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Direct calculation of the thermodynamic correction factor, Γ, from molecular dynamics simulations.

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The link between the Maxwell diffusion coefficient, D^M, and Fick's diffusion coefficient, D^F, is made through the thermodynamic correction factor, Γ, that gives the variation of the chemical potential of one species as a function of the variation of the number of molecules for a given volume and temperature. While D^M can be easily calculated from molecular dynamics (MD) simulations under equilibrium conditions, a lot of applications or softwares favor the use of D^F. D^F can be directly calculated from direct non-equilibrium molecular dynamics but it is not the most popular method to get it, as an alternative it is deduced from D^M and knowledge of Γ. Except for the case of ideal systems, the calculation of Γ requires additional simulations. The aim of this work is to propose a new route to obtain Γ directly and accurately from one molecular dynamics (MD) simulation (microcanonical or canonical) in which D^M also can be calculated.

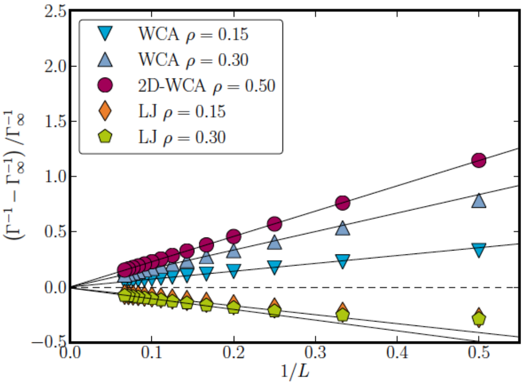

Figure 1 The variation in thermodynamic correction factor for small systems as a function of 1/L (L the system size). One set of simulations were performed in 2-dimensions with WCA-particles, while the rest were performed in 3-dimensions with LJ and WCA particles. The densities ρ are given in reduced units.

As it is well known, small parts of a large system behave like a grand-canonical ensemble. Under these conditions Γ can be directly calculated from the fluctuations of the number of particles, N, in sub-volume, V, at fixed temperature, T:

$$\Gamma^{-1} = k_B T \left(\frac{\partial \ln N}{\partial \mu} \right)_{T,V} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle},$$

where μ and k_B are the chemical potential and the Boltzmann constant.

We applied this formula to different systems, n-heptane in zeolite [1] and fluid argon [2] and obtained excellent agreement with previous methods. For argon systems we compared different atomic models (LJ: Lennard-Jones and WCA: Weeks Chandler Andersen) and we predicted and verified important small size scaling effects, see Figure 1. As we showed in [2], the deviation of Γ^{-1} from the value at the thermodynamic limit is linear with the inverse of the length of the volume investigated. From a single simulation, the calculations of Γ^{-1} using different sizes of sub-volumes lead by a simple linear extrapolation to the value of Γ_{∞}^{-1} at infinite volume. The results of the Figure 1 were computed from grand-canonical Monte-Carlo simulations they perfectly agree with MD simulations in canonical and microcanonical ensembles.

These results confirmed that small sub-systems of a larger one behave like a grand-canonical ensemble and that the fluctuation equation can be used to calculate directly the thermodynamic correction factor from a N constant molecular dynamics simulation. As a consequence, the Maxwell and the Fick's diffusion coefficients, can be easily computed in the same simulation using this fluctuation approach.

References

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