Steady-state molecular dynamics simulation of vapour to liquid nucleation with McDonald's dæmon

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Scientifically, the most interesting step of condensation is the droplet formation up to the critical size. In a closed system, this is an instationary process, as the vapour is depleted by the emerging liquid proto-phase. This imposes a limitation on direct molecular dynamics (MD) simulation of nucleation by affecting the properties of the vapour to a significant extent so that the nucleation rate varies over simulation time.

A new molecular simulation method for sampling both nucleation kinetics and steady-state properties of a supersaturated vapour is introduced in the present work. The idea behind the new approach is to simulate the production of droplets up to a given size for a specified metastable state. This is achieved by combining grand canonical MD and an ≪intelligent being≫ that continuously removes all large droplets: McDonald's dæmon [Am. J. Phys. 31 (1962): 31]. In this way, nucleation is studied by a steady-state simulation.

A series of simulations at temperatures between 0.7 T_3 and 0.9 T_c, where T_3 and T_c are the triple point and critical temperature, respectively, is conducted for the truncated and shifted Lennard-Jones fluid which accurately describes the fluid phase coexistence of noble gases and methane. A comparison to canonical ensemble MD simulation as well as Monte Carlo simulation with forward flux sampling confirms the viability of the new method. The classical nucleation theory is found to underpredict the nucleation rate by two orders of magnitude and to overstate the free energy of droplet formation.