238e Assessing the Van Der Waals and Platteeuw Theory of Gas Hydrate Thermodynamics Using Monte Carlo Calculations of Hydrate Free Energies

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The van der Waals–Platteeuw (vdWP) theory is the most widely used theory of gas hydrate thermodynamics. It is a cell theory based on the idea that the properties of a hydrate can be understood in terms of the motion of the guest molecules in cages created by the water molecules, which are assumed to be in a static configuration. We have recently used isobaric semi-grand ensemble Monte Carlo simulations to calculate the free energy and chemical potentials for water and methane in models of methane-hydrates. Here we use these results to test the predictions of the vdWP theory for the model systems. Our results indicate that the chemical potentials in these systems are sensitive to the interactions between methane molecules in different cages as well as motion of the water molecules away from a static lattice configuration. These effects are neglected in the vdWP theory. We show that the vdWP theory does benefit from some partial cancellation of errors.