Computer Simulation of Interfacial Tensions

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In this contribution we will analyze the calculation of interfacial tensions using computer simulation methods. We will focus the discussion on the case of interfaces between vapor and liquid phases (at equilibrium) of one component systems. However, most of the ideas and conclusions can be applied to other types of interfaces.

The calculation of the surface tensions of liquid-vapor interfaces can be carried out using different methods.[1] Most of the techniques can be classified in two groups: (a) Simulations of systems with explicit interfaces, and (b) Binder procedures[2,3].

Explicit Interfaces: The simulations are carried out (for one component systems) in the canonical ensemble using periodic boundary conditions(PBC). The density is taken as an intermediate value between those of the vapor and liquid phases at equilibrium at the corresponding temperature. The simulation box is chosen to be elongated in one direction, and the interfaces are built (and expected to stay) perpendicular to that direction. The surface tension, γ, is computed as the derivative of the Helmholtz energy function with respect to the surface area at constant volume.

These procedures are quite straightforward, but some care has to be taken to avoid spurious finite-size effects[4,5]. On the other hand, these methods can not be used to compute interfacial tensions of lattice models.

Binder Procedures: For the liquid-vapor case, the usual approach is to use a grand-canonical-like calculation (with PBC and eventually with elongated boxes) to compute the Helmholtz energy function, $A(N|V,T)$, at given conditions of volume, V, and temperature, T, for different values of the number of particles N. With the results of $A(N|V,T)$ it is possible to determine the conditions of liquid-vapor equilibrium (LVE) (i.e. the values of the chemical potential, μ_e, and pressure p_e of the transition), and then to extract the surface tension by considering that the grand potential, $\Omega_e(N) \equiv A(N) - N\mu_e$, is expected to fulfill, if two phases coexist, $\Omega_e(N) = -p_e V + \gamma \mathcal{A}(N)$, where $\mathcal{A}(N)$ is the interfacial area.

Within this framework the interfacial tension is not computed as a derivative but as a difference between the values of Ω_e at coexistence situations and those of the pure phases. This fact alleviates most of the problems with finite-size behavior that appear in the differential methods. Nevertheless, Binder methods require for most cases non-standard simulation methods[3,6] to get reliable results for $A(N,V,T)$ in the two-phase region. In fact γ is often computed as a by-product of the finite-size scaling analysis of the LVE close to the critical point.

Finite-size effects: In the poster, we will illustrate the facts commented above showing results from both kinds of techniques applied to the LVE of a Lennard-Jones fluid. Special attention will be paid to the dependence of the results with the different system lengths.

Thermodynamic Integration techniques: Given the non-monotonic dependence of γ with the interfacial area that appears in the explicit interface methods[4,5] (at least for small systems) we could think on the possibility of using Thermodynamic Integration (TI) procedures to compute γ for liquid-vapor interfaces, with the aim of keeping the relative simplicity of the explicit interface simulation procedures while using a non-differential route to compute γ. TI methods have been proposed to compute the interfacial free energy of systems near a hard wall[7].

In our case the TI is build up to go from the system divided into two non interacting phases to the system with the two phases connected through the corresponding interface. Some preliminary results using TI on lattice gas models will be shown, and compared with those attained using the Binder method. Finally, possible ways of adapting TI techniques to compute γ for atomistic models will be discussed.

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