Molecular Simulation and the Derivation of Fluid Properties for Fluid Flow and Reactive Transport Simulations

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1. Fluid flow simulations, equations of state, and transport properties

Currently, simulations of fluid flow in "realistic" 3-D geological models start to become feasible. Many unknowns in such simulations (e.g. permeabilities) may be approximated by assumptions based on field evidence. Probably the most severe limitation for increasingly realistic simulations is the lack of accurate equations of state (EOS as well as correlations for transport properties) for fluids other than pure water. However, the available EOS for H_2O-NaCl usually only cover a restricted PTX range and therefore do not provide the necessary data for flow simulations. Palliser and McKibbin (1998a,b,c) tried to design correlations specifically for flow simulation but close inspection reveals that the model has some severe problems around the critical temperature of water making it essentially useless for flow simulations. In addition to problems with EOS, parameters such as the dynamic viscosity have only been measured over very limited P-T-X ranges and extrapolations may be in error.

While the problems in the critical/supercritical region may be solved by choosing adequate mathematical expressions, the lacking knowledge about various parameters is severe. The production of accurate experimental data would require much more time than desirable given the fact that the flow simulations are possible *now* while the data production would require at least several years. Molecular simulation techniques are well suited to derive data of presumably reasonable accuracy in regions where experiments are tedious and difficult. Several simulations of the H_2O-NaCl system have shown that experimental pressures of simulated solutions at a given T-X-ρ can be reproduced reasonably well. Since pressure and viscosity in a molecular simulation are both derived from the pressure tensor, the prediction of the viscosity should be acceptable as well. Some results for this system using the will be presented in comparison to experimental data.

2. Towards a unified chemical scheme for reactive transport simulations at high T

The interpretation of chemical processes requires the assumption of a chemical model. At low temperatures the assignment of thermodynamic properties to well-defined species usually is a good starting point with powerful predictive capabilities. On a molecular scale, this approach frequently breaks down in the case of high temperatures and/or more concentrated solutions because the definition of a species becomes arbitrary: at low concentrations and low temperatures the "associated" and "dissociated" states can be distinguished because in the "associated" case two ions, say, Na^+ and Cl^- will be in a deep minimum in the potential of mean force (PMF) curve while the small thermal energy will only occasionally allow them to leave this minimum ("dissociate"). At high temperatures this happens more frequently and intermediate states (such as the "solvent-shared ion pair") will contribute significantly to the overall state of NaCl in solution. In such cases only a statistical mechanical interpretation based on the PMF is appropriate (Chialvo et al., 1997).

The situation gets worse when the concentration is high. The spatially close position of the ions combined with the high thermal energy lets the relative importance of the occupation of minima on the PMF surface (= "associated") decrease and the contribution of "undefined" (with respect to "species") states increases. While ion clusters in the solution may be identified in MD simulations (Driesner et al., 1998) and an average stoichiometry may be seen in spectroscopic data (Seward et al., 1999), the definition of when, for example, an Na_3Cl_3 cluster exists is totally arbitrary and has little predictive thermodynamic potential.

This situation has been treated in the "Pitzer model". Unfortunately, at high temperatures experimental data are too scarce to parameterise Pitzer models. Molecular simulation may help to identify trends in the parameter values. I compare the results from MD simulations with parameters deduced from experiment. Molecular simulation also provides diffusion coefficients of the ions in solution: we directly get the bulk diffusion coefficient for Na^+ in the state the Pitzer-based activity coefficients pertain to. Such combined equilibrium and transport parameters from molecular simulation results greatly reduce the complexity of the specific chemical model in a reactive transport simulation. However, great care has to be used in the molecular simulations since system size effects play a large role at high concentrations.

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