Thermodynamic properties and cavitation mechanism of water at negative pressure

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Bubble nucleation is relevant in many different technological contexts, such as explosive boiling[1], cavitation erosion[2] and sonochemistry[3]. In spite of the practical relevance of these phenomena, the mechanism by which the vapor phase nucleates from a homogeneous, metastable liquid is still under debate. In order to be able to study bubble nucleation of water, one needs to have a potential model capable to predict the equation of state in the metastable region with high accuracy. In this work, we report numerical calculations of a number of thermodynamic properties of TIP4P/2005 water at negative pressures, such as the equation of state, the spinodal and the cavitation lines, the line of maximum densities (TMD) and the speed of sound. To be able to capture the kinetics of bubble formation, we perform Molecular Dynamics simulations of the TIP4P/2005 water model[4] with the GROMACS 4.5 package[5]. TIP4P/2005 is an interaction potential that represents water as a rigid and non-polarizable molecule. When available, we compare our results to recent experimental results from Professor Caupin's group in Lyon.

Even in the stable liquid phase, spontaneous density fluctuations occur in the bulk system. In a superheated liquid, some of these local density fluctuations may grow to nucleate a bubble of the stable vapor phase. Wang and coworkers have recently reported a Molecular Dynamics study of homogeneous bubble nucleation in a Lennard-Jones fluid[6], observing that cavitation started with compact bubbles rather than with ramified structures as suggested by Ref.[7] and that local temperature fluctuations were strongly correlated to the subsequent bubble formation. In the same year, Wedekind and coworkers studied the opposite phenomenon, vapor condensation, in the same monoatomic Lennard-Jones fluid and observed a crossover between a "nucleation-and-growth" and a "spinodal decomposition" regime, depending on the supersaturation. More recently, Pereza and Rubio[9] investigated condensation of the super-saturated vapor of TIP4P/2005 water, using Mean First Passage Time[10] to analyze the influence of charged species on nucleation dynamics. The authors found that the presence of charged species had a dramatic impact on the dynamics and that the TIP4P/2005 water model predicted anions inducing faster formation of water clusters than cations of the same charge. However, as far as we are aware, bubble nucleation from an over-stretched metastable liquid water has never been tackled so far.

In our work, we investigate the cavitation mechanism at negative pressures by means of Mean First Passage Time[10]: we compute the nucleation rate and study how the nucleation mechanism changes depending on the supersauration from the spinodal line of the metastable liquid. When studying cavitation, we also investigate the effect of the chosen order parameter by comparing the nucleation rate computed using a local order parameter (the volume of the largest vapor bubble in the system) to the one obtained using a global order parameter (the total volume of the vapor in the system). Moreover, to identify a vapor bubble in the metastable liquid, we define two independent local order parameters: one sensitive to the formation of large, connected void spaces (as in Ref.[6]) and another based on a Voronoi tesselation[11]. An example of a nucleating bubble at a state point not close to the spinodal line is given in Fig.1.

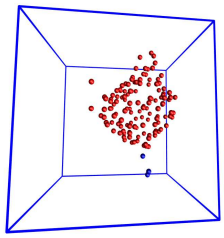

FIG. 1. Snapshot of the a nucleating bubble (in red) at T=280K and p=-2630bar.

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