

**The influence of colour on the floating velocity of rubber ducks**

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*Cover image:* fractal map from a photography of a circuit board of a smartphone, done with GIMP code on 02 February 2018.

# **The influence of colour on the floating velocity of rubber ducks**

**You won't expect the results**

**Thesis**

to obtain the Degree of Doctor of Philosophy at Pablo de Olavide University under the authority of the Rector Magnificus, Prof. Vicente Guzmán Fluja, to be defended in public on 23th March 2018 in the morning, in accordance with the decision of the  
Doctoral Committee

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**PhD External Committee:**

The research leading to these results was performed at very funny place. This dissertation has been supported with a predoctoral fellowship from the Glorious Andalusian Emirate.



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# Preface

How you expect to run with the  
wolves come night when you spend  
all day sparring with the puppies?

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Omar, The Wire

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Gracias.

# Summary

This thesis is focused on the study of nanoporous soft crystals. Atoms in crystalline material in general fluctuate around their equilibrium positions. External stimuli and thermal effects distort the atoms, possibly resulting in a loss of crystallinity. The main **hypothesis** of the dissertation that I present is: *a)* the lack of crystalline regularity has an impact on the microscopic porosity, the void-channels and pockets available to guest molecules, and an effect in the sorption- and transport-properties, but likewise *b)* adsorbates could affect the pore structure, in a bidirectional causal relation, and *c)* these phenomena can be modelled with appropriate simulation techniques.

The aim and scope of the thesis is twofold:

1. To study thermal-induced and guest-induced distortions in soft nanoporous materials by means of computer simulation.
2. To develop new computational algorithms which improve the efficiency of simulations and ensure convergence to true equilibrium.

This thesis is structured as follows:

Chapter 1 covers ...

The final part is dedicated to the conclusions as well as a brief discussion on the perspective this work can have for future work-directions.



# Resumen

Esta tesis está orientada al estudio de cristales nanoporosos flexibles. Como se verá a lo largo del desarrollo del trabajo, algunas consecuencias y consideraciones emergen al tener en cuenta que los átomos del cristal pueden moverse más allá de los límites que marcan las fluctuaciones térmicas. A esto hay que añadir una posible pérdida de la regularidad cristalina. La principal **hipótesis** de este trabajo de tesis es: *a)* la disminución de regularidad cristalina tiene un impacto en la porosidad microscópica accesible, en general, a adsorbatos, y un efecto en las propiedades de adsorción y transporte, pero a su vez *b)* los adsorbatos pueden afectar la estructura del poro en un proceso de retroalimentación causal, *c)* siendo estos fenómenos modelables usando las técnicas apropiadas de simulación.

Los objetivos de esta tesis son:

1. Estudiar las distorsiones inducidas por la temperatura y por moléculas adsorbi-das en materiales nanoporosos flexibles mediante simulación por ordenador.
2. Desarrollar algoritmos computacionales que mejoren la eficiencia de estas simu-laciones y que aseguren una convergencia real a estados de equilibrio.

La tesis se estructura de la siguiente manera:

El Capítulo 1 está dedicado a ...

La parte final de la tesis está dedicada a las conclusiones y discusión breve de la proyección que puede llegar a tener este trabajo en el futuro.



# Chapter 1

## Introduction

There were many paths that led up into those mountains, and many passes over them. But most of the passes were infested by evil things and dreadful dangers.

---

*The Hobbit, J. R. R. Tolkien*

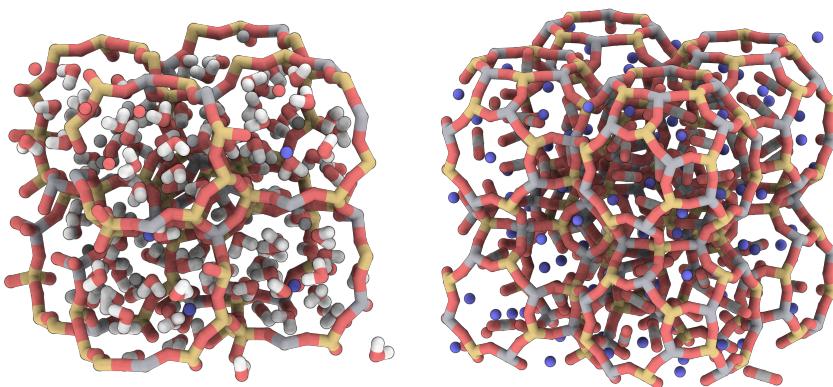
### 1.1. Nanoporous materials

Nanoporous crystals –such as zeolites, metal-organic frameworks (MOFs) or covalent-organic frameworks (COFs), form an interesting family of materials. Its relevance in the scientific community has been growing in the last decades.<sup>1</sup> These nanoporous crystals exhibit a huge variety of structural properties which are characterised by high surface area and pore volume. They possess a wide range of structural topologies with tunable regularity structures and interesting host-guest complexation behaviour [1].

Zeolites were the first porous crystals to be widely studied. Towards the end of the 1930s zeolitic structures such as analcrite, cancrinite, natrolite and sodalite, were reported by Taylor [2], Pauling [3] and Bragg [4] and Taylor [5]. Nowadays, more than 230 different zeolite topologies are identified [6] by diffraction techniques. Zeolites have a three-dimensional framework of  $\text{TO}_4$  tetrahedra, assembled through oxygen atoms in Secondary Building Units (SBUs) such as cubes (double four-rings or D4R) or octahedra (single eight-ring, S8R), among other configurations. These units are linked in

---

<sup>1</sup>Although this growing interest is not restricted to the scientific community. They have a wide variety of uses, including separation and storage of different compounds. Most compounds frequently used in the chemical or pharmaceutical industry are naturally found in an impure state and nanoporous materials act as molecular sieves for this indispensable separation. Synthetic drugs, petroleum industry or purification of metals are examples of the polyvalency of these crystals.



**Figure 1.1:** Left: Hydrated CHA-type zeolite or Chabacite with  $\text{Si}/\text{Al} = 2.5$  with  $\text{Na}^+$  and  $\text{Ca}^{2+}$  cations. Right: Adsorption of  $\text{CO}_2$  in dehydrated Linde Type A (LTA) with  $\text{Si}/\text{Al} = 1$  and 96  $\text{Na}^+$  per unit cell. All snapshots are taken from molecular dynamic simulations at 300 K.

a way that form a regular 3-dimensional structure (framework), which contains *pores*, *windows* and *channels* of molecular size (circa 3–10 Å in diameter). This porosity is reflected the fact that between 20 and 50% of the volume of a zeolite structure is empty and, in general, accessible to guest molecules. The central T atom is usually either silicon or aluminium. However, in the last decades new materials have been synthesised where the  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$  ion are substituted by  $\text{Ga}^{3+}$ ,  $\text{Br}^{3+}$  or  $\text{Ge}^{4+}$ . Aliovalent substitutions change the overall charge within the framework, but the zeolite must remain neutral. This negative charge is, then, balanced by an extra-framework cation. The chemical formula of aluminosilicate zeolite is:  $\text{Me}_{x/n}^{n+}[(\text{AlO}_2)_x(\text{SiO}_2)_{1-x}]@w\text{H}_2\text{O}$ , where Me is the cation (organic or inorganic),  $n$  their valence,  $x$  the molar fraction of Al atoms and  $w$  the number of water molecules in the unit cell of the structure. The  $\text{Al}^{3+}/\text{Si}^{4+}$  cation-ordering stability is governed by well-known rules, established by Lowenstein and Dempsey [7, 8]. They state that no Al-O-Al chains are allowed and the number of Al-O-Si-O-Al chains must be minimised (or, what is equivalent the Al-Al pair distance is maximised). In some particular cases, however, these rules are broken. The presence of divalent cations  $\text{Me}^{2+}$  allows the Al-O-Si-O-Al chains are stabilised. As a matter of fact, the heteroatom distribution in zeolite frameworks has been subject of major interest for a long time, with some controversial issues arising, such as the much debated  $\text{Si}^{4+}/\text{Ge}^{4+}$  cation distribution.

Extra-framework cations are linked to the oxygen atoms of the framework through relatively weak ionic interactions compared to the stronger covalent bonds of the atoms that form the framework. For this reason, extra-framework cations have a high degree of mobility and can *migrate* from its preferential cation sites to another. We will see that these extra-frameworks cations play a very important role in adsorption

properties at zeolites because of their electrostatic nature.

Zeolites normally exhibit high surface area, thermal stability (at high Si/Al ratio at least), ion exchange capacity and, of course, catalytic capacity. A notable feature of the high Si/Al ratio zeolites (those that appear in nature, also called natural zeolites) is its hydrophilic character, which is the reason behind the fact that these zeolites are often saturated with water. This hydrophilic character is due to various reasons : 1) relative large ratio of surface area per crystal volume, 2) presence of extra-framework cations, 3) existence of dipoles between crystallographic defects of aliovalent substitutions in tetrahedra. The two last conditions become weaker as Si/Al ratio increases, which eventually leads to a phase transition from hydrophilic to hydrophobic behaviour for ratios close to 8–10. As an example of this behaviour we have the silicalite structure (MFI-type pure silica structure or ZSM-5), which has a higher adsorption for paraffin compared to water [9].



# Chapter 2

---

## Methodology

Never trust a computer you can't throw out a window.

---

Stephen Wozniak

In this chapter, we will discuss the different techniques employed in our study. The main methodology used in this study is Molecular Dynamics (MD) simulation, in which particles trajectories are calculated by integrating the equations of motion. Energy minimisation calculations (EM) are used too. Here, we minimise the total energy of the lattice in order to determine the structure, employing interatomic potentials. In order to perform simulations of adsorption of guest molecules in the pore of the structures, Monte Carlo (MC) simulations were used. Moreover, we have verified some of the structural changes and point-charges calculations with electronic structure techniques using Density Functional Theory (DFT) i.e. quantum calculations. DFT is a powerful but time consuming technique, so we only use it in few key cases, in order to check the results obtained with classical calculations.

### 2.1. Molecular Dynamics

Intuitively, Molecular Dynamics simulations are the *simplest* type of simulation: particles move around in the system, following trajectories determined by Newton's laws (or by the Hamilton Equations ??). In an iterative scheme, the forces they exert on one another are calculated from their positions; based on the forces, the velocities are updated; and these velocities, kept fixed for one time-step  $\tau$ , yield the new positions one time-step away.

The velocity-Verlet algorithm is the most widely used method for integrating the equations of motion [10]. This is implemented in most of simulations codes according

to the following equations:

$$\vec{r}_i(t + \tau) = \vec{r}_i(t) + \vec{v}_i(t)\tau + \frac{\vec{f}_i(t)}{2m}\tau^2 + \mathcal{O}(\tau^3) \quad (2.1)$$

$$\vec{v}_i(t + \tau) = \vec{v}_i(t) + \frac{\vec{f}_i(t) + f_i(t + \tau)}{2m}\tau + \mathcal{O}(\tau^3) \quad (2.2)$$

where  $\vec{r}_i(t)$ ,  $\vec{v}_i(t)$  and  $\vec{f}_i(t)$  are the position, velocity and force vector at time  $t$ , respectively.  $\tau$  is the time-step and  $m$  the mass of the atom  $i$ . Note that this algorithm is time-reversible. An unphysical drift in the energy appears after long integration time or as a results of the use of large time-steps,  $\tau$ . To test this energy drift for a given time-step after  $\lambda$  integration steps, we can check the integration validity by requiring the drift is lower than a typical energetic value  $\delta$ :

$$\sum_{i=1}^{\lambda} \|1 - E^{(i\tau)}/E(0)\| < \delta \lambda \quad (2.3)$$

There are several ensembles in which we can run calculations, depending on the conserved quantities:  $NVE$ ,  $NVT$ ,  $NPT$ , etc. In this thesis, we mainly use the  $NVT$  and  $NPT$  ensembles. The numerical integration was performed using the Nose-Hoover style non-Hamiltonian equations of motion, which are designed to generate positions and velocities sampled from  $NVT$  and  $NPT$  ensembles following the scheme of Martyna et al. [11] and Tuckerman et al. [12].

The ergodic hypothesis states that ensembles averages can be obtained from time averages. So, the time average value,  $\langle \dots \rangle_t$ , of a generic property  $A$  can be obtained by the following expression

$$\langle A \rangle_t = \lim_{t \rightarrow \infty} \frac{1}{t} \int dt A(x, t). \quad (2.4)$$

where  $x \equiv \{\vec{r}^N\}$ . If Equation ?? is equal of the Equation 2.4 the system is **ergodic**.

An important dynamic quantity is the self-diffusivity coefficient  $D_s^\alpha$  (in the directions  $\alpha = x, y, z$ ) of  $N$  particles, which can be computed by evaluating the mean-square displacement, which reads in three dimensions

$$D_s^\alpha = \frac{1}{2N} \left\langle \sum_{i=1}^N (r_{i\alpha}(t) - r_{i\alpha}(0))^2 \right\rangle_t \quad (2.5)$$

where  $r_{i\alpha}$  is the  $\alpha$ -component of the center-of-mass of particle  $i$ . The directionally averaged diffusion coefficient is given by

$$D = \frac{D_x + D_y + D_z}{3} \quad (2.6)$$

We have used the order- $n$ -algorithm incorporated in the RASPA code [13, 14] to measure accurate mean-square displacements at long times in a fast way.

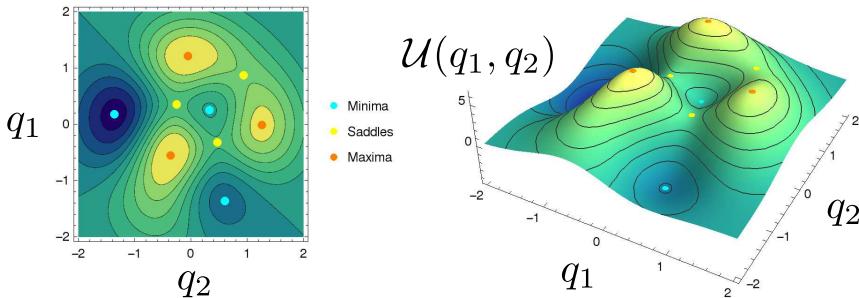
## 2.2. Lattice energy minimisation

In the previous Chapter 1, in Section ??, different models for calculating the energy of the systems have been presented. We are interested in finding the minimum state of the system.<sup>1</sup> However, the calculations presented in this section are performed at  $T = 0K$ . That is, they do not include thermal effects. This state corresponds to a minimum in the potential energy hypersurface, in which:

$$\frac{\partial \mathcal{U}(\vec{r}^N)}{\partial r_i} = 0 \quad \forall i = 1, \dots, N \quad (2.7)$$

where  $\mathcal{U}(\vec{r}^N)$  is the total potential energy of the system, as defined in Equation ??, and  $N$  is the number of atoms.

Transition states and local minima also satisfy Equation 2.7, therefore it is necessary to calculate the second derivative to distinguish between a minimum and a transition state (see Figure 2.1).



**Figure 2.1:** Cartoon of the potential energy surface of two generalised coordinates  $\mathcal{U}(q_1, q_2)$  in a fictional system. Local and global minima (cyan dots) and maxima (red dots) and saddle points (yellow) are indicated on the surface.

There are several minimisation algorithms. The simplest algorithm is the **Steepest Descents** (SD) method [15], which follows the force vector from an initial configuration to a zero in the force:

$$\vec{x}_{n+1} = \vec{x}_n - k_n \vec{\nabla} f(\vec{x}_n) \quad (2.8)$$

where  $k_n$  is a self-adjustable parameter for each minimisation step. However it is known to converge slowly in *stiff* systems [16]. The **Conjugate Gradient** (GC) method

<sup>1</sup>After some considerations can be proved that, under certain conditions, the state of energy minimum state is the most probable.

requires both the energy and first derivative evaluations, and is the most efficient method at intermediate distances from the minimum. The CG method improves upon the SD method by following conjugate search directions instead of always following the force. In the LAMMPS code it is implemented the Polak and Ribiére [17] version of the CG algorithm:

$$\vec{x}_{n+1} = \vec{x}_n - k_n \vec{h}_n \quad \text{with} \quad \vec{h}_n = \vec{\nabla} f(\vec{x}_n) + \gamma_n \vec{h}_{n-1} \quad (2.9)$$

where

$$\gamma_n = \frac{\vec{\nabla} f(\vec{x}_n) \left( \vec{\nabla} f(\vec{x}_n) - \vec{\nabla} f(\vec{x}_{n-1}) \right)^T}{\left\| \vec{\nabla} f(\vec{x}_{n-1}) \right\|^2} \quad (2.10)$$

The norm of the gradient is checked to ascertain whether to switch from one method to another. When the system is very close to the energy minimum this method is very slowly convergent. When that happens we switch to the **Newton-Raphson** method [18], which makes use of the second derivatives of the energy, in order to reach rapidly the energy minimum. Newton-Raphson method approximates the objective function by a quadratic surface at each step and moves to the minimum of that surface:

$$\begin{aligned} f(\vec{x} + \Delta \vec{x}) &\simeq f(\vec{x}) + \vec{\nabla} f(\vec{x})^T \cdot \Delta \vec{x} + \frac{1}{2} \Delta \vec{x}^T \cdot \mathcal{H} \cdot \Delta \vec{x} \\ \vec{\nabla} f(\vec{x} + \Delta \vec{x}) &\simeq \vec{\nabla} f(\vec{x}) + \mathcal{H} \cdot \Delta \vec{x} \\ \Delta \vec{x} &= -\mathcal{H}^{-1} \cdot \vec{\nabla} f(\vec{x}) \end{aligned}$$

where  $\mathcal{H} := (\partial^2 u / \partial x_i \partial x_j)$  is the Hessian. This method has a computationally high CPU cost. The most expensive and memory demanding part of Newton-Raphson method is the calculation of the Hessian. The basic Newton-Raphson method requires the Hessian to be non-singular and tends to develop problems if any of its eigenvalues become negative. A simple fix for this is to add a regularisation matrix (often a unit matrix)

$$\Delta \vec{x} = -(\mathcal{H} + \lambda \mathcal{S})^{-1} \cdot \vec{\nabla} f(\vec{x}) \quad (2.11)$$

**Rational Function Optimization** (RFO) introduces a step size dependent denominator [19], which prevents the algorithm from taking large steps:

$$f(\vec{x} + \Delta \vec{x}) \simeq f(\vec{x}) + \frac{\vec{\nabla} f(\vec{x})^T \cdot \Delta \vec{x} + \frac{1}{2} \Delta \vec{x}^T \cdot \mathcal{H} \cdot \Delta \vec{x}}{1 + \Delta \vec{x}^T \cdot \mathcal{S} \cdot \Delta \vec{x}} \quad (2.12)$$

Both Newton-Raphson and RFO minimisation methods were used to ensure convergence to true energy. However, RFO behaves better than Newton-Raphson in the vicinity of inflection points. Both methods are included in the GULP code [20]. Baker [21] and Banerjee et al. [22] developed a Eigenvector-Following method. This method

solves this limitation of the Newton-Raphson technique by shifting some of the eigenvalues to change their sign and achieve the desired curvature. This algorithm is included in the RASPA code [23].

We have used RASPA, GULP and LAMMPS codes [14, 20, 24] for energy minimisation calculations and to locate saddle points between structural phase-transitions.



# **Part I**

# **Block 1**



# Chapter 3

## Structural distortions by cosa migration and cosation: LOL-type zeolite I

Molecular valves are nanostructured materials that are becoming popular, due to their potential use in bio-medical applications. However, little is known concerning their performance when dealing with small molecules, which are of interest in energy and environmental areas. It has been observed experimentally that zeolite RHO shows unique pore deformations upon changes in hydration, cation siting, cation type, and/or temperature-pressure conditions. By varying the level of distortion of double 8-rings it is possible to control the adsorption properties, which confers a molecular valve behaviour to this material. We have employed interatomic potentials-based simulations to obtain a detailed atomistic view of the structural distortion mechanisms of zeolite RHO, in contrast with the averaged and space group restricted information that can be retrieved from diffraction studies. We have modeled the pure silica zeolite RHO as well as four aluminosilicate structures, containing  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  cations. It has been found that the distortions of the three zeolite rings are coupled, although the four-membered rings are rather rigid and both six- and eight-membered rings are largely flexible. A large dependence on the polarising power of the extra-framework cations and with the loading of water has been found for the minimum aperture of the eight-membered rings that control the nanovalve effect. The energy barriers needed to move the cations across the eight-membered rings are calculated to be very high, which explains the origin of the experimentally observed slow kinetics of the phase transition, as well as the appearance of metastable phases.

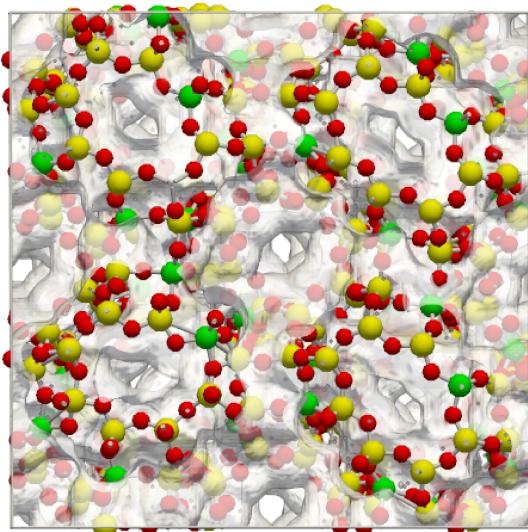
The publication related with this section can be found in:

- S. R. G. Balestra, S. Hamad, A. R. Ruiz-Salvador, V. Domínguez-García, P. J. Merkling, D. Dubbeldam and S. Calero. “Understanding Nanopore Window Distortions in the Revers-

ible Molecular Valve Zeolite RHO”.. *Chem. Mater.* 27, 5657–5667, 2015. DOI: 10.1021/acs.chemmater.5b02103. arXiv: 1605.06338.

### 3.1. Introduction

Molecular valves are a class of molecular devices that allow molecular transport in a controlled way through gate opening or trapdoor mechanisms. Valve action is typically performed by a molecule that is attached to the material, either by covalent bonds, hydrogen bonds or supramolecular interaction. In presence of external stimuli, such as temperature, pressure, pH, molecular or ion chemical potential, this molecule is able to change its configuration to allow the molecular flow. This ability has attracted huge attention during the last years, due to its impact in delivering medium and large size active molecules for medical applications [26–29].



**Figure 3.1:** Snapshot of a distorted form of RHO-type zeolite obtained by Molecular Dynamics. An isoenergy surface is shown in translucent gray. Extra-framework cations are omitted for clarity.

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# **Part II**

# **Block 2**



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# Chapter 4

## Structural Cosas: LOL-type zeolite III

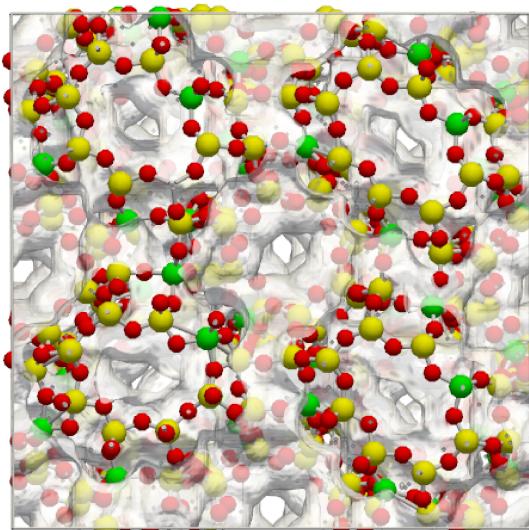
Molecular valves are nanostructured materials that are becoming popular, due to their potential use in bio-medical applications. However, little is known concerning their performance when dealing with small molecules, which are of interest in energy and environmental areas. It has been observed experimentally that zeolite RHO shows unique pore deformations upon changes in hydration, cation siting, cation type, and/or temperature-pressure conditions. By varying the level of distortion of double 8-rings it is possible to control the adsorption properties, which confers a molecular valve behaviour to this material. We have employed interatomic potentials-based simulations to obtain a detailed atomistic view of the structural distortion mechanisms of zeolite RHO, in contrast with the averaged and space group restricted information that can be retrieved from diffraction studies. We have modeled the pure silica zeolite RHO as well as four aluminosilicate structures, containing  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  cations. It has been found that the distortions of the three zeolite rings are coupled, although the four-membered rings are rather rigid and both six- and eight-membered rings are largely flexible. A large dependence on the polarising power of the extra-framework cations and with the loading of water has been found for the minimum aperture of the eight-membered rings that control the nanovalve effect. The energy barriers needed to move the cations across the eight-membered rings are calculated to be very high, which explains the origin of the experimentally observed slow kinetics of the phase transition, as well as the appearance of metastable phases.

The publication related with this section can be found in:

- S. R. G. Balestra, S. Hamad, A. R. Ruiz-Salvador, V. Domínguez-García, P. J. Merkling, D. Dubbeldam and S. Calero. “Understanding Nanopore Window Distortions in the Reversible Molecular Valve Zeolite RHO”.. *Chem. Mater.* 27, 5657–5667, 2015. DOI: 10.1021/acs.chemmater.5b02103. arXiv: 1605.06338.

## 4.1. Introduction

Molecular valves are a class of molecular devices that allow molecular transport in a controlled way through gate opening or trapdoor mechanisms. Valve action is typically performed by a molecule that is attached to the material, either by covalent bonds, hydrogen bonds or supramolecular interaction. In presence of external stimuli, such as temperature, pressure, pH, molecular or ion chemical potential, this molecule is able to change its configuration to allow the molecular flow. This ability has attracted huge attention during the last years, due to its impact in delivering medium and large size active molecules for medical applications [26–29].



**Figure 4.1:** Snapshot of a distorted form of RHO-type zeolite obtained by Molecular Dynamics. An isoenergy surface is shown in translucent gray. Extra-framework cations are omitted for clarity.

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# Conclusions

The **main finding** in this thesis is that it is possible to obtain molecular insights into flexibility of soft nanoporous crystals by descending to atomic level. As we assume in the hypothesis, there is strong interplay between structural changes and sorption and transport properties on nanoporous crystals. Molecular simulation can be an extremely useful tool: calculating and predicting observables which can be compared with experimental findings, to obtain knowledge on the nature of the flexibility of these materials.

The  $\text{Al}^{+3}/\text{Si}^{4+}$  cation distribution has minor impact on the phase transition associated to the flexibility of zeolite RHO. Therefore, pure silica structure provides an initial model for the study of the phase transition between acentric and centric space groups. The role of point charges and atom polarisability is crucial to describe the structural distortion, the volume, cell size and cell shape. The main conclusion in Chapter ?? is that interatomic potentials from molecular mechanics (those that involve an appreciable sort of interactions for bonds, bendings, and torsion) are unable to correctly reproduce the structure because they try to linearise a strictly energetic non-linear problem. The use of a polarisable force field and anharmonic potentials in Chapter 4, like the shell model for instance that stabilises low-symmetry structures, is mandatory for this purpose.

A novel method, based on cycles of the combined use of Monte Carlo, Energy Minimisation and Molecular Dynamics methods, has been proposed for the study of structural changes of high flexible nanoporous materials that are associated to the effect of temperature or guest molecules. The method provides crystallographic-quality structures (0.07-0.2% deviation from experimental values) of zeolite RHO exchanged with different extra-framework cations and different water content. A close relation was found between the polarising power of the extra-framework cations and the effective pore windows. The amount of water also modulates the effective pore windows. By choosing the right combination of extra-framework cations and water content, one can design the size of the effective pore windows for targeted molecular separations.

The



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# Appendices



# Appendix A

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## Cosas apartes

The publication related with this section can be found in:

- S. R. G. Balestra, S. Hamad, A. R. Ruiz-Salvador, V. Domínguez-García, P. J. Merkling, D. Dubbeldam and S. Calero. “Understanding Nanopore Window Distortions in the Reversible Molecular Valve Zeolite RHO”.. *Chem. Mater.* 27, 5657–5667, **2015**. DOI: 10.1021/acs.chemmater.5b02103. arXiv: 1605.06338.

### A.1. Introduction

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## Appendix bibliography

- [1] S. R. G. Balestra, S. Hamad, A. R. Ruiz-Salvador, V. Domínguez-García, P. J. Merkling, D. Dubbeldam and S. Calero. “Understanding Nanopore Window Distortions in the Reversible Molecular Valve Zeolite RHO”. *Chem. Mater.* 27, 5657–5667, 2015. DOI: 10.1021/acs.chemmater.5b02103. arXiv: 1605.06338. (Cit. on p. 41).



# List of publications

The following publications are directly related with this Thesis:

## Peer reviewed journals

- S. R. G. Balestra, J. J. Gutierrez-Sevillano, P. J. Merkling, D. Dubbeldam and S. Calero. “Simulation Study of Structural Changes in Zeolite RHO”.. *J. Phys. Chem. C* 117, 11592–11599, **2013**. DOI: 10.1021/jp4026283.
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- S. R. G. Balestra, R. Bueno-Perez, S. Hamad, D. Dubbeldam, A. R. Ruiz-Salvador and S. Calero. “Controlling Thermal Expansion: A Metal–Organic Frameworks Route”. *Chem. Mater.* 28, 8296–8304, **2016**. DOI: 10.1021/acs.chemmater.6b03457. arXiv: 1610.08122.
- S. Hamad, S. R. G. Balestra, R. Bueno-Perez, S. Calero and A. R. Ruiz-Salvador. “Atomic charges for modeling metal–organic frameworks: Why and how”. *J. Solid State Chem.* 223, 144–151, **2015**. DOI: 10.1016/j.jssc.2014.08.004. arXiv: 1802.08771.
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- J. J. Gutiérrez-Sevillano, S. Calero, S. Hamad, R. Grau-Crespo, F. Rey, S. Valencia, M. Palomino, S. R. G. Balestra and A. R. Ruiz-Salvador. “Critical Role of Dynamic Flexibility in Ge-Containing Zeolites: Impact on Diffusion”. *Chem. Eur. J.* 22, 10036–10043, **2016**. DOI: 10.1002/chem.201600983.
- A. Torres-Knoop, S. R. G. Balestra, R. Krishna, S. Calero and D. Dubbeldam. “Entropic Separations of Mixtures of Aromatics by Selective Face-to-Face Molecular Stacking in One-Dimensional Channels of Metal-Organic Frameworks and Zeolites”. *ChemPhysChem* 16, 532–535, **2014**. DOI: 10.1002/cphc.201402819.

### Non-peer reviewed journals

- S. Rodriguez-Gomez. “El metodo Monte Carlo”. *MoleQla* 5, 133–135, **2012**. ISSN: 2173-0903.
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### Software

- S. R. G. Balestra, R. Bueno-Perez and S. Calero. *Genetic Algorithm IAST*. 2016. DOI: 10.5281/zenodo.165844. We use Ideal Adsorbed Solution Theory (IAST) to predict the loading of the gas mixture on the bundle, based only on the knowledge of the pure adsorption isotherms of the individual components.

### Unpublished work

- R. T. Rigo, S. R. G. Balestra, S. Hamad, A. R. Ruiz-Salvador, S. Calero and M. A. Camblor. “The Si-Ge substitutional series in the chiral STW Zeolite Structure Type”. submitted Chem. Mater., Manuscript ID: cm-2018-00786e. 2018.
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