



# Hydration of a polyamide reverse-osmosis membrane



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## ABSTRACT

Over the last decades only a few atomistic simulations were performed to investigate water transport through polyamide reverse osmosis membranes at the molecular scale. In most reported simulations water uptake by the membrane was fixed on the basis of scarce experimental data available in the literature but it has never been predicted directly from explicit molecular simulations of water transport across the membrane/water interface. This was attempted in the present work by using a technique based on non-equilibrium molecular dynamics simulations. The prediction of the membrane water uptake is indeed of the utmost importance for (i) validating an atomistic model of a polymer membrane and (ii) getting an accurate picture of the molecular mechanisms ruling water transport through the membrane. Simulations performed in the present work led to a water content inside a cross-linked fully aromatic polyamide membrane around 24 wt% in very good agreement with reported experiments. We further showed that this high water uptake results from favorable interactions between the polyamide membrane and water molecules, which compensates the decrease in the number of hydrogen bonds between water molecules inside the membrane. Eventually, it was shown that water molecules confined in the membrane formed an interconnected hydrogen-bond network made of cyclic and linear aggregates.

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## 1. Introduction

Polyamide (PA) membranes are extensively used in reverse osmosis (RO), which is now the world-leading desalination process. These membranes are thin-film composite (TFC) materials with a thin and dense PA top-layer that controls the separation performance. Currently, this active layer is synthesized by the so-called interfacial polymerization process, in most cases from metaphenylene diamine (MPD) and trimesoyl chloride (TMC) monomers [1–3]. In order to optimize separations it is needed to understand water transport through membranes and then to rationalize PA/water interactions. Transport of water through RO membranes has been essentially described from macroscopic approaches, notably by means of the well-known solution–diffusion model. However, information at the molecular scale, which is crucial for a deep understanding of transport of water, ions or small organic solutes cannot be obtained in this way and then more sophisticated molecular simulation tools, such as molecular dynamics (MD), are needed.

The first challenge in molecular simulation of water transport

through RO membranes lies in the construction of the PA membrane model. Pioneering works were carried out by Kotelyanskii et al. [4,5] and more recently by Hughes and Gale [6] who first generated un-crosslinked PA membranes that were further cross-linked by connecting some TMC and MPD fragments. However, in both cases the degree of cross-linking achieved was much less than that of actual PA membranes. Harder et al. [7] and Luo et al. [8] used a different methodology, starting from TMC and MPD monomers which were polymerized during the course of the simulation. This procedure resulted in a ratio of cross-linked to linear segments of 37:63 [7]. More recently Ming et al. built a highly cross-linked (>80% based on pending carboxylic groups or >93% based on total nitrogen in the membrane) PA membrane model by inserting additional MPD monomers inside a network of PA linear chains [9–11] while Kolev and Freger [12] succeeded in generating a PA membrane with a cross-linking degree of 93% by improving the approach proposed by Harder et al. [7] and Luo et al. [8]. Henceforth, it therefore seems that the construction of atomistic models of PA membranes is now well controlled.

In most reported studies, however, membrane hydration was performed by random insertion of water molecules in the membrane structure. In most cases, the number of water molecules to be inserted was set on the basis of the experimental water uptake mentioned in Ref. [4], namely 23 wt% (note that very little works reported on the experimental determination of water uptake by

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polyamide RO membranes [4,13,14]). Indeed, the density of PA frameworks is too high to determine water uptake by using a Grand-Canonical scheme. As in adsorption-based processes, water uptake by membranes is a key property because it rules water structure and dynamics inside the membrane and thus water transport. Because of the very limited experimental data available, due to challenging issues related to the experimental determination of water uptake by the active layer of TFC membranes, it is interesting to see whether molecular simulations could be used to predict such an essential property of RO membranes. Moreover, the comparison with experimental data could provide additional conclusions regarding the relevance of the force fields used to generate atomistic models of RO membranes. This work therefore aimed at predicting quantitatively the water content inside an all-atom model of a highly cross-linked PA membrane from a non-equilibrium molecular dynamics technique. Molecular dynamics simulations performed at equilibrium were further carried out in order to investigate membrane/water interactions and thus gaining insight into polyamide membrane/water affinity at the molecular level.

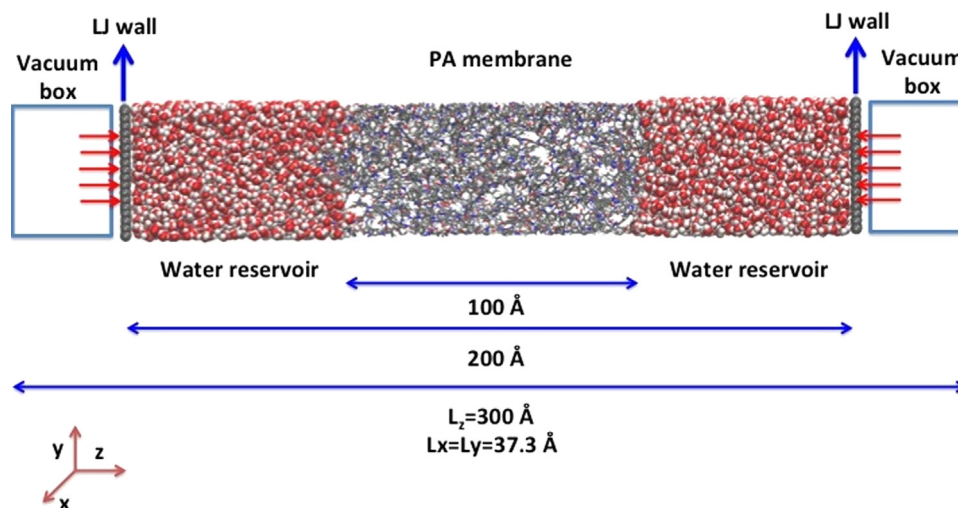
## 2. Computational procedure

### 2.1. Method, initial configuration, force field and MD details

Cross-linked PA membranes was built by following a recent hybrid protocol combining Monte Carlo and Molecular Dynamics simulations [9,10]. The so-obtained dry PA membrane had an oxygen to nitrogen ratio of 1.14, which is in very good agreement with experimental values estimated for commercial membranes [3,15–18]. A cross-linking degree of 80.8% was reported in [9,10]. It is worth mentioning that this value was calculated on the basis of pending carboxylic groups (COOH). Considering a single pending COOH per polymer unit (before cross-linking) the cross-linking degree was defined as  $100(\text{COOH}_{\text{initial}} - \text{COOH}_{\text{final}}) / \text{COOH}_{\text{initial}}$ . On the other hand Kolev and Freger defined the cross-linking degree as  $100N / (N + \text{COOH})$  [12]. Considering this definition the cross-linking degree of our membrane was found to be slightly higher than 93%, i.e. similar to that reported by Kolev and Freger. Our construction method was also shown to provide a membrane density and an average cavity size in line with experiments [10]. Details of the membrane construction and its equilibration can be found

elsewhere [9,10]. Studying water transport across the membrane involves considering explicitly PA/water interfaces. Therefore two water reservoirs surrounding the dry PA polyamide membrane were added to the simulation box. A snapshot of the initial configuration and the dimensions of the simulation box are given in Fig. 1. In order to generate water transport through the PA membrane two flexible walls acting as pistons were added on each side of the membrane/reservoir system along  $z$  direction (Fig. 1). These walls were composed by Lennard–Jones (LJ) particles. Simulations were carried out in the canonical ensemble (NVT) and an external force generating a pressure of 1 bar was applied on each LJ wall. Let us note that this method is similar that non-equilibrium molecular dynamics simulations where two different external forces are applied to model a transmembrane pressure difference [11]. The pressure  $P$  exerted on each wall is obtained from the external force ( $f_{\text{ext}}$ ) applied on each LJ particle by  $P = N_{\text{LJ}} f_{\text{ext}} / S$  where  $S$  is the wall surface area and  $N_{\text{LJ}}$  the number of LJ particles constituting the wall. Eventually, two vacuum boxes were added on each side beyond both walls in order to avoid interactions between two walls because of periodic boundary conditions. Dimensions of the different elements in the simulation box are provided in Fig. 1. Our study was divided into two parts, (i) a non-equilibrium MD simulation (NEMD) aiming at filling the PA membrane with water molecules (membrane hydration) and (ii) an equilibrium MD (EMD) simulation the initial configuration of which corresponded to the final configuration of the previous NEMD simulation (note that both LJ walls and vacuum boxes were removed in the EMD simulation). Indeed, the analysis of PA/water interactions should be performed in a statistical ensemble where thermodynamic, chemical and mechanical equilibria are fulfilled.

The PA framework was modeled by means of the AMBER99 force field [19,20]. Details of the PA force field can be found elsewhere [9–11]. Water molecules were modeled by means of the non-polarizable rigid TIP4P/2005 model [21]. Lennard–Jones parameters of the LJ walls were  $\sigma = 3.219 \text{ \AA}$  and  $\epsilon = 0.237 \text{ kJ mol}^{-1}$ . The flexible feature of the walls was achieved by considering a harmonic bond potential between a given particle and its neighbors. The equilibrium distance was  $2.29 \text{ \AA}$ , the force constant ( $k_b$ ) was set to  $2000 \text{ kJ mol}^{-1}$ . We checked that the final configuration was independent of the  $k_b$  value. Intermolecular interactions were computed by means of the Lennard–Jones and Coulombic potentials. Both contributions were truncated at  $12 \text{ \AA}$ . Electrostatic interactions were calculated by means of the Ewald sum method



**Fig. 1.** Snapshot of the initial configuration of the polyamide membrane surrounded by two water reservoirs. Carbon atoms are in grey, hydrogen atoms in white, oxygen atoms in red and nitrogen atoms in blue. The origin of box is located at the centre of the box. The red arrows indicate the external force applied on the LJ walls acting as pistons. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

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