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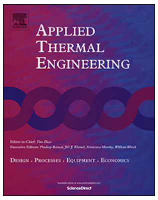

Research Paper

Protocols for atomistic modeling of water uptake into zeolite crystals for thermal storage and other applications

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HIGHLIGHTS

- Numerical protocols for modeling water adsorption and infiltration into zeolite.
- A priori screening of new materials for heat storage and desalination is possible.
- Water uptake isotherms for bridging atomistic and engineering scales.

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ABSTRACT

We report numerical protocols for describing the water uptake process into microporous materials, with special emphasis on zeolite crystals. A better understanding and more predictive tools of the latter process are critical for a number of modern engineering applications, ranging from the optimization of *loss free* and compact thermal storage plants up to more efficient separation processes. Water sorption (and desorption) is indeed the key physical phenomenon to consider when designing several heat storage cycles, whereas water infiltration is to be studied when concerned with sieving through microporous materials for manufacturing selective membranes (e.g. water desalination by reverse osmosis). Despite the two quite different applications above, in this article we make an effort for illustrating a comprehensive numerical framework for predicting the engineering performances of microporous materials, based on detailed atomistic models. Thanks to the nowadays spectacular progresses in synthesizing an ever increasing number of new materials with desired properties such as zeolite with various concentrations of hydrophilic defects, we believe that the reported tools can possibly guide engineers in choosing and optimizing innovative materials for (thermal) engineering applications in the near future.

1. Introduction

In the last decades, the increase in worldwide human population, industrialization and technological development have been causing a growth in the use of fossil fuels, which in turn has increased greenhouse gas emissions and fuel prices [1]. Those events motivate a more extensive and efficient exploitation of the various renewable energy resources, such as solar, tidal, wind or geothermal technologies [2]. To this end, one of the major limiting factor is the mismatch between most renewable energy availability and user demand, which is particularly the case of solar energy due to its intrinsically intermittent and unpredictable nature [1,3,4]. Therefore, energy storage technologies can play an increasingly important role towards a better equilibrium between energy supply and demand, with the additional aim to make accessible everywhere and every time electrical and thermal power.

Particularly focusing on thermal energy, sensible [5] or latent [6] heat storage systems are the most studied and established solutions in the field. However, due to unavoidable energy losses, those approaches are often not suitable for long-term applications [7]. On the contrary, storage systems based on sorption phenomena show high energy density, negligible heat losses and allow repetitive storage operations [8]. Systems using water as a sorbate present the additional advantages of no toxicity, low cost and large availability. In this context, zeolite materials are showing great potential for heat storage applications [1].

Zeolites are aluminosilicate materials that nowadays can be easily synthesized with a precise chemical composition and structure of the micropores [9]. The significant increase in the surface to volume ratio and the peculiar physical properties of water under nanoconfined conditions are the main motivations of the growing interest for zeolite materials in several fields [10,11]. In fact, the increased solvent accessible surface area enhances the solid–liquid interactions, which in turn modify the liquid transport properties due to nanoconfinement effects [12,13]. Generally speaking, such effects are of interest in modern engineering as they can be

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exploited for finely tailoring mass and energy transport properties in next-generation devices [14–16].

In particular, zeolite crystals present both large heat of adsorption and the capability to accommodate a significant amount of water without noticeable structure degradation, thus allowing durable heat release/accumulation cycles, respectively [17,18]. Zeolite sorbents are typically non-toxic and present low mass density [19] in addition to a relatively low desorption temperature: all these features make them materials of great interest in thermal science for both heating [20,21] and cooling purposes [22–24].

However, while the nanometer size of zeolite pores allows the sorption process to take place with large surface to volume ratios (as a rule of thumb, a teaspoon of zeolite or MOF materials have a inner pore surface equal to the area of a football field [25]) thus with high energy densities, it also involves nontrivial nanoscale effects on the mass transport of water inside the nanopores, such as surface barriers, single-file diffusion and nanoconfinement [26–30].

Therefore, modeling of the above phenomena is a non trivial task and it can often be accurately accomplished only by resorting to detailed atomistic tools, namely Monte Carlo (MC) and Molecular Dynamics (MD). In Fig. 1, the fundamental tool for linking atomistic results to the engineering level is schematically represented: the connection of those drastically disparate scales can be achieved by constructing the *water uptake isotherms*. In this work, atomistic numerical protocols are used to investigate on the mechanism of both water adsorption and infiltration into zeolites with different hydrophilicity thus enabling to fully construct those isotherms.

In the low-pressure regime (i.e. below the saturation pressure), curves in Fig. 1 are typically referred to as adsorption isotherms and, along with the value of the isosteric (adsorption) heat, are sufficient to reconstruct the isosteric field in the Clapeyron diagram. The latter is a convenient tool for the thermodynamic optimization of thermal storage cycles [31].

On the other side, in the high-pressure regime (larger than tens or hundreds of bars), curves in Fig. 1 are referred to as infiltration isotherms, which are relevant for water-solute separation processes such as desalination by reverse osmosis. In fact, it is worth noticing that microporous materials can be also used for manufacturing selective membranes.

To this respect, thanks to sub-nanometer pore sizes, excellent rejection rates are expected when using zeolite crystals, or other materials with a narrow pore size distribution. Better selective membranes can indeed help in the near future in lowering the overall energy requirements in water desalination and other separation processes. The permeability of a microporous membrane depends on both the solubility coefficient, definable on the basis of the infiltration isotherms (the more hydrophilic the more permeable), and the water mobility (diffusion coefficient, D) within the pores [12] (the more hydrophilic the less permeable). Given that it is *a priori* unclear which property (solubility or diffusivity) dominates the overall transport behavior [32], the right-hand side of Fig. 1 represents an essential piece of information when it is to predict the membrane engineering performances.

In summary, computational materials design is a very promising research area, because it allows a more systematic investigation of novel materials for several applications [33]. This is particularly true for nanostructured materials, where macroscale properties are strongly affected by nanoscale characteristics and experiments are often limited by fabrication and visualization techniques, and thus

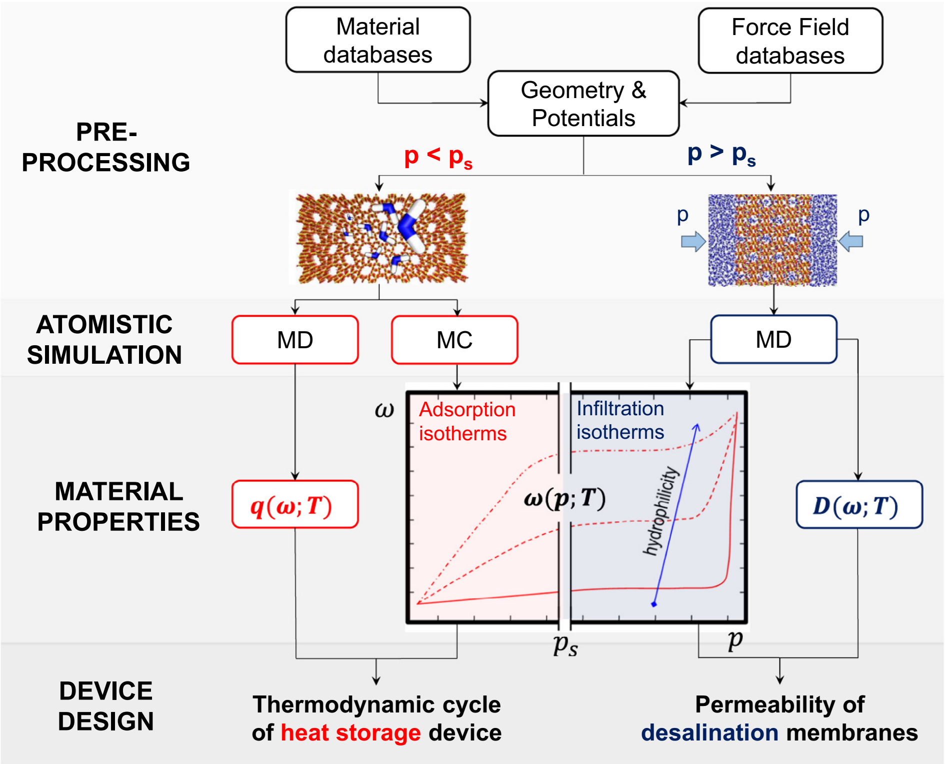

Fig. 1. Protocols for the atomistic modeling by Molecular Dynamics – MD and Monte Carlo – MC methods of properties of nanoporous materials for thermal storage or desalination applications. Starting from the geometrical structure and force field, atomistic simulations are carried out to compute: (i) the isosteric heat $q(\omega;T)$ and adsorption isotherms $\omega(p;T)$, at $p < p_s$ (p_s being the saturation pressure); (ii) the infiltration isotherms $\omega(p;T)$ and the solvent diffusivity $D(\omega;T)$ for evaluating the membrane permeability, at $p > p_s$. Water uptake isotherms can be regarded as a convenient linking tool for bridging the disparate space and time scales between atomistic simulations and engineering applications. The reported protocol may support computational design of devices based on nanostructured materials, such as modern thermal batteries and desalination membranes.

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