

## Interactions between perfluoroalkyl substances and polyethylene through molecular dynamics simulation

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### Abstract

This study addresses two contaminants that have been causing concern due to their omnipresence in the environment. One is microplastics (MPs) and other is per- and polyfluoroalkyl substances (PFAS). MPs, particles smaller than 5 mm, are known for adsorbing substances such as Persistent Organic Pollutants (POPs), which include some PFAS listed in the Stockholm Convention. PFAS, with their strong carbon-fluorine bonds, are highly persistent in the environment. This research evaluates the interactions between MPs and PFAS, exploring potential synergistic effects through molecular dynamics. The MP selected for this study is polyethylene (PE), while the PFAS studied are perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). The model constructed for this analysis includes 50 PE polymeric chains, each with 36 monomers, and 5133 SPC/E water molecules, using the OPLS-AA force field. Two PE structures were examined: crystalline and semi-crystalline. The OPLS-AA force field was also applied to PFOA and PFOS. The umbrella sampling (US) method and the Weighted Histogram Analysis Method (WHAM) were employed to determine the potential of mean force (PMF) profiles for PE and PFAS interactions in water. The collective variable was the projected distance between the centers of mass of PE and PFAS along the  $\hat{z}$ . For both crystalline and semi-crystalline PE, PFOS exhibited a more favorable interaction than PFOA. Comparing the two studied PE structures, both PFOA and PFOS interacted favorably with the semi-crystalline structure.

*Keywords:* Microplastics; Umbrella sampling; Molecular Dynamics; Perfluoroalkyl substances.

### 1. Introduction

Microplastics (MPs) and per- and polyfluoroalkyl substances (PFAS) are two contaminants causing significant concern. MPs are increasingly studied due to their environmental persistence and potential health impacts [1]. PFAS, used in various industries, are persistent and have been restricted by the Stockholm Convention. Despite this, their environmental levels remain high due to the substitution with shorter-chain PFAS, which, although less bioaccumulative, still persist [2,3].

MPs and PFAS are ubiquitous, prompting studies on their effects on humans. PFAS can interfere with the vitamin D receptor and prenatal exposure is concerning [4,5]. MPs have been found in human blood, saliva, placenta, and other organs, potentially causing cancer and other diseases [6].

### 2. Methodology

In the environment, dispersed MPs and PFAS can be found in very diluted quantities within the same medium. Therefore, this work focuses on analyzing how two different PFAS – PFOA and PFOS – at infinite dilution interact with virgin PE in pure water. It was assumed that the size of PFAS molecules is much smaller than that of PE microplastic, which can reach sizes of up to 5 mm. Consequently, PFAS perceives the PE as a slab.

#### 2.1 General Remarks

The simulation boxes were built using Packmol [7] and Playmol [8] to mitigate sampling issues and prevent molecule overlap, thus minimizing excessively repulsive interactions. LAMMPS software was used to carry out MD [9,10]. Since the simulations require a significant computational

effort, this work used resources from the CENAPAD-SP.

Periodic boundary conditions were applied in the three directions. For PE, PFOA, and PFOS, the OPLSS-AA [11] was employed, whereas the SPC/E force field [12] was used for water. The Lennard-Jones (LJ) potential with a cutoff set at 12 Å was used. However, for intramolecular 1,4-interactions, a weighting factor of 0.5 was considered. Geometric combination rules were applied for  $\sigma$  and  $\epsilon$  [11]. For distances less than 12 Å, direct calculation of long-range Coulombic interactions was conducted. Conversely, for distances beyond this cutoff, the Coulomb contribution to the potential energy was computed in k-space by the PPPM method [13] with a precision of  $10^{-4}$ , which tends to converge faster because it utilizes Fast Fourier Transform. The same weighting factor on 1-4 atom pairs of LJ interactions was used for Coulombic interactions. For all simulations, the timestep was set to one femtosecond.

## 2.2 System modeling

The parameters OPLS-AA force field for PE were acquired from the PolyParGen website [14]. Fifty PE chains with 36 monomers were inserted into a box (90 Å x 90 Å x 90 Å), and the system was simulated for 0.5 ns in the NpT ensemble at 500 K and 1 atm to overcome energy barriers. The system underwent cooling down to a temperature of 300 K for 0.5 ns, the dimensions of the box changed to approximately 46 Å x 46 Å x 46 Å.

The question arose as to whether the structure of the PE was semi-crystalline or if the simulated model was representing a local minimum, with insufficient energy for further crystallization, that is, in a metastable equilibrium. Therefore, the box was rebuilt with a crystalline PE structure. Fifty PE chains were inserted using Playmol and Packmol. The structure was pre-equilibrated for 0.5 ns using an NVE ensemble. Subsequently, 5133 water molecules were inserted into each simulation box. The first box (semi-crystalline PE) was simulated for 234 ns and the second box (crystalline PE) for 45 ns at 300 K and 1 atm in an NpT ensemble.

In each case, the position of the PE interface was measured, and the pollutants were positioned around 15 Å from this interface (Fig. 1). As the objective of this study is to evaluate the interaction of the two PFAS in the same medium, a neutral pH was considered. Due to the pKa value varying

between -0.2 and 2.8, both PFAS were deprotonated. The OPLS-AA parameters for PFOA and PFOS were obtained from LigParGen, which is a website that generates force field parameters for organic molecules or ligands [16,17], and the charges were adjusted so that the residual charge was -1.

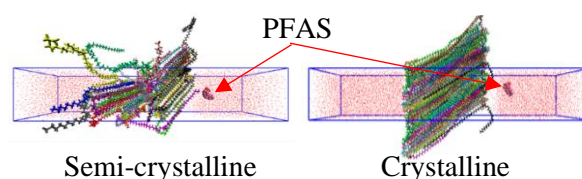


Fig. 1. Representation of the simulation boxes with PFAS at 15 Å from the interface, each polymer chain is represented by a color.

## 2.3 Umbrella sampling and WHAM

With the contaminants positioned, they were pulled at pre-defined intervals towards the center of mass of the PE, generating initial configurations for each window. Each interval represented a window where PFAS contaminants were constrained around a specific  $z$  value. The force constant of  $10 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$  was used for the US method, with a default simulation time of 4 ns per window. Simulations were performed at 300 K and 1 atm on an NVT ensemble using the Colvars module in LAMMPS. This module allowed the application of constraint potentials to guide the system through different thermodynamic states, resulting in a histogram distribution for each window. When good sampling was achieved, adjacent histograms overlapped. The PMF profile was then obtained using WHAM algorithm [18], with a tolerance of  $10^{-5}$ .

## 3. Results and discussion

### 3.1 Simulation with semi-crystalline PE and PFOA

The first simulation analyzed involves inserting the PFOA anion into structured boxes with semi-crystalline PE. Initially, PFOA was placed 15 Å from the PE-water interface, with the distance from the PE center of mass to the contaminant center of mass being 49.4 Å, later moved to 30.4 Å. This

distance was divided into 20 windows, each with 1.0 Å centers. Some windows required longer simulation times due to inadequate initial configurations. Specifically, windows 9, 13, and 16 needed an additional 4 to 8 ns. Histograms from neighboring windows were analyzed for overlaps to generate the PMF using the WHAM method. The PMF revealed a constant free energy in initial windows, a decline indicating attraction between PFOA and PE around 43 Å, reaching a minimum at 36 Å (Fig. 2A). Below 36 Å, the energy profile increased. The PFOA showed consistent behavior, with its hydrophobic tail aligning with PE and the hydrophilic head facing water (Fig. 3A).

### 3.2 Simulation with semi-crystalline PE and PFOS

In the semi-crystalline model with the PFOS anion, it was initially placed 15 Å from the PE interface and equilibrated for 19 ns. The simulation used windows spaced 1 Å apart, running for 4 ns each with a force constant of 10 kcal mol<sup>-1</sup> Å<sup>-2</sup>. However, PFOS showed greater resistance to equilibration, requiring adjustments in some windows. In window 17, insufficient histogram centralization led to resimulation with a higher force constant of 15 kcal mol<sup>-1</sup> Å<sup>-2</sup>, but this did not fully resolve the issue. Additional windows and extended simulation times were used to address instability and improve the PMF profile. Despite these efforts, some resistance persisted around windows 20 and 21. Ultimately, 20 windows were maintained, with PFOS showing greater interaction with PE than PFOA, as indicated by a lower minimum free energy of interaction around -43 kJ mol<sup>-1</sup> (Fig. 2A). Just like PFOA, PFOS has aligned with PE (Fig. 3B).

### 3.3 Simulation with Crystalline PE and PFOA

In the simulation, PFOA was initially positioned at  $z_1 = 51.0$  Å in the box. The reaction coordinate was divided into 19 windows, with steered molecular dynamics used to generate initial configurations. Each window underwent 1 ns of equilibration followed by 4 ns of sampling using the US method. The resulting histograms showed good overlap, allowing for the construction of the PMF. The PMF analysis revealed that PFOA initially has a favorable interaction with PE, reaching a

minimum energy of -24 kJ mol<sup>-1</sup> around 41.5 Å (Fig. 2B). The energy fluctuates between -24 kJ mol<sup>-1</sup> and -22 kJ mol<sup>-1</sup> from 39 Å to 36 Å, and then increases beyond this range. The snapshot of the last simulated window is shown in Fig. 3C.

### 3.4 Simulation with Crystalline PE and PFOA

In the system containing PFOS and crystalline PE, 17 initial windows were simulated, with  $z_1$  set at 50 Å and PFOS reaching its final position at 34 Å. Each window had central points spaced 1 Å apart. An energy peak was observed at around 35.5 Å between windows 15 and 16, prompting additional simulations. Despite these efforts, the energy peak persisted, suggesting strong attraction between PFOS and crystalline PE. Four more windows were generated, revealing a minimum energy of approximately -36 kJ mol<sup>-1</sup> (Fig. 2B). PFOS exhibited a strong attraction to PE in both crystalline and semi-crystalline models, aligning its tail with PE and orienting its hydrophilic head towards water. This behavior is due to the hydrophilic nature of the heads and the interactions between fluorine in PFOS and hydrogen in PE (Fig. 3D). The PMF indicated attempts of PFOS to penetrate PE, but absorption was unlikely due to repulsion from the polar heads.

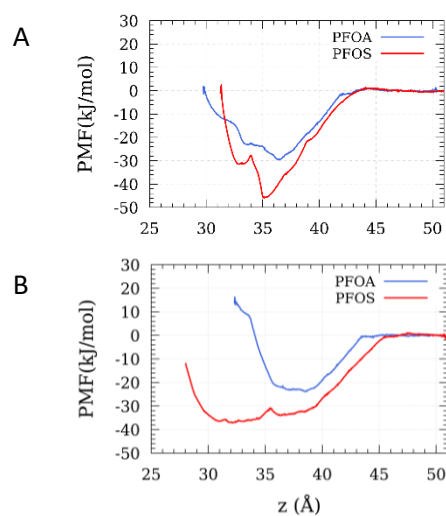


Fig. 2. Potential of mean force obtained by umbrella sampling for PFOA and PFOS in the semi-crystalline (A) and crystalline PE (B) simulation box.

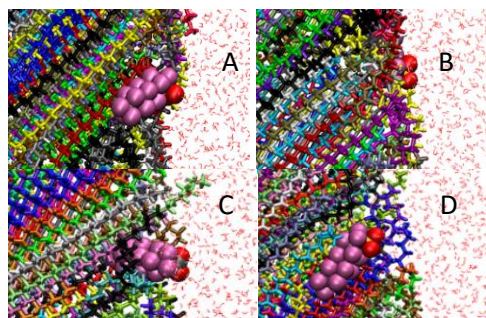


Fig. 3. The figure shows a snapshot of the last window of each simulation. In (A) PFOA and semi-crystalline PE; in (B) PFOS and semi-crystalline PE; in (C) PFOA and crystalline PE and in (D) PFOS and crystalline PE.

#### 4. Conclusion

In all models, the contaminants aligned their tails with the PE structure and their heads toward the water. The PMF generated for each system showed similar behaviors, with PFOA and PFOS showing different minimum Helmholtz free energies. In the semi-crystalline model, PFOA minimum free energy was around  $-30 \text{ kJ mol}^{-1}$ , while in the crystalline model, it was  $-24 \text{ kJ mol}^{-1}$ . For PFOS, the values were  $-46 \text{ kJ mol}^{-1}$  and  $-36 \text{ kJ mol}^{-1}$ , respectively, indicating a stronger attraction to the semi-crystalline structure.

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