Non-photochemical laser-induced crystal nucleation by evanescent wave

Martin R. Ward, Alasdair Rae and Andrew J. Alexander*

School of Chemistry, University of Edinburgh, Edinburgh, Scotland, EH9 3JJ

**e-mail: andrew.alexander@ed.ac.uk*

Abstract

Crystal nucleation at a glass-solution interface has been demonstrated by evanescent-wave laser-induced nucleation for the first time. Nucleation was induced in supersaturated aqueous potassium chloride (KCl) solutions. The interaction volume was estimated to be less than 2 nL, localized to within approximately 100 nm of the interface. Measurements of the power dependence of nucleation events showed a laser-power threshold that was approximately 3 times higher than experiments in bulk solution; the average number of nucleation events above threshold was similar to bulk. Surfaces treated with a hydrophobic polydimethylsiloxane-based coating showed no nucleation over the coated regions. The localization offered by this method has significant potential benefit for studies of nucleation mechanism, or for patterning of crystal nuclei in two dimensions.

1. Introduction

The process of nucleation of a solid phase from liquid is both economically important and of fundamental scientific interest. The major challenge to studying spontaneous, homogeneous nucleation is its random nature, making it impossible to predict where or when it will occur. Some control over the locus and time of nucleation would offer tremendous advantages to studying the mechanism. Recently, the advent of pulsed-laser methods has opened up new possibilities for studying nucleation.¹⁻⁴ Laser-induced nucleation experiments typically involve passing short timescale (< 20 ns) laser pulses through samples that are in a metastable state, e.g., supersaturated solutions. At the highest power densities ($\sim \text{GW cm}^{-2}$) and shortest pulse-durations (< 10 ps) used for laser-induced nucleation, the mechanism may be classed as photochemical (e.g., resulting from ion or radical formation); by contrast, non-photochemical laser-induced nucleation (NPLIN) employs longer pulse durations (> 100 ps) and much lower power densities ($\sim \text{MW cm}^{-2}$).⁵⁻⁹

Several mechanisms have been put forward to describe NPLIN. The *pre-nucleating cluster mechanism* is based upon the existence of clusters of solute prior to nucleation; these clusters are thought to be dense, disordered (possibly “liquid-like”) aggregates of solute and solvent.¹⁰⁻¹² The transient electric field of the laser pulse lowers the free-energy of the cluster through interaction with its polarizability, causing it to re-arrange its structure to become a nucleus. An alternative is a

photothermal mechanism, through which nanoparticles in the solution may be heated by the laser pulse, causing a rapid increase in temperature leading to a localized shockwave, or transient bubble formation.^{6, 13} In practice, different NPLIN mechanisms may be difficult to distinguish and may operate under different experimental conditions.

Aside from the underlying mechanism, it is clear that NPLIN offers a significant degree of control over the timing of nucleation, and better control over the spatial location of nucleation. Early NPLIN experiments probed large ($\sim 1 \text{ cm}^3$) volumes of the bulk sample.^{1, 11, 14} To achieve more localized control, Sugiyama, Masuhara and co-workers nucleated crystals of glycine by means of focusing of an intense continuous-wave laser beam using a microscope objective with a high numerical aperture.¹⁵⁻¹⁸ Using an agarose gel, Duffus *et al.* demonstrated localization of KCl nucleation to within $\sim 0.1 \text{ mm}$ with unfocussed, pulsed-laser light.¹⁹ More recently, Fang *et al.* have demonstrated nucleation in levitated aqueous KCl microdroplets (diameter $\sim 25 \text{ }\mu\text{m}$) using laser pulses.²⁰ There may be limitations on spatial localization, however. Tight focusing of the laser beam using objective lenses is not ideally suited to NPLIN because of the reduced probability of illuminating precursor particles or clusters. Focusing also tends to increase the power density to a regime where photochemical nucleation will occur, e.g., causing ionization or breakdown of the solvent. Because of the short penetration depth, we considered that evanescent waves might be useful for localizing NPLIN.

The word evanescent comes from the Latin *evanescere*, meaning “to vanish”. Evanescent waves can be formed at the point of total internal reflection (TIR) of an electromagnetic wave at an interface (Figure 1). The critical angle of incidence for total internal reflection is given by $\theta_c = \sin^{-1}(n_2 / n_1)$, where the refractive index changes from n_1 to n_2 at the interface. The evanescent wave results from boundary conditions on the continuity of the electromagnetic field at the interface.²¹ The electric field penetrates into the second medium (n_2) perpendicular to the interface, and its amplitude decays exponentially with distance propagated. In the present paper we demonstrate evanescent-wave NPLIN (ew-NPLIN) in droplets of aqueous supersaturated potassium chloride at a glass interface.

2. Experimental Methods

2.1 Power dependence

A Dove prism (Knight Optical) was used to study ew-NPLIN (Figure 1). The prism was first cleaned thoroughly with ethanol and deionized water and then dried in an oven for 1 hour at $70 \text{ }^\circ\text{C}$. At all stages of sample preparation the prism was kept covered as often as possible, to keep the surface

free from contamination. Potassium chloride (Sigma, 99+%) and de-ionized water (Fisher, HPLC grade), were used as-purchased. The saturation concentration (molality) of KCl at 23 °C was $C_{\text{sat}} = 4.688 \text{ mol kg}^{-1}$. Supersaturated aqueous KCl ($S = C/C_{\text{sat}} = 1.08$) was filtered through a 0.22- μm syringe filter (Millex GP, polyethersulfone membrane) and deposited gently onto the top of the prism. In preliminary experiments it was found that the nucleation count at $S = 1.06$ was low (but not zero), and therefore a higher concentration was used to facilitate counting. The droplet was contained inside a glass ring capped with a coverslip; the miniature chamber was sealed using ultraviolet-curing adhesive (Norland Optical Adhesive 63). The sealed environment prevents ingress of dust and evaporation of the solvent. Each sealed sample was re-used a maximum of 3 times before producing a fresh sample. The glass ring was removed from the prism by soaking in chloroform overnight; fresh samples were prepared using the procedures outlined above.

An atomic force microscope (AFM) operating in contact mode (Veeco, Nanoman VS) was used to determine the quality of the prism surface. Images taken over a number of 20 μm^2 patches of the surface of the Dove prism showed the surface to be very smooth, suggesting an average deviation in depth of $< 2 \text{ nm}$ over large areas of the prism (see Supporting Information).

Figure 1. (a) Schematic illustration of the Dove prism with dimensions $L_1 = 68$ mm, $L_2 = 36$ mm, $h = 16$ mm, $\alpha = 45^\circ$. We take the z -axis to point upwards in the page, with $z = 0$ at the prism–droplet interface. The glass ring was 15 mm in diameter and 3 mm high. The prism was made from BK7 glass, with refractive index $n_1 = 1.519$ at 532 nm. The critical angle for TIR (assuming a droplet of supersaturated KCl with $n_2 = 1.365$) was $\theta_c = 64^\circ$; the internal reflection angle used was calculated to be $\theta = 73^\circ$. (b) Photograph illustrating the beam path through the prism using a continuous-wave laser beam: the beam travels from left to right, entering the prism at (1). Note that the enclosing ring and coverslip were not used for this demonstration. The projection of the spatial profile of the Gaussian beam at the reflection interface is elliptical, as illustrated by fluorescence in an aqueous droplet of rhodamine 610 dye at position marked at (2).

Prior to shooting with the laser, the prism and droplet apparatus was placed in an oven at 50 °C for 1 hour to dissolve any crystals that had formed, and was allowed to cool slowly to ambient temperature (23 °C). The light used was the second harmonic ($\lambda = 532$ nm) from an Nd³⁺:YAG laser (Continuum Surelite II-10) producing pulses with full-width at half-maximum (FWHM) of 5 ns. The beam diameter was reduced from 8 mm to 2.5 mm using an optical telescope. Starting at a mean laser power of $P = 10$ mW, the sample was shot with 10 single pulses; if no nucleation was observed after 3 minutes, the mean power was increased by 10 mW and the sample was shot again with 10 pulses. This process was repeated until nucleation was observed. After the sample had nucleated, the power at which nucleation occurred was recorded and the sample was refreshed as described above. In total 16 droplets were nucleated.

It should be noted that for an ideal interface (assuming zero absorption in both media) no energy is transferred across the interface. However, species that are present near the interface can absorb due to the penetration of the electromagnetic field of the evanescent wave into the second medium.²² The effective peak laser power density delivered to the evanescent wave can be calculated as

$$j_{\text{peak}} = \frac{c_f c_{\text{ew}} P}{qaT} \quad (1)$$

The area ($a = 0.21$ cm²) of the elliptical beam at the glass–droplet interface was calculated using a ray-tracing method; P is the mean laser power of the input beam, measured with the laser operating at $q = 10$ pulses s⁻¹; T is the integral pulse duration of the laser (5.3 ns).⁹ The two polarization-dependent factors, c_f and c_{ew} , account for reflection losses at the input face and enhancement of the field intensity at the glass–droplet interface, respectively.

The laser power incident on the prism was controlled by passing the beam through a Glan-laser polarizer mounted with the polarization axis at some angle with respect to the linearly polarized

output of the YAG laser. The fractions of s and p-polarized light entering the prism are determined from the angle of the Glan-laser polarizer with respect to the scattering plane (the plane of the page for Figure 1a) at each laser power. The reflection losses at the input face of the prism were calculated using Fresnel's equations:²¹ the resulting transmission factor c_f lies in the range $c_f = 0.92\text{--}0.95$. The intensity of the evanescent wave is proportional to the square of the electric field amplitude. For internal reflection angles close to the critical angle, the intensity at the surface ($z = 0$) is enhanced with respect to the incident wave. The enhancement factors for s and p-polarized light are²²

$$c_{\text{ew}}(\text{s-pol}) = \frac{4 \cos^2 \theta}{1 - n^2} \quad (2)$$

$$c_{\text{ew}}(\text{p-pol}) = \frac{4 \cos^2 \theta [2 \sin^2 \theta - n^2]}{n^4 \cos^2 \theta + \sin^2 \theta - n^2} \quad (3)$$

where θ is the angle of incidence at the interface, and $n = n_2 / n_1$ is the ratio of the refractive indices (Figure 1). We calculate the overall enhancement c_{ew} as the weighted sum of eqs 2 and 3: in the present work we find the factor c_{ew} lies in the range $c_{\text{ew}} = 1.9\text{--}2.1$. As a guide to the conversion, an incident laser power of $P = 200$ mW corresponds to $j_{\text{peak}} = 33$ MW cm⁻².

2.2 Surface modification

The effect of surface modification on ew-NPLIN was investigated by chemical functionalization to form a hydrophobic coating. The surface of the prism was first cleaned by washing with a solution of HCl in methanol, followed by soaking the prism in concentrated H₂SO₄ overnight.²³ After soaking, the Dove prism was rinsed with deionized water and dried in an oven at 70 °C. The surface was patterned with a 2 mm-wide hydrophobic strip across the width of the prism. The strip was made by masking with tape, and the unmasked portion was then left to soak for 20 minutes in a commercially available solution containing hydroxy-terminated polydimethylsiloxanes (PDMS) in ethanol (Rain-X). The mask was removed and the prism rinsed and placed in an oven to cure at 70 °C for 15 minutes. The process was repeated to ensure good coverage. We attempted to image the boundary of the PDMS strip, but the results were inconclusive. This may be due to our inability to locate the edge of the 2-mm wide strip within the range of travel of the AFM probe, and also due to the small vertical extent of the surface modification, assumed to be monolayer.

After the prism surface was functionalized a droplet of supersaturated KCl solution ($S = 1.08$) was placed across the hydrophobic strip and sealed within a glass ring and coverslip, as outlined in section 2.1. The droplet was placed so as to straddle the strip, thereby keeping it in good contact with

both hydrophilic and hydrophobic portions of the surface. The droplet was then shot at a peak power density of 61 MW cm^{-2} , well above the threshold observed for nucleation.

3. Results

The intensity of an evanescent wave decays exponentially with distance propagated (z),²¹⁻²²

$$I(z) = I(0) \exp\left(-\frac{z}{z_p}\right). \quad (4)$$

The penetration depth z_p is given by

$$z_p = \frac{\lambda_0}{4\pi} (n_1^2 \sin^2 \theta - n_2^2)^{-\frac{1}{2}}, \quad (5)$$

where λ_0 is the vacuum wavelength of the light, and n_1 and n_2 are the refractive indices of the prism and the second medium, respectively. For the supersaturated KCl solution on the glass prism with $\theta = 73^\circ$ we calculate $z_p = 86 \text{ nm}$.

A series of images of the growth of KCl crystals taken after firing of the laser pulse are shown in Figure 2. A plot of the cumulative fraction of samples nucleated (f) versus the peak power density of the laser pulses is shown in Figure 3. The use of the cumulative fraction assumes that a sample nucleating at a given power would have nucleated at higher powers; in previous work on KCl we have verified that this assumption is justified.²⁴ The results have been fitted with a Poisson nucleation model that accounts for the probability of forming multiple nuclei at higher laser powers,²⁴

$$f(j_{\text{peak}}) = 1 - \exp\left[-m(j_{\text{peak}} - j_0)\right]. \quad (6)$$

In eq 6, j_0 is the threshold peak power density and m is the lability. The lability is the slope of the power dependence at threshold; higher lability indicates solutions that nucleate more easily with increasing laser power density.

In Table 1, the results are compared to previous NPLIN experiments on KCl solutions in glass vials ($S = 1.06$).²⁴ The threshold determined for ew-NPLIN is a factor of 3 higher compared to samples in glass vials. Although the supersaturation is slightly higher in the present work, previous work suggests that j_0 does not depend strongly on S .¹¹ The lability observed in the ew-NPLIN experiments is remarkably close to the value observed for bulk solution. Previous experiments with bulk solutions at 1064 nm showed that samples at $S = 1.08$ were approximately 1.5 times more labile than samples at $S = 1.06$.

Figure 2. Images showing growth of KCl crystals nucleated using ew-NPLIN. Images were taken at (a) 10 s, (b) 30 s, (c) 60 s and (d) 300 s after nucleation. The approximate footprint of the evanescent beam is outlined with the dashed ellipse. The scale bar represents 2 mm.

Figure 3. Graph of cumulative fraction of samples nucleated (f) versus laser peak-power density (j_{peak}). Solid circles represent the experimental points; uncertainties were calculated at 95% confidence using the Wilson score interval.²⁵ The solid line represents a fit to the points using a Poisson model of the nucleation probability (eq 6). The model returns a threshold peak-power density $j_0 = 17 \pm 1 \text{ MW cm}^{-2}$, and lability (slope at threshold) $m = 0.059 \pm 0.004 \text{ cm}^2 \text{ MW}^{-1}$.

	Supersaturation (S)	Threshold peak-power density (j_0) / MW cm ⁻²	Lability (m) / cm ² MW ⁻¹
evanescent (present work)	1.08	17 ± 1	0.059 ± 0.004
vials ²⁴	1.06	5.6 ± 0.5	0.057 ± 0.004

Table 1. Threshold peak-power density (j_0) and lability (m) for experiments using an evanescent wave (ew-NPLIN, present work) compared to previous experiments where the beam was passed through bulk solutions contained in glass vials.²⁴ Uncertainties represent standard errors from the nonlinear least-squares fit. Note that the supersaturation used in the present work was slightly higher than in vials.

Sample images of crystals nucleated on a PDMS-functionalized prism surface are shown in Figure 4. Out of 10 trials, no nucleation was observed to occur over the hydrophobic strip. On several occasions, nucleation was observed on either side of the hydrophobic strip after a single pulse. Once nucleated, crystals were seen to grow, unhindered, across the hydrophobic region.

Figure 4. Images of ew-NPLIN on partially functionalized prism surfaces. The images were taken several minutes after nucleation. The supersaturated KCl droplet straddles a hydrophobic strip indicated by the solid diagonal lines; the surface of the strip was functionalized with PDMS. The approximate spatial footprint of the evanescent wave formed by the laser pulse is indicated by the dashed ellipse. Nucleation was only observed to occur outside of the region of the hydrophobic strip; however, once growth commenced, crystals appeared to grow unhindered over the strip. Scale bars represent 2 mm.

4. Discussion

The power threshold observed in ew-NPLIN was higher than NPLIN in vials (Table 1). The reason for this is not clear. Classical nucleation theory applied to heterogeneous nucleation on surfaces shows that the barrier to nucleation is lowered if the nucleus wets the surface; this would mean that nucleation should occur more easily.²⁶ The higher threshold for ew-NPLIN could indicate that nucleation is taking place in the solution and not on the interface. This seems unlikely as the

highest intensity is at the surface, but there may be a boundary layer of inactive solution above the interface, so that higher powers are needed to reach the active solution above this layer.

Our results are consistent with various pre-nucleating cluster mechanisms where the presence of the electric field in the wave can interact with the polarizability of the cluster.¹⁰⁻¹² On its own, the pre-nucleating cluster mechanism does not account for a threshold.^{12, 24} Only nucleation events where macroscopic crystals are formed are counted, however; there may be nuclei that don't survive.²⁷ A photomechanical mechanism may operate, involving localized absorption of the electric field by nanoparticles, casing them to be heated (see comments preceding eq 1). Such nanoparticles are expected to be exceedingly rare (~1 per nL) and so frustration of the evanescent wave will be negligible. For this mechanism we would expect a threshold temperature below which the heat transfer to the solvent is not sufficient to cause nucleation. We are currently investigating this mechanism using intentional doping of supersaturated solutions.¹³

To understand the lability of our ew-NPLIN system, we follow the arguments advanced by Garetz and co-workers for nucleation in microdroplets.²⁰ They pointed out that the volume of solution irradiated was substantially smaller for a droplet than in bulk vials. In the present work we found that the overall exposure time required for nucleation was very similar between evanescent-wave and samples in vials, certainly to within an order of magnitude. This suggests that the mechanisms for ew-NPLIN and NPLIN in bulk are similar. The classical nucleation rate density (J) can be written,²⁸

$$J = AS \exp\left(-\frac{B'\gamma^3}{(\ln S)^2}\right) \quad (7)$$

where A is a pre-exponential factor, S is supersaturation, and B' depends on the thermodynamics of the nucleating system; for clarity of the discussion we have separated out the crystal-solution interfacial tension, γ . The parameter B' for the KCl system can be calculated as

$$B' = \frac{16\pi v^2}{3(k_B T)^3} \quad (8)$$

where v is the volume of a KCl unit in a crystal, k_B is the Boltzmann constant and T is temperature; for the present case we calculate $B' = 9.5 \times 10^5 \text{ m}^6 \text{ J}^{-3}$. It should be noted that we do not explicitly include any factor for the effect of the laser in the exponential of eq 7. We assume that this term will be small and similar in magnitude for the two cases that we compare (vials and evanescent-wave).

The average number of nucleation events can be written $N = J V t$, where V is the volume irradiated, and t is the duration of exposure to laser light. The average number of nucleation events observed were very similar, and we write (1 = vials, 2 = evanescent-wave)

$$J_1 V_1 t_1 = J_2 V_2 t_2 \quad (9)$$

We have $t_1 \approx t_2$, $S_1 = 1.06$, $S_2 = 1.08$, and $V_1 = 0.345 \text{ cm}^3$; the volume irradiated for ew-NPLIN we approximate as a cylinder $V_2 = a z_p = 1.8 \times 10^{-6} \text{ cm}^3$ (1.8 nL). Substituting eq 7, re-arranging and solving for the unknown interfacial tension, we find $\gamma = 4.6 \text{ mJ m}^{-2}$. This value compares favorably with previous values of 5.3 mJ m^{-2} of Ward et al.²⁴ (vials) and 3.6 mJ m^{-2} of Fang et al. (droplets).²⁰ Due to the exponential decay of the evanescent wave we have overestimated V_2 . Repeating the calculation outlined above with a volume $V_2 = 1 \times 10^{-7} \text{ cm}^3$ (100 pL) corresponding to a penetration depth of 4.8 nm, we obtain $\gamma = 5.0 \text{ mJ m}^{-2}$.

The apparent lack of nucleation on surfaces functionalized with the PDMS suggests that the hydrophobic coating has a strong effect on nucleation near the surface. Assuming that the surface coating is monolayer, and that the chain length of PDMS molecules is 15 dimethylsiloxane units, the surface layer would be approximately 2 nm thick. This is too small for significant absorption of light by the coating. A hydrophobic surface would be expected to increase the crystal–surface interfacial tension, thereby decreasing the nucleation rate on the interface.²⁹ The hydrophobic surface would also be expected to alter the solution structure directly at the interface, but it seems unlikely that this perturbation would penetrate far enough into the solution to cause such a clear inhibiting effect. The coating could simply act to reduce bumps or asperities where impurities or particles could be trapped; as noted above, results from the AFM were inconclusive. Further experiments on coating, including two-dimensional template patterns, are being investigated.

5. Conclusions

In summary, we have demonstrated nucleation over a glass–solution interface using evanescent-wave non-photochemical laser-induced nucleation (ew-NPLIN). Localization of time of nucleation was within 5 ns, and localization of one spatial dimension was within 100 nm. The dependence of nucleation on laser power by evanescent wave was similar to previous work in bulk solution above a power threshold; however, the threshold was significantly higher with the evanescent wave. Experiments involving chemical functionalization at the interface showed that the nucleation is suppressed by hydrophobic coatings. The present work could have applications where two-dimensional patterns of nuclei at a surface are required, or where the localization could aid studies of nucleation mechanisms.

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Supporting Information Available

Atomic force microscopy image of the surface of the dove prism. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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