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Molecular simulation of the hydrodynamics of water in contact with hydrophilized poly(vinylidene fluoride) surfaces

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ABSTRACT

Modeling electro-kinetic effects of aqueous solutions on charged polymer surfaces constitute great challenges. The interplay of water pH and salt concentration with surface charges at the nanoscale and macroscopic collective hydrodynamics leads to a rich phenomenology, including the hydrophobic/hydrophilic nature of the polymer surface. The present work aimed at contributing to the modeling of these phenomena for a specific system: Poly(vinylidene fluoride) (PVDF), including a surface functionalization by carboxylic groups. We report on molecular dynamic simulation of water interactions under imposed hydrodynamics with a flat PVDF surface functionalized with charged groups and buffered by sodium ions. Using this approach, we simulate the velocity and density profiles of water as a function of the functionalization. By using averaged charge distributions, the electrostatic surface potential at the mean field level, and hence the zeta potential, is also given. Deviations from Navier–Stokes type hydrodynamics at nanoscales are given and we found, in accord with experimental findings, that PVDF gets wet in contact with water. The observed dependencies of the hydrodynamics at nanoscales sheet light on the potential use of functionalized PVDF for instance as a membrane material for water filtration purposes.

1. Introduction

Poly(vinylidene fluoride) has received great attention in many applications due to its outstanding properties. Compared to other polymeric materials PVDF shows high mechanical strength, thermal stability, chemical resistance, and bio-compatibility, see [1,2]. It is also possible to process PVDF by phase inversion, therefore PVDF is an attractive material for instance in membrane technologies. However, PVDF is moderately hydrophobic (water contact angle around 89°), which is a drawback for specific applications. Hydrophobic polymer surfaces in general are susceptible to fouling in contact with aqueous solutions containing active pollutants, which can easily absorb on the surface. In contrast, hydrophilic polymer surfaces show reduced fouling because of their affinity for water. Water is strongly bound to these surfaces, so foulants do not interact directly with the polymer surface and therefore do not accumulate.

Surface modification is a way to hydrophilize a surface and at the same time to maintain the bulk characteristics [3–5]. Surface modifications of polymers can be classified into two categories: surface coating and surface grafting. Surface coating temporarily improves the surface hydrophilicity by depositing a thin functional layer onto membrane surfaces. Surface grafting on the other hand is one of the most promising methods to modify a polymer surface through covalent bonding of functional groups [6,3,5]. Plasma grafting of specific functional groups, such as carboxylic groups, is an efficient way to anchor the graft groups on the surface of PVDF. Plasma treatment is usually limited to the polymer surface and bulk properties are usually unaffected at the usually chosen plasma treatment conditions [3,7,8]. These functional groups may have a strong influence on the hydrodynamics close to the polymer surface as they introduce charged sites which strongly interact with the dipole moment of water molecules. A rich phenomenology is known from simplified models, see [5], but many details, in especially in the field of micro- and nano-fluidics, are still unexplored.

In this paper we investigate the hydrodynamics of aqueous solutions at solid/liquid interfaces depending on the concentration of carboxylic groups, grafted to a PVDF surface, by classical molecular dynamics (MD). We explore physical phenomena in systems on a molecular level, usually at nanometer scale, where the physical characteristics are often difficult to measure using experimental methods. For this reason, MD became popular in studies of interactions between liquids and solidified polymers [9–13]. For

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example, molecular simulations have been successfully used to characterize the hydrodynamics of water at various solid interfaces [11,14]. Effects of the surface roughness and the surface charge density were studied for instance in [15,16,14], respectively. In all the above studies, the atoms comprising a polymer surface were fixed in space, thus the effect of the surface relaxation at the solid/liquid interface was not considered. Here, we used a surface model with full molecular flexibility at the water interface in order to assess the wetting properties of PVDF as observed in experiment [17], in addition to possible relaxation effects of the PVDF surfaces while interacting with water molecules. In order to construct a PDVF surface model, we introduced a stochastic growth mechanism, since a full MD simulation of the polymer surface formation would fail due to the enormous relaxation times, as compared to feasible MD simulation times, in polymers in general. Also our construction scheme leads to fully amorphous PVDF samples, and does not reproduce the crystal phase which is experimentally known to be above 50% [2]. However, the simulated PVDF samples are mechanically stable. Therefore, we believe that our model reproduces the functionalized surface properties with respect to the hydrodynamic interactions with water reasonable well and allows for the identification of the hydrodynamic properties of the systems studied at nanoscales.

2. Models and methods

2.1. Molecular dynamics

The molecular dynamic simulation method in the NVE ensemble is based on Newton's second law or the equation of motion

$$\vec{F}_i = m_i\vec{a}_i = -\nabla_i U_{total}, \tag{1}$$

where F_i is the force exerted on the particle i, m_i is its mass and a_i is its acceleration. ∇_i denotes the 3D gradient operator along the coordinates of particle i. The total potential energy U_{total} describes the energy contributions of stretching, bending, and the torsion of atoms forming a molecule (the intermolecular interactions), the non-bonded intermolecular interactions, and interactions with external fields:

$$U_{total} = U_{bond} + U_{angle} + U_{dihedral} + U_{VdW} + U_{Coulomb} + U_{external}, \tag{2}$$

where U_{bond}, U_{angle} and $U_{dihedral}$ account for the stretching, bending, and torsion that occur in atoms forming a molecule, respectively. $U_{VdW}, U_{Coulomb}$ and $U_{external}$ describe non-bonded intermolecular interactions of Van der Waals and Coulomb type, respectively. $U_{external}$ accounts for possible external fields. In this work, we use as the potential energy function for intramolecular interactions the so called CHARMM force field [18]. All non-bonded interactions between particles are described by Lennard-Jones (LJ) and Coulomb potentials:

$$U_{VdW}(r_{ij}) + U_{Coulomb}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} + \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon r_{ij}}, \tag{3}$$

where r_{ij} is the distance between atoms i and j, q_i is the partial charge of atom i, and σ_{ij} and ϵ_{ij} are the Lennard Jones parameters defined by the conventional Lorentz–Berthelot mixing rules [19]. A cutoff radius of 16 Åwas used for LJ interactions and Ewald summation to compute long-range electrostatic interactions. All molecular dynamics simulations were performed with the parallel version of NAMD code [20] and visualized with the molecular visualization package VMD [21]. The electrostatic charges of the PVDF atoms were taken directly from report [22]. The charge distribution after functionalization with carboxylic groups was adopted with CGenFF programm for automatic parameterization of Molecular Mechanics Force Field [23].

2.2. Molecular model of PVDF layer

PVDF is a highly non-reactive fluoropolymer produced by the polymerization of vinylidene difluoride, forming a repeating unit of –CH_2–CF_2–. More precisely, PVDF is composed of linear chains of tetravalent carbon atoms to which two hydrogen or fluoride atoms are attached in an alternating fashion. The PVDF structures used in this work were constructed by a Monte Carlo method using a self-avoiding random walk algorithm on a diamond lattice [24]. This building technique is based on the fact that any tetravalent atom fits nicely on a diamond lattice.

First, we constructed a diamond lattice in a periodically replicated simulation box. The box sizes were specified in such a way that the final structure is a thin layer with a square surface. At the borders of the simulation box reflective boundary conditions were used in order to simulate a single polymer chain. Then, a carbon chain on the diamond lattice was constructed by adding one carbon atom to the end of the growing chain in each step. The next position is always chosen as a non-occupied diamond lattice site. In the unlikely event that all neighboring sites are already occupied, the construction routine backtracks until at least one free neighbor site is found. In our simulation, the distance between two sites is chosen to be a carbon–carbon bond length and the angle between two neighboring bonds is equal to a carbon–carbon–carbon angle in a PVDF chain. Therefore, bond and angle energy terms are directly minimized using this construction procedure. In the last step, we attach two hydrogen and two flour atoms to the carbon atoms in the chain in an alternating fashion while respecting the H–C–H and F–C–F bonding angles and the torsion angles between H–C–C–F bond sequences.

An important parameter characterizing equilibrium polymers is the mean square end-to-end distance of the real chain. According to Flory's theory of random coils [25], the mean square end-to-end distance of any polymer chain in the bulk at equilibrium is proportional to the number of bonds n with length l:

$$\langle R^2\rangle_0 = C_\infty n l^2, \tag{4}$$

where C_∞ is a dimensionless characteristic number of a polymer. For polyethylene, $C_\infty = 6.7$, and this number may also used for poly(vinylidene difluoride) [26]. It is know that the correct end-to-end distance can be reached with the Molecular dynamics method within a simulation time of the order of $O(n^3)$ with a large pre-factor [27]. For the relatively large structures we are interested in, this high computational demand precludes the use of MD for a structure formation simulation. Therefore, we have used a construction scheme based on Flory's results. With this method the final position of the atom is chosen within a distance equal to the value given by Flory's end-to-end distance distribution:

$$W(\vec{R})d\vec{R} = \frac{1}{(2/3\langle R^2\rangle_0\pi)^{3/2}}\exp\left[-\frac{3\vec{R}^2}{2\langle R^2\rangle_0}\right]d\vec{R}, \tag{5}$$

where $\vec{R}$ is the total end-to-end vector of a piece of the chain.

The algorithm constructed runs as follows:

- We start at a randomly chosen lattice point.
- We choose the next lattice point randomly within the 3 remaining directions and exclude self intersections.
- When 1000 lattice points are occupied, we check criterion (4). If the end-to-end distance of this subsequence is lower than the radius given by Eq. (4) at $n = 1000$, we proceed with the next 1000 steps. If the end-to-end distance is larger, we