Free energy calculations of molecular inclusions in short capped nanotubes: Targeted Molecular Dynamics and Grand Canonical Monte Carlo Calculations

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Short capped nanotubes are hemispherical polyarene formed of 50 carbon atoms ($C_{50}H_{10}$) that comprise a complete end-cap and the beginnings of the sidewalls of a carbon nanotube. These structures can be used as small hydrocarbon templates for uniform growth of nanotubes.

Crystallization of these structures has been achieved by slow evaporation of a solution in CS_2, and the crystal structure obtained reveals that the cavity of every nanotube is occupied by a carbon disulfide molecule. The target of this research is to estimate the free energy of the CS_2 inclusion into the short nanotube, showing the tendency of these nanotubes to host molecules and estimate the estability of the resulting system in the presence of the solvent and without it. Molecular inclusion free energy is calculated by Targeted Molecular Dynamics simulation[2] and by Monte Carlo simulation in the Grand Canonical Ensemble[3].

Firstly, Targeted Molecular Dynamics Method considers spontaneous transitions between known end structures in order to estimate profiles of free energy and transition rates along the reaction coordinate. To this end, suitable defined distances are necessary to provide a first conjecture for the reaction coordinates of desired activated processes[2]. Finally, the required transitions are carried out by decreasing the constrained distance during a molecular dynamics simulation.

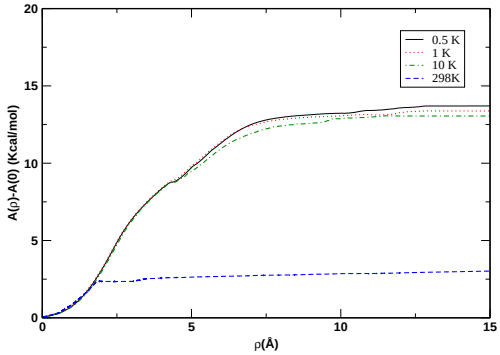

FIG. 1. Capped nanotube - CS_2 molecule binding free energy by Targeted Molecular Dynamics. The free energy profile has been given for different temperatures and belongs to vacuum conditions

In this case, we have taken the CS_2 molecule from the inside of the capped nanotube until a point far enough to avoid interaction between the nanotube and the CS_2 molecule. This is controlled by means of a reaction coordinate ρ, which measures the root mean square separation from the equilibrium positions of the CS_2 molecule inside the nanotube.

Figure 1 corresponds to the work (free energy) needed to drag the CS_2 molecule from the cage in vacuum. In Figure 2 we represent the corresponding work for a system at 298K, in presence of Cl_3CH as solvent, which stabilizes the inclusion. As a reference we also plot the work required to drag a single CS_2 molecule in the bulk solvent.

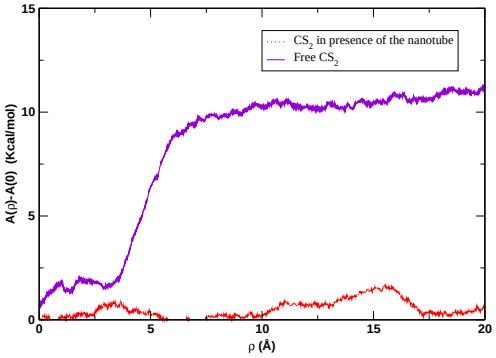

FIG. 2. Capped nanotube - CS_2 molecule binding free energy by Targeted Molecular Dynamics. The free energy profile has been given for T=298K and corresponds to the presence of solvent.

We will illustrate that the choice of a proper simulation length is crucial in the TMD calculations, so as to minimize kinetic energy effects in the corresponding free energy calculations.

Free energies will also be calculated by Monte Carlo simulation in the Grand Canonical Ensemble[3]. This second method has some benefits such as the independece of the simulation with the starting and ending positions, and with the nature of the binding site.

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