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

Model and Simulation Details

Potts Lattice Gas (PLG) Model
Each lattice site has two degrees of freedom: species (solute or solvent) and orientation (with 2 possible orientations). Nearest neighbors interact according to:

\[ H = -J \sum_{\langle i,j \rangle} \delta_{s_i s_j} \delta_{\sigma_i \sigma_j} + K \sum_{i} \delta_{\sigma_i \sigma} \]

Mis-aligned solute-solute
Any solvent-solute
Aligned solute-solute
A controls the freezing point of the pure solute
K controls the solubility of the 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.4,5
• Three types of moves are attempted with equal probability:
  • Particle identity swap (colors represent orientations)
  • Nearest-neighbor swap (translation)
  • Particle reorientation (colors represent orientations)

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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. Nucleation is needed to induce nucleation. We show how the threshold depends on supersaturation. Could bubbles cause nucleation of crystals? In argonated water that is co-supersaturated with glycerin, glycerin crystals form hours after argon bubbles are released. For the control with no argon, glycerin remains in solution.

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
• NPLIN 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. Furthermore, we and others only investigated nucleation enhancement at a few wavelengths. More thorough studies of wavelength dependence are needed to exclude or assert photochemistry.

Non-photochemical?

Test of Optical Kerr Hypothesis

Test for effect of induced orientational bias for both mechanisms

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 CO2 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.
• enhanced solute alignment should not help form a CO2 bubble, so if bubbles form there is a non-Kerr effect at work.

References


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