Liquid-liquid transitions crystallize new ideas for molecular liquids

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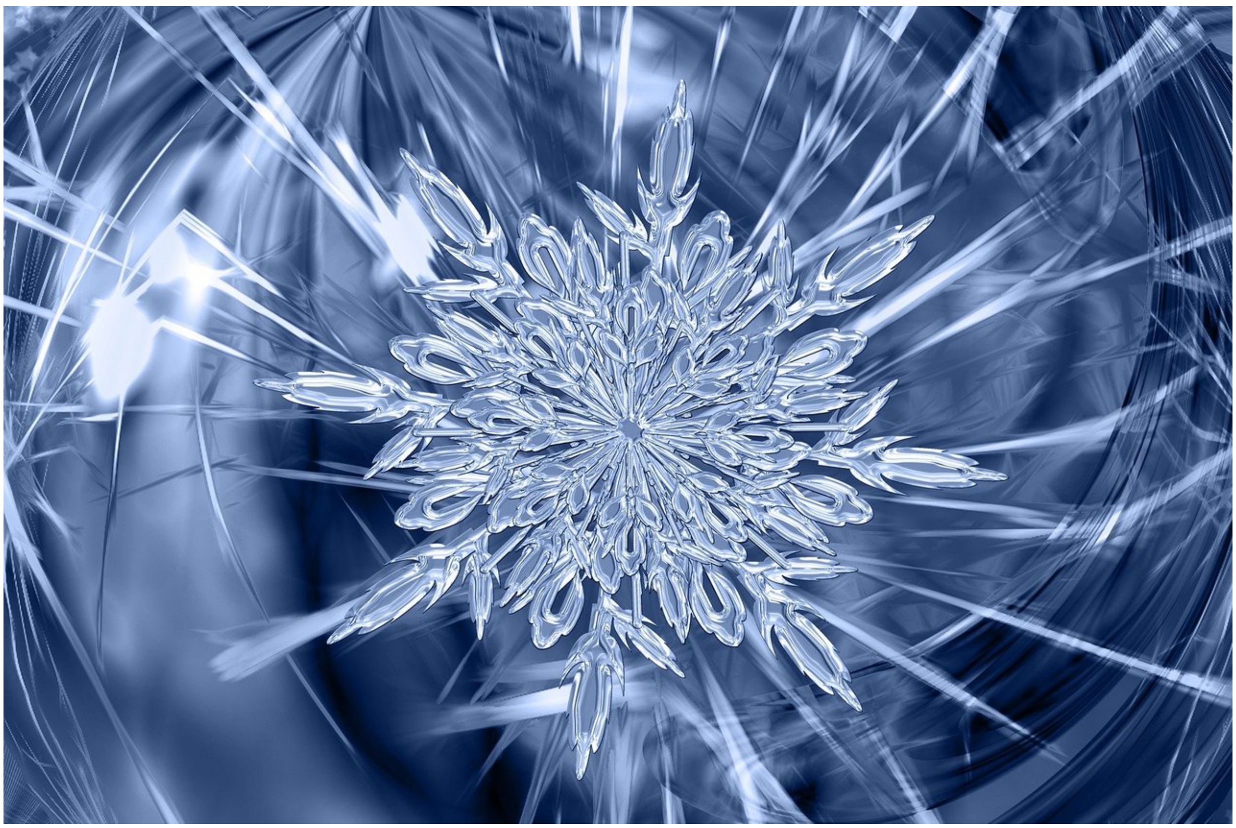

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Crystallization describes the formation of ordered structures from the disordered constituents of a liquid. Although the fundamental theory of crystal formation has been widely investigated and is generally well established, gaps in the understanding still remain. Researchers from The University of Tokyo, Institute of Industrial Science, and Tokyo Metropolitan University have reported experimental findings that reveal coupling between phase transitions that leads to drastic enhancement of crystal formation. Their findings are published in *PNAS*.

Within a liquid—even liquids made up of only one component—there can be multiple distinct phases with different properties. Variations in the experimental conditions can make the liquid change from one of these phases to another in a process called liquid-liquid transition (LLT). If these transitions occur just below the melting point of the crystal, they can affect its initial formation, known as nucleation. However, the mechanism for such effects and the general applicability of these observations remain unknown.

The researchers report a significant coupling of crystallization and LLT for the molecular liquid triphenyl phosphite. By annealing—cooling and keeping—the liquid at temperatures related to the LLT of the material, they were able to considerably enhance the nucleation rate and frequency of the subsequent crystallization.

"We were able to separate the kinetic and thermodynamic factors that contribute to crystal formation," study lead author Rei Kurita explains. "The LLTs caused by annealing lead to changes in the local order of the molecules. Because of the link we identified between crystallization and LLTs, these changes cause similar ones in the crystal phase, which lowers the energy between the crystal and liquid phases making it easier for crystals to nucleate. We hope that our findings can be used as a handle to direct crystallization behavior."

As well as leading to control and tailoring of crystallization effects, the researchers believe that their findings could also be used to probe material properties by identifying LLTs in materials where their effects are obscured by crystallization. For example, the approach could be used to gain a deeper understanding of water, silicon, germanium, and metallic liquid systems.

"Our findings provide useful insight for understanding and controlling crystallization," study author Hajime Tanaka explains. "We believe our work could have significant implications for both fundamental studies and industrial applications; for example, in achieving protein crystals for use in disease research, or in nanocrystalline materials for use in technology."

More information: Rei Kurita el al., "Drastic enhancement of crystal nucleation in a molecular liquid by its liquid–liquid transition," *PNAS* (2019). www.pnas.org/cgi/doi/10.1073/pnas.1909660116

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