

MOLECULAR DYNAMICS SIMULATIONS AND ISOTHERMAL HOMOGENEOUS NUCLEATION

R. Halonen, E. Zapadinsky and H. Vehkamäki

Department of Physics, P.O.Box 64, FIN-00014 University of Helsinki, Finland
email: roope.halonen@helsinki.fi

Two distinct molecular simulation techniques are widely used to predict the nucleation rates: Monte Carlo (MC) and molecular dynamics (MD) simulations. Using MC we obtain isothermal nucleation rate whereas in MD nucleation studies the applied thermostats do not completely thermalize the systems [1, 2]. In this study we compare the nucleation rates obtained with these two different approaches using Lennard-Jones potential.

The homogeneous nucleation process is directly observed in the large-scale molecular dynamics (MD) simulation procedure presented by Tanaka *et al.* [3]. Here the system is thermostatted with velocity scaling method, yet the cluster energy distribution deviates from the one corresponding to ambient temperature [1]. Using nonisothermal nucleation theory [1, 4] these results can be extrapolated to higher concentration of the carrier gas when the completely isothermal conditions can be expected. *Contra* MD, to calculate the nucleation rates *via* MC the time-independent results are supplemented to a classical treatment of cluster population dynamics. Here the classical kinetic model for the steady state nucleation rate expressed by Becker and Döring can be used. The work of cluster formation is calculated by semigrand canonical Metropolis Monte Carlo method [5].

Most of the MD results demonstrate one–two order of magnitude lower nucleation rates than the ones obtained by MC simulations. Discrepancy between MC and MD with using velocity scaling thermostats is bigger for lower nucleating vapour concentrations and lower temperatures. There is good agreement of MC results with the points obtained by extrapolation to high carrier gas concentrations of MD results.

Application of MC simulation to nucleation studies implies the validity of the kinetic scheme and using such thermodynamic properties like free energy for small quasi-stable clusters. MD simulations are free from these assumptions even if the kinetic equation is used to calculate the nucleation rate. Our results support the idea that usage of thermostats for MD simulations related to nucleation problems brings uncertain degree of thermalization. This problem grows with lowering down the nucleating vapour concentrations *i.e.* with approaching to real experimental conditions. The only known option is to use carrier gas as a thermostat in MD simulations studies of nucleation.

- [1] J. Wedekind *et al.*, J. Chem. Phys 127 (2007) 064501.
- [2] S. Toxvaerd, J. Chem. Phys 144 (2016), 164502.
- [3] K.K. Tanaka *et al.*, J. Chem. Phys 134 (2011), 204313.
- [4] J. Feder *et al.*, Advances in Physics 15 (1966), 111-178.
- [5] H. Vehkamäki and I.J. Ford, J. Chem. Phys 112 (2000), 4193.