Calculating Atmospherically Relevant Cluster Free Energies Using Non-Equilibrium Molecular Dynamics

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Atmospheric aerosols play a key role in affecting climate, pollution and human health by influencing the properties and lifetimes of clouds and precipitation. There is therefore great motivation to understand the underlying molecular mechanisms involved in the nucleation of liquid droplets. One important quantity in nucleation studies is the *excess free energy*. In this work, we extract this property using a novel disassembly method (Hoi and Ford [1]) based on the Jarzynski relation [2]. We first investigate clusters of pure water (using the TIP4P/2005 model [3]) followed by sulfuric acid-water clusters since sulfuric acid is a key player in terms of acting as condensation nuclei. Our first study evaluates the free energy of splitting a *2N* water cluster into two *N* sub-clusters to obtain the curvature-dependent surface tension and the results are compared to other reports in the literature. We then move on to simulating complete disassembly of water clusters to extract the excess free energy curve, which was established to be in good agreement with internally consistent classical theory (ICCT) [4]. Furthermore, the nucleation rate is calculated using the classical Becker-Döring equations and compared to experimental values by Brus et al. [5-6] It was found that our values lie within two orders of magnitude of the experimental data within the range of supersaturation studied at 300 K. Finally, investigations into the excess free energy surface are begun for sulfuric-acid water clusters using a newly developed potential model based on empirical valence band (EVB) theory [7].

References

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