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Properties of Supercooled Water Clusters from Nucleation Rate Data with the Effect of Non-ideal Vapour Phase

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There is a continuous interest to properties of supercooled liquid water due to it's importance in atmospheric phenomena and in scientific and technical applications. For example, in experimental studies of homogeneous water nucleation, quite high saturation ratios are needed to produce highest nucleation fluxes and correspondingly smallest critical clusters. Due to the exponential temperature dependence of saturation vapour pressure and thus saturation ratio, high enough supersaturations are achieved only when temperature is lowered below the freezing point of water. This now leads to situation, where also nucleating clusters are in a metastable, supercooled state. Sizes and excess energies of these clusters can be found using the first and second nucleation theorems, which give a model independent way to evaluate these properties directly from the slopes of nucleation rate data with respect to saturation ratio and temperature, respectively. However, the usual procedure here neglects the non-ideal behaviour of supersaturated vapour at low temperatures. In this work, we have evaluated the importance of these non-ideal effects using the second virial coefficient data.

Due to previously mentioned interests, most of the thermodynamic properties of supercooled water are known quite accurately and even reviewed recently, though some are still subject to debate. However, at the moment there does not exist any correlation for the second virial coefficient, $B(T)$, of water that is recommended to be used below 300 K. Main reason for this is that it is extremely hard to measure needed properties (e.g. *pVT*-data or Joule-Thomson coefficients) accurately enough even above 273.15 K, not to mention measurements with respect to colder, supercooled water, where condensation losses within measurement system introduce increasing uncertainties. This problem has recently been tackled by numerous simulation studies. Meta-analysis of these studies shows that both *ab initio* and semiempirical pair potentials can give reliable information on the second virial coefficient of supercooled water when both the flexibility of water monomer and higher order quantum corrections (in case of *ab initio* pair potentials) are taken into account. These data also allow us to compare the existing correlations for the second virial coefficient in temperatures below 273.15 K, and thus evaluate $B(T)$ at temperatures relevant for nucleation studies. It will also allow the comparison of various semi-phenomenological models of nucleation with the experimental data.

In this presentation we will give results of analysis of the effect of vapour phase non-ideality to the properties of critical supercooled water nuclei as well as comparison with the classical capillary drop model.

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