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Research paper

Accessing the structural and thermodynamic properties of ultra-thin layers of C32 adsorbed on a SiO_2 surface

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ABSTRACT

Medium-chain alkanes are important molecules with applications in biology and industry. Notably, their structural properties are scarcely understood. To assess structural and thermodynamic properties of dotriacontane (C32) molecules adsorbed on a SiO_2 surface, we conducted all-atom molecular dynamics (MD) simulations. By analyzing potentials of mean force, order parameters and self-diffusion, we compared the stability and preferential orientation between ordered and disordered systems. Our data confirm the presence of one parallel layer of C32 followed by a mixture of disordered C32 segments exhibiting no thermodynamic preference. This semi-ordered structural model shed light to the interactions between C32 and a SiO_2 surface.

1. Introduction

Medium-chain alkanes are the main constituents of several molecules with biological and industrial relevance. They are important for biosensing and bio-remediation of fossil fuels [1], as microlubricants, anticorrosive agents, and surfactants [2]. Consequently, their structural and dynamical properties have been the focus of both experimental and theoretical studies [3–10]. Given their simplicity and due to their role as prototypes for more complex polymers including biologically relevant molecules such as membranes, alkanes have been used to study the behavior of nano-scale materials such as polymeric thin films [11,12]. Using a variety of tools including atomic force microscopy, X-ray diffraction, high-resolution ellipsometry and more recently, molecular dynamics, it is currently accepted that the behavior of alkane thin films is mainly dominated by surface effects [5,10,13–16].

According to experimental evidence published by Volkmann et al. [17,18], the growth of dotriacontane ($C_{32}H_{66}$, C32) thin films, a linear medium-chain alkane, supported on amorphous silica surfaces covered with their native oxide layer (SiO_2) begins with the formation of a bilayer of C32 molecules with their long axis orientated parallel to the surface. On top of this parallel bilayer, a perpendicular layer is formed, i.e., a layer of C32 molecules with their long axis lays perpendicular to the surface. This layer will continue to grow adding as much perpendicular layers, one on top of each other, as more C32 molecules are added to the system, until the formation of mesoparticles is achieved. This mechanism is known as Stranski-Krastanov growth and is commonly accepted as the growth mechanism for medium-sized alkanes supported on inorganic surfaces such as SiO_2 [19–21]. Despite the advancements represented by these studies, fundamental questions remain to be answered regarding the nature of the physicochemical properties governing the interaction between inorganic surfaces and organic molecules. Moreover, shading lights on these questions is a key step to support the development of nanotechnological systems with application in biotechnology [9,12].

A relevant tool to gain insights with atomic resolution on the behavior of molecules is by using a whole spectrum of computer simulation techniques called Molecular Dynamics (MD). MD techniques offer a set of methods suitable to investigate complex interactions between molecules in heterogeneous systems. During the last years, it has emerged as a powerful tool to study diverse phenomena at the atomic scale, ranging from protein folding, structure-function relationships in proteins, to inorganic/biological interactions [9,12]. In particular, several molecular dynamics simulations of alkanes have been previously reported [3,4,6,8,11,13–16,22–26]. Most simulations performed to date have used united

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atom models, in which groups of atoms bonded covalently are replaced for pseudo-atoms whose physicochemical properties account for the whole group [4,11]. These approaches allow longer simulation times, saving precious computational power by neglecting high frequency interactions. Unfortunately, these models tend to oversimplify the studied systems in such a way that important microscopic details may be overlooked. For instance, in recent reports of MD simulations of alkanes, all-atom representations were always necessary to accurately reproduce key structural and physicochemical properties of the systems, such as melting [22,24]. Other reports have shown overestimation of certain parameters such as self-diffusion [27,28]. Although all-atom models impose high requirements in terms of computational time, the availability of increased computational power and the constant development of parallel algorithms for molecular dynamics allow, nowadays, the use of these detailed models.

In this work, we aim to get insights on the structural and thermodynamic properties of C32 molecules adsorbed on a SiO_2 surface. To do so, we rely on a set of all-atom MD simulations at room temperature considering two possible ordered scenarios: (i) a parallel arrangement of three C32 layers, and (ii) a single perpendicular C32 layer on top of two parallel C32 layers (Fig. 1). Next, in order to assess the self-organization of these systems, we performed several MD simulations considering three thin films (Fig. 2) and five temperatures ranging from room temperature, below C32's bulk melting point, to below its bulk boiling point. Our results are presented as time-averages of well-known parameters that have been previously applied to the study of alkanes and other molecules [23,29–32] such as density, order parameters, and self-diffusion. Moreover, by computing the potential of mean force, we evaluated the structural preference of all the assessed conformations of C32 adsorbed on SiO_2. Our results confirm the presence of one parallel layer of C32 in close contact with the SiO_2 surface. Above this layer, the simulations revealed a mixture of C32 segments ordered either parallel or perpendicular to the surface exhibiting no thermodynamic preference producing a semi-ordered structure. By comparing our results to physicochemical properties of C32, we validate our model proposing that this semi-ordered structural model could help to the understanding of the structural and thermodynamical properties governing the interactions between C32 and a SiO_2 surface.

2. Methods

2.1. Systems preparation

An amorphous solid SiO_2 surface of dimensions $11 \times 11 \times 2$ nm^3 was built as described elsewhere [33]. The surface has a mean mass density of 2.15 g/cm^3, which is in good agreement with experimental data [34], and a hydroxyl surface density of 0.73 OH/nm^2 on its upper side. For the ordered systems, each parallel layer was composed by 3 rows of 26 C32 molecules in all-trans configuration, in order to cover the whole SiO_2 surface, while the perpendicular layer was built by rotating by 90° one of the rows composing the parallel layer and replicating it 28 times. The parallel-only (PO) system comprised 3 parallel layers of C32 (Fig. 1A and C), while the parallel/perpendicular (PP) system was composed by two parallel layers and one perpendicular layer (Fig. 1B and D) of C32. For the disordered systems, a C32 box was built by equilibrating a single molecule in vacuum using the NAMD 2.7 simulation package [35] and the CHARMM36 force field parameters for lipids [36]. After equilibration, the C32 molecule was replicated using the Packmol software package [37] taking into account the experimental bulk density of C32 (about 0.812 g/cm^3 at room temperature) and the area of the SiO_2 surface. An initial box of 514 C32 molecules was generated and equilibrated following the MD simulation protocol described below. The resulting box was employed to build three systems representing C32 films of dif-

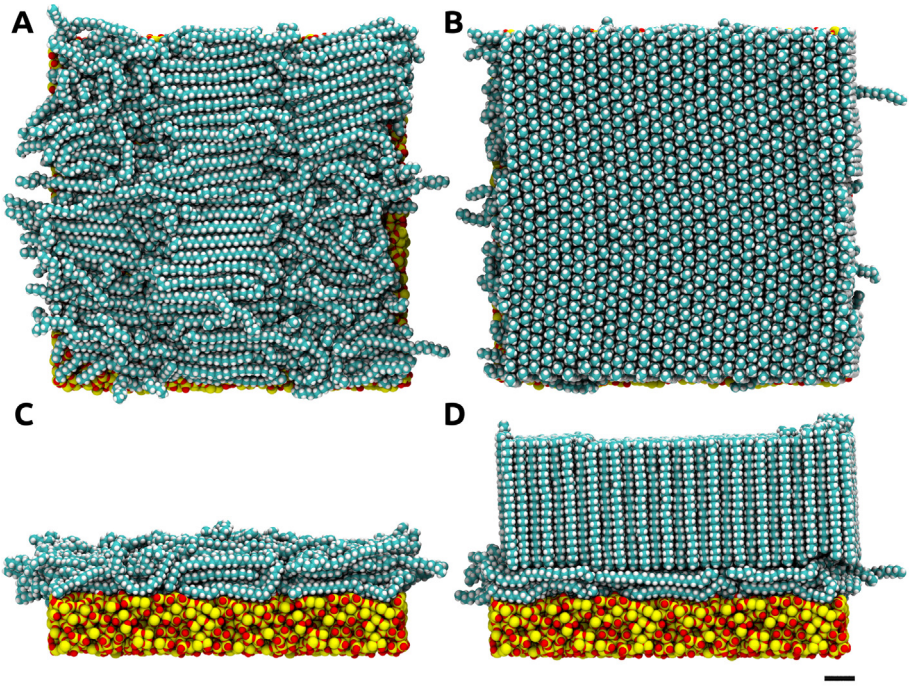

Fig. 1. Representative images of the ordered systems. Top (A and B) and front (C & D) views of both ordered systems. The PO system (A and C) corresponds to a triple parallel layer of C32, whereas the PP system (B and D) corresponds to a double parallel layer with a perpendicular film on top. Both systems are supported on the same SiO_2 surface. Colors correspond to the usual convention: cyan for carbon, white for hydrogen, red for oxygen and yellow for silicon. All molecules are depicted in van der Waals representation. The scale bar corresponds to 10 Å. All images were obtained with the VMD program [43]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)