Calculation of Phase Equilibrium for Gas Hydrate Systems Using Monte Carlo Simulation and Theory

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In this paper, we consider the calculation of phase equilibria for methane-water mixtures, including clathrate hydrate phases, using the Monte Carlo simulation and theory for models of the intermolecular forces in the systems. We have developed two simulation approaches for obtaining the free energy of the hydrate phase. The first is an adaptation of the Frenkel-Ladd thermodynamic integration from an Einstein crystal. This is directly applicable to the fully occupied hydrate phase. In the second method, we use an isobaric semigrand ensemble to construct a reversible path from a fully occupied hydrate to an empty hydrate. This latter method is useful for obtaining free energy information about partially occupied hydrate phases. We consider two classes of models for the interactions. The first is a mixture of hard spheres and associating hard spheres with dispersion forces added to a mean field. This is one of the simplest models for hydrophobic effects in methane-water mixtures. We also supplement this model by the addition of a dipole to the associating hard spheres. For the fluid phases we use thermodynamic perturbation techniques developed by Nezbeda and coworkers. In addition, we report some calculations with the SPC/E model for water and the Lennard-Jones potential for methane. In addition to the calculation of the water-methane phase diagram, we use our calculations to assess the accuracy of approximations such as the rigidity of the hydrate lattice that appear in theories of hydrate stability, such as the van der Waals-Platteuw theory.