

1) Molecular Simulation of Vapor-Phase Nucleation of Complex Fluids Under Tension

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Despite the practical importance of “stretched” metastable liquids under negative pressures; e.g., as occurring in water transport from the roots to the leaves in trees, our understanding of homogeneous nucleation under such conditions remains limited. Recent experimental efforts have shown that deviations from the predictions of Classical Nucleation Theory (CNT) for the cavitation pressure occur for many fluids but the extent of departure can differ very widely. Past simulation studies have mainly looked at either the rate or the free energy for bubble nucleation, and at positive pressures. Using novel simulation methods, we propose to determine free energy barriers, nucleation rates, and detailed pathways to characterize the mechanism of bubble nucleation in metastable liquids under tension as the stability limit is approached. Simulations will be conducted for an array of fluids of increasing complexity, from water (to elucidate the effect of interfacial hydrogen bonding formation), to alkanes of different length (to elucidate the role of molecular conformational entropy), and to alkane mixtures (to elucidate the effect of spatial composition partitioning across bubble interfaces). It is expected that these results would provide a stringent test of theoretical approaches (e.g., of the prefactor in the CNT rate expression, and of the suitability of the bubble’s spherical-shape assumption in CNT and Density Functional Theory) and guide new experiments toward ultimately assembling the rules of metastable phase behavior for liquids under tension.