67f Making Room for Intuition in Molecular Simulation

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Molecular simulation provides perhaps the most detailed picture possible of the underlying nature of material behaviors. It is a very fine microscope, one that can examine behavior with sixteen digits of precision. Of course, the usefulness of all this information depends greatly on the quality of the model that is being examined with it. But even if the model were perfect, we would remain at risk of being awash in more data than we can interpret. The collection of data is not equivalent to the development of understanding. It is important to have a conceptual framework in which to collect and organize the detailed picture. This framework informs, and is informed by, our physical intuition.

Thermodynamics is the first framework in which to process data from molecular simulations. It naturally averages out the detailed molecular picture, and connects to the macroscopic world we experience every day. When the molecular picture is appropriate, we need also the tools of statistical mechanics, which provide useful constructs for interpreting and retaining molecular-scale information.

An increasingly common question inquires about the behavior of not an individual system, but about two systems, and how they compare. In molecular simulation this question arises in one form as the free-energy calculation. Knowledge of free-energy differences is central to the understanding of many important phenomena, including phase equilibria, stability, and even kinetic processes. In molecular simulation, a popular type of free-energy calculation method is highly prone to inaccuracy, and in some cases it is easy to proceed correctly and yet obtain very precise numbers that are quite wrong. An intuitive picture of the way two systems relate from a molecular perspective can be formed by examining the relation between parts of phase space important to each. This relation can be quantified by the relative entropy, which differs from the thermodynamic entropy. Intuitively appealing constructs can be developed from this picture, and their application can guide the use of molecular simulation so that it provides results that are both precise and accurate. We consider such ideas in this presentation.