Estimation of the Three Phase Coexisting Line for Carbon Dioxide Type I Hydrates using Molecular Dynamics

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The interest on CO_2 hydrates characterization has increased remarkably over the last few years due to the possibility of using them for waste CO_2 recovery, capture and storage. The feasibility of replacing CH_4 by CO_2 in hydrate deposits existing in nature has been discussed, and seems to be a promising alternative with evident environmental benefits in the near future. Nevertheless, the modelling of CO_2 or mixed hydrates has received less attention so far, and the theoretical estimation of their phase equilibria and thermophysical and transport properties still needs further contributions. In this case, rigid non polarizable molecular models have been used to describe H_2O and CO_2, and the three phase CO_2 Hydrate-Liquid H_2O-Liquid CO_2 equilibrium line has been determined using Molecular Dynamics and the direct coexistence technique. The influence of the initial occupancy rate of the different cells of the type I hydrate has been evaluated, as well as the effect of the different parameterizations of the molecular models in each case. It has been found that, although correct qualitative results are found for this type of models up to high pressures, the H_2O model version plays a key role in the precise determination of the phase boundary location, which is by far less sensitive to the CO_2 model version employed.