

# A coarse-graining model for ions in water

Author: Guillem Güell Paule

Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.\*

Advisor: Giancarlo Franzese

**Abstract:** Over more than 100 years, water diffusivity in ionic solutions has been a matter of debate and still some gaps need to be filled in order to understand and reproduce experimental results at their best. Here a coarse-grained model for ions in water is used to test the empirical Jones-Dole relation as well as to study the behaviour of the so-called “structure breaker” and “structure maker” ions. The model reproduces qualitatively the experimental phenomenology by assuming that the main effects of the ions is on the intensity of the water hydrogen bonds. The model clarifies that, at fixed temperature, the Jones-Dole relation holds only for a limited range of concentrations that depends on pressure. The breakdown of the Jones-Dole marks also the end of the simplified distinction between “structure breaker” and “structure maker” ions.

## I. INTRODUCTION

Water is by far one of the most familiar substances to humankind as it is essential for life. Still, after centuries and efforts trying to understand its properties there are at least sixty anomalies that are documented for water dynamics, thermodynamics and structure, whose explanations lack general scientific consensus [1]. Here we focus on ionic water solutions and their dynamics when both ion concentration and pressure of the solution change, at constant temperature. Starting from the experimental observation, we develop a phenomenological model based on the Franzese-Stanley (FS) coarse grained water model.

Our everyday experience tells us that adding salt to water changes its properties as its boiling temperature, its density, or its conductivity, among others. Studies on this topic date back from 1847 Poiseuille’s experiments on the effect of some ions in water viscosity. It was not until 1929 that Jones and Dole proposed [3] an empirical expression that relates the viscosity of an ionic solution,  $\eta$ , to the viscosity of pure water,  $\eta_W$ , and to the ion concentration,  $c$ :

$$\frac{\eta}{\eta_W} = 1 + Ac^{1/2} + Bc + O(c^2), \quad (1)$$

where  $A$  and  $B$  are ion-dependent coefficients. While  $A \geq 0$  for almost all the cases,  $B$  is either positive or negative depending on the solute. In literature, ions with  $B > 0$  are said *structure makers* (kosmotropes), while those with  $B < 0$  are called *structure breakers* (chaotropes). As in general  $|B| \gg |A|$ , structure maker ions are related to an increase in the viscosity respect to pure water ( $\eta > \eta_W$ ) and structure breakers to a decrease ( $\eta < \eta_W$ ). In Eq. (1),  $O(c^2)$  and higher-order terms are usually neglected.

Molecular dynamics simulations of salts in atomistic water models have shown to be unable to reproduce the

experimental results [2]. In particular, simulations of rigid, nonpolarizable models at room temperature show that none of the commonly used force fields (SPC/E, TIP3P, TIP4P, TIP4P/2005, and TIP5P water models), neither the most used polarizable water models (SWM4-DP and AMOEBA), each combined with the corresponding force fields for ions, can reproduce the experimentally observed trend for the concentration dependence of diffusivity and viscosity for both structure-breaking and structure-making salts [2].

Here, to study the validity of the empirical Jones-Dole relation, we adopt a coarse-grained model and perform diffusive Monte Carlo simulations to calculate, at fixed ion concentration  $c$ , pressure  $p$  and temperature  $T$ , the water diffusion coefficient  $D$  defined as

$$D \equiv \lim_{\tau \rightarrow \infty} \frac{\langle [\bar{r}(\tau + t_0) - \bar{r}(t_0)]^2 \rangle}{4\tau}, \quad (2)$$

where  $r(t)$  is the position of a water molecule at the time  $t$  and the thermodynamic average is performed over all the water molecules. Assuming valid the Stokes–Einstein relation at constant  $T$  ( $\eta \propto D^{-1}$ ), we evaluate the Jones-Dole relation.

## II. METHOD

### A. The FS water model at zero ion concentration

For sake of simplicity, we consider the FS model in its version for a water nanoconfined monolayer, with periodic boundary conditions in the plane and height  $h = 0.5$  nm, and total volume  $V$ , hydrating structureless hydrophobic walls [4–6]. The system is kept at constant  $T$  and  $p$ , allowing  $V$  to fluctuate, with a constant number  $N$  of water molecules. The volume  $V$  is partitioned into  $\mathcal{N}$  equal cells in a square lattice, each with volume  $v \equiv V/\mathcal{N}$ . The square lattice reproduces the structure of four-coordinated water, as observed in the experiments for a water monolayer in hydrophobic nanoconfinement [7]. At full hydration,  $N = \mathcal{N}$ , each cell is

---

\*Electronic address: gguellpa20@alumnes.ub.edu

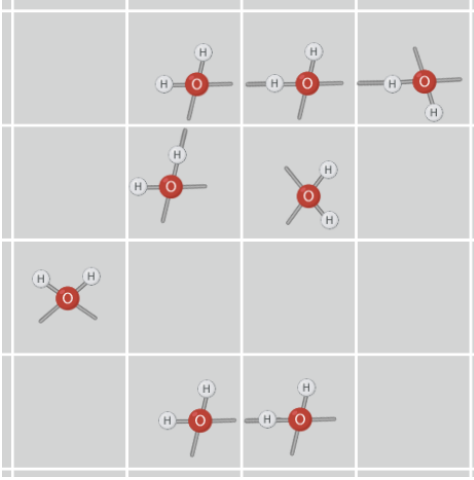


FIG. 1: Cartoon of the model with oxygens (in red), hydrogens (in white) and acceptor pair of electrons (gray sticks) of each molecule. In the model acceptor and donor electrons are treated equally. Hydrogen bonds are displayed as gray sticks between water molecules, while not connected sticks represents broken hydrogen bonds. The partitioning is shown by the white square grid.

chosen with a volume equal to the average proper volume of each water molecule. Hence, if  $v_0$  is the van der Waals (vdW) volume of a water molecule,  $v_0/v$  is the water density. Here, to facilitate the diffusive dynamics, following Ref. [8], we consider the surface at 75% hydration, hence  $N = \mathcal{N} \times 75\%$ , and we assign a variable  $n_i = 1$  to each occupied cell  $i$ , and  $n_i = 0$  otherwise.

The Hamiltonian of the model is defined as it follows:

$$\mathcal{H} \equiv \mathcal{H}_{vdW} + \mathcal{H}_{HB} + \mathcal{H}_{Coop}, \quad (3)$$

where the first term refers to the vdW attraction between molecules and repulsion of the electrons, described by a Lenard-Jones interaction:

$$\mathcal{H}_{vdW} \equiv \sum_{ij} U(r_{ij}) \equiv 4\epsilon \sum_{ij} \left[ \left( \frac{r_0}{r_{ij}} \right)^{12} - \left( \frac{r_0}{r_{ij}} \right)^6 \right] \quad (4)$$

for distances  $r_0 < r_{ij} < r_c$ , with  $r_0 \simeq 2.9\text{\AA}$ , the vdW water diameter, and  $r_c = 5r_0$ , the cut-off distance, above which by definition we set  $U(r_{ij}) = 0$ .  $\epsilon$  is the vdW energy parameter.

Two neighbour molecules are considered bonded if the hydrogen bond (HB) between them is set. Each water molecule can form up to four HBs, i.e., has four bonding indices. Defining the bonding index of a molecule  $i$  with respect to a molecule  $j$  as  $\sigma_{ij} = 1, \dots, q$ , being  $q$  the different possible states, the HB is set if the two molecules have indices in the same bonding state:  $\sigma_{ij} = \sigma_{ji}$ . Because in real space this happens when the hydrogen atom between the two coupled oxygens forms an angle  $\widehat{OOH} \in [-30^\circ, 30^\circ]$  with respect to the O-O axis, and this corresponds to  $60^\circ/360^\circ = 1/6$  of all the possible orientations in the plane defined by the three

atoms, we set the number of bonding states equal to  $q = 6$ , to correctly account to the configurational entropy decrease for each molecule due to a HB formation. For each formed HB, the total energy decreases by  $J$ . This is accounted for in the Hamiltonian term  $\mathcal{H}_{HB}$ :

$$\mathcal{H}_{HB} \equiv -JN_{HB} \equiv -J \sum_{\langle ij \rangle} n_i n_j \delta_{\sigma_{ij}, \sigma_{ji}}, \quad (5)$$

where the sum runs over the nearest neighbours (nn) and  $\delta_{\sigma_{ij}, \sigma_{ji}} = 1$  if  $\sigma_{ij} = \sigma_{ji}$  and 0 otherwise.

When the number of HBs,  $N_{HB} \equiv \sum_{\langle ij \rangle} n_i n_j \delta_{\sigma_{ij}, \sigma_{ji}}$ , is large, HB cooperativity, i.e., the effect of non-additive many-body quantum interactions, becomes relevant. This effect is modeled via the third Hamiltonian term:

$$\mathcal{H}_{Coop} \equiv -J_\sigma \sum_i n_i \sum_{(k,l)_i} \delta_{\sigma_{ik}, \sigma_{il}}, \quad (6)$$

where  $(l, k)_i$  runs over the six pairs of bonding indices  $\sigma_{ij}$  between the molecule  $i$  and its four nearest neighbours. By setting  $J_\sigma \ll J$  we guarantee that the cooperative rearrangement of the HBs only occurs when  $N_{HB}$  is large.

Under this condition, i.e.,  $N_{HB} \gg 1$  with many cooperative HBs, water molecules rearrange as in tetrahedrons (that are distorted in a monolayer, but still present), inducing a decrease of the total water density. This is accounted for in the model by adding for each formed HB, an average volume increases,  $v_{HB} \ll v_0$ , so that the total water volume is by definition

$$V_W \equiv Nv_0 + N_{HB}v_{HB}. \quad (7)$$

Following previous works [4–6, 8, 9], we set  $v_{HB}/v_0 = 0.5$ ,  $\epsilon \simeq 5.5$  kJ/mol,  $J/4\epsilon = 0.5$ ,  $J_\sigma/4\epsilon = 0.05$ .

## B. The FS water model with ions

As shown in calculations with monovalent ions [10], HB strength depends linearly on the charge transfer between ions and water molecules but also whether the ions are cations or anions. Here, we hypothesise that this effect can be included in the FS model by considering that on average the parameter  $J$  depends on the ion concentration  $c$ , at least as long as the ions are homogeneously distributed in water and fully solvated.

If every ion affects both water molecules participating in a HB with probability  $p(c)$ , at low ion concentrations, we can approximate the HB energy between the two water molecules, at the first order, as

$$J(c) \sim J_W - f(T)p(c)^2, \quad (8)$$

where  $f(T)$  is a temperature dependent coefficient and  $J_W \equiv J(c = 0)$ . The probability that an ion affects the entire hydration shell of a single water molecules is  $p_{hs}(c) = p(c)^4$  and, within mean-field approximation,  $p_{hs}(c) \sim c$ . This leads to  $J - J_W \propto c^{1/2}$ .

Depending if  $J - J_W > 0$  or  $J - J_W < 0$ , two situations can be identified. In the first case,  $J$  is larger than in pure water, which results in an increase of the HB strength, as assumed for the structure-maker ions. On the other hand,  $J$  is smaller than in pure water, which results in a decrease of the HB strength, as hypothesised for the structure-breaker ions.

Based on these considerations, we can rewrite the Jones-Dole relation, Eq. (1), as

$$\frac{\eta}{\eta_W} = 1 + A'(J_W - J) + B'(J_W - J)^2 + \dots, \quad (9)$$

and, assuming  $\eta \propto D^{-1}$ ,

$$D^{-1} = D_W^{-1} + A''(J_W - J) + B''(J_W - J)^2 + \dots, \quad (10)$$

where  $D_W$  is the diffusion constant of pure water and all the other coefficients are as in Eq. (1) apart from constant factors.

### C. Monte Carlo simulations

We perform diffusive Monte Carlo (MC) simulations of  $N = 1200$  water molecules situated in a square lattice with  $M \times M$  cells and  $M = 40$ , corresponding to 75% hydration. Each simulation has  $25 \times 10^6$  MC steps, and each step is made of  $5 \times N$  trials. In each trial, a random water molecule and a random integer  $n \in [0, 4]$  are selected. Depending on the value of  $n$ , we have two different cases:

1. If  $n = 4$ , we attempt to move the molecule to one of its nearest cells, at random, and the move is accepted with probability  $P$ :

$$P \equiv \min \{1, \exp\{-\beta(\Delta H - T\Delta S)\}\}, \quad (11)$$

where  $\beta \equiv 1/k_B T$ , being  $k_B$  the Boltzmann constant, and  $\Delta H \equiv H^{new} - H^{old}$ ,  $\Delta S \equiv S^{new} - S^{old}$  are the differences in enthalpy and entropy between the new and the old configuration. These are calculated as

$$\Delta H = \Delta \mathcal{H} + p\Delta V, \quad (12)$$

$$\Delta S = Nk_B \ln \left( \frac{V^{new}}{V^{old}} \right), \quad (13)$$

where  $p$  is the pressure.

2. If  $n \neq 4$ , we set the bonding indices  $\sigma_{ij}$  at random to one of the  $q = 6$  possible states, and we accept the move with probability  $P$  in Eq. (11).

Finally, at each trial, we choose at random a sign and a value  $0 < |\Delta V| < v_{HB}$  and accept the change from  $V$  to  $V + \Delta V$  with probability  $P$  in Eq. (11). For each MC step, we calculate the new total energy and save the new configuration.

At each pressure and ion concentration, we use the first  $5 \times 10^6$  MC steps for equilibration. We divide the next  $20 \times 10^6$  MC steps in 400 groups of  $5 \times 10^4$  MC steps each, and save the calculations every 500 MC steps. In each group, we calculate the mean square displacement  $\langle [\bar{r}(\tau + t_0) - \bar{r}(t_0)]^2 \rangle$ . Finally, we average the calculations over all the 400 groups.

To estimate the errors, we simulate several state points ( $J^* \in \{-0.1, 0.1, 0.3, 0.5, 0.7, 0.9, 1.1\}$ ) with six different seeds of the random numbers generator to get statistically independent averages and we compute their mean value and standard deviations. Notwithstanding, as it can be seen in the figures of the Results section, error bars, where calculated, are smaller than the symbols size. Hence, we assume that the statistical errors are small also for those state points where we did not calculate them explicitly. Further commentary on the effect of seeds is reported in the Appendix.

## III. RESULTS

In the following we use reduced quantities:  $J^* \equiv J/4\epsilon$ ,  $J_\sigma^* \equiv J_\sigma/4\epsilon$ ,  $T^* \equiv k_B T/\epsilon$ ,  $p^* \equiv pv_0/\epsilon$ . We set  $T^* = 0.7$  and pressures vary from  $p^* = 0.2$  to  $p^* = 0.8$ .

We calculate the diffusion constant  $D$ , Eq. (2), as described in the Appendix, and check, for  $J^* \equiv J^*(c) \in [-0.1, 1.1]$ , when  $D^{-1} - D_W^{-1}/(J_W^* - J^*)$  has a linear dependence on  $J_W^* - J^*$ , as predicted by the Jones-Doyle relation, Eq. (10). We find a linear regime for each considered pressures, for both  $J^* > J_W^*$  and  $J^* < J_W^*$  (Fig. 2). However, we observe clear deviations from linearity, in particular, at  $J^* > J_W^*$  and low pressure.

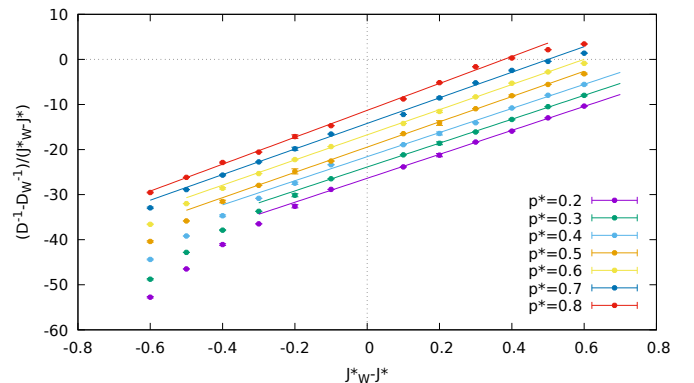


FIG. 2: Checking the Jones-Dole relation at  $T^* = 0.7$  and  $p^* \in [0.2, 0.8]$  for  $J^* \in [-0.1, 1.1]$ . The linear fits of  $(D^{-1} - D_W^{-1})/(J_W^* - J^*)$  as a function of  $J_W^* - J^*$  mark where the relation holds.

For  $J^* > J_W^*$ , at any pressure,  $(D^{-1} - D_W^{-1})/(J_W^* - J^*) < 0$ , hence  $(D^{-1} - D_W^{-1}) > 0$ , i.e., the viscosity in the ionic solution is larger than in pure water. This is consistent with our hypothesis that setting  $J^* > J_W^*$  is

enough to reproduce the behavior expected for structure makers.

For moderate  $J^* < J_W^*$  and moderate pressure,  $(D^{-1} - D_W^{-1})/(J_W^* - J^*) < 0$ , hence  $(D^{-1} - D_W^{-1}) < 0$ , i.e., the viscosity in the ionic solution is smaller than in pure water. This is consistent with our hypothesis that setting  $J^* < J_W^*$  is enough to reproduce the behavior expected for structure breakers.

However, for high enough  $J_W^* - J^*$  and pressure, we find  $(D^{-1} - D_W^{-1}) > 0$ , i.e., a viscosity increase that is apparently inconsistent with the simple interpretation of structure breakers. For  $p^* = 0.8$  this happens around  $J^* = 0.1$  ( $J_W^* - J^* = 0.4$ ) and for  $p^* = 0.7$  somewhere near  $J^* = 0$ . We will discuss this apparent inconsistency in the conclusions.

Using our assumptions,  $c^* \propto (J^* - J_W^*)^2$  if  $J^* > J_W^*$  and  $c^* \propto (J_W^* - J^*)^2$  if  $J^* < J_W^*$ , and the validity of the Stokes–Einstein relation, we can calculate how the relative viscosity  $\eta/\eta_W$  changes as a function of ion concentration  $c$  (Fig. 3). Again, also in this representation of our results, we observe clearly that structure makers always lead to a viscosity larger than in pure water, while structure breakers decrease the viscosity at low pressure for all the concentrations, but not at high  $p^* \geq 0.7$  and large  $c^* > 0.16$ . The effect can be further emphasized by representing  $D/D_W$  as a function of  $c^*$  (Fig. 4). Structure makers always induce a decrease of the relative diffusion coefficient  $D/D_W < 1$ , while structure breakers show a non monotonic behavior at any pressure and large enough  $c^*$ , and for  $p^* \geq 0.7$  lead to  $D/D_W < 1$ .

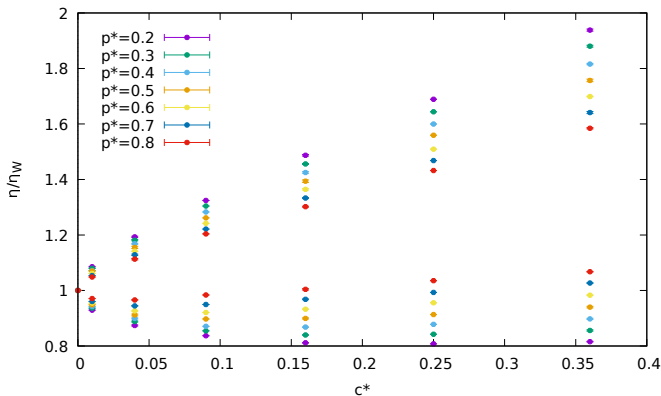


FIG. 3: Relative viscosity  $\frac{\eta}{\eta_W}$  of ionic solutions with respect to pure water as a function of ion concentration  $c^*$  for  $T^* = 0.7$  and  $p^* \in [0.2, 0.8]$ :  $\frac{\eta}{\eta_W} > 1$  corresponds to structure maker ions, while  $\frac{\eta}{\eta_W} < 1$  to structure breakers. Note that at high enough pressure and large enough  $c^*$ , the ionic solution can change from breaker to maker.

#### IV. DISCUSSION AND CONCLUSIONS

The Monte Carlo simulations of the FS coarse-grained water adapted to ionic solutions, presented here, displays

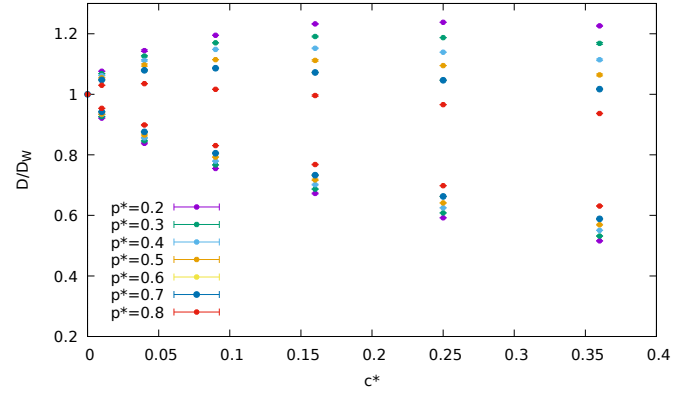


FIG. 4: Relative diffusion  $\frac{D}{D_W}$  as a function of  $c^*$  for  $T^* = 0.7$  and  $p^* \in [0.2, 0.8]$ , show a behavior that is monotonic and decreasing for structure maker ions, but is non-monotonic for structure breakers.

a behavior that is in apparent contrast with the starting hypothesis of the model. In particular, we assume that the model can account for the effect of ions homogeneously solvated in water by tuning the water-water HB strength  $J^*$  as a function of the ion concentration  $c^*$ . By mean field reasoning, we argue that  $c^* \propto (J_W^* - J^*)^2$ , with  $J^* > J_W^*$  of pure water if the ion is a structure maker and  $J^* < J_W^*$  if it is a structure breaker. Next, we find that for makers the diffusion constant is always smaller than for pure water and decreases monotonically with increasing  $c^*$ , consistent with the starting hypothesis, while for breakers, the diffusion constant has a non-monotonic behavior that depends on pressure, and at high enough pressure and  $c^*$  the breakers become makers, at variance with what expected.

Surprisingly, this unexpected behavior is perfectly consistent with the experiments, as shown in Fig. 3 of Ref. [11] and discussed in Fig. 1 of Ref. [2]. Furthermore, it cannot be reproduced by atomistic models at room temperature, even if polarization is included [2], clearly showing that classical water models do not account correctly for many-body effects.

The FS model, instead, is built on the basis that the interplay of many-body interactions with competing pair interactions is the origin of the water anomalies, including those related to the diffusion [8]. Hence, it is able to account for the subtle effect of solvated ions on the water HB network.

In particular, the model is able to show that the empirical Jones-Dole relation holds only in a pressure-dependent range of salt concentrations. When the Jones-Dole relation fails at large enough concentration for the breakers, the simple interpretation of breakers shows its limitation. Therefore, we can conclude that the distinction between structure maker ions and structure breaker ions loses its sense under extreme conditions. Although we observe this effect at high pressures, our results suggest that this conclusion would be true also for lower

pressures but at higher ions concentrations. Under these conditions, we expect, as well, that the Jones-Dole relation would be no longer valid. Further work is necessary to test this prediction.

## V. APPENDIX

We check the convergence of the results with different seeds for the random number generator and a number of values of  $J$  and pressure (Fig. 5 and Fig. 6). Although there are fluctuations, these are within the fourth decimal digit and practically do not deviate from the mean value.

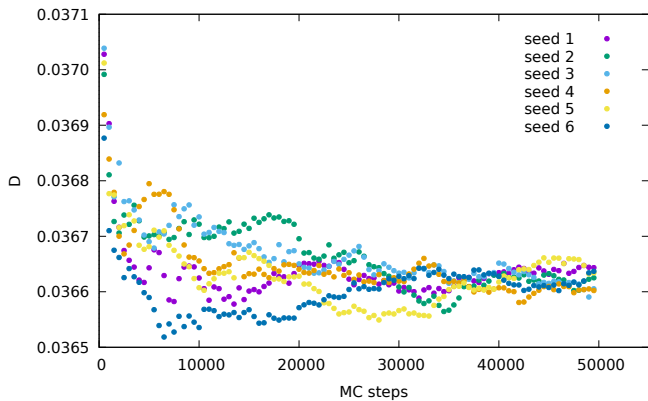


FIG. 5: Evolution of the average of the diffusion coefficient  $D$ , calculated in different time intervals, for  $J^* = 0.1$  and  $p^* = 0.2$ , and different seeds of the random number generator.

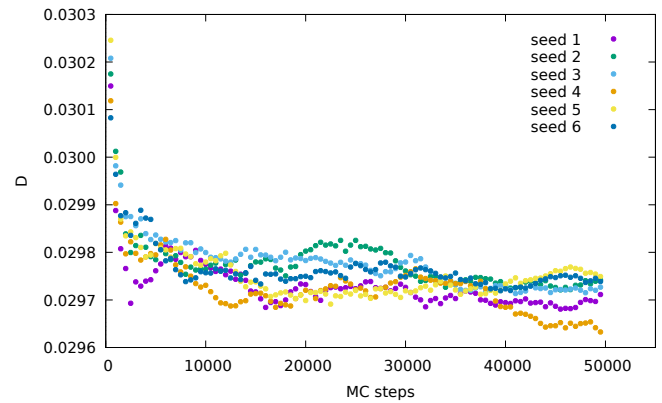


FIG. 6: Evolution of the average of the diffusion coefficient  $D$ , calculated in different time intervals, for  $J^* = 0.5$  and  $p^* = 0.2$ , and different seeds of the random number generator. The deviation of the behaviour of seed number 4 with respect to the others seems to change the results, but after propagating the uncertainties in  $D$  and  $D_W$ , the deviation lays within the error bars.

## Acknowledgments

I want to express my deep gratitude to Giancarlo for advising this work. I am also grateful to professor Francisco de los Santos for providing the main code used in this project and for solving different issues related to it. My special thanks as well to my family and friends who have been supporting me all this time.

- 
- [1] Valentino Bianco et al. “Water and anomalous liquids. In *Proceedings of the International School of Physics “Enrico Fermi”* **176**, *Complex Materials in Physics and Biology*, F. Mallamace and H. E. Stanley eds. (2012), pp. 113–128.
  - [2] Jun Soo Kim et al. “Self-Diffusion and Viscosity in Electrolyte Solutions”. In: *The Journal of Physical Chemistry B* **116.39** (2012), pp. 12007–12013.
  - [3] Grinnell Jones and Malcom Dole. “The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride”. In: *Journal of the American Chemical Society* **51.10** (1929), pp. 2950–2964.
  - [4] Giancarlo Franzese and Harry Eugene Stanley. “Liquid-liquid critical point in a Hamiltonian model for water: analytic solution”. In: *Journal of Physics: Condensed Matter* **14.9** (2002), pp. 2201–2209.
  - [5] Valentino Bianco and Giancarlo Franzese. “Critical behavior of a water monolayer under hydrophobic confinement”. In *Scientific Reports (Nature Publishing Group)* **4.4440** (2014).
  - [6] Luis Enrique Coronas et al. “The Franzese-Stanley Coarse Grained Model for Hydration Water”. In *CRC Press* **2004.03646** (2020).
  - [7] R. R. Nair et al. “Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes”. In: *Science* **335.6067** (2012), pp. 442–444.
  - [8] Francisco de los Santos and Giancarlo Franzese. “Relations between the diffusion anomaly and cooperative rearranging regions in a hydrophobically nanoconfined water monolayer”. In: *Physical Review E* **85.1** (2012).
  - [9] Kevin Stokely et al. “Effect of hydrogen bond cooperativity on the behavior of water”. In: *Proceedings of the National Academy of Sciences* **107.4** (2010), pp. 1301–1306.
  - [10] Tomaz Urbic. “Ions increase strength of hydrogen bond in water”. In: *Chemical physics letters* **610-611** (2014), pp. 159–162.
  - [11] K.J. Müller and H.G. Hertz. “A Parameter as an Indicator for Water-Water Association in Solutions of Strong Electrolytes”. In: *The Journal of Physical Chemistry* **100.4** (1996), pp. 1256–1265.
  - [12] Created with BioRender.com