t} \right)$$

Taking into account these forces as well as boundary conditions and a few assumptions a theoretical estimate of levitation time was calculated in [2]. These assumptions include a perfectly spherical drop with no temperature gradients. Using these, the levitation time is estimated to be

$$t = t_{\text{liquid}} + t_{\text{freeze}} + t_{\text{solid}}$$

where t_{liquid} is the time required to cool the drop to its freezing point, t_{freeze} is the time required to freeze the drop, and t_{solid} is the time needed to cool the solid drop to T_{LF} . According to [2] these times are

$$t_{\text{liquid}} = \frac{m_d (C_p)_d (T_{\text{init}} - T_{\text{freeze}})}{(hA)_d (T_{\text{freeze}} - T_{LN})}$$

$$t_{\text{freeze}} = \frac{m_d L_d}{(hA)_d (T_{\text{freeze}} - T_{LN})}$$

$$t_{\text{solid}} = \frac{R(\rho C_p)_{\text{solid}}}{3h} \ln \left| \frac{T_{\text{melt}} - T_s}{T_{LF} - T_s} \right|$$

where

$$h = \frac{11k_v}{R} + \left[\frac{2\rho_d \rho_v g k_v^3 L_{LN}}{9\eta_v R (T_d - T_{LN})} \left(1 + \frac{C_v (T_d - T_s)}{2L_{LN}} \right) \right]^{\frac{1}{4}}$$

Summing these, the expected levitation time of a liquid droplet on the surface of LN is

$$t = \frac{2R\rho_d}{3h} \left[\frac{(C_p)_d (T_{\text{init}} - T_{\text{freeze}}) + L_d}{T_{\text{freeze}} - T_s} + \frac{\rho_{\text{solid}} (C_p)_{\text{solid}}}{2\rho_d} \ln \left| \frac{T_{\text{freeze}} - T_{LN}}{T_{LF} - T_{LN}} \right| \right]$$

Some experimental data was reported in [2], but for only a single liquid (water) and a very limited radius range. We seek to embark on a more comprehensive study to test the theoretical predictions with experimental data. We investigate a much larger

radius range and vary parameters by using different liquids and water mixtures. Ethylene glycol mixtures are particularly of interest as it is the active ingredient in antifreeze and depresses the freezing point of water to well studied values.

Methods

The experimental setup is not terribly complex, but there are some subtleties of importance. The LN pool is contained in a vacuum-insulated glass dewar, but there is still some boiling due to an influx of heat from room temperature. The dewar is a cylinder of radius 15.25 cm and height 30.5 cm, with a LN boil off rate of $1.85 \times 10^{-7} \text{ m}^3/\text{s}$. The nitrogen boiling is somewhat energetic and tends to disrupt the surface. To create a quiescent nitrogen surface a Pyrex funnel is partially submerged to deflect rising bubbles from the inner partition towards the outer edge, while allowing droplets to float on the liquid surface inside the funnel cone, and then to escape through the funnel tip. A nice surface is important to ensure that unwanted fluctuations do not influence the levitation time of droplets. A smooth surface also eases the determination of the moment when the drop sinks, and keeps the drop from being kicked around and freezing to the container walls. The system works well; with a little positioning we have been able to completely shield the surface from disruption by the bubbles.

We wish to study the dependence of levitation time on the radius of the droplet and thus need a consistent method of creating drops of a particular size. Our solution is to use variable volume pipettes with detachable tips that can be cut to the needed sizes. To create the drops we used three different pipettes of volume ranges 0.5-2.5 μL , 5-50 μL , and 10-250 μL . The pipettes allowed the creation of droplets in the radius range 0.5-3.9 mm with only a small gap between 0.84-1 mm. Finally, the levitation time was measured using one of two methods. Either videos were recorded using a digital camera and analyzed later, or a stopwatch was used. Uncertainties arising from the methods are smaller than fluctuations in the raw data. Most often roughly twenty trials comprise the data for each drop size.

Results

Levitation times

Drops of water, ethylene glycol mixtures, acetone, and 30% hydrogen peroxide were placed onto the surface of LN for comparison with theory developed in [2]. We record the levitation times and compare with the theory. We also briefly look at the motion of the levitating drops. They move with a nearly constant velocity in straight lines over the surface of the LN pool, “bouncing” nearly elastically from the liquid meniscus at the edge of the pool.

Water

We first consider the levitation of water above a pool of LN. Water is one of the easiest liquids to work with, as the data is relatively consistent. Figure 2 shows the time of levitation as a function of drop radius. The blue diamonds with error bars are our experimental data and the red triangles are data from [2]. The dotted line indicates the theoretical prediction from [2], which uses $T_{\text{LF}}=126 \text{ K}$. The solid line shows the same

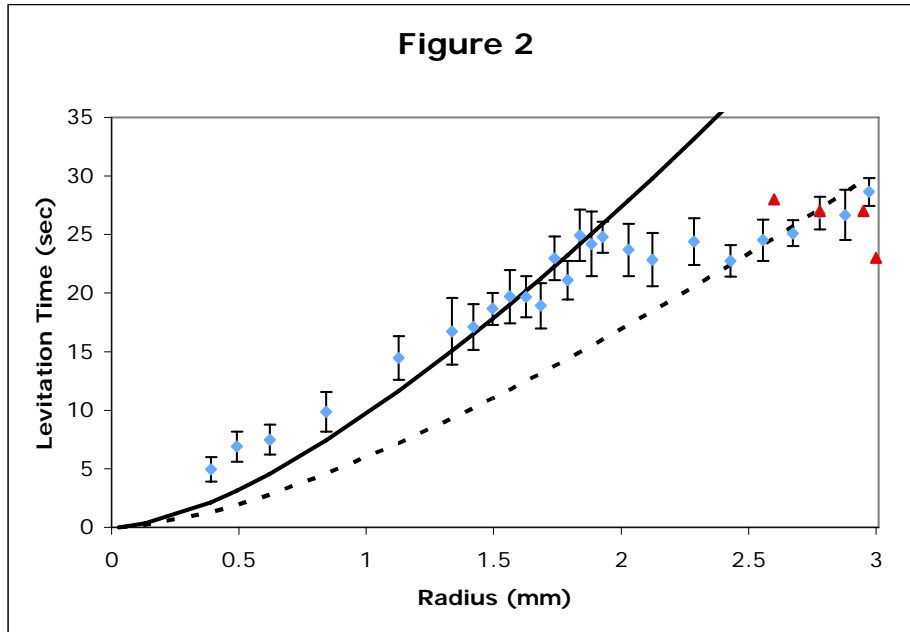


Figure 2. Levitation time of water droplets as a function of drop radius. The dotted line is the theory developed in [2] and the solid line is our version with revised T_{LF} . The blue diamonds are our data and the red triangles are data from [2].

theory but using $T_{LF}=81$ K, and this clearly gives a better fit for drop radii less than 2 mm. Although the $T_{LF}=126$ K estimate from [2] approaches the data at large radius, we believe that the revised T_{LF} is more accurate. This is a large adjustment of T_{LF} from its estimated value and is much closer to the boiling point of liquid nitrogen.

There are several possible reasons why the data at large radii noticeably diverge from the theoretical predictions. Above 2 mm gravitational forces begin to outweigh the effects of surface tension, flattening out the spherical shape of the drop and thus facilitating greater heat transfer due to increased surface area.

Another effect which becomes important is that drops with radius above ≈ 2 mm have a tendency to split apart. The hypothesized mechanism for the splitting is that the outer surface freezes before the innermost water. As the innermost water freezes it expands and the pressure becomes great enough to split the water droplet apart. The split is sometimes very violent and more accurately described as an explosion, with an acoustic “crack” and chunks of ice launching into the air. The splitting of droplets becomes more frequent with increasing drop size and quickly becomes more frequent than non-splitting. When taking data, the drops that split/explode are left out, as they clearly do not relate to the phenomena being investigated. However, a cracking sound could sometimes be heard even for drops that did not split apart and were included in the data set, and this could be responsible for the decrease in levitation time for the larger drops. A small crack in ice could allow the liquid to leak out to the surface causing a quicker cooling of the drop as a whole and thus shorter levitation times.

Ethylene Glycol Mixtures

We now consider the levitation of mixtures of ethylene glycol and water above the surface of LN. We tested mixtures of 5%, 20%, 50% and 70% ethylene glycol by

mass. Ethylene glycol mixtures could not be studied at radii as small as water droplets because of problems with long-lasting drops that will be discussed later. In order to compare with theory, many thermodynamic properties of these solutions must be known. Unfortunately T_{LF} has not even been estimated for substances other than water. Also, we were unable to locate values for $(C_p)_{solid}$, and ρ_{solid} . Thus the values of T_{LF} and the product $(C_p)_{solid} \rho_{solid}$ were estimated based on the values for water as well as the best fit of data (the parameters $(C_p)_{solid}$, and ρ_{solid} only appear as a product). The values of T_{LF} and $(C_p)_{solid} \rho_{solid}$ used for the plots as well as the freezing points of the mixtures are recorded in Table 1. The values for water are also included to use as a reference.

The mixture of 5% ethylene glycol is very reminiscent of water as data and theory agree for smaller radii but the theory again overshoots for larger ones, as shown in Figure 3a. It is apparent that the data, like that of water, levels off at 2 mm before increasing again. Also, like water, it is believed that a radius of 2 mm is the point where the drop's deviation from spherical becomes important. Unlike water, however, splitting may not be an issue. There were no observed cases of 5% ethylene glycol droplets splitting apart so it either does not occur or is less violent.

The data for the solution of 20% ethylene glycol agrees well with theory for radii below 2 mm and deviates otherwise, as shown in Figure 4. As the drop radius is increased beyond 2 mm, the levitation time first decreases and then begins to slightly increase again. This is in agreement with the liquids already considered. Amazingly, however, drops larger than 2.6 mm radius experience no levitation at all. Instead, the drops sink immediately and violently boil off nitrogen while plummeting to the bottom of the container. This means that the force of gravity has exceeded the vapor force acting on the drop.

Figure 5 shows that 50% ethylene glycol behaves in the same manner as 20%. The experimental data follows the theoretical predictions for radii below 1.8 mm. For larger radii levitation times are decreased and levitation ceases altogether for radii above 2.3 mm. Similarly, Figure 6 shows that 70% ethylene glycol matches theory for radii below 1.7 mm, then diverges and ceases levitation for radii above 2.2 mm.

Acetone

We now consider the levitation of acetone above the surface of LN. Acetone is also a relatively difficult liquid to work with as it has a tendency to freeze to the walls of the funnel while levitating above the nitrogen. Freezing to the walls allows convection between acetone and Pyrex, but only heat transfer with nitrogen vapor is of interest and thus all acetone trials in which the droplets stick to the container walls must be scrapped. Acetone's affinity for other surfaces also makes drops hard to form using the pipettes, reducing the size range over which drops can be studied.

Figure 7 shows that the experimental data for acetone is relatively noisy (large error bars) and has an upper limit of theory agreement at a smaller radius than the other substances discussed. The acetone loses spherical shape at smaller radius than water, because of its small surface tension (less than a third that of water), and this may cause the deviation from theory.

The acetone data required a larger Leidenfrost temperature ($T_{LF}=100$ K) to fit the theory than the other substances. Since values are not available in the literature, we used $(C_p)_{ice}\rho_{ice}=1.5 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$. Acetone has an exceptionally low thermal conductivity

| Mass % Ethylene Glycol | T_{LF} (K) | $(C_p)_{ice}\rho_{ice}$ ($J m^{-3} K^{-1}$) | Freezing Point (K) [3] |
|------------------------|--------------|---|------------------------|
| 0 (Pure Water) | 81 | 1.854×10^6 (Known) | 273 |
| 5 | 80 | 1.85×10^6 | 271 |
| 20 | 79.5 | 1.8×10^6 | 266 |
| 50 | 79 | 1.1×10^6 | 239 |
| 70 | 78 | 1.0×10^6 | 222 |

Table 1. Estimates of T_{LF} and $(C_p)_{ice}\rho_{ice}$ used to generate theory curves in Figures 2-7.

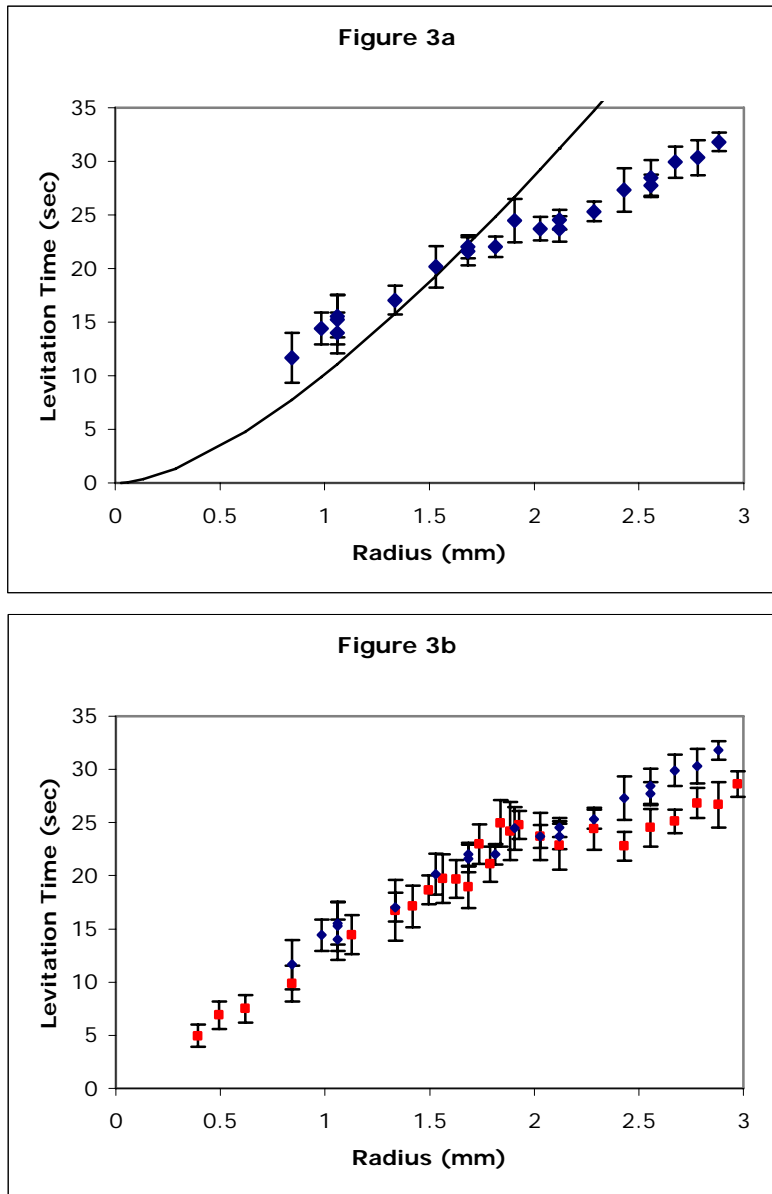


Figure 3. Figure 3a shows the levitation time of 5% ethylene glycol as a function of drop radius with the theoretical prediction. Figure 3b shows the same plot but with the experimental data for water replacing the theoretical prediction. The 5% ethylene glycol data is again represented by blue diamonds and the water data is represented by the red squares.

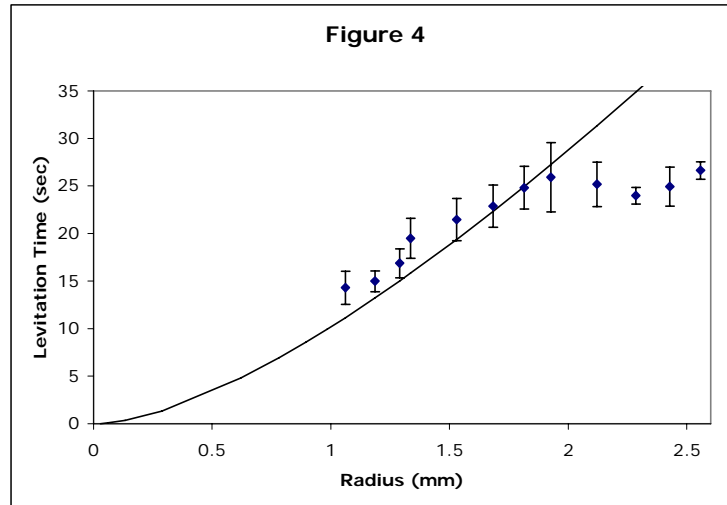


Figure 4. Plot of levitation time versus radius for 20% ethylene glycol solution. The solid curve is a result of the theory developed in [2] with $T_{LF}=79.5\text{K}$ and $(C_p)_{ice\rho_{ice}}=1,800,000\text{ J m}^{-3}\text{ K}^{-1}$.

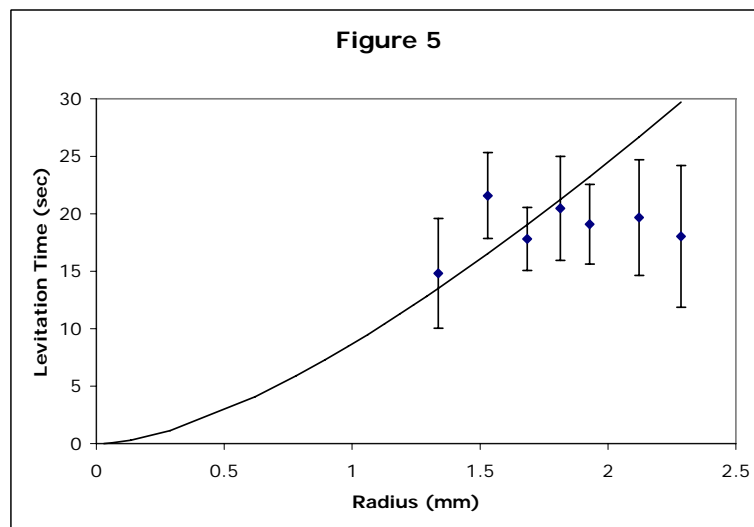


Figure 5. Plot of levitation time versus radius of 50% ethylene glycol. The solid curve is a result of the theory developed in [2] with $T_{LF}=79\text{ K}$ and $(C_p)_{ice\rho_{ice}}=1.1\times 10^6\text{ J m}^{-3}\text{ K}^{-1}$.

(about a quarter that of water) which may explain this behavior. A low thermal conductivity indicates that acetone will have large temperature gradients that result in a large average drop temperature when the surface reaches 77 K.

Hydrogen Peroxide

We now consider the levitation of hydrogen peroxide droplets above the surface of LN. We used a solution of 30% hydrogen peroxide by mass in water. Hydrogen peroxide is also a difficult liquid to work with as it too has a tendency to stick to the walls of the Pyrex funnel. As Figure 8 shows, hydrogen peroxide can only be studied over a small range of radii as it is plagued by absurdly long levitation times at small (<1mm) radii and no levitation at large (>2 mm) radii. The long-lasting problem is discussed in

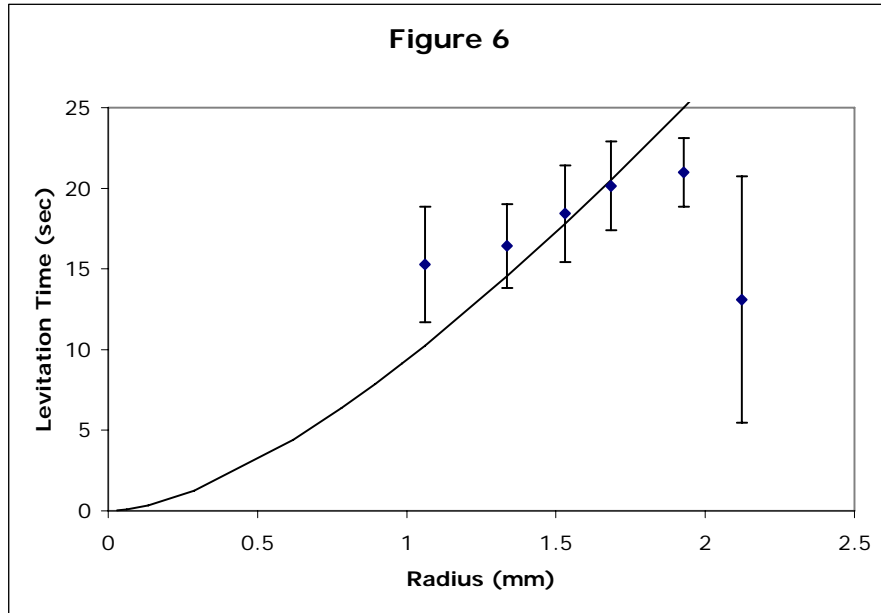


Figure 6. Plot of levitation time versus radius of 70% ethylene glycol. The solid curve is a result of the theory developed in [2] with $T_{LF}=78\text{K}$ and $(C_p)_{ice}\rho_{ice}=1.0\times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$.

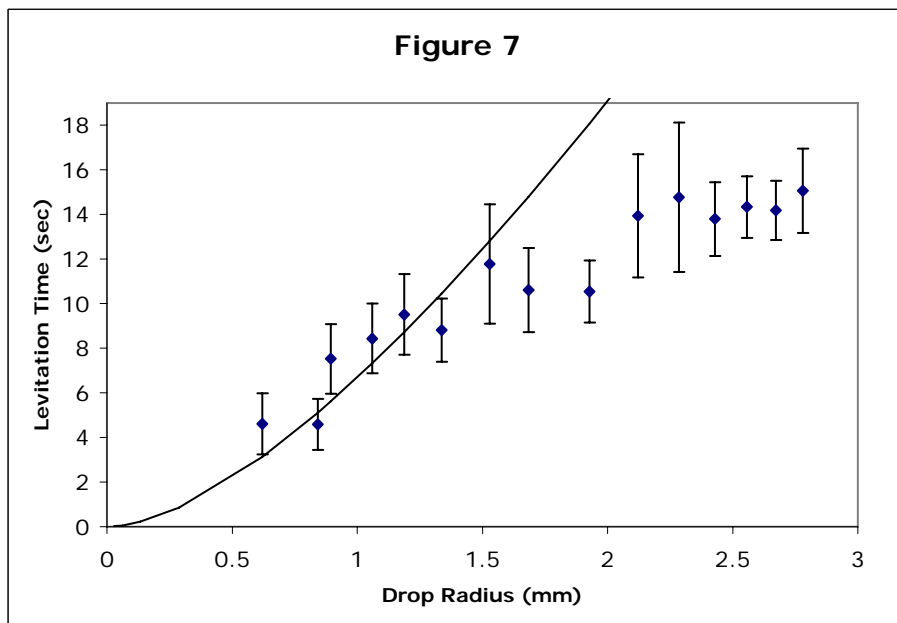


Figure 7. Plot of levitation time versus radius of acetone. The solid curve is a result of the theory developed in [2] with $T_{LF}=100\text{K}$ and $(C_p)_{ice}\rho_{ice}=1.500 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$.

the next section.

The hydrogen peroxide mixture data does not agree well with theoretical predictions. The theory curve in Figure 8 also assumes values for the unknown constants that best fit the data and are in an acceptable range; the curve assumes $T_{LF}=79\text{K}$ and $(C_p)_{ice}\rho_{ice}=2.0 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$. The data is monotonically increasing with radius until 1.9

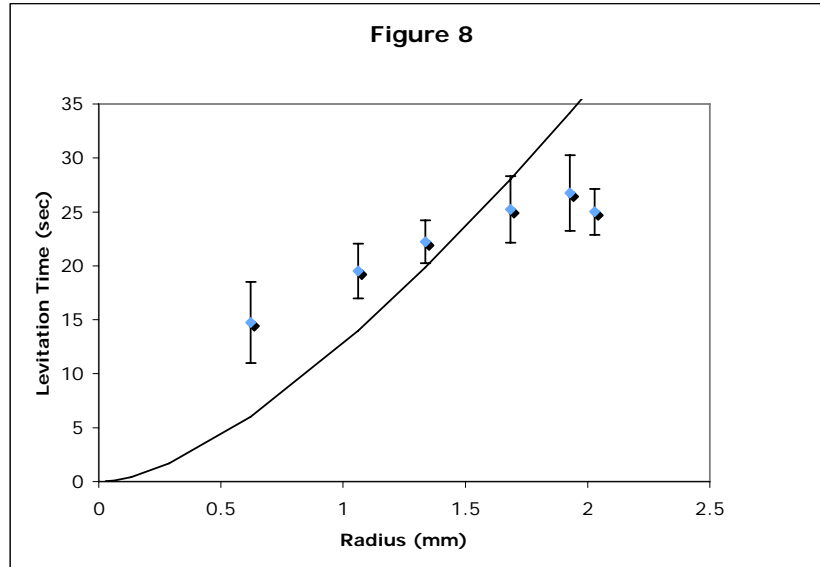


Figure 8. Plot of levitation time versus radius of 30% hydrogen peroxide. The solid curve is a result of the theory developed in [2] with $T_{LF}=79\text{K}$ and $(C_p)_{ice}\rho_{ice}=2.000 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$.

mm, at which point the levitation time decreases and then quickly drops to zero, as seen in some ethylene glycol mixtures.

Long-lived drops

In the small radius regime, drops of the ethylene glycol mixtures as well as hydrogen peroxide behave in a strange manner. Some of the small drops levitate for expected periods of time while others float for as long as half an hour or more. The strange behavior is increasingly more frequent for smaller drops of the liquids that demonstrate the behavior. It has been observed that disruptions of the nitrogen surface will finally cause the long-lasting drops to fall. We believe that the drops may be supported by chemical repulsion between the hydrocarbon surface and the liquid nitrogen, and so this data is not included in the levitation times. Although throwing data out is somewhat subjective, the “bad” data is usually obvious as the droplets float for times much greater than what is expected from Leidenfrost support. Perhaps the same effect influences all small drops, though. This could explain why the theory always slightly undershoots experimental observations.

Velocity

The velocity of droplets floating above the surface of LN is another interesting quantity. Regardless of initial velocity (even if it is zero), the droplets approach a terminal velocity and reach it in about 1-4 seconds. The drops then coast at constant velocity until bouncing off of the container walls. After bouncing they continue at the same speed in a new direction. The drops continue this pattern until nearing the end of their levitation, at which point deceleration and spin-up occur.

It was first believed from qualitative observations that the velocity depended on drop size, but quantitative measurements presented in Figure 9 have shown this not to be

the case. The speed of the drops is about 0.05 m/s regardless of drop size. To determine the velocities, videos were recorded and the position of the drop monitored as a function

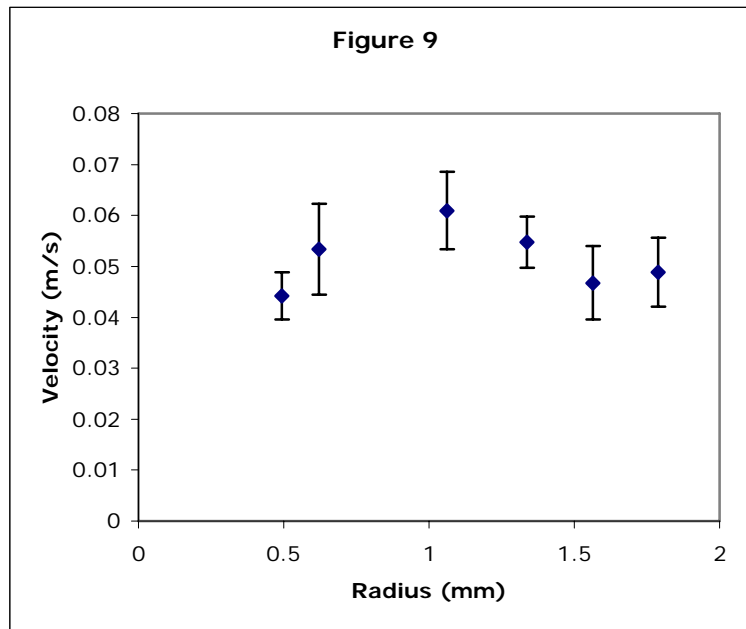


Figure 9. The velocity of water droplets is plotted a function of drop radius. The velocity appears to be independent of drop size.

of time. The speed was then calculated from the displacement of the drop over a 1/6 second time interval. Roughly twenty measurements were done for each drop size shown in Figure 9.

We believe that drop velocity is the result of a fluctuation in the separation distance between itself and the LN surface. Once the droplet is a tiny amount closer to the LN on one side than the other, it proceeds in that direction. More evaporating nitrogen is forced out of the side with the larger opening, driving the droplet. Qualitative evidence does support this theory as a jet of vapor is often observed surging in the direction opposite the drop's motion.

Conclusions

Our study shows that the theoretical predictions developed in [2] are generally in agreement with the data, but a readjustment of the Leidenfrost temperature to a value closer to that of the LN is necessary to fit the data at smaller drop sizes. Large drops do deviate from theory and we speculate that shape effects and cracking may cause this. The phenomena observed is interesting and there is much still to be studied. Unusual effects such as long-lived drops and no levitation are observed to occur and are not completely understood. Also, the dynamics are peculiar, as there appears to be a characteristic velocity across the surface for water droplets. This is not well understood, and the question still remains if other liquids behave the same way.

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