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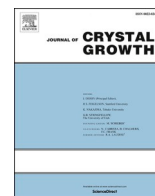
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# Mechanical shock-induced nucleation in solution: Is cavitation necessary?

Yuchen Sun, Andrew J. Alexander\*

School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, Scotland EH9 3FJ, UK

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## ABSTRACT

Mechanical shock-induced nucleation (MSIN) of crystals from aqueous supersaturated solutions of ammonium chloride is reported. A simple apparatus was constructed to expose solutions in glass vials to a single impact, while images were recorded using a fast camera. A strong correlation between cavitation in the liquid and nucleation of solid ammonium chloride was revealed. The measured fraction of solutions nucleated as a function of impact height was fitted using a Poisson model. The mean number of solution samples nucleated increased quadratically with impact height above a threshold height. Analysis of images showed that the accelerations achieved were sufficient to induce cavitation based on the cavitation number proposed by Pan et al. [Proc. Natl. Acad. Sci. USA 114 (2017) 8470]. The use of a hydrophobic coating on the internal glass surface was shown to significantly increase both the number of cavities observed and the probability of MSIN of solid crystals. The results presented suggest that MSIN of ammonium chloride salt is mediated by cavitation.

## 1. Introduction

The nucleation of solid from a metastable liquid by mechanical shock is a phenomenon that is familiar to most chemists. By the term mechanical shock we mean particularly by impact, but there are a variety of interactions including stirring, shaking, or scratching a vessel wall that might share the same mechanism. [1] In many cases, MSIN is considered as trouble and is carefully avoided, for example, when preparing high-quality single crystals for X-ray diffraction. MSIN can be demonstrated easily at home, by hitting a bottle of beer which has been first supercooled in a domestic freezer ( $-20\text{ }^{\circ}\text{C}$ ) for about two hours. Despite widespread familiarity with MSIN, the mechanism for the effect is not certain. The majority of previous studies have focused on single-component supercooled liquids. In the present report, we explore the mechanism for MSIN in supersaturated solutions. As we shall discuss in more detail below, our interest stems from work in our group on laser-induced nucleation, where there appear to be some common mechanistic features. [2]

The first systematic studies of nucleation by impact were conducted by Young and co-workers in 1911. [3,4] It was at first thought that collisions between solid particulate impurities were important. [5] Berkeley, however, suggested that waves of high transient pressure, both positive and negative amplitude, could increase local supersaturation, resulting in nucleation. [6] Uhara et al. studied nucleation by MSIN and by fracture of solids submersed in supercooled liquids. [7] They

concluded that shock waves cause localised bond rupture and ionization, leading to a transient metallic state which promotes structural order. Uhara et al. also considered chemical and physical properties, such as viscosity, that likely prevent MSIN from being achieved in some systems.

The water–ice system has received special interest due to its relevance to atmospheric science and meteorology. The use of rockets and explosive charges to control precipitation of hail stretches back at least to the 14th century, with revivals in interest in these methods in the 19th and 20th centuries. [8] Goyer and co-workers used explosive detonating cord to mimic lightning in a study of ice formation from water droplets at Old Faithful geyser in Wyoming, USA. [9,10] Experiments by Hunt and Jackson suggested that for nucleation of ice from supercooled water, it is the collapse of a cavity that is responsible for nucleation. [11]

Cavitation is the formation of a gas-filled volume within a liquid, caused by negative differential pressure. [12] Cavitation can be induced by shear of the liquid, e.g., near the tip of a rotating blade. The cavity formed is normally short-lived because the pressure difference cannot be sustained. The collapse of a cavity can produce tremendously high local pressures that can cause damage, e.g., to nearby surfaces. A practical method of controlling impact is the shock tube, which employs an explosive release of a gas at high pressure. Sivakumar and Dhas recently used a shock tube to demonstrate precipitation of minerals from groundwater and seawater, which they attributed to acoustic cavitation. [13]

\* Corresponding author.

E-mail address: [andrew.alexander@ed.ac.uk](mailto:andrew.alexander@ed.ac.uk) (A.J. Alexander).

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There is significant interest in external methods of inducing nucleation, such as laser-induced nucleation.[14–17,2] Cavitation in liquid samples can be achieved by focussing laser pulses into supersaturated solutions, and these events can cause crystal nucleation.[18–21] MSIN has been achieved by directing high-energy laser pulses onto an absorbing material in contact with the sample of interest.[22–24] Fischer et al. employed a thin steel boat floated on the surface of a supersaturated solution, which was irradiated with nanosecond laser pulses.[22] With supersaturated glycine solutions, tiny crystals were seen to rain down from the bottom of the boat. The results were explained in terms of lowering of the free-energy barrier to nucleation by the pressure waves transmitted into solution. Non-photochemical laser-induced nucleation (NPLIN) typically employs unfocussed laser pulses passing through a supersaturated solution to induce crystal nucleation. Kacker et al. directed unfocussed nanosecond laser pulses onto an absorbing material in contact with the solution, rather than through it, and observed no nucleation. They concluded that acoustic pressure waves (or resulting cavitation) were not responsible for NPLIN.[25]

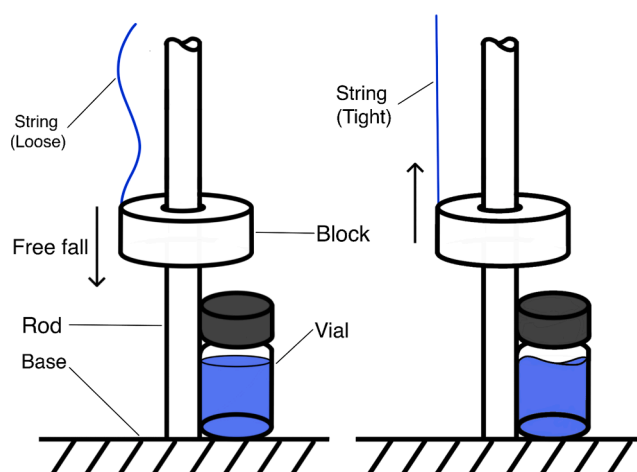
In recent work, our group has compared mechanisms for NPLIN, MSIN and sonocrystallization.[26,27] A leading candidate for the mechanism of NPLIN is cavitation due to transient heating of impurity nanoparticles.[28,29,2] The heating causes fluid in contact with a nanoparticle to vaporize, i.e., spontaneous boiling, also called thermocavitation.[30,31] In the present report, we shall refer to these events simply as cavitation. Just as in cavitation induced by negative pressure, a cavity formed by transient heating will not survive, and will deposit energy on collapse. Although cavitation seems to be a common feature of external nucleation methods, we observe important differences in the product crystals: including size, number and polymorph. For example, in the case of glycine, we suggested that the cavitation events of NPLIN are more energetic, resulting in a preference for the  $\gamma$ -glycine polymorph at lower supersaturations than MSIN or sonocrystallization.[26,32]

The aim of the present work was to explore the mechanism for MSIN in aqueous supersaturated solutions, in particular whether cavitation is involved or not. A simple mechanical apparatus was constructed to make systematic observations. The results indicate a strong correlation between cavitation and nucleation of crystals. In addition, we show that introduction of a hydrophobic interface can enhance the probability of MSIN, and therefore may have applications to control nucleation in some systems.

## 2. Methods

The experimental setup was inspired by Young's experiments.[3,4] It involves hitting the sample vials with a falling block, as illustrated in Fig. 1. The block consisted of a detachable mass mounted on a linear bearing flange, giving a total mass in the range 66–200 g (see Supporting Information for details). The block was mounted on a steel rod (length 1 m, diameter 12 mm) fixed to an iron base. The liquid samples as targets were contained in glass screw-cap vials (volume 10 mL) placed directly under the sliding block, either on the iron base, or on a softer material secured on top of the iron base. A variety of base materials were tested, including layers of paper (80 gsm), sponges (10 and 35 Shore D hardness), and a rubber mat (2 mm thick). We will refer to the iron base as 'hard floor', and the other materials collectively as 'soft floor'. The sliding block was released from a defined impact height ( $d$ ) in the range 5–40 cm. Secondary collisions by the block were prevented by use of an attached tether. Images were recorded with a high-speed digital camera (Huawei P40-Pro) at 7680 frames per second. Illumination was provided with a high-intensity white LED screen (PIXEL k80-sp) placed 30 cm behind the vial.

Samples tested included water, carbonated water (soda water), and aqueous solutions of ammonium chloride salt ( $\text{NH}_4\text{Cl}$ ). The saturation concentration ( $C_{\text{sat}}$ ) of  $\text{NH}_4\text{Cl}$  in water at 25 °C is 7.39 mol  $\text{kg}^{-1}$  (molality).[33] Stock solutions were prepared by dissolving solid  $\text{NH}_4\text{Cl}$



**Fig. 1.** Schematic diagram of the experimental setup. A block (66–200 g) consisting of a weight mounted on a linear bearing, was dropped from a defined height (5–40 cm) onto a glass vial. The surface under the vial was either a hard floor (iron base), or a soft floor (a compressible layer secured onto the iron base). In order to prevent secondary collisions after rebound, the block was recaptured using a tether (denoted by the string).

(99.5%, Tianjin ZhiYuan Chemical Reagent Co. Ltd, China) in deionised water. At a given temperature ( $T$ ) and concentration ( $C$ ) the supersaturation is defined as  $S = C / C_{\text{sat}}$ . Solutions were dissolved at 70 °C, transferred while hot to sample vials, and allowed to cool slowly to 25 °C. To study the effects of a hydrophobic interface on nucleation, half of the inner surfaces of glass vials were coated with a commercially available solution (Rain-X) of hydroxy-terminated polydimethylsiloxane (PDMS) in ethanol and left to dry in air. The coating was applied using a cotton swab soaked in the Rain-X solution. To study the effect of intrinsic impurities, solutions of  $\text{NH}_4\text{Cl}$  were filtered (Millex-GP, 0.22  $\mu\text{m}$  polyethersulfone membrane) at 45 °C into clean vials and allowed to cool. The filtered samples were compared against samples prepared in the same way but without filtering.

## 3. Results and discussion

### 3.1. MSIN of ammonium chloride solutions

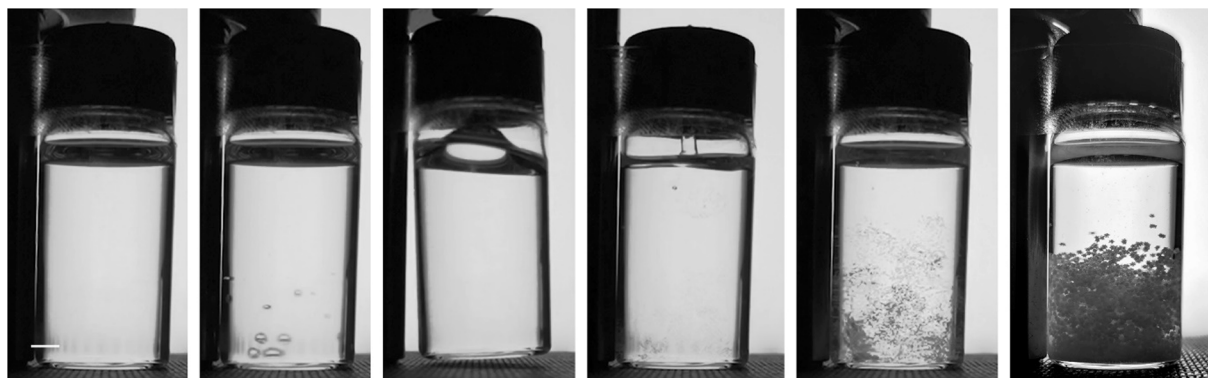
A typical cavitation event resulting in crystal nucleation is shown in Fig. 2. On impact, cavities were seen in the bottom half of the vial, which is where crystal nucleation was also observed. The lifetime of these cavities was approximately 2 ms, and the first crystals were observed at approximately 100 ms. On very few occasions, nucleation appeared to start higher in the solution. Microfiltration of the solutions was found to have no effect on the probability of crystal nucleation.

The initial potential energy of the block  $V$  can be written as

$$V = mgd \quad (1)$$

where  $g$  is the standard acceleration due to gravity ( $g = 9.81 \text{ m s}^{-2}$ ),  $m$  is the mass and  $d$  is the release height of the block. For a 200 g block released at 40 cm, we calculate  $V = 0.785 \text{ J}$ . At 25 °C, these conditions were not sufficient to induce crystal nucleation in solutions at  $C = 8.50 \text{ mol kg}^{-1}$  ( $S = 1.15$ ). However, at  $C = 8.88 \text{ mol kg}^{-1}$  ( $S = 1.20$ ) solutions could be nucleated readily. When the temperature was increased to 35 °C ( $S = 1.09$ ) the 8.88 mol  $\text{kg}^{-1}$  solution could still be nucleated, but at 40 °C ( $S = 1.03$ ) it had become very difficult to induce nucleation by impact. Unsurprisingly, attempts to nucleate crystals from undersaturated solutions failed.

The effect of impact energy was studied systematically by varying the release height. The experiments were carried out with  $m = 66 \text{ g}$  at 35 °C ( $C = 8.88 \text{ mol kg}^{-1}$ ,  $S = 1.09$ ) which gave a good spread in the



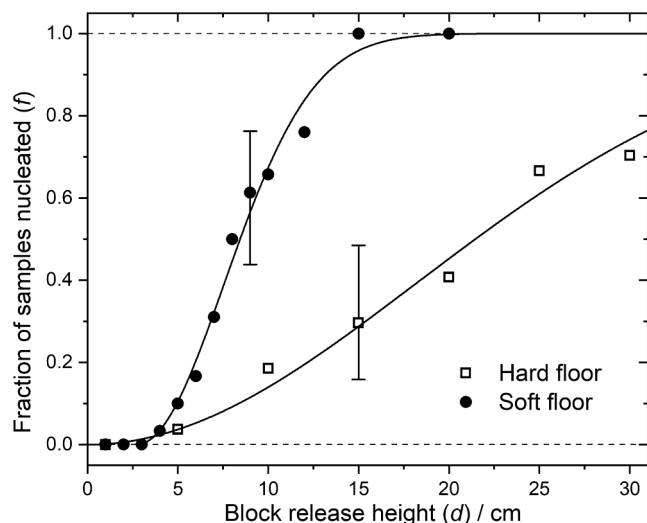
**Fig. 2.** Image sequence of MSIN within glass vial of supersaturated  $\text{NH}_4\text{Cl}$  in water ( $S = 1.20$  at  $25^\circ\text{C}$ ). The vial was hit by a block of 200 g dropped from 40 cm height, with a soft floor (rubber mat) as base. Images from left to right: (1) 1 ms before hitting, showing a clear solution; (2) during impact, cavities can be observed; (3) 10 ms; (4) 100 ms; (5) 1 s; (6) 10 s after impact. The average lifetime of cavities in this example was approximately 2 ms; crystals were first visible approximately 100 ms after hitting. The scale bar represents 5 mm. See corresponding video S1 in the Supporting Information.

number of samples nucleated, as shown in Fig. 3. The probability of nucleation was higher with the soft floor compared to the hard floor. The soft floor allows for some vertical displacement of the vial during the collision, which we discuss further below. The fraction of samples nucleated was seen to increase with impact height, and the data suggest there is a threshold height below which nucleation is not achieved.

The results in Fig. 3 were modelled using a Poisson distribution by considering the probability of obtaining at least one crystal nucleus following impact,

$$p(n \geq 1) = 1 - p(0) = 1 - e^{-\lambda} \quad (2)$$

where  $p(n)$  is the probability of obtaining  $n$  nuclei, and  $\lambda$  is the mean number of nuclei at a given impact height. We previously used a Poisson model to fit results of NPLIN of aqueous KCl solutions, where  $\lambda$  was found to be linearly dependent on the energy of the pulsed (nanosecond) laser light. [34] In contrast to the NPLIN results, we found that the MSIN data here cannot be fitted adequately assuming that  $\lambda$  is linearly proportional to the impact height. A quadratic dependence  $\lambda \propto d^2$  was the simplest model that fitted the data reasonably well. It should be noted



**Fig. 3.** Fraction of samples resulting in crystal nucleation versus block release height. The results were obtained for supersaturated  $\text{NH}_4\text{Cl}$  solution with  $C = 8.88 \text{ mol kg}^{-1}$  at  $35^\circ\text{C}$  ( $S = 1.09$ ). The mass of the sliding block was 66 g, released from various heights ( $d$ ). Experiments were conducted with a hard floor (iron base) or soft floor (rubber mat). At least  $N = 25$  samples were tested at each height. Solid curves represent Poisson-model fits to the data (see text for details). The error bars represent 95% confidence intervals (Wilson score).

that there is no physical justification for this dependence: we note only that it implies  $\lambda \propto v_0^4$ , where  $v_0$  is the impact velocity of the block. The experimental fraction of samples nucleated  $f(d)$  were thus modelled as

$$f(d) = 1 - \exp[-c(d - d_0)^2] \quad (3)$$

where  $c$  is the lability of a sample, i.e., how sensitive the sample is to MSIN, and  $d_0$  is a threshold impact height. [35] The threshold heights were determined to be  $0 \pm 2.1 \text{ cm}$  and  $2.7 \pm 0.4 \text{ cm}$  for hard and soft floors, respectively. The fits reveal uncertainty on whether or not there is a threshold height using the hard floor. The lability obtained for the soft floor  $(2.1 \pm 0.3) \times 10^{-2} \text{ cm}^{-2}$  was higher than that for the hard floor  $(1.5 \pm 0.3) \times 10^{-4} \text{ cm}^{-2}$ .

The images in Fig. 2, and the observation of a threshold release height for the soft floor, strongly suggest that cavitation precedes crystal nucleation in solution. To test for a causal link, a set of 30 trials was conducted using different materials at the base, including hard and soft floors. On review of the video images, each result was classified as to whether cavitation, nucleation, or both, were observed. The results are summarized in Table 1, which illustrates clearly that when cavitation was observed, crystal nucleation was always observed. When no cavitation was observed, the chances of seeing nucleation were approximately one in three.

We analysed the data in Table 1 using Boschloo's Exact Test, at 95% confidence level (see Supporting Information for details). The null hypothesis was  $H_0$ : nucleation is independent of cavitation.  $H_0$  was rejected with a p-value of  $7.1 \times 10^{-5}$ , which indicates that it is highly unlikely that the strong correlation between cavitation and crystal nucleation was obtained by chance alone.

Our experiments are constrained by the ability to see cavities: so, it is possible that cavities were too small, or cavity lifetimes too short, to be observed. Cavities observed with a hard floor were always significantly smaller than those seen with a soft floor, making observations more difficult. The curvature of the cylindrical glass vial also makes it difficult to observe objects nearer the vertical walls of the vial. On the other

**Table 1**

Contingency table correlating the number of vials that showed cavitation and crystal nucleation. A set of 30 trials was conducted, with mass of block 200 g, impact height 20 cm, concentration  $8.88 \text{ mol kg}^{-1}$  ( $S = 1.20$  at  $25^\circ\text{C}$ ). Different materials were used as the base under the vial, including both hard and soft floors. It is evident that when cavitation was observed, crystal nucleation was always observed.

		Crystal nucleation?	
		Yes	No
Cavitation?	Yes	16	0
	No	5	9



hand, there may be mechanisms for MSIN that do not involve cavitation. The strong correlation demonstrated in Table 1 suggests that cavitation is necessary for crystal nucleation under the conditions tested.

### 3.2. Factors affecting cavitation pattern

To understand better how mechanical shock induces nucleation, we investigated several factors that affect the cavitation pattern: (i) use of soft versus hard floor; (ii) shaking vials before impact; and (iii) hydrophobicity of the internal walls of the glass vials.

Fig. 4(a) shows a comparison of impact on distilled water using soft versus hard floors. As was found in ammonium chloride solutions, cavities are observed predominantly near the bottom of the vial. The bottom of the vial is the region where the water is stretched due to its adhesion to the glass and the inertia of the liquid, as illustrated schematically in Fig. 4(b). As noted above, a hard floor prevents downward displacement of the vial, and therefore hinders the stretching of the liquid, so less cavitation was observed.

Pan et al. have recently proposed a dimensionless parameter to predict whether cavitation will occur under conditions of high acceleration, as used in the present work.[36] The cavitation number,  $Ca$  is calculated as

$$Ca = \frac{p_r - p_v}{\rho ah} \quad (4)$$

where  $p_r$  is the external (reference) pressure;  $p_v$  and  $\rho$  are the vapor pressure and density of the liquid, respectively;  $a$  is the acceleration; and  $h$  is the height of the column of liquid in the vessel. A broad range of experimental trials from two research groups validated the proposal that  $Ca < 1$  is a likely indicator for cavitation.[36].

For saturated aqueous  $\text{NH}_4\text{Cl}$  ( $S = 1$ ) at 25 °C we determined values  $p_v = 2512$  Pa and  $\rho = 1074$  kg m<sup>-3</sup> from data available in the literature. [33,37] Experiments were conducted on an undersaturated solution of aqueous  $\text{NH}_4\text{Cl}$  ( $S = 0.9$ ), using a block with  $m = 66$  g, release height  $d = 20$  cm, and sponge as soft floor. The height of liquid in vials was  $h = 3.5$  cm, and the external pressure was  $p_r = 101325$  Pa (1 atm). By analysis of frames from high-speed video, we estimated  $a = 3190$  m s<sup>-2</sup>. Using Eq. (4) we calculate  $Ca = 0.81$ , showing that these conditions would be expected to result in cavitation, as was observed. Experiments at lower values of  $d$ , for which cavitation was not observed, yielded values  $Ca \geq 1$ , again in good agreement with Pan et al. (see Supporting Information for details).

The results above provide a useful indicator for how to increase the number of crystals nucleated by MSIN, by modifying pressures (numerator of Eq. (4)) or the inertial forces on the liquid (denominator of Eq. (4)). For example, MSIN may be promoted by using solvent mixtures with lower vapour pressure or by lowering the external

pressure. Higher accelerations, increasing the density of the solvent, or increasing the column length of fluid in the vessel would also enhance MSIN. It is not possible to make quantitative predictions of the number of nuclei, however, since Eq. (4) tells us only if cavitation is likely, but not how many cavitation events will occur. Moreover, we do not know how many crystal nuclei are produced by a single cavitation event.

### 3.3. Influence of shaking and additives

It was found that shaking the vial prior to being struck can alter its cavitation pattern under impact. This effect was first noticed from a vial that fell to the floor. Fig. 5 shows one vial, containing an undersaturated aqueous solution of  $\text{NH}_4\text{Cl}$  ( $S = 0.14$ ), which was struck 10 times in sequence. However, before the 6th impact, the vial was shaken by hand: the next impact produced many more, and smaller, cavities. This effect was observed to decline during subsequent impacts over the period of about a minute. Such a decline occurred whether the vial was hit or not

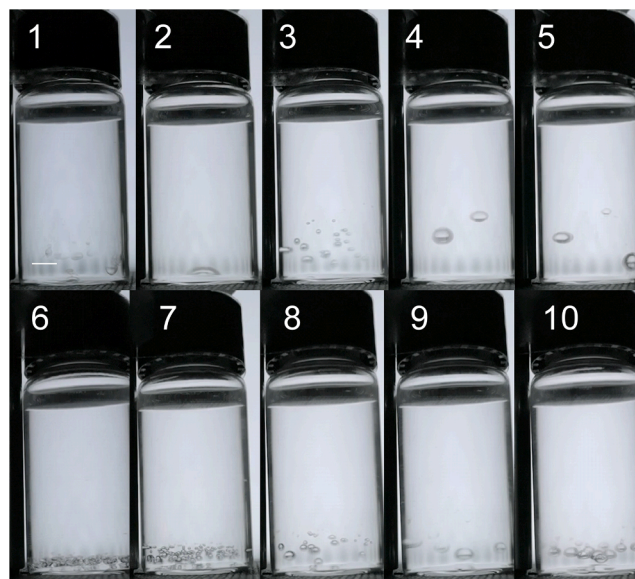


Fig. 5. Demonstration of the effects of shaking a vial. The vial contains an undersaturated aqueous solution of  $\text{NH}_4\text{Cl}$  ( $C = 0.98$  mol kg<sup>-1</sup>,  $S = 0.14$ , 25 °C). The conditions used were  $m = 200$  g,  $d = 20$  cm, soft floor (rubber mat). The same vial was hit 10 times repeatedly (numbered in sequence) with a pause of 10 s between hits. Before the 6th impact, the vial was shaken by hand. It can be seen that, as a result of the shaking, subsequent impacts created significantly more and smaller cavities. From impacts 6 to 10 the effect of shaking diminished quickly. The scale bar in image 1 represents 5 mm.

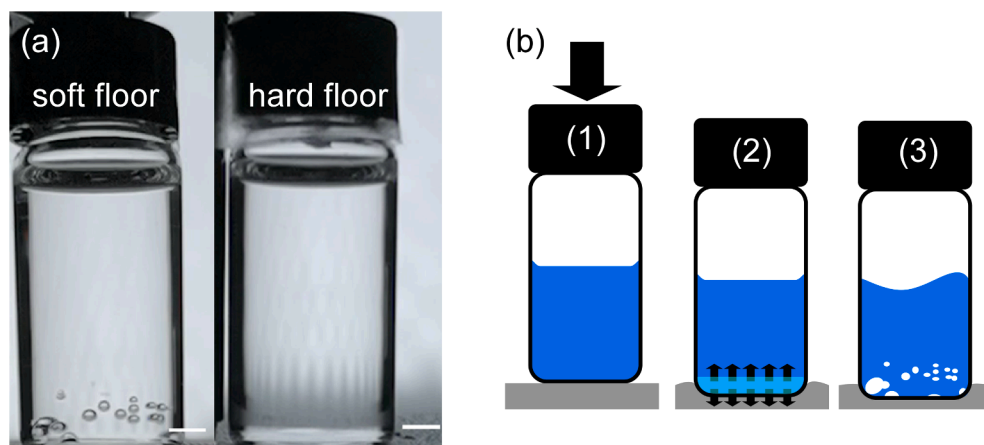


Fig. 4. (a) Cavitation patterns observed at the moment of impact on distilled water at 25 °C using the soft floor (left), and hard floor (right). The scale bars represent 5 mm. Many cavities were observed with soft-floor materials, e.g., rubber mat. The vertical fringe patterns seen in the images are an artifact of the LED screen. (b) Schematic diagram illustrating the cavitation mechanism. (1) The glass vial experiences the impact force and moves downward; (2) water at the bottom of the vial is stretched due to adhesion and the inertia of the liquid, resulting in a low-pressure region; (3) water in the low-pressure region is ruptured to form cavities.

during this period. The same effect of shaking was observed with vials containing water or undersaturated aqueous NaCl solutions.

The increased number of cavities observed following shaking is likely due to dispersion of sites where cavities can be nucleated. It seems most likely that the act of shaking entrains gas from the headspace in the vial, and disperses microscopic bubbles of gas. A gas-filled bubble has sufficient internal pressure to survive longer than a transient cavity. These microbubbles act as nucleation points for cavitation during subsequent impacts. Over time, the microbubbles will coalesce or dissolve, such that the effect disappears in about a minute.

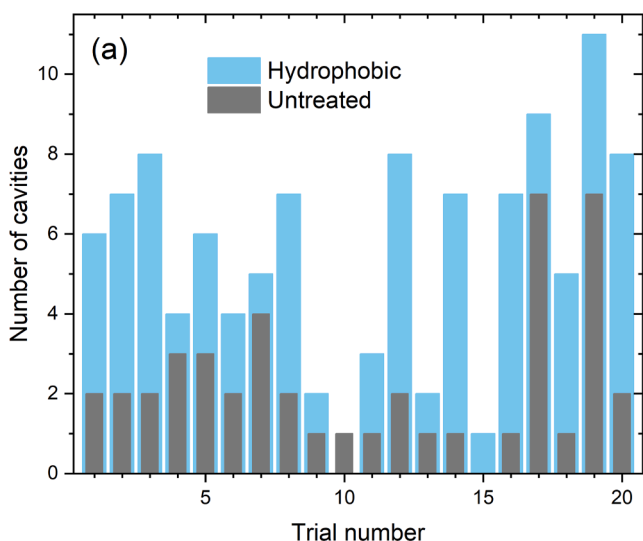
In NPLIN with pulsed lasers it is believed that heating of solid impurity nanoparticles, such as iron oxide, causes cavitation that results in crystal nucleation. It was found that filtration substantially reduces NPLIN due to removal of impurity particles.[28,38] To determine if solid impurities affect MSIN, mechanical shock tests were carried out on water samples doped with 10 ppm insoluble  $\text{Fe}_2\text{O}_3$  fine particles. No significant difference in cavitation was observed. This result is consistent with our prior observation (Section 3.1) that filtration did not affect the nucleation of  $\text{NH}_4\text{Cl}$  by MSIN.

We found that adding small quantities (1% w/w) of liquid detergent or acetic acid to water did not visibly change the cavitation observed. These additives might have acted as surfactants to stabilise microbubbles or hinder coalescence. According to Craig et al., simple salts such as NaCl and  $\text{NH}_4\text{Cl}$ , dissolved at concentrations  $C > 0.3$  M in water, can act to hinder bubble coalescence.[39] We found that aqueous solutions of NaCl ( $0.90 \text{ mol kg}^{-1}$ ,  $S = 0.15$ ) and  $\text{NH}_4\text{Cl}$  ( $0.98 \text{ mol kg}^{-1}$ ,  $S = 0.13$ ) at  $25^\circ\text{C}$  did not show noticeable differences in cavitation pattern compared to distilled water. Saturated  $\text{NH}_4\text{Cl}$  solution ( $7.93 \text{ mol kg}^{-1}$ ,  $S = 1$ ) did produce more cavities under impact, though this was judged to be a relatively weak effect.

As a practical method of enhancing MSIN, rapid shaking of the solution would be expected to increase the nucleation of solid in two ways: (a) by increasing the inertial forces exerted, as per Eq. (4); and (b) promoting dispersion of gaseous nucleation sites throughout the liquid. Other methods could be employed to increase the dissolved gas content prior to shaking, but if the concentration of gas is too high, it could promote nucleation of the gas itself, hindering cavitation and reducing MSIN of crystals.

### 3.4. Effect of hydrophobic surface on MSIN

It can be seen in Fig. 4 that some cavities are nucleated at the glass wall of the vial. To study the effect of the glass interface, a direct comparison was made by treating half of the inner glass surface of vials with



a hydrophobic coating, leaving the other half untreated. Samples of water were exposed to impact as before, and the results are shown in Fig. 6. It was found that there were consistently more cavities in the treated, hydrophobic side compared to the untreated side of each vial. The counts in Fig. 6 were analysed using a paired, two-tail  $t$ -test (95% confidence level) with null hypothesis  $H_0$ : cavitation is independent of surface treatment.  $H_0$  was rejected with a  $p$ -value of  $1.4 \times 10^{-6}$ .

We observed that differences in cavitation between the hydrophobic and untreated sides of the vial became less obvious at both lower and higher impact energies. At low impact energies, few cavities were observed, so the correlation was not clear. At higher impact forces, the large number of cavitation events hindered accurate location and counting.

The preferential cavitation at a hydrophobic surface is consistent with a classical model of nucleation.[40,41] The free-energy barrier  $\Delta G(r, \phi)$  for heterogeneous nucleation of a vapor cavity of radius  $r$  on a flat surface can be written

$$\Delta G(r, \phi) = \Delta G_{\text{hom}}(r) \Psi(\phi) \quad (5)$$

where  $\Delta G(r)$  is the free-energy barrier for homogeneous nucleation of a vapour cavity in the bulk.  $\Psi(\phi) = \frac{1}{4}(1 + \cos\phi)^2(2 - \cos\phi)$  is a geometrical factor and  $\phi = \cos^{-1}[(\gamma_{\text{SV}} - \gamma_{\text{SL}})/\gamma_{\text{LV}}]$  is the contact angle between the spherical cap of the nucleating cavity and the solid surface (see Supporting Information). The contact angle is written in terms of the interfacial tensions  $\gamma$  at the solid–vapor (SV), solid–liquid (SL) and liquid–vapor (LV) interfaces. The case  $\phi < 90^\circ$  corresponds to a hydrophilic surface;  $\phi > 90^\circ$  for a hydrophobic surface. The value of the geometrical factor  $\Psi(\phi) \rightarrow 0$  as  $\phi \rightarrow 180^\circ$ , i.e.,  $\Delta G(r, \phi)$  will decrease as the affinity of the cavity for the hydrophobic surface becomes greater. Therefore, the barrier to nucleation of a vapour cavity on a hydrophobic surface is lowered compared to the bulk homogeneous value.

To determine if the hydrophobic treatment also increased the probability of nucleation of the solid, we conducted impact experiments on samples of supersaturated aqueous  $\text{NH}_4\text{Cl}$  solution ( $S = 1.09$ ,  $35^\circ\text{C}$ ). The results are shown as a sequence of images in Fig. 7. Note that this sequence was recorded at low frame rate, so cavitation was not observed directly. The results show that the solid nucleated exclusively in the left-hand side of the vial, which had been treated internally with the hydrophobic coating. The untreated (right-hand) side of the vial showed no nucleation of crystals.

The images in Fig. 7 warrant some further comments. Correlating precise locations of cavities with crystals in the current setup was difficult, mainly due to a limit on the duration that can be recorded at high frame rate, coupled with the long time for crystals to become



Fig. 6. (a) Counts of cavities, on the hydrophobic-coated side compared to the untreated side, for 20 trials using sample vials under identical conditions of mechanical shock ( $m = 200 \text{ g}$ ,  $d = 20 \text{ cm}$ , soft floor). The assignment of cavities formed near the vertical treated–untreated boundary were decided by the central point of the cavity. (b) Example image of a vial of distilled water at  $25^\circ\text{C}$  showing the resulting cavitation. The left half of the inner glass surface was given a hydrophobic coating; the right half was left untreated. The scale bar represents 5 mm. It can be seen that more cavities were formed in the half with the hydrophobic coating.



**Fig. 7.** Sequence of images demonstrating MSIN of  $\text{NH}_4\text{Cl}$  crystals. The scale bar represents 5 mm. See video S2 in the Supporting Information. The left half of the inner surface of the vial has been treated with a hydrophobic coating. The right half has been left untreated; the vertical boundary has been marked with a pen. The deformed liquid meniscus demonstrates the water repellent feature of the coating. The solution was aqueous supersaturated  $\text{NH}_4\text{Cl}$  ( $C = 8.88 \text{ mol kg}^{-1}$ ,  $S = 1.09$ ,  $35^\circ\text{C}$ ). The vial was struck with a block of mass  $m = 200 \text{ g}$  from a height  $d = 10 \text{ cm}$ , using a soft floor as base. Images from left to right: 2 s, 3 s, 10 s, 20 s and 60 s after impact. It can be seen that the solid nucleates exclusively in the hydrophobic half of the vial. After 10 s (third panel) the crystals have sedimented to the bottom. By 60 s there is evidence of secondary nucleation coupled with internal fluid flow.

visible (2 s). At 10 s after impact (third panel) the crystals have already sedimented to the bottom, and appear to form a semi-circle nearer the walls of the vial. Cavitation does not take place exclusively at the hydrophobic surfaces. The extreme distinction between the two sides shown in Fig. 7 was only observed in a window of conditions near to the threshold of crystal nucleation. In conditions that favour nucleation, e.g., higher supersaturation or greater impact acceleration, the distinction between hydrophobic and untreated sides became less obvious. The reason for this is an increase in the relative proportion of cavitation events originating in the bulk compared to the surfaces (e.g., see Fig. 2). In general, however, we found that more crystals were produced on the side with the hydrophobic coating.

The results shown in Fig. 7 support the strong correlation observed in Table 1, and the hypothesis that cavitation is necessary for MSIN of solid crystals. The results of Fig. 6 demonstrated that in water, more cavities were produced on the side of the vial with internal hydrophobic coating. With supersaturated salt solution at similar impact energies, it was demonstrated that nucleation of solid occurred exclusively on the hydrophobic side. It might be argued that the solid itself prefers to nucleate on the hydrophobic side, but this seems unlikely: the crystalline structure of ammonium chloride is not commensurate with either the amorphous glass surface, or the hydrophobic coating. More importantly, we have seen no evidence for enhancement of spontaneous nucleation of inorganic salts in vials with an internal hydrophobic coating. Since cavitation can be promoted by the hydrophobicity of the surface, it may be possible to define interfacial regions where MSIN of solids is more active: to control nucleation, for example, at specific locations within a tubular flow reactor.

#### 4. Conclusions

In summary, we have investigated the nucleation of solid crystals from supersaturated solutions exposed to mechanical impact. A simple experimental setup was constructed to drop a weight onto a sample vial while recording images at high frame rates. Analysis of images showed that the MSIN conditions were consistent with predictions using a cavitation number based on the inertial forces experienced by the liquid. The correlation between cavitation in the liquid and the nucleation of

solid was shown to be very strong. Experiments using hydrophobic coatings provided further support that MSIN is mediated by cavitation, at least for the system and conditions tested in the present work. Our study points to some simple measures that could be employed to increase the number of crystals nucleated. These measures include dispersion of gas nuclei in the liquid, for example by shaking prior to impact; and use of hydrophobic coatings, for example to promote MSIN or sonocrystallization at specific locations in a tubular crystallizer.

#### CRediT authorship contribution statement

**Yuchen Sun:** Methodology, Validation, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Andrew J. Alexander:** Conceptualization, Methodology, Formal analysis, Data curation, Visualization, Writing – review & editing, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcrysgro.2022.126786>.



## References

- [1] J.W. Mullin, *Crystallization*, 4th ed., Butterworth-Heinemann, Oxford, 2001.
- [2] A.J. Alexander, P.J. Camp, Non-photochemical laser-induced nucleation, *J. Chem. Phys.* 150 (2019), 040901, <https://doi.org/10.1063/1.5079328>.
- [3] S.W. Young, Mechanical Stimulus to Crystallization in Super-Cooled Liquids, *J. Am. Chem. Soc.* 33 (1911) 148–162, <https://doi.org/10.1021/ja02215a003>.
- [4] S.W. Young, W.J. Van, Sicklen, The Mechanical Stimulus to Crystallization, *J. Am. Chem. Soc.* 35 (1913) 1067–1078, <https://doi.org/10.1021/ja02198a002>.
- [5] S.W. Young, R.J. Cross, The Mechanical Stimulus to Crystallization. II, *J. Am. Chem. Soc.* 33 (1911) 1375–1388, <https://doi.org/10.1021/ja02221a013>.
- [6] Berkeley, Solubility and supersolubility from the osmotic standpoint, *Phil. Mag.* 24 (1912) 254–268.
- [7] I. Uhara, S. Doi, M. Makino, S. Teratani, Crystal nucleation given rise by fracturing or by mechanical shock, *Kolloid-Zeitschrift Und Zeitschrift Für Polymere.* 244 (1971) 218–222, <https://doi.org/10.1007/BF02291729>.
- [8] G.G. Goyer, Effects of Lightning on Hydrometeors, *Nature.* 206 (1965) 1203–1209, <https://doi.org/10.1038/2061203b0>.
- [9] G.G. Goyer, Mechanical Effects of a Simulated Lightning Discharge on the Water Droplets of 'Old Faithful' Geysers, *Nature.* 206 (1965) 1302–1304, <https://doi.org/10.1038/2061302a0>.
- [10] G.R. Edwards, L.F. Evans, S.D. Hamann, Nucleation of Ice by Mechanical Shock, *Nature.* 223 (1969) 390–391, <https://doi.org/10.1038/223390a0>.
- [11] J.D. Hunt, K.A. Jackson, Nucleation of Solid in an Undercooled Liquid by Cavitation, *J. Applied Physics.* 37 (1966) 254–257, <https://doi.org/10.1063/1.1707821>.
- [12] C.E. Brennen, *Cavitation and Bubble Dynamics*, Oxford University Press, New York, 1995.
- [13] A. Sivakumar, S.A.M.B. Dhas, Shock-wave-induced nucleation leading to crystallization in water, *J. Applied Crystallography.* 52 (2019) 1016–1021, <https://doi.org/10.1107/S1600576719009488>.
- [14] B.A. Garetz, J.E. Aber, N.L. Goddard, R.G. Young, A.S. Myerson, Nonphotochemical, Polarization-Dependent, Laser-Induced Nucleation in Supersaturated Aqueous Urea Solutions, *Phys. Rev. Lett.* 77 (1996) 3475–3476, <https://doi.org/10.1103/PhysRevLett.77.3475>.
- [15] T. Sugiyama, T. Adachi, H. Masuhara, Crystallization of Glycine by Photon Pressure of a Focused CW Laser Beam, *Chem. Lett.* 36 (2007) 1480–1481, <https://doi.org/10.1246/cl.2007.1480>.
- [16] T. Sugiyama, K. Yuyama, H. Masuhara, Laser Trapping Chemistry: From Polymer Assembly to Amino Acid Crystallization, *Accounts Chem. Res.* 45 (2012) 1946–1954, <https://doi.org/10.1021/ar300161g>.
- [17] Y. Liu, M.R. Ward, A.J. Alexander, Polarization independence of laser-induced nucleation in supersaturated aqueous urea solutions, *Physical Chemistry Chemical Physics.* 19 (2017) 3464–3467, <https://doi.org/10.1039/C6CP07997K>.
- [18] A. Soare, R. Dijkink, M.R. Pascual, C. Sun, P.W. Cains, D. Lohse, A.I. Stankiewicz, H.J.M. Kramer, Crystal Nucleation by Laser-Induced Cavitation, *Cryst. Growth Des.* 11 (2011) 2311–2316, <https://doi.org/10.1021/cg2000014>.
- [19] J.A. Jacob, S. Sorgues, A. Dazzi, M. Mostafavi, J. Belloni, Homogeneous Nucleation-Growth Dynamics Induced by Single Laser Pulse in Supersaturated Solutions, *Crystal Growth & Design.* 12 (2012) 5980–5985, <https://doi.org/10.1021/cg301024t>.
- [20] S.A. Gharib, A.K. El Omar, A. Naja, A. Deniset-Besseau, S.A. Denisov, P. Pernot, M. Mostafavi, J. Belloni, Anisotropic Time-Resolved Dynamics of Crystal Growth Induced by a Single Laser Pulse Nucleation, *Crystal Growth & Design.* 21 (2021) 799–808, <https://doi.org/10.1021/acs.cgd.0c01016>.
- [21] J. Yu, J. Yan, L. Jiang, Crystallization of Polymorphic Sulfathiazole Controlled by Femtosecond Laser-Induced Cavitation Bubbles, *Crystal Growth & Design.* 21 (2021) 3202–3210, <https://doi.org/10.1021/acs.cgd.0c01476>.
- [22] A. Fischer, R. M. Pagni, R. N. Compton, D. Kondepudi, Laser Induced Crystallization, in: P. Jena, A. W. Castleman (Eds.), *Nanoclusters: A Bridge across Disciplines*, Elsevier, Amsterdam, The Netherlands, 2010.
- [23] N. Mirsaleh-Kohan, A. Fischer, B. Graves, M. Bolorizadeh, D. Kondepudi, R. N. Compton, Laser Shock Wave Induced Crystallization, *Crystal Growth & Design.* 17 (2017) 576–581, <https://doi.org/10.1021/acs.cgd.6b01437>.
- [24] Y. Ren, J. Lee, K.M. Hutchins, N.R. Sottos, J.S. Moore, Crystal Structure, Thermal Properties, and Shock-Wave-Induced Nucleation of 1,2-Bis(phenylethynyl) benzene, *Crystal Growth & Design.* 16 (2016) 6148–6151, <https://doi.org/10.1021/acs.cgd.6b01119>.
- [25] R. Kacker, S. Dhingra, D. Irimia, M.K. Ghatkesar, A. Stankiewicz, H.J.M. Kramer, H. B. Eral, Multiparameter Investigation of Laser-Induced Nucleation of Supersaturated Aqueous KCl Solutions, *Cryst. Growth Des.* 18 (2018) 312–317, <https://doi.org/10.1021/acs.cgd.7b01277>.
- [26] Y. Liu, M.H. van den Berg, A.J. Alexander, Supersaturation dependence of glycine polymorphism using laser-induced nucleation, sonocrystallization and nucleation by mechanical shock, *Phys. Chem. Chem. Phys.* 19 (2017) 19386–19392, <https://doi.org/10.1039/C7CP03146G>.
- [27] E.R. Barber, M.R. Ward, A.D. Ward, A.J. Alexander, Laser-induced nucleation promotes crystal growth of anhydrous sodium bromide, *CrystEngComm.* 23 (2021) 8451–8461, <https://doi.org/10.1039/D1CE01180D>.
- [28] M.R. Ward, A.M. Mackenzie, A.J. Alexander, Role of Impurity Nanoparticles in Laser-Induced Nucleation of Ammonium Chloride, *Cryst. Growth Des.* 16 (2016) 6790–6796, <https://doi.org/10.1021/acs.cgd.6b00882>.
- [29] J.O. Sindt, A.J. Alexander, P.J. Camp, Effects of nanoparticle heating on the structure of a concentrated aqueous salt solution, *J. Chem. Phys.* 147 (2017), <https://doi.org/10.1063/1.5002002>.
- [30] M.R. Ward, W.J. Jamieson, C.A. Leckey, A.J. Alexander, Laser-induced nucleation of carbon dioxide bubbles, *J. Chem. Phys.* 142 (2015), 144501, <https://doi.org/10.1063/1.4917022>.
- [31] N. Hidman, G. Sardina, D. Maggiolo, H. Ström, S. Sasic, Numerical Frameworks for Laser-Induced Cavitation: Is Interface Supersaturation a Plausible Primary Nucleation Mechanism? *Crystal Growth & Design.* 20 (2020) 7276–7290, <https://doi.org/10.1021/acs.cgd.0c00942>.
- [32] D. Irimia, J.J. Shirley, A.S. Garg, D.P.A. Nijland, A.E.D.M. van der Heijden, H.J. M. Kramer, H.B. Eral, Influence of Laser Parameters and Experimental Conditions on Nonphotochemical Laser-Induced Nucleation of Glycine Polymorphs, *Crystal Growth & Design.* 21 (2021) 631–641, <https://doi.org/10.1021/acs.cgd.0c01415>.
- [33] D. Lide, ed., *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Boca Raton, FL, 2005.
- [34] M.R. Ward, A.J. Alexander, Nonphotochemical Laser-Induced Nucleation of Potassium Halides: Effects of Wavelength and Temperature, *Cryst. Growth Des.* 12 (2012) 4554–4561, <https://doi.org/10.1021/cg300750c>.
- [35] A.J. Alexander, P.J. Camp, Single Pulse, Single Crystal Laser-Induced Nucleation of Potassium Chloride, *Cryst. Growth Des.* 9 (2009) 958–963, <https://doi.org/10.1021/cg8007415>.
- [36] Z. Pan, A. Kiyama, Y. Tagawa, D.J. Daily, S.L. Thomson, R. Hurd, T.T. Truscott, Cavitation onset caused by acceleration, *Proc Natl Acad Sci USA* 114 (2017) 8470, <https://doi.org/10.1073/pnas.1702502114>.
- [37] G. Edgar, W.O. Swan, The Factors Determining the Hygroscopic Properties of Soluble Substances. I. The Vapor Pressures of Saturated Solutions, *J. Am. Chem. Soc.* 44 (1922) 570–577, <https://doi.org/10.1021/ja01424a014>.
- [38] N. Javid, T. Kendall, I.S. Burns, J. Sefcik, Filtration Suppresses Laser-Induced Nucleation of Glycine in Aqueous Solutions, *Cryst. Growth Des.* 16 (2016) 4196–4202, <https://doi.org/10.1021/acs.cgd.6b00046>.
- [39] V.S.J. Craig, B.W. Ninham, R.M. Pashley, The effect of electrolytes on bubble coalescence in water, *J. Phys. Chem.* 97 (1993) 10192–10197, <https://doi.org/10.1021/j100141a047>.
- [40] Volmer, Masunx, *Kinetik der Phasenbildung*, Verlag von Theodor Steinkopff, Dresden und Leipzig, 1939.
- [41] M. Gallo, F. Magaletti, C.M. Casciola, Heterogeneous bubble nucleation dynamics, *Journal of Fluid Mechanics.* 906 (2021) A20, <https://doi.org/10.1017/jfm.2020.761>.