269b The Role of Critical Cavities in Homogeneous Bubble Nucleation

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Previous computational and density-functional theory (DFT) studies[1,2] of cavities (regions devoid of particle centers) within the superheated Lennard-Jones (LJ) liquid revealed that there exists a so-called critical cavity, whereby the presence of cavities with radii larger than some critical radius caused the superheated liquid to become unstable, i.e., phase separate. In addition, the critical cavity was shown by DFT calculations to represent a true thermodynamic limit of stability for the superheated liquid. Furthermore, for the LJ fluid, the size of the critical cavity was found to be a strict lower bound to the size of the critical bubble while the reversible work of forming a critical cavity, Wc, was found to be a strict upper bound to the reversible work of forming a critical bubble, Wb. Wc, like Wb, was also shown to scale in a temperature independent fashion when plotted against the scaling parameter used by Shen and Debenedetti[3] in their DFT study of homogeneous bubble nucleation. These studies reveal a previously unexpected connection between the critical cavity and the critical bubble and suggest that the critical cavity is relevant, to some degree, to the molecular mechanisms of homogeneous bubble nucleation.

To study further the importance of cavities to bubble nucleation for a broader range of fluids, we present additional DFT and molecular simulation results for critical cavities inside model superheated liquids with varying intermolecular potentials. Our calculations reveal, as those in Ref. [4], that the radius of the critical cavity and the ratio of the work of formation of the critical cavity to the work of formation of the critical bubble as predicted by classical nucleation theory exhibit universal scaling across very similar intermolecular potentials. This scaling behavior was used to propose two new criteria for the kinetic spinodal of superheated liquids[4]. Our new results show, however, that the observed scaling across similar intermolecular potentials eventually breaks down for moderate to large differences in the attractive potential. An exploration of the effects of these larger differences in the attractive potential on the cavity-based criteria for the kinetic spinodal is discussed.

We also use DFT and molecular simulation to study the importance of cavities whose volume is defined via a “shell” particle (at least one particle in the spherical shell dv surrounding the volume v of the cavity). The focus on cavities in superheated liquids followed from an initial extension of the molecular theory of vapor-to-liquid nucleation[5], where a “shell” particle was used to define the droplet volume. A more rigorous extension of this approach to liquid-to-vapor nucleation strongly suggests that the cavity, as well as the bubble, should be defined by a shell particle taken from one of the particles assigned to the liquid. We introduce the shell particle into our DFT and computational studies of cavities in model superheated liquids and investigate the effects of using this rigorously defined volume scale.

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