Computational Prediction of Critical Properties of Energy-Related Compounds:

Jared Fern achieved a PhD with a dissertation titled "Methods for the Self-Consistent Determination of Thermophysical Properties from Two-Phase Molecular Dynamics Simulations." This work is the product of collaboration between UT and ORNL advisors, David Keffer and Bill Steele.

Jared's thesis described the calculation of critical properties for ethanol and ethanediol, substances of significant importance in engineering. Although critical properties are the cornerstones of equations of state used to represent all materials, there are less than 700 organic chemicals whose critical temperatures have been measured by experiment. This is largely due to thermal instability of most organic compounds in the critical region. Reliable methods for the estimation of critical properties are needed to fill the gaps, and will assist industry in attempts to save energy and increase efficiency in developing modern manufacturing techniques.

Estimation techniques developed to date have proved to be insufficient even for so-called "simple" substances. For 1,2-ethanediol (ethylene glycol; antifreeze) the "accurate" estimates available in the literature for the critical temperature range from 620 K to 770 K. The new method developed in this work, using Voronoi tessellations to determine the volume of every single molecule, can accurately describe the near-critical region. By coupling the molecular volume to statistical parameters, the phases can be determined self-consistently without arbitrary cut-offs or bins of any kind.

Jared's thesis also discussed results relating to the structure of both the liquid and gas phases for ethanediol and ethanol. For ethanol, hydrogen-bonding in the gas phase agrees with recent neutron diffraction work. For the diol, intra- hydrogen-bonding was shown to be more prevalent than inter- in the gas phase, but in contrast in the liquid phase, the glycol resembled a polymer with "very long" chains existing even close to the critical region.

This UT-ORNL collaboration has resulted in the preparation of three research papers to the *Journal of Physical Chemistry Part B*, two of which have now been published with the third under internal review prior to submission. In addition, several simulation research groups have shown interest in collaboration to further develop the methodology.

Fern, J. T.; D. J. Keffer, W. V. Steele "Measuring coexisting densities from a two-phase molecular dynamics simulation by Voronoi tessellations." *J. Phys. Chem. B* v. 111, 2007, 3469-3475.

Fern, J. T.; D. J. Keffer, W. V. Steele "Vapor-liquid equilibrium of ethanol by molecular dynamics simulation and Voronoi tesselation." *J. Phys. Chem. B*., published on Web 11/1/2007.

Fern, J. T.; D. J. Keffer, W. V. Steele "Vapor-Liquid Equilibrium of 1,2-Ethanediol by molecular dynamics simulation and Voronoi tesselation." In review prior to submission to *J. Phys. Chem. B*.

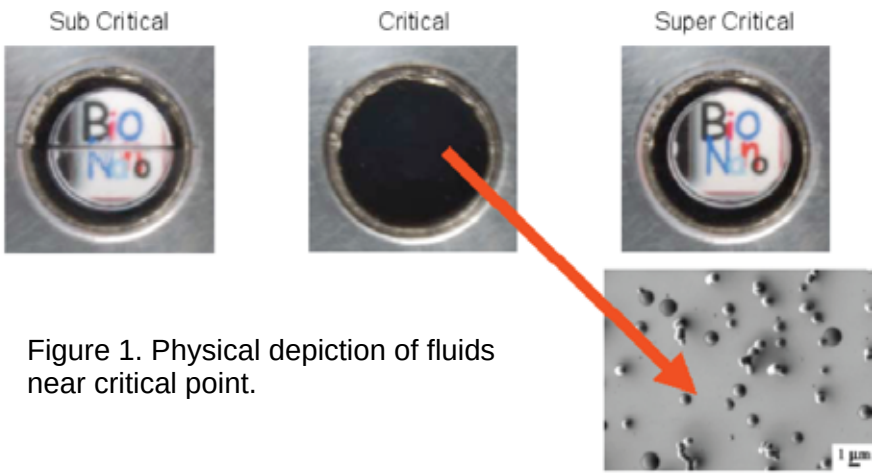

Figure 1. Physical depiction of fluids near critical point.

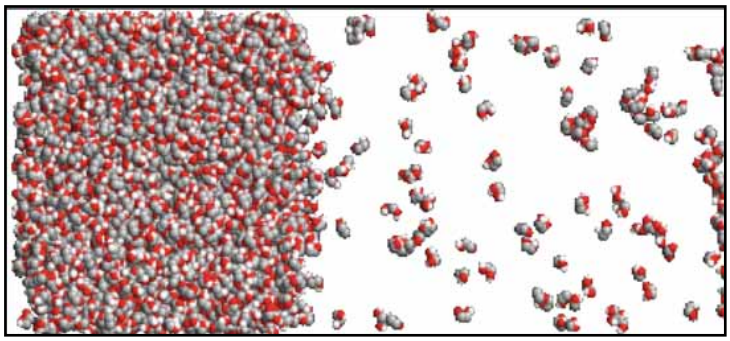

Figure 2. Molecular dynamics simulation of vapor and liquid resembles experiments. Interfaces are explicitly simulated.

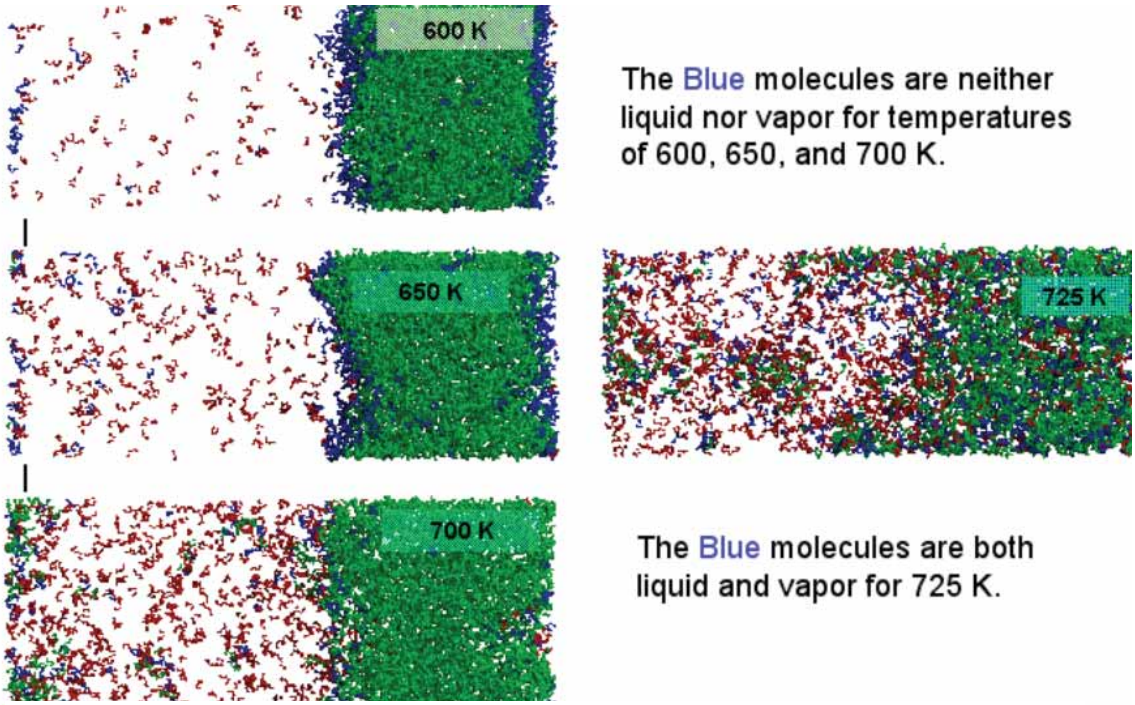

Figure 3. Configurations of molecules in simulations of ethylene glycol at temperatures between 600 and 725K. Molecules are color coded green for liquid, red for gas, and blue for interfacial, depending on the coordination number. The fraction of molecules that are neither fully liquid or gas increases and the segregated structure of the two phases is reduced as the critical point is approached.