ESR 7 UPDATES

MOLECULAR DYNAMIC AND MONTE CARLO STUDY OF WATER IN HYDRATES DURING DESORPTION AND RE-SORPTION

Presented by: Arifah Binti Abdu Rahaman

Academic Supervisor: Dr. D. Faux

Co-Supervisor: Prof. P. McDonald

Industrial Supervisor: Dr. A. Vichot

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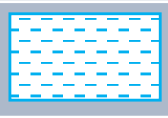
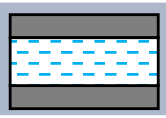
Outline

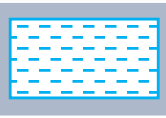
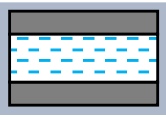
- Introduction
- Objectives
- Research Overview
- Theory
- Methodology
- Results
- Conclusion and Future Works
- ERICA Outreach and Secondment Plan

Introduction

- NMR is a powerful method to characterise water transport in porous media.
- However, it requires a model to understand the NMR relaxation times of water in cement pores.
- Two important issues in cement:-
  I. Paramagnetic ions in/on the solid surface.
  II. The effect of “structured water” around ions in solution which may not be paramagnetic.

Research Objectives

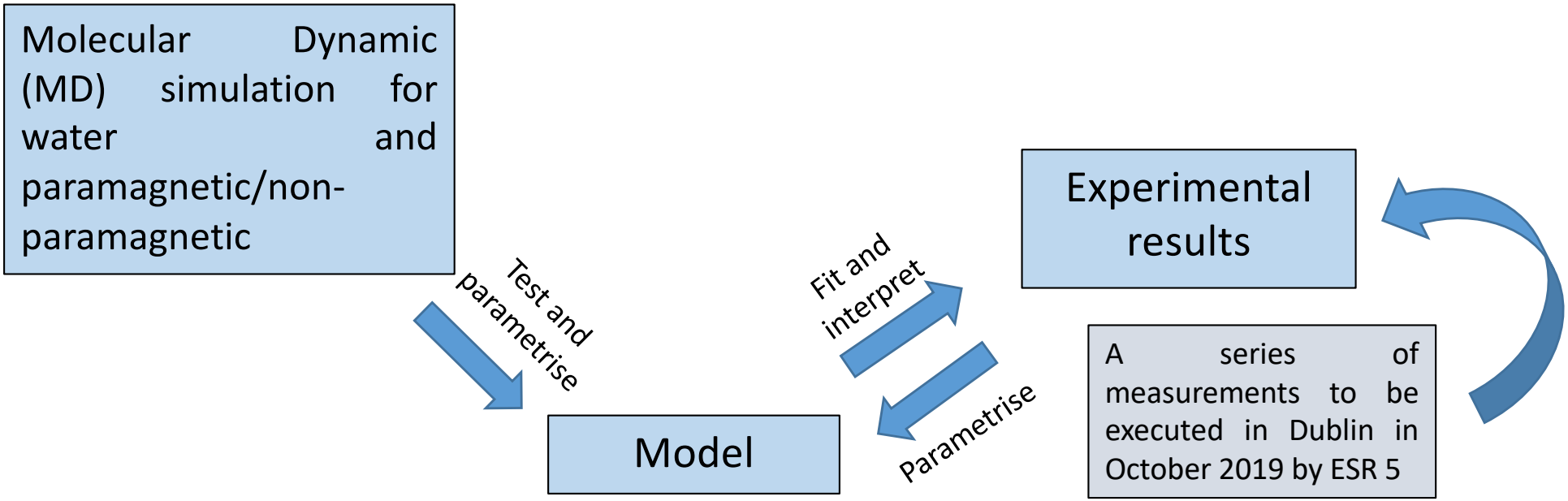
Paramagnetic (Fe^{3+}, Mn^{2+})		
	in solution	**in solid**
Bulk 	✘	-
Confined 	✘	✓

Non - Paramagnetic (Ca^{2+}, Na^{+})		
	in solution	**in solid**
Bulk 	✘	-
Confined 	✘	Not useful

✘ Objective of the research

Research Overview

- ✓ Molecular Dynamics (MD) simulation provides information about the dynamic of water and ion.
- ✓ Starting point: water + NaCl

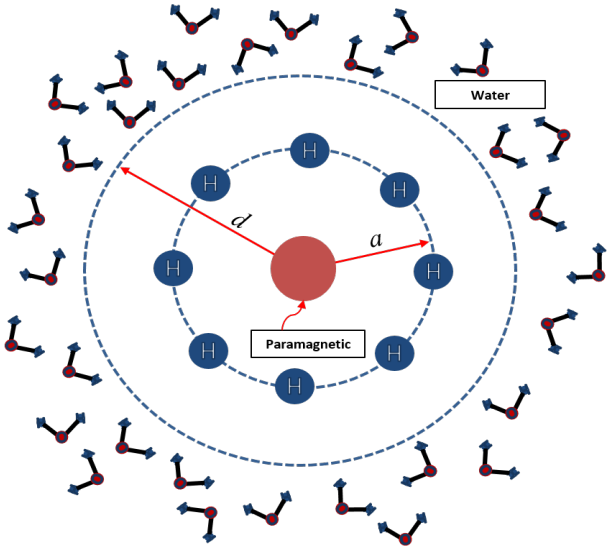


Theory

- There are two spin environments to describe the collection of spins attached to the ion, identified as **inner-sphere, *is*** and **outer-sphere**, ***os***.

- This research seeks to produce expressions for the dipolar correlation function, *G(t)* comprising contributions from each spin environment.

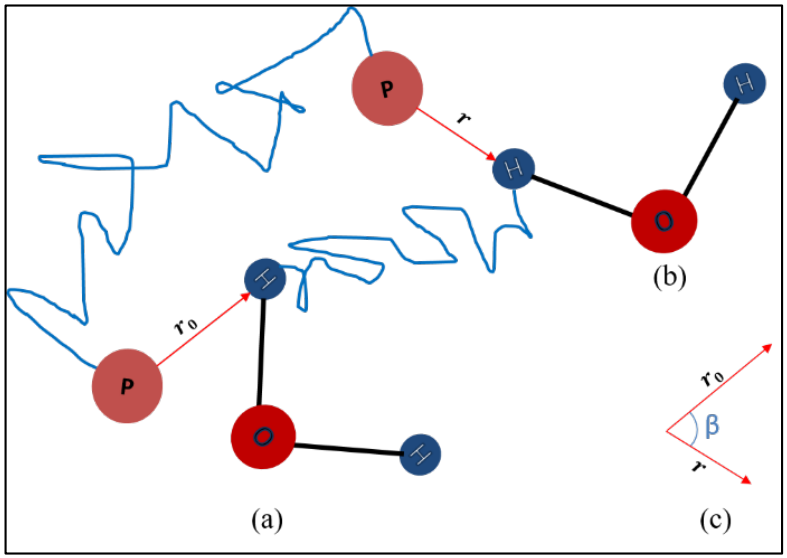
$$G(t) = Gi_s(t) + Go_s(t) \quad \Rightarrow \quad J(\omega) = 2\int_0^{\infty} G(t)\cos\omega t\, dt \quad \Rightarrow \quad R_1 = T_1^{-1} = \frac{1}{3}\beta[7J(\omega_s) + 3J(\omega_I)]$$



First shell: inner sphere
Second shell: outer sphere

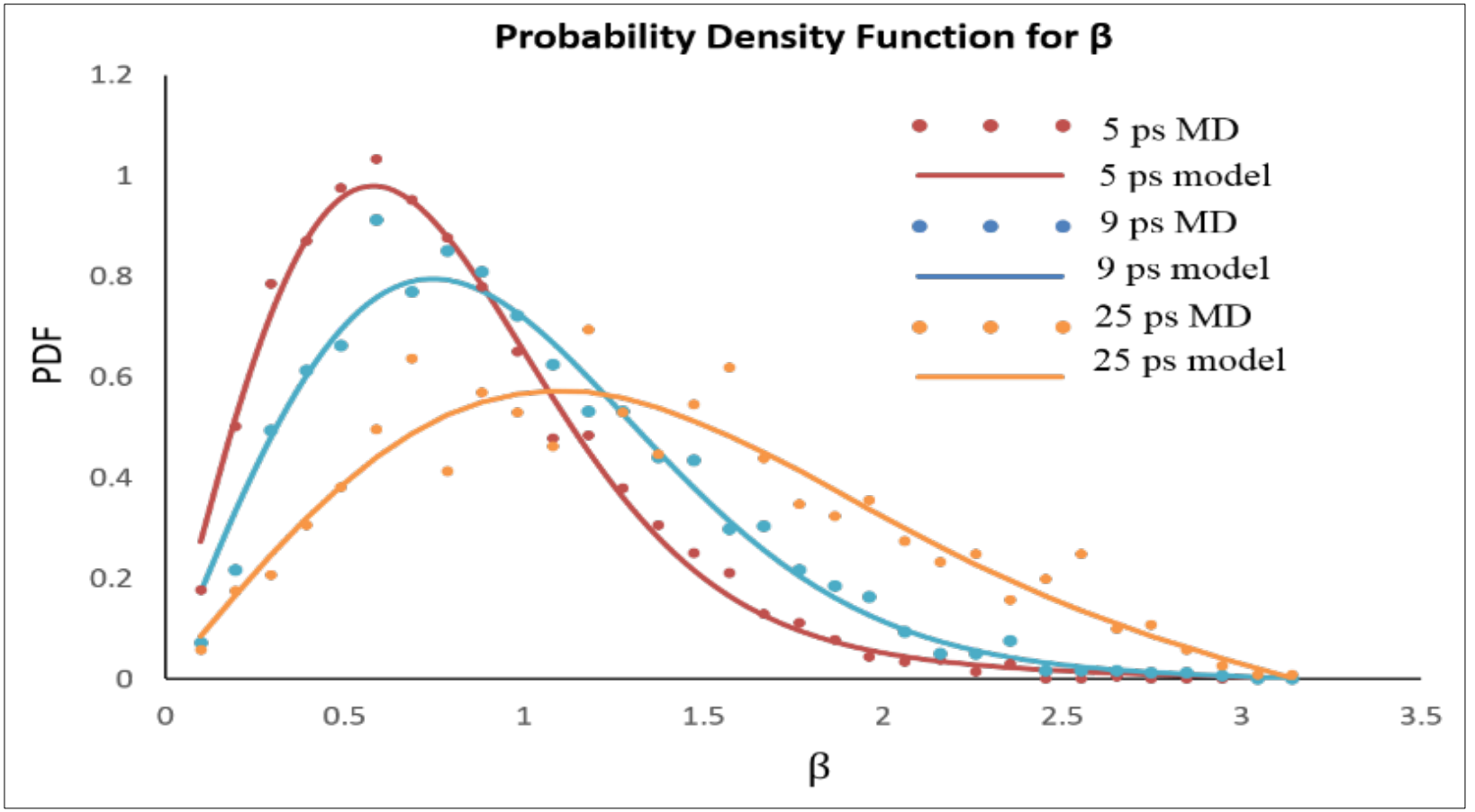
Methodology

- Molecular Dynamic (MD) simulations for modeling atomistic dynamics.
- Two objectives of the MD simulations:
  - ✓ To test the physics of a theoretical model
  - ✓ To provide guidance for model parametrisation
- The simulations are executed using SPCE model in a cubic box of side length 100 A for 100 ps.
- The simulation cell contains 27000 water molecules, 216 sodium and 216 chloride ions.
- Atomic displacements and the angle β are computed as shown.



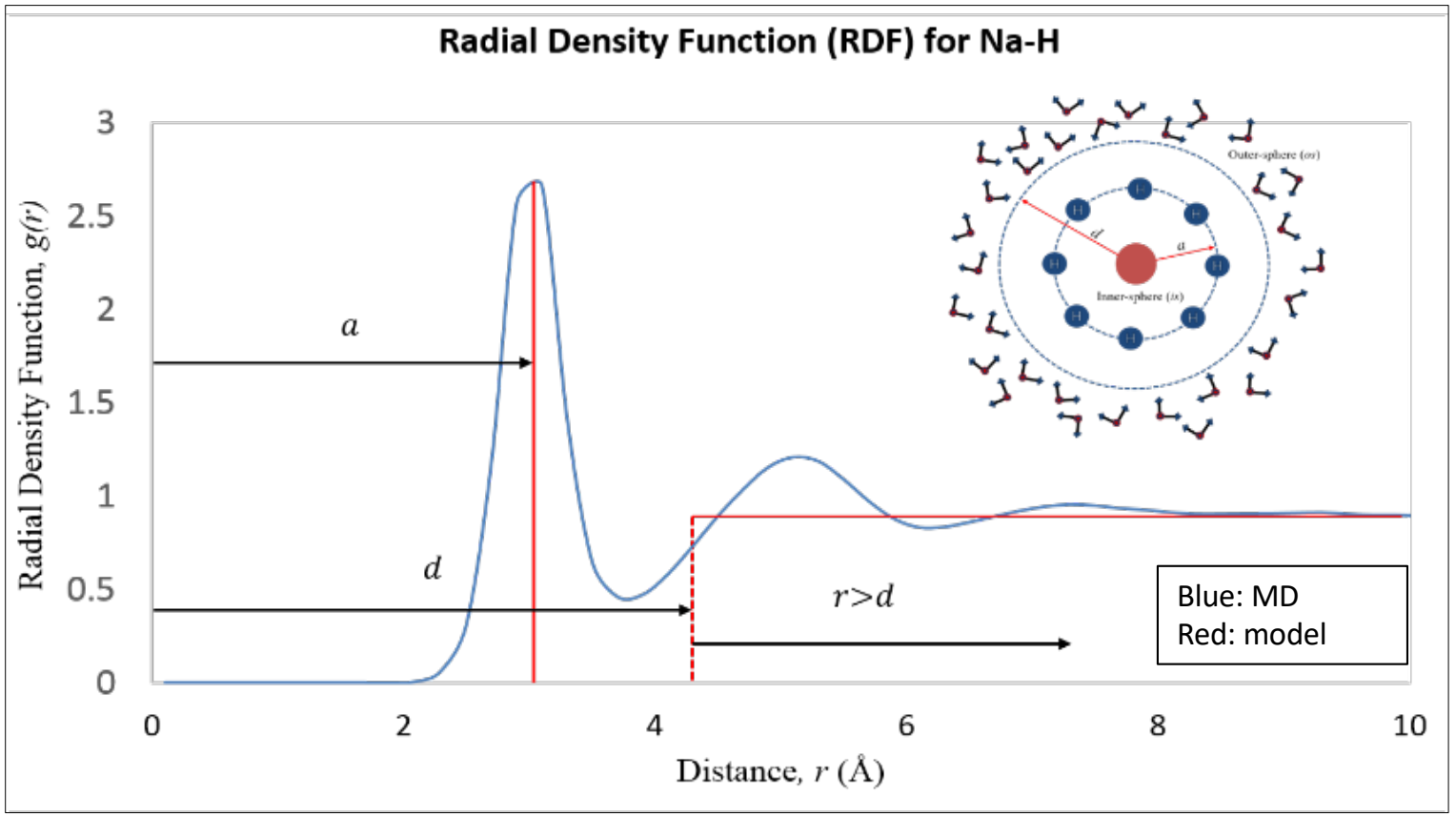
(a) At t=0, a water molecule is connected to the paramagnetic by a vector $\boldsymbol{r_0}$ at their original location. (b) After time t, both water molecule and paramagnetic travelled to a new location, linked by vector ***r.*** (c) The angle between two vectors is denoted as β.

Result - Probability Density Function (PDF)



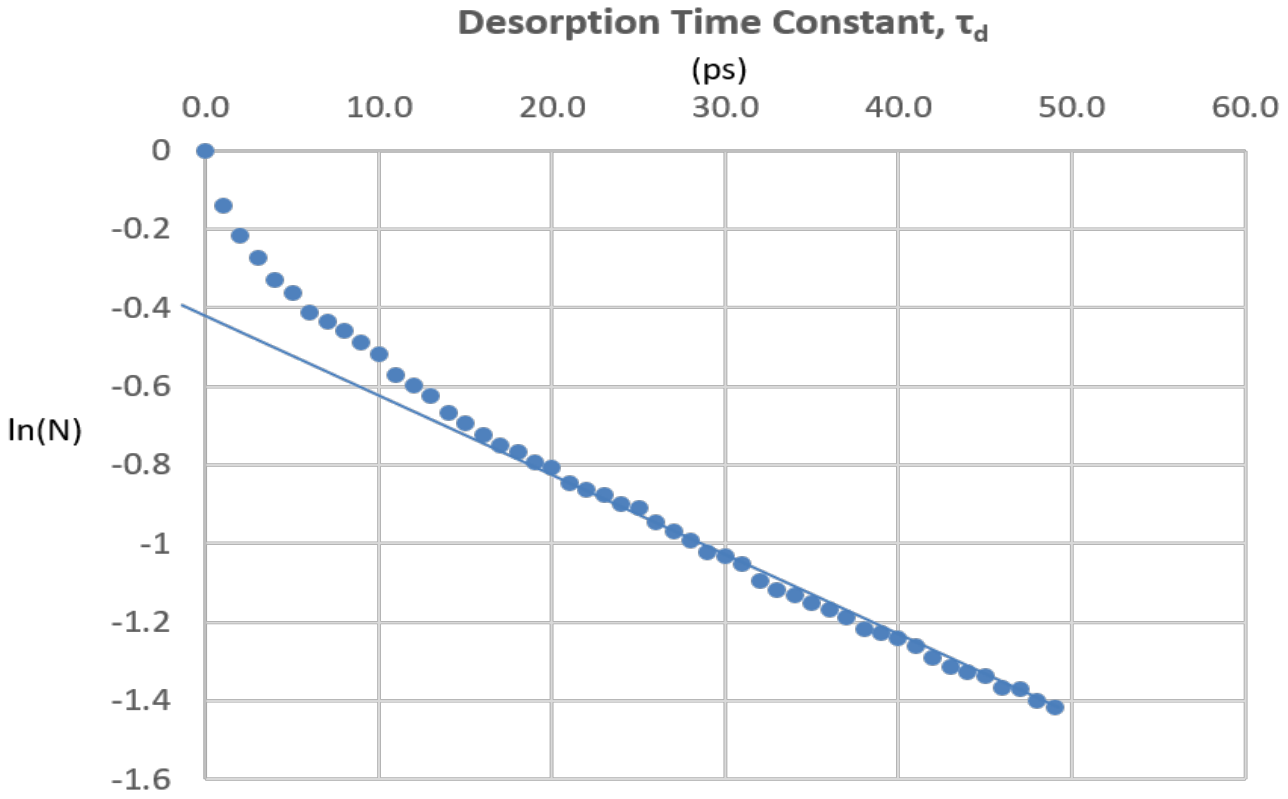
The probability density function shows the data fitting for β obtained from MD simulations and the model. The parametrisation is made using the data set at 5 ps.

Results – Radial Density Function (RDF)



The Radial Density Function graph illustrates the inner-sphere, *is* at distance *a* and the outer-sphere, *os* at distance r > d. Distance *a* ≈ 3.1 Å.

Results – Desorption Time Constant, τ_d



The desorption time constant, τ_d is calculated from the gradient indicating the number of hydrogen spins in the inner sphere shell. The τ_d is 50 ps from the graph.

Summary of the Results

List of parameters for the elucidation of the dipolar correlation function to describe the NMR relaxation rate

Parameter	Terminology	Value	Notes
τ_β	τ_β time constant	21 ps	Data fitting at 5 ps
α	Lévy parameter	2	Fit to MD gives 1.81
a	Distance of inner-sphere shell	3.1 Å	Deduced from MD
τ_d	Desorption time constant	50 ps	Deduced from MD
D	Diffusion coefficient of water	6.19×10^{-11} m^2/s	Deduced from MD
d	Cut-off distance for os water	3.9 – 4.2 Å	Estimated from RDF

Conclusion & Future Plan

- The results proved that the key physics behind the theoretical model are well captured to describe the nano-scale dynamics of the paramagnetic/non-paramagnetic and the water.
- In future, the model will predict the frequency dependent spin-lattice relaxation time $T_1(f)$ for a range of paramagnetic/non-paramagnetic to provide fits to experimental data.
- A series of experiments will be executed in Dublin in October 2019 by ESR 5.

Outreach Activity and Secondment Plan

Outreach

- ✓ Outreach program was conducted on 25 July 2019 at University of Surrey.

Secondment Plan

- ✓ The secondment plan is suspended due to maternity leave.