

Gas Hydrates Dissociation Temperature Determination Through Isenthalpic-Isobaric Molecular Dynamics Simulations

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Gas hydrates are crystalline solids composed of water and light gases, which occur most commonly in types I and II structures, depending on the shape and size of the gas molecules. The direct phase coexistence method is commonly used in the literature to determine the dissociation temperature of hydrates by molecular simulation. This method requires the execution of several simulations for a single equilibrium point, demanding a high computational cost. As an alternative, in this work we propose the use of the isenthalpic-isobaric (NPH) ensemble to determine the dissociation temperature of gas hydrates. In this ensemble, the system temperature evolves towards equilibrium based on the enthalpies of dissociation and hydrate formation in a single simulation, for each pressure condition. Energy conservation is a key factor in the convergence of the method. An extensive analysis of several preliminary simulations resulted in a methodology that includes the use of double precision, a 1 fs time step, the use of only one computational node to run the simulation, and the use of the Parrinello-Rahman barostat. Two systems are studied: a sI methane hydrate and a sII mixed methane and propane hydrate, both fully occupied. The dissociation temperature of both systems is determined for pressures of 40, 80, 150, 300, and 500 bar. Despite limitations regarding the convergence of the method, the NPH ensemble proved to be an efficient alternative to determine the dissociation temperature of more complex systems, such as hydrates, using an appropriate methodology to conserve the system's energy. Average deviations below 2% are obtained when compared to values from other molecular simulation works and experimental data. This demonstrates the good predictive capabilities of the method and models used.