Molecular Dynamic Simulations of Unstable and Metastable Regions

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Prediction of equilibrium and nonequilibrium interfacial properties with density functional theory [1], or description of nucleation processes [2] rely on thermodynamic properties from the metastable and unstable domains of the single-component fluid phase-diagram. Unfortunately, experimental investigation of most of these domains is currently out of reach due to spontaneous transformation into two phases by nucleation after the homogeneous nucleation limit is reached. In a small system, it is possible to prevent nucleation [2,3] and force the fluid to remain in a metastable single-phase state. This can be achieved by using computer simulations with a limited number of particles. The thermodynamic properties of fluids in small systems are, in general, different from those in the macroscopic limit. Computer simulations in small systems in combination with the thermodynamic framework developed by T. L. Hill [4] can possibly be utilized to extract information about the thermodynamic properties in the macroscopic limit. We discuss how this can be accomplished for the Lennard-Jones fluid, where computer simulations are carried out by using classical molecular dynamics in LAMMPS and HOOMD. Computer simulations are carried out for systems of varying size in order to explore the size effect on the properties of the system in the metastable and unstable regions of the fluid phase diagram.

References:

[1] Ø. Wilhelmsen, D. Bedeaux, and S. Kjelstrup, “Heat and mass transfer through interfaces of nanosized bubbles/droplets: the influence of interface curvature,” Phys. Chem. Chem. Phys., vol. 16, no. 22, pp. 10573–10586, 2014.
[2] Ø. Wilhelmsen and D. Reguera, “Evaluation of finite-size effects in cavitation and droplet formation,” J. Chem. Phys., vol. 142, no. 6, 2015.
[3] Ø. Wilhelmsen, D. Bedeaux, S. Kjelstrup and D. Reguera, "Communication: Superstabilization of fluids in nanocontainers" J. Chem. Phys., vol. 141, 071103, 2015.
[4] T. L. Hill, "Thermodynamics of Small Systems, Parts I & II"