455f Determination of Interfacial Tension in Binary Mixtures Using Transition-Matrix Monte Carlo

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Knowledge of the properties of fluid interfaces is key to understanding a wide variety of scientifically and technically important processes ranging from nucleation, heat transfer, to self-assembly. Because of the small length scales involved, interfacial phenomena are ideally suited to be studied by molecular simulation. A key quantity that characterizes a fluid-fluid interface is its interfacial tension. However, precise determination of this quantity for fluids over their entire phase-coexistence range by molecular simulation has remained elusive. The traditional approach to this problem has been to simulate directly the interfacial region and calculate the average values of the normal and transverse components of the stress tensor. The results yielded by direct simulation methods are known to be sensitive to system size and how long-ranged interactions are treated. Furthermore, the range of thermodynamic conditions for which these calculations are tractable is fairly limited. An alternative approach that circumvents many of the limitations of direct interfacial simulations is the use of so-called “flat-histogram” sampling methods in conjunction with finite-size scaling analysis [1-3].

Recently, the combination of grand-canonical transition matrix Monte Carlo and finite-size scaling has been shown to be a highly efficient approach to preceisely determine the surface tension of pure fluids at both sub-critical, near-critical, and critical temperatures [2,4]. In this work, we take an important step and extend the methodology to calculate the interfacial tension of binary mixtures. In particular, we use mixture transition-matrix Monte Carlo [5] to calculate the free energy barrier separating coexisting phases at various system sizes, and then use the finite-size scaling formalism introduced by Binder [1] to extrapolate these values to the infinitely large system limit, which corresponds to the *thermodynamic* interfacial tension. An important advantage of this approach is that the interfacial tension can be readily calculated across the entire composition range at fixed temperature in what usually amounts to four or five simulations. We demonstrate the utility and efficiency of the method by investigating the interfacial tension (liquid-vapor and liquid-liquid) of several binary Lennard-Jones mixtures.

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