

Control over phase separation and nucleation using a laser-tweezing potential

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Control over the nucleation of new phases is highly desirable but elusive. Even though there is a long history of crystallization engineering by varying physicochemical parameters, controlling which polymorph crystallizes or whether a molecule crystallizes or forms an amorphous precipitate is still a poorly understood practice. Although there are now numerous examples of control using laser-induced nucleation, the absence of physical understanding is preventing progress. Here we show that the proximity of a liquid-liquid critical point or the corresponding binodal line can be used by a laser-tweezing potential to induce concentration gradients. A simple theoretical model shows that the stored electromagnetic energy of the laser beam produces a free-energy potential that forces phase separation or triggers the nucleation of a new phase. Experiments in a liquid mixture using a low-power laser diode confirm the effect. Phase separation and nucleation using a laser-tweezing potential explains the physics behind non-photochemical laser-induced nucleation and suggests new ways of manipulating matter.

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Background

- Crystallization is one of the “voodoo” arts of Chemistry
 - Massively sensitive multi-parameter phase transition:
 - Solvent (and a near-infinite choice of mixtures of solvents)
 - Temperature
 - Heating and cooling rates
 - Concentration
 - Stirring rate
 - Size and material of the vessel
 - Traces of water or other impurities

Background

- Thermodynamics of solid \leftrightarrow liquid phase transitions are extremely complex, and not fully understood
 - No *a priori* models for predicting melting points exist!
 - Along with poorly-understood crystallization, this indicates a lack of understanding of transitions to (or out of) an ordered solid phase
- This has major consequences for separations processes
 - Protein crystallography
 - Azeotropic cracking
 - Pharmaceutical purification

Background

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Nonphotochemical, Polarization-Dependent, Laser-Induced Nucleation in Supersaturated Aqueous Urea Solutions

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We report a new photophysical phenomenon in which 1.06 μm pulses from a Q -switched Nd:YAG laser induce crystallization in supersaturated solutions of urea in water. Because the solutions are transparent at the incident wavelength, a photochemical mechanism is unlikely. The needle-shaped crystals that initially form tend to be aligned parallel to the electric field vector of the light, suggesting a Kerr-like field-induced alignment of urea molecules that aids in organizing prenucleating clusters. The effect has application to pump-probe nucleation studies and to clean nucleation in sealed systems. [S0031-9007(96)01456-1]

- Discovered in 1996 that shining a small, bright laser beam into a concentrated solution can induce crystallization
 - Long-standing disagreement over how that works
 - Originally proposed to be example of Kerr-like Effect

Kerr Effect

Enhancement of media refractive index due to susceptibility to external electric field

$$\mathbf{P} = \varepsilon_0 \chi^{(1)} : \mathbf{E} + \varepsilon_0 \chi^{(2)} : \mathbf{E}\mathbf{E} + \varepsilon_0 \chi^{(3)} : \mathbf{E}\mathbf{E}\mathbf{E} + \dots$$

In the case of a laser, the monochromatic wave acts as this field:

$$\mathbf{E} = \mathbf{E}_\omega \cos(\omega t)$$

$$\mathbf{P} \simeq \varepsilon_0 \left(\chi^{(1)} + \frac{3}{4} \chi^{(3)} |\mathbf{E}_\omega|^2 \right) \mathbf{E}_\omega \cos(\omega t)$$

Leads to a laser intensity-dependent refractive index

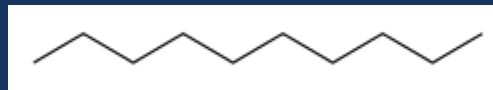
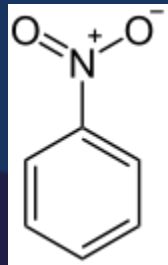
$$n = (1 + \chi)^{1/2} = (1 + \chi_{\text{LIN}} + \chi_{\text{NL}})^{1/2} \simeq n_0 + \frac{3\chi^{(3)}}{8n_0} |\mathbf{E}_\omega|^2 = n_0 + n_2 I$$

Background

- Evidence for Kerr-like effects in crystallization have been inconsistent and inconclusive
- Present work asserts that laser-induced crystallization is due not to polarization effects, but by the formation of concentration/depletion zones
 - Crystallization separations typically done on saturated/supersaturated solutions
 - In this solution, solid crystal phase is the thermodynamic ground state
 - Phase transition still has energetic / potential barrier, typically overcome by addition of nucleation seed / external perturbation

Background

- Authors propose that formation of concentration/depletion zones is capable of inducing crystallization **in solutions near transition**
- Application as separation technique for highly miscible solutions
 - Concentrating one component together, and “skimming” it off
 - Not unlike selectively separating cream from coffee
 - Or rosiner from boller....
- Paper deals with easier test case – miscible liquid/liquid solution of nitrobenzene / decane



Mixing Model

- Binary nitrobenzene / decane solution modeled as *regular solution* (non-ideal)

$$\Delta H_{mix} = \beta x_A x_B$$

$$\Delta G = \Delta H - T\Delta S = RT(x_A \ln x_A + x_B \ln x_B) + \beta x_A x_B$$

- Free energy of system is function of mole fractional composition x_i

$$\Delta H'_{laser} = -n^2 I$$

- Laser adds additional enthalpy term for the added electromagnetic energy
 - Lowers system free energy, “trapping” highest n component

Methods

- Used 785 nm (near-infrared) laser to stimulate a $\sim 12\mu\text{m}$ thick sample
 - Laser power ranged $0 < P < 200\text{ mW}$
 - Sample mixture held on dual-cryo-cooled stage of microscope
 - Temperature held 280 – 300 K, to maintain stable mixture (miscible solution)
- Impact of laser-induced phase separation (LIPS) verified by:
 - Phase-contrast microscopy – converts optical path length \rightarrow intensity, used to “image” refractive index
 - Fluorescence imaging – methylene blue dye added to mixture
 - Dye’s fluorescence quenched \propto nitrobenzene concentration
 - Visual highlighting of phase composition

Methods

Nitrobenzene-rich fraction w/ 4.5 μm FWHM, depletion region w/ $\sim 10\text{ }\mu\text{m}$ radius

Stable \rightarrow unstable phase transition induced by increasing laser power

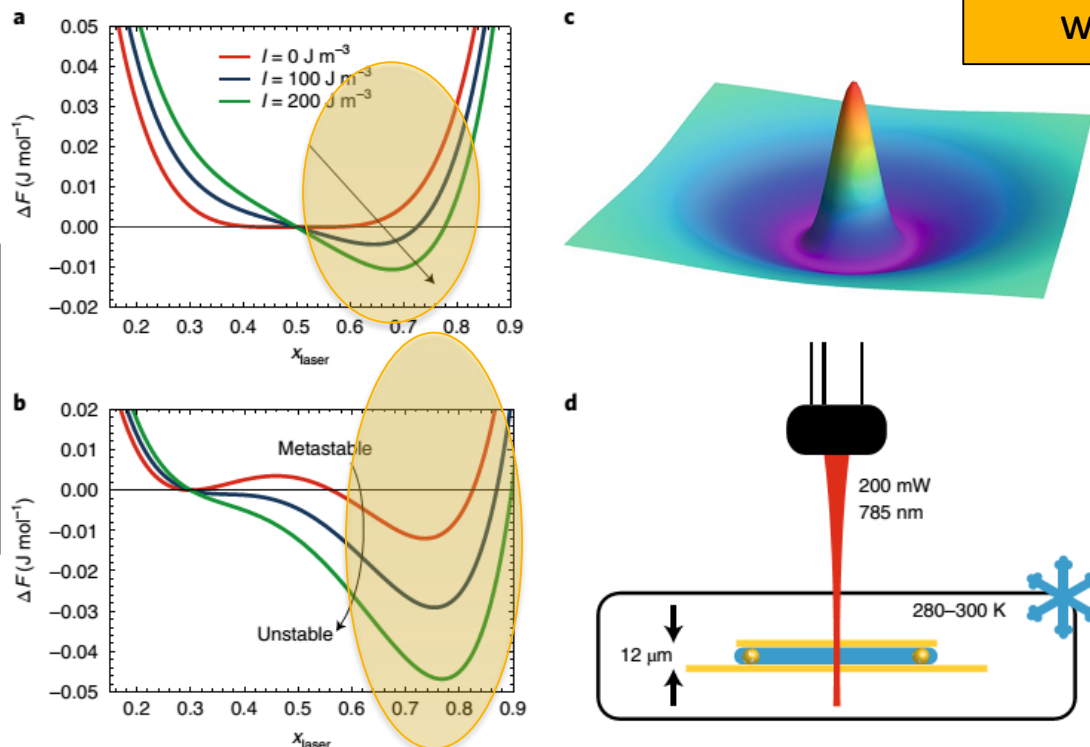
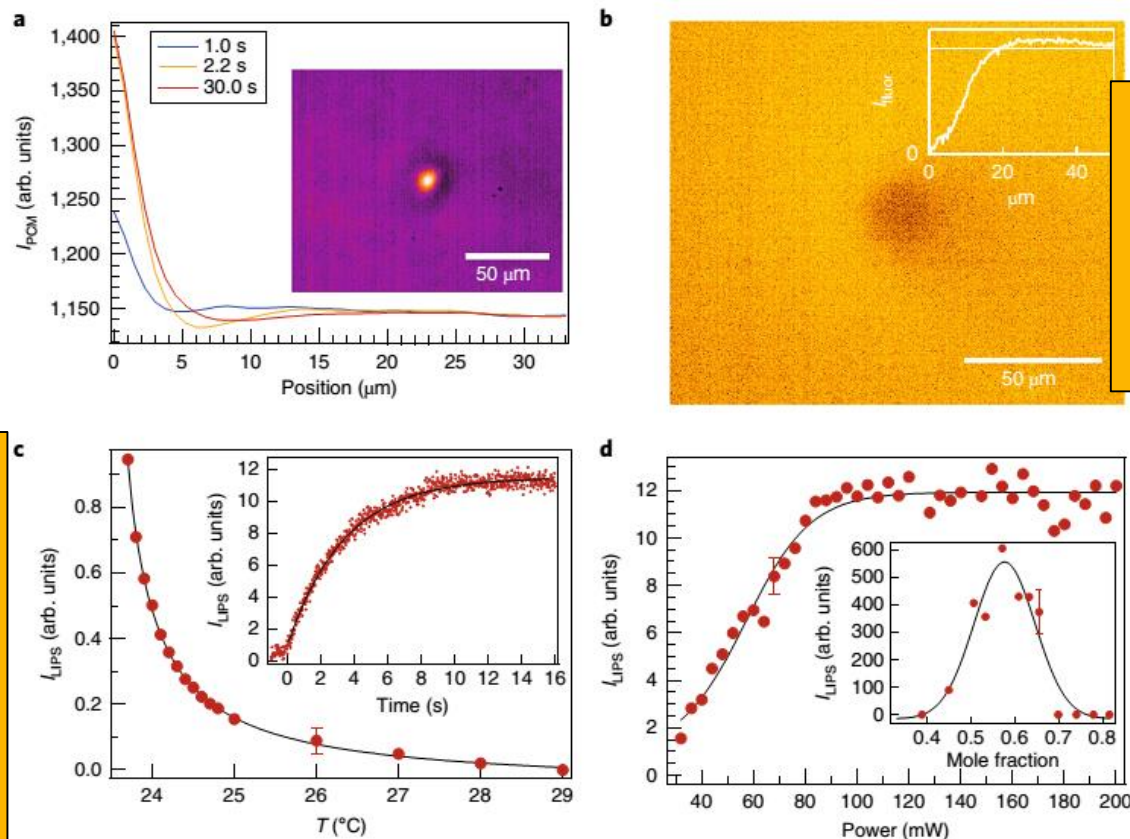


Fig. 1 | Summary of the LIPS and laser-induced nucleation experiments. **a**, A plot of the change in free energy, ΔF , in a nitrobenzene–decane mixture of mole fraction x_0 when the mole fraction is changed to x_{laser} in a small volume. Here the initial nitrobenzene mole fraction is $x_0 = 0.5$, the laser intensities are $I = 0$ (red), 100 (blue) and 200 (green) J m⁻³. The other parameters are appropriate to a stable nitrobenzene–decane mixture (Supplementary Section 1). As can be seen, when the laser power is increased, the minimum in the free-energy potential shifts to a higher mole fraction causing phase separation through a diffusive concentration process. **b**, As in **a** but with initial mole fraction $x_0 = 0.3$ and the other parameters appropriate to a metastable nitrobenzene–decane mixture. When the laser is off, a free-energy barrier prevents the system from phase separating spontaneously. However, with increasing laser power the barrier lowers and then disappears entirely, causing the system to transition from metastable to unstable, hence inducing nucleation of a new phase. **c**, A three-dimensional plot of the position-dependent nitrobenzene mole fraction near the focus of a tweezing-laser. Laser-induced phase separation causes the nitrobenzene concentration to increase in the laser focus leaving behind a temporary depleted volume. **d**, Cartoon of the experimental setup consisting of a diode laser focused in the sample, which is contained in a temperature-controlled cell (Methods).

Evolution of phase transition is time-dependent. Established within ~1s, stabilizes around 30s

Phase separation enhanced by lower-temperatures → dampening of diffusion, which counteracts LIPS



Fluorescence confirms “tweezed” droplet is nitrobenzene-rich component

Fig. 2 | Experimental LIPS through the tweezing effect. **a**, Radial distributions of the LIPS droplet (mole fraction $x = 0.575$) measured using phase-contrast microscopy (PCM). They show a time-dependent enhancement of the nitrobenzene mole fraction in the focus of the tweezing laser and a depletion region at a radius of 4 to 10 μm . The vertical axis is the phase-contrast intensity at each point. Inset is a false-colour PCM image of the droplet. **b**, False-colour fluorescence image of a LIPS droplet (dark region) showing fluorescence quenching demonstrating that it is nitrobenzene enriched. The inset shows the radial distribution of the fluorescence intensity. **c**, Temperature dependence of the magnitude of the LIPS effect (defined as the mean phase-contrast intensity within a droplet) at $x = 0.575$ fit to an inverse power-law function demonstrating that the LIPS effect maximizes on the liquid-liquid demixing binodal line. Inset is the magnitude of the LIPS effect as a function of delay time after the tweezing-laser switch on. The 3.4-s rise time is consistent with diffusion of nitrobenzene into the droplet. **d**, The magnitude of the LIPS effect as a function of incident laser power. The inset shows the dependence on mole fraction (at an incident laser power of 70 mW) demonstrating enhancement of the LIPS effect near the liquid-liquid critical point. For more information, see the Methods section.

Laser on: potential induction

Laser off: temperature drops, crashing mixture below bimodal

Nucleation induced!

Stable after ~30s, remains stable for 10's of minutes

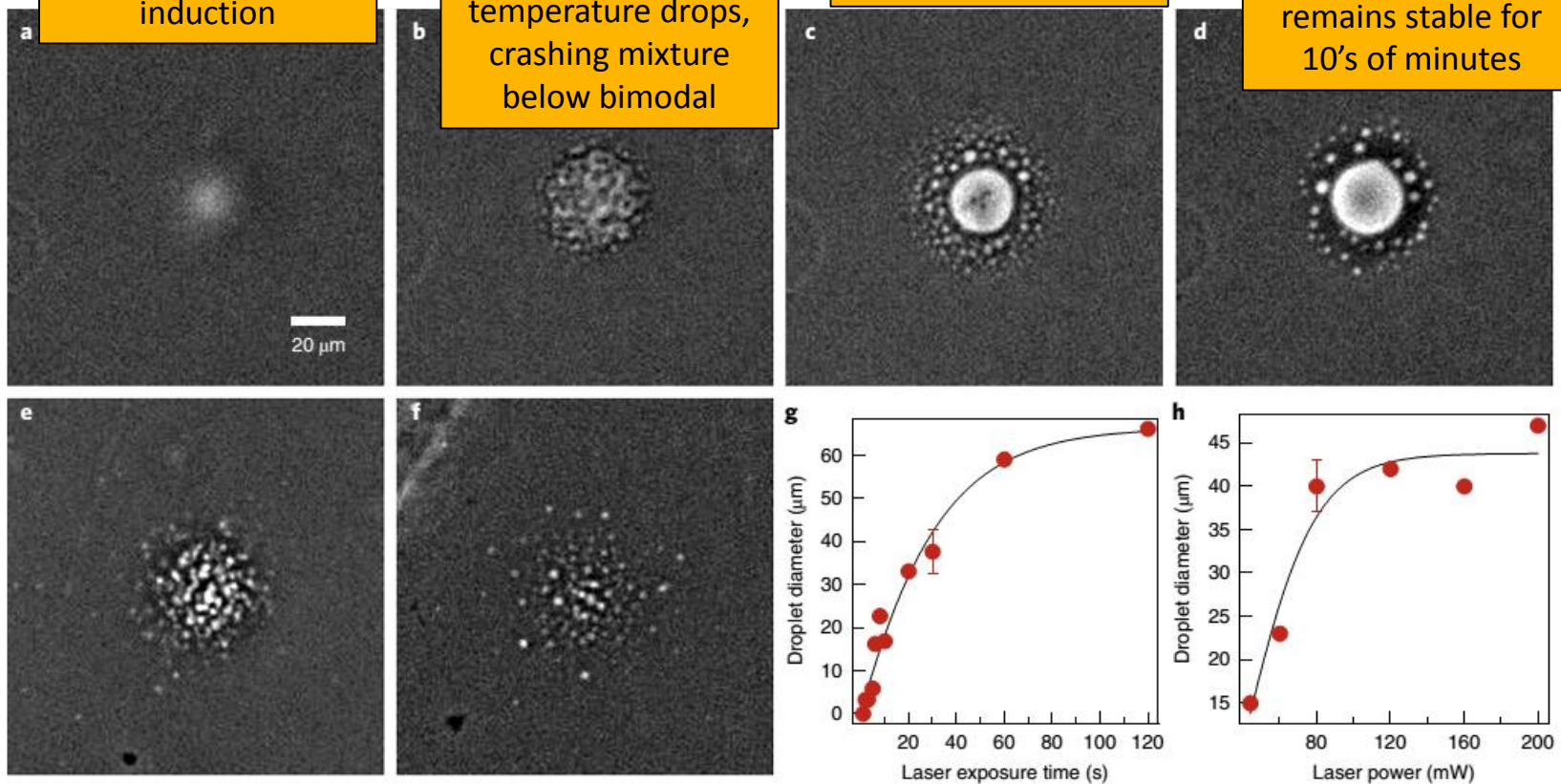


Fig. 3 | Laser-induced nucleation triggered via the LIPS effect. **a**, In the mixed regime near a binodal, the LIPS effect combined with heating produces a droplet enriched in nitrobenzene surrounded by a depleted volume. ($x=0.632$, $T=23.9^\circ\text{C}$, incident laser power 100 mW for 30 s, measured using PCM.) **b**, Switching off the laser, puts the depleted volume in the metastable region, triggering nucleation after <1 s. **c**, Nucleation is followed by Ostwald ripening (frame at 4 s). **d**, The ripened droplet remains stable for tens of minutes (frame at 14 s). **e**, Further away from the critical point (here $x=0.657$) the effect decreases (frame at 4 s). **f**, As in **e** for $x=0.675$ with a further diminished effect. **g,h**, The diameter of the nucleated droplet (at $x=0.632$) increases with laser exposure time (**g**) and also with laser power (**h**). For more information, see the Methods section.

Conclusions

• “This is a **generic effect that does not only apply to poorly mixing liquids but to any mixture or solution**. However, the ease with which the laser-tweezing potential can initiate phase separation is enhanced near a liquid–liquid demixing critical point or binodal line. Phase manipulation and **nucleation can be induced with a straightforward low-power laser diode**. This suggests that this **effect can be used to control matter in a range of practical applications**.”

- Mostly applicable for solutions already close to critical / phase transition point!
- Way to “reverse” entropy and cause phase separations, and isn’t that energy intensive!
- Interesting potential applications for difficult separations of exotic/small-scale systems
 - Isotopic separation?