

# Molecular Simulation of the Adsorption of Molecules from Dilute Solutions

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The adsorption of biomolecules on surfaces is a perennial and general challenge relevant to many fields in biotechnology. In adsorption of complex molecules like proteins and nucleic acids an essential question concerns the conformation of the adsorbed molecule. Direct investigations by molecular simulations are difficult as adsorption usually occurs on a long time scale. However the most favourite position, orientation, and configuration of the adsorbed molecule will be determined by the minimum of the free energy. The present contribution is concerned with the calculation of the change of the free energy during adsorption of a molecule by molecular simulations.

The change of free energy can be obtained both by integration over the mean force (MF) on a molecule and via the local density. The first method is physically obvious as it says that the change in free energy is the work required on a reversible path. Thus, we fix the molecule to be adsorbed in a certain position and calculate the MF exerted on it from the surface and the fluid particles. Over integration along an appropriate path one obtains the PMF. The latter route yields the potential of mean force (PMF) over the logarithm of the local density which is obtained by simulations of freely moving particles. It has been shown previously that this local density distribution may not be directly accessible from molecular simulations in some cases. Hence the route via calculating the MF at fixed positions of the molecule may be more appropriate [1].

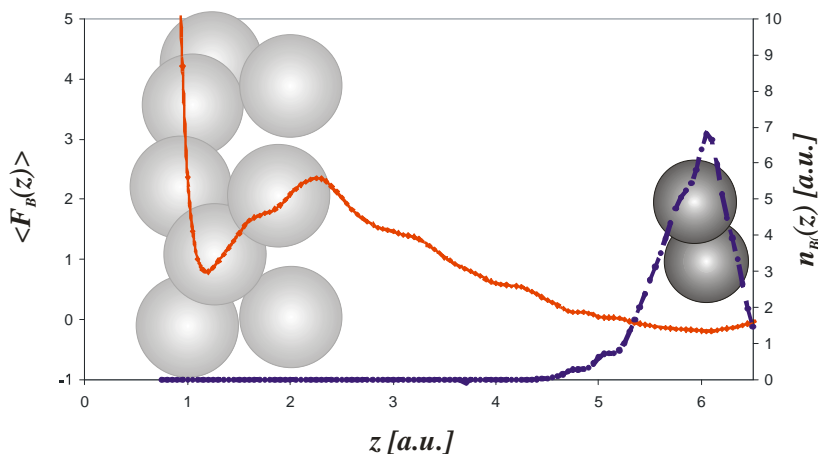


FIG. 1. Mean force  $\langle F_B(z) \rangle$  (red solid line) and local density  $n_B(z)$  (blue dashed line) of the dilute component B as function of the distance  $z$  from the wall as obtained by integration of the MF. The system is a binary mixture of a dumbbell (B) diluted in LJ-spheres (A) and in contact with a 9/3-LJ wall ( $\sigma_{BB} = 0.8\sigma_{AA}$ ,  $\epsilon_{BB} = 2\epsilon_{AA}$ ,  $\epsilon_{SA} = 5\epsilon_{AA}$ ,  $\epsilon_{SB} = 15\epsilon_{AA}$ ). Circles on the left side indicate rather densely packed A-particles close to the wall. The dumbbell on the right side represents a B-particle in its most likely conformation at the maximum of the local density.

Obviously the B-particle is shielded off from the wall by the A-particles.

Based on abovementioned theory we first considered rather simple systems of 1-centre [1] and 2-centre-Lennard-Jones (LJ) mixtures at a 9/3-LJ wall (see FIG. 1). Eventually the algorithm has been applied for the adsorption of benzene from aqueous solution at a carbon surface. The surface itself remained either untreated or has been activated by carboxyl groups. Since aromatic molecules like benzene are considered to act as active sites in larger molecules (i.e. proteins) this system is of special interest in biotechnology.

- [1] W. Billes, F. Bazant-Hegemark, M. Mecke, M. Wendland, and J. Fischer, Change of Free Energy during Adsorption of a Molecule, *Langmuir* **19**, 10862-10868.