

## Direct calculation of the thermodynamic correction factor, $\Gamma$ , from molecular dynamics simulations.

*Sondre K. Schnell<sup>a</sup>, Thijs J.H. Vlugh<sup>a</sup>, Jean-Marc Simon<sup>b</sup>, Signe Kjelstrup<sup>a,c</sup>, Dick Bedeaux<sup>c</sup>*

<sup>a</sup>Process and Energy Laboratory, Delft University of Technology, Leeghwaterstraat 44,  
2628CA Delft, The Netherlands

<sup>b</sup>Laboratoire interdisciplinaire Carnot de Bourgogne, UMR 5209, 9 avenue Alain Savary,  
CNRS-Université de Bourgogne, F-21078 Dijon, France, [jmsimon@u-bourgogne.fr](mailto:jmsimon@u-bourgogne.fr)

<sup>c</sup>Department of Chemistry, Faculty of Natural Science and Technology, Norwegian  
University of Science and Technology, Trondheim, Norway

The link between the Maxwell diffusion coefficient,  $D^M$ , and Fick's diffusion coefficient,  $D^F$ , is made through the thermodynamic correction factor,  $\Gamma$ , 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  $\Gamma$ . Except for the case of ideal systems, the calculation of  $\Gamma$  requires additional simulations. The aim of this work is to propose a new route to obtain  $\Gamma$  directly and accurately from one molecular dynamics (MD) simulation (microcanonical or canonical) in which  $D^M$  also can be calculated.

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

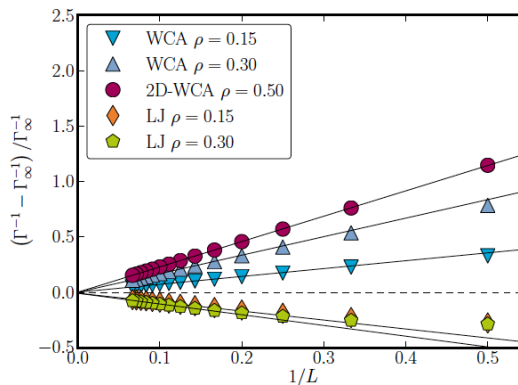


Figure 1 The variation in thermodynamic correction factor for small systems as a function of  $1/L$  ( $L$  the system size). One set of simulations were performed in 2-dimensions with WCA-particles, while the rest were performed in 3-dimensions with LJ and WCA particles. The densities  $\rho$  are given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

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

where  $\mu$  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  $\Gamma^{-1}$  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  $\Gamma^{-1}$  using different sizes of sub-volumes lead by a simple linear extrapolation to the value of  $\Gamma_{\infty}^{-1}$  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

- [1] Floquet, N.; Simon, J.-M.; Coulomb, J.-P.; Bellat, J.-P.; Weber, G.; Andre, G. *Microporous Mesoporous Materials* 122 (2009) 61.
- [2] Sondre, K.S.; Vlugt T. J. H.; Simon, J.-M.; Bedeaux, D.; Kjelstrup S.; *Chem. Phys. Let.* 504 (2011) 199.