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# On the structure and rejection of ions by a polyamide membrane in pressure-driven molecular dynamics simulations

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## HIGHLIGHTS

- We report Pressure-Driven Molecular Dynamics Simulation of an electrolyte solution in a PA RO membrane.
- Time evolution of the structure of water and ions was investigated.
- For the first-time Pressure-Driven Molecular Dynamics Simulation of a PA membrane was carried out.

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## ABSTRACT

Pressure-driven molecular dynamics simulations were carried out to investigate both structural and transport properties of a sodium chloride solution through a highly cross-linked polyamide membrane. Transport properties were characterized from the calculation of water permeability and salt rejection while the local structure was analyzed through hydration number, hydrogen bond number and radial distribution functions.



## 1. Introduction

During the last century Earth has faced a dramatic industrial development that has been accompanied by an almost exponential growth of the world population. As a result, humanity is now facing the significant challenge of overcoming freshwater shortage. The lack of freshwater available for human consumption and ecosystems is further aggravated by factors such as pollution and the inequality of its distribution. People's access to drinking water is therefore a major challenge for the coming decades, not only for developing countries but also for the industrialized states [1]. The only methods to increase water supply beyond what is available from the hydrological cycle are desalination and water reuse after appropriate treatments [2]. Membrane separation processes are already recognized worldwide as promising tools to deal with this issue in a strategy of process intensification, i.e. a strategy leading to the development of cleaner and more energy-efficient technologies. Notably, reverse osmosis (RO) has been widely used for seawater desalination. It has progressively replaced some of the thermal desalination technologies including multi-effect distillation, multi-stage flash and vapor compression distillation, notably thanks to its lower energy consumption [3].

Thin-film composite polyamide membranes are currently the main class of RO membranes available on the market. The skin layer of these membranes is formed on top of a composite support (usually made of a coarse-porous polymer covered by a mesoporous polysulfone layer) by interfacial polymerization [4,5]. For most commercial membranes, this polycondensation reaction is performed from m-phenylenediamine (MPD) and trimesoyl chloride (TMC). A fully aromatic polyamide film quickly forms at the interface and grows on top of the polysulfone layer of the support membrane because of the low solubility of the acid chloride monomer in water and the better solubility of the amine monomer in the organic solvent [5–7]. Despite years of intense research on the transport of water and solutes through RO membranes, the physical phenomena that control transport through the active layer are not yet fully understood, particularly at the atomistic level.

Molecular dynamics (MD) is an attractive technique for gaining insights into RO membrane features such as polymer configuration, free volume distribution, and transport phenomena [8–11]. Indeed, it offers unique opportunities to connect some macroscopic properties

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to a microscopic description of the physical phenomena involved in the separation. Although MD has been already applied to investigate both water and ion transports through nanopores with well-defined geometries [12–18], the limited information about the three-dimensional molecular structure of RO polyamide membranes makes the use of this computational method much more challenging. As a result, the identification and the understanding at a microscopic level of the underlying mechanisms governing water and ion transport through RO membranes are proceeding very slowly and only few studies reported on the attempt of building full atomistic models of RO polyamide membranes [19–25].

In this work we apply a recent approach proposed by our group for building atomistic models of RO polyamide membranes [23,24] in order to investigate both ion and water transport from pressure-driven molecular dynamics simulations.

## 2. Models & computational details

### 2.1. Models and interactions

Polyamide material was described from the AMBER99 (Assisted Model Building with Energy Refinement) force field [26] developed from the AMBER94 force field [27] and re-parameterized by Wang [26] for molecular dynamics of biomolecules and many organics. Cross-linked polyamide (PA) was generated by following the procedure developed in Refs. [23,24]. In the first stage of our construction protocol several linear chains of polyamide are packed into a simulation box according to a well-established method combining Monte Carlo (MC) and MD simulations. An additional MD simulation is then performed by randomly adding a given number of MPD monomers inside the free volumes of the un-crosslinked network. At the end of this simulation the polymer chains are cross-linked artificially by bridging free carboxylic acid groups on the polymer chains and some of the added MPD monomers on the basis of a heuristic distance criterion. Proceeding this way the degree of cross-linking can be easily controlled by tuning the number of additional MPD monomers inserted in the simulation. Computational details of our construction are given in Refs. [23,24]. The simulation box is orthorhombic such that the box lengths according to the $x$ and $y$ directions are $L_x = L_y = 37.3$ Å while $L_z = 100$ Å (the thickness of the polyamide membrane is about 100 Å). As shown in Fig. 1a the cross-linked membrane was surrounded by two water reservoirs along the $z$ axis. Water was modeled by means of the non-polarizable and rigid TIP4P/2005 model [28]. Ions were modeled by an unpolarizable model [29] because it has been shown that the polarizability of NaCl does not affect substantially the structure and the transport properties of water and ions [30]. The total configurational energy $U$ is defined as $U = U_{\mathrm{INTRA}} + U_{\mathrm{INTER}}$ where $U_{\mathrm{INTRA}}$ and $U_{\mathrm{INTER}}$ are the intramolecular and intermolecular contributions, respectively. The intramolecular interactions include contributions from stretching, bending, torsion energy and non-bonded Lennard-Jones interactions of the PA membrane. The intermolecular interactions are composed of the repulsion-dispersion and electrostatic contributions that are represented by Lennard-Jones and Coulombic potentials, respectively. The LJ interactions were truncated at 12 Å. The electrostatic interactions were calculated using the Ewald sum method [31].

### 2.2. Non-equilibrium molecular dynamics: pressure-driven molecular dynamics simulations

The effect of a transmembrane pressure difference can be mimicked in MD simulations by applying a constant force $F_z$ in the $z$-direction on all water molecules and ions, as illustrated in Fig. 1a. $F_z$ was applied only on the oxygen atom of water molecules so as to avoid a spurious rotational dynamics. Here we assume that the membrane is fixed in

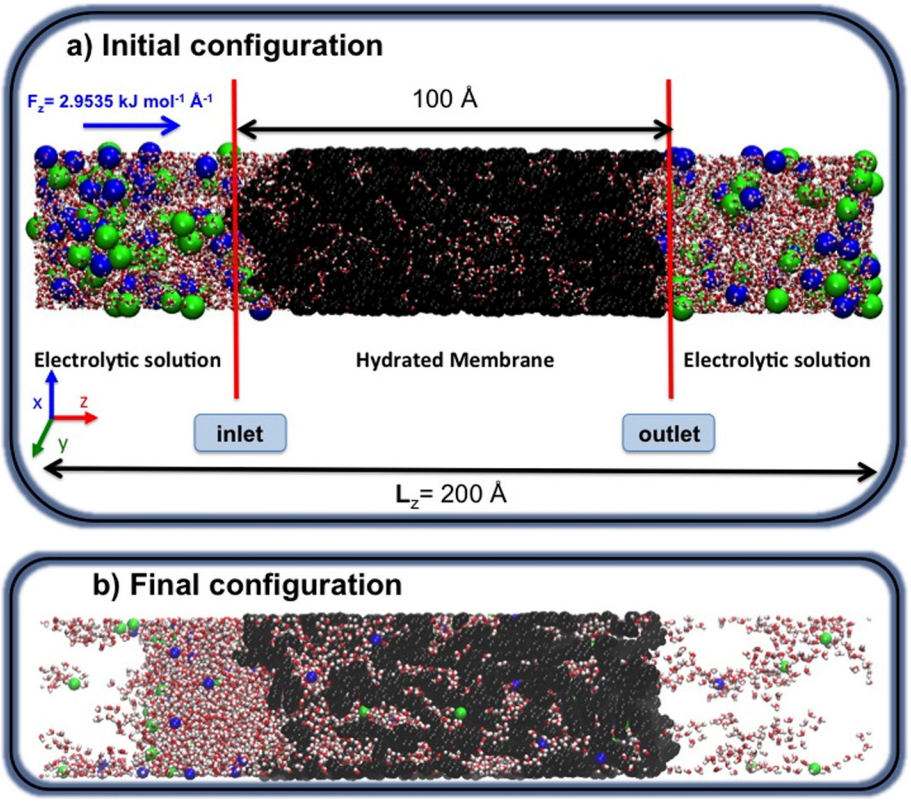


**Fig. 1.** Snapshot of the a) initial and b) final configurations of hydrated polyamide surrounded by two water reservoirs. The atoms of the PA membrane are represented in black, hydrogen atoms in white, oxygen atoms in red, $Na^+$ ions in blue and $Cl^-$ ions in green. The vertical lines indicate the approximate positions of the membrane/solution interfaces. The origin of the simulation box is located at the center of the box. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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