Mechanistic Studies of Laser-Induced Nucleation

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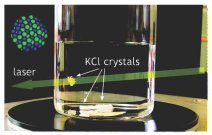
Background

Nonphotochemical Laser-Induced Nucleation (NPLIN)

- Exposure of transparent supersaturated solutions to intense, nanosecond laser pulses can dramatically reduce the induction time for nucleation of crystals.[1] Laser polarization can also influence polymorph selection.[2]
- NPLIN has been demonstrated in supersaturated aqueous solutions of urea,[2] glycine,[3] proteins,[4] and potassium chloride.[5]
- The optical Kerr hypothesis is that the laser aligns solutes according to their most polarizable axes during a pulse and thereby promotes crystallization.[1,2,3]



(Picture from Ref. 5)

Model and Simulation Details

Potts Lattice Gas (PLG) Model

- Each lattice site has two degrees of freedom: species (solute or solvent) and orientation (with Q possible orientations).
- Nearest neighbors interact according to:

$$H = -\sum_{<ij>}\left[\delta_{n_i=n_j=1}[(K-\frac{A}{Q})+\delta_{s_i=s_j}A]+\delta_{n_i=n_j=0}K\right]$$

Mis-aligned solute-solute; Aligned solute-solute; Any solvent-solvent

- A controls the freezing point of the pure solute
- K controls the solubility of solute in solvent

Semigrand Canonical Monte Carlo (SGCMC) "Dynamics"

- SGCMC maintains fixed volume, temperature, and fugacity ratio between solutes and solvents, i.e. fixed chemical potential difference.[6,7,8]
- Three types of moves are attempted with equal probability:
- Particle identity swap

fugacity ratio sets concentration

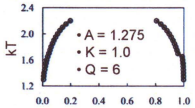
$$P_{ACC}(n_1 \to n_0) = \min\left(1, \frac{f_0}{f_1}\exp\left[\beta\left(H_{n_0}-H_{n_1}\right)\right]\right)$$

- Particle reorientation (colors represent orientations)

- Nearest-neighbor swap (translation)

Phase diagram[8]

Parameters in simulations are for structureless solvent.



Orientational bias to mimic optical Kerr effect (OKE) of laser

- The OKE proposes that the laser biases solutes to align their most polarizable axis with the oscillating field direction.[1,2,3] Sun, et al., give the degree of alignment with a linearly polarized laser field in the x-direction as:[3]

Orientational order parameters:

- $K_x^{LP}=\frac{1}{3}+\varepsilon \quad K_y^{LP}=\frac{1}{3}-\frac{\varepsilon}{2} \quad K_z^{LP}=\frac{1}{3}-\frac{\varepsilon}{2}$

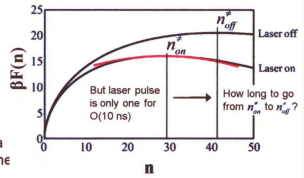
$$\varepsilon = \frac{\Delta\alpha E^2}{45k_BT}$$

molecular polarizability difference; oscillating field

- Bias included through Monte Carlo generation probability

Diffusive Dynamics On Barrier

- Diffusivity along the reaction coordinate at the barrier top is a crucial parameter in mean first passage time rate constants and in comparing rates through competing reaction pathways.
- Barrier crossing time is important because NPLIN laser pulses are of short (nanosecond) duration.
- Common to obtain diffusivity along reaction coordinate at the top of a barrier from MSD vs. time (Einstein relation):



$$\left\langle (n(t)-n(0))^2 \right\rangle = 2Dt$$

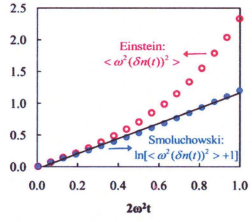
- Einstein does not account for drift induced by curvature in the PMF. The effect of drift can be included by starting from Smoluchowski equation and a parabolic approximation to barrier top:

$$\beta F(n) = \beta F(n^*) - \frac{1}{2}\omega^2(n-n^*)^2$$

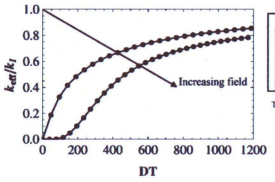
- new relationship between MSD, time, and PMF curvature:[9]

$$\ln\left[\left\langle \omega^2(n(t)-n^*)^2\right\rangle + 1\right] = 2\omega^2 Dt$$

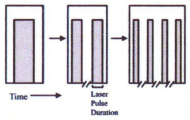
- MSD data from PLG simulations plotted using the Einstein relation (with both axes multiplied by curvature ω^2) and the Smoluchowski relationship (with best fit line).[9]
- The Smoluchowski relation describes the dynamics accurately for longer times than the Einstein relation.[9]
- How do laser pulse time T and dynamics along barrier influence the effective rate enhancement?[9] Literature hypotheses imply a threshold laser pulse **duration**



$$k_{eff}(I,T) = \frac{1}{T}\int_0^T dt\, 2k_f \int_{-\infty}^{\infty} dn\, H[n-n_0^*]P(n,\infty|n',T)\int_{-\infty}^{\infty} dn'\, \rho_I(n',T-t)$$



(dimensionless pulse time)



enhancement relative to enhancement from very long pulses at same total exposure (prediction from theory and simulations)[9]

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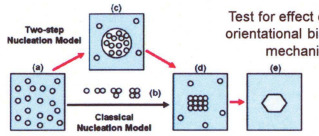
Test of Optical Kerr Hypothesis

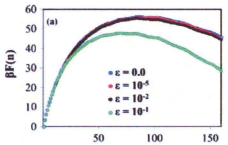


Test for effect of induced orientational bias for both mechanisms

(Figure from Ref. 10)

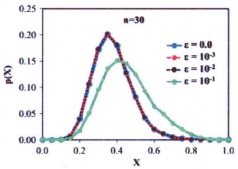
By classical mechanism?

- How does orientational bias influence work to form nucleus of size n? In experiments,[12] the oreientational bias is $\varepsilon \sim 10^{-6}$
- In PLG model, a much larger orientational bias (ε) is required for appreciable barrier reduction.



By second step in two-step nucleation?

- Can orientational bias facilitate crystallization of an amorphous nucleus?
- Need measure of crystallinity: X=(solid bonds in cluster) /(total bonds in cluster)
- solid bond is a pair of nearest-neighboring solutes with the same orientation.



- The optical Kerr effect can promote crystallization of an amorphous nucleus. However, the effect requires field strengths that are orders of magnitude stronger than those in the experiments.

Non-photochemical?

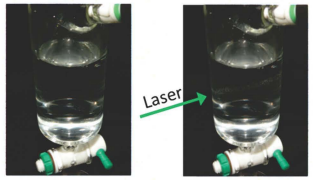
Nucleation is a rare event: important but rare precursors may not be visible in the absorption spectrum of the bulk solution. Thus a lack of absorption bands is not strong enough to exclude photochemistry. Furthermore, we and others only investigated nucleation enhancements at a few wavelengths. More thorough studies of wavelength dependence are needed to exclude or assert photochemistry.

Conclusions

- relation for mean squared displacement from barrier top vs. time captures effect of curvature in PMF
- predicted threshold laser pulse *duration* for nucleation enhancement if mechanisms that lower barrier cause NPLIN
- lattice model simulations show that optical Kerr alignment can enhance crystal nucleation, but only at field strengths that are orders of magnitude stronger than in experiments.
- demonstrated that the same lasers that induce crystal nucleation can also induce nucleation of volatile solute *bubbles* from solution. confirms there is a mechanism other than the optical Kerr effect.
- threshold intensity for laser-induced nucleation in carbonated water increases as supersaturation decreases.
- Argon bubbles can induce crystal nucleation even without a laser
- photochemistry and cavitation mechanisms need further study

Laser-Induced Bubble Nucleation Experiments

- To test the hypothesized optical Kerr mechanism for laser-induced crystal nucleation (Myerson, Garetz, et al.) we tested whether a laser could induce nucleation of CO_2 bubbles from carbonated water
- Cavitation was not observed in laser-induced crystal nucleation experiments by Myerson et al., but small transient bubbles might not be seen.
- in our experiment ,any nanoscale or larger bubble will grow to become a macroscopic bubble and be seen.
- enhanced solute alignment should not help form a CO_2 bubble, so if bubbles form there is a non-Kerr effect at work.

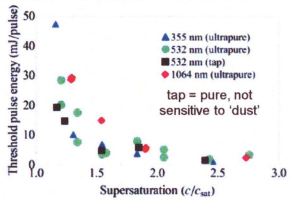


Laser:
- λ = 532 nm
- 7 ns pulse
- 5mm beam diameter
- 5cm vessel diameter like NPLIN for crystals

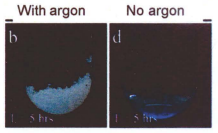
*(right) taken just after a single 7 ns pulse of energy 280 mJ. even if *all* of the pulse energy is absorbed by the irradiated zone, the temperature rise of the solution is only $O(10^{-4})$ K.

- Previous investigatiors[5,13] found that a minimum pulse intensity is needed to induce nucleation. We show how the threshold depends on supersaturation.

the pulse energy that gives 0.1 bubbles per pulse over many pulses is defined as the threshold pulse energy.



Could bubbles cause nucleation of crystals? In argonated water that is co-supersaturated with glycine, glycine crystals form hours after argon bubbles are released. For the control with no argon, glycine remains in solution.



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