Solubility of methane in water and its connection to the hydrate nucleation

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Differently than in the case of the formation of ice, the process of the formation of a hydrate requires the presence of two different compounds – water and a guest molecule. Because of their low solubility in water, hydrophobic guest molecules are a limiting factor in the process of nucleation and growth of a hydrate. As a result, studies of these processes by the means of molecular dynamics can be challenging. In this work we shall determine the solubility of methane in water when in contact either with the hydrate or with the gas phase using two-phase direct coexistence simulations using TIP4P/Ice model for water and a single Lennard-Jones site model for the methane. The solubility will be computed at several temperatures along the 400 bar isobar. The impact of the curvature of the interface on the solubility of methane will be analyzed. The solubility curves obtained from two phase simulations (via a planar interface), where liquid solution of methane in water was in contact with either the methane gas phase or the hydrate phase, will be used in order to determine the triple point (T_3) at the studied pressure of 400 bar. This result will be then compared to the value of T_3 obtained by the three phase direct coexistence method – it will be shown that both results are in good agreement and give the value of T_3 of 295(3) K. The analysis of the impact of the curvature of the interface (either gas-liquid or solid-liquid) on the solubility of methane in water will also be presented. It will be shown that the concentration of methane in water can be increased above the solubility limit by introducing curved interfaces. In the last section, the change in chemical potential for the formation of the hydrate will be evaluated along the 400 bar isobar and it will be shown that the supersaturation of the solution increases the driving force for nucleation dramatically.