Non-Photochemical Laser-Induced Nucleation in Supercooled Water

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Abstract

Non-photochemical laser-induced nucleation is a method for how lasers can change the molecular structure of the supercooled water into crystals leading to a transition into a solid state, ice. In this study experiments were conducted in order to determine if a Pharos laser with a wavelength of 1030nm could be used to induce nucleation and if the different powers of the laser had different effects on the nucleation. This could be achieved by using a Nd:YAG, Brilliant B, Q-switched laser with a wavelength of 532nm to illuminate a vacuum sealed chamber through which a stream of water droplets were injected. The Pharos laser was used to induce nucleation while a camera took pictures of the droplets hit by the laser. There was no nucleation visible in the pictures despite varying degrees of power output from the laser. The result remained relatively stable throughout all power levels. Thus a conclusion was made that the laser did not induce nucleation.

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Contents

1 Introduction

Non-photochemical laser induced nucleation, NPLIN, is a method on how lasers can create a crystalline structure in supercooled water causing a phase change. The knowledge about crystallization of water is essential for many fields of science and technology - e.g. atmospheric sciences and food preservation [1]. Crystallizing can for instance be observed in supercooled rain that freezes upon reaching the ground which affects traffic safety [2]. Understanding this phenomenon allows for the possibility to come up with methods that can aid in these areas and prevent detrimental situations [1].

1.1 Applications

Inducing nucleation in supercooled water through the use of lasers allows for improved control over the nucleation process. Atmospheric sciences will be impacted by contributing to the knowledge of cloud formation and supercooled rain. This knowledge will ultimately lead to a better understanding of possible solutions to prevent climate changes [3]. Furthermore, the pharmaceutical and food industry could potentially benefit from the knowledge that is obtained from the laser-induced nucleation. Controlling nucleation is imperative in the synthesis of medicine. Supercooled water that controllably crystallizes into ice can also be used to, for example, cryopreserve food. Cryopreservation can be used to decrease food wasting since it is then possible to contain food for a longer period of time. [2]

1.2 Aim of Study

This study aims to examine how nucleation is affected by lasers, or more specifically, to determine the lower power threshold in which nucleation is induced by a laser, and how it could be utilized to control said nucleation. Due to the stochastic nature of the nucleation, the time required for the process to occur is unknown. The droplets that have laser-induced nucleation are to be compared with the spontaneous nucleation. [2]

1.3 Theoretical Background

Alexander, Andrew J. and Philip J. Camp have experimentally determined in their study that lasers may induce nucleation, which is what this study is based upon [4]. It is also based upon previous research done by Prof. Kaemtz that state that pure water can be in a liquid phase below 273 K [5].

1.3.1 Supercooled Water

Supercooled water is liquid water with temperatures below the general freezing point (273.15 K) which can reach 233 K in optimal conditions for supercooled water to occur. The water should not have external particles that interfere with the water molecules once below the freezing point, as the interference can induce nucleation. By having pure water in vacuum the risk for external interference is severely decreased [5]. Once crystallization begins, the ice fraction measures the proportion of the water which has transformed - it was estimated by dividing the amount of frozen droplets by the total amount of droplets captured by the camera.

1.3.2 Nucleation

Nucleation is the first instance in which a liquid or vapour begins to form a crystallised structure, e.g. when water initially transitions into ice. It can either be homogeneous or heterogeneous. Heterogeneous is where an external force causes nucleation to begin, this is largely found in nature. An example of this is when water naturally freezes to ice. A particle makes the molecules less active leading to reduced surface energy and in turn to crystallization [6]. Homogeneous nucleation, on the other hand, is completely spontaneous and happens without any external interference. The molecules simply line up in a formation, transforming it into crystals. This happens when the water is pure and consequentially supercooled. Homogeneous nucleation is the process that occurs in pure supercooled water that makes it form crystals. At 233 K spontaneous homogeneous nucleation occurs often and many droplets freeze [7]. One useful measure of nucleation is the nucleation rate, which measures how many nuclei are formed in a given time. A lower temperature usually leads to a higher nucleation rate. Nucleation can be synthetically initiated in different ways, one hypothesised method is to utilise lasers [7]. Lasers can be used to align the needle axes parallel to the applied electric fields and cause the so-called Kerr effect [8]. The Kerr effect is when a substance is subjected to an electrical field and changes the refractive index, the needles which do form are parallel to the electric field in the laser. This suggests the mechanism is dependent on the laser [9].

2 Method

The method this study has chosen was designed to decrease the possibilities of heterogeneous nucleation. For example there was no substrate that freezes the droplets which reduces the external interference. [4]

2.1 Experimental Setup

In order to conduct the experiment different components were necessary. Two lasers were used for this experiment, one to illuminate the chamber [Nd:YAG, Brilliant B, Q-Switch, 532 nm] so it could be observed and recorded. Another laser was used to induce nucleation in the supercooled water. The illumination laser was synced with the camera so that it took a picture every time the laser sent out a pulse and the water droplets became illuminated and were seen by the camera. The camera was a Complementary Metal Oxide Semiconductor camera and it was set up with a microscope close to the chamber, as two separate entities, allowing the camera to take pictures on a microscopic scale. A lens to concentrate the light towards the camera and a filter to remove short wavelengths that could damage the camera were also used. Among these wavelengths were the one the laser used, 532 nm, which makes the images black and white. When the chamber had less than 1 mbar of pressure, the illuminating laser began sending pulses and the camera was adjusted to have the droplets in focus. The Pharos laser [1030 nm, 1 mJ] was used to alter the molecular formation of the water and thereby induce nucleation. To control the lasers' route, several mirrors, shields and lenses were used.

The nozzle was where the water droplets were injected into the vacuum chamber from. It had a tip of 10 µm and its consequential water droplets were between 15 – 25 µm in diameter. The size and frequency of the droplets were controlled by a built-in piezoelectric actuator. A piezoelectric actuator is a motor made out of a material that converts the mechanical energy into electrical when deformed and vice versa [10]. The height from which the drops were injected could be altered by calibrating the height of the nozzle. After the nozzle was adjusted to the correct height and the droplets were clearly visible, the nucleation laser was initiated. A tube of liquid nitrogen was placed below the bottom of the chamber before the trials could begin so that the chamber and water became supercooled. In order to keep a steady flow of the water, 99% pure nitrogen gas pressurised a container of 99% pure water. The chamber had to be vacuum sealed and a sequential vacuum was retained. The stream of droplets needed to start before the vacuum to clean the nozzle at any retained air in its path. The data could then be recorded and analysed. The ice fraction was taken to be the ratio between ice droplets and total number of droplets, calculated by counting the number of droplets that froze. This can indicate whether or not the laser had an effect on the nucleation. In figure 1 the different types of droplets are shown. When the droplets freeze and are in a solid-state they can look slightly different as shown in the bottom line of figure 1. The liquid droplets can either have a clear light point in the middle or be slightly darker.

2.2 Calculations

In order to know how long the time of flight of the droplets was the speed had to be calculated. This could be done with the frequency and the spacing between the droplets. The frequency of the droplets was calculated using the flow rate and either diameter or volume of the droplets. Temperature was also noted by calculating according to the Herz-

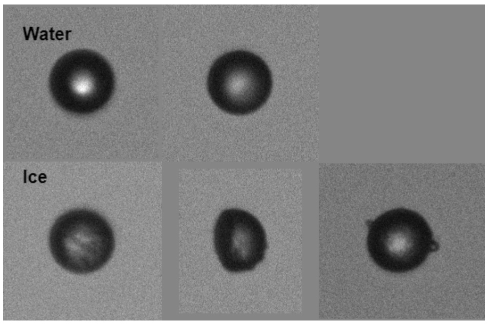


Figure 1: Differences between frozen and liquid droplets.

Knudsen theory. The most important was to calculate the nucleation rate for conclusions. The diameter and spacing was taken as an arithmetic average of the pictures the camera took.

2.2.1 Temperature Estimation

The further away from the nozzle the droplets traveled the lower the temperature of the droplets became. The Hertz-Knudsen theory can then be applied to predict the heat-flow of the droplets. Where $\frac{dTs}{dt}$ is the surface temperature rate of the droplet, $\gamma_e J_{e,max}(T_s) = \frac{P_s(T_s)-P_v}{\sqrt{2\pi m k_B T_s}}$ is the Hertz-Knudsen evaporation rate, (T_s) is the surface temperature, $A_s(t)$ is the surface area of the droplet, $\rho(T_s)$ is the density of the droplet, $\frac{4\pi}{3}(r_{100}^3 - r_{99}^3)$ is the volume between the radius of the whole droplet and the full radius minus one hundredth of the radius, $C_p(T_s)$ is the specific heat capacity and $\Delta H_{vap}(T_s)$ is the enthalpy of evaporation [11].

$$\frac{dTs}{dt} = -\gamma_e J_{e,max}(T_s) \frac{A_s(t)\Delta H_{vap}(T_s)}{\frac{4\pi}{3}(r_{100}^3 - r_{99}^3)\rho(T_s)C_p(T_s)} \tag{1}$$

2.2.2 Speed Estimation

The speed is vital for the calculation of the nucleation rate. To calculate the speed, the flow rate and frequency was used. The spacing and diameter of the droplet need to be used as well. The frequency can be calculated using equation 2. In equation 2, f_{drop} is the frequency of the droplets, Q is the flow rate, D is the diameter of the droplets and V is the volume of the droplets. [12]

$$f_{drop} = \frac{Q}{V_{drop}} = \frac{Q}{\frac{4\pi}{3}(\frac{D_{drop}}{2})^3} \tag{2}$$

Equation 3 uses the spacing and frequency to calculate the speed of the droplets, where s is the speed of the droplets and l_{drop} is the length between the droplets, the spacing.

$$s = l_{drop} \cdot f_{drop} \tag{3}$$

2.2.3 Nucleation Rate

The count of liquid and solid droplets can be used to calculate the nucleation rate using the central nucleation theory. If the nucleation rate is positive, the amount of nucleation increases. If the nucleation rate is zero the amount of nucleation does not change. In order to calculate the nucleation rate, the speed and ice fraction is used. In equation 4, J is the ice nucleation rate, f_{ice} is the ice fraction of the droplets, t is the time it takes the droplets to leave the tip of the nozzle and be captured on an image, V_{drop} is the volume of the droplets, n and n+1 is two consecutive points in time [13].

$$J(t_{n+1/2}) = -\frac{\ln[\frac{(1-f_{ice}(t_{n+1}))}{(1-f_{ice}(t_n))}]}{V_{drop}(t_{n+1} - t_n)} \tag{4}$$

3 Results

In figure 2, the water droplets are visible and in a liquid state. When the droplets left the nozzle they had a formation similar to the figure. They separated shortly after and a few went out of focus from the camera. The longer time of flight the more droplets were out of focus. Frozen droplets were not recorded before the water had reached a temperature of 236 K. The flow rate was 68.5 $\mu L\,min^{-1}$ on average. The diameter of the droplets was in average 25 µm and the spacing between the droplets was in average 95 µm.

In table 1 the different energies of the laser that was used can be examined. Table

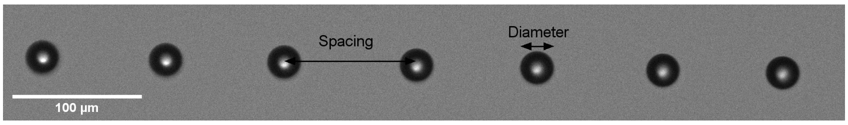


Figure 2: An image of the water droplets from the tip of the nozzle.

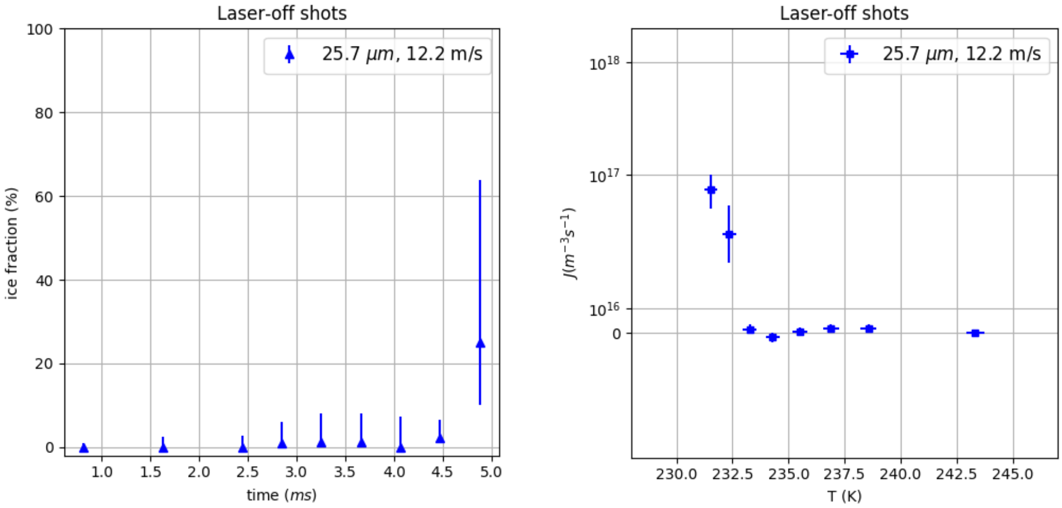
2 shows the different distances form the nozzle the water began to freeze at. Before the height of the nozzle was 40 mm no ice was captured on images and there was no ice fraction. When the height was 50 mm no ice was captured on images either. At 55 mm and 60 mm of distance the ice fractions had increased. Figure 3a, shows the relation between ice fraction and time of flight of the droplets for the laser-off shots due to spontaneous nucleation and figure 3b, shows the relation between the nucleation rate and temperatures for the same shots as in figure 3a. Figure 3b, shows that the lower the temperature the higher the nucleation rate became. Figure 4, shows that the energy did not have a significant impact on the ice fraction.

Total of focused droplets	Water	Ice	Ice fraction (%)	Power (W)	Energy (µJ)
25	25	0	0	3	15
43	41	2	4.65	3	3
90	87	3	3.33	5	5
45	42	3	6.67	7	7
23	22	1	4.35	10	10

Table 1: Ice fraction at 50mm distance with different laser power.

Distance (mm)	Total of focused droplets	Water	Ice	Ice fraction (%)
10	351	351	0	0
20	151	151	0	0
30	141	141	0	0
35	109	108	1	0.92
40	78	77	1	1.28
45	80	79	1	1.25
50	48	48	0	0
55	425	415	10	2.35
60	48	36	12	25

Table 2: Different distances and respective ice fractions without the laser.



(a) A graph depicting ice fraction (%) relative to time (ms).

(b) A graph showing nucleation rate ($m^{-3}s^{-1}$) relative to temperature (K).

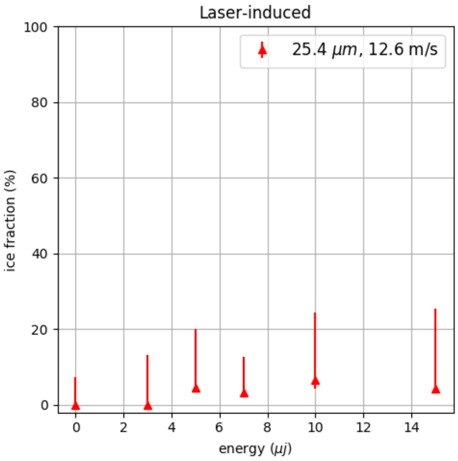


Figure 4: A graph showing ice fraction (%) over energy (µJ).

4 Discussion

This study provided evidence that indicate that the nucleation rate drastically spikes when the water reaches 233 K and that the laser did not have a major effect on the nucleation rate at the specified powers. The graphs indicate that the laser did not have a major effect on the nucleation. Figure 4 shows no big difference between the ice fraction caused by a low powered laser and a fraction caused by a high powered laser. This could have been due to the range of power being too weak. The lower threshold might be above the power levels that was experimented with in the trials. When the laser-induced trials were compared with the non laser-induced, there was limited evidence that the laser had caused any nucleation. Therefore nucleation most likely happened due to its spontaneity and the stochastic nature. The nucleation and spontaneity increased by how long the droplets were in flight and was adjusted by altering the nozzle height. The temperature declined in proportion to how much the time of flight increased. The water could be in a liquid form below 273.15 K which normally would be the freezing point. This was because the droplets were cooled through evaporation. When the droplets have a temperature of less than 235 K the nucleation drastically increases. It is assumed that the nucleation that is happening in this temperature region, is fully homogeneous since, according to figure 4, the laser did not have a major impact and there should therefore be no heterogeneous nucleation due to the laser. The nucleation rate slowly escalates before it reaches the critical freezing point around 233 K and after that the nucleation rate increases rapidly. Since the nucleation rate is based on the ice fraction they should correlate. The results show that the nucleation rate is negative around 234 K which leads to the conclusion that the ice melts to water, and then reforms ice again at a higher nucleation rate than before. The negative nucleation rates are due to the low statistics around some of the measured points and may not be accurate. The ideal nucleation rate should in theory be higher as the droplets get colder. A sufficient number of shots need to be collected in order to avoid poor statistics and consequently, the unexpected drop in the nucleation rates. Shortly after, the results show a dramatic increase of the nucleation rate and water transitions back into ice again faster than previously. The results also included that the focused droplets varied from each trial even though the same amount of images were captured. No frozen droplets were recorded before the water had reached a temperature of 236 K.

4.1 Conclusion

In conclusion this study presents evidence that the laser at the tried power levels could not induce a nucleation process on supercooled water. Therefore future studies does not need to measure these power levels and can start from this study's upper threshold. The nucleation that happened were most likely spontaneous. This study provides evidence that for pure water in vacuum conditions, the transformation to ice occurs close to 233 K. In order to continue this project later, one can try to focus the beam on a spot inside the droplet using focusing lenses to form a bubble that can act as a nucleation site. In this case, the nucleation happens at the surface of the hollow being made inside the droplet. This can give us a lot of information about the time scales when the nucleation has been triggered and can be used for future studies. Information provided by this study states that the tried power levels of the laser did not induce nucleation, therefore this study could be used as a lower threshold for future studies.

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