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A simple model for solute–solvent separation through nanopores based on core-softened potentials

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HIGHLIGHTS

- Simple model for solute–solvent separation based on core-softened potentials.
- Molecular dynamics simulations of complex fluids.
- Reverse osmosis for water desalination.

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ABSTRACT

We propose an effective model for solute separation from fluids through reverse osmosis based on core-softened potentials. Such potentials have been used to investigate anomalous fluids in several situations under a great variety of approaches. Due to their simplicity, computational simulations become faster and mathematical treatments are possible. Our model aims to mimic water desalination through nano-membranes through reverse osmosis, for which we have found reasonable qualitative results when confronted against all-atoms simulations found in the literature. The purpose of this work is not to replace any fully atomistic simulation at this stage, but instead to pave the first steps towards coarse-grained models for water desalination processes. This may help to approach problems in larger scales, in size and time, and perhaps make analytical theories more viable.

1. Introduction

The separation of dissolved solute from a solution is an important subject from both technological and scientific perspectives. The canonical example is the purification of water, in which water must be separated from solutes, as ions or heavy metals, for example, in order to be suitable for consumption. Processes for obtaining clean water are generally inefficient and in most cases tend to be prohibitively expensive. The seawater desalination seems to be a promising alternative: despite approximately 97% of the water is concentrated in the oceans and seas the percentage of potable water obtained through salt–water separation is still very small [1]. Examples of water–salt separation processes are distillation, reverse osmosis (RO), thermal desalination and freezing [1–6]. Reverse osmosis is particularly important and it consists

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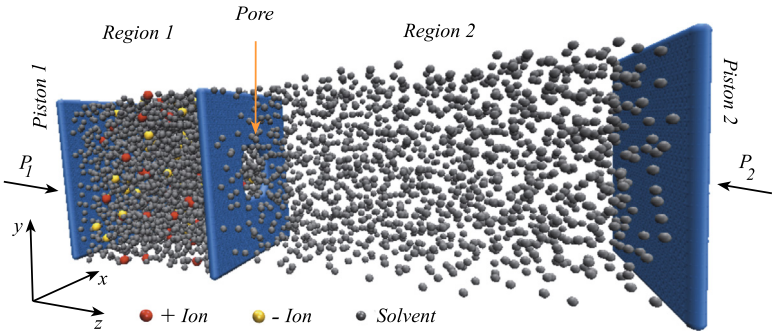

Fig. 1. System model we used for separating solute from solvent through nanopores. The mixture of solvent and ions, initially localised in the Region 1, is pushed by a piston against a middle membrane. The circular pore in its center prioritises the passage of solvent once ions are effectively bigger than solvent particles.

of forcing water to pass through a semipermeable membrane by applying an external pressure bigger than the osmotic pressure of the fluid, while the membrane is responsible to retain most of the particles dissolved in the water. Conventional RO membranes used for this purpose are expensive and not very efficient: water transport is slow and there are issues in controlling the membrane selectivity [7]. Researches in this area generally aim to reduce the specific energy consumption, increasing water recovery and lowering the pressure difference between feed and permeate sides [8–11].

RO mechanisms for water desalination based on nanostructures as semipermeable membranes have obtained encouraging results [7,12–21]. The size exclusion promoted by nanopores seems to be an important ingredient when such structures are used as filters.

In this context, the water–ions separation through nanostructures subject gained attention from scientific community, who have intensified the efforts in order to understand the main mechanisms responsible for water desalination in such a nanometric level [7,13,14,17,18,22–37].

For example, Qi Chen and Xiaoning Yang have recently reported a molecular simulation study of pyridinic nitrogen doped nanoporous graphene as desalination membrane [20]. Their results indicate that these membranes are capable of rejecting salt ions and increase the water flow and permeability in several orders of magnitude if compared with existing processes of water–salt separation. The authors have established that the desalination performance is sensitive to pore size and membrane's hole chemical functionalisation [20].

Despite the cited encouraging results, the water desalination problem is typically macro. Considering the modern computational power available, it is literally impossible to study this problem using an all-atoms approach in a macro size scale. In this sense, it is important to seek for cheaper, alternative procedures to tackle this problem. An alternative to computationally model water-like fluids in an effective manner relies on core-softened potentials. Systems modelled through these potentials generally present several features present in water. For example, they possess density, diffusion, and structural anomalies. Many core-softened potential based systems show a liquid–liquid critical point separating a high density liquid phase from a low density liquid one, as hypothesised for liquid water [38–58]. Core-softened potentials treat anomalous fluids (water being the most famous case) in an effective way, in a manner that there is no directionality (interactions between particles are pairwise only) neither the presence of charges. No major arguments seem necessary in order to convince the reader that the absence of these ingredients turn core-softened models extremely cheap to simulate.

Those kinds of models were explored in depth not only by computer but also by means of theoretical tools due to their simplicity [57–68]. Successive good results gave support to the use of core-softened potentials in more complicated environments, such as mimicking a salty solution [69], water in nanotubes [70,71], confined between plates [72–74] and in contact with nanopores [75]. Following this spirit, we propose in this work the use of core-softened potentials as a building block for a simple system able to reproduce the main features of water–salt separation all-atoms simulations. We show that it is possible to build a system which qualitatively reproduces the results of more sophisticated systems in a fraction of time. Even though some work are still necessary to fine tuning the core-softened based model presented in this work, we believe this study is a first step to extrapolate the water desalination through nanostructures process to a more realistic number of particles scale.

This paper is organised as follows. Computational details are given in Section 2 while the results and discussion are made in Section 3. Section 4 ends the text with the conclusions of the work.

2. Computational details

Our system model is shown in Fig. 1. We used a simulation box with dimensions of $25 \times 25 \times 75$ (in units of solvent particles size σ) in the x, y and z, directions, respectively, and two pistons, one initially located at $z = 0$ (Piston 1) and another one at $z = 75\sigma$ (Piston 2). In all simulations we apply external pressures in the Piston 1. The Piston 2 may either be static or mobile, subject to external pressures as will be discussed later. Finally, there is a middle wall whose position is fixed at $z = 25\sigma$, and which separates the Region 1 (feed side) from Region 2 (permeate side). The middle wall has a circular pore