

Change of Free Energy During Adsorption of a Molecule

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A crucial question in the adsorption of complex molecules is that about their conformation. One possibility to answer that question is to calculate the change of the free energy during adsorption of a molecule by simulations. Starting from the canonical partition function a general result is that the change in the free energy is the change in the potential of mean force. This is physically obvious as it says that the change in free energy is the work required on a reversible path. Another general result is that the potential of mean force is related to the logarithm of the local density. Hence, there are two independent routes for the calculation of the change of the free energy. The first one is to calculate the local density of the species to be adsorbed under the condition that all molecules move without constraints. The second route is to fix the molecule to be adsorbed in a certain position and to calculate the mean force exerted on it from the wall and the fluid particles; thereafter this mean force has to be integrated over an appropriate path to yield the potential of mean force. The final question of interest is the performance of both routes. In particular we expect that the local density may not be easily accessible from molecular simulations in some cases, e.g. in the case of protein adsorption, and hence the route via calculating the mean force at fixed positions of the molecule may be more appropriate.

In the present contribution we present results obtained from the two routes for the case of simple systems consisting of a 9/3-Lennard-Jones wall and several Lennard-Jones fluids. Most of the results were obtained by molecular dynamics simulations. In some cases we show for comparison also local densities from solutions of the Born-Green-Yvon equation.