Computational Quantum Mechanics: An Underutilized Tool in Thermodynamics

S.I. Sandler[C, S]
Department of Chemical Engineering, University of Delaware, Newark, DE, U.S.A.
sandler@udel.edu

With continual improvements in computing power, the use of molecular simulation has increased in the last two decades. At the simplest level, simulation can be used to test statistical mechanical and applied thermodynamic models. This is usually done using simple force fields, such as a hard sphere or Lennard-Jones potential neglecting nonpairwise additivity, and as the theory and model use the same potential the simulation provides a test of the model. At the next level, simulation can be used to provide insight into phenomena, for example local compositions, that may not easily be probed by other methods because of the length or time scales involved. Insights may be obtained with approximate empirical potentials, though caution is needed in interpretation as the predictions of some phenomena can be very sensitive to the force field used. For example, which of several crystal structures is found to be the most stable can depend on slight differences in the potential. The highest level is the holy grail of simulation, the accurate prediction of properties completely from first principles. This requires an accurate force field that may be obtainable from quantum mechanics, and which will not be of the simple forms typically used in simulation. However, as the Schrodinger equation cannot be solved exactly for a multi-electron system, approximations are needed. Nonetheless, this area of research has progressed to the point where in some cases quite accurate first principles predictions of equilibrium and transport can be made from the combination of quantum mechanics and statistical mechanics. Some examples of the successes and failures of this procedure will be presented.