

Molecular Simulation of the Thermodynamic Properties of Natural Fluids: Liquid/Vapor Equilibria in and Around the Critical Region in the Water System

The purpose of this research program is to develop methods for predicting the thermodynamic properties of the system $\text{H}_2\text{O}-\text{NaCl}-\text{CH}_4-\text{CO}_2$ (SWS) based on interactions at the molecular level. Molecular simulation methods are fairly straightforward but there are several important problems that today limit the direct calculation of the thermodynamic properties of natural mixtures. Among the most important of these are the following: 1. Phase coexistence predictions require extremely accurate free energy calculations. Even the highest-level quantum chemistry calculations have difficulty reaching this accuracy for calculations of weak intermolecular interactions. 2. To produce simulation results that can replace experimental data, parameters, such as the number of particles included in the simulation, and simulation times required to obtain reliable statistics or to produce thermodynamic averages (e.g., free energies) are large. In SWS, the most difficult interactions to model at the molecular level are those of water molecules interacting with each other and with other species in the system. Water is a strongly polar system, and the effects of its hydrogen bonding are responsible for many of its solution properties. Since the basic work of Rahman and Stillinger (1971), hundreds of articles dealing with MD/MC simulation of water have been published and over twenty water potential functions have been proposed. Most of these potentials are based on a spherically symmetrical short range potential with hydrogen bonding effects incorporated by placing several charges in the molecule. For some applications these potentials

work rather well. However, to predict the observed field behavior in natural systems, the required accuracy is very high (Weare 1987). In Fig. 1 (partially taken from Boulougouris et. al. (1998)) we show the predicted liquid-vapor coexistence of water using most of the well-known simulation potentials. The errors in all of these calculations (are discussed below) are too large to provide meaningful interpretation of field measurements. Here we present predictions of PVT properties, energetics and phase coexistence calculations for the water-water interactions using a potential due Reimers and Watts (1982). This potential was parameterized from a large database, including ice data and spectroscopic data. Phase coexistence results are included in Figure 1. In addition, we have calculated and will present results of PVT properties for a large range of temperature, pressure and vapor pressure calculations. All of these properties agree well with experimental data. In addition to simulations we discuss the development of a phenomenological representation of the data that forces the correct behavior in the critical region. Common equations of state give a very poor representation of the data in this region. However, this method, based on the work of Moldover and Rainwater (1988), can be used to fit both measured and simulated data, therefore providing a convenient means for accurate interpolation and extrapolation of mixed system predictions. We have shown that this method significantly improves representation of the PVTX properties in the critical region.