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Atomistic Monte Carlo and molecular dynamics simulation of the bulk phase self-assembly of semifluorinated alkanes



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HIGHLIGHTS

- We have simulated **F12H12** using both MD and MC atomistic simulation algorithms.
- We have used large simulation cells containing up to 144,000 atomistic units.
- The Monte Carlo runs have been executed in parallel on NVIDIA GPUs.
- Below its melting point, **F12H12** is predicted to self-assemble in ordered lamellae.
- Lowering the temperature causes a transition from monolayer to bilayer ordering.

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ABSTRACT

Results are presented for the conformational, thermodynamic, structural and solid-state chain organization properties of the semifluorinated alkane $F(CF_2)_{12}(CH_2)_{12}H$ (termed perfluorododecyl dodecane and abbreviated as **F12H12**) from detailed, atomistic-level Molecular Dynamics and Monte Carlo simulations in the isothermal–isobaric ensemble using large simulation cells containing up to 144,000 atomistic units. To cope with the large requirements in CPU time accompanying the use of super-cells in our simulations, we identified the Monte Carlo subroutines with the largest demand in computational resources and took advantage of parallelization by multithreading on NVIDIA graphics processing units (GPUs) to improve code performance by almost one order of magnitude. Consistent simulation results for the most important properties of the system have been obtained from the two methods, especially at the higher temperatures where their predictions for the density, average square chain-end-to-end distance and dihedral angle distributions are indistinguishable (practically identical). Driven by experimental data that provide evidence for two first-order phase transitions in **F12H12**, we have further investigated its bulk-phase assembly by carrying out gradual cooling runs from an initial configuration of randomly distributed chains. For both methods, the study of the average-squared end-to-end molecular distance indicates that **F12H12** molecules prefer to be aligned in ordered zones (lamellae), whereas the dihedral distributions exhibit a favorable *trans* state with decreasing temperature and/or increasing pressure, verifying the tendency of perfluorododecyl dodecane to undergo a structural transition at these conditions. Our simulations support a spontaneous transition of **F12H12** from an isotropic phase to a smectic-like phase at a low enough temperature (close to $T=315$ K based on cooling experiments), at a pressure $P=100$ atm. Intermolecular pair distribution functions and atomistic configurational snapshots show that the simulated smectic phase consists of bilayer lamellae with a variety of directions, involving tilted and non-interdigitated chains. Experimentally, two solid phases are proposed for **F12H12**: a high-temperature one consisting of monolayer lamellae and a low temperature one consisting of bilayer lamellae with interdigitated hydrocarbon and fluorocarbon blocks. Despite that

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our simulations cannot unambiguously predict a second (solid–solid) phase transition, they provide convincing evidence for the co-existence of many ordered lamellae in **F12H12** below its melting point T_m both in monolayer and bilayer arrangements, with the relative population of bilayer ones increasing with decreasing temperature.

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1. Introduction

Semifluorinated alkanes (SFAs) are diblock molecules consisting of two immiscible and incompatible moieties, the perfluorinated segment $(CF_2)_m$ and the hydrogenated segment $(CH_2)_n$, which are covalently linked to form the copolymer with the general chemical structure $F(CF_2)_m(CH_2)_nH$, abbreviated as **FmHn**. The $(CF_2)_m$ and $(CH_2)_n$ segments have different conformations: the first adopts a twisted 15/7 helical structure whereas the second prefers an all-*trans* zigzag conformation. Due to the incompatibility between the two segments and their asymmetric structure, SFAs are capable of exhibiting remarkable phenomena, such as structural transitions, formation of ordered structures (Hopken and Moller, 1992; Russell et al., 1986; Rabolt et al., 1984) and aggregation in non-polar solvents (Turberg and Brady, 1988; Binks et al., 1996) influenced by the existence of significant dipole moment and surface activity. Despite the absence of a hydrophilic polar head group, SFAs possess an amphiphilic character forming Langmuir monolayers at the air/water interface (Krafft and Riess, 2009; Broniatowski and Dynarowicz-Latka, 2008). Furthermore, because of their biocompatibility and tendency to stabilize interfacial films and control several properties of biological colloidal systems, they are used as additional components in fluorocarbon-in-water emulsion applicants to artificial blood formulation (Krafft and Riess, 2009; Riess et al., 1994), in phospholipid liposomes that act as drug delivery systems (Broniatowski and Dynarowicz-Latka, 2008; Krafft, 2001), in ophthalmology as endotamponades, in vitreoretinal surgery and in lung surfactant therapy (Krafft and Riess, 2009).

Experimental and computational efforts to predict the solid state packing of SFAs with comparable segment lengths (especially of the F12 series) in the bulk and their phase behavior arising from the incommensurable cross-section of the two opposing moieties have attracted the scientific interest in the literature since many years (Hopken and Moller, 1992; Russell et al., 1986; Rabolt et al., 1984; Turberg and Brady, 1988; Binks et al., 1996; Krafft and Riess, 2009; Broniatowski and Dynarowicz-Latka, 2008; Riess et al., 1994; Krafft, 2001; Fujiwara et al., 2005, 2006; Hopken et al., 1988; Viney et al., 1989; Escobedo and Chen, 2004; Kim and Shin, 1999; Marczuk and Lang, 1998; deViguerie et al., 2011; Nunez et al., 2008; Lee et al., 2009; Pierce et al., 2008). By carrying out DSC measurements Rabolt et al. (1984) observed the existence of solid–solid phase transitions for F12Hn diblocks with $n=8, 10$ and 12 ; additional SAXS and electron density profile measurements below the melting point pointed out to the formation of two different crystal packings with layered structure. Later, Russell et al. (1986) proposed that bulk systems of F12Hn with $8 \leq n \leq 14$ form an antiparallel monolayer packing (see Fig. 1a) below their melting point, followed by the transformation to a tilted bilayer lamella (see Fig. 1b) at a lower temperature based on the observation that the measured Bragg spacings were larger than the end-to-end distance of individual molecules. For the same series (F12Hn), Hopken and Moller (1992) referred to a mesomorphic phase below the melting transition which they described as a *smectic liquid crystalline phase* since the hydrogenated segment keeps its fluid-like character at the solid–solid transition. The X-ray scattering study of Marczuk and Lang (1998) indicated a structure at high

temperatures which was in accordance with the one suggested by Russell et al. (1986) but they concluded that at lower temperatures F12Hn with $8 \leq n \leq 14$ display a double-layered undulating lamella with interdigitating hydrogenated segments.

Computer simulations have also addressed issues related with the structural characterization of **FmHn** SFAs in the bulk and at interfaces. Escobedo and Chen (2004) have studied the liquid crystalline behavior of F10H10 applying three different united-atom force fields. Special care was taken by Escobedo and Chen (2004) of the H–F atom interaction through a correction parameter in the Berthelot mixing rule between interspecies of alkyl and perfluoroalkyl groups in order to match as accurately as possible experimental data. Then, to predict the phase transition from a smectic isotropic to an isotropic phase, they performed heating Monte Carlo (MC) runs in the isothermal–isobaric ensemble using a nematic-like structure as the starting configuration; through such a procedure (heating), they managed to identify two types of smectic phases whose structure, however, does not seem to be consistent with the experimentally proposed ones. Fujiwara et al. (2005) have also studied the density and transition behavior of semifluorinated alkanes of the type F10Hn with n equal to 6, 8, 10 and 12 through a constant pressure molecular dynamics (MD) cooling procedure using a united-atom model. Their results confirmed the spontaneous transition from an isotropic to an ordered state with a layered structure. The obtained layered structures and the estimated densities were in reasonable agreement with those inferred from the experimental studies. Additional MD simulations of a Langmuir monolayer of the F12H18 semifluorinated alkane by Kim and Shin (1999) (again with a united-atom model) indicated the formation of highly ordered monolayer structures after quenching at low temperatures an initial configuration of randomly distributed chains in the simulation cell.

Clearly, given the simplicity of their molecular structure, the phase behavior (smectic ordering) and physicochemical properties of semifluorinated alkanes (the so called *primitive surfactants* by Turberg and Brady (1988) to emphasize the absence of polar groups) are unusual, surprising and fascinating. Motivated, in particular, by the recent interest in the Langmuir monolayers formed by these molecules when they are spread at the air/water interface and their unique viscoelastic response to an applied interfacial stress, we have embarked on a new project aiming at the detailed computer simulation of these diblock molecules both in the bulk and as Langmuir monolayers, and at the understanding of the relationship between chain length and liquid crystalline formation. Our goal is to develop robust and powerful simulation algorithms capable of describing the remarkable phenomena exhibited by SFAs and explaining their uncommon properties due to the incompatibility (immiscibility) of the two moieties (F and H). As a model system, we have chosen perfluorododecyl-dodecane or **F12H12**; this is a linear, symmetric amphiphilic diblock that exhibits interesting morphologies both at the air/water interface (where it forms Langmuir monolayers consisting of *spherical cap* substructures with the orientation of the perfluorocarbon segment on the air) (deViguerie et al., 2011) and in the bulk state. We mention, e.g., the DSC experiments and the thermodynamic pressure–volume temperature measurements of Nunez et al. (2008) which provided evidence for two first-order

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