# Abstract

For the first time, molecular dynamics simulations (MD) have been used to study the homogeneous vapor–liquid nucleation of argon below the triple point. First, a new method for the precise determination of nucleation rates from MD simulations is developed based on the concept of mean first-passage times (MFPT). This new method proves to be a powerful and universal tool to gain additional information on nucleation, such as the critical cluster size, directly from the kinetics. Second, a comparison of different thermostats shows that the errors arising from the simplest isokinetic thermostat are negligibly small for argon. Third, a study of finite-size effects arising from the vapor depletion and the small system volumes enables an optimization of the systems in terms of their size. Using this knowledge, six nucleation rate isotherms are obtained for the first time in the literature. Only isotherms facilitate the use of the nucleation theorem (NT) to deduct the critical cluster size. The rates are based on more than 7500 simulations and span 3 orders of magnitude about $10^{23} \leq J / \mathrm{cm}^{-3}\mathrm{s}^{-1} \leq 10^{26}$ in a temperature range of $45\ \mathrm{K} \leq T / \mathrm{K} \leq 70\ \mathrm{K}$. The results deviate from the classical nucleation theory (CNT) by 2 – 7 orders of magnitude, which is much smaller than the more than 26 orders of magnitude encountered in recent experiments in a similar temperature range. The theory by Reguera and Reiss shows excellent agreement with the simulation results within one order of magnitude over the entire temperature range studied in this work. The deviations with the experimental results remain huge. The critical cluster sizes obtained from the NT agree well with the prediction of the Gibbs-Thomson (GT) equation, again supporting the notion that CNT succeeds in estimating the location of the nucleation barrier but severely fails to predict its height. In addition, the critical cluster sizes obtained from the MFPT method are consistently higher than those of the NT and the GT equation due to limitations of the Stillinger cluster definition.