

DFT and molecular dynamics simulations of a Langmuir monolayer

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A Langmuir monolayer is a mono-molecular film formed at the air-water interface, usually composed of organic molecules like amphiphilic compounds. In this study, we have focused on a monolayer composed of palmitic acid molecules ($C_{15}H_{31}COOH$). In the formation of a Langmuir monolayer, the polar head group of amphiphilic molecules will be oriented towards the water-face, leaving the hydrophobic hydrocarbon tail tilted a certain angle (β) with respect to the normal surface.

The dominant interactions involved in this type of compounds are dispersive forces, which arises from the formation of dihydrogen bonds ($-C-H \cdots H-C-$) between neighboring molecules. Despite dihydrogen bond are one of the weakest intermolecular forces in the nature, the accumulation of many of them makes the total interaction appreciable. Dihydrogen bonding is highly anisotropic, and the strength of the interaction depends not only on the distance between the molecules but also on the orientation of the participating atoms [1]. It is therefore necessary to characterize this force by means of an accurate DFT method, since, for example, a Lennard-Jones type potential approximation would not adequately reproduce this behavior. In this context, different Van der Waals (VdW) exchange-correlation functionals (available in the DFT SIESTA package) have been tested to compare the geometries and interaction energy values of different dimers of alkanes molecules with that obtained by *ab initio* perturbative methods MP2 at a high level of calculation [2]. As a result of this study, we have obtained the most adequate VdW functional for this system, as well as optimized convergence parameters. It has been proved in this work that the interaction between several molecules can be approximated as the sum of the pairwise interactions and the monomers can be assumed as a rigid solid in the dimer formations, since the structures obtained before or after this formation are virtually identical.

To describe the different structures adopted by monomers relative to the water-air interface, three parameters have been established that define, in an univocal way, the relative position of them (see Fig. 1). In this study, we have assumed that the chains are aligned according to the normal to the aqueous interface ($\beta = 90^\circ$), which occurs in all phases of high

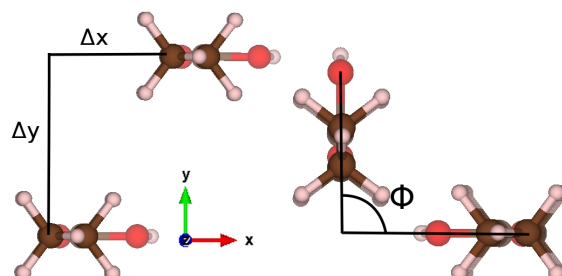


Fig. 1. Relevant parameters of the relative position of the molecules in the dimer.

pressure. The rest two parameters will refer to the relative displacement between the molecules and the relative orientation of both chains. By varying these two parameters, the potential energy surface (PES) of the intermolecular interaction of a dimer of palmitic acid has been calculated, including the basis set superposition error (BSSE) correction, which is relevant for this system.

Using the calculated PES, molecular dynamics simulations have been carried out to find both dynamic and equilibrium properties of this system. By varying the temperature controlled by a thermal bath to the simulation, as well as the concentration of the molecules in the surface, we have obtained different equilibrium structures corresponding to the different phases of the monolayer. Using the Green-Kubo expressions, we have also calculated the shear viscosity of this system at different temperatures. In addition, we compare the calculated value with experimental results, in which an anomalous behavior of the shear viscosity is observed.

[1] J. Echeverría, G. Aullón, D. Danovich, S. Shaik, and S. Alvarez, Dihydrogen contacts in alkanes are subtle but not faint, *Nat. Chem.* **3**, 323-330 (2011).

[2] S. Tsuzuki, K. Honda, T. Uchamaru, and M. Mikami, Magnitude of interaction between n-alkane chains and its anisotropy: High-level *ab initio* calculations of n-butane, n-pentane, and n-hexane dimers, *J. Phys. Chem. A* **108**, 10311-10316 (2004).