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INSTITUTO DE FÍSICA “LUIS RIVERA TERRAZAS”

“COALESCENCE OF LEIDENFROST DROPS”

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Coalescence of Leidenfrost drops

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Resumen

El efecto Leidenfrost es un fenómeno en el que un líquido, en contacto con una superficie cuya temperatura sea mayor que el punto de ebullición del líquido, produce una capa de vapor aislante que evita que el fluido se evapore rápidamente. Aunque este fenómeno se ha estudiado para una gota líquida sobre una superficie sólida o, incluso, sobre una superficie líquida, se conoce poco sobre el efecto de dos gotas de líquidos diferentes que interactúan entre sí sobre la misma superficie sólida a temperatura Leidenfrost. En este estudio, se caracterizó el comportamiento de once líquidos cuando están a su temperatura Leidenfrost y se encontró que el tiempo de vida de los líquidos en estas condiciones varía linealmente a una razón de $\frac{1}{\kappa}$, donde κ es la conductividad térmica del vapor producido por el líquido. Luego, se investigó la coalescencia de diferentes líquidos en el estado Leidenfrost y se propuso un mecanismo que explica porqué no hay una coalescencia directa entre líquidos distintos cuando interactúan en estas condiciones, a saber, *el triple efecto Leidenfrost*.

Abstract

The Leidenfrost effect is a phenomenon in which a liquid, in contact with a surface warmer than the boiling point of the liquid, produces an insulating vapor layer preventing the fluid from evaporating rapidly. Although well understood for a liquid droplet over a solid or, even, a liquid surface, nothing is known about the effect of two droplets of different liquids interacting with each other over the same solid surface. In this study, we characterize the behavior of eleven different liquids when they are at their Leidenfrost temperature and we find that the life time of liquids under these conditions varies linearly at a rate of $\frac{1}{\kappa}$, where κ is the thermal conductivity of the vapor produced by the liquid. Regarding coalescence of different liquids in the Leidenfrost state, we introduce a mechanism that explains why there is no direct coalescence of different liquids when interacting at these conditions, namely *the triple Leidenfrost effect.*

Contents

Introduction

What happens when you put a drop of water on a hot surface? Intuition tells us: it evaporates, and it will do it faster the hotter the surface is, this is how it happens when there is nucleated evaporation. However, when a certain temperature is exceeded, we can observe a phenomenon called Leidenfrost effect, in which the liquid droplet not necessarily evaporates faster the hotter the surface is, that liquid droplet presenting Leidenfrost effect is called Leidenfrost drop.

This document contains the results and reflections of a series of experiments that we carried out with the aim of studying the coalescence dynamics of two droplets of miscible liquids when they are in Leidenfrost state, to explain what factors determine the direct non-coalescence and their life time. For it, we show the experimental setup and we describe the observation techniques that allowed us to analyze how two Leidenfrost drops of different liquids coalesce. We describe each of the experiments we carry out and give a strong hypothesis, based on our observations, to explain how drops coalesce in the Leidenfrost state.

In the first section, we present some indispensable theoretical foundations for studying the behavior of liquid materials on hot surfaces; we describe how evaporation processes can be and their implications in the Leidenfrost effect, we show some of the most relevant studies about the Leidenfrost effect and we highlight important concepts to take into account about droplet miscibility and coalescence.

In the second section, we present how the experimental setup is configured and, therefore, what the observation techniques were. We present the liquid substances with which all the experiments were carried out and the properties that were fundamental for the analysis of results, such as the latent heat of vaporization, the molecular dipole moment, the boiling point, surface tension, capillary length, etc. Consequently, we relate to each of the experiments carried out, the results obtained accompanied by images taken by a high-speed camera and a discussion of our considerations about what these results might imply. Thus, we report the Leidenfrost temperature of each liquid; the coalescing relationships between liquids, it means, how the liquids interact with each others; the interaction between water and mixtures of water and ethanol; and the size of the droplets when coalescing.

Finally, we present the conclusions that we can draw from the work done, thus arguing our hypothesis. We discuss some of the questions that remain at the end of this study and provide some suggestions for how this topic could continue being researched.

1. Fundamental concepts and previous studies

Boiling and nucleated evaporation

Knowing the vaporization process will allow us to better understand how a Leidenfrost drop can survive over a hot surface without having quick vaporization and later disappear, just as intuition dictates.A Leidenfrost drop levitates on its own vapor, which acts as a thermal insulator, however, the drop does evaporate faster than at room temperature even though the liquid is not boiling.

Vaporization is the main process by which a substance changes from a liquid to a gaseous state. This process can take place through *boiling* or *nucleated evaporation*; it is called boiling when the change of state occurs due to an increase in the temperature inside the liquid; the boiling point is the temperature at which a given liquid boils (also depends on atmospheric pressure), and remains constant during the state change process. For its part, nucleated evaporation occurs when the liquid state slowly changes to a gaseous state, after acquiring enough energy to overcome surface tension. Unlike boiling, evaporation occurs at any temperature, the rate of evaporation being proportional to the increase in temperature.

Vaporization, therefore, can be distinguished between boiling and nucleated evaporation; the difference is that when the transition from liquid to gaseous takes place in the entire mass of the substance, it is a matter of boiling, whereas if the change of state only takes place on the surface of the liquid, the phenomenon known as evaporation. In that sense, a Leidenfrost drop goes through the nucleated evaporation process and not through the boiling process, because just the bottom surface is suffering a quick change of state.

The Leidenfrost effect

As mentioned before, the Leidenfrost effect is a phenomenon in which a liquid, in contact with a surface warmer than the boiling point of the liquid, produces an insulating vapor layer preventing the fluid from evaporating rapidly. It is known that when a drop of a liquid is dropped on a hot solid, at a temperature close to the boiling point of the liquid, the drop evaporates and disappears in a short time. However, if the solid temperature is much higher than the boiling point of the liquid, the drop ceases to have contact with the surface of the solid, instead, levitating on its own vapor. In previous studies it has been observed that a drop of water of one millimeter size deposited on a metal surface at approximately 180 °C can levitate for up to one minute [1]. In addition, thanks to the fact that there is no contact between the liquid and the solid, there is no bubble nucleation, so the drop does not boil, but evaporates slowly. These levitating drops have been called "Leidenfrost drops", due to the name of Johann Gottlob Leidenfrost, who first reported the phenomenon in 1756 [2]. A simple scheme of the phenomenon can be seen in Fig. 1.1.

According to the last, a common technique used for determining the Leidenfrost temperature requires measuring evaporation times of liquid droplets of a given initial volume over a range of surface temperatures to produce a droplet evaporation curve as shown in Fig. 1.2. The curve displays droplet evaporation lifetime versus surface temperature and exhibits four distinct heat transfer regimes; In the single-phase regime, characterized by long evaporation times, heat from the surface is conducted through the liquid film and is dissipated by evaporation at the liquid-gas interface. In the nucleate boiling regime, vapor bubble production and the corresponding heat flux increase dramatically, thus decreasing the droplet lifetime. The upper limit of the nucleate boiling regime, known as critical heat flux, corresponds to maximum heat flux and minimum drop lifetime. In the transition regime, a non continuous, insulation vapor layer is developed below portions of the droplet, leading to reduced evaporation rates and increased drop lifetime. At the upper end of the transition boiling regime, referred to as the Leidenfrost point, the vapor layer grows substantially to prevent any significant contact between the drop and surface and the droplet evaporation time reaches a maximum. At surface temperatures above the Leidenfrost point, the droplet remains separated from the surface by a thin vapor layer through which heat is conducted [3].

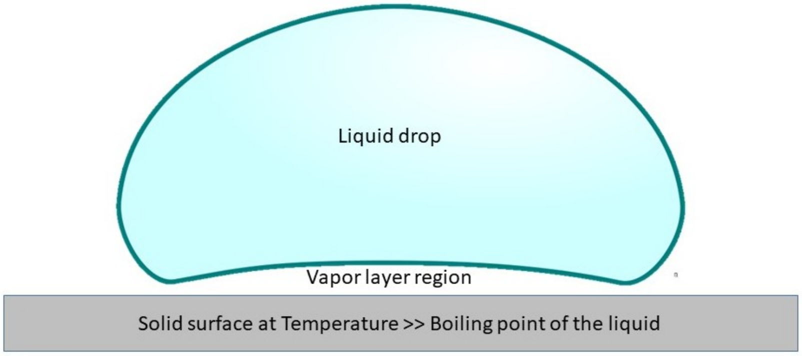


Figure 1.1: The water droplet does not touch the hot surface, instead, there is a region of vapor between the liquid and the solid that doubles as an insulating layer, which allows the slow evaporation of water.

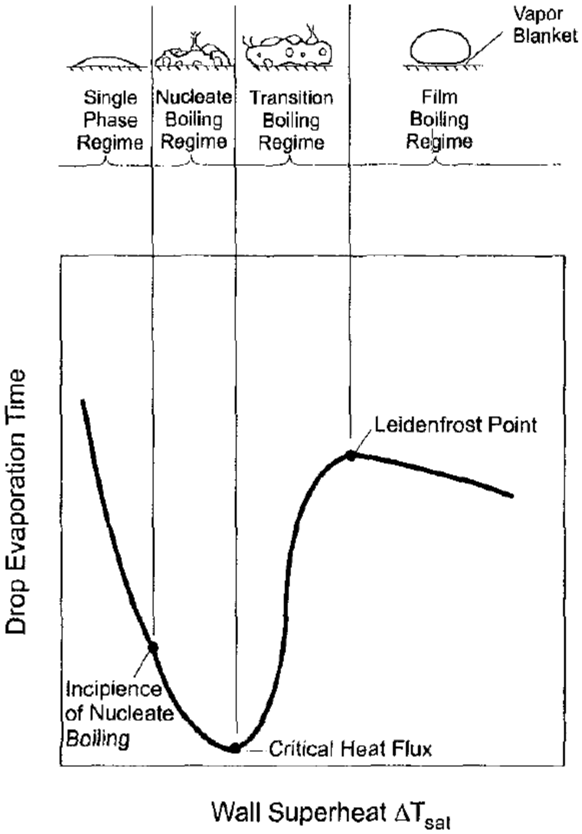


Figure 1.2: Droplet evaporation lifetime versus temperature of a solid surface.The curve goes through four distinct heat transfer regimes and in each one the droplet lifetime varies depending on the phenomenon that occurs. [3]

The first quantitative study of this phenomenon disclosed the shape of the Leidenfrost water droplets, the characteristics of the vapor layer on which they float and how they relate to the size of the drop [4]. It was found that the drop of water, when floating on its own steam, does not moisten the hot solid on which it was deposited. Concerning the characteristics of the vapor layer, it was found that it becomes unstable for large drops. In addition, it was stated that the life time of the drop depends on its size compared to its capillary length, λ_c. This constant value is characteristic of each liquid and indicates the competition of the surface tension force and the gravitational force, as it is shown in eq. 1.1, where σ is the surface tension of the liquid, ρ is its density and g the gravitational acceleration. Fig. 1.3 shows how the shape of the drop changes depending on its volume due to the capillary length.

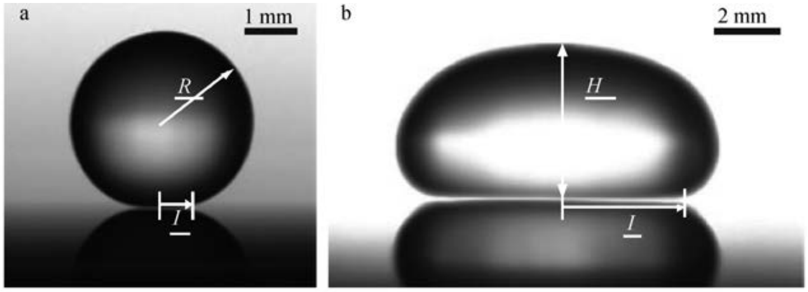


Figure 1.3: A water droplet is shown, in (a), as a quasi-sphere and, in (b) as a puddle because its size is larger than its capillary length. [5]

$$\lambda_c = \sqrt{\frac{\sigma}{\rho g}}. \tag{1.1}$$

In this sense, the ability of the water drop to remain spherical is due to its capillary length, which depends on the surface tension of the liquid. This concept is the same one that prevents, when pouring a liquid into a glass, before it overflows, the liquid forms a dome above the edge of the glass. This kind of dome is formed thanks to the cohesive properties of the liquid's molecules, that is, its tendency to stick together. Cohesion refers to the attraction that molecules have for others of the same type, for example, water molecules have strong cohesive forces thanks to their ability to form hydrogen bonds between them [6].

Cohesive forces are responsible for surface tension, this phenomenon is the tendency of a liquid's surface to resist rupture when subjected to tension or stress. For example, the water molecules at the surface, at the interface between water and air, form hydrogen bonds with their neighboring molecules, just like the molecules found deeper in the liquid. However, since they are exposed to the air on one side, they have fewer water molecules to bond with and therefore, the bonds formed between them will be stronger. The surface tension causes the water to form small spherical drops and allows it to support small objects, such as a piece of paper or a needle [7]. It is important to note that the concept of surface tension could imply an extensive definition, given that it is one of the most studied properties of fluids. Nevertheless, for what concerns us in this study, it is a priority to highlight what factors affect the surface tension of a liquid and what are the bases of the concept.

The previous concepts and other aspects were included in equation 1.2, which was found in order to clarify which parameters determine the size of a Leidenfrost drop. It is important to highlight that the relevance of this research lies in the fact that it addressed basic questions about Leidenfrost drops, which allowed important statements about the behavior of fluids on hot surfaces. According to such study [4], the radius of the water drop as a function of time is given by:

$$R(t) = R_0 \left(1 - \frac{t}{\tau}\right)^2 . \tag{1.2}$$

where,

$$\tau = 2 \left(\frac{4\rho a L}{K\Delta T}\right)^{\frac{3}{4}} \left(\frac{3\eta}{\rho_v g}\right)^{\frac{1}{4}} R_0^{\frac{1}{2}} . \tag{1.3}$$

Where R_0 the radius of the drop at t = 0 and τ is the life time of the drop. In equation 1.3, ρ is the density of the used liquid, a the capillary length of the drop, L the latent heat of evaporation, K the thermal conductivity of the vapor of the used liquid, ΔT is the difference between the temperature of the hot surface and the boiling temperature of the liquid, η is the viscosity of the gas, ρ_v is the density of the vapor and g is the gravitational acceleration.

The shape of the vapor layer that is generated between the drop of water and the hot surface of a solid was determined using interference from a laser light and with the help of high-speed images, the work team managed to measure the radius, curvature and height of the vapor film. Thus, it was determined that the geometry of the vapor layer depends mainly on the size of the drop and not on the temperature of the substrate. In addition, it was found that there are significant fluctuations in the central steam region and around the lateral edges of the drop, through which the steam escapes [8]. These properties are of vital importance for one of the most striking phenomena that can be generated with Leidenfrost drops, namely droplet propulsion.

A droplet deposited on the hot ratchet, in addition to levitating, is self-propelled in a certain direction and at a defined speed. This is caused by the fact that the flow of the steam that escapes from below the drop is rectified because of the presence of asymmetric textures, thus, the liquid in levitation receives a directed thrust, which is determined by the direction of the ratchet teeth [9], as it can seen in Fig. 1.4. One conclusion to highlight is that the friction between the drop and the surface on which it is propelled is minimal, up to one hundred times smaller than the driving force. Also, the main idea that is important to this thesis work is how the steam released from the drop can move the droplet despite its weight.

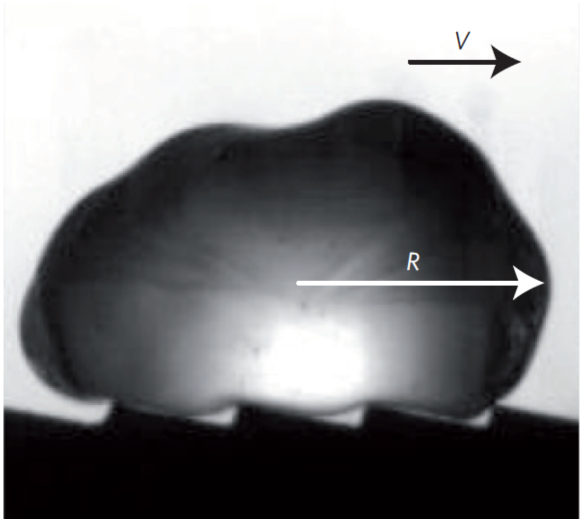


Figure 1.4: A drop deposited on a hot ratchet self-propels in the direction indicated by the arrow. The equatorial radius of the droplet is 3 mm. The ratchet is made of brass and brought to a temperature 350 °C, greater than 200 °C, the Leidenfrost temperature for ethanol which was found in this research work. The teeth have a length of 1.5mm and a height of 300 μm. The drop moves at a constant velocity of 14 cm/s, after a short period of acceleration. [9]

The steam-based propulsion system is not limited to liquid droplets. By dropping hydro-gel spheres onto hot surfaces, it was found that, rather than hovering, they energetically bounce several times for long periods. It was shown that these otherwise-hidden agitations constitute work cycles that harvest mechanical energy from the vapour and sustain the bouncing [10], as it can be seen Fig. 1.5. Although it is true that these experiments reveal that the mechanism behind this behaviour is the coupling between vapour release and elastic deformations, which leads to microscopic work cycles at the sphere/substrate interface that inject mechanical energy, it also gives rise to thinking if a liquid drop can present a similar process of bouncing depending on the surface with which the liquid may enter the Leidenfrost state, or in function of the properties of the liquid.

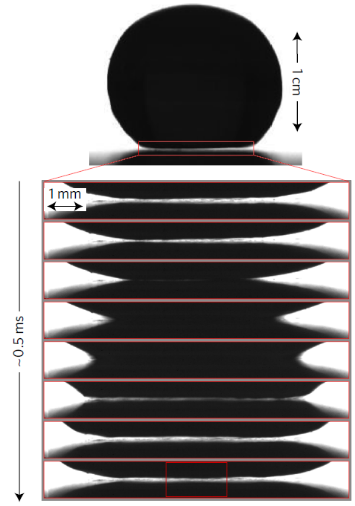


Figure 1.5: High-speed video images of a single impact of a hydro-gel sphere after falling from 3.5 cm high, at high magnification and a frame rate of 15,625 fps (frames per second) reveal that a minute gap below the sphere rapidly opens and closes many times during each impact. [10]

The behavior of Leidenfrost drops on an irregular surface of a solid is different from that of the drop on a solid and flat surface.This phenomenon was investigated by depositing water in hot conical bowls, as it can be seen in Figure 1.6. It is found that, on these conical surfaces, there is the Leidenfrost effect even for large quantities of a liquid, quantity which depends on the inclination angle of the surface and on the liquid itself. In addition, it is concluded that the curvature of the surface does not change the total evaporation time, with the advantage that the confinement allows controlled levitation of large volumes of liquid for a considerable time. These statements give rise to think about possible low friction applications using confined structures [12].

Figure 1.6: 20 ml of water preserving the Leidenfrost state on a conical surface. Even when the surface curvature does not change the total evaporation time considerably, the confinement allows the controlled levitation of large volumes of liquid for a long time [12]

In the same way that Leidenfrost drops on flat solids and other morphologies have been studied, there are also investigations about the implications of generating a Leidenfrost drop on the surface of a liquid. For example, it was studied, experimentally and theoretically, the Leidenfrost drops deposited on a pool of hot liquid, emphasizing the importance of the substrate nature in the Leidenfrost effect. It was experimentally demonstrated that, on a water body, a state of Leidenfrost is possible as soon as the surface-acting liquid is warmer than the boiling point of the drop. This is due to the fact that a liquid substrate has no roughness unlike solids. Experiments have also revealed that the final stage of the life of the drop is different on a liquid and on a solid substrate; instead of being removed from the surface, as it is usually the case with solids surfaces, the drop comes into contact with the liquid surface [13].

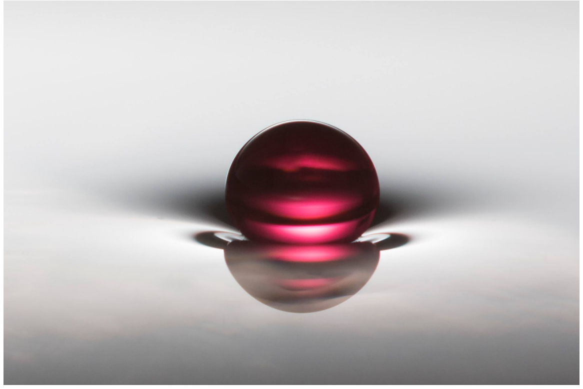


Figure 1.7: An ethanol drop (which was dyed red) levitates over a pool of silicone oil V20, because of the Leidenfrost effect between the two droplets. The ethanol drop radius is 1.2 mm and the pool is at 79 °C while the boiling point of ethanol is 78 °C. [13]

In that sense, it is a fact that the Leidenfrost temperature of a liquid depends only on the boiling point of the liquid and the roughness of the hot surface which has contact with the liquid. This implies that the Leidenfrost temperature tends to the boiling point of the liquid as the surface roughness tends to zero.

The previous one is an interaction between liquids where one of them is at higher temperature than the other one and its molecular dipole moments are different. This invites us to ask ourselves how liquids interact when varying characteristics of what miscibility depends on.

Droplet Coalescence

The aforementioned research is suggestive in the sense that it opens a series of questions around how fluids interact in relation to the Leidenfrost effect, for example, what happens if we put two drops in Leidenfrost state? What if those drops are from the same liquid, from different miscible liquids or different non-miscible liquids?. We know that two drops of miscible liquids on contact at room temperature coalesce, but we wanted to observe what happens when two droplets interact in the Leidenfrost state. Thus, it is consistent with consulting about the basic relationships that may exist between some of the best known liquids and, therefore, most used to experiment around their behavior.

The term *miscibility* refers, in chemistry, to the property that allows different liquids to mix in any proportion, forming a solution. Water and ethanol, for example, are miscible in any proportion, in addition, they are easily accessible and that is why they are two of the most used liquids to study interaction phenomena between liquids. On the other hand, liquids are classified as immiscible if they are not capable of forming a homogeneous phase. For example, water and oil are immiscible with each other since they both have different polarities, water is, obviously, a hydrophilic compound, which has an affinity for water, while oil is a hydrophobic compound, which does not have an affinity for water.

Several factors that determine the possibility of drops of different liquids coming together as a manifestation of the coalescence phenomenon. In principle, the miscibility of two liquids implies that one dissolves in another to obtain a homogeneous mixture, thus, for two liquids to be miscible, it is necessary that one of them act as a solute and the other as a solvent; one compound only dissolves in another if the attractive forces between the solute and solvent particles change to form new forces that bind them together. Furthermore, the solubility of a molecular compound depends on the polarity of its molecules, since this determines the types of inter-molecular force of attraction. A polar solvent is a compound with a charge separation at chemical bonds, they have an affinity for water and dissolve in it easily. Ethanol, for example, is a polar solvent, which is soluble in water. Generally speaking, a polar solute dissolves in a polar solvent, in the same way that a non-polar solute dissolves in a non-polar solvent [14].

It has been studied how small drops of ethanol and water coalesce and the reasons why they do so in the first moment they are found [15], this through an ingenious experimental setup that forces the drops to collide with each other. In this work, factors such as the surface tension of liquids, the amount of substance used and some chemical properties that can affect miscibility are considered.

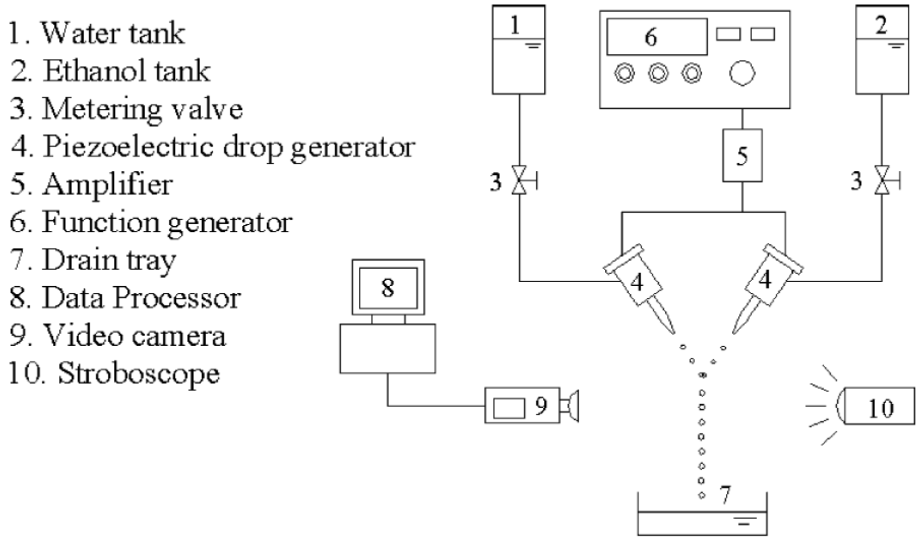


Figure 1.8: Experimental setup to observe the coalescence between water and ethanol droplets. Two piezoelectric drop generators were used to generate two droplets streams of equal size in the range 400–600 μm. Water and ethanol were provided through separate pressurized containers. Only one function generator was used to drive these two-drop generators and the two streams of drops collided pair by pair in front of a stroboscope. The frequency of the stroboscope was synchronized with the drop-generating frequency so that the collision outcome may be recorded by the video camera in slow motion. The measurements were then made on the recorded frames of the video. [15]

The results showed that because of the large difference in surface tension for water and ethanol, an action of Unbalanced Surface Force (which they named USF) is observed on the water drop. In that sense, they concluded that due to the USF action, in high-impact parameter collisions, the water drop is elongated and can split into two drops; for collisions of medium impact parameter, a liquid finger due to USF action can be observed and it can separate from the combined mass; for head-on collisions, coalescence or reflex separation occurs and at least one USF satellite is produced; the mixing rate for unlike-drop collisions is higher than that for like-drop collisions.

Four coalescence systems have been reviewed, namely, the coalescence of two droplets freely suspended in a fluid; the coalescence of two sessile droplets on a solid substrate; the coalescence of a falling droplet and a sessile droplet on a solid substrate; and liquid marble coalescence.

Now, when two droplets interact in Leidenfrost state, they behave the same way as at room temperature? Taking into account the factors described throughout this section, the interaction of liquids in the Leidenfrost state is considered as a branch of study that has left several questions uncovered, among them, which gives rise to the object of study of this research work, namely, to study how the coalescence of two drops of different liquids that are in the Leidenfrost state occurs.

2. Individual characterization of liquids in Leidenfrost state

The seminal observations

In 2019, while different phenomena related to with the Leidenfrost effect were being studied in the GrainsLab laboratory, linked to IF-BUAP, it was observed that if a drop of ethanol and another of water, both in the Leidenfrost state, collide with each other, the drops do not coalesce as easily as they would do it at room temperature. Instead, the drops bounce off each other for a certain time interval, until eventually, they come together in a homogeneous mixture.

The phenomenon that has just been described arouses the curiosity of those who hope to work in the line on research of the behavior of liquids. Since the discovery of the Leidenfrost effect, it has been developed observation techniques increasingly precise, which have allowed obtaining valuable information on the natural behavior of liquids on hot surfaces. In this way, solving to some extent the questions raised here is essential for the field of study.

In this sense, this section describes what is the experimental setup, how it was used for each experiment, what were the experiments carried out and the results obtained in order to explain how Leidenfrost droplets from different liquids coalesce. Although we have deepened in observe the interaction between water and ethanol, it was necessary to observe the behavior of eleven different liquids and their interaction with each other. The liquids studied here were; Water, Ethanol, Methanol, Dimethylformamide, Isopropyl alcohol, Ethyleneglycol, Acetone, Acetonitrile, Hexane, Chloroform and Toluene. All of these liquids were chosen by their different physical and chemical properties as boiling point, surface tension, polarity, etc, which can be observed in Table 2.1.

Liquid	**Boiling point** [°C]	**Surface tension at boiling point** [N/m]	**Liquid density at boiling point** [Kg/m^3]	**Liquid dynamic viscocity at boiling point** [mPa*s]	**Capillary length at boiling point** [m]	**Latent heat of vaporization** [KJ/Kg]	**Molecular dipole moment** [D]
Water	100	0.0588	939.8	0.284	0.00253	2256	1.85
Ethanol	78.37	0.0174	747.8	0.418	0.00154	846	1.66
Methanol	64.7	0.0188	725.3	0.296	0.00163	1100	1.7
Dimetyl formamide	153	0.0364	926	0.92	0.00200	578	3.86
Isopropanol	82.5	0.0159	724.1	0.523	0.00150	779	1.55
Ethylene glycol	197	0.046	1091	0.74	0.00207	800	2.27
Acetone	56	0.0189	711.1	0.242	0.00165	518	2.69
Acetonitrile	82	0.0219	713.9	0.224	0.00177	729	3.92
Hexane	68	0.027	633	0.201	0.00209	365	0.09
Chloroform	61	0.0225	1411.3	0.398	0.00128	247	1.15
Toluene	110	0.028	842	0.419	0.00184	351	0.36

Table 2.1: Liquid properties that are of primary relevance to this study. Most of the data are reported experimentally, however, rare data, such as certain properties that vary as a function of temperature and of the liquids themselves, were found using simulations that give an approximate result of the property value. [17], [18]

Experimental setup

In order to analyze the behaviour of the water and ethanol droplets interacting with each other over a solid surface, we used a system with a metal plate about 4cm wide, which has an inclination of 2° to the center for keeping the droplets over the plate, so the drops always tend to go to the center, forcing each other to collide. The plate is gradually warmed. It is important to highlight that several measurements were made at different times, in the first instance, we measured the lifetime τ of a droplet of each liquid for different values of temperature of the plate. Once these values are known, we put a droplet of water over the plate and instantly we put an ethanol droplet, so that we can observe that the ethanol drop begins to bounce off the drop of water, we timed how long it takes for the drop of ethanol to disappear in favor of the drop of water. Besides, we used a high speed camera and filmed from above how the size of drops changes (Fig. 2.1), so this experimental setup also allows us to observe carefully the interaction between droplets and to measure how big the droplets are at the moment of coalescence.

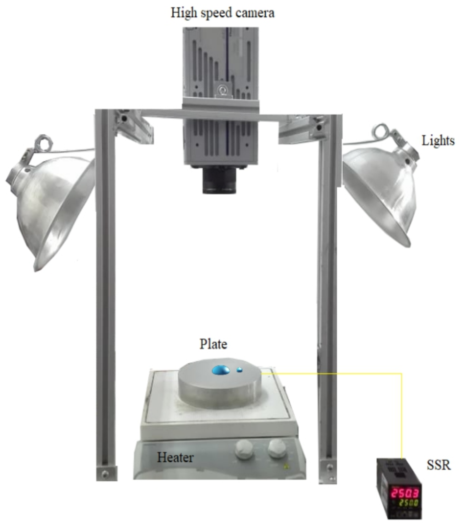


Figure 2.1: Experimental setup. The bigger droplet represents water, the other one represents ethanol. At the bottom of the system the metal plate is located; at the top of it a high speed camera is settled; and on the right of the set up is the temperature controller, which allows to set the temperature of the plate.

Finding the Leidenfrost temperature

First, the life times of all liquids at different temperatures were measured in order to find their Leidenfrost temperature, for this the same surface and the same amount of liquid (1 ml) were used in all cases. Independently, a drop of the liquid to be studied was placed on the aluminum plate and the temperature of the plate was gradually increased in such a way that the life time of the drop was taken every 5 °C. Through this process, the Leidenfrost temperature of each liquid was found under the conditions of the laboratory. As an example, in Fig. 2.2 we show the process of how the mean lifetime of 1 ml drops of water, ethanol and methanol varies depending on the temperature of the surface on which they are deposited. The lifetime of the droplets approaches to 0 seconds (s) as the temperature of the aluminum plate approaches to the boiling point of the liquid, but at temperatures considerably higher than the boiling point, the lifetime of the droplets increases and we can found a certain temperature at which the lifetime of the droplet is maximum, that temperature is called Leidenfrost temperature of the liquid.

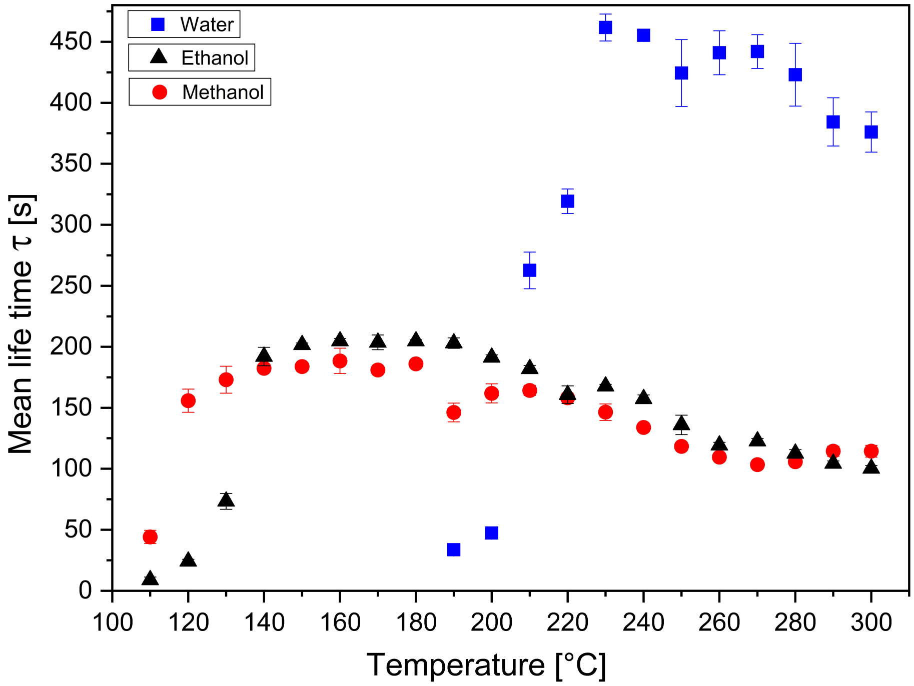


Figure 2.2: Mean lifetime τ of water, ethanol and methanol droplets as a function of the temperature of the surface on which they are deposited. The temperature at which the lifetime of each droplet is maximum is called Leidenfrost temperature.

Following the same process, we measured the mean lifetime of all liquids and found their Leidenfrost temperature. The data obtained for all liquids can be seen in Fig. 2.3.

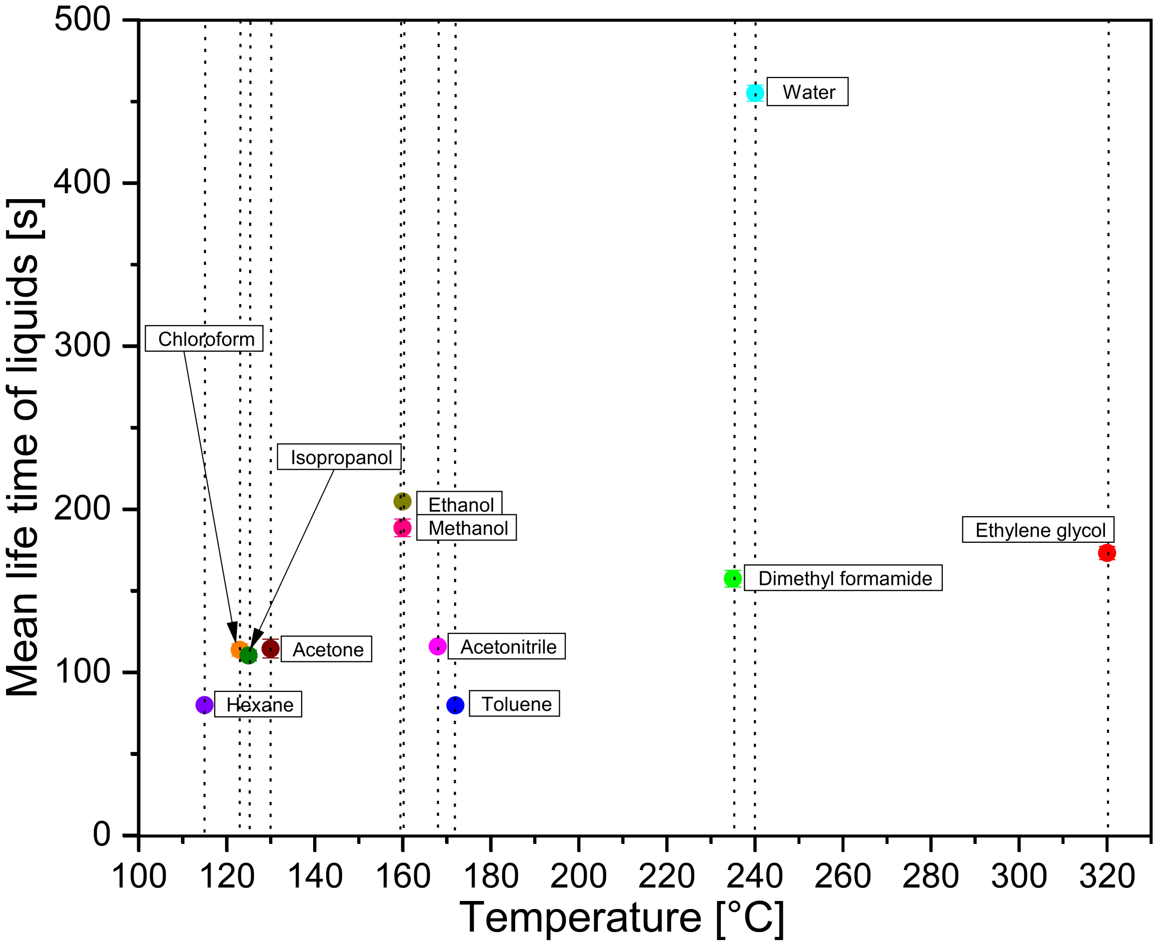


Figure 2.3: Leidenfrost temperatures L_T for different liquids, each color point represents the Leidenfrost temperature of each liquid in the horizontal edge and its lifetime in the vertical edge. From left to right the liquids are Hexane, Chloroform, Isoporpanol, Acetone, Methanol, Ethanol, Acetonitrile, Toluene, Dimethylformamide, Water, Ethylene glycol.

On Figure 2.3 it is important to highlight that the Leidenfrost temperatures found for each liquid are valid in the laboratory conditions in which we carry out all the experiments. As explained in the previous chapter, the Leidenfrost temperature depends only on the boiling point of the liquid and on the roughness of the surface on which it is deposited. Thus, the Leidenfrost temperatures that can be read in this Figure are valid only on the aluminum plate that we use for all experiments and in the city where our laboratory is located, that is in Puebla, Mexico, at 2135 metres above mean sea level, which implies that the boiling points of the liquids used are slightly lower than those reported. [11]

Now, the lifetime of water is significantly higher than that of the other liquids, also, as can be seen in Table 2.1, the highest latent heat of vaporization is that of water too. Therefore, we thought there could be a relationship between latent heat of vaporization, which is a constant of each liquid, and the lifetime of a droplet of the liquid at its Leidenfrost temperature. So that, in Fig. 2.4 can be observed how these two values dependents on each liquid can be related.

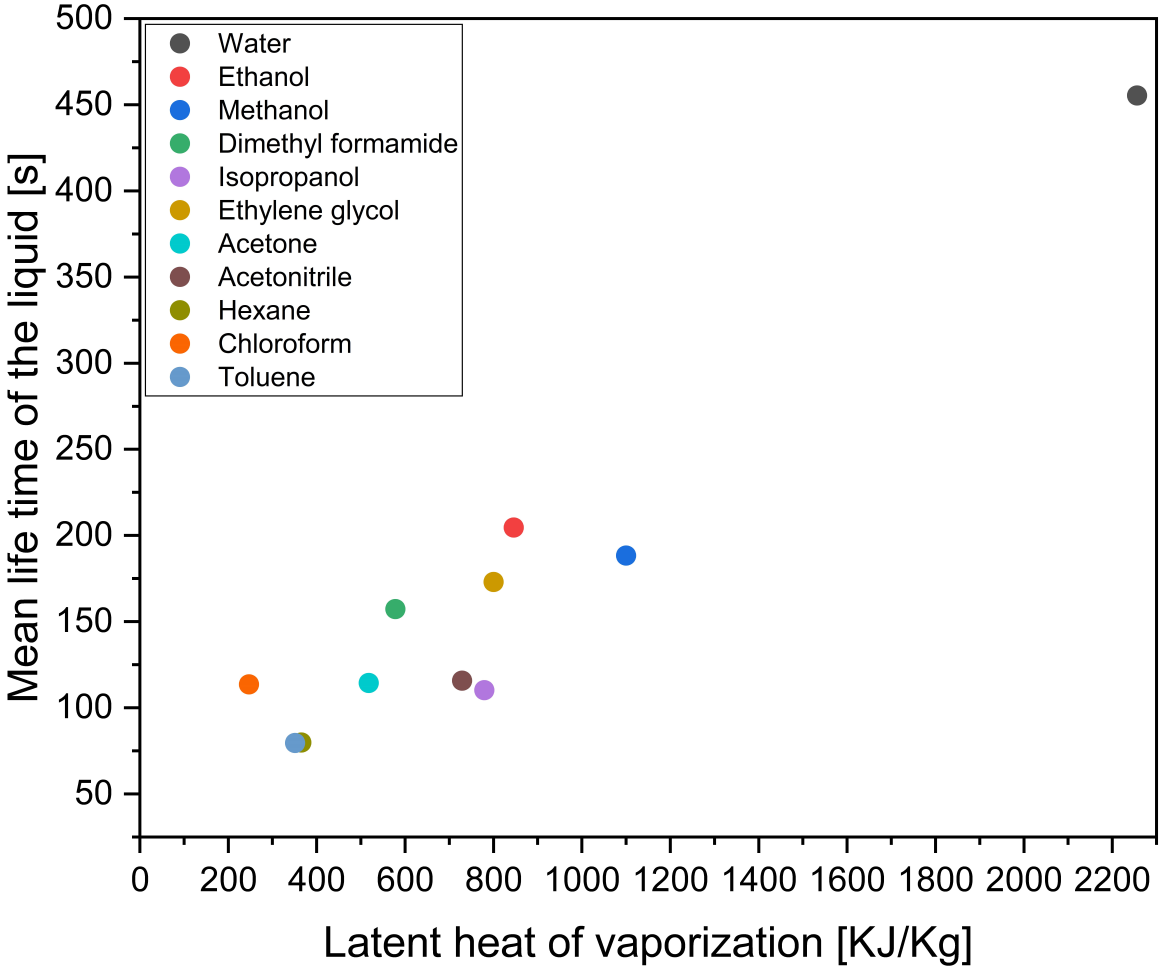


Figure 2.4: Graph showing how the life time of 1ml of liquid at its Leidenfrost temperature is related to its latent heat of vaporization.

As the figure shows, there does exist a relationship that seems to be linear between the life time of liquids at their Leidenfrost temperature and the latent heat of vaporization of each of them. If we find the best linear fit as in Fig. 2.5, we can link these results to the analyzes made at the time by Biance-Clanet-Quéré, so that we can remember on of their equations, eq. 2.1, which provides the lifetime of a Leidenfrost drop ($R_0 < a$), which is found to be slightly more sensitive to temperature than a puddle, and much more dependent on the size [4], where, remember, ρ is the density of the liquid,L is its latent heat of vaporization, ΔT is the temperature difference between the Leidenfrost temperature and the boiling point, *R_0* is the initial radius of the spherical droplet and κ is the thermal conductivity of the vapor layer produced by the liquid

$$\tau \sim \frac{\rho L}{\kappa \Delta T} R_0^2. \tag{2.1}$$

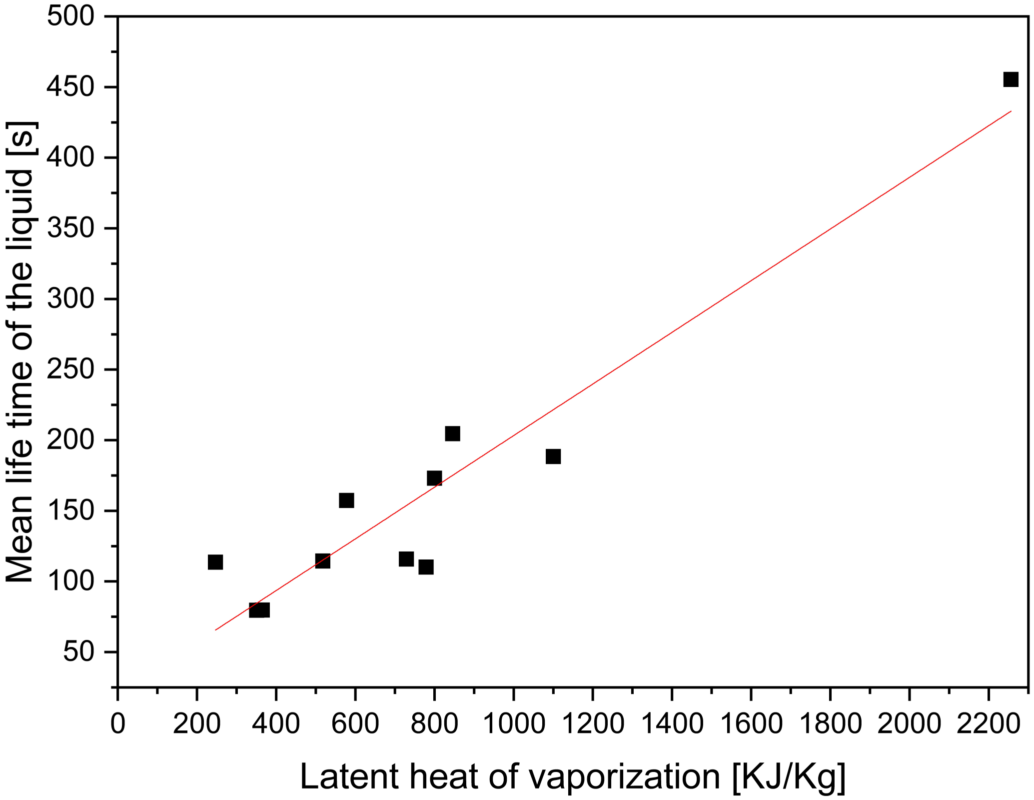


Figure 2.5: Linear fit representation of how the life time of 1ml of liquid at its Leidenfrost temperature is related to its latent heat of vaporization.

In Fig. 2.5 the coefficient of determination is 0.90, which implies that there is indeed a linear trend. In order to specify the relationship between the mean lifetime of the droplet and the parameters on which it depends, we took into account the magnitudes that we obtained experimentally for the factors of the previous equation. Thereby,in addition to the latent heat of vaporization, we consider now the density of the liquid at its boiling point and the temperature difference between the Leidenfrost temperature and the boiling point for each liquid.We did not include the thermal conductivity of the vapor layer because it is a value we do not know experimentally, nor did we include the radii of the drops studied because this value is constant, since the volume used for the observation of all the drops is the same. Thus, this new linear fit is shown in Fig. 2.6. We could realize that, in fact, the density of the liquid at the boiling point and the temperature difference contribute to the coefficient of determination to be 0.98, which is a more precise linear fit.

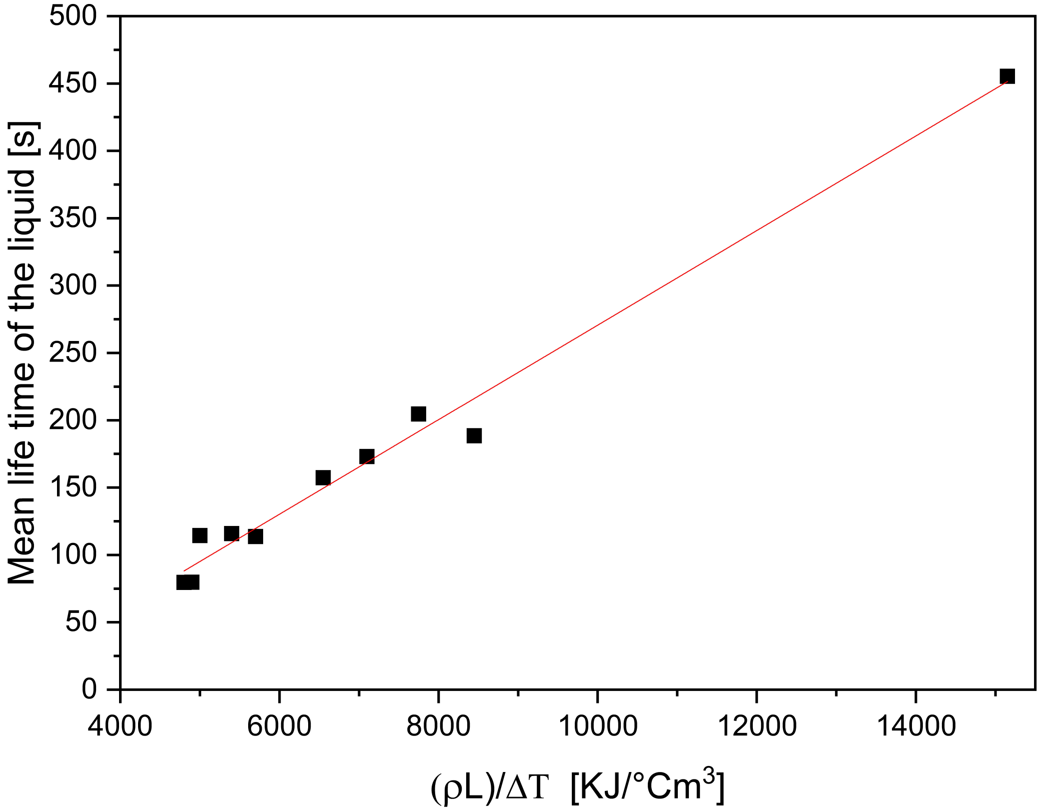


Figure 2.6: Linear fit representation of how the life time of 1ml of liquid at its Leidenfrost temperature is related to its latent heat of vaporization, its density at the boiling point and the temperature difference between the Leidenfrost temperature and the boiling point.

Taking into account the results of the experiment and the exposed relationships, we think that we found a dependency similar to that of eq. 2.1, which implies that there is a constant ratio when describing the lifetime of the drop. We can affirm, then, that the combination of parameters changes such that R_0 remains constant. Thus, $\frac{1}{\kappa}$ is the ratio which determines the increase in the lifetime of the droplet in Leidenfrost state, once known its latent heat of vaporization, its density at the boiling point and the temperature difference between the Leidenfrost temperature and the boiling point of the liquid.

It is evident that Fig. 2.6 shows a much clearer linear relationship between the quantities studied than in the previous case, Fig. 2.5. This is how we can realize that, unlike the study carried out by Biance-Clanet-Quéré, where they find that proportionality ratio for τ as a necessary condition for the results that they obtained only for the case of water be possible, in this study we graph how this relationship is true for various liquids and is indisputably linear, based on experimental data.

This is an important finding insofar as it could lead to the development of a measurement technique to find the thermal conductivity of the vapor of certain liquids. In other words, if we know the lifetime in Leidenfrost state of a drop of a liquid whose density, boiling point and latent heat of vaporization are known, we could easily find the thermal conductivity of the vapor of that fluid. To do this, the next step would be to investigate thoroughly other liquids and corroborate if they behave similarly to the liquids that have been studied here. Also, to answer the question of what type of liquids fit into the model we have just discussed, it is necessary to determine what these liquids have in common or if the model can be applied to all known liquids.

3. The coalescence of Leidenfrost drops

Interaction between water and mixtures of water and ethanol

At first, we thought only about the question of why water and ethanol do not coalesce in the Leidenfrost state in the same way that they do at room temperature. We did tests with water and methanol to realize that the same thing was happening as in the first case, so we wondered if the same would happen when observing interactions of water and other liquids. But before, we wanted to know how changing the surface tension of liquids affected when interacting and thus to know if the rebound effect between miscible liquids was produced by the difference in surface tensions between interacting liquids.

By adding an amount of ethanol to the water, the surface tension of that mixture will be less than the surface tension of pure water. In this experiment, various mixtures of water and ethanol were made at different concentrations, a drop of mixture was taken and it was put into interaction with a drop of pure water while the two were in Leidenfrost state. The objective was to measure at what concentration of ethanol in the water there were bounces between the drop of the water-ethanol mixture with the drop of pure water, with the intention of knowing if there was a value for the surface tension from which there would be rebounds and not direct coalescence between a drop of liquid and a drop of water in the Leidenfrost state.This experiment was repeated with water and mixtures of water and methanol.

We used the same parameters in both cases, the temperature of the plate was 250°C, like in all the experiments, the volume of the water droplet was 1 ml and the volume of the mix water-ethanol droplet was 0.250 ml. The variable to set was the percentage of ethanol in water and the resulting variable was whether or not there were bounces between the two drops when they were in the Leidenfrost state.

First, the interaction between the drop of water and a drop of water whose 10%

was ethanol was observed, the procedure was repeated with 20% ethanol for the second drop and so on until the case in which the second drop consisted of 40% ethanol. In the last case, there were always rebounds between the two drops, while in the immediately previous case, when the second drop consisted of 30% ethanol, there were never rebounds between the drops. So tests were done increasing the percentage of ethanol in the water-ethanol mixture by one at a time from 30% to 40% in order to find a better approximation to the percentage in which there were bounces between the drop of the mixture and the drop of water for the first time.

We found that 33% was the percentage in which the droplets started to bounce with each other, so that we calculate the mole fraction of ethanol in the mixture, which turned out to be 0.163, which means that the density of the mixture is $0.925*10^{-3}$ Kg/m^3, its viscosity $0.934*10^3$ Pa*s and its surface tension 29.24 mN/m [16]. We did the same experiment but instead of water-ethanol mixture we observed the interaction between water and water-methanol mixture. In this case, we found that 37% of methanol in water-methanol mixture was the percentage in which droplets started to bounce with each other, then the mole fraction of methanol is 0.255 and, hence, its surface tension is approximately 32.5 mN/m [19].

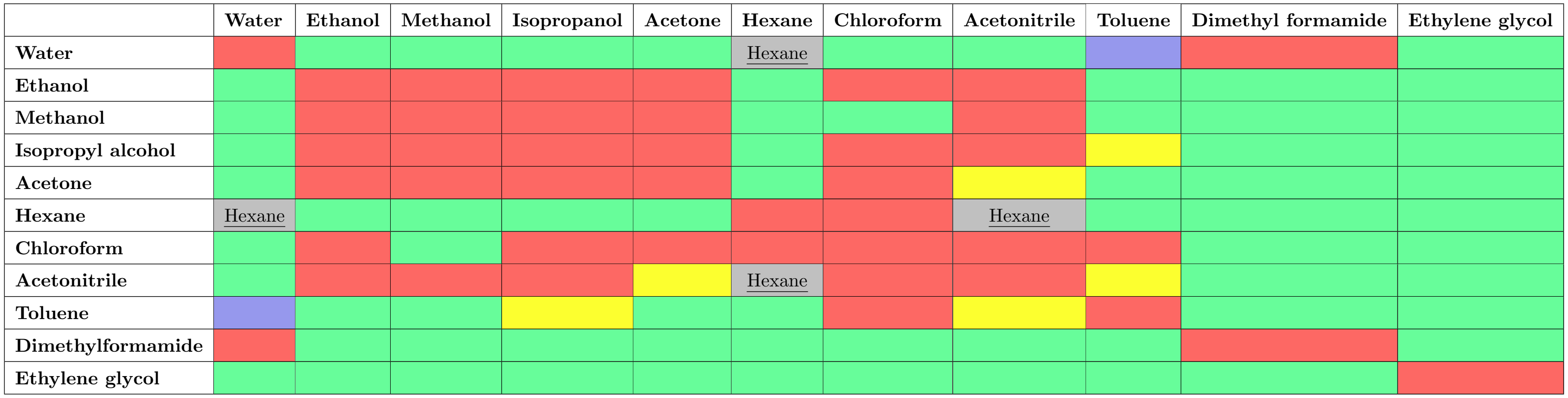
In summary, we realized that the difference between the surface tensions of liquids was a factor to consider when observing the phenomenon. So it was time to think about analyzing the interaction of water and other liquids, which would be a great challenge considering that not only would the surface tension vary, but also other characteristics of the liquids themselves.

Coalescing relationships between liquids

It has already been described how the phenomenon occurs in which a drop of ethanol bounces with a drop of water when both are in the Leidenfrost state.That led us to wonder if this phenomenon was typical of water and ethanol or happened between water and other liquids, so we decided to use nine liquids in addition to ethanol to determine how they interact with water. In this case, we were able to see that most of the liquids bounced from the water drop and we found no obvious reason for those that presented direct coalescence. In other words, the liquids that did not bounce with water had nothing in common, so we thought that we could extract more information if we observed the interaction of all liquids among themselves.

In this experiment, the plate temperature of 250 °C was maintained as a parameter, making an exception in the case of ethylene glycol, which Leidenfrost temperature is above 320 °C. The volume of the liquids when interacting was also constant, we used 1 ml of liquid in all cases. All tests were carried out under the same conditions inside a fume hood to avoid inhaling the fumes expelled from the used liquids.

The way to proceed was as follows. Once the aluminum plate was at a constant temperature of 250 °C, we deposited in it the two drops of which we wanted to know the interaction, one of each liquid, trying to make them both enter the Leidenfrost state at the same time. Subsequently, we observed what type of phenomenon they presented when they came into contact and we filmed the last seconds before coalescence. In this way, we were able to establish, at least qualitatively, what the interactions of each liquid were with the others.



	Water	**Ethanol**	**Methanol**	**Isopropanol**	**Acetone**	**Hexane**	**Chloroform**	**Acetonitrile**	**Toluene**	**Dimethyl formamide**	**Ethylene glycol**
Water	🟥	🟩	🟩	🟩	🟩	Hexane	🟩	🟩	🟦	🟥	🟩
Ethanol	🟩	🟥	🟥	🟥	🟥	🟩	🟥	🟥	🟩	🟩	🟩
Methanol	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟥	🟩	🟩	🟩
Isopropyl alcohol	🟩	🟥	🟥	🟥	🟥	🟩	🟥	🟥	🟨	🟩	🟩
Acetone	🟩	🟥	🟥	🟥	🟥	🟩	🟥	🟨	🟩	🟩	🟩
Hexane	Hexane	🟩	🟩	🟩	🟩	🟥	🟥	Hexane	🟩	🟩	🟩
Chloroform	🟩	🟥	🟩	🟥	🟥	🟥	🟥	🟥	🟥	🟩	🟩
Acetonitrile	🟩	🟥	🟥	🟥	🟨	Hexane	🟥	🟥	🟨	🟩	🟩
Toluene	🟦	🟩	🟩	🟨	🟩	🟩	🟥	🟨	🟥	🟩	🟩
Dimethylformamide	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟩
Ethylene glycol	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥

Table 3.1: Table where the interaction between all the studied liquids is indicated. A Green cell indicates there are bounces between the liquids and after a considerable period of time there is coalescence. A Red cell indicates there are no bounces of any kind, which implies a direct coalescence of the liquids. A Yellow cell indicates there are cases with few rebounds and cases with direct coalescence. The Gray cells correspond to a special case in which there are bounces and the underlined liquid evaporates before coalescing. The Blue cells correspond to a rare phenomenon in which liquids are arranged so that they look like a fried egg, it means, there is a liquid in the center and the other liquid surrounds the first.

The results showed five fundamental types of interaction, as can be seen in Table 3.1, in which the majority of cases correspond to liquids that collapse directly (Red) or there are bounces between them for a prolonged period until they eventually coalesce (Green). Three pairs of liquids were impossible to classify in these last two categories (Yellow), since they bounced in some tests and presented direct coalescence in others no matter the number of tests that were made. Consequently, these cases increase the question of what determines whether or not there is direct coalescence between liquids in the Leidenfrost state.

The other cases draw even more attention, since they present phenomena that we did not expect to observe, such as the particular case of hexane-acetonitrile and hexane-water interactions (Gray), in which the drops bounce for so long that even hexane evaporates completely and, therefore, they never coalesce. Also, the case of water and toluene is very particular (Blue), there are no bounces or direct coalescence between them, instead, the water drop remains in the center of the plate, while the toluene drop is defaced to fit around the water drop and completely enclose it, as you can see in Fig.3.9, which is a very similar arrangement to that of a fried egg, where there is liquid of one type in the center and a liquid of another type surrounds the first. Accordingly, both drops remain together in that arrangement until the liquids evaporate.

Now, it is essential to show how some of the liquids that we have described in the table interact in order to highlight the way in which our observations allowed us to extract valuable information to analyze the phenomenon.

First of all, it is important to observe how the phenomenon of coalescence occurs between two drops of the same liquid that are in the Leidenfrost state. We report that all liquids behave in the same way when they interact with drops of the same nature in the Leidenfrost state; there is direct coalescence between the drops. As an example, in Fig. 3.1 we show a series of images where you can see how two drops of water coalesce on an aluminum plate at 250 °C, where 0 seconds (s) represents the moment when the drops come together, as well as the negative sign indicates time elapsed before coalescence and the positive sign indicates time elapsed after coalescence. The photos were taken from a high-speed video recorded at 1000 frames per second (fps), but the times indicated correspond to real time of observation.

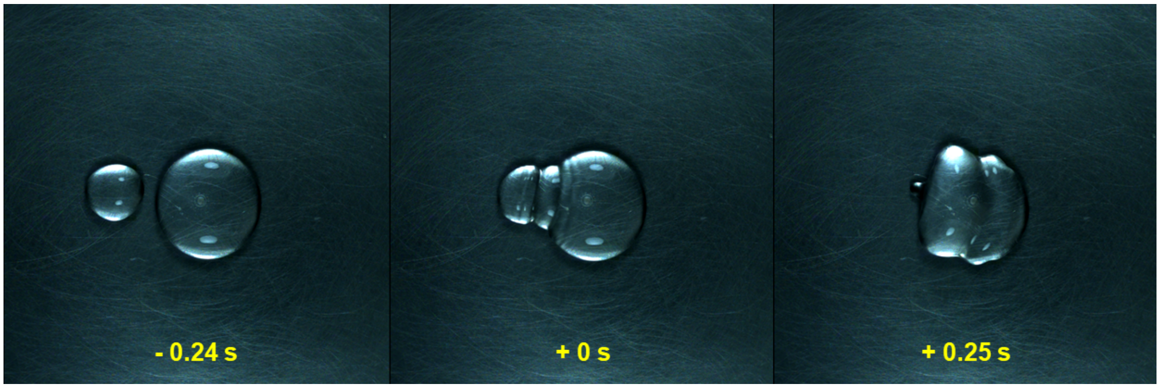


Figure 3.1: Series of images taken from a high-speed video recorded at 1000 frames per second (fps) about how two drops of water coalesce on an aluminum plate at 250 °C. The image with 0 seconds (s) text represents the moment when the drops come together, the negative sign that accompanies the time value indicates the time elapsed before coalescence as well as the positive sign indicates the time elapsed after coalescence.

Now, remembering that our main interest was to study the non-coalescence of water droplets and ethanol in the Leidenfrost state, we will focus on the interaction between these two liquids to exemplify what, in general terms, happens when two liquids of different nature interact in the Leidenfrost state. We report that all liquids have a similar behaviour to that of water and ethanol except for occasions in which coalescence is direct or anomalies occur, as explained in Table 3.1. Thus, in Fig. 3.2 we show the last 38 s before the coalescence of a drop of ethanol with a drop of water. The central and transparent drop corresponds initially to 1 ml of water and the small drop corresponds initially to 0.25 ml of ethanol, which was stained with methylene blue in order to facilitate the observation of the process and determine if there was a transfer of mass between the drops.

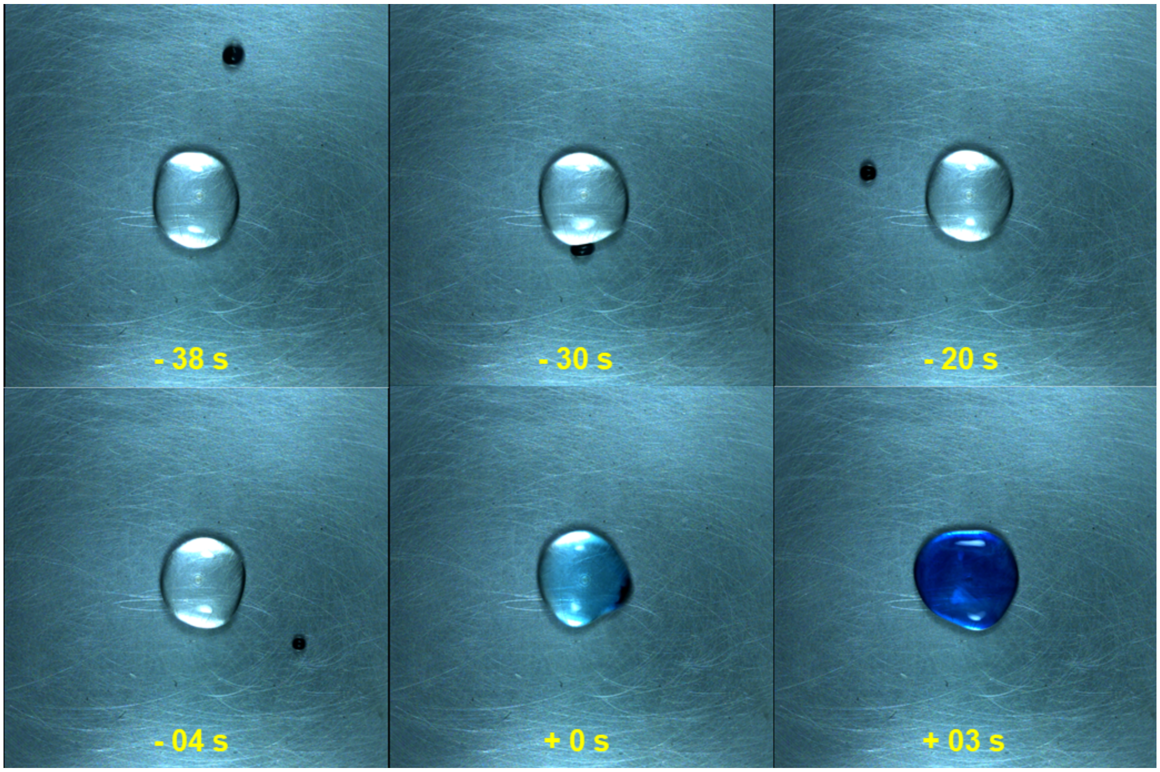


Figure 3.2: Series of images taken from video recorded at 60 fps about the process before coalescence of a drop of ethanol with a drop of water on an aluminum plate at 250 °C. The central and transparent drop corresponds initially to 1 ml of water and the small drop corresponds initially to 0.25 ml of ethanol, which was stained with methylene blue.The image with 0 s text represents the moment when the drops come together, the negative sign that accompanies the time value indicates the time elapsed before coalescence as well as the positive sign indicates the time elapsed after coalescence.

As is evident, the drop of ethanol decreases in size as the moment of coalescence approaches, which is consistent when remembering that the two drops evaporate faster than at room temperature while on the hot plate. This happens with all liquids whose interaction is based on several rebounds before coalescing. Furthermore, it is notable that after coalescence the two liquids make a homogeneous mixture, as it happens with the other liquids that do not fall under the exceptions mentioned above, thus showing that the liquids used are, in general terms, miscible.

We show that, as in the case of water and ethanol, there is no mass transfer during the interaction of liquids before coalescence, which suggests that the surface tension of liquids only vary by the temperature at which they are during the experiment. Furthermore, it caught our attention the fact that the rebounds seem random in terms of the maximum distance between the drop of water and the drop of ethanol after each contact between them, so we decided to follow the path of the ethanol droplet, from the video which is the basis of the Fig. 3.2, during those 38 s before coalescence. We repeated this process for all liquid interactions that had similar behaviour, that is, in which there were rebounds before coalescence.This can be seen in Fig. 3.3.

Figure 3.3: Path of the ethanol droplet, from the video which is the basis of the Fig. 3.1, during the last 38 s before coalescence. The white space in the center that corresponds to the place where the drop of water is and the black line corresponds to the path that the ethanol droplet follows.

There is a white space in the center that corresponds to the place where the drop of water is all the time, the black line represents the path that the ethanol droplet follows from 38 s before coalescing until it joins the drop of water in a homogeneous mixture. As you can see, it is difficult to determine, with the naked eye, the maximum distances between the two drops after each bounce, so that we decided to do a coordinate transformation to represent the distance traveled by the ethanol droplet in a Cartesian plane and observe how this distance varies as the time elapses before the coalescence, as can be seen in Fig.3.4 .

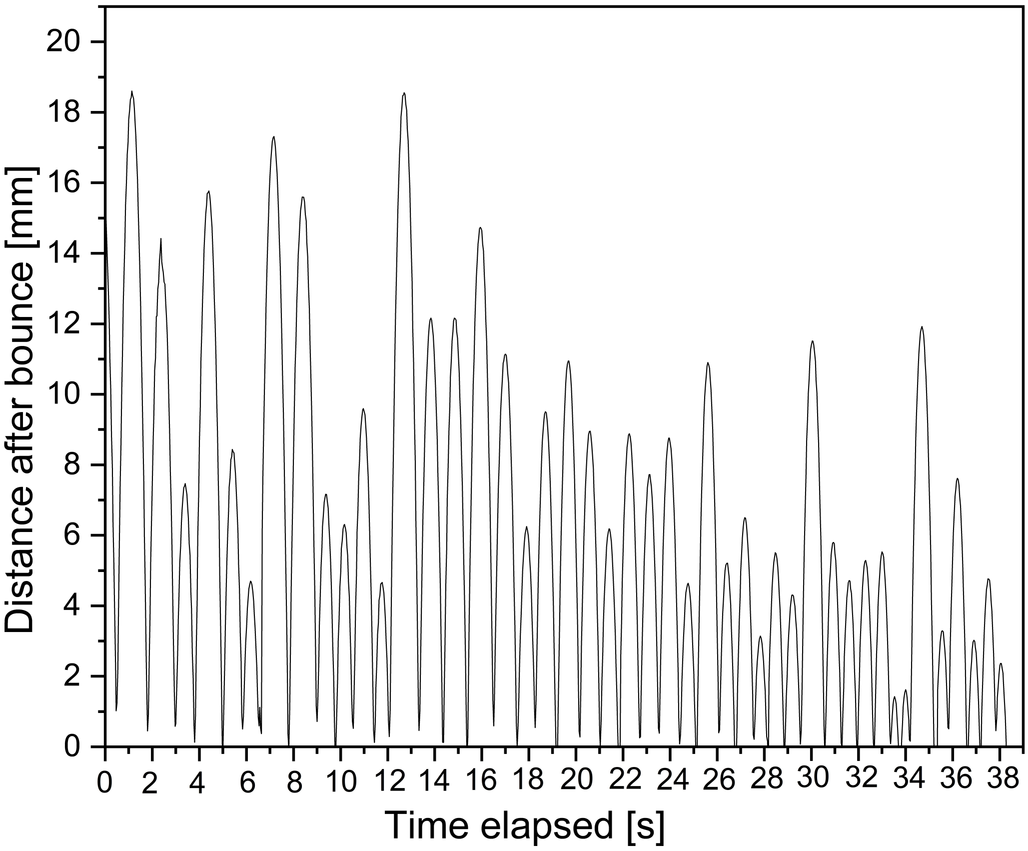


Figure 3.4: Representation of the distance traveled by the ethanol droplet after each bounce, from Fig. 3.2, in a Cartesian coordinate system. It can be observed how the distance varies as the time elapses before the coalescence.

From the previous figure we can see that although the way in which the ethanol droplet bounces on the water droplet does seem random, the distance after the bounce tends to decrease as the interaction time increases. It is also notable that some rebounds result in the maximum distance traveled even if the previous rebounds corresponded to much shorter distances traveled. This means that the distance after the bounces does not simply decrease in time, there are also times when it increases, which could indicate that in some way the ethanol droplet is propelling itself, that is, it is acquiring energy that allows it to overcome the distances traveled thanks to previous rebounds.

As mentioned before, all the liquids that bounced with the water drop in the Leidenfrost state had a behavior very similar to that of ethanol. Among them, we highlight isopropanol and chloroform; the first one because it reached the longest distances after bouncing and the last one because it reached the shortest distances after bouncing. In Fig. 3.5, we use again the Cartesian coordinate system to compare the distances after bounces reached by the isopropanol and chloroform drops with that already observed for the ethanol in Fig. 3.4, this in the last 38 seconds before the coalescence of each drop with the water drop, because that was the maximum time interval the high-speed camera could record in our conditions.

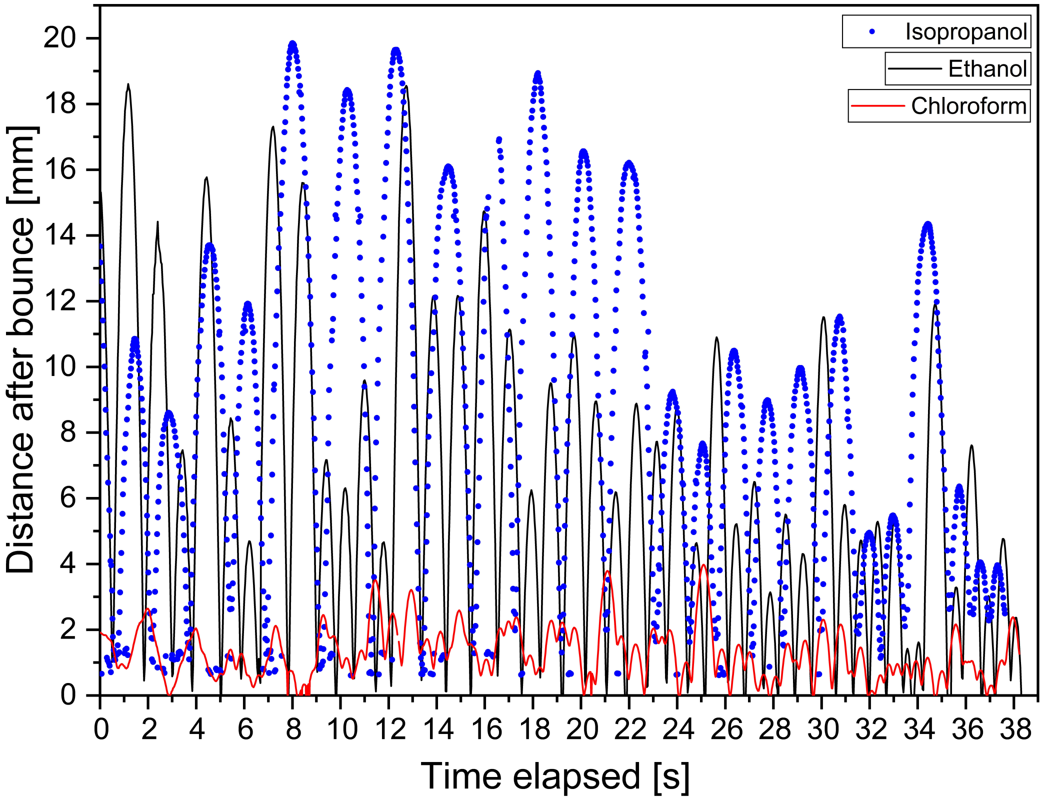


Figure 3.5: Representation of the distance traveled by ethanol (black line), isopropanol (blue dotted line) and chloroform (red line) droplets after each bounce in the last 38 seconds before the Coalescence of each drop with a water drop in a Cartesian coordinate system. It can be observed how the distance varies fro each liquid in a different way.

We could see how in the three graphs some rebounds result in a great height even if the previous rebounds corresponded to lower heights. We observed the same behaviour for all liquids and we realized there were different trends, it means, the distance after bounce is different for all liquids. Thus, we continued thinking the droplets were acquiring energy that allows it to overcome the distances traveled thanks to previous rebounds but we wondered how that energy changed from one liquid to another. We thought the heights observed in Fig. 3.5 could give us enough information to determine it, so that we calculated the potential energy of these three types of droplets each time the drop were in a peak, that is, in the maximum distance that the drop could reach after bouncing and before falling back towards the drop in the center of the plate. Afterward, we calculated the average potential energy for each case.

It is important to remember that in all cases we used a central water droplet of 1 ml and the droplet to vary was always of 0.25 ml ($2.5*10^{-7}$ m^3), however, because of the density of each liquid at its boiling point (see Table 2.1), the masses were different, so that the mass of the ethanol droplet was 0.18695 gr, 0.352825 gr for chloroform and 0.181025 gr for isopropanol. The average distance after bounce in the peaks of each liquid was 8.50 mm for ethanol, 2.01 mm for chloroform and 11.94 mm for isopropanol. Thus, taking into account the arrangement of the system as in the diagram in Fig. 3.6, we used eq. 3.1 to obtain the average potential energy of each droplet, where m is the mass of the droplet, g is the gravitational acceleration, h is the maximum height or the peak of distance after bounce and the sin(2) is because of the inclination of the plate surface was 2 degrees with respect to the horizontal

$$U = mgh\sin(2). \tag{3.1}$$

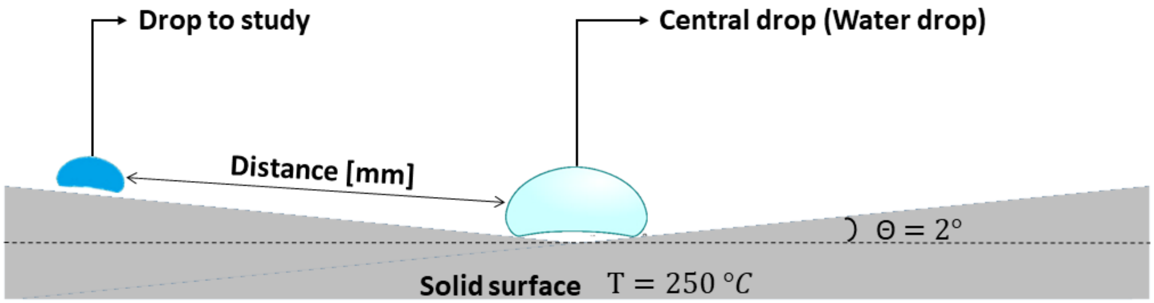


Figure 3.6: Diagram showing the experimental setup to measure the height reached by a drop of a liquid to study after bouncing on a water drop that always remains in the center of the aluminum plate, which is at a temperature of 250 °C. The plate has a surface inclination of 2 degrees with respect to the horizontal, which forces the drops to go towards the center of the plate. The distance between the drops is measured in mm using a high-speed camera that records all the activity of the interaction between the drops.

The results were 0.541 μJ (5.41*10^{-7} Jules) for ethanol, 0.242 μJ for chloroform and 0.739 μJ for isopropanol. In the case of chloroform, as expected, the energy is lower than in the other two cases because, although its mass is greater than the other two droplets, the average maximum height is considerably less than the distance after bounce in the other two cases. In other words, in the case of chloroform we can see the least energy because this droplet presents the shortest distance after each bounce.

What is remarkable in this comparison is that the potential energy for ethanol and isopropnaol turned out to be very different despite the great similarities between the two liquids. We can only associate this difference in potential energies to the difference in average maximum heights that each drop reaches. However, this indicates that the apparent injection of energy that allows the rebounds depends on the nature of the liquid itself and in addition to a factor that we do not appreciate at a glance.

It is impossible to ignore the fact that this rebound phenomenon is similar to the previously discussed study about rebound of hydro-gel spheres in the Leidenfrost state, where it was found that, rather than hovering, the spheres energetically bounce several times for long periods of time. It was shown that these otherwise-hidden agitations constitute work cycles that harvest mechanical energy from the vapour and sustain the bouncing [10]. Knowing these previous studies, we ask ourselves, is it possible that there is a mechanism during the interaction of the drops that, in addition to preventing direct coalescence, propels the drop with less mass?

Unlike the observations made on the rebounds of hydro-gel spheres, the materials that we observe are totally liquid and we cannot predict when a rebound occurs after which the drop travels a distance greater than or equal to that previously traveled. This leads us to think that, if there is a similar mechanism that causes the absence of direct coalescence and the propulsion of the drop, the mechanism that enables the phenomenon that we have observed depends only on the liquids themselves.

Non-coalescence mechanism: The triple Leidenfrost effect

After considering various perspectives from which this phenomenon could be explained, we prioritize the hypothesis of a possible triple Leidenfrost effect in the system. Remembering that the reported boiling temperatures for water and ethanol are 100 °C and 78.37 °C respectively [11], it is consistent to think that, although water and ethanol are miscible, it is possible that at extreme temperatures there is a Leidenfrost effect of one substance on the other in addition to the Leidenfrost state that each liquid presents with the solid surface.

Clearly, it was necessary to make several observations to determine whether or not there is a vapor layer that is generated when two drops in the Leidenfrost state come into contact and that can also function as a thermal insulator. With the high-speed camera we filmed the interaction of each liquid studied with all the others and observed in detail if we found evidence of a vapor layer between the two drops of liquid. Although we were close to observing what was expected in several cases, we did not obtain forceful images of the existence of the vapor layer in the middle of the liquids when they collided, except for one interaction, namely that of ethylene glycol-chloroform.

In Fig. 3.7 we show a series of images where you can see how a chloroform droplet, stained with methylene blue, bounces twice on a ethylene glycol droplet on an aluminum plate at 320 °C, where 0 s represents the initial moment in which the two droplets are deposited over the hot surface. The actual total time interval of the interaction is 2.4 s from the drops being deposited until moments after the second collision.The photos observed were taken from a high-speed video recorded at 500 fps, but the times indicated correspond to real time of observation.

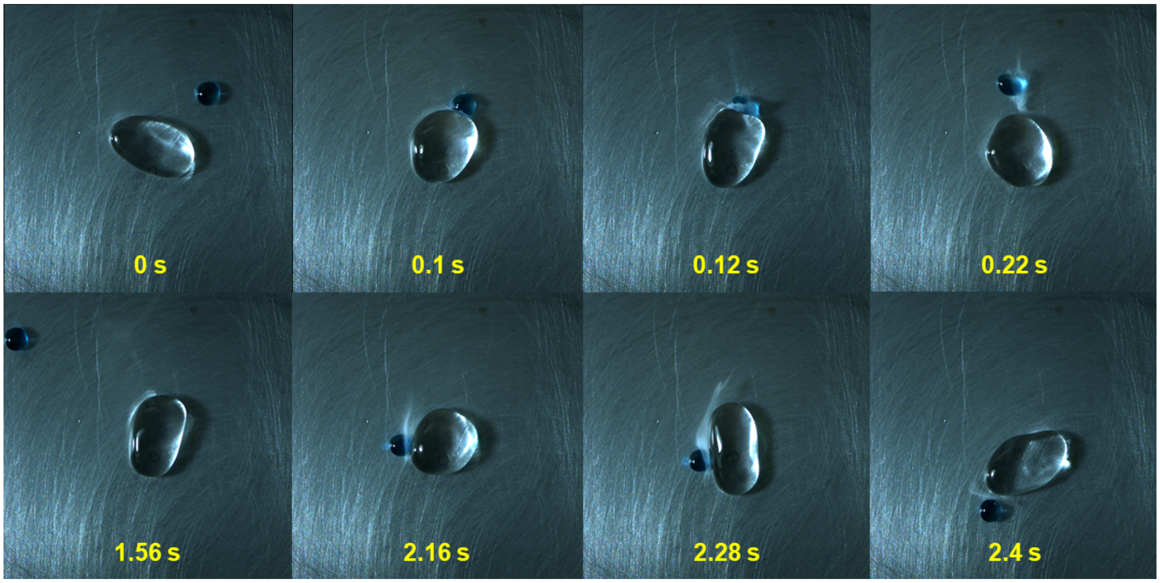


Figure 3.7: Series of images taken from a video recorded at 500 fps about the process of a chloroform droplet bouncing twice on a ethylene glycol droplet on an aluminum plate at 320 °C. The central and transparent drop corresponds to 0.5 ml of ethylene glycol and the small drop corresponds to 0.2 ml of chloroform, which was stained with methylene blue. The 0 s text represents the initial moment in which the two droplets are deposited over the hot surface. The actual total time interval of the interaction is 2.4 s.

As is evident, there is a large amount of vapor that can be observed only when the two drops are in contact. In the image at 0 s the drops have not had contact with each other and it is clear that there is no evident vapor around them. In the 0.1 and 0.12 s images we record how the steam expelled from the contact region of the drops is more evident the greater the contact area between the drops. The image at 0.22 s is a record of the first moments after the first bounce between drops, it can be seen how the steam resulting from the contact moves in the same direction that the chloroform drop does. After 1.56 s the droplets are even more distant than in their initial position and are about to present a second collision, as can be seen, there is no obvious vapor between the droplets. In the moments at 2.16 and 2.28, once again, the drops collide and, as in the first collision, we report that there is evident steam only when the drops are in contact and the amount of steam that we can observe increases as the contact area of one drop with the other. At the end of the two-bounce process, at 2.4 s, we see how the chloroform drop bounced in a different direction from the initial position and the first bounce and, as happened in the first bounce, the steam resulting from the collision moves in the same direction that the chloroform drop does.

Recalling the values of boiling point and Leidenfrost temperature of the liquids and that in previous studies it was shown that the Leidenfrost temperature of a liquid depends only on the boiling point of the liquid and the roughness of the hot surface which has contacted the liquid [13], so that the Leidenfrost temperature tends to the boiling point of the liquid as the surface roughness tends to zero, it is consistent to think that there is a Leidenfrost state between chloroform and ethylene glycol if they are at the temperature treated in this experiment. Thus, we can affirm that the reason why the chloroform drop did not coalesce with the ethylene glycol drop and, in addition, it was propelled to show multiple rebounds, is related to the evident vapor layer that arises only when the drops come into contact.

In this sense, the results and the discussion previously exposed suggests to us to think that, in the Leidenfrost state, the explanation that there is no direct coalescence and that there is propulsion of liquid drops over others is due to a third Leidenfrost effect that occurs between one drop and the other. This, taking into account that we were able to observe the vapor layer between ethylene glycol and chloroform due to the volatility of the liquids, but for other interactions, a better observation tool would be necessary to allow more detailed analysis of the contact regions of the drops. A diagram of this explanation can be seen in the Fig. 3.8.

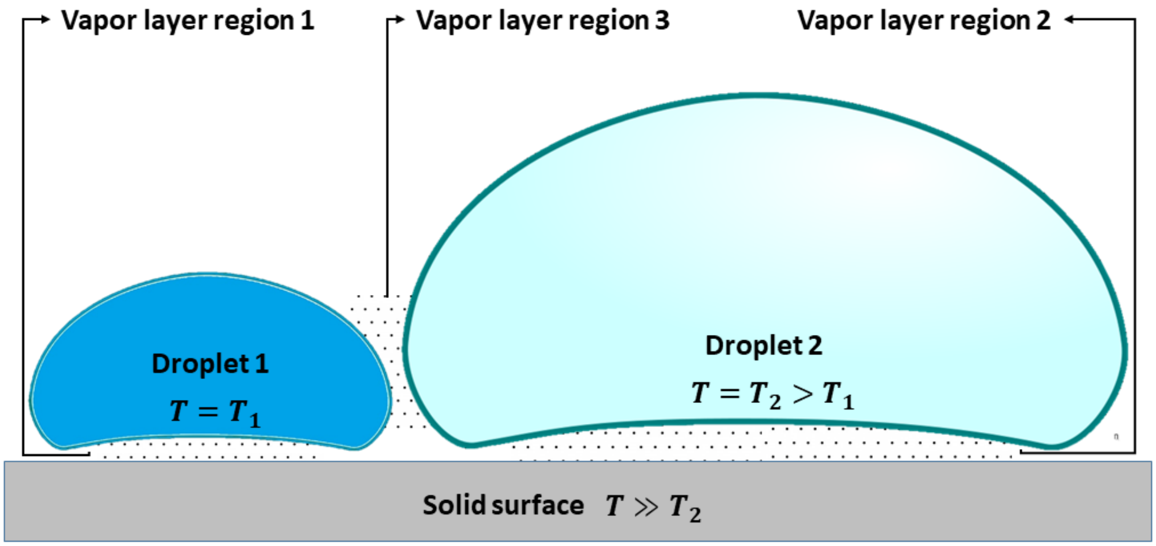


Figure 3.8: Diagram of how the triple Leidenfrost effect works. Each of the drops is at its boiling point, while the solid surface is at a much higher temperature than the boiling points of liquids, therefore there is a Leidenfrost effect between each drop and the hot surface. Furthermore, drop 1 is at a lower temperature than drop 2, and since the liquid surface of the hottest drop has negligible roughness, a Leidenfrost effect occurs between the drops. Therefore, there are 3 regions of vapor layers generated independently in the interaction, so the phenomenon is called the triple Leidenfrost effect.

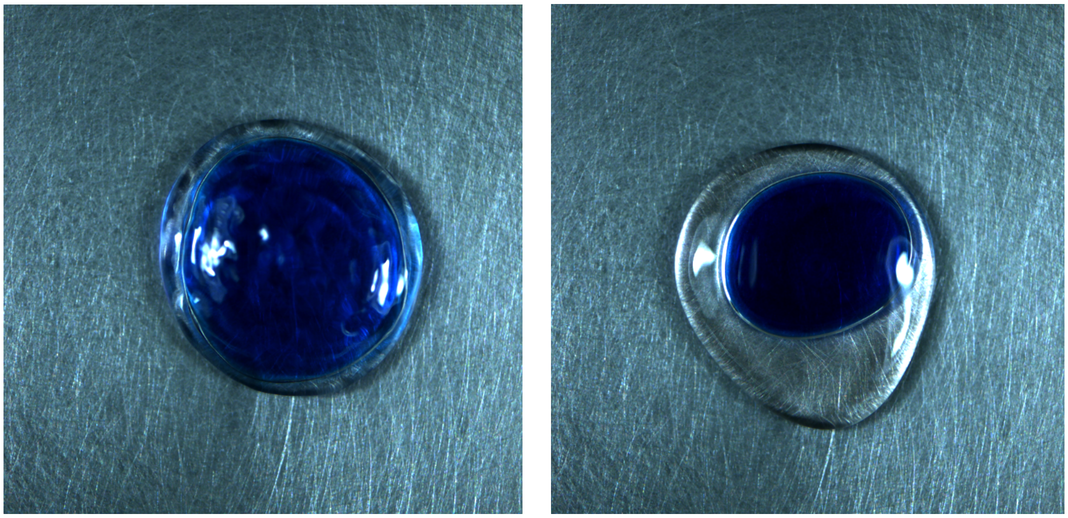
Droplet size when coalescing

As mentioned before, when there are bounces between drops of liquids in the Leidenfrost state, they generally coalesce after a certain period, when the droplets are smaller. Since liquid droplets are smaller when they coalesce than when they are deposited on the aluminum plate, we know the drops are slowly evaporating as they interact. This fact led us to consider whether the size at which the drops coalesce could give information about the factors that determine the coalescence of drops in the Leidenfrost state. Specifically, we wanted to find out if the size at which the coalescing droplet was random, constant, or varied depending on the properties of the liquid.

In that sense, we carried out this experiment which was about measure the size of each of the two droplets when they coalesce. For it, the temperature of the plate was constant at 250 °C since, as it can be seen in Fig. 2.3, almost all liquids are in Leidenfrost state at this temperature. We established as constant one of the drops to be as accurate as possible in the data collection, so in all cases water was used as the central drop or reference liquid. It was put the water droplet of 1 ml in the center of the plate and immediately a droplet of a second liquid of 0.1 ml is deposited, we observed and filmed at high speed the interaction between them, so after the coalescence we observed the video and used the software ImageJ for measuring the size of each droplet in the instant just before they coalesce. Then, we repeated the procedure around five times. Later we did the same experiment but now with 0.2 ml of the second liquid, after that with 0,3 ml and so on until the droplet of the liquid was stable, it means, the capillary length of the liquid allows to conserve the shape of spherical droplet. We repeated this process for all the liquids in interaction with the central drop of water.

Once the droplets were measured with the help of the software, for the easy observation of the data we proposed graphs, which can be seen in Figures from 3.10 to 3.16,in which the mean size of coalescence was plotted against the initial volume of liquid that compounds the droplet of the liquid to be analyzed. The graphs corresponding to the following interactions are not present for various reasons: when it comes to water-dimethyl formamide and water-water, there are no rebounds of any kind between these substances, as evidenced in Table 2; the water-ethylene glycol interaction was also not taken into account because at 250 °C ethylene glycol does not achieve a Leidenfrost state and we think that it would be better to analyze results under the same parameters.

We did not consider either the water-toluene interaction, because it does not apply to this experiment due to the phenomenon that has been mentioned before, that is, as you can see in Fig. 3.9, the water drop remains in the center of the plate, while the toluene drop is defaced to fit around the water drop and completely enclose it, which is a very similar arrangement to that of a fried egg, where there is liquid of one type in the center and a liquid of another type surrounds the first. Accordingly, both drops remain together in that arrangement until the liquids evaporate.



(a) Interaction water-toluene few seconds after their first contact

(b) Interaction water-toluene after more than thirty seconds from the first contact

Figure 3.9: Images of the behavior of the liquids when Toluene and water interacting in Leidenfrost state. The water, of blue color because it was dyed with methylene blue, remains in the center while the Toluene, the transparent liquid, surround the water. A few seconds after their first contact (a), the toluene seems to vibrate on water and approximately thirty seconds later (b) the liquids do not seem to vibrate. The two liquids evaporate and remain together until eventually the toluene evaporates to a point where the toluene layer on the water cannot be distinguished on high speed imaging. Finally, the drop of water evaporates as if it had always been alone.

We have some ideas of what can cause the strange phenomenon just mentioned, but we did not hypothesize about it because this was the only case in which we observed something like this and we had to choose between determining how this arrangement occurs between the liquids or continue analyzing the interactions between liquids that show similarity between them and, therefore, can be analyzed. We think that this case of water and toluene is very particular and requires its own investigation, in which it can be studied in detail and thus determine if there are other liquids that interact in a similar way and vary the parameters that can intervene in said interactions.

In this sense, we focus only on liquids that we have studied in more detail throughout the text. Thus, in Figures from 3.10 to 3.16 can be seen the graphs in which the mean size of coalescence was plotted against the initial volume of liquid that compounds the droplet of the liquid to be analyzed.

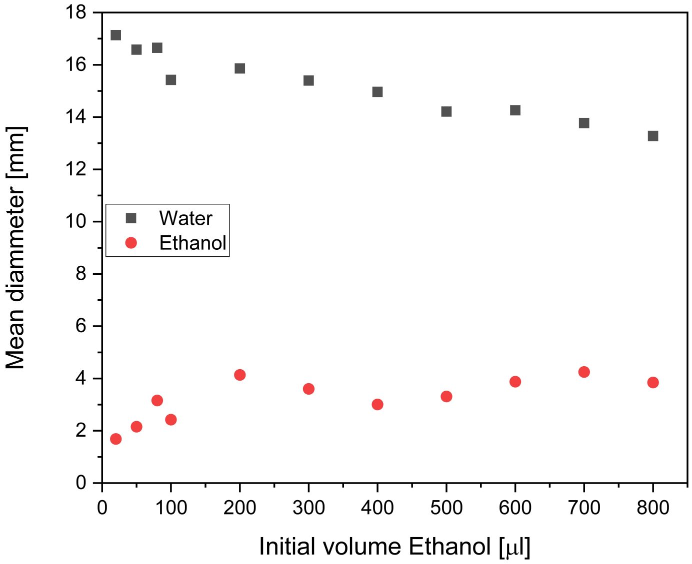


Figure 3.10: Graph of mean size of coalescence of water and ethanol droplets against initial volume of ethanol

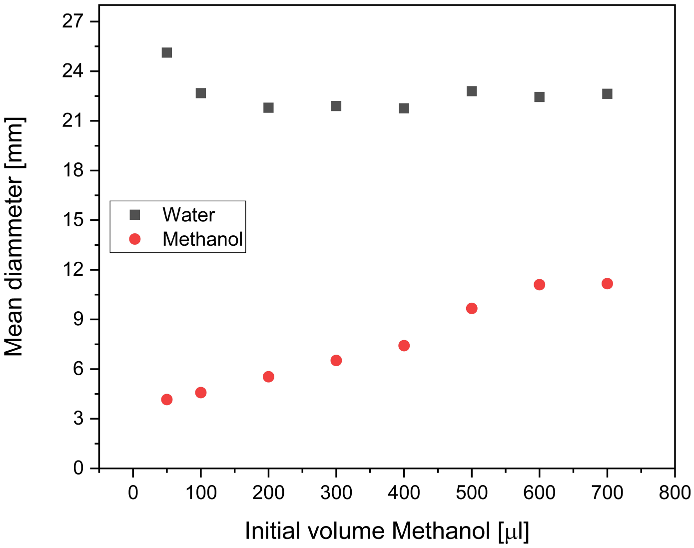


Figure 3.11: Graph of mean size of coalescence of water and methanol droplets against initial volume of methanol

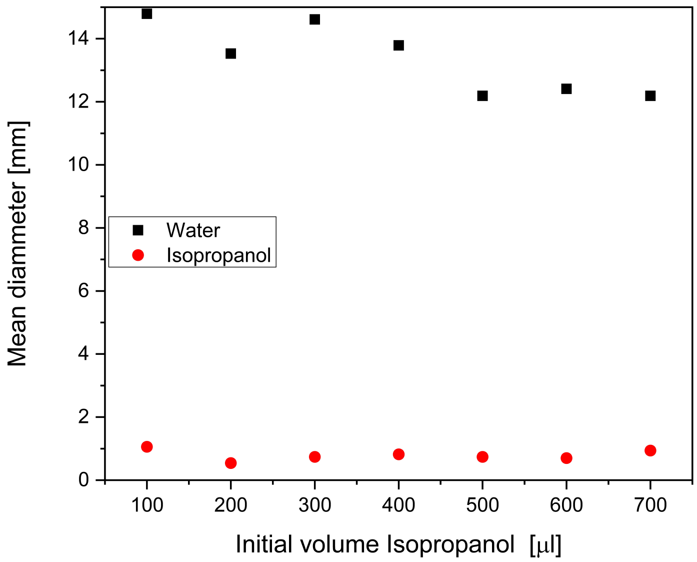


Figure 3.12: Graph of mean size of coalescence of water and isopropanol droplets against initial volume of isopropanol

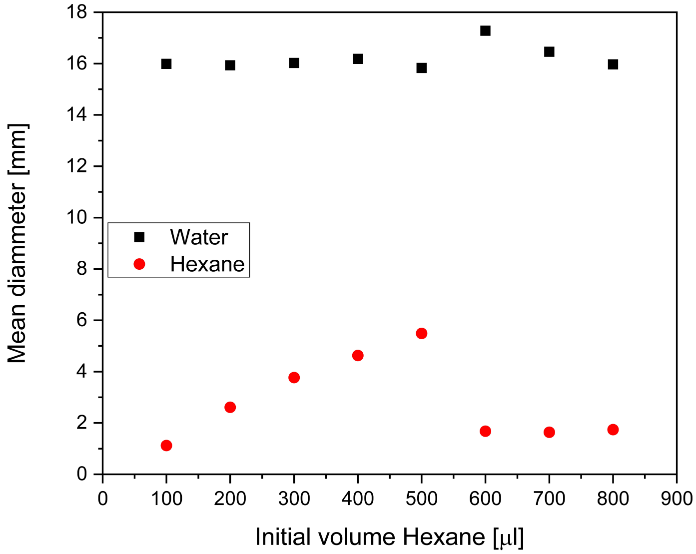


Figure 3.13: Graph of mean size of coalescence of water and hexane droplets against initial volume of hexane

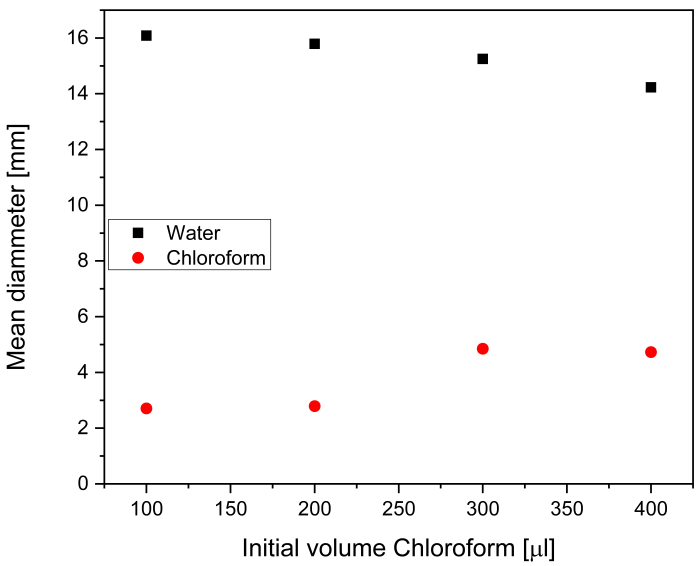


Figure 3.14: Graph of mean size of coalescence of water and chloroform droplets against initial volume of chloroform

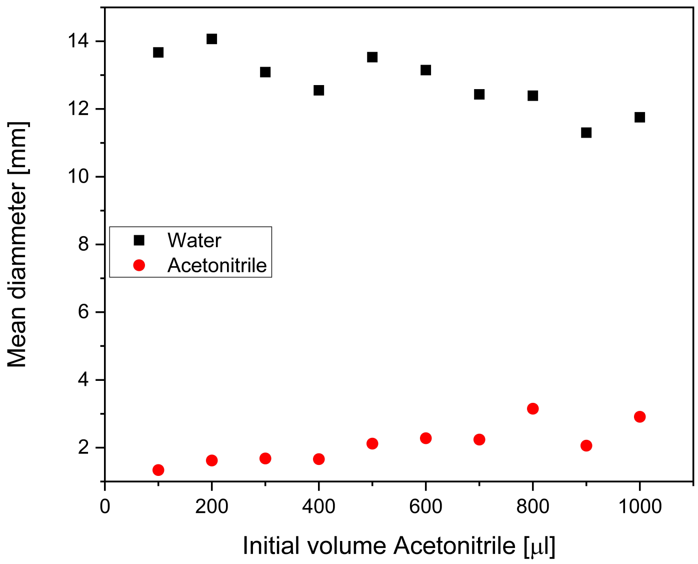


Figure 3.15: Graph of mean size of coalescence of water and acetonirtrile droplets against initial volume of acetonitrile

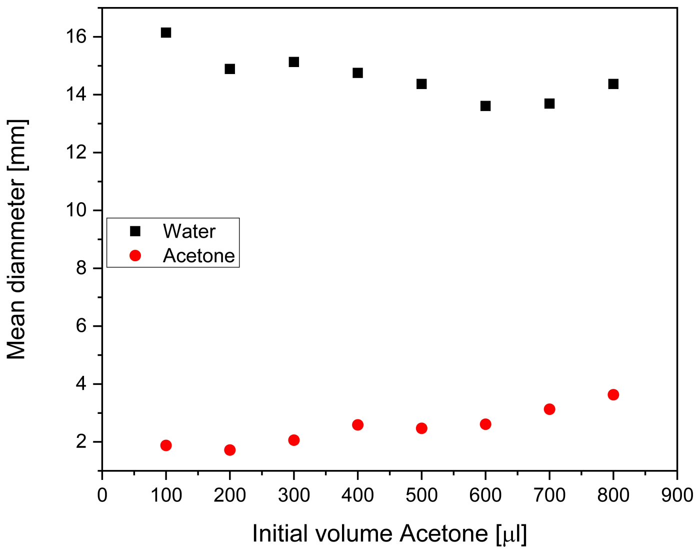


Figure 3.16: Graph of mean size of coalescence of water and acetone droplets against initial volume of acetone

The results showed that, when interacting with water, all the liquids had a behavior in common, which is that each liquid tends to collapse with the same size regardless of the amount of initial liquid.Although in some cases the coalescence size does not seem constant, in several of these graphs it can be seen how the relationship tends to be constant even for large initial amounts of liquid. For example, in Fig. 3.10 and Fig. 3.11, you can see how ethanol and methanol show a linear coalescence size relationship for small initial volumes of liquid, but as said initial volume is increased the ratios tend to be constant. This indicates that, in the Leidenfrost state, the moment of coalescence of a water drop with a drop of another liquid, which does not present direct coalescence with water, is related to the size reached by the second liquid after evaporating for a certain period of time.

4. Conclusions

Taking into account that this study turned out to be qualitative, it is important to mention those results that were decisive in characterizing the liquids studied and its behavior in the Leidenfrost state. First, we found that all the liquids studied, without exception, show a Leidenfrost effect on polished aluminum. In the literature it is rare to find studies on the Leidenfrost effect manifesting in liquids other than from water, so it is valuable to have experimental results that support the idea that in a certain variety of liquids the Leidenfrost effect occurs when working on one of the solids surfaces most used for this type of study, such as polished aluminum. This is essential to understand the behavior of liquid materials on hot surfaces, so we can affirm that we achieved a physical characterization of the studied materials.

We observed that some liquids have a different behavior from most liquids when they are at Leidenfrost temperatures. Because of the objectives of this study, we had to choose to continue analyzing the interactions between liquids that have direct coalescence or bounces with water. Therefore, we think that these special cases require its own deep research, in which it can be studied in detail in order to determine if there are other liquids that interact in a similar way and vary the parameters that can intervene in said interactions.

Thanks to the characterization process, it was found that for the mean lifetime of a Leidenfrost droplet the combination of parameters changes such that R_0 remains constant, following the relation of Biance-Clanet-Quéré. Thus, the ratio $\frac{1}{\kappa}$ determines the increase in the lifetime of the droplet in Leidenfrost state, once known its latent heat of vaporization, its density at the boiling point and the temperature difference between the Leidenfrost temperature and the boiling point of the liquid. Thereby, we now know that the Leidenfrost effect is a physical issue in the framework in which there is a balance between the weight of the drop and the vapor pressure that supports the droplet. This means, in this study we found, based on experimental data, how this relationship is true for various liquids and it is indisputably linear. This is important because little emphasis has been made on how the lifetime of different liquids varies in Leidenfrost temperatures and it could lead to the development of a measurement technique to find the thermal conductivity of the vapor of certain liquids.

The most important finding regarding coalescence of different liquids in the Leidenfrost state is the mechanism that explains why there is no direct coalescence of various different liquids when interacting at these conditions, namely the triple Leidenfrost effect. Although there was no quantitative analysis of how the triple Leidenfrost effect works, evidence was obtained that allowed us to qualitatively describe the operation of this mechanism. This is, additional to that there is a Leidenfrost effect between each drop and the hot surface, a Leidenfrost effect occurs between the drops due to there is a temperature difference between the two droplets and the liquid surface of the hottest drop has negligible roughness. Therefore, there are three regions of vapor layers generated independently in the interaction, so the phenomenon is called the triple Leidenfrost effect. In this way, our research leaves an open door for a more detailed study on coalescence of Leidenfrost drops, where tests could be carried out with a greater variety of liquids and from a rigorously mathematical perspective.

In closing, we want to point out that from this study, multiple work plans can be designed to continue investigating these phenomena that correspond to the coalescence of Leidenfrost drops in order to obtain quantitative results consistent with the observations. Specifically, the objective would be to accurately describe how the Leidenfrost triple effect mechanism prevents direct coalescence between drops of miscible liquids and also propels the droplets of less mass during interaction. We think that the first step to do this could be using an experimental setup that allows a more detailed observation of the moment when two drops collide. In this way, it could be determined if there is a vapor layer between all the liquids and if there are oscillations in the droplet surfaces that are playing an important role in the interaction.

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