



University of Sheffield

Development of Positron and Neutron Experimental Techniques for the Investigation of Hierarchical Materials

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A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

University of Sheffield

July 9, 2025

Declaration

The work described in this thesis was undertaken by the author at the University of Sheffield between October 2020 and October 2024 under the supervision of Doctor Andrew Parnell. Unless otherwise stated, this work has not been submitted in whole or in part for any other degree at this or any other institution.

Joseph Orgill
October 2024

Abstract

The experimental investigation of polymer coatings is of great interest, partly due to their use in corrosion protection. Epoxy-amines are currently used extensively as industrial corrosion-resistant coatings. However, these systems contain volatile organic chemicals with severe environmental and health side effects and are therefore being replaced by water-based latex coatings. This thesis investigates epoxy-amine and water-based coatings using positron annihilation lifetime spectroscopy (PALS) and spin-echo small angle neutron scattering (SESANS). In the process, both techniques have been developed and their use for the investigation of corrosion-resistant coatings has been tested.

The PALS instrument in Sheffield has been upgraded and a new data fitting procedure was established. This instrument was then used to investigate corrosion-resistant epoxy coatings alongside molecular dynamics simulations. Two characteristic free-volume void diameters were identified at 4.7 Å and 7.0 Å using PALS and a similar two-peak distribution was identified by molecular dynamics.

SESANS is a recently developed neutron scattering technique with access to information on larger length scales than conventional scattering. This technique therefore requires a new calibration sample. Multiple samples were trialled including various nanoparticle dispersions and colloidal crystals. The samples suggested for future calibrations of the device are 500 nm SiO_2 colloidal crystals and polystyrene nanoparticle dispersions.

SESANS is then used to investigate water-based latex coatings. These systems require the use of surfactants for latex particle stability, however, residual surfactants in the final film can cause defects and create pathways for corrosion reactants to penetrate the film. Surfactant distribution is therefore of great interest in corrosion-resistant coatings. Using a deuterated latex to gain contrast, the distribution of a range of surfactants were investigated and the internal structure of dried latex films was measured. Thanks to the unique length scales available to SESANS large (micron-sized) ellipsoidal surfactant clusters were identified and their size distribution was determined.

Publicly Presented Work

1. The influence of ambient cure chemistry and stoichiometry on epoxy coating surfaces. Callum Bannister, Alan Guy, Ralitsa Mihaylova, Joseph Orgill, Stephanie L Burg, Andrew Parnell, Richard L Thompson. RSC advances, Vol 12, Issue 44, p28746 (2023)
2. Quantifying the free volume distribution in a crosslinked epoxy-amine through a combined PALS and molecular dynamics simulation study. Joseph Orgill, Anthony Wright, Andrew Parnell, Stephanie Burg, John Patrick Anthony Fairclough, and Charlie R. Wand (Completed and to be submitted to Macromolecules)
3. IOP Physical Aspects of Polymer Science Conference, Edinburgh, 2024. Talk titled Free Volume in Epoxy Coatings: Experimentation Vs Simulation.
4. ISIS facilities development student conference, Didcot, 2024. Talk titled SESANS Calibration: Going to New Lengths.
5. ISIS facilities development student conference, Didcot, 2023. Talk titled SEM-SANS calibration: Advancements in Small-Angle Neutron Scattering for multi length-scale Characterization.
6. UK Neutron & Muon Science and User Meeting (NMSUM), Warwick, 2023. A poster titled Development of SEMSANS for the characterisation of large-scale structure systems.

Acknowledgements

This thesis was only made possible with the help and support of a vast number of people. Firstly, to my supervisor Doctor Andrew Parnell I would like to thank you for your constant help and wealth of knowledge of everything PhD and life-related. Thank you for always treating us as equals and prioritising our happiness. Throughout the last four years, I have developed as much as a person as I have as a scientist thanks to your exceptional mentorship. You have made this experience more enjoyable than I would have ever expected it to be.

Doctor Stephanie Burg, this work would have looked very different without your support, if it existed at all. Your extremely patient Python tutelage and over-text code troubleshooting skills are astonishing and I must thank you for the way they got this project off the ground. I must also thank you for always being there to answer endless questions from “What is a directory?” to “Have you seen Andy today?”. Not to mention your motivation (and slight scaremongering) when it came to the bitter end, without which I may have never submitted.

I would also like to thank the following people whose scientific input has truly shaped this project. To Doctor Robert Dalglish thank you for supporting me throughout my PhD, especially during my year in Didcot, with your extensive knowledge of all things neutron and also your knowledge of all the best pubs in the Oxford area. Professor Patrick Fairclough thank you for your valuable input and great scientific knowledge, this work has benefited from our meetings from start to end and for that, I am very grateful. Professor Richard Jones, thank you for taking the time to join our weekly meetings and seemingly never tiring of hearing about the fine details of why the PALS isn’t working, your pearls of wisdom have had a great impact on this work. It has been a pleasure and a privilege to have the unwavering support of such incredible minds for the duration of my PhD.

Francis “soon-to-be-doctor” Gurman, thank you for your camaraderie throughout and for being a permanent fixture of G12. I don’t think I could have managed it without you and your infinite epoxy stirring wisdom and never faltering commitment to the lab book even after the epoxies betrayed us and we had to take a trip to the Northern General. Thank you for running the PALS for me when I was on my tour of Didcot, and thank you for letting me win occasionally at Connect-4 to keep my morale high.

Thank you also to my collaborators. Doctor Charlie Wand for your work on my favourite chapter. To Doctor Mohammad Jamali and Doctor Lee Fielding, thank you

for providing exceptional latexes as well as joining us on perhaps the most tiring and enjoyable beamtime experiment. Doctor Steven Parnell, thank you for helping with beamtime proposals and also for letting me borrow your bike on a very enjoyable (albeit scientifically fruitless) trip to Delft.

Thank you to James “soon-to-be-doctor” Greer (Captain of the Sheffield additive manufacturing comity) for allowing me to use your 3D printer and help in CAD.

Thank you Billy “soonish-to-be-doctor” Callon for your steadfast optimism and “It will be alright on the night” attitude, and for always being available for a Jessy West meal deal when it all gets too much. Along with all my friends Joe, Brogan and all of Christmas Curry just to name a few, thank you for everything, you make Sheffield our home.

To My Family, Mum, Dad, Archie and Polly. I would have never been in this position without your relentless support and belief and for that I am truly thankful. Thank you for always being there (with a cold Corona in hand) whenever I need to leave work behind, I couldn’t wish for a better family.

And Finally, to my love Amy I would not have completed this without you. You have been with me through every part of this process and despite me asking so much of you, you are always there when I need you. Thank you for instinctively knowing when to ask about work and when I am far too over it to talk about it. Thank you for following me around the country and going through three career changes just to be by my side. You are my inspiration and I can’t wait for what will come next and wherever it will take us (it’s your choice next).

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Acronyms

M_w molecular weight

ACF autocorrelation function

AFM atomic force microscopy

CU coincidence unit

ER epoxy resin

FFV fractional free volume

FV free volume

MD molecular dynamics

oPs ortho-positronium

PALS positron annihilation lifetime spectroscopy

PMT photo-multiplier tube

pPs Para-positronium

Ps positronium

PSD pore size distribution

SANS small-angle neutron scattering

SAXS small-angle x-ray scattering

SEM scanning electron microscopy

SEMSANS spin-echo modulated small-angle neutron scattering

SESANS spin-echo small-angle neutron scattering

SLD scattering length density

Tg glass transition temperature

TOF time-of-flight

VF volume fraction

VOCs volatile organic compounds

Chapter 1

Introduction

1.1 Thesis Aims

The main motivation for this thesis is the development of experimental techniques for investigating polymer coatings systems. Two experimental techniques have been the main focus of this work; spin-echo small-angle neutron scattering (SESANS), positron annihilation lifetime spectroscopy (PALS). SESANS and PALS are both suitable tools for the investigation of polymeric systems. This work will describe the theory and data analysis of PALS and SESANS as well as describe the contributions that I have made to the development of both techniques. Furthermore, investigations into polymer coating systems have been carried out using both techniques. These experiments are described in detail along with in some cases, a comparison of results with computational simulations.

1.2 Polymer networks background

The systems investigated in this work are primarily polymer coatings, including both water-based latex and epoxy resin (ER) crosslinked coatings. The focus is on investigating these systems in the role of corrosion-resistant coatings.

1.2.1 Corrosion protection

Corrosion occurs when a material deteriorates due to a chemical or electrochemical reaction with chemicals in its environment [1]. Corrosion fundamentally impacts several critical sectors, including infrastructure (bridges, buildings, pipework), oil and gas, and travel (cars, boats and planes). Failures caused by corrosion can have catastrophic consequences, therefore the costs of corrosion mitigation and prevention are a vital necessity. The cost of corrosion is not only in preventative techniques but also in the inspection of structures and repairing damaged components. In 2016 the global cost of corrosion was estimated at 2.5 trillion US dollars, equivalent to 3.4% of the global economy [2].

Corrosion in metals is an oxidative process occurring when metal ions are hydrated in solution and take electrons from the metal (anode) to the acceptor (cathode) which can be; oxygen, oxidising agents, or hydrogen ions. In most cases for real-world systems an acceptor is the oxygen present in water or air in the metal’s environment [3]. Corrosion therefore requires the transfer of metal ions and water. Hence metals are most commonly protected by coatings forming a physical semi-impermeable barrier between the environment and the metal surface.

Organic coatings are most commonly used for corrosion protection of metals. An organic coating forms a physical barrier between a metal and its environment therefore inhibiting corrosion mechanisms. These protective coatings contain two main components, the polymer base, known as the binder, which contains additives such as pigments or fillers [4]. The properties of the pigment and binder both affect the overall effectiveness of the protective coating. Pigments are selected to change the appearance of a coating as well as improve corrosion resistance. An example of a pigment used to improve corrosion resistance is inhibitor particles. Inhibitor particles will leach out of a damaged coating layer to form a new coating on the metal surface, when it becomes scratched or abraded i.e. the coating is compromised.

1.2.2 Epoxy Resin Coatings

Epoxy resins (ERs) are commonly used as industrial corrosion-resistant coatings. These are highly suited for this role, due to their chemical and mechanical properties [5]. ERs are formed of a monomer containing a reactive epoxied group which opens and bonds either to another epoxy in a catalysed homopolymerisation reaction or with a chemical hardener, which can be a range of chemicals, often an aromatic amine, alcohol or ester [6]. In an industrial setting formulations will often consist of a combination of hardener and homo-polymeriser to ensure full conversion of the epoxy groups. ERs characteristics are highly tunable, hardener selection can affect the viscosity, cure temperature, surface properties and chemical, heat and electrical resistance.

The ERs used in this study are formed of diglycidyl ether bisphenol A (DGEBA) and m-xylylenediamine (MXDA), the chemical structures of which are shown in Figure 1.1. This formulation is used extensively in industrial corrosion-resistant coatings.

The epoxy reacts with the amine crosslinker to form a crosslinked network in a two-stage reaction. In the first stage, the nucleophile primary amine (belonging to MXDA) reacts with the electrophilic carbon in an epoxy ring (belonging to DGEBA). This forms a secondary amine which reacts with another epoxy ring, forming a three-dimensional crosslinked structure [7]. This reaction is shown in Figure 1.2. Due to each amine group reacting with two epoxy groups, a stoichiometric ratio consists of a 2:1 DGEBA:MXDA molecular ratio.

The resulting structure displays exceptional material properties, being tough and highly adhesive. The cross-linked structure also provides an excellent barrier to water and ion ingress [5]. In an industrial setting, this formulation will also include solvent as a viscosity modifier, to aid in spray coating, along with additive particles which can decrease permeability and some that act as corrosion inhibitors [3], leaching out of a

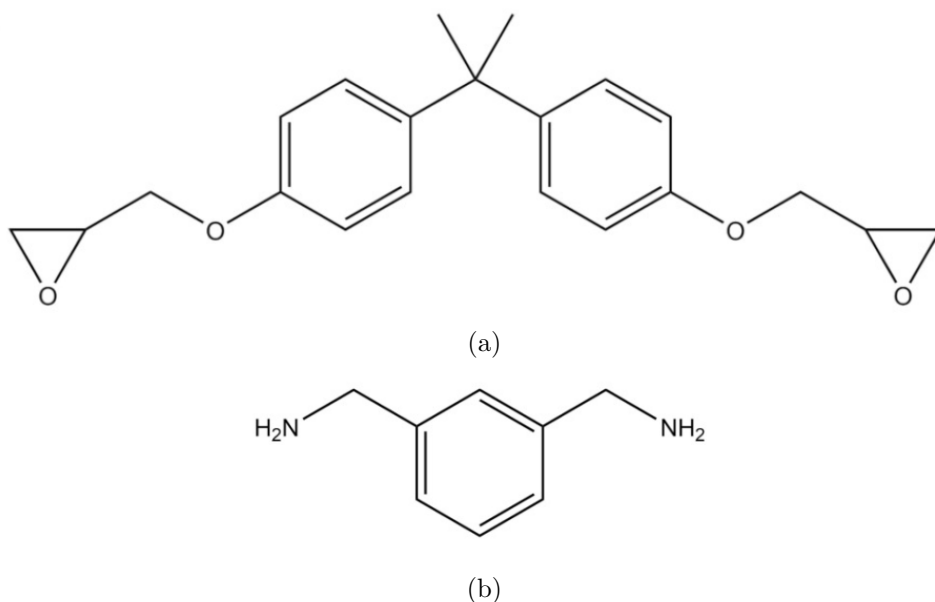


Figure 1.1: Chemical structure of the epoxy-amine used in this work. (a) DGEBA with epoxide group on each side of the molecule, and (b) MXDA crosslinker containing 2 primary amines.

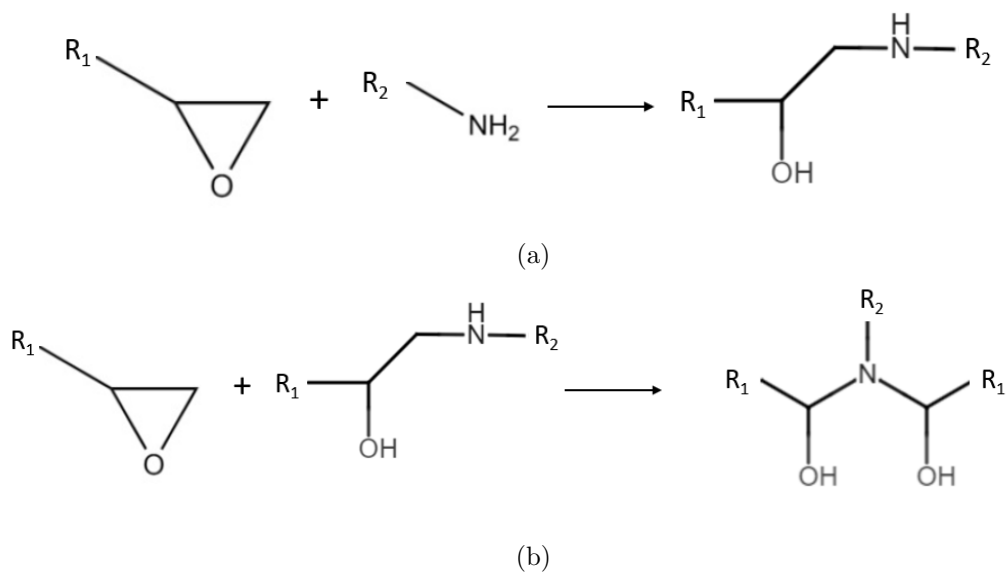


Figure 1.2: Epoxy-amine reaction, in which (a) an epoxy ring reacts with a primary amine forming a secondary amine. (b) the secondary amine then reacts with another epoxy ring. R_1 represents the remainder of the DGEBA molecule and R_2 represents the remainder of the MXDA molecule.

damaged coating to protect an exposed substrate.

1.2.3 Water-based Latex Coatings

Despite the benefits of using ERs for corrosion protection, there is a drive to use more water-based latex coatings in all industries. This is due to environmental concerns over solvent-based coatings, especially the use of volatile organic compounds (VOCs) [8]. VOCs are used as fluid carriers in solvent-based coatings to reduce viscosity and aid in application. VOCs raise considerable health, safety and environmental concerns [9] [10] [11]. Inhalation of VOCs can lead to damage to the central nervous system and cancer [12]. In the atmosphere, VOCs cause ozone and organic aerosol formation, contributing to climate change [13]. The reduction of VOCs in coatings and the investigation of alternate systems is therefore a top priority. Due to their intrinsic low viscosity, water-based coatings do not require the use of VOCs [14].

Decorative paints have already largely transitioned to water-based formulations, however, this is not true for industrial coatings, due to their current inferior barrier properties. It is, therefore, an aim of this work to investigate water-based coatings, to develop an understanding and aid in their development. Specifically understanding the internal structure of coatings formulated with a range of surfactants, investigated using SESANS.

Water-based coatings are mainly formed of polymer latex particles. Latex particles are applied to a surface as a dispersion in water. A continuous film is then formed in a four-stage process. As the water evaporates, particles first form a close-packed system. Particles then deform to fill the gaps, and finally, polymer diffusion between particles creates a homogeneous layer [15].

Surfactants play a crucial role in latex formulations as they act to keep particles in dispersion [16]. Surfactants are also used to improve the wettability of the coating, improving application and therefore the quality of the final film. However, the presence of residual surfactant in the final coating has an adverse effect on adhesion and corrosion resistance by forming channels for water to penetrate the coating [16] [17]. The investigation of surfactant distribution is therefore of great interest [18] [19].

Previous investigations have been carried out with a plethora of techniques including atomic force microscopy (AFM) [8], small-angle x-ray scattering (SAXS) [20], and small-angle neutron scattering (SANS) [21]. However, due to the length scale resolution available in a SESANS measurement, this work will provide a unique insight into the distribution of residual surfactants in latex films across many orders of length.

1.2.4 What we Would Like to Know

Due to the huge economic impact of corrosion on a vast range of industries, corrosion science has been the subject of countless experiments throughout the last century. A google scholar search for "corrosion" returns over 4 million results. Despite this deep interest over such a long time period the mechanisms underlying coating failure remain somewhat poorly understood [4]. By developing the PALS and SESANS techniques with a focus on their use for investigating polymer coatings the aim is to provide

instrumentation and instruction for the study of polymer coatings. There are several properties of polymer coatings that affect their efficacy as corrosion resistant coatings, all of which require further investigation before their effects will be fully understood. The physical properties of a polymer coating which affect corrosion resistance include: heterogeneity (defects and regions of low crosslinking), adhesion (how well the coating and protected surface are bonded) and additives (particles added to the polymer to aid corrosion resistance).

Heterogeneity

To form an effective barrier coating it is assumed that a homogeneous film is required. This means the coating must be free from defects and the crosslink density should be uniform throughout the 3D polymer network [22]. Defects and heterogeneity can lead to failures in polymer films. Nguyen *et al.* found that water uptake across a coating is non-uniform and higher at areas of low molecular weight and crosslinking [23]. Water uptake in a film leads to oxidation below the film and blistering and failure of the coating, due to volume change of metal oxides. Heterogeneity in films has been identified on the centimeter [24] and nanometer [22] scale.

There are many questions still to be answered about heterogeneity in polymer coatings including: what causes heterogeneity and how can it be avoided / minimised, where in the intact film is heterogeneity located, can they be identified before causing coating failure, what are the length scales of the heterogeneities?

Through the development of PALS and SESANS we aim to provide an insight into these questions. Thanks to the wide range of length scales available to SESANS it is well suited to provide information on film heterogeneity. As a non-destructive technique which probes the internal structure of bulk samples, no cutting or damage of any sort is required before measurement. Therefore, more reliable information is available on the unaltered internal structure of the sample. Again as a nondestructive technique SESANS can also provide information on a sample throughout its life cycle, telling us how defects are formed and develop during the operation of a coating.

PALS provides information on the distribution and sizes of free volume (FV) voids in a sample as well as the location of water in voids. This gives insight into how voids affect water uptake in polymer coatings.

Adhesion

The level of adhesion of a protective coating to the protected substrate greatly affects the quality of the protection [25]. Adhesion is a complex subject, made more so by the range of surfaces requiring protection from corrosion. Surfaces can range in material (metals/woods) but also surface roughness [26] and presence of oxide/hydrogen [27] layer. This subject is further complicated by the ever-changing conditions in which films are applied in the real world.

Research is required on the oxide or hydroxide layer between polymer film and substrate to determine if this layer grows during the lifetime of the coating and whether

it hinders performance. For this investigation to be carried out on intact films a highly penetrating probe particle is required such as neutrons.

Additives

The presence of additive particles in polymer coatings can aid in corrosion protection in a number of ways. The shape and size of pigments can affect water and oxygen diffusion through a polymer network. It was found that lamellar pigments in nano-clay composites can reduce water diffusion by 88% [4]. Corrosion inhibitor particles can also be included in formulations. Such particles are designed to leach out of a damaged surface and protect the exposed surface.

PALS and SESANS are useful tools in the investigation of additives. SESANS is an ideal technique for investigating size, shape and position of particles within a medium. isotopic substitution can be used to highlight the particles of interest. Also as a non destructive, highly penetrating technique neutron scattering lends itself to this work. PALS can also be used to investigate the effect of particles on polymer free volume and water uptake.

1.3 Instrumentation

1.3.1 Positron Annihilation Lifetime Spectroscopy Background

Positron annihilation lifetime spectroscopy (PALS) is used in this work to investigate free volume in epoxy-amine coatings. The PALS methodology is introduced in detail in Chapter 2 along with details of the Sheffield PALS (SPALS) instrument used in this study.

Contributions to the development of PALS were made in this work. First through the development of a custom data fitting program [28], and upgrades made to the Sheffield PALS instrument. Moreover, a comprehensive study compared PALS free volume measurements of a model epoxy-amine system, with free volume calculated for an identical formulation simulated using molecular dynamics. The comparison of these results validates both techniques and gives further insights into the structure of epoxy-amines.

The corrosion resistance of a polymer coating depends on how well it acts as a barrier to corrosion reactants (water, ions and oxygen). Several factors affect the barrier properties of a coating, including free volume voids in the polymer network [29], and interconnection of voids. The free volume of a polymer is defined by the size and distribution of voids in the polymer network including space between polymer chains that open under thermal motion, an important process in diffusion in polymers [30]. Making PALS a valuable tool in the analysis of epoxy networks [31] [32] and corrosion-resistant coatings [33] [34] including during ageing [35] [36].

1.3.2 Spin-Echo Small Angle Neutron Scattering Background

Spin-echo small angle neutron scattering (SESANS) is a relatively recently developed technique, which provides access to length scales not available in conventional scattering experiments. By manipulating the polarisation of a neutron beam using parallelogram-shaped magnetic fields, smaller scattering angles can be measured. Meaning that information is provided on larger length scales than in conventional SANS. SESANS is described in detail in Chapter 2.

As a relatively new technique, measuring commonly inaccessible length scales, SESANS requires a unique calibration standard. A large proportion of this work is dedicated to the development of a SESANS calibration standard. The length scales available to SESANS ($\sim 10\text{ nm} - \sim 40\text{ }\mu\text{m}$) [37] align with those present in polymer and colloidal systems. Meaning that the best candidates for calibration samples will likely be polymeric. A reliable calibration sample will also be stable over long time scales. For this reason, a glassy polymer would be ideal such as the polymer blends routinely used in conventional SANS.

Multiple candidate samples are trialled in Chapter 5 in an in-depth study combining a SESANS investigation and neutron ray-tracing simulations. Through this investigation, a systematic shift in SESANS data was also identified.

1.4 Thesis Structure

Chapter 1: Introduction and motivation behind the project.

Chapter 2: A detailed look at the experimental techniques used in this work. The theory of both PALS and SESANS is developed from first principles and data analysis methods are described.

Chapter 3: Article prepared for submission to *Macromolecules* on the free volume of epoxy-amines used for corrosion protection, measured using PALS and molecular dynamics. Free volume average void size measurements are compared between techniques as well as void size distribution. A combination of techniques (simulation and experiment) provides unique insight into these systems.

Chapter 4: A SESANS calibration sample investigation, in which potential samples are prepared and precharacterised using a range of techniques including AFM, scanning electron microscopy (SEM) and SANS. Samples are then analysed using pseudo monochromatic SESANS on the Larmor instrument at ISIS. Results are also compared with neutron ray-tracing simulations of the same instrument and sample set up in the McStas software.

Chapter 5: A study into surfactant distribution in water-based latex systems. Using SESANS and samples prepared with deuterated latex and a range of surfactants to provide an insight into the internal structure formed by residual surfactants. SESANS

is used to investigate internal structure on a length scale that is less commonly investigated. The implications of the findings are discussed in terms of what they imply for the use of water-based systems for the use of corrosion protection.

Chapter 6: Conclusions and future work. Here I will discuss the findings of this work and what they imply for the coatings industry. Also the proficiency of the techniques used and how our work has developed them. I will also discuss what further development of these techniques might look like and what this will mean for future investigations of polymer coatings.

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Chapter 2

Methods

2.1 Introduction

The two main techniques used throughout this work are Positron annihilation lifetime spectroscopy (PALS) and spin-echo small-angle neutron scattering (SESANS). In this chapter both techniques are introduced in detail. Theory is introduced from first principles and developed to describe the instruments and the practicalities of taking measurements. Data analysis and modeling for both techniques is also described in detail.

2.2 Positron Annihilation Lifetime Spectroscopy

Positron Annihilation Lifetime Spectroscopy (PALS) utilises the annihilation of a positron to measure the size of free-volume voids in a bulk sample. Using Fast plastic scintillators, photo-multiplier tube (PMT) and a coincidence counting unit the lifetime of the positron in the sample is measured. This lifetime is linked to the size of free volume voids by the Tao-Eldrup bubble model [1][2].

FV is a fundamental dynamic property of polymeric materials. Free volume voids exist in polymers due to the space-filling arrangement of polymer chains during polymerisation. Despite this, the size of voids is influenced by many factors. Free volume is inherently linked to molecular diffusion within a polymer. If the Van der Waals volume of a particular small molecule is similar in magnitude to the FV in a polymer system, diffusion is hindered [3]. Diffusion of ions and water in a polymer coating can lead to corrosion even under a fully intact coating. Corrosion under a coating can be dangerous and costly as it can cause catastrophic failures because it is hard to monitor and repair. The factors affecting FV in polymer systems have been previously investigated and include glass transition temperature, thermal history, crosslink density and pressure. The effect of crosslink density is of uppermost interest as it is readily tunable in epoxy resins by altering the ratio of crosslinker (amine) to epoxy.

The crosslink density of a polymer network is the number density of crosslinks in a polymer network, therefore increasing crosslink density increases the glass transition

temperature (Tg) of a polymer. This is up to a maximum value at which point the Tg plateaus, principally due to the reduction in chain free ends. Free volume increases when temperature rises above Tg [4] while the free volume of a polymer in its glassy state is sensitive to its thermal history. If a polymer is quenched rapidly the free volume will be larger than if it were cooled slowly. As polymer chain re-arrangement and relaxation are better able to take place if the polymer is cooled slowly near its Tg, due to the long timescales that are associated with polymer chain and polymer network relaxation.

2.2.1 The Positron

The positron is the anti-particle of the electron. Identical with the electron's rest mass, being 9.11×10^{-31} Kg or 0.511 MeV/C² and spin 1/2 but opposite charge.

Carl David Anderson first discovered the positron in 1932 [5], for which he was awarded the Nobel Prize in physics in 1936 [6]. It was discovered when studying cosmic rays in a Wilson cloud chamber. Anderson observed tracks in the cloud chamber that could only have been produced by a particle with the mass of an electron but with a positive charge. Anderson called this particle a positron [7] and deduced it was the antimatter pair of the electron. This was the first observation of antimatter, which Paul Dirac had predicted the existence of some time earlier in 1928 [8]. This was by the combination of general and special relativity, Dirac came to a solution with both positive and negative solutions. This led him to predict that every particle had an equivalent antiparticle with the exact properties but possessing an opposite charge. Dirac won the Nobel Prize for Physics for this work in 1933.

2.2.2 Positron Source

Positrons can be produced in a beam or as a point source by the decay of certain radioactive isotopes. For spectroscopic applications, a radioactive source is often the most practical and cost-effective option. In a PALS instrument, the most commonly used source is a sodium-22 (²²Na) radioisotope. ²²Na has a half-life of 2.6 years and can decay to form stable neon-22 (²²Ne) via 3 decay mechanisms [9]. The most frequent decay mechanism is via positron decay, shown in Equation 2.1 and 2.2.



In which ²²Na decays first via $\beta+$ decay to an excited state of ²²Ne, which rapidly decays to a stable energy state via emission of a 1.27 MeV gamma particle [10] within 3.7 ps of the $\beta+$ decay. Very rarely (0.1% of the time) ²²Na will decay directly to ²²Ne via $\beta+$ emitting a high energy gamma.



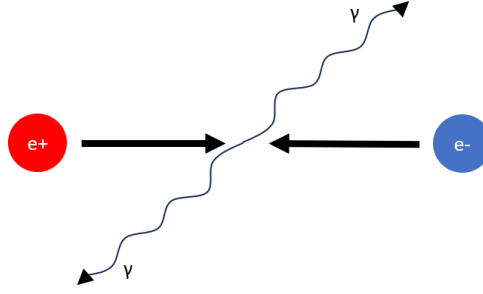


Figure 2.1: A positron annihilates with an electron and releases a pair of 0.511 MeV gammas.

Around 10% of the time electron capture will occur. In which an inner orbital electron is absorbed into the nucleus and a proton is converted into a neutron[11].



which is also followed by the emission of a gamma particle as in Equation 2.2

Positron Annihilation

As an anti-electron, a positron will annihilate with an electron releasing a pair of 0.511 MeV gamma particles, Figure 2.1.

In a PALS Instrument, the ^{22}Na positron source is sandwiched between two identical samples, as shown in Figure 2.2. This is to increase the coverage and therefore, the number of positrons that are emitted from the point source and annihilate in the sample. When a positron is injected into a solid or liquid sample it only has an energy in the KeV range, meaning it will quickly reach thermal equilibrium before annihilating [12]. The Positron will then annihilate in one of three modes, each having a characteristic lifetime (τ) (inverse of annihilation rate(λ)).

$$\tau_i = \frac{1}{\lambda_i} \quad (2.5)$$

The simplest annihilation mode is when a positron in its free state annihilates with a free electron via direct impact, the lifetime for this mode is $\tau_{e+} = 0.4 \text{ ns}$ [12]. During the thermalisation, secondary electrons are produced via ionisations in the sample. Thermalised positrons can combine with an electron to form a positronium (Ps) “atom”. The ground state of which exists as either a triplet state where the spin of the positron and electron are aligned in parallel called ortho-positronium (oPs) or a singlet state where spins are antiparallel called Para-positronium (pPs). In a vacuum, Ps would only annihilate by self-annihilation. Due to the conservation of parity, the self-annihilation of pPs and oPs happens on vastly different time scales. The anti-parallel singlet state pPs can decay into any even number of gammas, although 2 gammas is by far the most likely. This process is very likely and therefore results in a

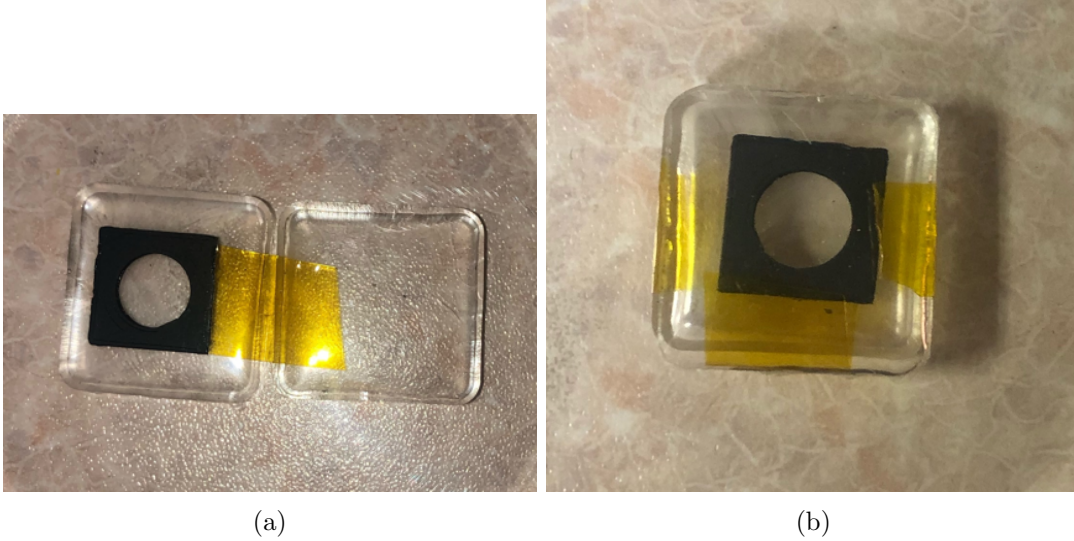


Figure 2.2: PALS ^{22}Na source is contained in Kapton tape and held in the black source holder. The source is placed on the first clear sample in (a) which is then covered by the second sample and taped on 3 sides in (b) to hold the source in place during measurement.

lifetime of only $\tau_{pPs} = 0.125$ ns [13]. However, the 2 quanta decay is forbidden for oPs meaning a less likely 3 quanta decay is required, giving a lifetime of $\tau_{oPs} = 142$ ns in a vacuum [14].

However, in a PALS measurement, the Ps will be decaying inside our sample at atmospheric pressure and not under vacuum. This does not affect the short lifetime of the pPs self-annihilation. However, interaction with the medium introduces another annihilation possibility which is more likely than the 3 quanta decay and therefore reduces the lifetime of the oPs. As the oPs is more stable in a vacuum it will seek out free volume voids. oPs is not fully stable in FV voids as it will annihilate with electrons from the surface of the void to overcome the forbidden 3 quanta decay in a process called pick-off annihilation. This reduces the lifetime drastically to between $\tau_{oPs} = 0.5$ and 3 ns [12], depending on void size. Consequently, the lifetime of the oPs can be used to probe free volume void size in materials.

2.2.3 Tao-Eldrup Bubble Model

The dependence of oPs lifetime on free volume void size is described mathematically by the quantum mechanical Tao-Eldrup Bubble Model [1] [2]. The model describes an oPs atom within a free volume void as a wave function in a spherical infinite potential well. Therefore, assuming a spherical void, the rate of decay of the oPs particle in the void is equal to the product of the probability of finding the oPs outside the void and the decay of the oPs in the bulk (λ_{bulk})[15].

$$\lambda_{oPs} = P\lambda_{bulk} \quad (2.6)$$

The probability of finding the oPs outside the potential well is given by P.

$$P = 4\pi \int_R^\infty \Psi_{out}^2(r) R^2 dr \quad (2.7)$$

Where R is the void radius. Tao simplified this by substituting a real potential well with a depth of U and added a broadening factor of Δ . This left the void volume the same and the value for Δ was experimentally determined using values for plastic crystals to be 0.166 nm. Giving a final expression for the decay rate of the oPs as

$$\lambda_{oPs} = 4\pi\lambda_{bulk} \int_R^{R+\Delta} \Psi_{in}^2(r) R^2 dr \quad (2.8)$$

Which can be solved to give the expression for oPs decay rate as a function of R.

$$\lambda_{oPs} = \lambda_{bulk} \left(1 - \frac{R}{R + \Delta} + \frac{\sin \frac{2\pi R}{R + \Delta}}{2\pi} \right) \quad (2.9)$$

λ_{bulk} is equal to the weighted average of the decay rates for oPs and pPs. The decay constant for the self-annihilation of oPs is neglected as in a solid it is two orders of magnitude smaller than the pick-off decay rate. λ_{bulk} is widely accepted as 2 ns^{-1} [16] [17]

Using the equation for the volume for a sphere $V = 4\pi r^3/3$ and Equation 2.5 we can plot the relationship between oPs lifetime and free volume, shown in Figure 2.3.

2.2.4 PALS Measurement

During a PALS measurement, the positron lifetime is measured by detecting the emitted gamma photons. As described earlier, for the most common decay mode of the ^{22}Na isotope a positron is emitted followed quickly by a 1.27 MeV gamma photon, see Equations 2.1 and 2.2. We call this the 'birth' gamma as it acts as a timestamp for the positron implantation into the sample. This positron then annihilates in the sample via one of the 3 annihilation modes and forms 2 simultaneous 0.511 MeV gammas in opposite directions, named the 'annihilation' gammas. The time between the birth and annihilation gammas is measured and recorded as the positron lifetime.

All PALS measurements in this work were performed on the Sheffield positron annihilation spectrometer (SPALS). SPALS detects gamma photons using 2 detector tubes (displayed in Figure 2.4) positioned at 180° from each other. Each detector tube contains a fast plastic scintillator and a photomultiplier tube (PMT). Specifically used in the SPALS instrument is a 51mm diameter 51mm length EJ-232Q-0.5% Fast Timing Plastic Scintillator and a Hamamatsu H1949-51 PMT.

For a positron annihilation or birth to be measured the relevant gamma photon must first interact with the scintillator in one of the 2 detector tubes. Within the scintillator, the photon is absorbed by an atom causing an excitation. The atom then

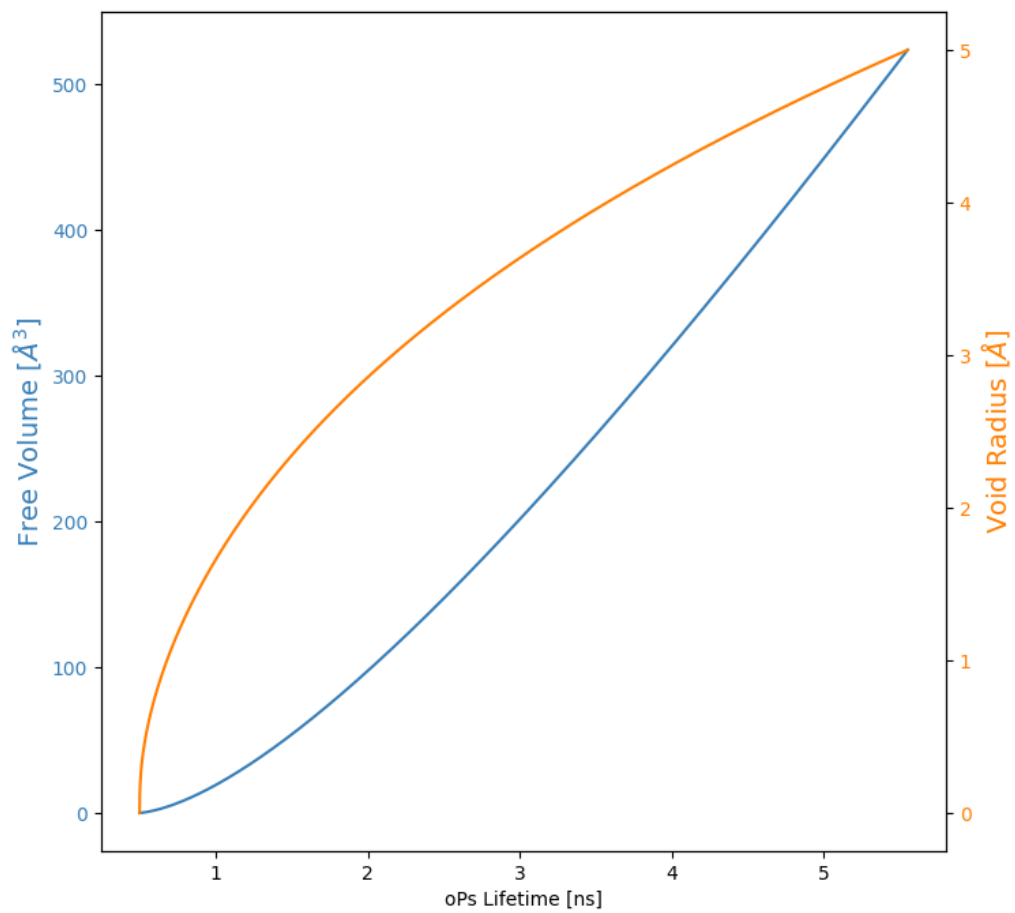


Figure 2.3: Tao-Eldrup Bubble model, giving the relationship between oPs lifetime and measured free volume void size.

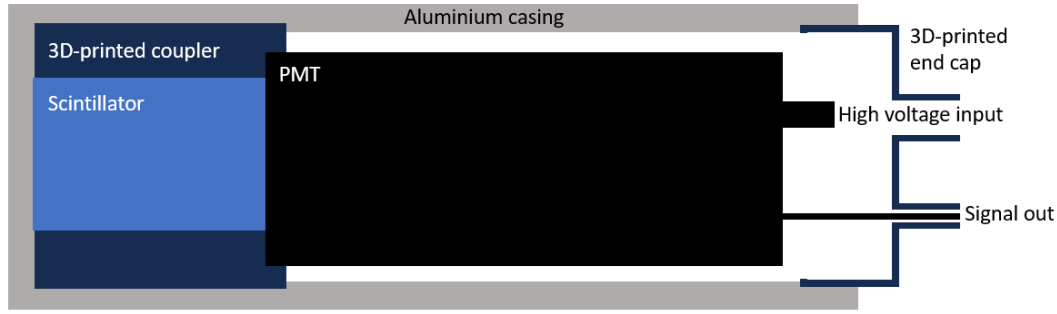


Figure 2.4: Schematic diagram of a PALS detector. Consisting of a fast plastic scintillator and a photo multiplier tube (PMT). The aluminium casing and the 3D-printed end cap keep the detector light-tight. A 3D-printed coupler ensures good contact between the scintillator and PMT.

decays back to its ground state via the emission of light photons, the emission spectrum of the EJ-232Q is shown in Figure 2.5. The rate at which this decay occurs is defined by the decay time of the scintillator. Fast plastic scintillators have short decay times which is essential for fast timing applications. With a decay time of only 700 ps the EJ-232Q is ideal.

Once the gamma photon has interacted with the scintillator material the light photons are then detected by the PMTs, which are coupled to the scintillators using a custom 3D-printed coupler and the contacting surfaces are covered with a thin layer of coupling gel for the best light transfer. The PMT then converts these photons to a detectable electric current.

Once photons have been converted into an electric signal this is passed into a coincidence unit (CU). This component discriminates between photons produced in a single positron birth-annihilation event and those produced by separate decays. This is done by only recording events that occur within 50 ns of one another. With an activity of 1.19 MBq, decays will occur on average once every 840 ns, therefore photons detected within 50 ns of each other are likely from a single positron being produced in the source and then annihilating in the sample. When two photons are detected within 50 ns the CU will trigger the digital oscilloscope to record these two events. Producing a measurement of both the photon wavelength and the positron lifetime. A histogram of positron lifetimes is then produced using the PALS acquisition software QTPALS [19].

Figure 2.6 Shows an example of 4 PALS histograms. As the free volume of the sample increases there are more, longer oPs decays. This is shown in Figure 2.6 as the polymer samples Polytetrafluoroethylene (PTFE) and epoxy-amine (DER354-MXDA) contain larger free volume voids and the histogram, therefore, contains more long lifetime events.

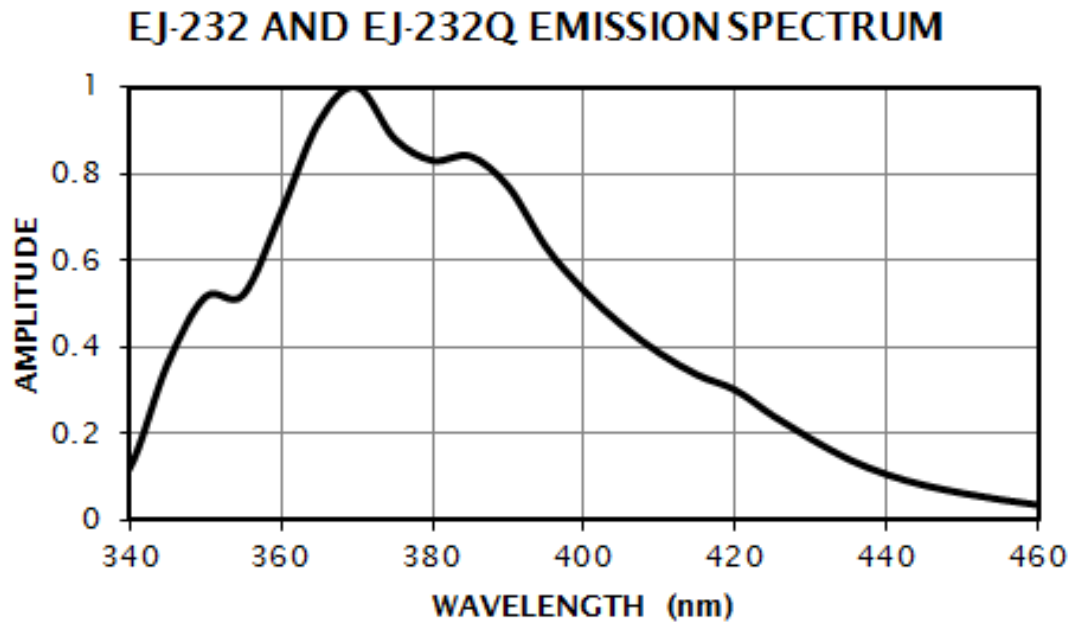


Figure 2.5: Wavelength emission spectrum for the fast plastic scintillator used in the SPALS instrument. This can be found at [18]

SPALS component specifications

Source	– ^{22}Na Positron source – 2.6 years half-life – Activity = 1.19 MBq (calculated from the original activity of 1.85 MBq given in [9]) – Active diameter = 5.08 mm – Overall diameter = 12.7 mm
Scintillator	– Type: EJ232Q 0.5% Benzophenone – Shape: cylinder – Diameter: 51 mm – Length: 51 mm – Scintillation Efficiency (Photons/keV): 2.9 – Light output (% Anthracene): 19 – Decay time (ps): 700 – Wavelength maximum emission (nm): 370
PMT	– Spectral range (nm): 300-650

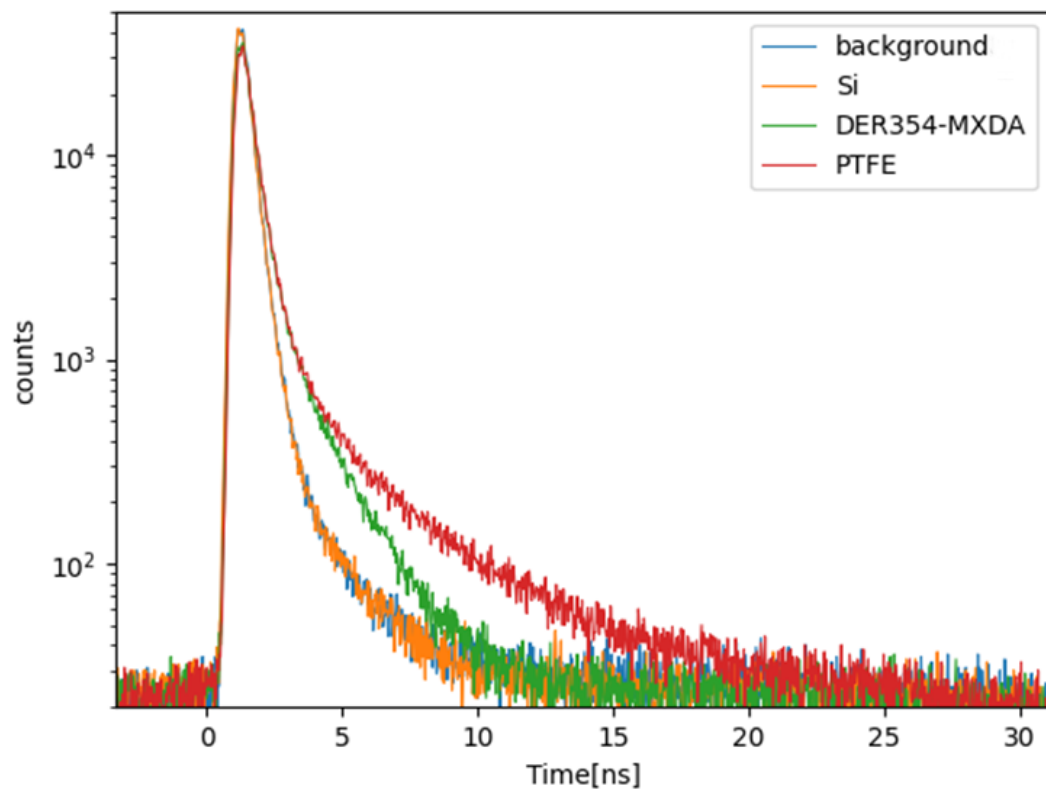


Figure 2.6: Four examples of PALS histograms lifetimes, showing the sensitivity of the instrument to different void sizes. The background (blue) is measured with no sample and is coincident with the Single crystal silicon (Si), measured using two silicon blocks. The remaining samples are polymers, a polymer network DER354-MXDA is an epoxy-amine and the polymer Polytetrafluoroethylene (PTFE).

- Peak efficiency wavelength (nm): 420
- Rise time (ns): 1.3
- Gain at optimal voltage: 2×10^7

2.2.5 PALS Data processing

The histogram of positron lifetimes must then be analysed to extract free volume information. This can be done in two ways. Firstly a custom written Python program was used to extract an average free volume void size. Furthermore, a void size distribution was then extracted using the DCONTINPALS program [20], this is a free program, available online [21].

The custom Python program was created as there is no standardised approach for fitting PALS histogram data [22]. This script was validated by comparison with a different fitting software, DQuickLTFit [23] (available online), using PALS data from a range of epoxy-amine samples. Two least squares fit modes were also compared (Trust Region Reflective and Levenberg-Marquardt), along with DQuickLTFit. The results from the 3 different fitting approaches are shown in Appendix A.1. For the data presented throughout the thesis, the Trust Region Reflective algorithm was used.

PALS Python

The custom Python program available on GitHub [24] calculates τ_{oPs} by fitting the PALS histogram to a function consisting of a Gaussian convoluted with 3 exponential decays (one for each positron lifetime).

$$f(x) = \frac{He^{(-x-P)^2}}{2\sigma^2} * Ae^{-l_1x} + Be^{-l_2x} + Ce^{-l_3x} \quad (2.10)$$

Where H is the height of the gaussian, P is its position relative to zero and σ is the width. The 3 exponential decays represent the lifetime of the 3 different types of positron annihilation, l_i is the lifetime of the positron and the letter (A,B,C) is the factor of decays of each type. Initial quesses and bounds are used to force each exponential to represent the desired positron type. The program therefore calculates τ_{oPs} and the intensity (I_{oPs}) of this decay. Free volume (FV) is then calculated from the Tao-Eldrup fit and fractional free volume (FFV) from the equation:

$$FFV = FV \times I_{oPs} \quad (2.11)$$

Fractional free volume is a measure of the percentage of the overall volume that is made up of free volume voids, as observed by the oPs.

DCONTINPALS

DCONTINPALS is a python program written by Dr. Danny Petschke available on GitHub [21]. The program runs the historical FORTRAN code CONTIN-PALS written by Provencher [25] and adapted by Gregory [26]. The program solves the Freholm

integral equations with convoluted exponential decays. It is, therefore, able to identify as many decays as the data may contain, instead of the predefined 3. By not defining the positron decay modes we are able to validate our model and also define multiple free-volume void sizes.

Figure 2.7 shows an example of the output data from DCONTINPALS for silicon and an epoxy-amine sample. The output shows that silicon gives a single short lifetime response due to its crystalline structure whereas the epoxy sample gives multiple lifetimes due to multiple characteristic free-volume void sizes. Due to the resolution of the SPALS instrument being 411 ps the decay of the pPs and free positron are contained in one peak below 500 ps.

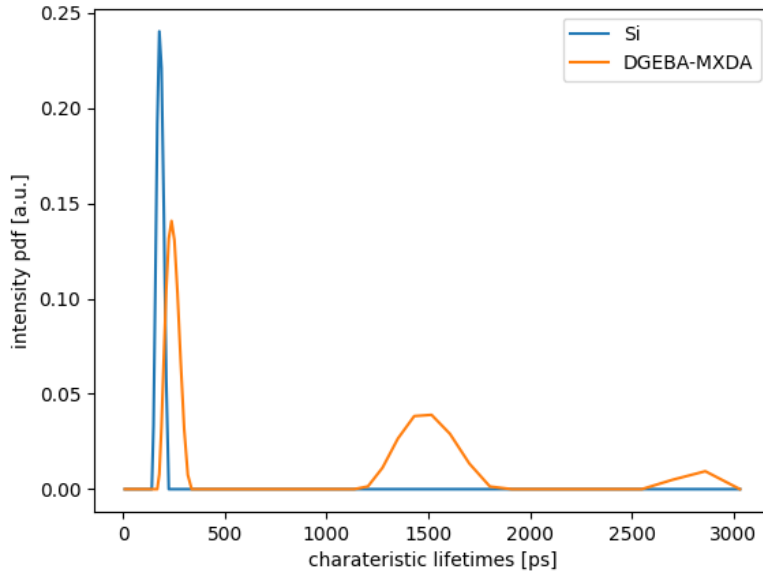


Figure 2.7: PALS positron lifetime distribution given by the DCONTINPALS program.

2.2.6 Development of the Sheffield PALS instrument

The SPALS instrument was upgraded as part of this work. First, the instrument hardware was updated by replacing the original EJ-232 plastic scintillator with a faster EJ-232Q, which has faster rise and decay times [18]. The instrument's timing resolution was calculated by measuring a silicon crystal sample (which gives a sharp single lifetime response) and fitting a full-width half maximum to the rise in the histogram data. Timing resolution improved from 470 ± 26 ps [9] to 411 ± 1 ps. Silicon data is then used as an instrument response function in the DCONTINPALS program.

Furthermore, a positron source holder and a scintillator-PMT coupler were designed using computer-aided design and 3D printing. Improving the usability of the instrument.

Finally as described above data fitting software was improved and tested. Before this point, SPALS data had only been fitted using the LTpolymers software [27]. However, we upgraded the fitting procedure by developing a custom-written Python script which calculates the average FV void size in a transparent and adaptable way. Also, a fitting procedure for the DCONTINPALS program was developed, giving access to lifetime and FV distribution.

2.3 Neutron Scattering Theory

Neutron scattering techniques have been used extensively throughout this work, specifically small-angle neutron scattering (SANS) and spin-echo small-angle neutron scattering (SESANS). Both these techniques use neutron beams incident on a sample and measure how the neutrons are elastically scattered. By doing so we are able to investigate the internal structure of the sample in a nondestructive manner. Where SANS simply measures a scattering angle using a position-sensitive detector, SESANS utilises a polarised neutron beam and encodes the scattering angle onto the polarisation. This allows larger structures to be measured with SESANS than is possible via conventional SANS. While SANS can measure length scales from $\sim 1 - 100$ nm [28], SESANS has access to length scales from 10's of nanometers to around 40 microns [29] [30].

Neutron scattering techniques are ideal for the investigation of soft matter systems. As highly penetrating techniques, neutrons access information on the interior structure of bulk samples. Neutrons will only slightly activate polymer systems, this along with being nondestructive allows for subsequent measurements with other methods on the same samples. A large beam cross-section also provides an averaging measurement across an entire sample volume.

2.3.1 Neutrons

Ernest Rutherford originally postulated a neutral particle with the mass of a proton in 1920 [31]. However, its neutral charge made the search for the particle a demanding task. After being wrongly identified as high energy gamma-rays in experiments by Irène and Frédéric Joliot-Curie in 1930 [32], James Chadwick correctly confirmed the existence of the neutron in 1932 [33] [34].

Neutrons used in scattering experiments have a typical wavelength of around 0.01-3 nm [35]. When considering polymers with a radius of gyration of around 1-10 nm it is obvious to see that neutrons are a better choice for making observations than visible light with a wavelength of 400 - 700 nm.

Neutrons and X-rays used in scattering experiments have similar wavelengths however, neutrons are far less destructive. Consider a neutron and an X-ray, both with a wavelength (λ) of 0.5 nm, typical in both scattering techniques. The X-ray energy is given by Planck's equation

$$E = hc/\lambda \tag{2.12}$$

where h is Planck's constant and c is the speed of light. This gives our X-ray an energy of $3.973 \times 10^{-16} \text{ J}$ (2.480 KeV). To calculate the neutron energy its mass of $m_n = 1.674 \times 10^{-27} \text{ Kg}$ ($939.6 \text{ MeV}/c^2$) must be considered along with the kinetic energy.

$$E = h^2/2m\lambda^2 = mv^2/2 \quad (2.13)$$

Giving an energy of only $5.243 \times 10^{-22} \text{ J}$ (3.2724 meV), 6 orders of magnitude smaller than the x-ray energy. Therefore, considerably less energy is deposited into the sample in a SANS experiment when compared with small angle x-ray scattering (SAXS). Making SANS far less destructive and preferable for soft matter and biological systems. From Equation 2.13 we also see how neutron velocity (v) and wavelength are inversely proportional.

$$v = h/m\lambda \quad (2.14)$$

As neutral particles neutrons can only interact with the nuclei of nonmagnetic materials via the strong nuclear force. Despite being strong the force is only short range allowing neutrons to penetrate deeply into a sample, before interacting with a nucleus. Unlike X-rays which will interact with orbital electrons via the electromagnetic force, which has an infinite range falling off with distance squared. Neutrons will therefore penetrate around 10 times deeper into a material [36]. Allowing bulk materials to be probed more easily with neutrons. However, this limits their effectiveness in poorly scattering materials. $3.5 \text{ \AA}$ neutrons have a transmission of 56.75% in 1 mm of water whereas the same wavelength x-ray will only have a transmission of 0.0007% [37].

As a spin half particle with a magnetic moment of $-1.913 \mu_N$ [38] the neutron will also interact with unpaired orbital electrons in magnetic materials via a dipole-dipole interaction. While this interaction also occurs with x-rays, it is vastly overwhelmed by the electromagnetic interaction so has negligible effect. Whereas in neutrons the magnetic and nuclear interactions occur at a similar rate. Meaning neutrons are able to probe the magnetic properties of materials.

2.3.2 Neutron Sources

Neutrons used for scattering applications must be produced in the form of an intense beam. This can be done by two different methods. A high-intensity single-wavelength beam can be produced using a nuclear fission source. During the decay of a uranium-235 atom, 2-3 neutrons are released. Once moderated one of these will be used to sustain the chain reaction while the others can be used for science, by focusing through instrument optics. With a power output of 58 MW [39] the Institute Laue-Langevin (ILL) in France is the highest flux reactor source in the world.

Alternatively, a spectrum of wavelengths can be produced by a spallation source, in which a heavy metal target is bombarded by accelerated protons. This is known as a time-of-flight (TOF) source. Neutrons separate according to their wavelength during flight from source to detector. The beam is therefore pulsed using choppers and each pulse consists of short wavelength neutrons that arrive first, through to the longest

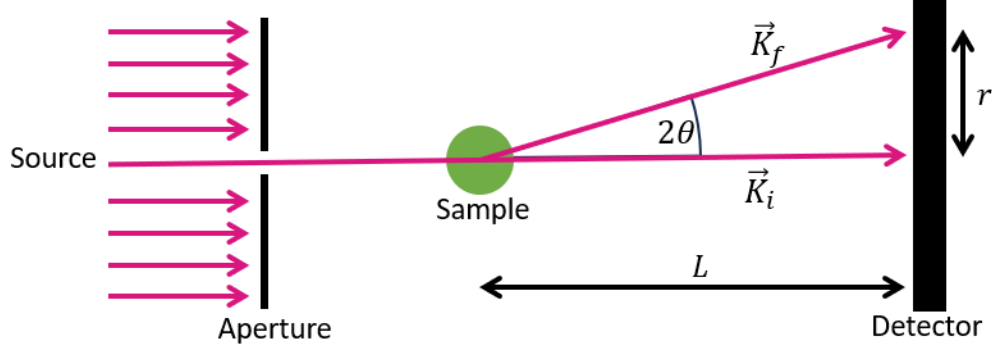


Figure 2.8: Schematic of a conventional SANS instrument. Neutrons are incident on the aperture from the left, once collimated they scatter from the sample through an angle of 2θ . Scattered neutrons are then recorded by the position-sensitive detector at a distance L from the sample at a radial distance of r . $\vec{K}_i$ and $\vec{K}_f$ represent the wavevectors of the incident and scattered neutrons respectively. Adapted from [40].

wavelengths that arrive at the end of the pulse. The ISIS neutron source is one of the highest flux spallation sources in the world and works by accelerating protons in a synchrotron to 800 MeV [35] before colliding them with a tungsten target. Neutrons are ejected from the nuclei in the target and moderated before focusing via neutron guides into instruments. Providing 50 pulses a second each consisting of neutrons of wavelengths $\sim 2 - 13 \text{ \AA}$.

2.3.3 SANS

SANS instruments operate by focusing a collimated neutron beam onto a scattering target and measuring how neutrons are scattered away from the direct beam using a position sensitive detector. A schematic of a SANS instrument is shown in Figure 2.8.

The scattering vector ($\vec{Q}$) describes how the wavevector of the neutron is changed as it is scattered from the sample. $\vec{Q}$ has units of inverse length and is the independent variable in a SANS experiment. Giving information on the sample length scales in reciprocal space. Momentum transfer is expressed as

$$\vec{P} = \hbar\vec{k}_i - \hbar\vec{k}_f = \hbar\vec{Q} \quad (2.15)$$

Therefore the change in wavevector is the definition of the scattering vector

$$\vec{Q} = \vec{K}_i - \vec{K}_f \quad (2.16)$$

In a SANS experiment the neutron is assumed to elastically scatter from a nucleus in the sample. The energy transfer is zero and the momentum transfer $\vec{Q}$ is the same as the magnitude of the scattering vector Q . And is only defined by the change in

angle between incident and scattered neutron and can be calculated via trigonometry using the triangle defined in Figure 2.8 where θ defines half the scattering angle, the hypotenuse is $-\vec{K}_f$ and the opposite has length $\vec{Q}/2$.

$$\vec{Q} = Q = 2\vec{K}_f \sin \theta \quad (2.17)$$

Taking into account the fundamental relation of wavevector and wavelength $k = 2\pi/\lambda$ this can be defined as

$$Q = \frac{4\pi \sin \theta}{\lambda} \quad (2.18)$$

At very small angles we can use the small angle approximation $\sin \theta \approx \tan \theta \approx \theta$. This is a reasonable assumption for a SANS experiment[35]. If we now consider a triangle with opposite and adjacent side lengths defined by r and L respectively, as in Figure 2.8. We can define

$$\tan 2\theta = \frac{r}{L} \approx 2\theta \approx \sin 2\theta \quad (2.19)$$

Therefore we can simplify Equation 2.17 to

$$Q \approx \frac{2\pi r}{\lambda L} \quad (2.20)$$

In a SANS instrument a 1D plot of intensity against Q is obtained by radially integrating the 2D detector image. Known as the scattering function or $I(Q)$. The scattering function in an idealised system, can be split into a product of two terms. These are the form factor, $P(Q)$, which relates to intraparticle correlations, and the structure factor, $S(Q)$, relating to inter particle correlations. A version of the total scattering function is shown in Equation 2.21, where I is the scattering intensity, n is the number concentration of particles, M is molar mass and $\Delta\rho$ is the scattering contrast factor[41].

$$I(Q) = nM^2(\Delta\rho)^2 P(Q)S(Q) \quad (2.21)$$

From this equation it is clear to see that the Q range of a SANS experiment can be altered by changing the wavelength of the neutrons or the length of the instrument. As Q is reciprocal space we measure small features of the internal structure of the sample at high Q and large features at low Q .

2.3.4 Neutron Scattering Length

Neutrons interact with nuclei in a sample as a point source due to the short range of the strong force, making neutron scattering isotropic. Considering the incident neutron beam as a plane wave travelling in the z direction, it can be expressed by

$$\psi_i = \psi_0 e^{ikz} \quad (2.22)$$

Where ψ_0 represents the incident flux. After elastically interacting with a point source neutrons move out radially so the wavevector of the scattered wave is parallel to the

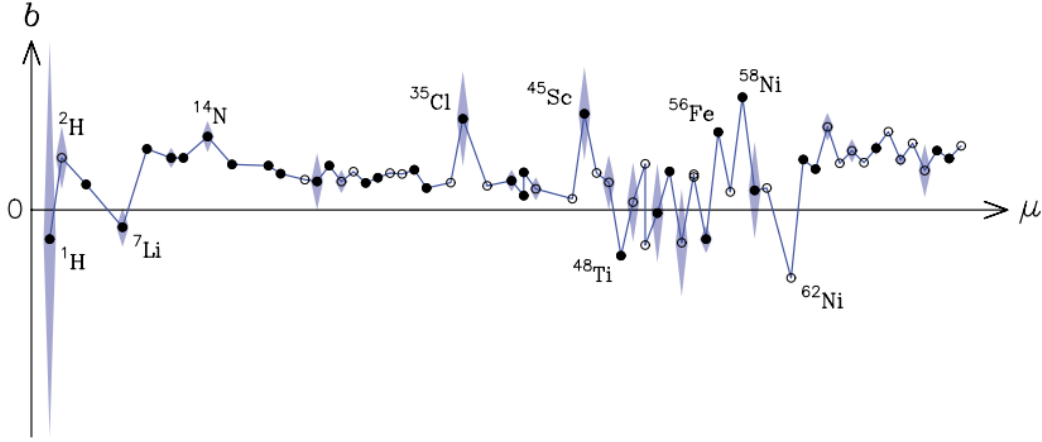


Figure 2.9: Neutron scattering lengths, b as a function of atomic mass, μ . Standard deviation represented by diamonds. Least common nuclei have been omitted. Taken from [36]

displacement vector $\mathbf{r}$ [36]. The flux of the scattered neutrons will fall off with r and the scattered beam can therefore be represented by

$$\psi_f = \psi_0 f(\lambda, \theta) \frac{e^{ikr}}{r} \quad (2.23)$$

In which $f(\lambda, \theta)$ is a function that defines the chance that a neutron of wavelength λ is scattered in the direction θ .

For neutrons $f(\lambda, \theta)$ tends to be independent of scattering angle and neutron wavelength. Meaning it can simply be described by the constant b , called the scattering length.

$$f(\lambda, \theta) = -b \quad (2.24)$$

The negativity of the scattering length is a matter of convention. The magnitude of b represents the scattering strength. Its sign indicates whether incident and scattered neutrons are in or out of phase. a positive value indicates in phase (coherent scattering) and a negative value indicates a (180°) out of phase (incoherent scattering).

Scattering length is isotope dependent and changes in a non-linear unpredictable fashion with atomic mass, as shown in Figure 2.9. Each nuclei's scattering length consists of a coherent and incoherent component but the dominant scattering type is represented by the sign. Only coherently scattered neutrons carry information about the structure of the sample [35].

In practice, it is more practical to consider scattering from molecules rather than atoms. For this, we consider the neutron scattering length density, which is analogous to the refractive index of a material but specific to neutrons. Scattering length density (ρ) is a function of b along with the bulk density (δ) and the molecular weight (M) of

a molecule. Scattering length density can be calculated by

$$\rho = \frac{\delta N_A}{M} \sum_i b_i \quad (2.25)$$

Where b_i is the coherent scattering length of the nucleus i .

In the same way that matching optical refractive indices can make a piece of glass invisible in water, manipulating ρ can hide or highlight features of a sample in a neutron experiment. As b is vastly different for hydrogen and deuterium this is often done by substituting part of a material's Hs with Ds. To match or contrast with another material, procedure known as contrast matching. H_2O has a scattering length density of $-0.561 \times 10^{-6} \text{\AA}^{-2}$ and D_2O has a value of $6.105 \times 10^{-6} \text{\AA}^{-2}$.

2.3.5 Limitations of SANS

To measure very large features (relevant for many polymer and biological experiments) we must measure at low Q values. Therefore, we must be able to distinguish neutrons that are scattered at a very small angle from those in the direct beam. It is impossible to measure scattering angles that lie within the direct beam at the detector position in a SANS instrument as the direct beam overwhelms the detector and is therefore blocked by a beam stop. SANS instruments that are designed to investigate large length scale systems must be built with a very large sample to detector distance, to separate scattered neutrons from the beam stop. Such instruments include D11 at the ILL, with a maximum sample-to-detector distance of 39 m[42]. Giving a Q range of $3 \times 10^{-3} \leq Q[\text{nm}^{-1}] \leq 8$. Such instruments are expensive to build as the regions in which the neutrons propagate must be kept under vacuum, necessitating large vacuum tanks and the ability to move the detector to any position in the tank.

However, we are still fundamentally limited in how low we can go in Q and the largest length scales we can measure with a conventional SANS instrument. Also, the flux of neutrons falls off linearly with Q meaning that count times are many times longer.

2.3.6 SESANS

Spin-echo small angle neutron scattering (SANS) overcomes the fundamental limit of SANS by manipulating neutron spin and encoding scattering angle onto the polarisation of the neutron beam. Therefore, scattering that falls within the direct beam can be measured. Neutron spin-echo was originally suggested as an experimental technique by Mezei [43].

Neutrons in a Parallelogram Magnetic Field

When considering a single neutron it is possible to define its spin as

$$\vec{s} = \frac{\hbar}{2} \vec{\sigma} \quad (2.26)$$

where σ is the Pauli spin matrix of the neutron [40]. When considering a beam of neutrons we must consider its polarisation ($\vec{P}$). This is the average of the Pauli spin matrices for all the neutrons in the beam.

$$\vec{P} = \langle \hat{\sigma} \rangle \quad (2.27)$$

When all neutrons in the beam have the same spin direction $|\vec{P}| = 1$ and the beam is polarised, whereas in an unpolarised beam, neutron spins are aligned randomly $|\vec{P}| = 0$.

Neutron magnetic moment is expressed as

$$\vec{\mu} = \frac{g_n \mu_N \vec{\sigma}}{2} \quad (2.28)$$

where $g_n = -3.826$ is the dimensionless neutron g-factor and $\mu_N = 5.051 \times 10^{-27} \text{ JT}^{-1}$ is the Nuclear magneton. Due to the neutron's magnetic moment, it will undergo Larmor precession in a magnetic field. As the neutron passes through the magnetic field of $\vec{B}$ it experiences a torque of

$$\frac{d\vec{\sigma}}{dt} = \vec{\mu} \times \vec{B} = \frac{g_n \mu_N}{2} (\vec{\sigma} \times \vec{B}) \quad (2.29)$$

Due to the cross-product, the neutron will feel no turning force if its spin is aligned with the magnetic field. Equivalently when we consider the polarisation of the neutron beam

$$\frac{d\vec{P}}{dt} = \frac{g_n \mu_N}{2} (\vec{P} \times \vec{B}) \quad (2.30)$$

As the beam passes through the field it is possible to define a Larmor frequency (ω_L), defined as the rate of precession of the magnetic moment. And calculated by

$$\omega_L = \frac{\Delta\varphi}{\Delta t} = |\gamma \vec{B}| \quad (2.31)$$

where γ is the gyromagnetic ratio of the neutron

$$\gamma = \frac{g_n \mu_N}{\hbar} \quad (2.32)$$

so that

$$\omega_L = \left| \frac{g_n \mu_N}{\hbar} \vec{B} \right| \quad (2.33)$$

If the neutron path length through the magnetic field has a length of L and the neutron has a velocity of v , it will precess by φ_L . As it spends a time of $t = L/v$ in the magnetic field. Given the velocity of the neutron is defined by Equation 2.14, this can be expressed by:

$$\varphi_L = \omega_L t = \left| \frac{g_n \mu_N}{\hbar} \vec{B} \right| \left(\frac{L}{v} \right) = \left| \left(\frac{g_n \mu_N M_n}{\hbar h} \right) \vec{B} \right| L \lambda = C \vec{B} L \lambda \quad (2.34)$$

By combining constants we can evaluate a single constant $C = 4.6368 \times 10^{14}$ [44] [45]

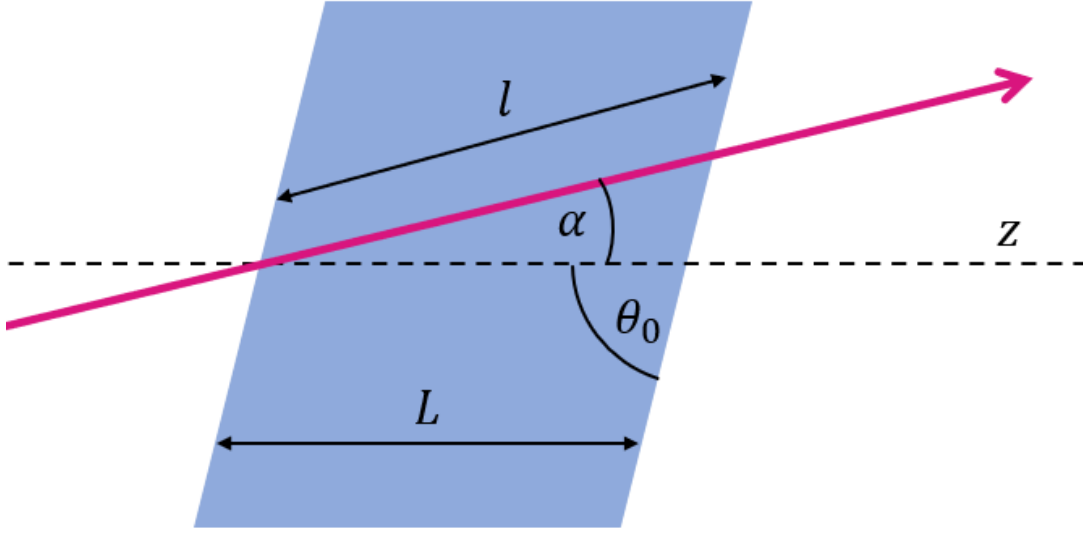


Figure 2.10: Neutron beam path through a parallelogram magnetic field of length L and angle of inclination θ_0 . The neutron beam (in pink) enters the field on the z axis at an angle α and experiences a path length in the field of l .

In a SESANS instrument, the neutron beam passes through 2 parallelogram-shaped magnetic field regions. When considering a parallelogramic field as used in a SESANS instrument the path length l of the neutron beam is defined by

$$l = L(1 + \alpha \cot \theta_0) \quad (2.35)$$

Where L is the width of the field region along the z -axis (optical axis of the instrument), α is the angle between the beam and the z -axis and θ_0 is the inclination of the field from perpendicular to the z -axis. Shown in Figure 2.10. Therefore, the angle that the neutron (Larmor) precesses through is

$$\varphi_1 = C\vec{B}\lambda L(1 + \alpha \cot \theta_0) \quad (2.36)$$

Spin-echo

A SESANS instrument consists of two parallelogram shaped magnetic fields of the same shape but with equal and opposite magnetic fields. If the neutron passes through the instrument unscattered it will precess equally in both fields but in opposite directions, returning its spin to the same direction as when it entered the first field. This condition of the spin returning to its original state is called spin-echo. However, if the neutron is perturbed by a scattering sample in between the fields any scattering will cause the path length to be different through the second field and the neutron will not precess by the same amount. In this case, the spin-echo condition is not met. The total precession

of the neutron will be given by $\Delta\varphi$

$$\Delta\varphi = \varphi_1 - \varphi_2 = C\vec{B}\lambda L(1 + \alpha_1 \cot \theta_0) - C\vec{B}\lambda L(1 + \alpha_2 \cot \theta_0) \quad (2.37)$$

$$\Delta\varphi = C\vec{B}\lambda L(\alpha_1 - \alpha_2) \quad (2.38)$$

Where α_1 and α_2 are the angles the beam is inclined to the z-axis in the 1st and 2nd precession regions, respectively. The difference between α_1 and α_2 is only due to the scattering angle 2θ . Therefore, $\alpha_1 - \alpha_2 = 2\theta$ and

$$\Delta\varphi = C\vec{B}\lambda L 2\theta \cot \theta_0 \quad (2.39)$$

Using Equation 2.18 and the small angle approximation of $\sin \theta \approx \theta$ we can remove scattering angle from the equation, by substituting

$$\theta \approx \frac{Q\lambda}{4\pi} \quad (2.40)$$

Therefore, arriving at a value for the total precession that only consists of instrument defined parameters and the scattering vector.

$$\Delta\varphi \approx \frac{C\vec{B}\lambda^2 L \cot \theta_0}{2\pi} Q = zQ \quad (2.41)$$

Where z is defined as the spin-echo length, defined by the set-up of the instrument and denoting the length scales probed.

$$z \equiv \frac{C\vec{B}\lambda^2 L \cot \theta_0}{2\pi} \quad (2.42)$$

Spin-echo length (z) has dimensions of length. This is best understood by the quantum mechanical treatment of SESANS. In which z denotes the distance the two neutron spin eigenstates are separated in the field region [45] [46]. This quantum mechanical treatment has recently been proven to be the correct interpretation by McKay et al [30].

SESANS Measurements

A SESANS instrument is shown in Figure 2.11. In the instrument the neutron beam is polarised before entering the first region and analysed before the detector. With both polariser and analyser in the same orientation. As shown before, any scattering in the sample causes a deviation from the spin-echo condition. Resulting in a drop in beam polarisation and therefore, a measured drop in intensity (I) at the detector. Meaning unlike SANS, SESANS does not require a position-sensitive detector as overall intensity is measured.

The instrument runs with neutrons aligned spin up and then spin down alternating between the two, and polarisation is found as

$$P = \frac{I_+ - I_-}{I_+ + I_-} \quad (2.43)$$

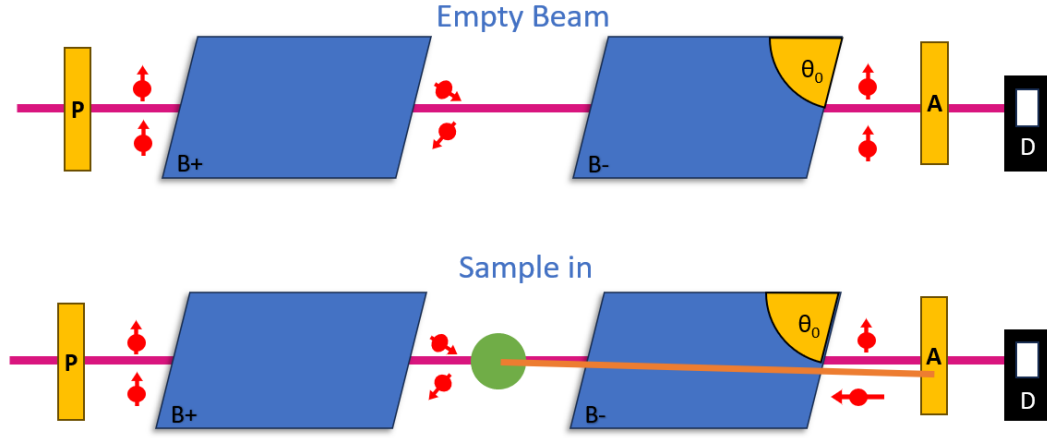


Figure 2.11: Schematic of a SESANS instrument with an empty beam and with a scattering sample in place. The neutron beam in pink is incident from the left and passes polariser (P) before two equal and opposite magnetic field regions B+ and B-, inclined a θ_0 . Before passing through the analyser (A) and being measured at the detector (D). Red arrows represent the direction of the neutron's spin.

Where I_+ is the intensity measured when the neutrons are aligned with spin up and I_- is spin down. The polarisation is measured initially for an empty beam (P_0). Due to the spin-echo condition, this is a maximum intensity at the detector accounting for any losses in the instrument. Secondly, a scattering sample is placed in between the fields and the polarisation is measured again ($P(z)$). The ratio of the polarisations (normalised polarisation) is calculated and relates to the total precession as

$$\frac{P(z)}{P_0} = \cos \Delta\varphi \quad (2.44)$$

and is a function of spin-echo length. This relates to the projection of the autocorrelation function $G(z)$ of a sample by [47]

$$\frac{P(z)}{P_0} = e^{\Sigma_t(G(z)-1)} \quad (2.45)$$

Where Σ_t is the fraction of neutrons that are scattered once. Given by

$$\Sigma_t = \lambda^2 t (\Delta\rho_0)^2 \sigma (1 - \sigma) \xi \quad (2.46)$$

where $\Delta\rho_0$ is the scattering length density of the sample, ϕ is the normalised volume fraction of the sample and ξ is the correlation length. The fraction of neutrons that are not scattered by the sample gives us the saturation of the polarisation (P_∞).

$$P_\infty = e^{-\Sigma_t} \quad (2.47)$$

And finally, the projection of the autocorrelation function can be related to values measures in a SESANS experiment by

$$G(z) = 1 - \frac{\ln \frac{P(z)}{P_0}}{\ln P_\infty} \quad (2.48)$$

Changing Spin-Echo length

In order to carry out a SESANS experiment we must scan across multiple spin-echo lengths. The way this is done depends on the neutron source and desired outcomes. Equation 2.42 shows that z depends on three instrument-defined variables, the magnetic field, neutron wavelength and inclination of the field. At a reactor source such λ is fixed and B is varied. At a TOF source neutrons arrive at the instrument in a pulse with varying wavelengths. Therefore, z is automatically varied across a pulse. To increase the accessible length scales further, the Larmor instrument at ISIS has the ability to change the shape of the field region and change θ_0 . In the standard operating mode measurements are carried out at a few different θ_0 angles depending on the length scales of interest. Larmor can also be operated in a pseudo-monochromatic mode in which θ_0 is varied incrementally and the data is binned by wavelength. Creating multiple single wavelength measurements.

2.3.7 Autocorrelation function

SESANS give a measurement that is analogous to the projection of the autocorrelation function for our sample. Therefore, it provides real-space information on the shape of features and their distribution in the interior structure of a sample. The autocorrelation function of a two phase stucture can be calculated mathematically by the procedure outlined here.

First, A two-phase system is defined by is density distribution ρ [40].

$$\rho(x, y, z) = \begin{cases} 1, & \text{Phase 1,} \\ 0, & \text{Phase 1.} \end{cases} \quad (2.49)$$

As the samples used in this work are all isotropic we can rewrite this for an isotropic system replacing x, y and z coordinates with r [47] (the distance from the center).

$$\rho(r) = \begin{cases} 1, & \text{if } r \text{ in inside phase 1,} \\ 0, & \text{otherwise.} \end{cases} \quad (2.50)$$

In conventional SANS intensities measured are proportional to the power spectrum ($I(q)$) of this distribution. This is the Fourier amplitude squared of $\rho(r)$

$$I(q) = \frac{1}{V\phi(1-\phi)} \left| \int_V e^{iqr} \Delta\rho(r) d^3r \right|^2 \quad (2.51)$$

In which V is the total volume of the system, ϕ is the volume fraction of phase 1, defined by

$$\phi = \frac{1}{V} \int_V \rho(r) dr \quad (2.52)$$

And $\Delta\rho$ is the density fluctuations around the average.

$$\Delta\rho(r) = \rho(r) - \phi \quad (2.53)$$

By calculating the inverse Fourier transform of $I(q)$ we arrive at the autocorrelation function ($\gamma(r)$).

$$\gamma(r) = \frac{1}{2\pi^2} \int_0^\infty \frac{\sin qr}{qr} I(q) q^2 dq \quad (2.54)$$

The projection of the autocorrelation function along the x axis is defined by

$$G(z) = \frac{2}{\xi} \int_0^\infty \gamma(x, 0, z) dx \quad (2.55)$$

where

$$\xi = 2 \int_0^\infty \gamma(x, 0, 0) dx \quad (2.56)$$

and is defined as the correlation length. For an isotropic density distribution, the projection $G(z)$ can be written in terms of r

$$G(r) = \frac{2}{\xi} \int_0^\infty \frac{\gamma(r) r}{\sqrt{r^2 - z^2}} dr \quad (2.57)$$

$G(r)$ therefore depends on the density distribution and hence the structure of the sample. In a SESANS experiment projection (G) is measured along the axis perpendicular to the beam direction and the direction of the polarisation. Hence, $G_y(x)$ is the projection along y with correlations in x.

Autocorrelation function of matrix of spheres

In this section, the projection of the autocorrelation function ($G_y(x)$) is calculated for a 3D matrix containing randomly distributed spheres. A 200x200x200 matrix was formed in Python containing spheres with a controlled radius and volume fraction (VF). Spheres were created one by one and prevented from touching or existing within one another for simplicity and to better represent a physical system. Pixels inside the spheres have a value of 1 and can be thought of as inside phase 1 as in Equation 2.50. Meanwhile, values outside spheres are 0 (outside of phase 1). An example of a phase matrix with sphere radius of 20 pixels and a volume fraction of 10% is shown in Figure 2.12.

Projection of the autocorrelation function was calculated for a range of VF matrices. Here a VF of 20% was generated. Firstly, a Fourier transform is performed on the phase matrix and the modulus squared is taken for every pixel. This gives an $I(q)$ matrix, such as a detector image in a SANS measurement. An inverse Fourier transform is

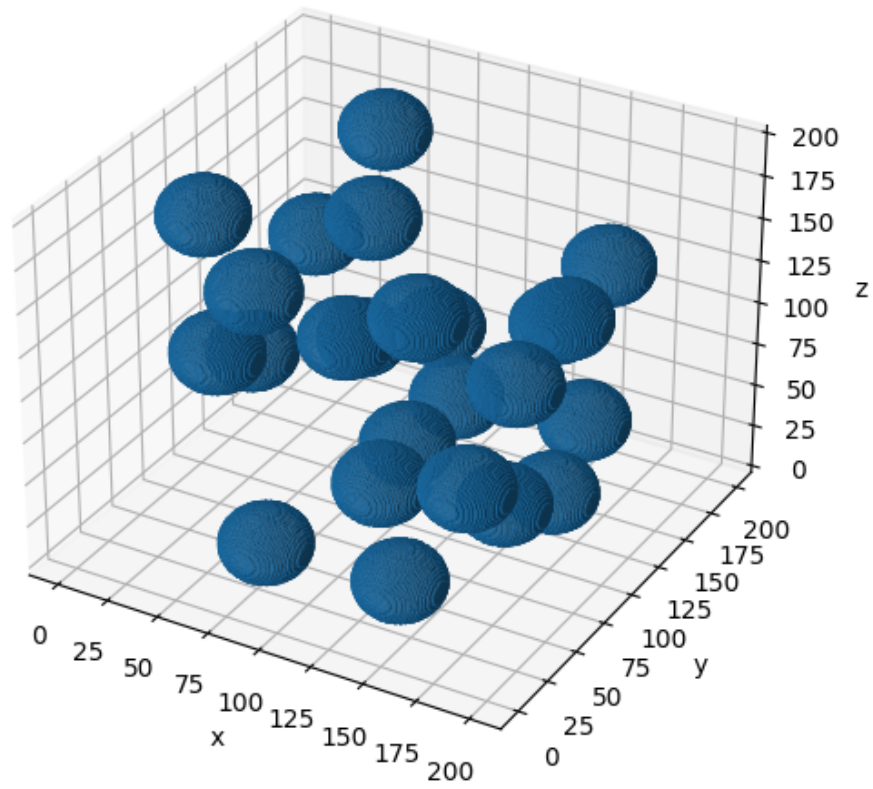


Figure 2.12: Model particle system used to probe $\gamma(r)$, for a 200x200x200 pixel box containing spheres with a 20 pixel radius at a 10% fill fraction.

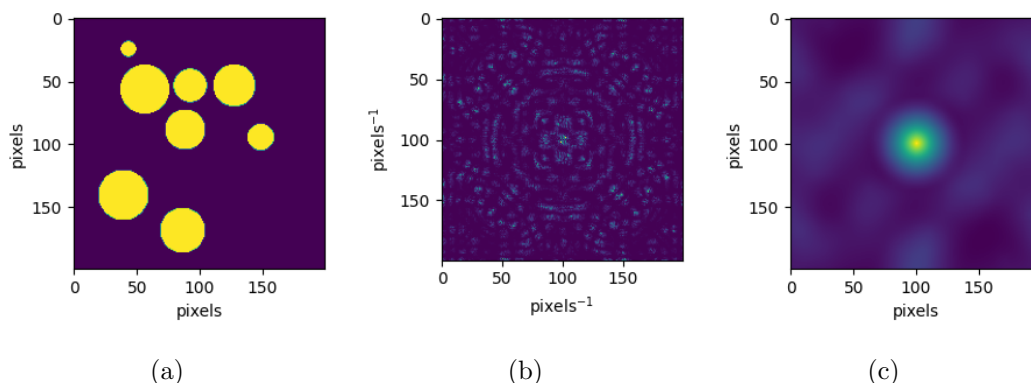


Figure 2.13: (a) A 2D slice of matrix containing random 20-pixel radius spheres, (b) modulus of the Fourier transform squared and (c) autocorrelation function. (b) represents $I(q)$ as measured in SANS and (c) represents a SESANS measurement.

then performed on this matrix resulting in the autocorrelation matrix $\gamma(r)$. 2D slices from the resulting matrices are shown in Figure 2.13.

The projection of the autocorrelation matrix is then calculated following Equations 2.55 and 2.56 giving a 1D data set. This is then repeated for 50 randomly generated phase matrices. The first 10 iterations along with the mean of all 50 are plotted in Figure 2.14.

This procedure was repeated for a range of VFs from 0.1% to 20% and the results are shown in Figure 2.15. This figure shows how increasing VF introduces a structure factor into the SESANS data in the form of an oscillation with periodicity at the correlation length.

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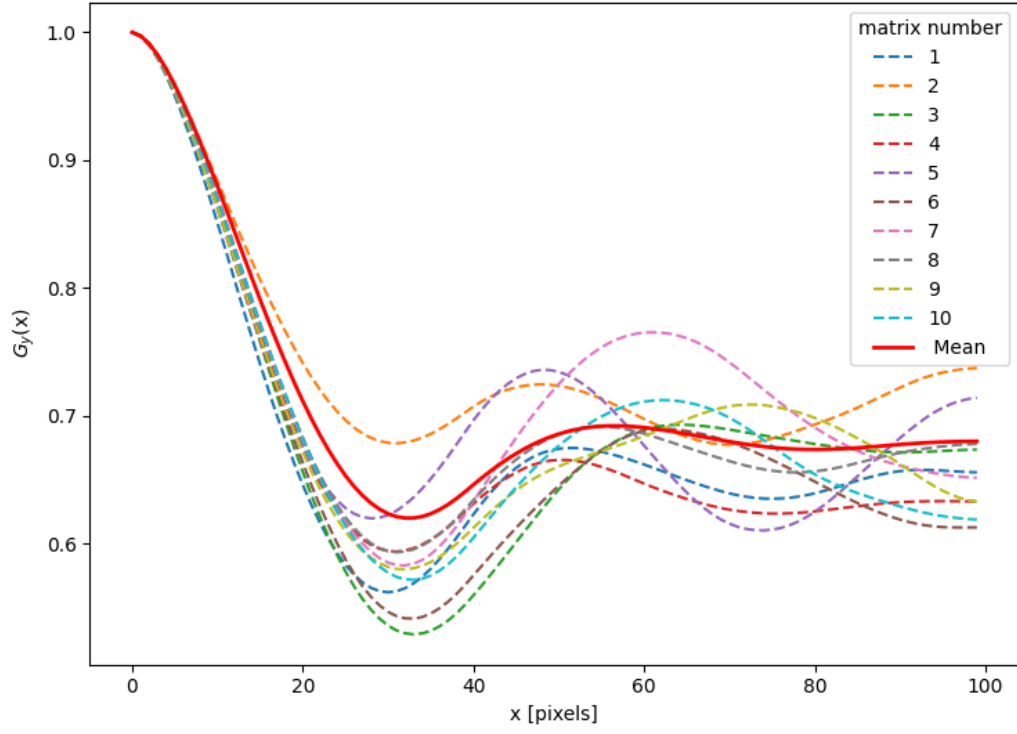


Figure 2.14: Projection of the autocorrelation function for spheres randomly arranged in a 3D matrix. Sphere radius of 20 pixels with a volume fraction of 20%. The matrix is simulated 50 times and $G_y(x)$ is calculated for each instance. Results for the 1st 10 matrices are shown along with the mean value for all 50.

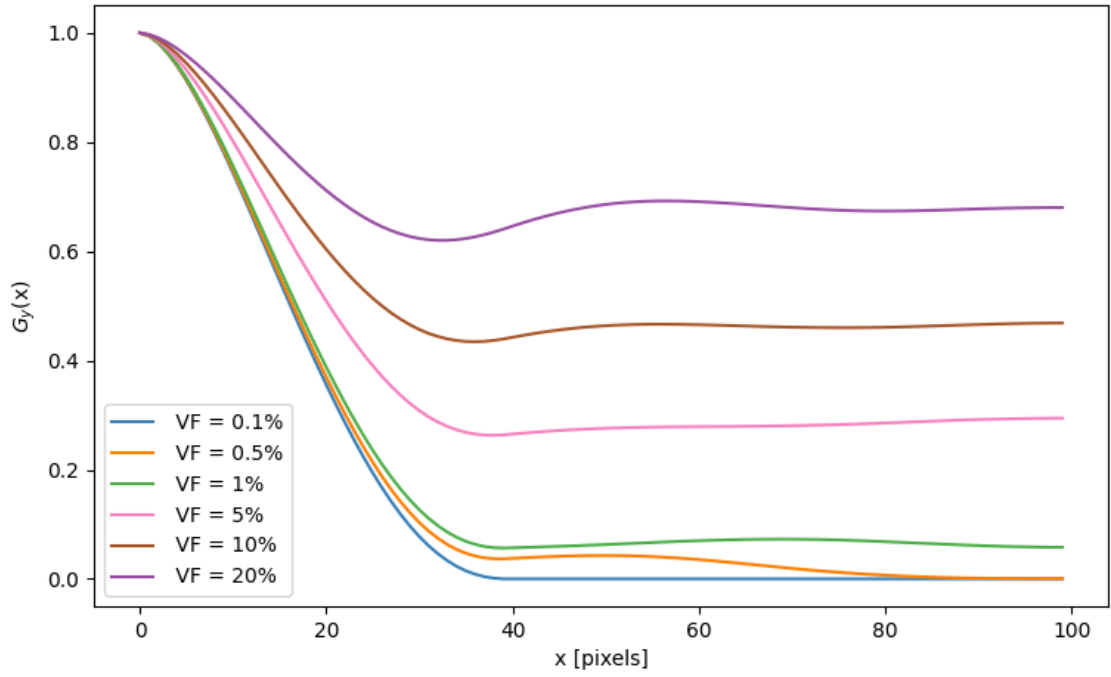


Figure 2.15: Projection of the autocorrelation function for 200x200x200 pixel matrices containing randomly positioned 20-pixel radius spheres at a range of particle volume fractions, denoted in the legend. Each line is the mean of 50 matrices of random spheres

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Chapter 3

Quantifying the free volume distribution in a crosslinked epoxy-amine through a combined PALS and molecular dynamics simulation study

In this chapter positron annihilation lifetime spectroscopy is used to measure the free volume in epoxy amine coatings. The experimental data from PALS is compared with molecular dynamics simulations. A simple solvent free, stoichiometric samples is used to best compare model systems. Both experimental and computational techniques found that epoxy amine coatings contained two discrete free volume void sizes. Through molecular dynamics simulations it was determined that the number of large voids increases with the level of cross-linking, possibly explained by increased packing frustration and a reduction in molecular mobility at high cross linking densities.

3.1 Foreword

This paper is prepared for submission to *Macromolecules*, this pending based on consultation with our industrial partners.

My contribution to this paper was the PALS measurements of the DGEBA : MXDA crosslinked networks. This involved experiments looking at solvent (water uptake) and its effects on the free volume along with utilising code that fitted a distribution of length scales rather than just a single free volume. The latter code was specifically written by myself and has previously been published in [1].

Supporting information is available in Appendix A.2.

3.2 Introduction

Crosslinked Epoxy-amine polymers are widely used in a variety of industries, including aerospace, automotive, and construction. The variety of uses ranges from corrosion protection [2] to prosthetic aortic heart valves [3]. The wide range of applications of epoxy-amines is made possible by the diverse characteristics and tunability of their mechanical and hence their barrier properties.

Globally the financial costs of corrosion are estimated to cost 3.4% of total world GDP (2013) [4] which equates to over \$2 trillion dollars. The high cost of corrosion comes from both preventing corrosion and also repairing the damage caused by the related effects of corrosion, damage that is not just limited to physical infrastructure. When corrosion causes damage, for instance in the oil and gas industry, the environmental impact can be catastrophic. For example in the 2008 Nigerian oil spill between 103,000 - 311,000 bbls of crude oil were spilled into the Bodo Creek area [5] causing the loss of income for many thousands of fishermen and huge environmental damage to large areas of mangrove forests.

The properties of an epoxy-amine coating depends on the specific combination of epoxy type and curing agent [6] along with the curing regime, i.e the thermal curing cycle time and temperature schedule which the formulation is exposed to. These are tuned to suit the required function. Epoxy-amines as corrosion-resistant coatings are often formulated with corrosion inhibitors to protect the substrate when damage occurs to the coating. High chemical resistance, toughness, and adhesion to a range of surface materials make for an excellent heavy-duty anti-corrosion coating [7]. Epoxy-amine systems are therefore the focus of much scientific and industrial investigation, aiming to optimise properties through a better understanding of the individual molecular components (epoxy resin and crosslinker) and the curing protocols used to produce these materials.

In corrosion protection, epoxy-amine coatings are usually mixed with solvents to allow the coating to be spray-applied. In this study a solvent-free formulation is used to gain a fundamental understanding of the epoxy-amine interactions and allow for direct comparisons to be drawn between experimental and computational results. This was seen as appropriate as all solvent is thought to be removed from the coating during the curing process.

Positron annihilation lifetime spectroscopy (PALS) is the primary technique throughout the literature for measuring free volume [8] [9]. PALS provides free volume information including void size and distribution in bulk samples. Whilst also being a low-cost and non-destructive technique. Free volume studies are used to analyse and explain the macroscopic properties of polymers and link them to the nanoscale structure. PALS measurements have been used by Cangialosi et al [10] to quantify how free volume changes in polycarbonate (PC) during physical ageing. It was shown that the size of free volume voids in PC remained consistent throughout ageing while the number of voids decreased, a process described by the polymer relaxation time. Furthermore, free volume effects of water absorption were analysed in epoxy amines by Wang *et al.* [11]. It was shown that void size decreased with water absorption. Moreover,

two characteristic void sizes were identified which both decrease in size with water absorption.

Here the aim is to both validate computational results by like-for-like comparison with experimental data, along with drawing further insight from experimental data. In corrosion-resistant polymer coatings, free volume is used to investigate, pore sizes and the relation to water and ion ingress. Along with the effects of water absorption on the polymer matrix. Physical ageing of coatings is also an important factor when considering coatings and their long-term performance.

Computer simulations, such as molecular dynamics (MD), can be used to analyse crosslinked polymers at the nanoscale level. This approach allows for more in-depth knowledge of epoxy-amine networks than is possible through experimental methods alone, for example calculating the binding energy of a single DGEBA molecule to an iron oxide surface[12, 13]. Unlike experimental systems, *in silico* methods allow for the precise control of crosslinked density. *In silico* methods also allow for the investigation of a wider range of epoxy-amines in a more cost-effective fashion. A non-trivial task in the simulation of crosslinked polymers is the generation of the crosslinked structures. In the literature several approaches have been used to construct polymer networks, these can broadly be split into three approaches; single step, multi step, and dendritic growth.

Yarovsky and Evans [14] used a single step process to create a virtual model of low molecular weight phosphate modified epoxy resins, in which all crosslinks are formed in one step. These resins are often used in water-soluble coatings and theoretical simulations have found qualitative agreement with experimental results in terms of their adhesion and barrier properties. A comparison of the single step method and a multi step method which features geometry optimisation or short MD runs between crosslinks formations has been investigated by Demir and Walsh [15] for diglycidyl ether bisphenol A (DGEBA) with a diethyltoluene diamine (DETDA) and by Monk *et al.* [16] for Novolac-type phenolic chains. In both cases, the multi step method was found to yield a higher degree of crosslinking and produce lower energy structures with less internal stress.

Lin and Khare [17] and Khare and Khare [18] used a slightly different single-step approach based on a Monte Carlo method to produce the optimum connectivity of the system in one step which is then relaxed. This approach was compared to a multi step relaxation scheme by Jang *et al.* [19] using DGEBA and poly(oxypropylene) diamine (POP) who found that the networks formed by the two methods are qualitatively different, with the single step process leading to fewer larger fragments than the multi step process when cutting each crosslink between the amines. However, they also found that this structural difference had limited impact on the mechanical and thermal properties of the system. Dendritic growth methods have been employed with the aim to capture heterogeneity of the crosslinked system by Bandyopadhyay and Odegard who found that the crosslink distribution had no discernible influence on the elastic modulus or the linear thermal expansion coefficient [20]. A multi step crosslinking mechanism is by far the most common in the literature as the multiple steps allow the system to relax between bond formation, however there is no overall consensus on the

simulation procedure, i.e. the length of MD runs, the cut-off used, and the reactivity of primary and secondary amines. Monk *et al.* [16] have quantitatively studied the influence of initial volume, crosslinking approach, relaxation time and equilibration temperature on the generated structures and found that for highly crosslinked systems (> 70%) they were all shown to influence the final structure. We also direct the reader to the review by Li and Strachan [21] for an overview of the different approaches.

Here we focus on a system of diglycidyl ether bisphenol A (DGEBA) and m-xylylenediamine (MXDA) that are used for corrosion protection coatings as shown in Figure 3.1. In this study, we measure the free volume (FV) and fractional free volume (FFV) of an epoxy-amine system based on DGEBA and MXDA, which is a simplified model of a corrosion-resistant coating, using PALS and MD modelling. FV is a measure of the average pore size present in a material, while the FFV is the overall percentage of pores in a material. FV and FFV are important parameters that influence the corrosion resistance of epoxy-amine coatings [22].

By using both PALS and MD in parallel throughout this study the aim is to gain further insight into a simplified corrosion resistant coating, while also validating the use of the combined technique. A simple solvent free DGEBA-MXDA coating at a stoichiometric ratio is used throughout this experiment as a standard example of a corrosion resistant epoxy coating. If proven for this sample the combined PALS/MD technique should be used on more complex systems and formulations to provide insight to these complex systems.

An additional aim of this work is to compare the results of PALS and MD in order to validate the MD findings. If MD is found to be reliable in the measurement of FV and FFV along with providing molecular detail of cured epoxy-amine systems, it could be used as a high throughput method to quickly analyse large numbers of formulations and cure conditions. This would allow formulations with preferable characteristics to then be synthesized and validated physically by PALS and other techniques (DSC, diffusion and uptake measurements). Due to the properties of epoxy-amine coatings being a complex result of formulation and cure procedure, this would save time and money in developing new and effective coatings that are developed and guided by simulation.

3.3 Experimental Details

3.3.1 Sample Preparation

Samples were prepared by mixing diglycidyl ether bisphenol A (DGEBA) and m-xylylenediamine (MXDA) in a glass beaker and stirring for 5 minutes with a glass rod. Both epoxy and amine were provided by Akzo Nobel and used as received. The samples were then left for 15 minutes at room temperature before pouring into 6 individual 25 mm square PTFE moulds. They were then cured in an oven at 60°C for 2 hours, 100°C for 1 hour and 160°C for 1 hour. All samples were prepared at stoichiometric ratio, using 12.17g of epoxy and 2.41g of MXDA.

Stoichiometry in this case is met when the number of epoxy molecules is half

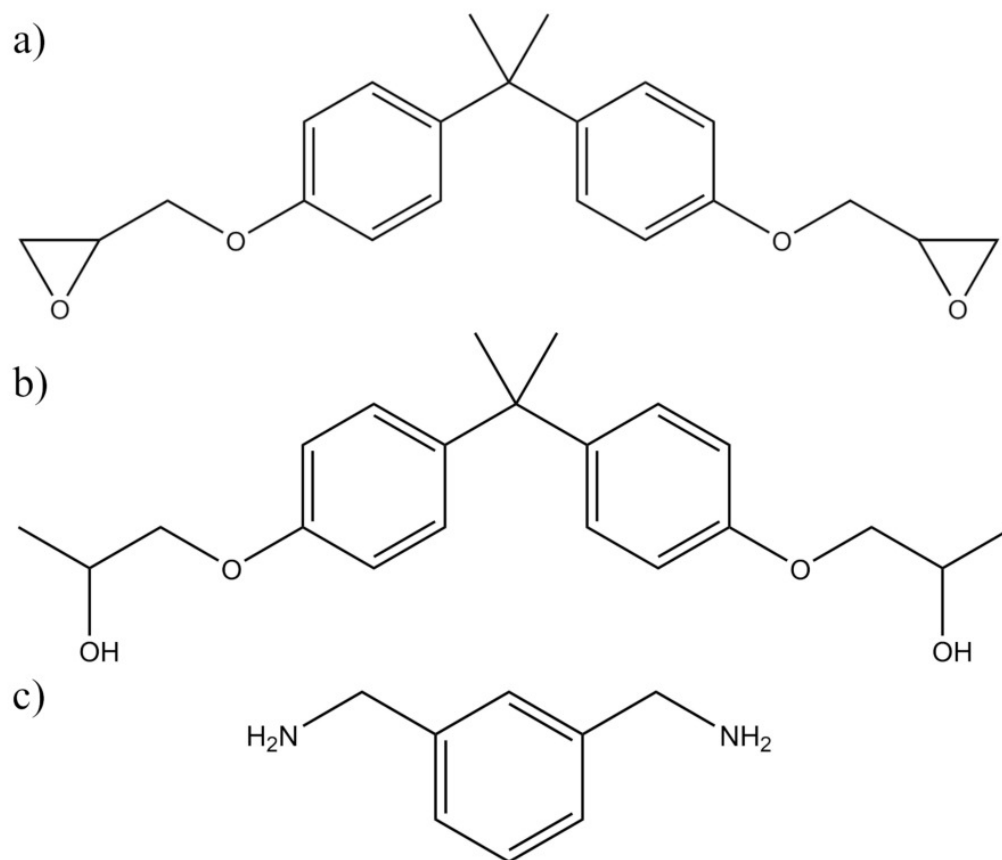


Figure 3.1: Chemical structure of a) DGEBA b) DGEBA with the epoxy rings opened as used in the molecular dynamics simulations, and c) MXDA

the number of amine molecules, allowing each amine's amino group to react with an epoxide ring once as a primary and then as a secondary amine. A stoichiometric ratio ensures as close to 100% crosslinked structure as possible. Although it is hard to know if 100% crosslinking is achieved across the entire sample. It has been shown by Fourier transform infra-red spectroscopy that cured samples can contain around 10% residual epoxy groups[23].

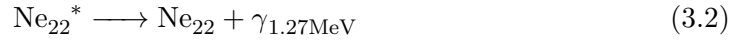
The resulting samples were 25mm translucent squares with a varying thickness of around 4 mm. Controlling the thickness of samples is difficult due to the meniscus effect of the viscous pre-cured mixture. However, slight deviations in thickness will not affect PALS results as this is intrinsically an averaging technique. Consideration was taken to keep the samples thin to decrease PALS measurement times. To ensure a consistent thickness milling would be required which could heat the surface and alter the structure.

For a PALS measurement, 2 identical samples are required to form a sample sand-

wich around the positron source. To allow for repeat measurements 6 identical samples were made.

3.3.2 PALS Theory

Free volume (FV) and fractional free volume (FFV) were measured experimentally using positron annihilation lifetime spectroscopy (PALS) using the custom-built Sheffield PALS instrument [24]. This instrument uses a sodium 22 positron source. The Na22 decays by releasing a positron, to a high energy state Ne22 which subsequently stabilises (within 3.7 ps) by the release of a 1.27MeV gamma, known as the “birth gamma”.



The resultant positrons are implanted into the sample where they quickly thermalise and then annihilate via 3 processes [25]. The 3 annihilation processes are: free annihilation where a positron decays with an electron (e^+), para-positronium decay (pPs), and ortho-positronium decay. The first two of these decays, e^+ and pPs, occur in 0.1-0.5 ns and 0.125 ns respectively and are independent of the material in which they occur. The 3rd decay process, via oPs, is dependent on the void size of the material, and is therefore the probe for free volume. In this process a positron and an electron form a positronium atom in a triplet state. This atom is more stable in vacuum. Here its lifetime is larger than 1 ns and depends on the void size. Lifetime is determined using the Tao-Eldrup bubble model [26] [27].

Within the Tao-Eldrup bubble model oPs is assumed to be trapped within an infinite potential well with spherical symmetry. For the positronium to annihilate its wavefunction must overlap with the wavefunction of the surrounding electrons. The annihilation rate of the oPs therefore depends on the overlapping integral of the functions and can be described by the following equation:

$$\frac{1}{\tau_{oPs}} = 2 \left[1 - \frac{R}{R + 1.66} + \frac{1}{2\pi} \sin \frac{2\pi R}{R + 1.66} \right] \quad (3.3)$$

Where τ_{oPs} is the annihilation rate and R is the free volume void radius.

When the oPs annihilates a pair of 0.511MeV gammas are released known as the “annihilation gamma”. A PALS instrument detects both the birth and annihilation gammas, using fast plastic scintillators and photomultiplier tubes and calculates the positron lifetime. A coincidence unit is used to discriminate any gammas arriving more than 50 ns apart, as these are assumed to be from separate decay events.

3.3.3 PALS Methodology

PALS measurements were carried out by placing the Na22 source between a pair of identical samples before placing this “sandwich” between the 2 detectors of the Sheffield PALS instrument. Data was recorded using the QtPALS software [28]. The instrument

was allowed to count until 1 million annihilations were observed (measurement time of around 6 hours). Each measurement was repeated twice for each sample pair, 3 pairs of samples made for a total of 6 measurements. All samples were initially measured dry, then water-saturated and measured wet before drying and then remeasuring.

Soaking Procedure

To measure the effect of water uptake on the FV and FFV of the samples they were then soaked in water in individual dishes at 50°C. The elevated temperature was to increase the diffusion rate of water into the sample and achieve water saturation faster. Due to the time to complete measurements for 1 sample being ~12 hours, soaked samples were measured on subsequent days, therefore samples were soaked for 5, 6, or 7 days. However, all samples had reached a state of saturation as mass had stopped increasing. The mass did not change on the additional days due to the slow fast uptake characteristics. Additional days soaking can be treated as wet storage. After measuring wet the samples were dried in a vacuum oven at 60°C until the mass returned to very close to the original dry mass value (around 4 days).

The uptake of each sample is given in Table 3.1. Sample number indicates which sandwich a sample was in and A and B are used to identify individual samples within a sandwich.

Free volume and fractional free volume is measured for each individual sample in 3 conditions; initial, wet and dried.

Sample	Days Soaked	Final Mass Uptake (%)	Mass Uptake/Loss After Drying (%)
1 A	5	1.319	-0.133
1 B	5	1.199	-0.115
2 A	6	1.266	-0.030
2 B	6	1.221	0.001
3 A	7	1.257	-0.086
3 B	7	1.635	-0.190
Average	6	1.316	-0.092

Table 3.1: Water uptake of each sample during soaking

3.3.4 PALS data treatment

Data from the QtPALS software is in the form of a histogram of oPs lifetimes. Once 1 million lifetimes were measured the data was analysed using custom-written Python code. The data was fitted to a convolution of a Gaussian and 3 exponential decays. Each of the exponential decays represents an annihilation process. The Python fit is shown in Figure 3.2. Here sample 1 is shown in all 3 stages of the soaking cycle; initial (stored in a decicator since cure), wet (soaked until water saturated), dried (dried in a vacuum oven post soak). The raw PALS data is presented along with Python fit and

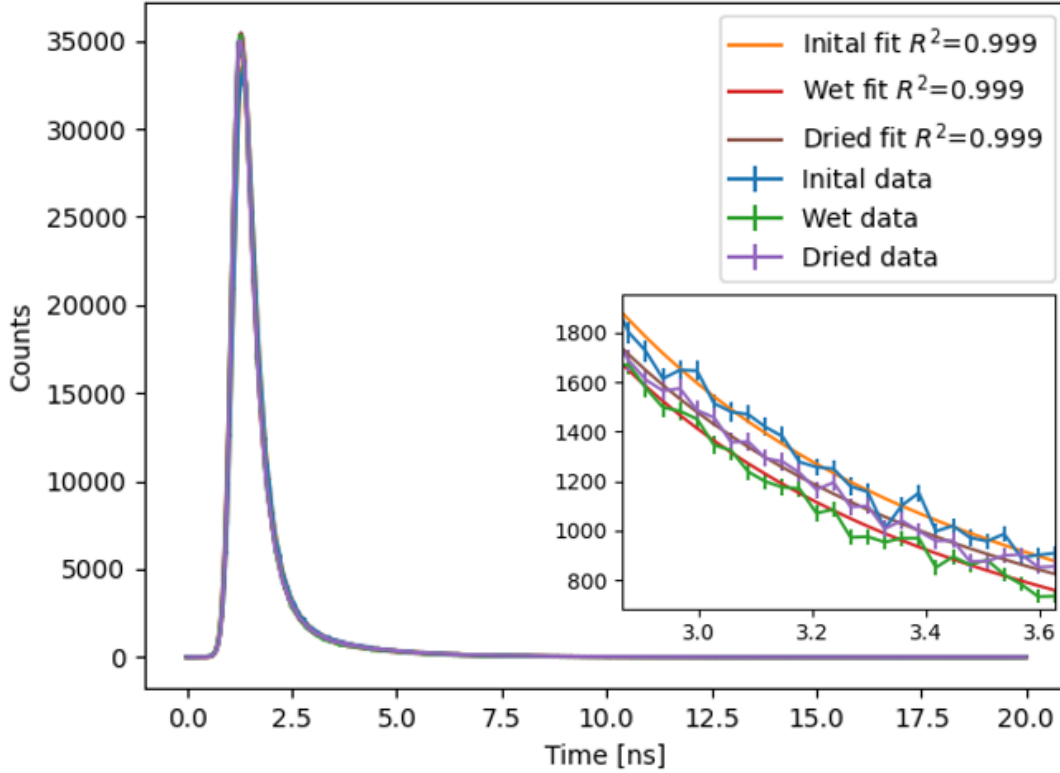


Figure 3.2: Raw PALS data for sample 1 throughout the soaking cycle. Plotted alongside Python fit with R^2 values reported in the legend. Insert contains a zoomed section in which there is clear separation in the data.

goodness of fit R^2 value. A consistent R^2 value of 0.999 show that the fit very closely fits the data in all cases.

The Tao-Eldrup model [27] [29] was then used to convert the decay rate of the oPs into an average free volume pore size. FFV is calculated by multiplying the FV by intensity.

$$FFV = I^3 * FV \quad (3.4)$$

Intensity is calculated by the ratio of the exponential heights, I^3 is the intensity of the oPs exponent calculated by:

$$\frac{I^3}{(I^1 + I^2 + I^3)} \quad (3.5)$$

Fractional free volume is a measurement of the total volume of the sample that is made up by free volume voids measured as a percentage of the total volume.

The PALS spectrum was also analysed using the CONTIN-PALS FORTRAN code originally developed by Provencher[30] and adapted for PALS by Gregory and Zhu[31]. This code was executed using a python version implemented by Petschke[32]. This program solves the Fredholm integral equations to identify multiple exponentials in

the lifetime data. We use a silicon wafer measured for 4 million counts to obtain an instrument resolution function. This was used because a highly ordered single crystal will provide a single lifetime response[31]. Silicon wafer was provided by Prolog Semicor, LTD with a thickness of 4 mm and a diameter of 50 mm. The wafer was test grade dilicon doped with boron, with an orientation of $100 \pm 1^\circ$ and a resistivity of $1 - 50 \Omega cm$.

3.4 Computational Details

Simulation details

In this work we have performed MD simulations for a crosslinked resin consisting of DGEBA and MXDA using LAMMPS [33] with a standard velocity-Verlet [34] algorithm to integrate the equations of motion using a timestep of 1fs. A Nosé-Hoover thermostat and barostat [35] [36] are used to maintain a constant temperature and pressure. The long-range electrostatic forces are handled using a standard particle-particle-mesh (PPPM) solver [37].

The OPLS-AA force field [38] was used and the systems were prepared using LigParGen [39] with SPC-flexible water [40], and charges assigned using the 1.14*CM1A utility [41]. In all cases standard Lorentz-Berthelot mixing rules are used to represent cross interactions with a cut-off radius of 10Å. More details of the parameters used and charges can be found in the SI.

Crosslinking procedure

Each system consists of 256 DGEBA molecules with 128 MXDA, corresponding to a stoichiometric ratio as each DGEBA molecule can form two cross links, whilst each MXDA can form four cross links. Note that here the epoxide group in DGEBA is modelled as already having been opened as shown in Figure 3.1(b).

Although there are several ways to produce a crosslinked structure many of these do not provide enough technical information or simulation specifics to follow the procedure. Demir and Walsh [15] have addressed this issue in their paper and produced a robust, easily reproducible protocol that has been specified for LAMMPS and shown to produce realistic crosslinked structures. Therefore, we adopt Demir and Walsh’s protocol which is summarized in Figure 3.3. Note that as we are using a different force field to the one used by Demir and Walsh (OPLS-AA v.s DRIEDING [42]) the relaxation values are slightly different.

The initial configuration is produced by randomly packing the molecules into a cubic simulation box with sides 7.0nm using PACKMOL [43]. The liquid mixture is then initialised and equilibrated by heating to a high temperature ($T = 1000K$) and cooling to the crosslinking temperature of 500K, where the system is then annealed by repeated heating and cooling between 500K and 1000K. In each annealing cycle, the radial distribution functions (RDFs) are calculated over the first 0.2ns and compared. The system is defined as having reached equilibrium when no visible change in RDFs

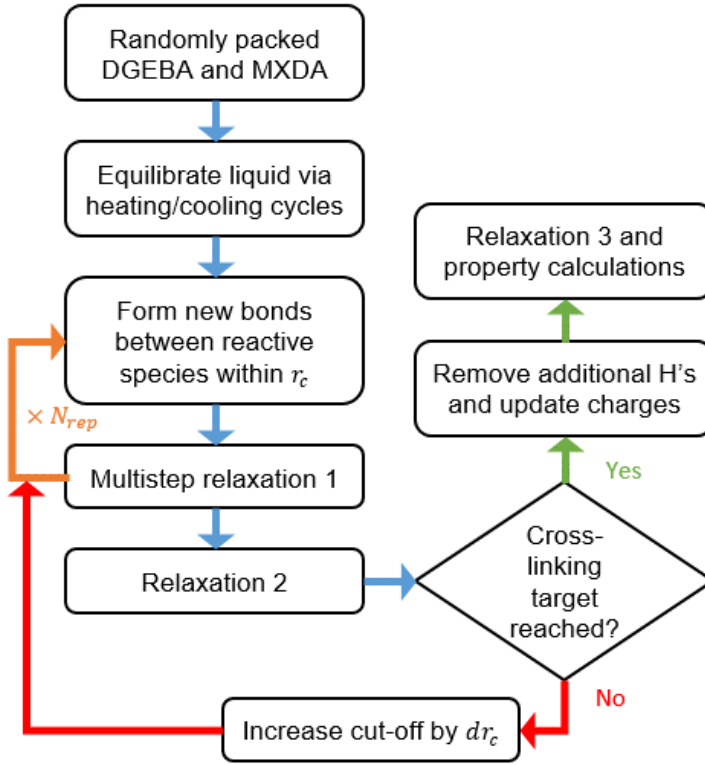


Figure 3.3: Flowchart of the MD crosslinking procedure

is observed. We use the central quarternary carbon in DGEBA and the carbon atom between the two substituted sites in MXDA as the reference atoms for the RDF calculations. The annealing step was repeated 6-8 times to ensure the system was fully equilibrated. Representative examples of the calculated RDFs can be found in the Supplementary Information (SI).

After the system is fully annealed, new bonds are formed between reactive groups that are closer than a specified cut-off distance r_c , initially taken as $r_c = 3\text{\AA}$. The newly formed bonds are initially far longer than the equilibrium length in OPLS-AA and therefore a multi step relaxation that gradually increases the bond constant and decreases the equilibrium length is used to relax the system. More details are given in the SI. This step is repeated $N_{rep} = 10$ times after which an isobaric-isothermal NPT simulation is run for 50ps at 500K and if the target number of crosslinks is not reached then the cut-off distance is changed as $r_c = r_c + dr_c$, where $dr_c = 0.5\text{\AA}$ and repeated until the target crosslinking amount is reached or until $r_c = 10\text{\AA}$. The system topology is then updated by removing the excess hydrogens and updating the partial charges on the atoms. Finally, the system undergoes a final relaxation run. In all cases the network properties are calculated over three independent crosslinked systems.

We have investigated systems with a crosslinking amount of 50, 80 and 98%, where

98% is the maximum crosslinking value achieved using this methodology. We have analysed the behaviour of each system with 0, 1, 2, 3, and 5%wt water content, corresponding to 0, 60, 120, 180 and 300 water molecules, respectively. In all cases, the water is added to the system in the initial configuration stage. To confirm that adding water prior to the crosslinks does not alter the properties of the structures, for the case of 5%wt water content, we deleted all the water molecules effectively, drying out the sample at a range of temperatures using *NPT* simulations. In all cases above 400K, the density of the system returned to that of the dry state. At 300K, to overcome the slow dynamics of the system, an annealing step is taken where the system is heated to 500K and cooled to 300K, at which point the density is that of the dry state for all crosslinking values (see SI for more information).

Simulation Analysis

The fractional free volume, pore size distribution and solvent accessible surface area (SASA) of the crosslinked system were calculated using Poreblazer [44], this was for frames taken every 50 ps over a 1 ns run. When calculating the free volume, the water molecules were removed and the SASA was calculated using a water probe and was then averaged over all frames and three independent runs for each condition.

3.5 Results and Discussion

3.5.1 PALS Results

Average free volume

The average free volume (FV) and fractional free volume (FFV) are plotted alongside the soaking status of the sample in Figure 3.4.

Figure 3.4 shows a clear reduction in free volume and fractional free volume when a sample is water soaked. FV reduced from $71.1 \text{ \AA}^3$ to $67.4 \text{ \AA}^3$ when the sample was soaked and then increased to $70.1 \text{ \AA}^3$ when dried. FFV followed a very similar trend reducing from 13.9% to 12.6% on soaking a decrease of 1.3% and increasing back to 14.0% on drying. This decrease in FFV on soaking corresponds almost exactly with the average water uptake of 1.3% by mass as shown in Table 3.1. The decrease in both FV and FFV indicate that the water penetrates the free volume sites and sits within the voids.

Figure 3.4 shows that there is some hysteresis, with a slightly lower value for both FV and FFV after soaking and re-drying the system. This is unlikely due to water remaining in the system as the final mass after drying is slightly lower than the initial mass for all samples as shown in Table 3.1. This indicates that the drop in FV and FFV between initial and dried samples is most likely due to water plasticizing the polymer and allowing the network to relax[45], forming a more dense system with smaller voids after the soaking cycle.[46]

Despite all the samples being prepared identically, significant differences were found between samples and consecutive measurements of the same sample (runs) (Figure 3.5).

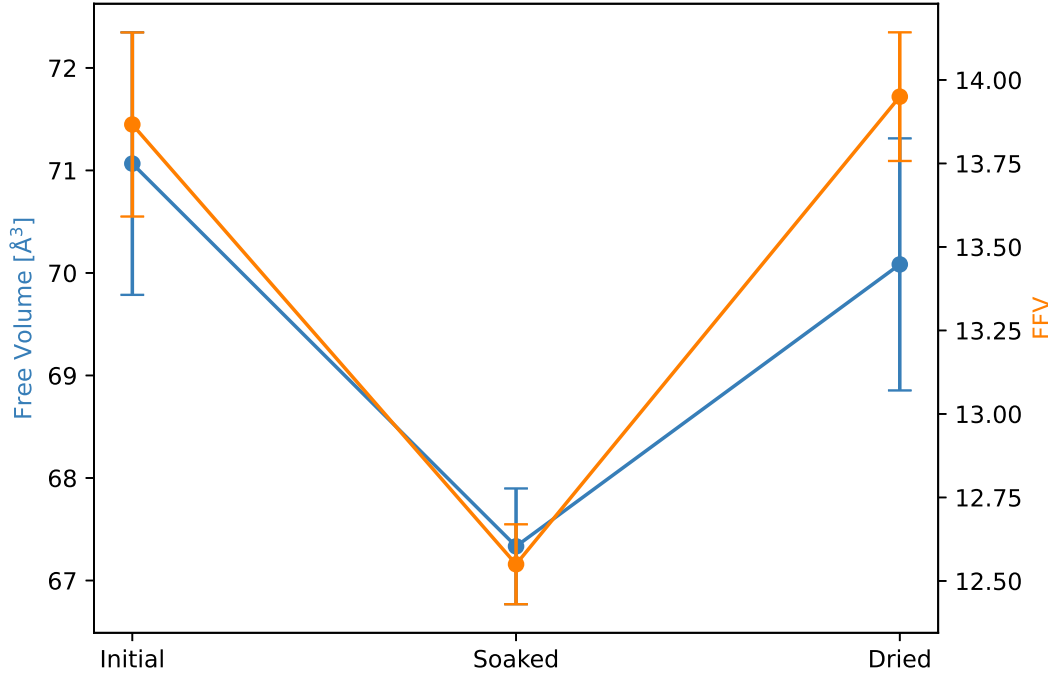


Figure 3.4: FV and FFV averaged between samples and runs, against sample soaking status. Error bars correspond to 1 standard deviation.

We found that the precision of the FV and FFV was similar for all time count lengths, however the time required to run the experiment increased drastically, with 16 million counts taking around 100 hours. This indicates that the precision of a PALS measurement is low. However, by taking the average of multiple samples, we are confident in our results and the trend. To attempt to understand the source of uncertainty we carried out a series of longer time count measurements at 2, 4, 8, and 16 million counts for a poly-lactic acid control sample. FFV results are more consistent than the FV, indicating the inconsistencies may result from the fitting.

Lifetime distribution

The lifetime distribution results from the CONTIN-PALS program were averaged between the 3 samples and 2 repeat measurements, shown in Figure 3.6 (individual spectra are available in SI).

The results show 3 or 4 distinctive peaks each attributed to a positron lifetime. The shortest lifetimes below 500 ps are due to the pPs and free positron annihilations. The two peaks above 500 ps are due to two different oPs annihilations[47]. An in-

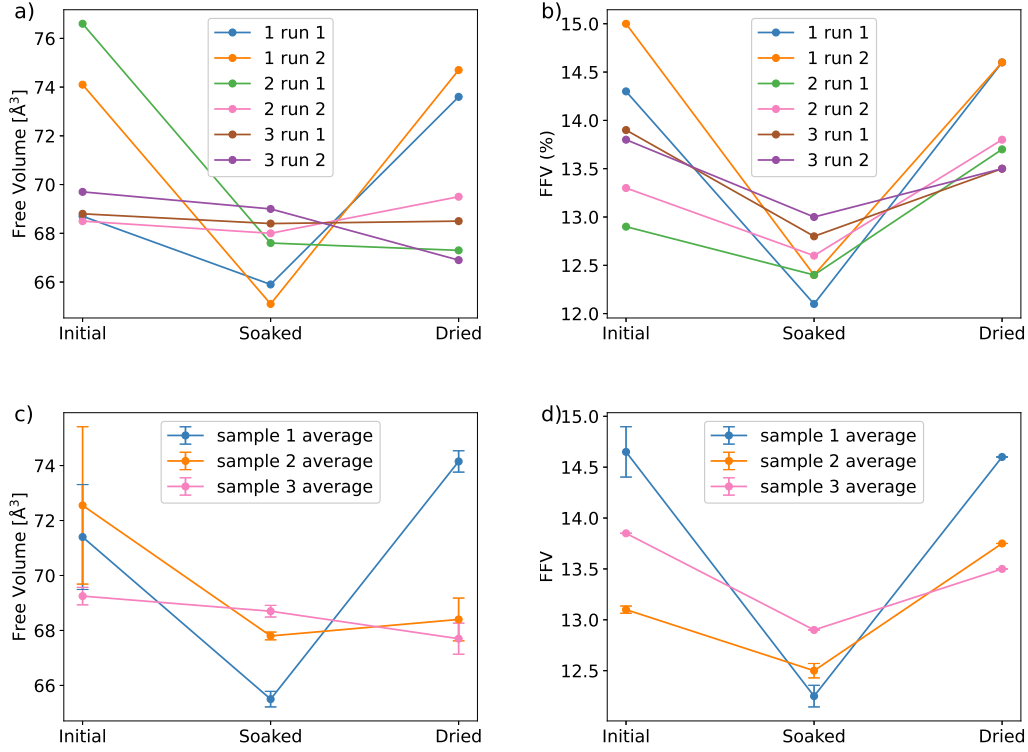


Figure 3.5: Individual sample PALS fitted data a) free volume and b) FFV results are shown, with each sample being measured twice. The average c) free volume and d) FFV for each sample is also shown.

crease in intensity in the free positron exponent has previously been attributed to the presence of hydrogen between water and the hydroxyl groups [11] however, we cannot draw conclusions from the peaks below 500 ps as they are below the resolution of our instrument. The resolution was calculated by measuring the full-width-half-maximum of the rise in the PALS spectrum for a silicon wafer, and found to be 411 ± 1 ps. This explains why we sometimes see both pPs and free positron peaks and sometimes they are combined into one. this pattern was also true for Polylactic acid standard samples measured multiple times at 2, 4, 8 and 16 million counts.

For clarity, we have re-plotted the data with only the oPs lifetimes furthermore, life-time has been converted into free volume diameter using the Tao-Eldrup model[29][27]. This data is presented in Figure 3.7. From the data, it is clear that in all states of the soaking-drying cycle there are 2 void sizes present, with diameters of 4.7 and 7 $\text{\AA}$. From this data, it is hard to draw conclusions as to how the distribution changes during the cycle.

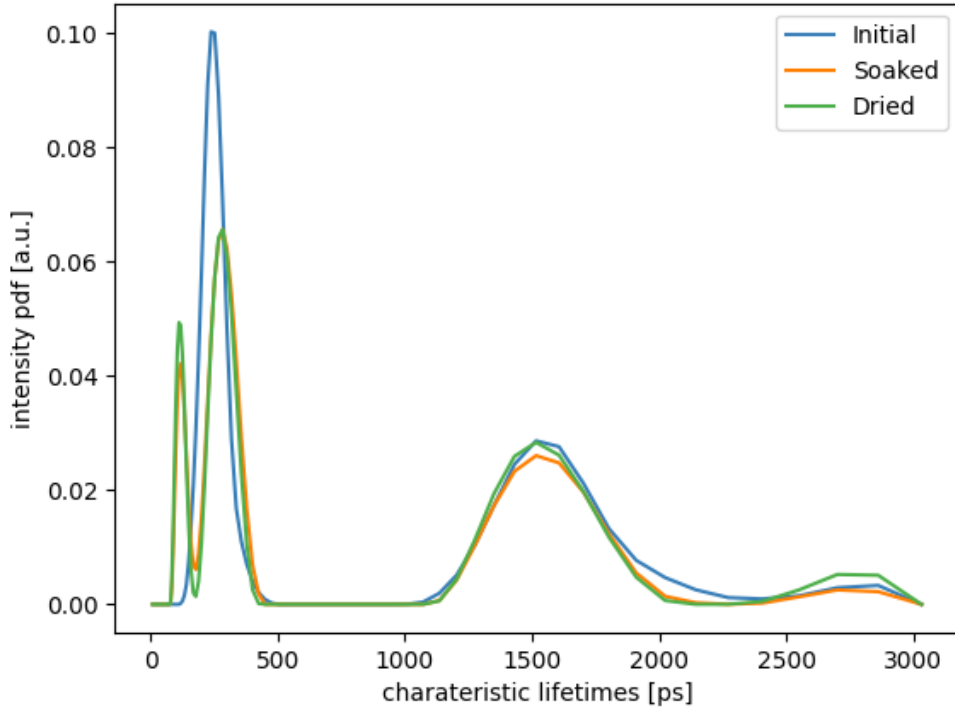


Figure 3.6: PALS Lifetime distribution of epoxy amine samples during the water soaking cycle

3.5.2 Molecular Dynamics Results

The atomistic model was validated against literature data for the glass transition temperature (T_g) and density (ρ) and the results are summarized in Table 3.2. For more details including how T_g is calculated, see the SI. In all systems the free volume formed

Property	Simulation value	Literature experimental value
DGEBA ρ / g cm ⁻³	1.06	1.16 [48]
MXDA ρ / g cm ⁻³	1.00	1.03 [49]
T_g / K at 0% crosslinking	275	237 [50]
T_g / K at 50% crosslinking	303	299 [50]
T_g / K at 80% crosslinking	388	353, [50] 330 [51]
T_g / K at 98% crosslinking	395	394 [50], 392 [51]

Table 3.2: Bulk properties calculated from the atomistic simulations and comparison with experimental findings in the literature.

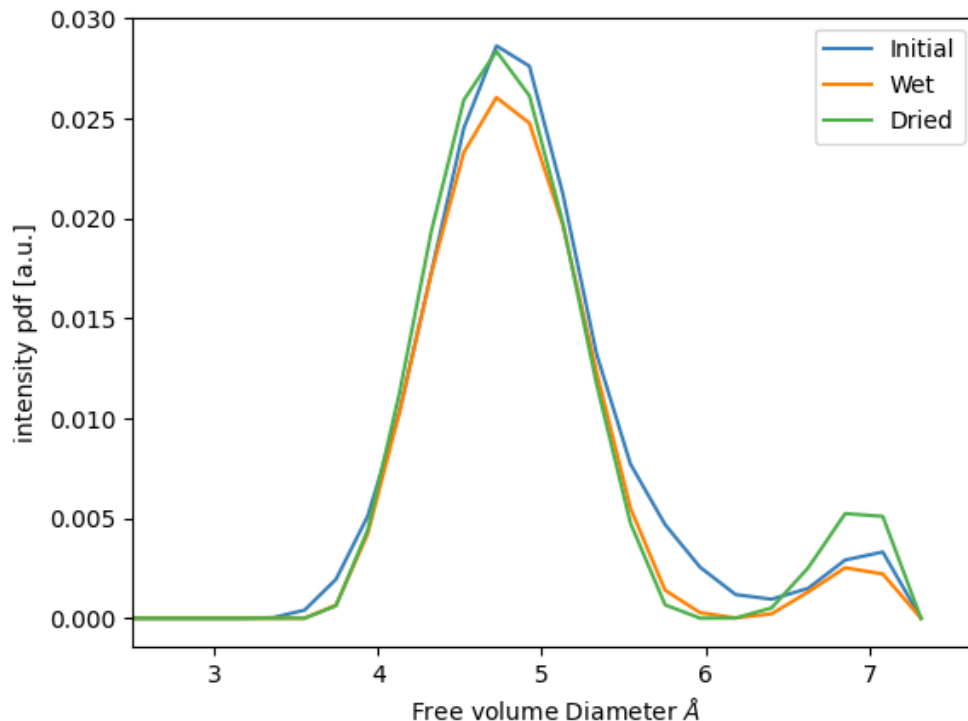


Figure 3.7: Distribution of Free Volume void diameter, as determined by CONTIN PALS fitted data

is in the form of isolated voids (Figure 3.8a) as opposed to interconnected networks. From visual inspection of the resulting atomistic structures presented in Figure 3.8a it appears that no phase separation occurs for all water concentrations probed. However, the pore size distribution (PSD) plots show that for the highest water content (5%wt) we observe the formation of larger pores at all crosslinking values. This observation is consistent with previously reported literature that finds the formation of water clusters above 4%wt water for a variety of epoxy-amine systems. It has previously been suggested that adsorption mechanism of water occurs through three stages; first water fills the intrinsic available free volume before forming clusters within the polymer matrix [52–56].

As water content increases, the density of the polymer matrix decreases and the free volume increases. Overall, the effect of crosslinking is independent of water concentration and as such, in the following two sections we will use the dry film as an example, however the analogous data and figures for the other water contents can be found in the SI.

The molecular dynamics simulations are able to investigate partially cured systems and look at how the pore distribution evolves during the crosslinking process. This

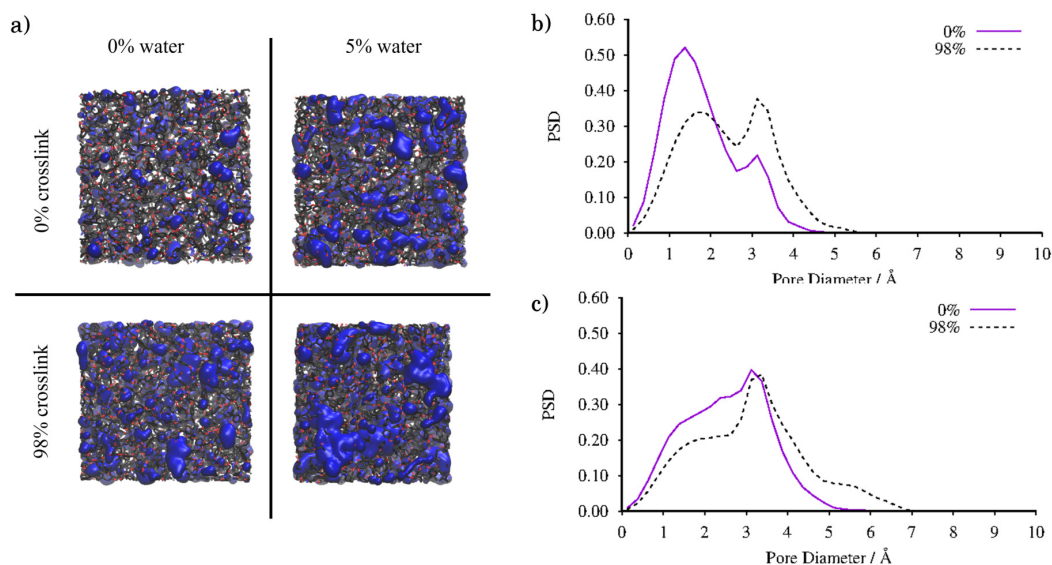


Figure 3.8: a) Example configurations for 0%wt and 5%wt water content with 0% and 98% crosslinking. The free volume is represented by blue surfaces, whilst the molecules are shown by the sticks (black = carbon, red = oxygen, blue = nitrogen). The hydrogen atoms in the polymer and the water molecules are not shown for clarity. b) and c) show the pore size distributions (PSD) for 0 and 5%wt water content respectively.

is not possible to do experimentally due to the curing time and PALS data collection duration. The fractional free volume (FFV) for all water contents show the same trend, with a large increase from 0-50% crosslinking and a more gradual linear increase from 50-98% crosslinking. This is echoed in the actual free volume change (given by system volume multiplied by FFV). We find a bimodal distribution of pore sizes at all crosslinking percentages, with a smaller pore at approximately 1.5 Å and a larger pore at approximately 3.5 Å. This bimodal distribution is in agreement with experimental findings by Shantarovich et al [57] who find a bimodal distribution with peaks at approximately 2.5-3.5 Å and 3.5-7.0 Å for a range of glassy polymers using PALS. The relative heights of these two peaks changes with crosslinking percentage, with the peak at the smaller radius decreasing in relative height and the larger radius as the crosslinking percentage increases. This indicates that larger pores are formed as more crosslinks are formed, which is also seen with the increasing fraction of large pores. This feature of large pores increasing in number with increase in crosslinking percentage is best displayed in Figure 3.9. In sub figure b pore size distribution is shown for a series of samples with changing crosslink percentage, showing an increase in the number of large pores with increased crosslinking. The smaller pore size at around 1.5 Å (present at 0% crosslinking) is an inherent property of the epoxy. whereas the larger pores at around 3.2 Å is a property of the crosslinked network. As the crosslinking increases and the molecule grows the number of larger voids increases the packing frustration in

% wt water	FFV		Mean pore volume / $\text{\AA}^3$		Largest pore volume / $\text{\AA}^3$	
	300K	430K	300K	430K	300K	430K
0	7.3 ± 0.3	8.5 ± 0.4	7.35	7.96	66.18	76.26
1	7.2 ± 0.3	8.5 ± 0.4	6.19	7.16	55.26	64.93
2	7.3 ± 0.5	8.8 ± 0.4	6.25	6.48	63.27	70.04

Table 3.3: Fractional free volume from MD simulations calculated without removing the water for a fully cured system (98% crosslinked)

the crosslinked network.

From the cumulative PSD, we can also calculate the probability of a pore being large enough to accommodate a water molecule $P(r > 3.125)$ (Figure 3.10). This follows the same trend as the FFV, that is it increases with crosslinking percentage.

3.5.3 Comparison

The PSD plots from the MD simulations in the previous section have had the water removed to gain fundamental understanding of the ER matrix. However, this means that these cannot be directly compared to the PALS results that have the water present which will influence the positron annihilation. Therefore we recalculate the PSD with the inclusion of water molecules to allow for comparison between the two methods for 0, 1 and 2% water. As the curing temperature is known to affect the microstructure and mechanical properties of the system, we looked at both room temperature (300K) and 160°C (430K) [58].

The FFV from PALS of the dry sample is approximately 13% whereas from the simulations for the fully cured system it is around 7% at 300K, rising to 8.5% at 430K. For the soaked experimental sample the FFV was slightly reduced to 12.55%, whilst for the simulations no change was observed in the FFV at either temperature (Table 3.3). The lack of change observed in the simulations could be due to the relatively small size of the simulations compared to the experiments. The simulations model a homogeneous cured network at the nanoscale. However, experimentally there is likely to be variation on a larger length scale due to improper mixing and vitrification, which can lead to local non-stoichiometric regions. This in turn will lead to lower crosslinking levels in these regions and poorer packing, leading to a larger overall FFV. Experimental literature has found regions of glassy highly crosslinked nodules ranging in size from 6nm to 70 μm within a softer matrix [59–61]

We can also compare the mean cavity volume from experiments and simulations. These pore sizes are significantly smaller than that observed experimentally for both the wet and dry samples. Indeed, the average volume of a water molecule in SPC-flexible water is 16.6 $\text{\AA}^3$, meaning that water cannot fit inside these small pores.

However, the largest cavity volume in the molecular dynamics simulations is comparable to that observed experimentally, ranging between 55.26 $\text{\AA}^3$ and 76.26 $\text{\AA}^3$. In both the experimental and simulations, there was a large spread in the values observed between the repeats, with a range of approximately 1-4 $\text{\AA}^3$ from the simulation results

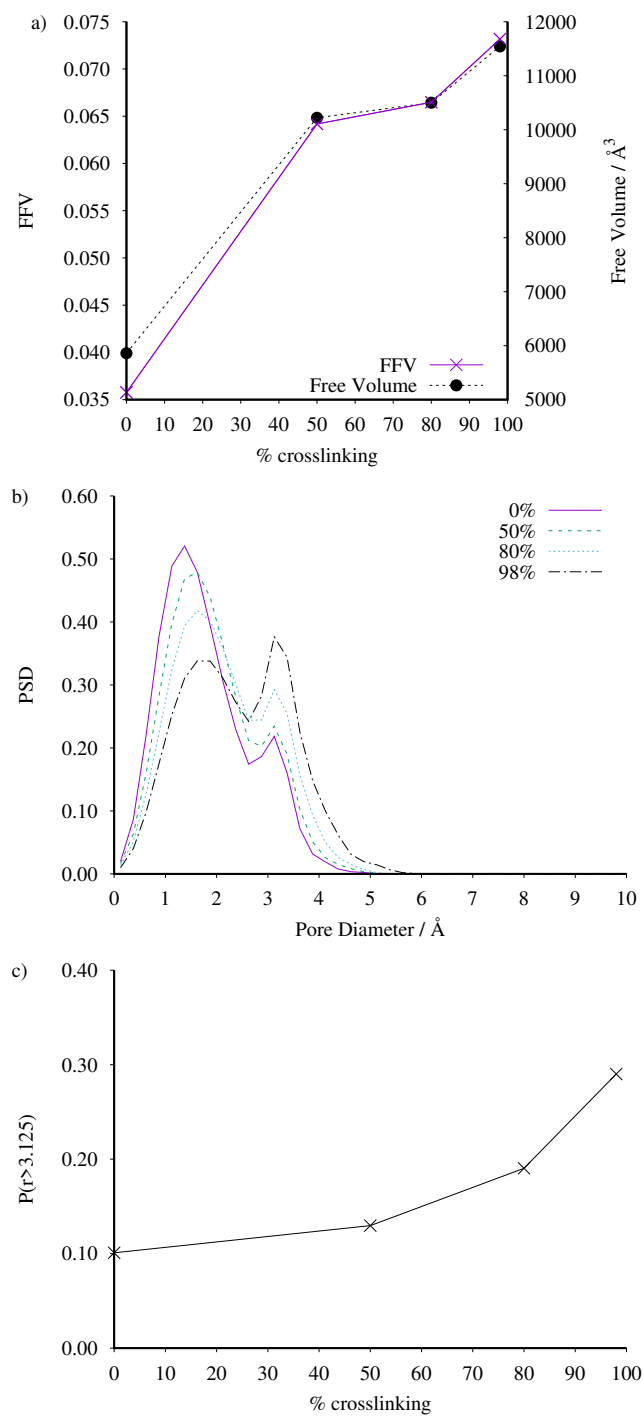


Figure 3.9: a) FFV and actual free volume, b) pore size distributions and c) probability of large pores at 300K for different crosslinking percentages.

and 5-7 $\text{\AA}^3$ from the PALS findings. From the PALS data alone, we attributed this to an overfitting of the positron annihilation spectra, however it could be an intrinsic variation in the pore sizes leads to a smearing out of free volume pore sizes. The lack of change of the FFV and pore size suggests that there is a significant fraction of empty pores, or free volume pockets within the structure.

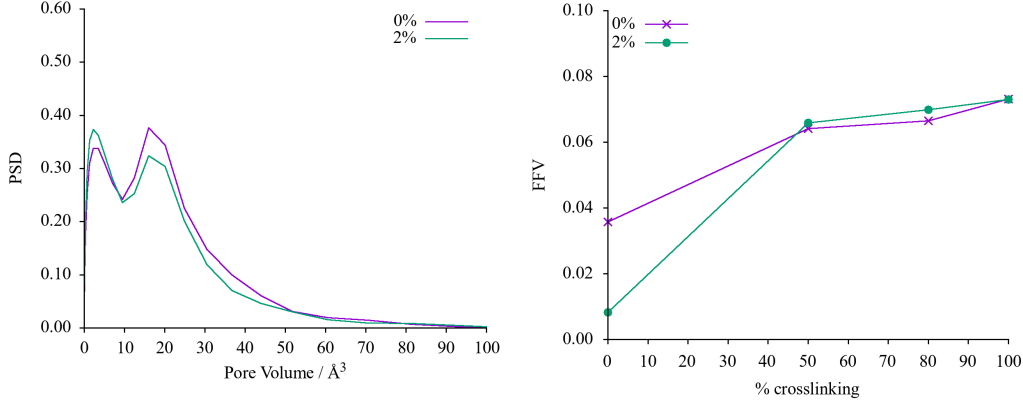


Figure 3.10: a) PSD distribution for the dry (0%wt water) and soaked (2%wt) water from the MD simulations including the water molecules. b) FFV with crosslinking percentage for the dry and wet systems from MD simulations at 300K

From Contin analysis of the PALS spectrum we see that there are clearly 2 distinct free-volume pore sizes present in the epoxy-amine. This corresponds well with the simulation results. There is a slight discrepancy in the size of experimentally measured voids and those found in the simulation. with diameters of 4.7 $\text{\AA}$ and 7 $\text{\AA}$ from PALS and 2.5-3.5 $\text{\AA}$ and 3.5-7.0 $\text{\AA}$ from simulation. this difference may be the result of the Tao-Eldrup's model assumption of spherical voids[29][27]. There is no such assumption in the FV void size calculation in the simulations.

In the simulation results the distribution of pore sizes changed slightly with the addition of water into the system. As shown in Figure 3.10 the distribution of smaller pores increased with 2%wt water. Some change in distribution is shown in the PALS results however intensity of both small and large pores appear to decrease. With the lack of error bars provided in the CONTIN-PALS program, it is hard to identify whether these changes are meaningful. However, both PALS and simulation did both show that while the distribution of the pores may change with soaking, the size of both small and large pores remains constant.

3.6 Conclusions

We have undertaken a combined PALS and molecular dynamics approach to understand the uptake of water in crosslinked epoxy-amine systems. Both techniques showed similar results in FFV of the samples and pore size distribution. PALS and molecular dynamics have been clearly shown to be complementary techniques in the investigation

of epoxy-amine nano-structure. PALS provides a validation of the simulated results by showing similar values and trends. Moreover, the simulations support experimental results by providing a better insight into exactly what the pores look like.

From the combination of the techniques, we have shown that the epoxy-amine samples contain isolated voids of two characteristic length scales. MD results also suggest that the distribution of smaller voids increases with water uptake. MD also showed that the percentage of large voids increased with crosslink percentage, indicating these voids may be formed late in the crosslinking procedure.

PALS revealed that FV decreased when the epoxy amine is saturated with water, and then reverts back to around its original value when water is subsequently removed. The FFV of the system followed the same pattern, with the total void volume decreasing by the same percentage as water uptake. Showing that water is filling free volume voids, then leaving voids unchanged when removed. We saw a decrease in mass when samples were soaked and then subsequently dried, this loss of mass could be due to leaching of uncured monomers. To better understand this system further soaking experiments should be carried out using Fourier transform infrared spectroscopy to validate the addition and removal of water in the system. Furthermore, pulsed nuclear magnetic resonance can be used to show the location of water in the soaked samples.

Results from MD gave a useful insight into the molecular structure of the epoxy-amine. When FV and FFV results did not align exactly with PALS results however the same patterns were seen, most importantly the presence of two discrete free volume void sizes. With further development MD could feasibly be used as a high throughput, preliminary analysis technique in the development of new corrosion resistant polymer coatings, *i.e.* a digital twin approach.

The combination of two techniques should be considered for further investigation of polymeric systems. Further work may include measuring the effect of solvent-processing of epoxy-amine systems. Solvent is used in industrial applications as a rheology modifier to aid in the spray coating application of epoxy-amines. From preliminary tests, it can be seen that these systems have a larger average FV void size.

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Chapter 4

Self-assembled Colloidal Particle Systems as SESANS calibration Samples, Investigated via Experimentation and Simulation

In this chapter a range of colloidal particle systems are synthesized, pre-characterised, and measured using pseudo-monochromatic SESANS. With the intention of analysing their validity as SESANS calibration samples. SESANS accesses unique length scales not available to conventional SANS and therefore requires a new calibration standard on the range of 100-500 nm. Resolution on this length scale is essential in the investigation of polymer systems. Through the investigation of several dry and dilute systems, 500 nm diameter silica colloidal crystals prepared on silicon disks showed potential as a potential stable calibration sample.

4.1 Introduction and background

Spin-echo small angle neutron scattering (SESANS) is a neutron scattering technique developed to access larger length scales than conventional small angle neutron scattering (SANS). Where SANS can measure structures in the 1 - 100 nm range [1], SESANS provides access to length scales from 10's of nanometers to around 40 μm [2] [3]. Access to these length scales requires calibration samples with structures on this scale to ensure accurate measurements and repeatable results for neutron facilities across the globe.

To be used as a calibration, it is paramount that a sample has a well-defined and understood structure. For this reason, the samples trialled in this work were chosen partially for their simplicity. Spherical particles of polystyrene (PS) and deuterated latex (DL) dispersed in water and D_2O at 5 or 10 wt% concentration, were tested. Alongside colloidal crystals formed of spherical silica particles. Furthermore, all samples went through rigorous pre-characterisation measurements.

The scattering function of spherical particles is well understood and the projection of the auto-correlation function (measured in SESANS) is defined numerically. Allowing experimental data to be fit with ease. Furthermore, there exists a model simulation of spherical particles in McStas (a neutron-ray-trace simulation software). Allowing us to compare our experimental measurements with those from an identical simulated instrument. All these factors make spherical particles the best option for this test.

An ideal SESANS calibration sample requires correlation over long-length scales due to SESANS beam sizes being around 1 cm^2 , an ideal sample would have repeating structures at the desired length scale (100's of nm) over the entirety of a cm scale sample. Samples of this nature are not common, and in this chapter I will present several potential candidates and measure and discuss their efficacy as SESANS calibration samples.

To be used as a calibration sample there are a number of criteria that must be met. A suitable calibration sample must be stable at room temperature and pressure and a range in humidity that would be common in a laboratory. This allows the sample to be stored in lab conditions without specialist treatment and allows it to be reused over multiple experiments. For reliable comparison of SESANS measurements across different neutron facilities, the sample must be easily accessible across the world. Therefore, it must be available to purchase internationally with tightly controlled specifications. Alternatively, it must be relatively easy to produce in a neutron facilities preparation lab with a high level of repeatability.

For these reasons the calibration sample used in small angle x-ray scattering is a hydrated rat tail tendon (RTT) [4] [5]. Biological samples are ideal as they are available worldwide and possess highly consistent internal nanostructure. RTT's are also stable if kept hydrated.

For conventional SANS a blend of hydrogenous and deuterated polystyrene are used as calibration samples. This blend provides contrast and enables measurement of the polymer R_g which can be compared to R_g 's measured using light scattering and gel permeation chromatography.

4.2 Sample preparation

All the samples trialled in this work are shown in Table 4.1. This section will describe how all the samples were prepared in the sample preparation lab at the ISIS neutron source.

4.2.1 Materials

Dry silica (SiO_2) Nanoparticles were supplied by General Engineering and Research (GE&R). According to the GE&R certificate of analysis the nanoparticles had a diameter of $200 \pm 20\text{ nm}$ and $500 \pm 50\text{ nm}$. Coefficient of variation was stated as $< 20\%$ for 200 nm and $< 10\%$ for 500 nm particles. A skeletal density of $2.1 - 2.2\text{ gcm}^{-3}$ and no impurities above 5 ppm was assured for both sizes. GE&R also provided SEM images of the particles showing perfectly spherical particles.

Bangs Laboratories Inc. supplied the polystyrene (PS) particles dispersed in water. Mean diameters of 102 nm and 190 nm were stated on the certificate of analysis for the two colloids. At a volume fraction of 10.2% and 10% for the 102 and 190 nm particles, respectively. Each dispersion also contained 0.1% sodium dodecyl sulfate and 0.05% sodium azide as an antimicrobial agent.

Polyvinylalcohol (PVA) used as a surfactant for the colloidal crystal samples was supplied in the form of crystals by Sigma Aldrich, under the product name of Mowiol and having a molecular weight of 130,000 g/mol.

4.2.2 Silica Colloidal Crystals

Silica colloidal crystals (samples 1 & 2 in table 4.1) were prepared by the method detailed by Rey *et al.* [6]. Rey *et al.* present a versatile strategy for forming homogeneous drying patterns of dispersed particles. High-molecular weight polymers (including PVA) are physisorbed onto the surface of colloidal particles (including silica) dispersed in water, enhancing the steric stability and causing a homogeneous pattern to form as the water evaporates. Alterations were made to the technique (described below) as sample sizes around 1 cm² are required, due to the size of the neutron beam therefore, larger droplets were used.

Each of the 2 colloidal crystal samples consisted of 9 silicon wafers with a silica crystal layer on one side. This was done to allow total sample thickness to be tuned in the SESANS measurement by adding or removing wafers, to optimise the scattering signal. Samples were stacked in the SESANS beam in custom 3D printed racks, as shown in Figure 4.1b. Each silica crystal was formed by depositing 3 ml of a PVA-grafted silica dispersion onto the wafer and allowing it to dry on a hot plate maintained at 40°C, see Figure 4.1a.

PVA-grafted silica was prepared by stirring together 0.77 g of SiO₂ with 0.766 g of PVA in a glass vial with 39 ml of deionised water. Stirred overnight using a magnetic stirrer at 1200 rpm and 100°C. After stirring the PVA should be grafted to the surface of the silica particles and act as a surfactant and prevent particles from clumping. Excess PVA was then removed by centrifugation. Solutions were diluted to 240 ml and centrifuged at 4000 rpm for 20 minutes in an Eppendorf 5810 centrifuge. The supernatant was removed before re-dilution to 240 ml sonicating to redisperse and repeating a total of 3 times. It was clear that excess PVA was removed after centrifuging 3 times as the supernatant would not froth when shaken. After the removal of excess PVA, the resultant PVA-grafted silica particles were redispersed in 39 ml of water by sonication and shaking. Resulting in around 40 g of a 0.02% dispersion.

This was then pipetted in 0.5 ml droplets onto the 9 silicon wafers. Droplets dried in around 1 hour on a hot plate set to 40°C, Figure 4.1a. After drying another drop was added and repeated 6 times until a total volume of 3 ml of the dispersion was deposited.

This process was repeated for 200 nm and 500 nm SiO₂ particles.



(a)



(b)

Figure 4.1: Silica colloidal crystal samples. a) Showing the dispersion drying process and b) showing the dry samples in place in 3D printed mounts and on the SESANS instrument

Sample	Particle material	Diameter [nm]	Concentration [wt%]	Medium	Contrast $(\rho_p - \rho_m)$ $[10^{-6} \text{Å}^{-2}]$
1	SiO ₂	500	74*	air	3.432
2	SiO ₂	200	74*	air	3.432
3	PS	190	10	H ₂ O	1.971
4	PS	190	5	H ₂ O	1.971
5	D-Latex	118*	10	H ₂ O	4.261
6	D-Latex	118*	5	H ₂ O	4.261
7	PS	102	10	D ₂ O	-4.965
8	PS	190	10	D ₂ O	-4.965
9	PS	102	5	D ₂ O	-4.965
10	PS	190	5	D ₂ O	-4.965

Table 4.1: Calibration samples tested. Samples 1 and 2 are colloidal crystals, and 3-10 are particles dispersed in water or D₂O. All properties are known before the SESANS measurement excluding the * starred ones, which were determined by fitting the SESANS data. scattering length density (SLD) for particles (ρ_p) and mediums (ρ_m) are calculated in the NIST Neutron activation and scattering calculator [7], and used to calculate contrast.

4.2.3 Dilute samples

The PS samples (3-4 in table 4.1) are particles suspended in water. PS particles with a 190 nm diameter were used as supplied for sample 3 and loaded into a 1 mm quartz liquid cell before measuring. Similarly, sample 2 was diluted by half before loading into the cell. For Samples 7-10 the H₂O was exchanged for D₂O using dialysis. Using a 3 ml Thermo Scientific Slide-A-Lyzer Dialysis Cassette with a membrane molecular weight cut off of 10,000 g/mol. Dispersions were added to the cassette which was then immersed in a 500 ml beaker of D₂O for over 24 hours, replacing the D₂O twice.

D-latex dispersions were made by Dr. Mohammed Jamali of The University of Manchester, via emulsion polymerisation. D-styrene D8 (34.4 g), 2EHA (25.4 g), MMA (1.35 g), MAA (0.242 g), Rhodapex (0.648 g), Ammonium persulphate (0.961 g) and deionised water (102 g) were stirred on a magnetic stirrer at 300 rpm and heated to 90°C under a nitrogen atmosphere. Latex poly(D-styrene-co-methyl methacrylate-co-2-ethylhexyl acrylate-co-methacrylic acid) (P(D-STY/MMA/2EHA/MAA)) particles were formed dispersed in water with 50% w/w water and 1.34% w/w surfactant (Rhodapex). Full synthesis details are given in section 5.2.

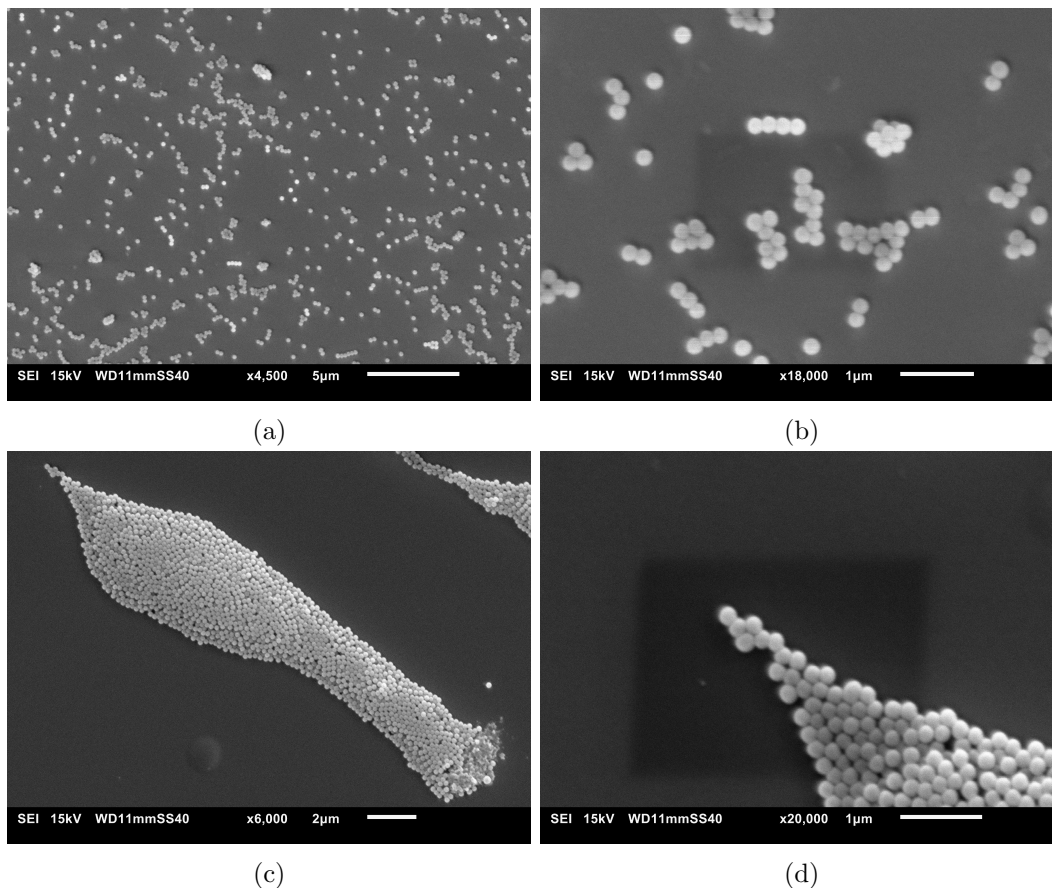


Figure 4.2: 200 nm SiO_2 Particles imaged using SEM. Scale bars are shown in each image. b) is a zoomed-in section of a). And d) is a zoomed-in section of c).

4.3 Sample precharacterisation

4.3.1 Silica particles

Before preparing the colloidal crystal samples the dry 200 nm SiO_2 particles were characterised by a range of techniques to validate their size and shape were as stated by the manufacturer. The particles were measured using scanning electron microscopy (SEM), dynamic light scattering (DLS), helium pycnometry and SANS.

Samples for SEM were prepared by spin-coating a dispersion of SiO_2 particles in ethanol onto an SEM stub topped with conductive carbon tape and then sputter-coated with gold. Samples were prepared by spin-coating in an attempt to create a thin layer of particles, in order to best observe and measure the size and shape of individual particles in the SEM. The resulting images are shown in Figure 4.2. From the images, we see that the spheres have a very uniform size and shape. Image analysis in ImageJ found the mean diameter of 20 particles to be 200 ± 4 nm. Subfigures 4.2c and 4.2d also illustrated the tendency to aggregate, this was found to be the case for

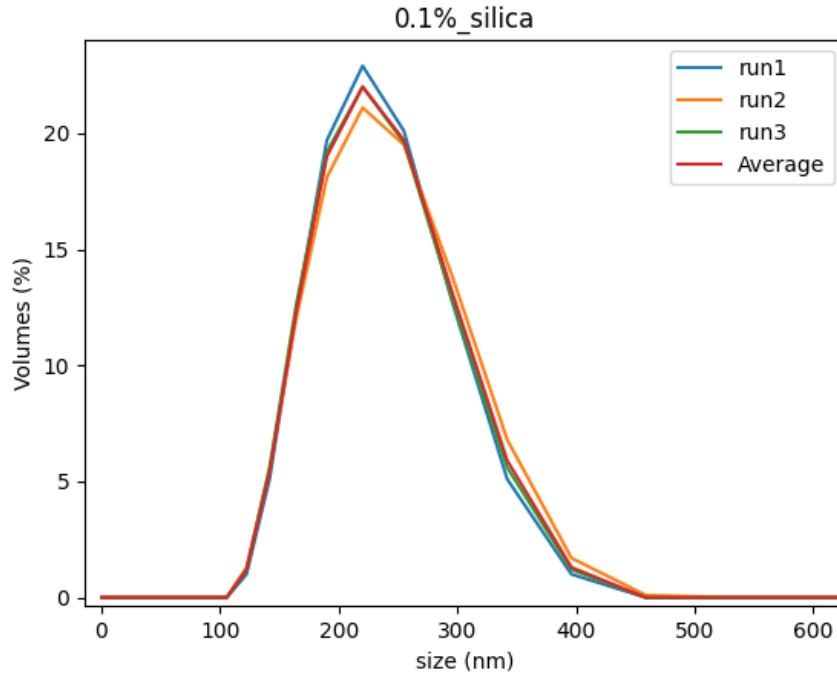


Figure 4.3: Dynamic light scattering results for a 0.1%w/w SiO_2 dispersion in water.

high-concentration dispersions.

For dynamic light scattering a dilute dispersion of 0.1%w/w SiO_2 in water was made up and sonicated for 5 minutes to effectively disperse the particles, i.e. make sure they were not aggregated. A total of 3 measurements were taken and an average result was calculated, shown in Figure 4.3. A sharp peak indicated monodisperse particles with a well-defined diameter. The hydrated diameter was calculated as 213.2 nm with a polydispersity index of 0.02, indicating a highly monodisperse sample dispersion.

Helium pycnometry was used to find a density of the particles of 2.0503 gcm^{-3} with a standard deviation of 0.0017 gcm^{-3} , slightly below the value of $2.1\text{-}2.2 \text{ gcm}^{-3}$ quoted by the manufacturer.

To calculate an accurate scattering length density (SLD) for the 200 nm SiO_2 particles SANS measurements were carried out on a series of dispersions in different ratios of $\text{D}_2\text{O}:\text{H}_2\text{O}$. SANS was carried out on the Larmor instrument at ISIS. Dispersions were made up of 0.5% w/w SiO_2 in 0, 25, 35, 40, 50, 55, 60, 65, 75 and 100% D_2O mixtures. By measuring intensity at a single scattering vector for each mixture it is possible to calculate the D_2O ratio that best matches the SLD of the particles, as shown in Figure 4.4. A parabola is fit to the intensity data and the minimum is taken as the contrast match point. This was found to be at 57.9% D_2O , giving a SLD for the particles at $3.432 \times 10^{-6} \text{ \AA}^2$.

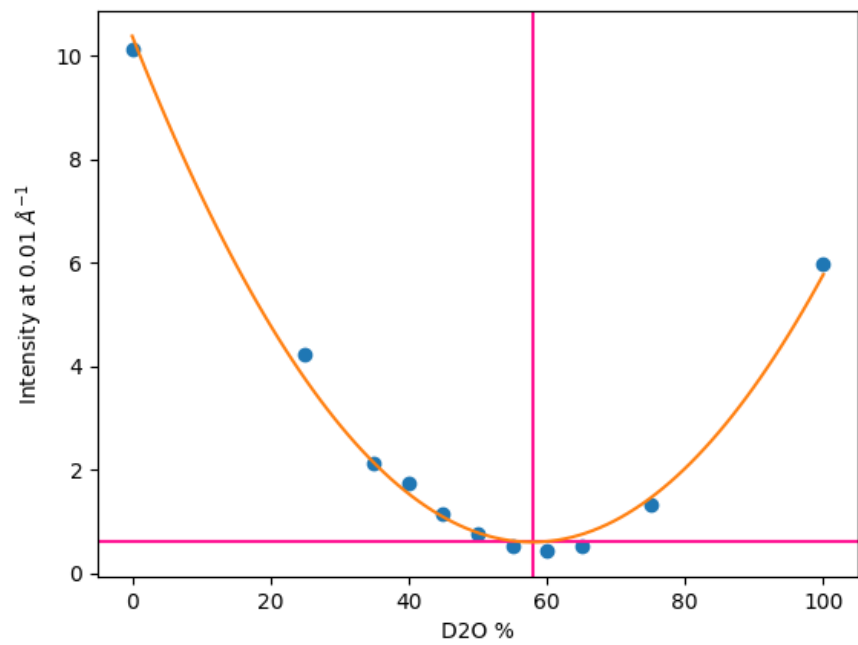


Figure 4.4: Scattering intensity at $0.01 \text{ \AA}^{-1}$ for a contrast series of 200 nm SiO_2 particles at $0.5\%w/w$ in a $H_2O + D_2O$ mixture. Data is fitted with a parabola (orange) and the minimum taken as the contrast match point (pink cross).

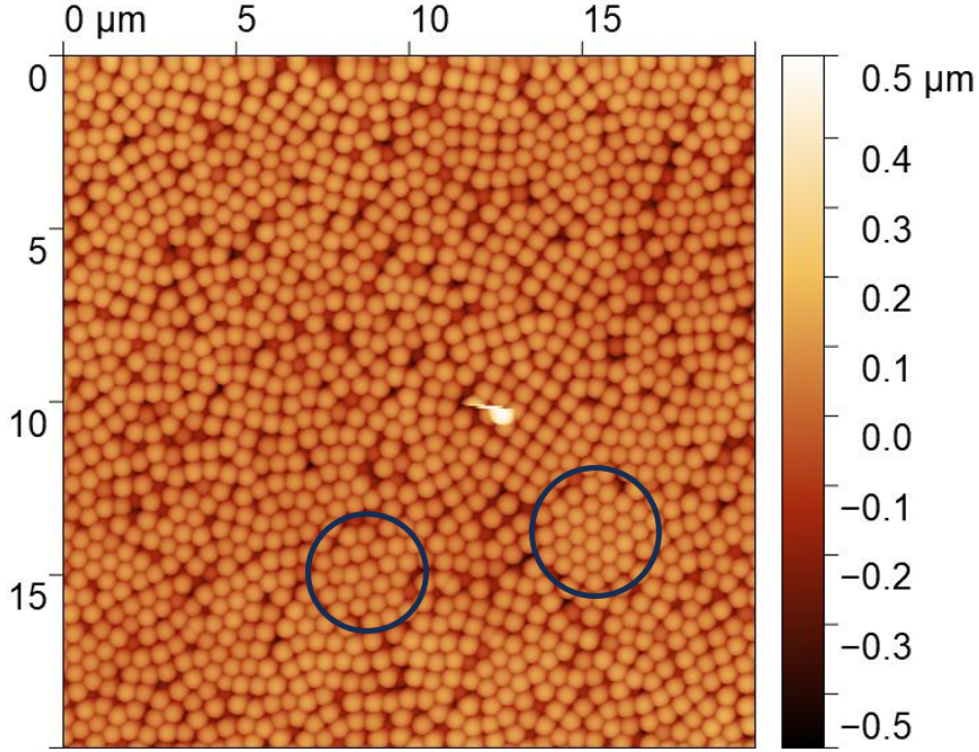


Figure 4.5: AFM height image of a colloidal crystal consisting of SiO_2 particles with a PVA surfactant. Regions which display hexagonal close packing are circled.

4.3.2 Colloidal Crystals

Colloidal crystals prepared by the method in section 4.2.2, underwent further pre-characterisation. The sample was imaged using atomic force microscopy (AFM) at the materials characterisation lab at ISIS. An AFM height image is shown in Figure 4.5. The AMF imaging showed that the SiO_2 kept their spherical shape and are arranged into regions of hexagonal and square close packing.

4.4 Experimental Methods

The neutron scattering measurements were performed on the Larmor instrument at ISIS. Larmor was set to measure in a pseudo-monochromatic SESANS mode.

SESANS measures larger length scales than SANS by the manipulation of a polarised neutron beam, encoding scattering angle onto polarisation. By passing a polarised neutron beam through two identically shaped but opposite-direction magnetic fields spin-echo is achieved. This is where unperturbed neutrons precess out of their polarised state in the first field and then complete the same number of precessions in the opposite direction in the second, returning to their initial state. When a scattering sample is introduced between the fields, a scattered neutron will follow a different

path through the second field. Due to the fields' parallelogramic shape, any scattering angle causes a different path length through the second region. Causing the neutron to precess by a different amount and the spin-echo conditions are not met. By polarising the beam after the second field this is measured as a drop in intensity. By comparing measurements with and without a sample in place, the drop in polarisation is calculated. Polarisation is measured as a function of the real space parameter spin-echo length, z [8]. Spin-echo length is defined by the instrument parameters, equation 2.42 [9].

$$z = \frac{C|\vec{B}|\lambda^2 L \cot \theta_0}{2\pi} \quad (4.1)$$

Here B is the magnetic field, λ is the neutron wavelength, θ is the angle of inclination of the magnetic field (also called the pole shoe angle) and C is a constant equal to $4.6368 \times 10^{14} T^{-1} m^{-2}$ [10].

Spin-echo length can be understood by the quantum mechanical treatment of Larmor precession, in which the two spin states of the neutron are separated over a distance z in the first field region and return in the second [11][12]. This quantum description of spin-echo was recently described and strongly supported as the correct model by McKay et al [3].

The polarisation is then used to calculate the projection of the autocorrelation of the sample, $G(z)$ using equation 4.2.

$$G(z) = 1 - \frac{\ln \frac{P(z)}{P_0}}{\ln P_\infty} \quad (4.2)$$

In which empty beam polarisation is P_0 , and P_∞ denotes the saturation level of the polarisation.

This result gives information on the form factor of particles and the structure factor i.e. how the particles are arranged.

As ISIS is a spallation source, the Larmor instrument has access to polarised neutrons with wavelengths of 1.7 - 13.0 Å [13]. Larmor is routinely operated in a time-of-flight operating mode. In this case, the spin-echo length (z) is varied by the neutron wavelength. In this mode a constant pole shoe angle is used for each measurement however this can be changed to take measurements over different spin-echo ranges. A typical experiment may use two or three pole shoe angles. In this experiment, however, we used Larmor in the less commonly used pseudo-monochromatic mode. Here pole shoe angle was varied in small steps and neutron wavelength remained constant. As the beam is made up of all accessible wavelengths this meant binning data by wavelength. In this mode, different measurement ranges are accessed by selecting different wavelengths. Each sample was measured for 20 μA at pole shoe angles of -89° to -63° at 1-degree intervals and at -61° . Data was binned into 1Å wavelength bins. Resulting in 27 data points for each wavelength and 10 wavelength bins, with average wavelengths of 3.5Å to 12.5Å.

4.5 Experimental Results and Discussion

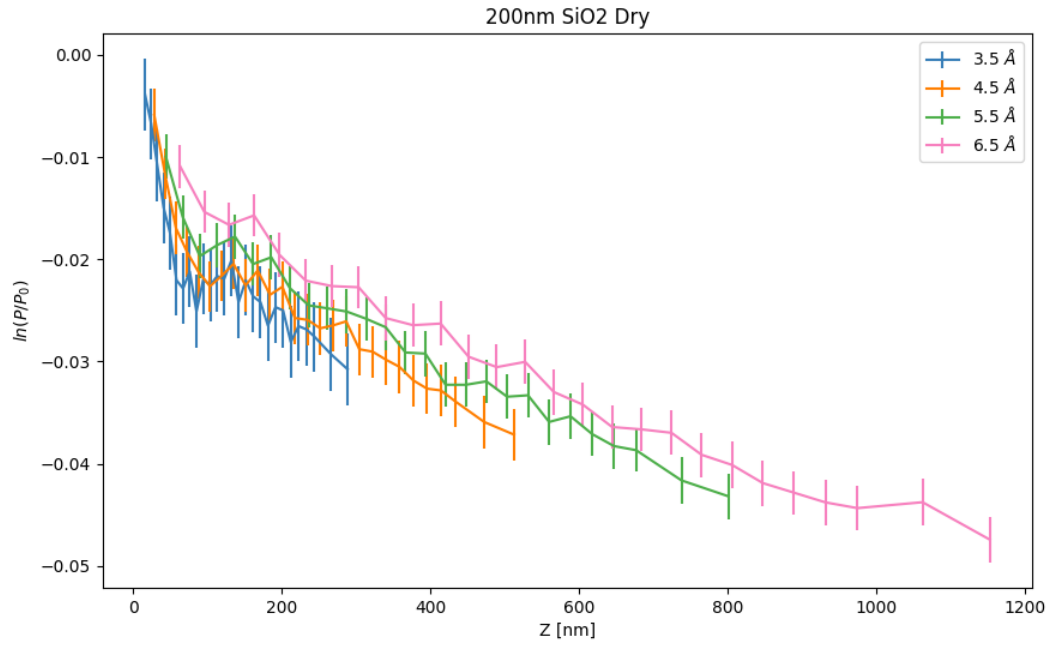
Measurements taken on the Larmor instrument are shown below. Operating in a pseudo-monochromatic mode provided 10 data sets per sample (one for each wavelength bin), here we show a selection of the data sets. However, all the data is available in appendix A.3.

The data presented here is the raw SESANS data for all our samples. Presented as the logarithm of the normalised polarisation versus spin-echo length (Z).

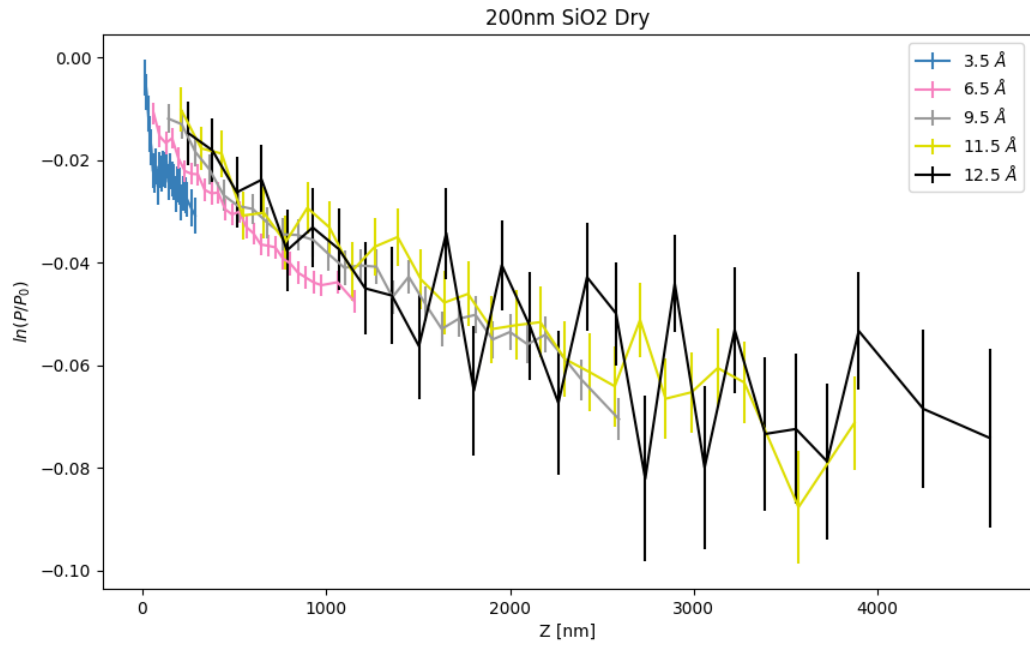
Figure 4.6 shows pseudo monochromatic SESANS data for colloidal crystals made from 200 nm SiO₂ (sample 1). For this sample, two graphs are shown with different Z ranges. The first graph shows data from the 3.5, 4.5, 5.5 and 6.5 Å wavelength bins. This gives good details in the 100's of nm range. It shows a peak in the data at 200 nm as expected for this sample. However, this has not plateaued as expected. This indicates the presence of a large feature outside this range of length scales accessed. For this reason, a second graph is shown containing the longest wavelength and therefore the largest accessible spin-echo length, Figure 4.6b. The data here has still not reached a plateau showing this sample contains a length scale larger than 5 μ m. Particles are likely forming into large aggregations and not one continuous repeating pattern across the entire sample. This data also shows a large increase in error for the longest neutron wavelength data.

Figure 4.7 shows data for the 500 nm SiO₂ colloidal crystal. This data has an oscillating pattern that peaks at around 500 nm. The oscillating pattern shows that the sample has a well-defined repeating structure factor. By fitting the 7.5 Å data in sasview it is calculated to have a particle diameter of 374 nm and a volume fraction of 36% with a χ^2 value of 0.64, shown in Figure 4.7a. This shows that our data is skewed as we know our particle diameter is close to 500 nm. We also expect a volume fraction of around 74% as AFM images showed a hexagonal packing structure. Figure 4.7b shows where this error may originate. This figure contains a range of wavelength data for this sample and clearly shows as the wavelength is increased, data shifts up and right. All these lines should lie directly on top of each other and their first minima should lie exactly on 250 nm (the radius of our particles). The source of this shift is unknown and was seen for all samples. Highlighting the need for a calibration sample. It may be the case that during data reduction a scaling factor should be applied to the data to show accurate length scales.

The same shift in the data was seen for samples 3 and 4 (PS in H₂O) however here just the first wavelength is shown along with the sasview fit, Figure 4.8. This graph illustrates how SESANS data changes with volume fraction as both samples are identical but with 5% or 10% volume fractions. The 10% volume fraction sample shows more depolarisation and therefore a lower plateau due to more scattering. This data also shows a structure factor as the line dips and then rises. In the fits a the hardsphere sasview model [14] [15] [16] was used and only radius and volume fraction were not fixed. The fits here showed 130 nm and 127 nm diameters and volume fractions of 11% and 5.5% for samples 3 and 4, respectively. While the volume fraction was as expected diameter was yet again far from the real value of 200 nm. However, both samples

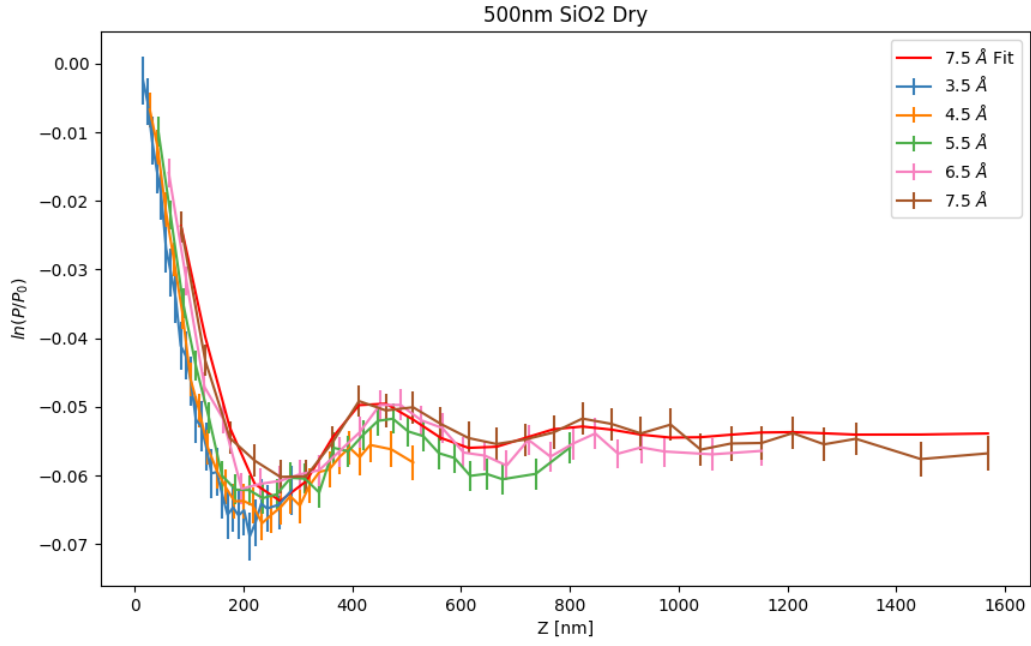


(a)

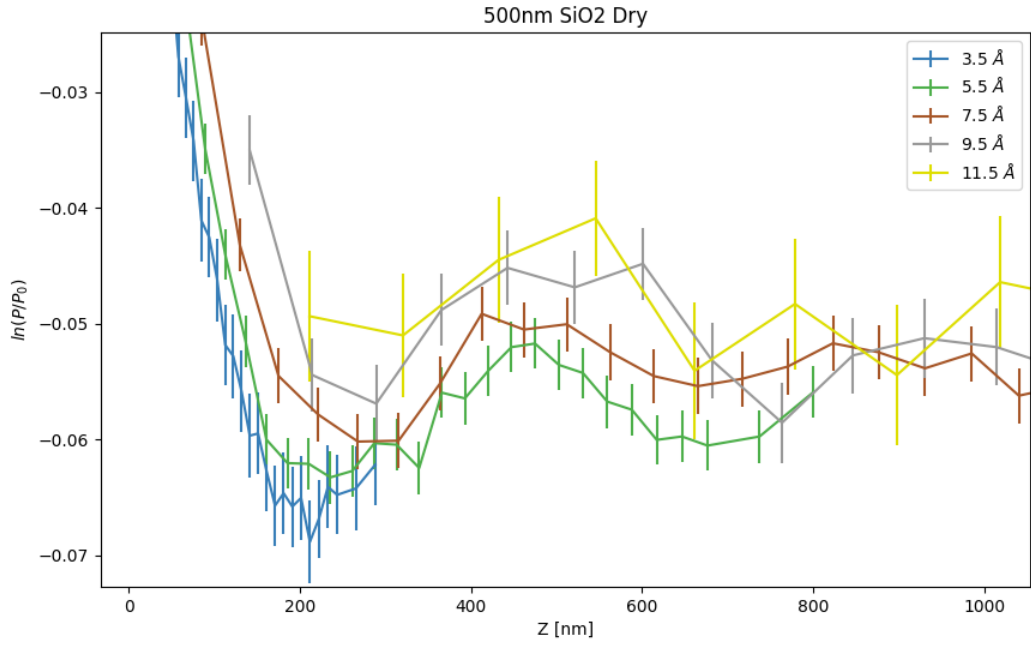


(b)

Figure 4.6: Pseudo Monochromatic SESANS Data for a 200 nm SiO₂ colloidal crystal. Showing short-range scale in (a) and long-range scale in (b). Neutron wavelength is given in the legend.



(a)



(b)

Figure 4.7: Pseudo Monochromatic SESANS Data for a 500 nm SiO₂ colloidal crystal. Including a fit of the 7.5 Å data in (a) and a zoomed-in section containing longer wavelengths in (b).

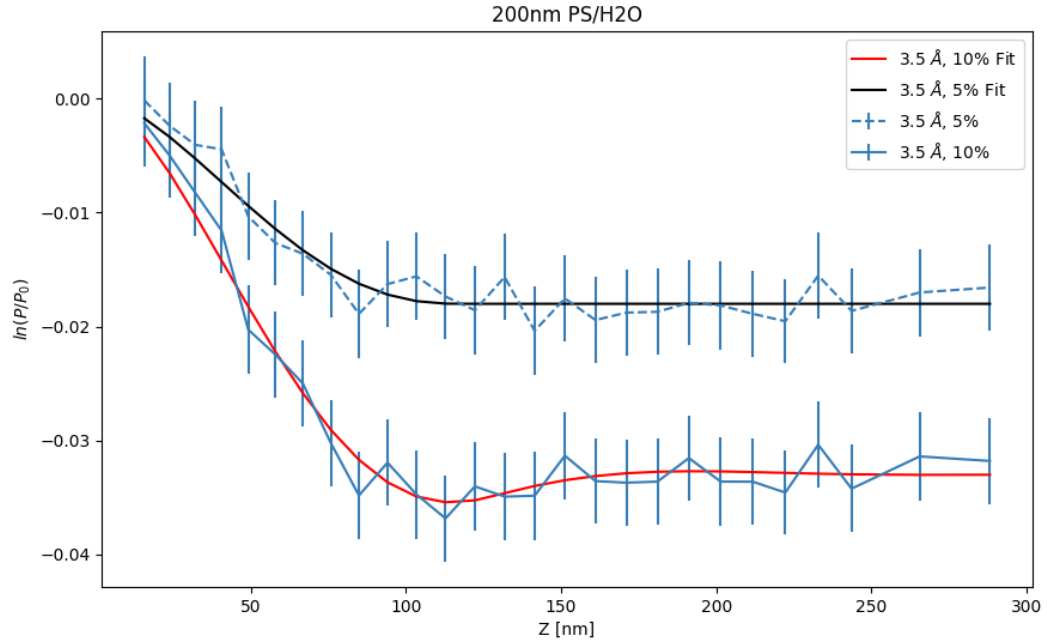


Figure 4.8: SESANS data for dilute 200 nm polystyrene spheres, fit using the hard-sphere sasview model. only 3.5 Å neutron data shown.

showing the same radius show that these samples do have a reliable and consistent diameter.

Figure 4.9 shows SESANS data for deuterated latex particles dispersed in water at 50 and 10% volume fraction (VF). Here we see again that the data moves up and right with increasing neutron wavelength. Here the shift affects both samples by a similar amount. The 3.5Å data was fit using the same model and the diameter was calculated as 119 nm for 10% VF and 118 nm for 5% VF. Again we see a good correlation between samples. However, as less pre-characterisation was carried out on these particles the true diameter is not known accurately, by different techniques. This sample therefore is not suitable as a calibration in this instance.

Figure 4.10 shows data for 4 variations of dilute polystyrene (PS) particles at a single neutron wavelength. These are 200 nm PS dispersed in H₂O and D₂O at 5 and 10% VF (samples 3, 4, 8 & 10). This data shows the difference in contrast between H₂O and D₂O samples. The SLD's for the sample components are [7] :

- Polystyrene = $1.41 \times 10^6 \text{ Å}^{-2}$
- H₂O = $-0.561 \times 10^6 \text{ Å}^{-2}$
- D₂O = $6.375 \times 10^6 \text{ Å}^{-2}$

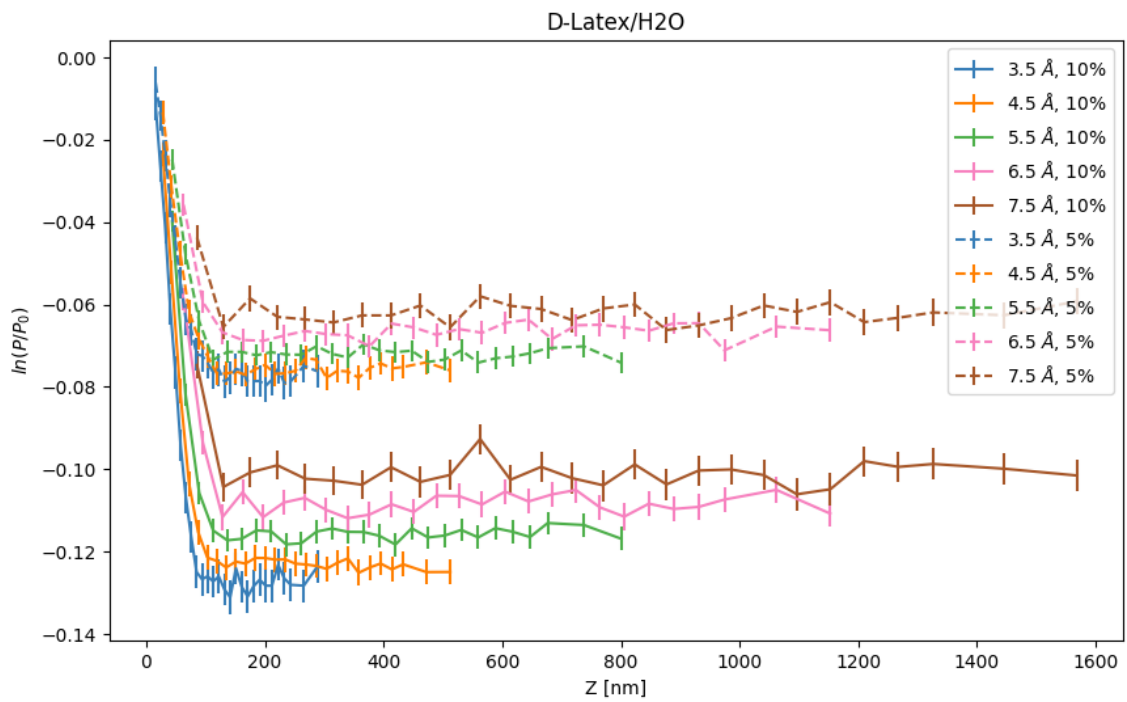


Figure 4.9: SESANS data for deuterated latex particles in water. Neutron wavelength, followed by sample volume fraction is given in the legend.

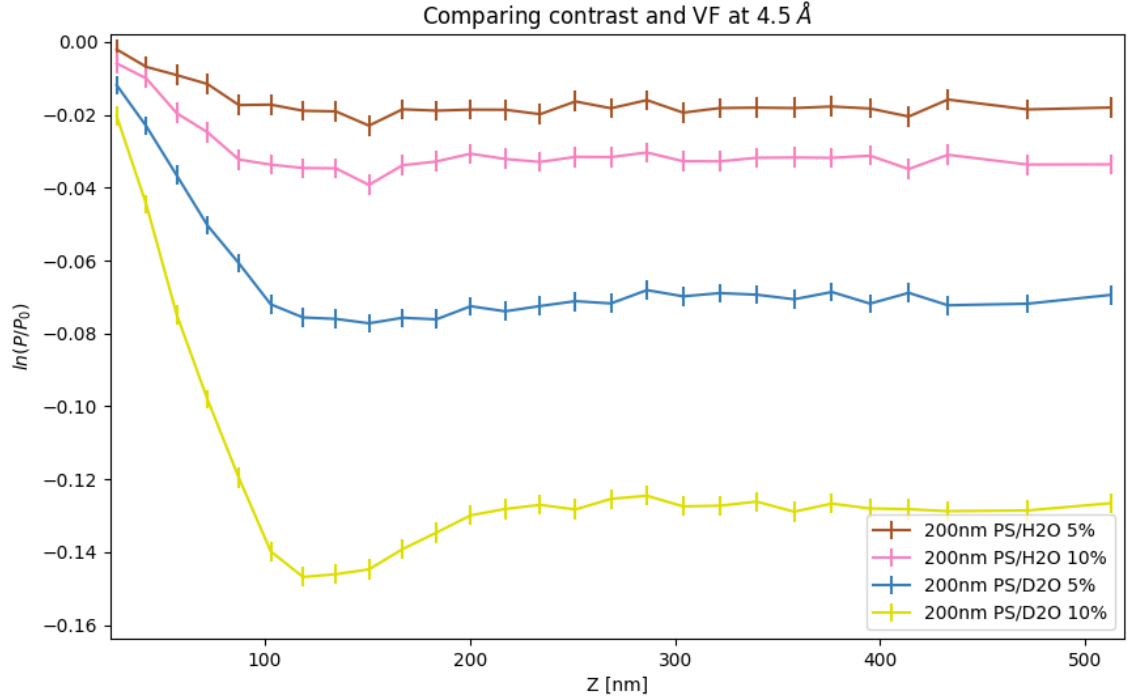


Figure 4.10: SESANS data for polystyrene particles dispersed in water and D₂O at 10 and 5% volume fraction.

Giving H₂O/PS samples a contrast of 1.971 and D₂O/PS a contrast of 4.965. D₂O samples having a larger contrast and cause more scattering and therefore a larger drop in polarisation. Similarly, 10% VF samples scatter more than 5% causing more depolarisation.

In a SESANS experiment, there is always a payoff between increasing scattering enough to get the neutron beam to depolarise but not to fully depolarise the beam. These samples therefore act as a useful series to find the optimal amount of scattering. Here our 10% VF 200 nm PS particles in D₂O give us the most depolarisation without losing resolution in a fully depolarised beam, making it the most effective calibration sample out of the four. With the largest signal to noise ratio and the most accurate fitting.

Furthermore, different particle sizes and VF are compared in Figure 4.11 which displays SESANS data for 100 and 200 nm diameter PS particles in D₂O at 5 and 10% VF (samples 7-10). This data demonstrates the increased depolarisation with increasing VF and also shows how SESANS results change with particle size. Here the increased particle size not only moves the position of the minima but also increases depolarisation.

The height of the polarisation curve i.e. the amount of depolarisation is described

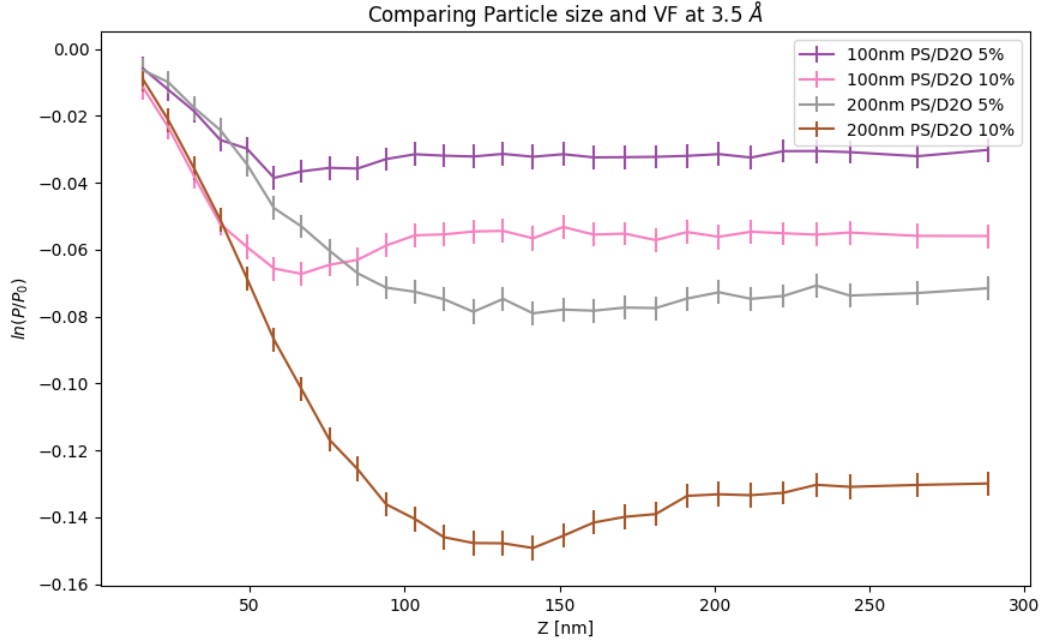


Figure 4.11: SESANS data for polystyrene nanoparticles in D₂O

by Andersson *et al.* [8] by

$$1 - \exp[-\lambda^2 t (\Delta\rho_0)^2 \phi(1 - \phi)\xi] \quad (4.3)$$

depolarisation is therefore proportional to scattering length density ($\Delta\rho$), neutron wavelength (λ), sample thickness (t), packing fraction(ϕ) and correlation length (ξ) of the sample inhomogeneities. In the case of figure 4.11 the increase in particle size therefore results in a larger level of depolarisation.

4.6 SasView Problem and Report

The Sasview fitting software, originally designed for conventional small-angle scattering, can also fit SESANS data. However, it was found during this work that the SESANS fitting contained a bug. When a fit is created for a data set and then applied to another set with different bin spacing, the fit moves. For our data, we would ideally fit one wavelength data set and apply the fit to all other wavelengths. To see how the data changes between wavelengths with more detail. However, as the point spacing changes between data sets, this was not possible.

To test this bug multiple model SESANS data sets (.ses files) were created in Python. The model data sets were made to resemble real SESANS data by adding Gaussian noise and error bars.

Firstly, a SESANS data set is loaded and fit using the sphere model where scattering intensity is calculated by

$$I(q) = \frac{scale}{V} \left[3V(\Delta\rho) \frac{\sin qr - qr \cos qr}{qr^3} \right]^2 + background \quad (4.4)$$

in which V is the volume of the scatterer, r is the radius of the sphere and $\Delta\rho$ is the difference in SLD between the solvent and sphere. SLD, solvent SLD and radius are allowed to float. Scale and background are fixed at the default values of 1.0 and 0.001 respectively. Then a second data set with different binning is sent to fitting using the swap data mode. The fit is then applied to this data using the show plot button. Therefore, all parameters are unchanged, and the two fit lines should lie directly on top of each other. However, we found that if the spacing between points increased, then the fit line would move up. In Figure 4.12 two identical data sets are shown, the only difference being the 1st has 10 points and the second has 50. The 50-point set was initially fit in sasview, and the fit was then applied to the 10-point set. It can be seen here that the fit has moved up despite the parameters being unchanged.

Model data sets were also tested with changing range and this did not move the fit. This bug was reported to the Sasview team in a detailed report.

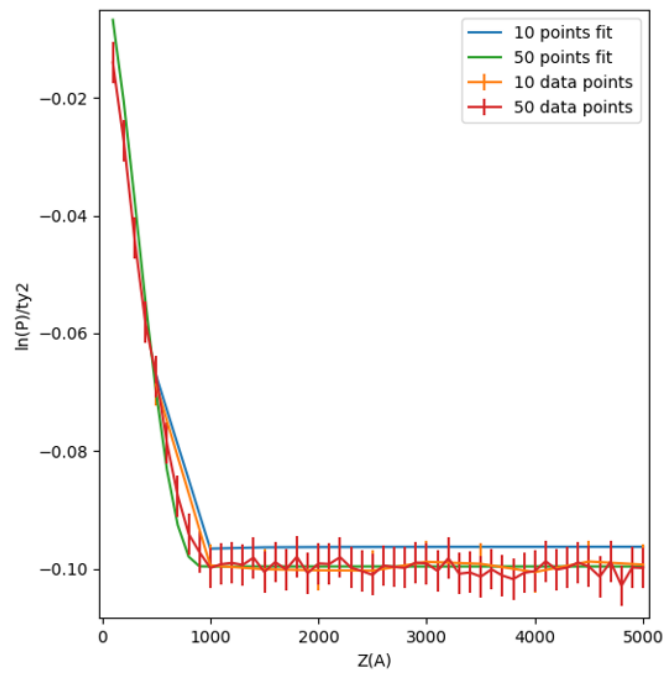
4.7 McStas Simulations

To further understand these pseudo-monochromatic SESANS results a virtual SESANS instrument was built in McStas. McStas is a neutron ray-trace simulation package using Monte Carlo statistics to simulate neutrons in a virtual instrument [17][18][19][20][21][22].

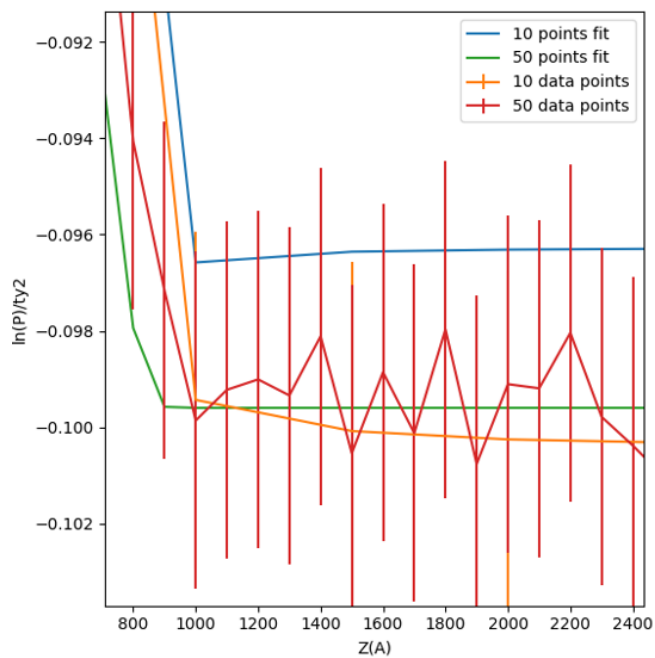
The Larmor instrument was built by adapting the existing Delft SESANS instrument written [23] by Bouwman et al. [24]. This virtual instrument consists of two parallelogram field regions, each formed of two foil flipper magnets [25]. Foil flipper magnets consist of a rectangular magnetic field with an angled magnetic foil inside that acts as a spin-flipper, flipping neutron spin into a direction non-parallel to the applied magnetic field. As the neutron only experiences a torque when its spin is not parallel to the field direction it effectively experiences a triangular field region. A parallelogram field region is created by placing two of these components in the neutron beam. The beam then passes through the scattering sample, here we use the Sans spheres2 component [26]. After scattering, the beam passes through another parallelogram field formed of two foil flippers with opposite magnetic field to the first. The beam is polarised before and after the magnetic fields before entering the detector where total beam intensity is measured.

The instrument was adapted to have Larmor's dimensions by increasing the sample-detector distance to 4.4 m and changing the size of the detector to match the size of the Larmor SESANS detector. The virtual instrument is displayed in Figure 4.13 and the code is given in A.3.1.

Three neutron wavelengths were used, 2.165, 6.495 and 10.825 Å. The SANS spheres sample was set to be 1 mm thick with a particle diameter of 200 nm and a

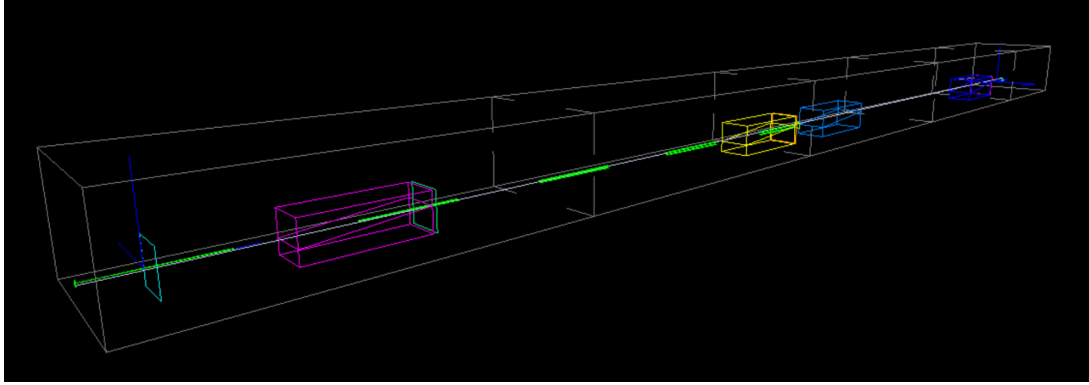


(a)

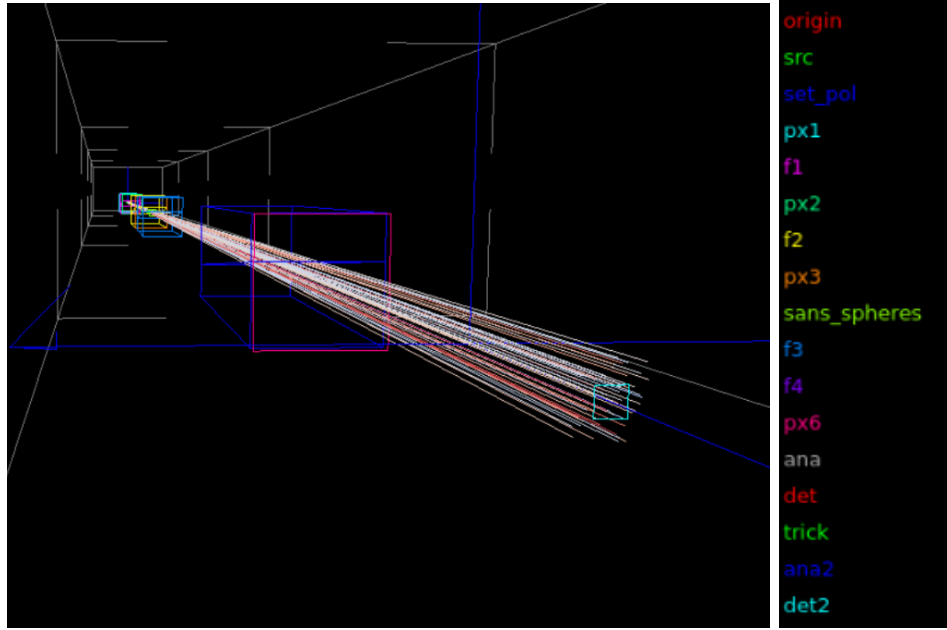


(b)

Figure 4.12: Model SESANS data sets fit using the Sasview sphere model. Two model data sets with the same shape and range but one containing 10 points and the other 50. The fit is created for the 50-point data and then applied to the 10-point data. The fit moves up and left, away from the data. (b) is a zoomed-in section of (a) showing the plateau in more detail.



(a)



(b)

(c)

Figure 4.13: Virtual Larmor instrument, built in McStas from the existing Delft SESANS instrument. Two angles are shown (a) a side view with neutrons traveling left to right and (b) a view from behind the detector. Components are colour-coded using the legend colours (c). Components f1 and f2 make up the first parallelogram magnetic field region and f3 and f4 the second. The polariser and analyser are denoted by set pol and ana, sans spheres and det2 are the sample and main detector. Other components include diagnostic detectors and monitors. The full instrument code is given in A.3.1.

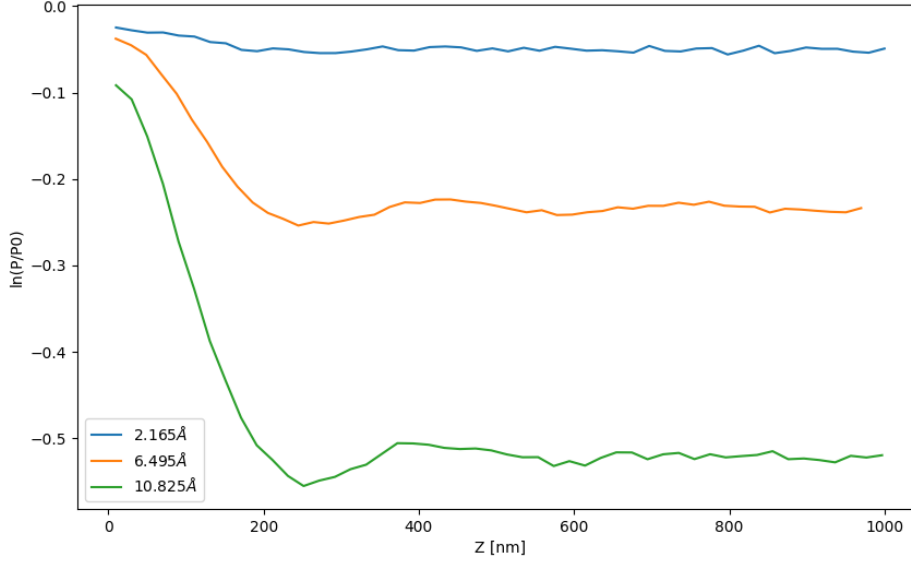


Figure 4.14: McStas simulation results. Spherical particles with 200 nm diameter at a 10% volume fraction.

VF of 10% to mimic our dilute samples. Field angle was kept constant and spin-echo length was varied by changing the strength of the magnetic field (B_y). A different B_y range was used for each wavelength to keep the spin-echo range constant at 10-1000 nm, given in table 4.2.

Wavelength [$\text{\AA}$]	B_y start [T]	B_y end [T]
2.165	1.856×10^{-4}	1.856×10^{-2}
6.495	2×10^{-5}	2×10^{-3}
10.825	7.4×10^{-6}	7.4×10^{-4}

Table 4.2: McStas Larmor instrument wavelengths and magnetic field ranges

As in a SESANS experiment, an empty beam and sample in intensity were measured and the logarithm of the ratio was plotted. The results of the McStas Larmor simulation are presented in Figure 4.14. All three data sets have a minimum at the same Z value (around 200 nm as expected for our particle size. However, the longer wavelengths experience more depolarisation. This is due to longer neutron wavelengths being scattered over a larger angle. However, it is the opposite of the trend we see in the experimental data, in which longer wavelength data sets move up and right.

Figure 4.15 shows experimental data for 10% 200 nm PS nanoparticles in D_2O at 4 neutron wavelengths compared with simulated data at 10.825 $\text{\AA}$. The simulated data has been scaled in the y axis by a factor of 1/4 to appear next to the experimental data.

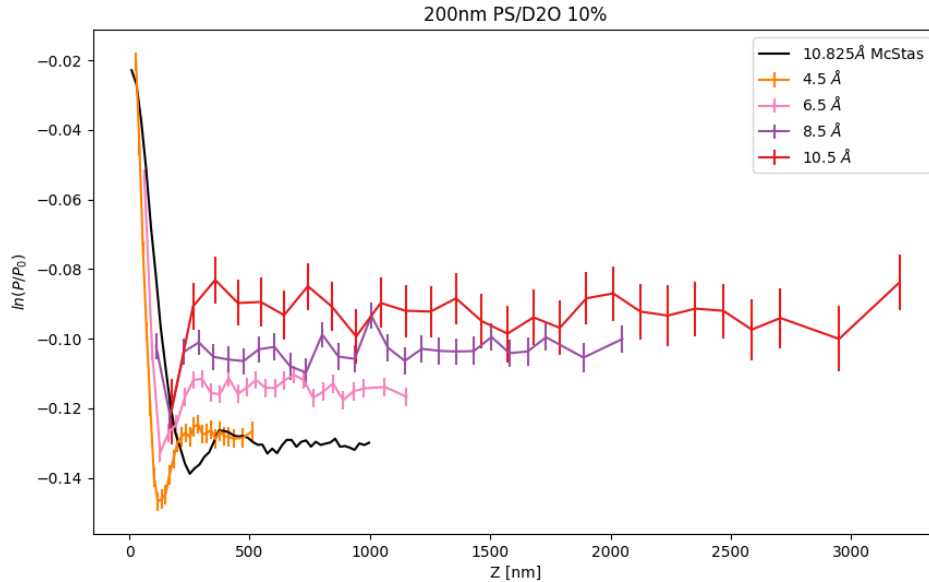


Figure 4.15: psuedo monochromatic SESANS data for a 10% concentration of 200nm PS nanoparticles in D₂O at 3 neutron wavelengths, along with scaled McStas simulated data at a single neutron wavelength of 10.825 Å.

This shows that our experimental data has a minimum that is smaller than expected for 200 nm spheres. Also as we increase wavelength the minima move towards its true value but does not reach it.

4.8 Conclusions

Developing a reliable calibration sample has led us to discover several issues with the current SESANS data acquisition and fitting process. In turn, this emphasises the need for calibration samples. It was found that when operating in the pseudo-monochromatic mode changing the neutron wavelength drastically changes the data. Using this unique SESANS mode enabled us to identify how data moved with wavelength however it is obvious that this feature will affect all operational modes. This may indicate that there is a fundamental problem with how polarization is measured and normalised. More investigation of the practical aspects of data acquisition and normalisation is needed to mitigate this problem. It may be the case that a correction factor is applied to data dependent on wavelength.

While using Sasview to fit SESANS data it was also found that a fit applied to data varies due to data binning. This bug was reported. Sasview is invaluable for the analysis of scattering data and the ability to fit SESANS means it will be extensively used during experiments. However, this problem must be resolved to ensure accurate

analysis of data.

Through simulation of the Larmor instrument in McStas, it was found that there is also a shift in spin echo length between simulated and experimental data. With experimental data trending towards simulation with increasing wavelength. A shift in minima position with increasing wavelength was not seen in the simulated data as it is in the experimental data.

Out of the 10 calibration samples tested a few stood out as the most practical. Due to its reliable size and long-range order, the self-assembled 500 nm SiO₂ colloidal crystal is one of the best options for a calibration sample. Being a dry sample also means this is easily imaged using AFM. This is a valuable method of investigating the sample and ensuring it has a well-known structure, essential knowledge for a practical calibration sample. Being a dry sample also means long-term stability and easy storage. Allowing it to be reused for consecutive SESANS experiments over the years. Self-assembly of the sample also means it can be relatively easily made in neutron facilities across the world with a reliable structure.

Another sample that showed promise as a calibration standard was polystyrene nanoparticle dispersions. Through experimentation, it was found that the best resolution was achieved using volume fractions of 10% in D₂O. Having both 100 and 200 nm diameter particles available will allow for a good calibration over a range of spin echo lengths. These samples are also very easily prepared by dialysis, a procedure that is commonly carried out at neutron facilities.

These reliable calibration samples should now be used to refine the SESANS measurement procedure on the Larmor instrument device. They should also be used on SESANS instruments at other facilities to ensure consistency between experiments.

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Chapter 5

SESANS Investigation of Surfactant Clusters in Water-Based Deuterated Latex Films.

Water-based polymer coatings are an alternative to epoxy-resin coatings, with low volatile organic compound content. Water-based polymer coatings are widely used as coatings for commercial uses (indoor wall paint). However, more development is needed in this area before water-based systems will have the corrosion protection ability of epoxy systems. Surfactants are used in water-based latex coatings to provide colloidal stability to the latex dispersion, and also to improve wettability on the substrate. In this chapter, we have investigated the residual surfactants in deuterated latex films by spin-echo small angle neutron scattering (SESANS) measurements. We have shown that surfactant clusters exist on a length scale that is readily accessible by SESANS, proving its utility in the investigation of these materials.

5.1 Introduction

Polymer coatings are used in a vast range of industries for many different applications. These applications can be decorative (paints used for aesthetics and branding), functional (adhesive coatings), or protective (preventing corrosion) [1]. They can also be used to modify the properties of surfaces such as create a hydrophobic layer, provide bacterial resistance [2], or prevent the build-up of marine life (biofouling) [3] and so increase the efficiency of ships.

The use of volatile organic compounds (VOCs) in solvent-based coatings aids in application and drying as well as improving coating characteristics. However, VOCs have severe adverse effects on human and animal health, as well as the environment [4] [5] [6]. Inhaling VOCs causes eye, nose and throat irritation and can lead to nausea, damage to the central nervous system and cancer [7]. VOCs released into the

atmosphere also contribute to atmospheric ozone formation, organic aerosol formation and photochemical smog formation [8] ultimately leading to global warming. For this reason, there is currently a drive to move away from the use of VOCs and solvent-based coatings, and towards water-based systems. Water-based polymer coatings contain up to 80% water and are below the legal limit of 350g of VOCs per litre of water [9].

Water-based polymer coatings are formed mainly of latex particles dispersed in water. Once applied to a surface the water evaporates and a continuous film is formed, this is a complex drying process widely agreed to contain 4 discreet steps [10], and depicted in figure 5.1. Initially, Latex particles are stored as a dilute dispersion in water (known as stage I). As water evaporates particles move closer together and eventually come into contact forming a close-packed system (stage II). Next, driven by a reduction in interracial free energy, through capillary pressure [11] further water is removed and particles deform to fill the gaps created (stage III). Finally, (if the system is above the glass transition temperature (T_g)) polymers diffuse across particle boundaries, forming a continuous homogeneous network with no solid-solid interfaces (stage IV).

Surfactants are used in water-based polymer coatings to provide colloidal stability to the latex dispersion [12], And also to improve wettability on substrates. Surfactants are also used as antimicrobials [9] to increase shelf life, which in commercial paints and coatings needs to be 3 years. In the film formation process, surfactants aid in particle ordering in the formation stages. Surfactants are essential for the storage and application of the coating however once the film is formed they must redistribute to form a homogeneous film. Exactly where the surfactant goes is not well understood and has been the subject of multiple investigations [11]. Surfactants can collect in the film or migrate towards the surface, both of which can have negative effects. The presence of surfactants inside the final film can affect water resistance and aesthetic properties of the coating changing the optical clarity, while migration of the surfactant towards the coating-substrate interface can reduce adhesion [13] [12].

Surfactants accumulate at the particle-particle interface and inhibit polymer diffusion in stage IV of film formation. Creating an inhomogeneous film with reduced barrier properties, allowing for increased water and ion diffusion through the film [14]. The hydrophilic nature of the surfactants also increases the permeability of water through the film with clusters forming channels in the dried film [1]. These factors limit the efficacy of water-based coatings as corrosion-resistant coatings. By understanding the structures that different residual surfactants form we can aid in the development of water-based polymer coatings for the use of corrosion-resistant coatings. Corrosion is a vital area for scientific development as it has substantial economic and environmental costs globally. With costs originating from repairing and replacing structures damaged by corrosion, along with the cost of preventing corrosion via the repeated application of coatings.

Previous investigations have been carried out on the distribution of surfactants in dried water-based coatings. These include in situ small angle neutron scattering (SANS) measured during the film drying process, carried out by Martin-Fabiani *et al.* [11]. Here the film formation process was followed as spherical latex particles coalesced

to form a continuous film. leaving behind scattering signal from clusters of residual surfactant. The clusters were found to take the form of oblate spheroids with a polar radius of 170 nm. Clusters were also shown to grow with increased drying time.

Surfactant investigations have also been carried out using a multitude of other techniques including, Rutherford backscattering [15], SAXS [16], [17], SEM and AFM [18] [1].

Tizitzinou et.al. [18] observed using AFM, that surfactant clusters in latex films evolve from a thin uniform layer and coalesce to form large hemispherical 'blobs'. These features were shown to be present on the sample surface and were as large as 10 μm . The morphology is suggested to be caused by a reduction in surface energy. A higher surfactant concentration was also observed near the film-air interface, by Rutherford backscattering measurements. This observation was further investigated by Lee et.al [15], identifying a 30-50 nm surfactant rich surface layer.

Previous work has shown that surfactant cluster sizes are around the upper limit of length scales accessible by conventional SANS. Scattering techniques are essential for the investigation of soft matter systems as unlike imaging techniques they allow the investigation of the internal structure of a sample without the need for cutting or fracturing the sample. Imaging techniques can provide essential insight, often through freeze fracturing a sample and imaging the internal structure. However, without correlating images with scattering results it is impossible to know if the structure was damaged or changed in the process. Scattering techniques also have the added benefit of averaging over a large beam size and hence large sample volume, ensuring results represent the sample as a whole and not a local phenomenon that may be shown in an image and so unrepresentative. Neutron scattering is able to use large beam sizes (around 1 cm^3), along with highly penetrating beams due to neutrons interacting with the sample nuclei. Neutron scattering also benefits from isotopic sensitivity, allowing specific regions of a sample to be investigated through isotopic substitution and contrast matching.

In previous work by Chi Him Lo [14] the corrosion protective properties of the same surfactant systems as used in this experiment has been measured using a variety of techniques. Prohesion testing was carried out in which a coating on a metal substrate is exposed to a 2-hour wet (high sulphate solution fog at 25°C) and dry (air at 35°C) cycle over a 70, 250 and 750-hour life cycle. Lo discovered that excess AOT (2.5% w/w) has severe adverse effects on adhesion and corrosion protection properties. It was also discovered that coatings containing 2.5% w/w PSS 70k exhibited good corrosion protection and adhesion. The poor adhesion of AOT samples was put down to excess low molecular weight (M_w) surfactant at the coating-metal interface. In contrast, it was also theorised that PSS improves adhesion and corrosion protection by forming a polymer layer at the interface, based on AFM-IR results.

Lo also saw very similar corrosion protection properties between PSS surfactants with different molecular weights. In another prohesion experiment 3 M_w s were tested; monomer, 70 K and 1 M. Corrosion resistance and adhesion were shown to increase with M_w .

Spin-echo small angle neutron scattering (SESANS) provides access to larger length

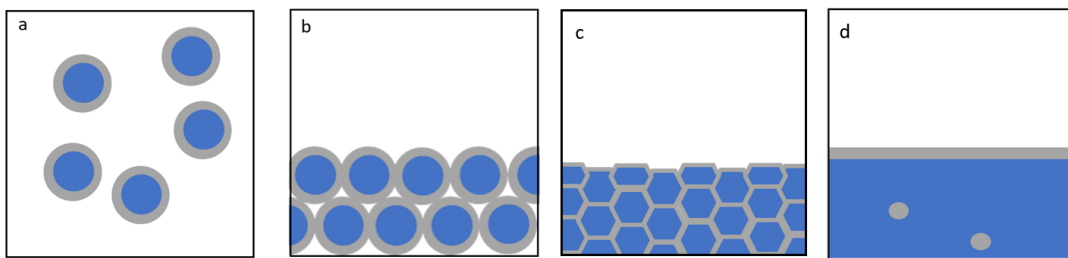


Figure 5.1: Polymer latex film formation of latex particles (blue) coated with a surfactant layer (grey). The four basic stages of film formation are depicted left to right in a-d. Firstly, dilute latex particles are dispersed in water (a), water evaporates and particles come in to contact with each other and become ordered (b). Further evaporation leads to particle deformation (c), and finally, a homogeneous film is formed as polymer molecules diffuse across particle boundaries (d). Residual surfactant can collect inside the film or on the surface (d).

scales than conventional SANS by mapping very small scattering angles onto the polarization of a neutron beam. By measuring scattering angles that would be lost in the beam stop on a SANS instrument, SESANS can measure length scales from 10 nm to 20 μm (4 orders of magnitude) [19] and theoretically with access up to 100 μm [20]. Compared with a conventional SANS instrument with lengthscale sensitivity in the range of 1 - 100 nm. Therefore, this makes SESANS an ideal choice for the study of surfactant clusters in film-forming water-based latexes.

5.2 Deuterated Latex Synthesis

Deuterated Latex (d-latex) films were prepared by Dr Mohammed Jamali of Manchester University. Closely following the procedure described in the thesis of Chi Him Lo [14], A student also sponsored by AkzoNobel and working with AkzoNobel Sassenheim (Netherlands).

5.2.1 Materials

Deuterated styrene D8 monomer (d-styrene) was supplied by Polymer Source (Quebec, Canada).

Methyl methacrylate (MMA), 2-ethylhexyl acrylate (2EHA), methacrylic acid (MAA) and ammonium persulphate (APS) were supplied by Sigma-Aldrich (Gillingham, UK). Rhodapex CO436 (CO436), was supplied by Solvay Group. Dipropylene glycol n-butyl ether (DPnB) under the brand name Dowanol was supplied by AkzoNobel Sassenheim.

The surfactants: Polystyrene 4-sulfonic acid co maleic acid (PSSMA), Poly(sodium 4-styrenesulfonate) with 70k and 1M molecular weight (PSS 70k & PSS 1M), 4-vinyl benzene sulphonate (4VB), and Aerosol OT (AOT) were supplied by Sigma Aldrich UK.

5.2.2 D-Latex synthesis

The Latex used in this experiment was poly(styrene-co-methyl methacrylate-co-2-ethylhexyl acrylate-co-methacrylic acid) (P(STY/MMA/2EHA/MAA)) with a desired Tg of 49°C. This was synthesised using Rhodapex CO436 as the anionic surfactant and ammonium persulfate as the thermal initiator. The latex was synthesised with d-styrene and prepared by seeded semi-batch emulsion polymerisation. D-styrene D8 (34.4 g), 2EHA (25.4 g), MMA (1.35 g), MAA (0.242 g), Rhodapex (0.648 g), Ammonium persulfate (0.961 g) and deionised water (102 g) were stirred together at 300 rpm and heated to 90°C under a nitrogen atmosphere

The final solids content of the latex by weight was:

- 71.1% d-styrene
- 25.6% 2-ethylhexyl acrylate (2EHA)
- 2.8% Methyl methacrylate (MMA)
- 0.5% Methacrylic acid (MAA)

With 50% w/w water and 1.34% w/w surfactant (Rhodapex)

5.2.3 Coating Formulation

The 6 coatings investigated in this experiment were all formed from the deuterated latex described above and all but 1 (control) were spiked with 2.5% w/w of an additional surfactant. Below is a list of additional surfactants that were trialled:

- Polystyrene 4-sulfonic acid co maleic acid (PSSMA)
- 4-vinyl benzene sulphonate (4VB)
- Poly(sodium 4-styrenesulfonate) $M_W = 70K$ (PSS 70k)
- Poly(sodium 4-styrenesulfonate) $M_W = 1M$ (PSS 1M)
- Aerosol-OT (sodium bis(2-ethyl-1-hexyl) sulfosuccinate) (AOT)

These additional surfactants were slowly added to the latex as the dispersion was stirred on a automatic stirrer. DPnB was added at the same time at a concentration of 6.6 % w/w in all samples. DPnb acted as a cosolvent, lowering the T_g of the latex enabling it to film form at room temperature.

5.2.4 Casting of Free-standing films

Once the cosolvent and additional surfactants were added free-standing films were formed by pipetting the dispersion onto a polypropylene lid, which contained the film in the liquid stage and allowed for easy removal once the film was dry and had film formed. The films were then left to air dry for several days before being removed during the SESANS experiment. Each film was cut into several circles using a scalpel. 10 individual circles were cut per sample.

5.3 Experimental Methods

All SESANS measurements were carried out on the Larmor instrument at the ISIS neutron and muon source in Oxfordshire. Unlike conventional scattering techniques that measure correlations in inverse space, SESANS measures the real-space autocorrelation function (ACF) of a sample. Therefore, direct insights into the lengthscales present without the need for model fitting and so the results are readily interpreted. In particular, the largest scattering feature of a sample is represented in the ACF as a plateau. In the case of dried latex films, the entire sample would ideally be a homogeneous layer therefore the presence of large scattering features will indicate a film that has voids on a large lengthscale.

SESANS works by first polarising the neutron beam. This polarised beam then passes through a parallelogram-shaped magnetic field, in which the neutrons will undergo Larmor precession. The beam then passes through an equal but opposite-direction magnetic field. If the beam is unscattered between the fields each neutron will precess by the same amount in the opposite direction as it did in the first, returning the beam to its initial polarised state. This condition is called spin-echo. When a scattering sample is placed in the beam between the fields any small angle scattering will result in the spin-echo condition not being met. Smaller scattering angles are measured here than is possible in a SANS measurement, meaning SESANS is sensitive to larger length scales than SANS. By analysing the beam after the second field and measuring the intensity, scattering is represented as a drop in intensity between an empty beam and the sample being measured. The drop in polarisation gives the ACF of the sample.

Lengthscales probed in a SESANS measurement are given by the spin-echo length (z), which is defined in terms of the instrument parameters, neutron wavelength (λ), magnetic field (B) length of the field region (L) and inclination angle of the magnetic field region (θ_0). Along with a constant $C = 4.6368 \times 10^{14} T^{-1} m^{-2}$ [21].

$$z \equiv \frac{C \vec{B} \lambda^2 L \cot \theta_0}{2\pi} \quad (5.1)$$

Larmor is a time-of-flight (TOF) instrument with access to neutrons of wavelength 2 - 12 Å and therefore a range of spin-echo lengths are achieved in a single measurement, providing a range of λ in equation 5.1. In this experiment, the accessible z range was also increased by measuring at 3 different angles (θ_0) also called pole shoe angles. Pole shoe angles of 89°, 70° and 30° gave access to length scales from 50 nm to 8 μm.

Free-standing film disks were stacked to achieve sufficient scattering and held in the neutron beam in an aluminium sample holder, with a circular aperture. Held in place by a quartz disc on each side of the sample stack, as shown in figure 5.2.

For all samples, we had 10 individual sample disks. All samples were initially measured by SESANS dry then each sample batch was split into 2 for separate soaking measurements. The first batch (wet 1) was soaked in water for 1 hour and 40 minutes, uptaking an average water percentage of 15%. This batch was then measured wet while the second batch continued soaking. The second batch (wet 2) was left soaking for 15

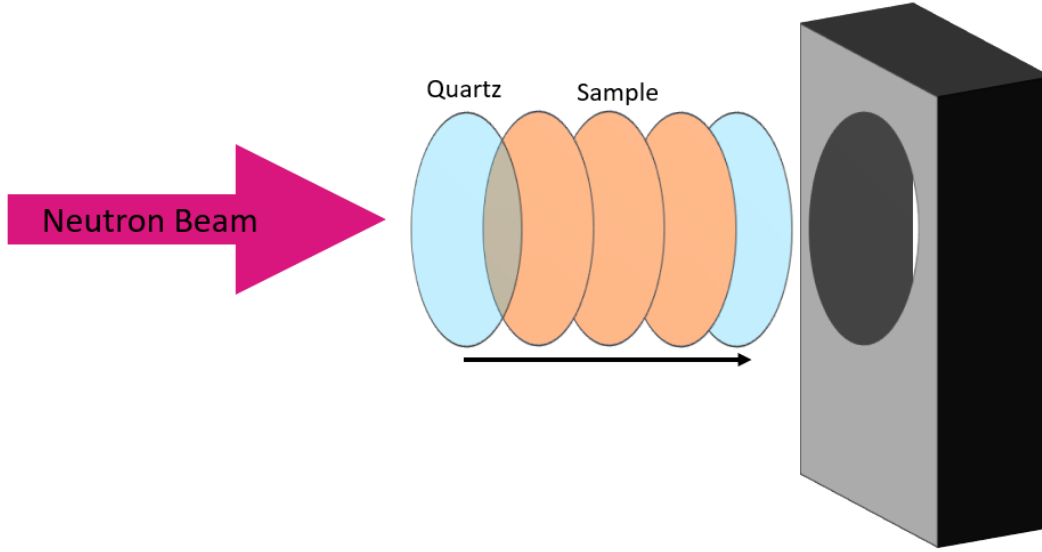


Figure 5.2: SESANS sample holder. Free-standing films are arranged inside an aperture in an aluminium holder, sandwiched by two quartz disks.

hours, uptaking an average of 36% of their original mass. One disk of each sample in wet 2 was then measured using SESANS while the others were taken out of the water and left to dry in a fume cupboard. After 6.5 hours the average uptake had dropped to 1.9% of the original mass and the samples were then measured dry (wet 2 dry), further details are given in table 5.1.

Along with free-standing films, d-latex particles were also measured dispersed in water at volume fractions of 5% and 10%. These were held in 1 mm thick silica cells and measured using the conventional TOF SESANS mode. These were only measured at a pole shoe angle of 89° as the particles are small and only require access to short

Sample	t [mm]	Dry		Wet 1		Wet 2		Wet 2 Dry	
		L	$I_{mass}[g]$	L	$W_{mass} [\%]$	L	$W_{mass} [\%]$	L	$W_{mass} [\%]$
Control	0.168	8	0.0296	3	0.135	1	0.175	1	-0.0542
PSSMA	0.12	8	0.0267	3	0.111	1	0.321	1	-0.0136
4VB	0.158	8	0.0383	3	0.239	1	0.656	1	0.178
PSS 70k	0.109	9	0.0231	3	0.129	1	0.519	1	0.0309
PSS 1M	0.777	6	0.0540	3	0.216	1	0.517	1	0.114
AOT	0.932	7	0.0213	3	0.0755	1	0.0296	1	-0.142

Table 5.1: Sample details. Where t is the mean film thickness measured for a dry film. L is the number of sample layers used in each measurement. I_{mass} is the average initial sample mass. W_{mass} is the average water uptake at the start of the measurement, calculated as a percentage of the initial mass.

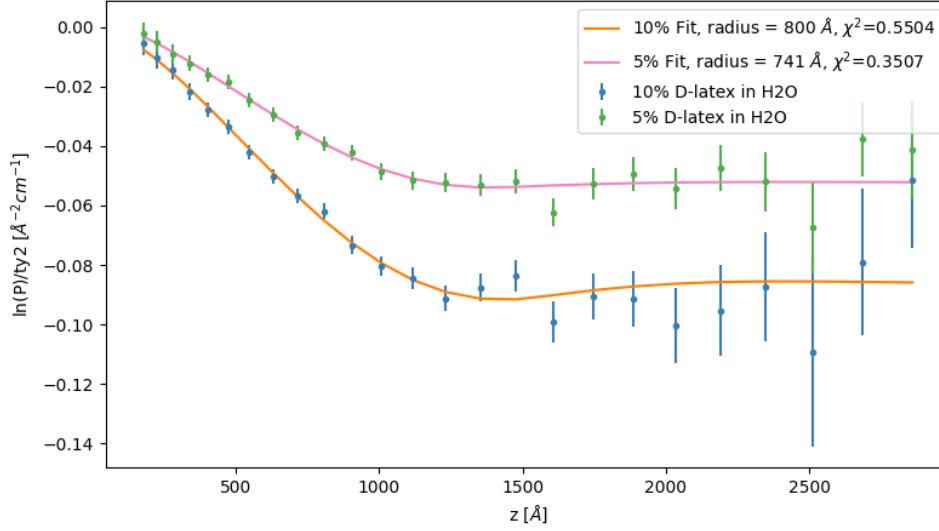


Figure 5.3: SESANS data for deuterated latex particles dispersed in water, at 10% and 5 % volume fraction. Fit with a hard sphere model in SasView, fit radius and χ^2 value are shown in legend.

spin-echo lengths.

Along with SESANS measurements, a limited number of samples were analysed using scanning electron microscopy (SEM). Two free-standing films were imaged; the control, and a sample prepared with additional surfactant PSS 1M. Samples were prepared for imaging the internal structure via freeze-fracture. This process consisted of dipping the sample disk into liquid nitrogen for around 30 seconds, before being removed and split in half by hand. Samples were then placed on an SEM stub and sputter coated with a 10 nm gold layer.

5.4 Results and Discussion

5.4.1 D-Latex Dispersion

Measurement of d-latex particles dispersed in water allowed a measurement of the particle size before they underwent the film-forming procedure. The SESANS results are shown in figure 5.3. Data was fit in SasView using the sphere model [22]. The fit identified particles with a radius of 800 Å for the 10% dispersion and 741 Å for 5%.

5.4.2 Dry films

All SESANS data for the dry free-standing films is shown in figure 5.4. Each data set contains all 3 pole-shoe angles, giving detailed information on length scales ranging

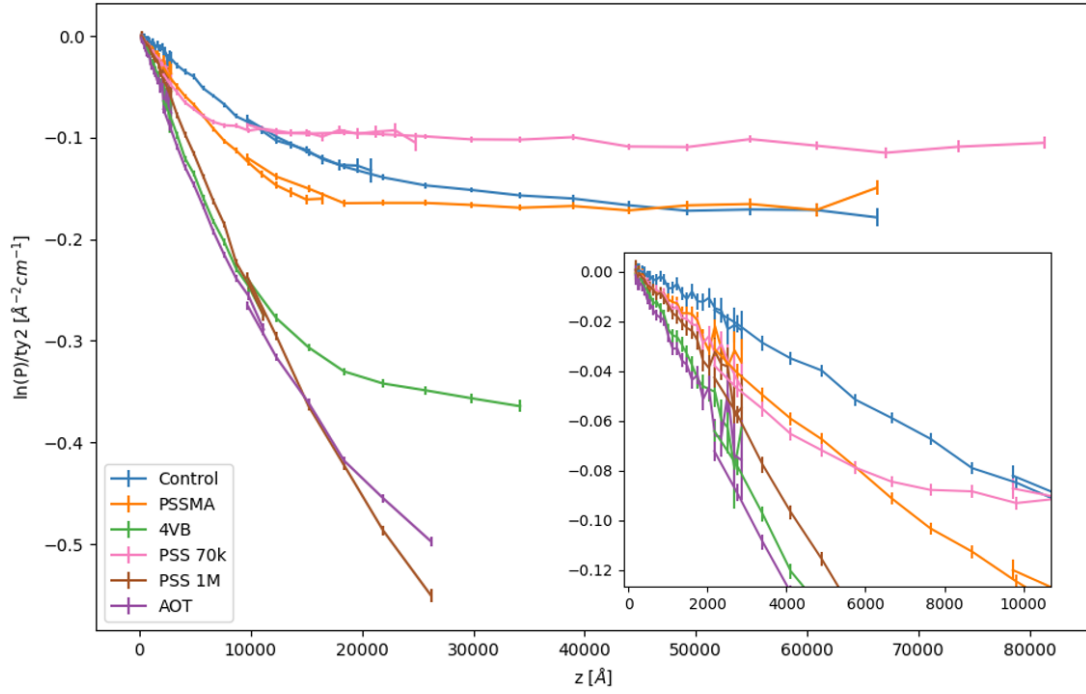


Figure 5.4: SESANS data for dry free-standing d-latex films. Data from 3 pole-shoe angles (89° , 70° and 30°) are stitched together. The legend shows the additional surfactant used in the specific formulation. Insert is a zoomed in section of the small length scales.

Sample	Sphere fit		Lamellae fit		Ellipsoid fit		
	r [Å]	χ^2	t [Å]	χ^2	Polar r [Å]	Equatorial r [Å]	χ^2
Control	11230	6.1059	5014	1.3191	3626	30765	0.41142
PSSMA	7480	5.9772	2473	10.98	2612	14914	1.5764
4VB	7388	21.21	3393	4.853	2419	20029	2.4023
PSS 70k	3915	2.9292	1163	8.923	1451	8070	1.286
PSS 1M	11418	19.444	7830	8.8168	5152	70142	6.3342
AOT	8921	51.929	4824	17.896	3110	57204	14.325

Table 5.2: Dry free-standing film fit parameters for sphere, lamellae and ellipsoid SasView fits. r and t represent the radius and thickness for the relevant fits.

from 100's of Å to 10's of thousands. A pole-shoe angle of 89° gives a z range from 20-280 nm, 70° gives $220 \text{ nm} < z < 2.5 \text{ }\mu\text{m}$ and 30° gives $1 \text{ }\mu\text{m} < z < 6.6 \text{ }\mu\text{m}$. For clarity, all graphs are shown in Å. All of the sample data overlaps well at the intersection of pole-shoe angles, showing that the films were stable.

In each case the SESANS data plateaus orders of magnitude above the initial size of the latex particles before film formation. The plateau in SESANS data shows the size of the largest scattering feature, therefore latex particles in all samples had gone through the film formation stage and polymer diffusion had occurred over the particle boundaries forming a continuous film, the surfactants did not stop film formation. The sample that plateaus first was PSS 70k at $1 \text{ }\mu\text{m}$, showing this film contains no scattering structures over $1 \text{ }\mu\text{m}$. Three samples are yet to plateau in this data set (4VB, AOT and PSS 1M). These three samples fully depolarised the neutron beam at long wavelengths meaning the largest length scale data is cut off. As all samples were of a similar thickness, it is easy to qualitatively say that these 3 samples contained more, larger scattering features. This indicates that these 3 surfactants cause more heterogeneity in the final film. This is likely to lead to films with less effective barrier properties. As these "surfactant" domains will preferentially allow water to diffuse much easier than in the polymer regions [1].

Each data set in figure 5.4 was then fit in SasView, to further investigate the shape and size of residual surfactant clusters. Three models were selected due to the likely structures that the surfactant can form; sphere [22], lamellae [23] and ellipsoidal [24]. In each fit the solvent SLD was fixed at the value calculated for the d-latex while radius/thickness and particle SLD were fit. The results for each fit are shown in table 5.2 and each fit is plotted in figure 5.5.

The best fit for all samples was found for the ellipsoid model, with the lowest χ^2 value in all cases. The fit for 4VB, AOT and PSS 1M data gives a larger χ^2 value due to the data not reaching a plateau. Therefore, it is harder for the fit to identify the size of these features.

This supports the findings of Martin-Fabiani *et al.* [11] who identified the formation of oblate spheroidal surfactant clusters in dry latex films. however, the clusters identified had average equatorial and polar radii of 170 nm and 25 nm, whereas our clusters had average polar and equatorial radii of 306.2 nm and 3352 nm. As a SANS

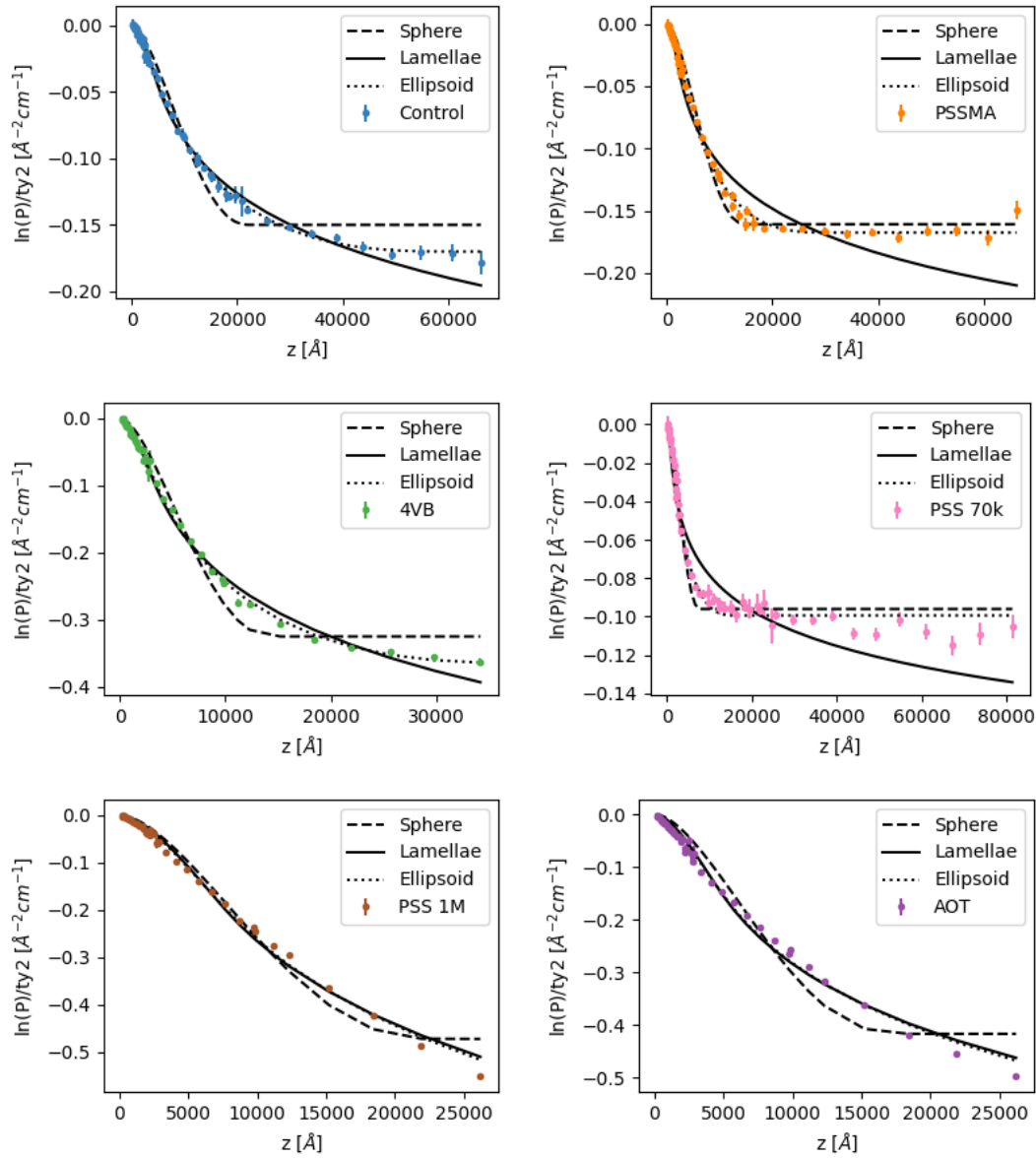


Figure 5.5: SESANS data for dry films containing additional surfactants. Fit using the software SasView, with the Sphere, lamellae and ellipsoid models.

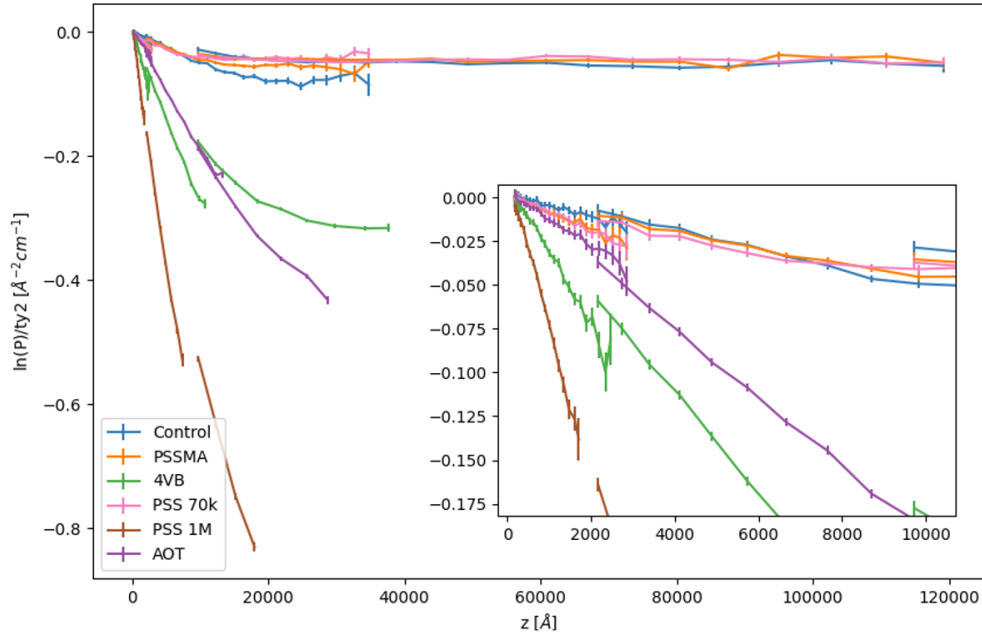


Figure 5.6: SESANS data for d-latex films soaked in water for 1 hour and 40 minutes (wet 1), containing different additional surfactants. Containing data from 3 pole-shoe angles (89° , 70° and 30°). The legend identifies the additional surfactant and the insert shows a zoom-in of the small length scales.

experiment, the available q range in [11] was 0.0015 - $0.25 \text{ \AA}^{-1}$ giving a real space range of ~ 400 - 2.5 nm . Therefore, it is possible that larger features were present and just not detected.

5.4.3 Soaked films

Figure 5.6 shows the SESANS data collected for samples after being soaked in water for 1 hour 40 minutes (wet 1). As with the dry data, it is clear that the three films containing (4VB, AOT and PSS 1M) contain larger scattering features, and therefore don't reach a plateau.

All 6 samples were first measured at a pole shoe angle of 30° before changing to 70° , and finally 89° . Meaning there was around 3 hours between subsequent measurements for each sample. Due to the sample holder not being air-tight this meant that water was lost by evaporation between measurements. Therefore, the data from different pole-shoe angles does not overlap. The wet sample data is therefore unsuitable to be fit in the same way as the dry data.

For this reason, the samples soaked for 15 hours (wet 2) were only measured at a single pole-shoe angle (89°), shown in figure 5.7. There is little information to be gained from this data as it is far from reaching the maximum length scales in each sample.

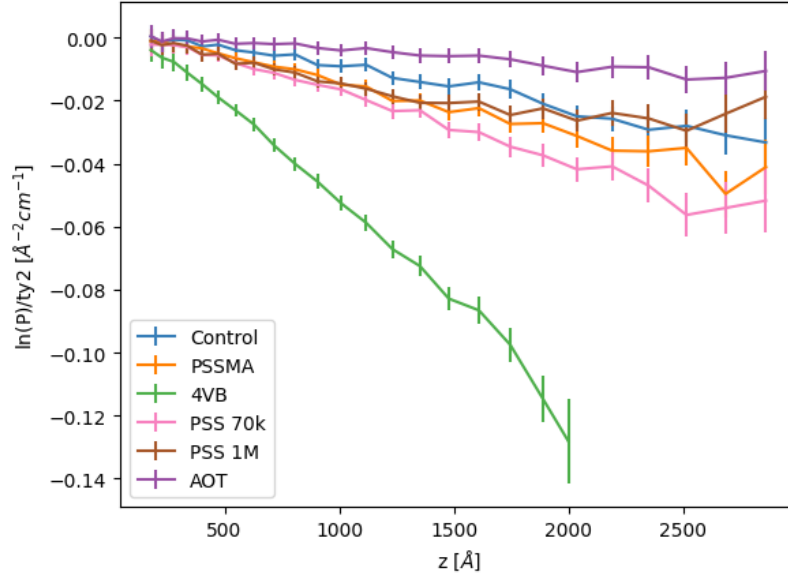


Figure 5.7: SESANS data for deuterated latex films soaked in water for 15 hours (wet 2). Measured at a pole shoe angle of 89° only.

5.4.4 Soaked and Dried Films

The 15-hour soaked samples were dried and measured using SESANS. The data for all wet-2-dry samples is shown in figure 5.8. In this measurement, all samples (apart from AOT and PSS 1M) plateaued before $2 \mu\text{m}$, inside the z range of the 89° and 70° measurements. Therefore, only AOT and PSS 1M were measured at 30° .

Like the wet results, there is evidence of water loss between measurements. Showing the samples were not fully dry when measured. Most evident between the 70° and 30° data in PSS 1M where water loss resulted in a reduction in scattering, causing the data not to overlap. This is the case despite PSS 1M dropping below its original dry mass, as shown in table 5.1. This is evidence of loss of material, either surfactant is being washed from the sample in the soaking and drying process or polymer and surfactant are leaching from the sample.

This data shows a similar pattern to the initial dry samples, where 4VB, AOT and PSS 1M scatter more strongly than the other samples. Showing that after soaking and drying they still contain more internal structure due to the residual surfactant forming clusters/domains. However, in this case, the 4VB data does reach a plateau at around $2 \mu\text{m}$. Showing the size of the largest scattering features has reduced during the drying and soaking procedure.

All data sets were fit with the ellipsoid model in SasView, fits are shown in figure 5.9 and the parameters are given in table 5.3 where they are compared to the dry data fits. The fit is poor on PSS 1M ($\chi^2 \simeq 62$) due to the disjointed data, caused by mass

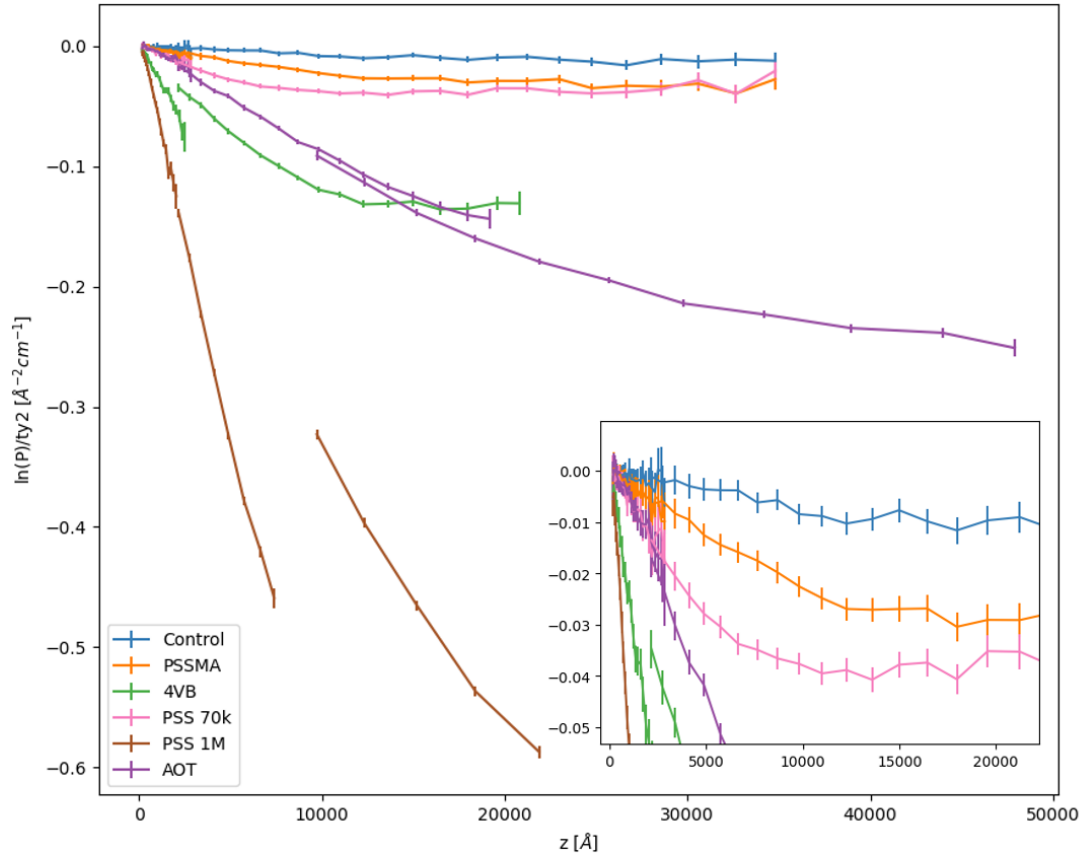


Figure 5.8: SESANS data for soaked and subsequently dried samples (Wet 2 dry). All data sets include measurements at pole-shoe angles of 89° and 70° , PSS 1M and AOT also include 30° . Insert shows a zoom-in at small length scales. Measured in the order 89° then 70° and finally 30° .

Sample	Ellipsoid fit			Change from Dry	
	Polar r [$\text{\AA}$]	Equatorial r [$\text{\AA}$]	χ^2	Polar r [%]	Equatorial r [%]
Control	2709	39976	0.25401	-25.3	+29.9
PSSMA	2085	23786	0.31466	-20.2	+59.5
4VB	834	23859	6.597	-65.5	+19.1
PSS 70k	2667	11661	0.52392	+88.5	+44.5
PSS 1M	2839	2551600	61.834	-44.9	+3540
AOT	5629	65820	2.7373	+81.0	+15.1

Table 5.3: Wet 2 dry data fit with an ellipsoid model using SasView. The percentage change in each radius from the dry data is also given.

loss.

The fitted data shows the ellipsoidal surfactant clusters remain but have changed size. Control, PSSMA and 4VB have all increased in the larger (equatorial) radius and decreased in the smaller (polar) radius. In these cases, the soaking cycle has formed asymmetric flatter clusters. In the case of PSS 70k and AOT, the clusters have increased by a significant margin in both dimensions, likely caused by clusters joining together, aided by the reorganisation and relaxation of the polymer network during the soaking cycle.

5.5 SEM Images

The SEM image shown in figures 5.10, 5.11 and 5.12 are of a free-standing film prepared with additional PSS 1M surfactant. This particular sample disk has been soaked for 1 h 40 min in water (wet 1) and subsequently dried in ambient conditions for over a week. The cross-section was accessed by freeze-fracture, revealing the internal structure. The first image (figure 5.10) shows the film on a large scale on top of the SEM stub. The surface of the film is smooth showing a continuous film.

Figure 5.11 shows the same film in cross-section on a much smaller scale. The rough surface along the cross-section is a feature of the freeze-fracture process. The figure also shows the presence of lighter spherical features. The features are more clear near the top surface of the film but can be seen throughout the cross-section. Figure 5.12 shows a zoomed-in section of the same image, near the film's top surface, displaying the features more clearly. These features are likely surfactant clusters.

The cluster size was analysed by image analysis in the ImageJ software. 20 clusters were measured across their longest axis revealing a mean radius of $1.09 \pm 0.04 \mu\text{m}$. While these clusters appear severely less ellipsoidal than the clusters identified in the SESANS data they are of the same order of magnitude. SESANS detected ellipsoidal surfactant clusters in the dry PSS 1M sample with a polar radius of $0.5 \mu\text{m}$ and an equatorial radius of $7 \mu\text{m}$. The freeze-fracture process could alter the shape of cluster additionally the cluster shape may be changed if surfactant leaves the system via the new opening created by the freeze fracture.

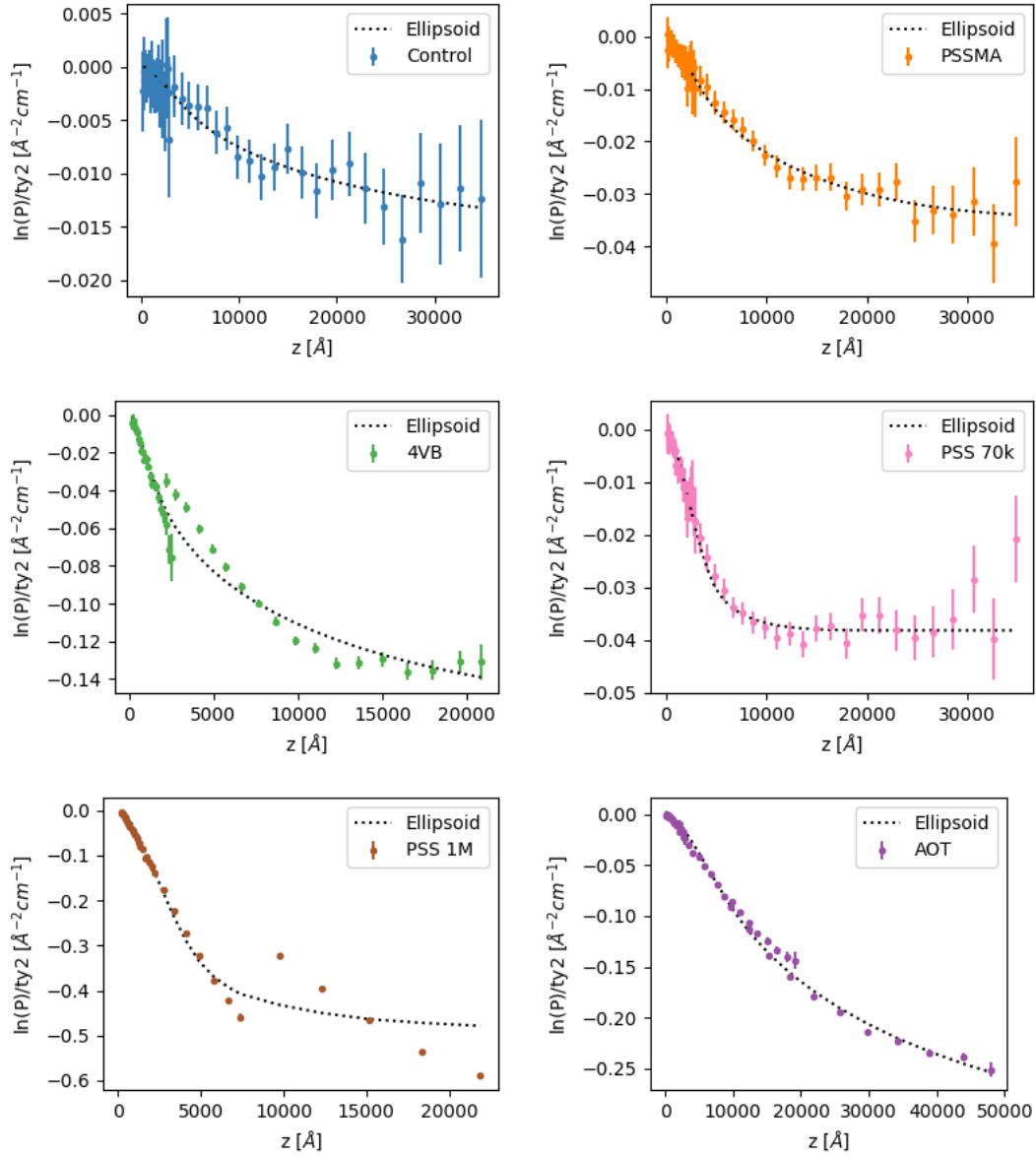


Figure 5.9: SESANS data for soaked and dried d-latex films, fit with the SasView ellipsoid model.

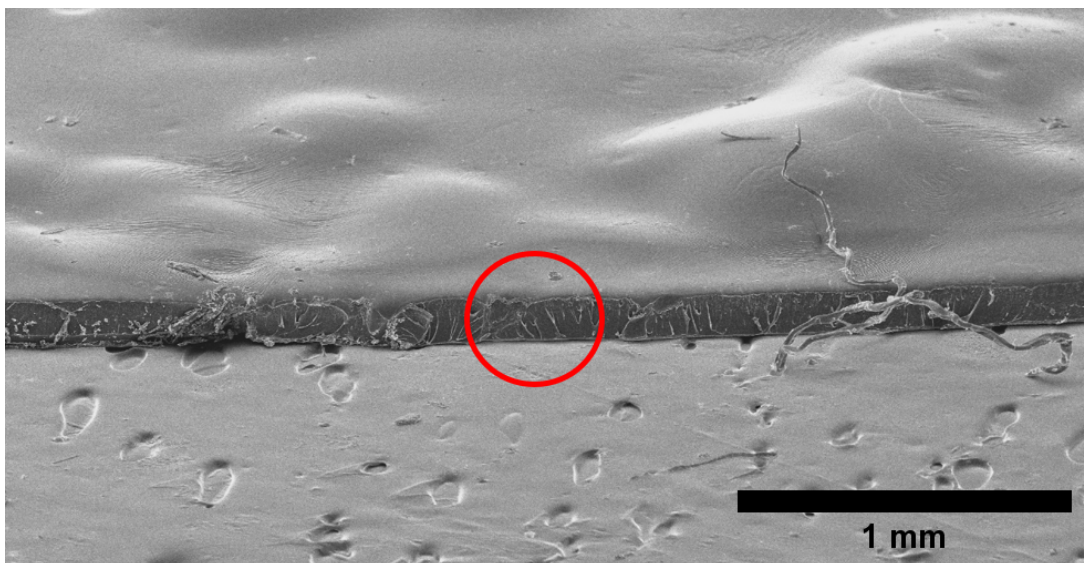


Figure 5.10: SEM image of deuterated latex film prepared with additional PSS 1M surfactant. The film is freeze-fractured revealing an internal cross-section (circled in red).

5.6 Conclusions

Residual surfactants in water-based latex films were investigated by SESANS measurements of deuterated latexes with a range of additional processing surfactants. It was found that surfactants form large ellipsoidal clusters in dried films. The additional surfactant severely affects the internal structure of the final film. PSSMA and PSS 70k show substantially less scattering, indicating a more homogeneous film, and are likely to exhibit better barrier characteristics.

In work by Chi Him Lo [14]

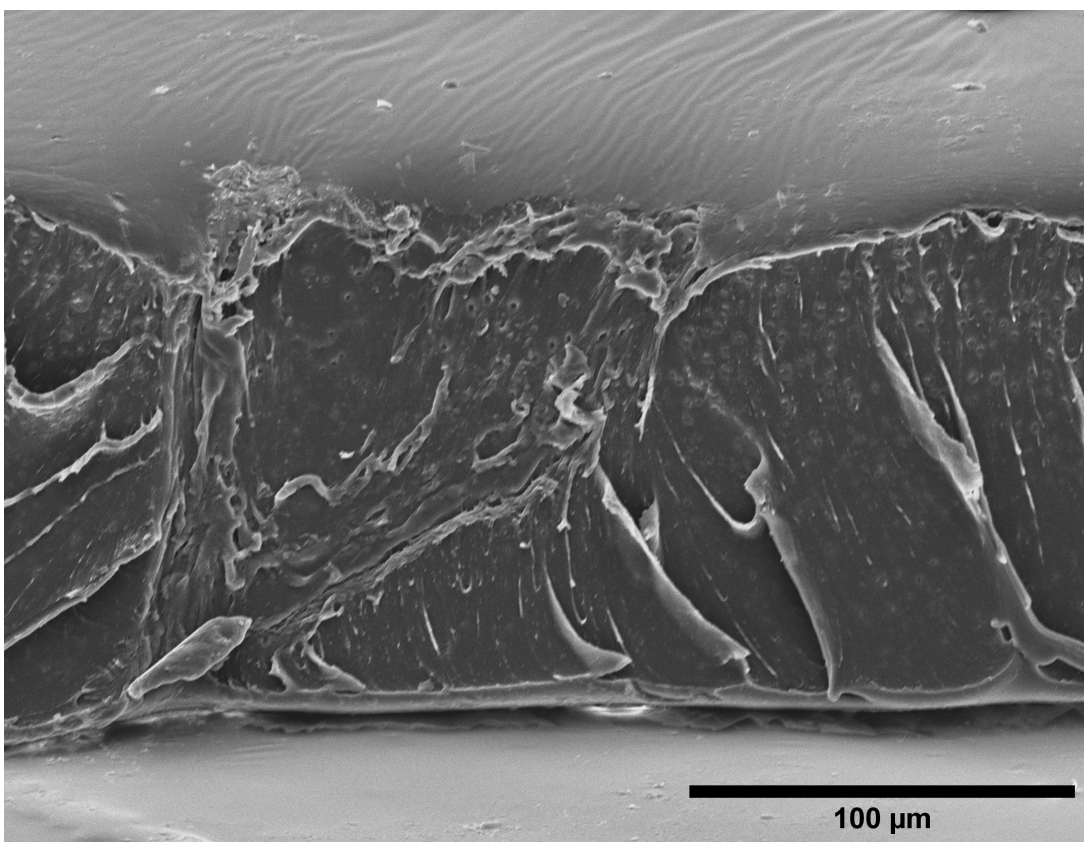


Figure 5.11: higher magnification SEM image of the film shown in figure 5.10, displaying voids in the cross-section. Mean void diameter along its longest axis $2.179\text{ }\mu\text{m}$ from 20 measurements.

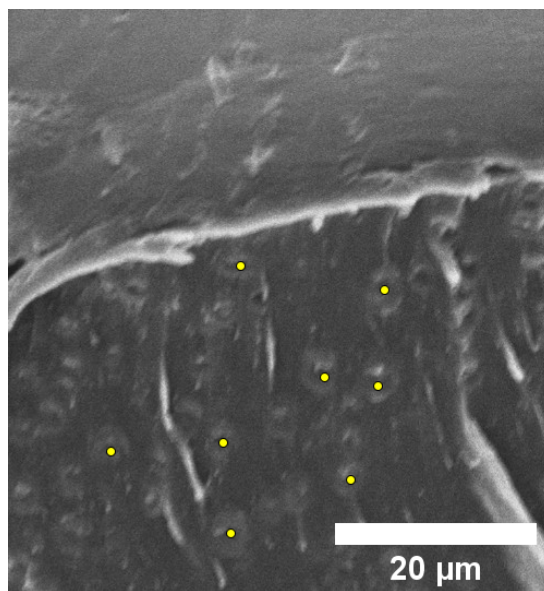


Figure 5.12: Zoomed in section of figure 5.11. Voids are marked in yellow.

Chapter 6

Conclusions and Suggested Future work

6.1 Conclusions

The aims of this thesis, as set out in Chapter 1, were twofold. They were to develop the experimental techniques of positron annihilation spectroscopy (PALS) and spin-echo neutron scattering (SESANS). While in the process using the techniques for the investigation of polymeric systems, focusing on their use as corrosion-resistant coatings.

Chapter 2 Introduced the theory of both experimental techniques in detail, starting with a description of the probe particles (positrons and neutrons) and developing the theory through to the final instrument output. Data analysis pathways are also described. For PALS this includes the introduction of a custom-written Python program which analyses data by fitting convoluted Gaussian and exponential functions and uses the Tao-Eldrup model to calculate a mean free volume void size and a fractional free volume. This program was written out of dissatisfaction with the current data analysis software used for PALS data analysis.

SESANS theory was detailed from first principles which includes a description of conventional SANS theory. The practicalities of a SESANS experiment were detailed along with a detailed description of SESANS results. Finally, SESANS results were simulated for a matrix containing randomly arranged spheres at different volume fractions using Python. This is a very similar system to those investigated in the following experimental chapters.

Chapter 3 is a paper written for submission in *Macromolecules* which compares PALS free volume measurements of an epoxy-amine corrosion-resistant coating with molecular dynamics simulations of the same system. Both techniques showed the presence of 2 discrete free-volume void sizes. PALS identified characteristic voids with diameters of 4.7 Å and 7.0 Å, while molecular dynamics identified characteristic void diameters of 2.5 - 3.5 Å and 3.5 - 7.0 Å. The combination of MD and PALS validated the results of both techniques while also giving better insight into this system. Through MD FV measurements at varied crosslink percentages, it was found that the proportion

of large voids increases as the crosslink percentage increases. Indicating they may be formed late in the curing process.

PALS fractional free volume (FFV) measurements were also found to be sensitive to water uptake in the system. With FFV decrease being equal to the percentage of water uptake. Showing that water occupies free volume voids in corrosion-resistant epoxy-amines.

Chapter 4 details the work carried out in the search for a reliable SESANS calibration sample. By investigating systems with a well-defined structure we were able to compare SESANS measurements with neutron ray-trace simulations. It was found that SESANS data shifted with neutron wavelength, this was not seen in the simulated data.

Multiple colloidal systems were trialled and samples with the greatest potential for use as calibration samples were 500 nm silica colloidal crystals and polystyrene nanoparticles of 100 and 200 nm diameters dispersed in D_2O . The colloidal crystal provided long-range repeating order and reliable particle size that is straightforward to image with AFM to ensure a consistent sample. Being a dry sample also gave the advantage of easy storage and stability. Polystyrene nanoparticle dispersions had the advantage of easy preparation as they are supplied already dispersed in water, and also provided a good calibration at a range of length scales.

The use of a reliable calibration sample will aid in the development of the SESANS technique by validating results and providing consistency across instruments at different institutes, including between spallation and reactor sources.

Chapter 5 is a SESANS investigation into water-based latex coatings prepared with a range of surfactants. SESANS was shown to be a valuable tool in the investigation of these systems, accessing length scales from 50 nm to 8 μm . Ellipsoidal regions of residual surfactant were identified in all samples with radii along the long axis ranging from 0.8 to 7 μm in dry samples. Ellipsoidal voids were also identified by SEM imaging of a freeze-fractured sample expected to be left over from surfactant clusters after the surfactant had left the coating. The presence of clusters and voids has adverse effects on the corrosion protection abilities of water-based coatings, SESANS provides unique insight into these systems over a crucial length scale range.

6.2 Future Work

In the process of compiling this thesis, I have identified a number of areas for further research as well as improvements that could be made to experimental procedures carried out in this work.

6.2.1 PALS and MD Experiments

In Chapter 3 we investigated a model epoxy-amine system at a stoichiometric ratio and not containing any additives or solvents. In an industrial setting corrosion resistant epoxy-amine coatings are formulated with additive particles to improve barrier properties and high solvent content to modify viscosity and allow for spray application.

For a more in depth investigation, these additives should be included. Work is already underway in adding solvent to the molecular dynamics simulations.

To further investigate the presence of two characteristic void sizes PALS measurements should be made at different cross-linking percentages. This had considerable experimental challenges and would mean either measuring samples which have been prevented from fully curing, by changing epoxy ratio or somehow prematurely halting the cross-linking procedure. Alternatively, the sample could be measured in situ as it cures. However, this would involve a heated stage or a room temperature cure. Also the current cure process takes around 6 hours and a PALS measurement with the current set up takes around 7 hours.

6.2.2 SESANS Calibration

As stated above, the most practical SESANS calibration samples should now be tested at other facilities, including reactor facilities with monochromatic SESANS instruments. This will allow SESANS results to be more compatible between instruments.

The identified wavelength shift in SESANS results measured at on Larmor should be investigated further. There may be wavelength corrections needed in the data processing or alternatively changes in the way the empty beam measurements are made in the instrument.

These samples should also be used for the calibration of spin-echo modulated spin-echo modulated small-angle neutron scattering (SEMSANS) instruments. SEMSANS is a development of the SESANS technique which enables simultaneous measurements with SANS. SEMSANS will benefit from these calibration samples as it has access to a similar range of length scales.

6.2.3 SESANS D-latex investigations

The investigation of water-based coatings could be improved upon. Firstly, through careful measurement of sample thickness and a more consistent preparation technique, SESANS measurements could be more accurately compared between samples and between wet and dry samples.

Furthermore, the use of an airtight sample holder would prevent water loss between measurements. Resulting in more consistent data that overlapped between pole shoe angles. This would allow better fitting of wet sample data and therefore a better idea of how water affects residual solvent and internal structure of water-based corrosion-resistant coatings.

An in situ SESANS measurement of the coatings during the curing process or during soaking in water would supply information on how surfactant domains and internal structures change during these processes. The recent updates the the Larmor instrument will aid in this investigation due to a factor of 70 increase in detector efficiency.

Previous SANS investigations of water-based coatings identified ellipsoidal domains on a smaller length scale to those identified in this work. A SEMSANS investigation would allow for multi length scale evaluation, validating both results.

Appendix A

Appendix

A.1 chapter 2 python code validation

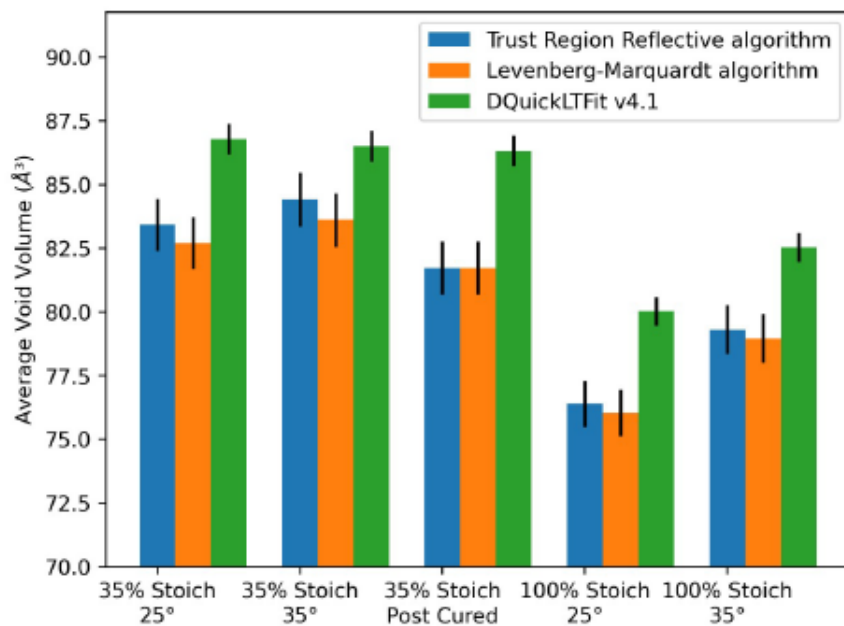


Figure A.1: comparison of three different approaches to fitting the decay lifetimes of the orthopositronium signal, the signal responsible for probing the free volume in the different epoxy samples prepared at different temperatures and stoichiometric ratios. As can be seen the shift in magnitude is small and they are all similar, n.b. the y axis scale.

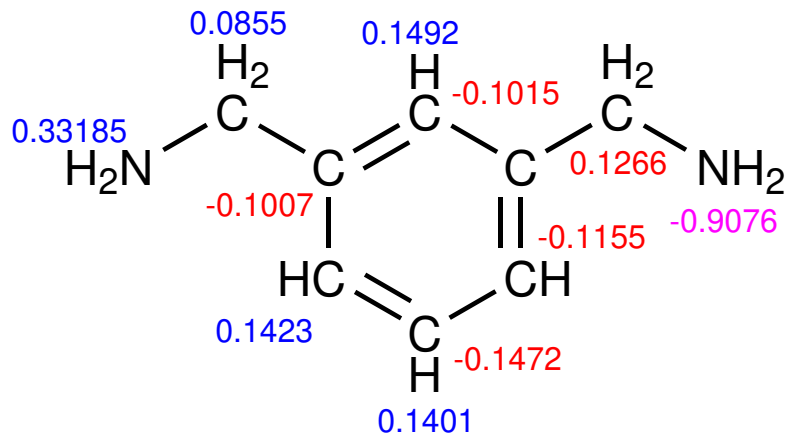


Figure A.2: Structure of MXDA showing the charges assigned for each atom environment. For ease of clarity, C charges are given in red, H charges in blue and N charges in pink

A.2 Chapter 3 SI

A.2.1 Model Parameters

These parameters were taken from the OPLS force field [1] and the charges were generated using LigParGen [2] and the 1.14*CM1A utility [3]. The water model is SPC-flexible water [4]. The water charges are -0.82 and 0.41 for oxygen and hydrogen respectively.

Atom type	ϵ	kcal mol ⁻¹	σ Å
alkyl C	0.066	3.500	
alkyl H	0.030	2.500	
aromatic C	0.070	3.550	
aromatic H	0.030	2.420	
O in OH	0.170	3.120	
H in OH	0.000	0.000	
ether O	0.140	2.900	
amine N	0.170	3.300	
amine H	0.000	0.000	
water O	0.1553	3.166	
water H	0.000	0.00	

Table A.1: Parameters used in the simulation

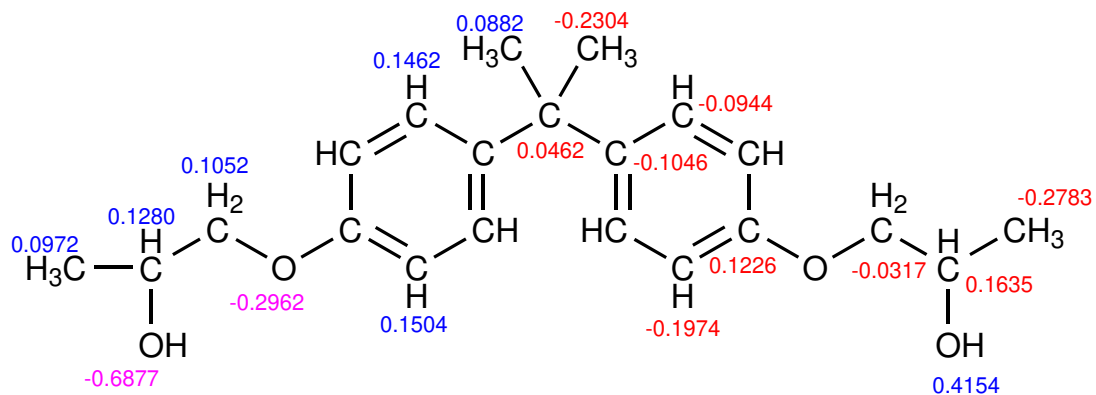


Figure A.3: Section of DGEBA showing the charges assigned for each atom environment. For ease of clarity, C charges are given in red, H charges in blue and O charges in pink

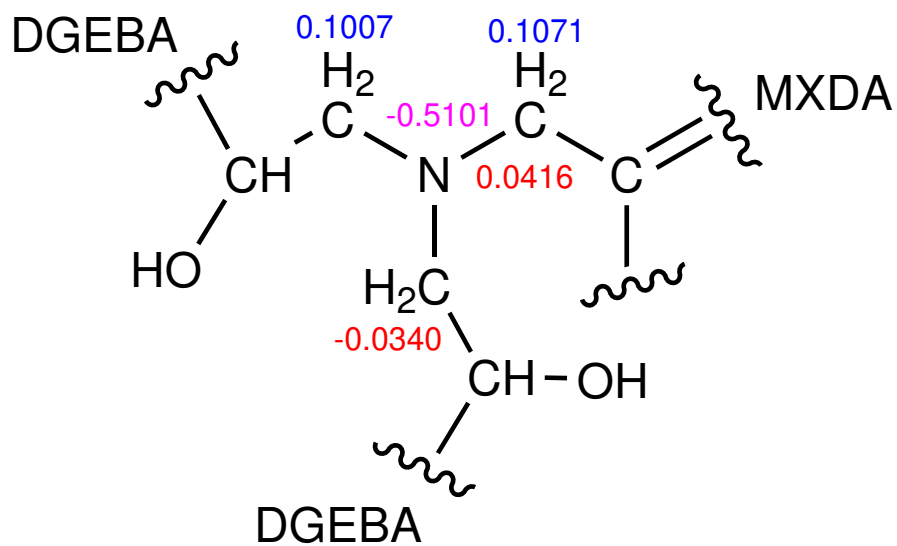
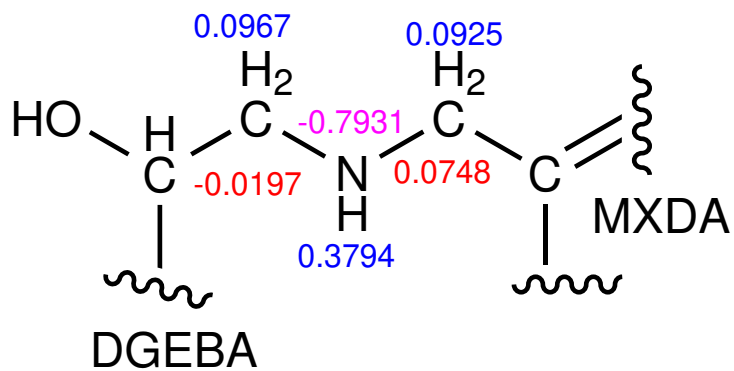


Figure A.4: Section of mono- (top) and di- (bottom) substituted MXDA after cross-linking reaction has occurred showing the charges assigned for each atom environment. For ease of clarity, C charges are given in red, H charges in blue and N charges in pink. Only charges that have changed after cross-linking are shown

A.2.2 Cross-linking procedure details

Details of the simulation steps run in the cross-linking procedure.

Initialisation step

-
- | | |
|------|---|
| i. | Geometry optimization using a conjugate gradient method at 0K |
| ii. | <i>NVT</i> linear temperature ramp 0-1000K for 50ps |
| iii. | <i>NVT</i> at 1000K for 400ps |
| iv. | <i>NVT</i> linear temperature ramp 1000-500K for 500ps |
| v. | <i>NVT</i> at 500K for 100ps |
| vi. | <i>NPT</i> at 500K for 300ps |
-

Table A.2: Simulations used in the initialization step (STEP 0)

Annealing step

-
- | | |
|------|--|
| i. | <i>NVT</i> at 500K for 200ps |
| ii. | <i>NVT</i> linear temperature ramp 500-1000K for 200ps |
| iii. | <i>NVT</i> at 1000K for 1000ps |
| iv. | <i>NVT</i> linear temperature ramp 1000-500K for 500ps |
-

Table A.3: Simulations used in the annealing step (STEP 1)

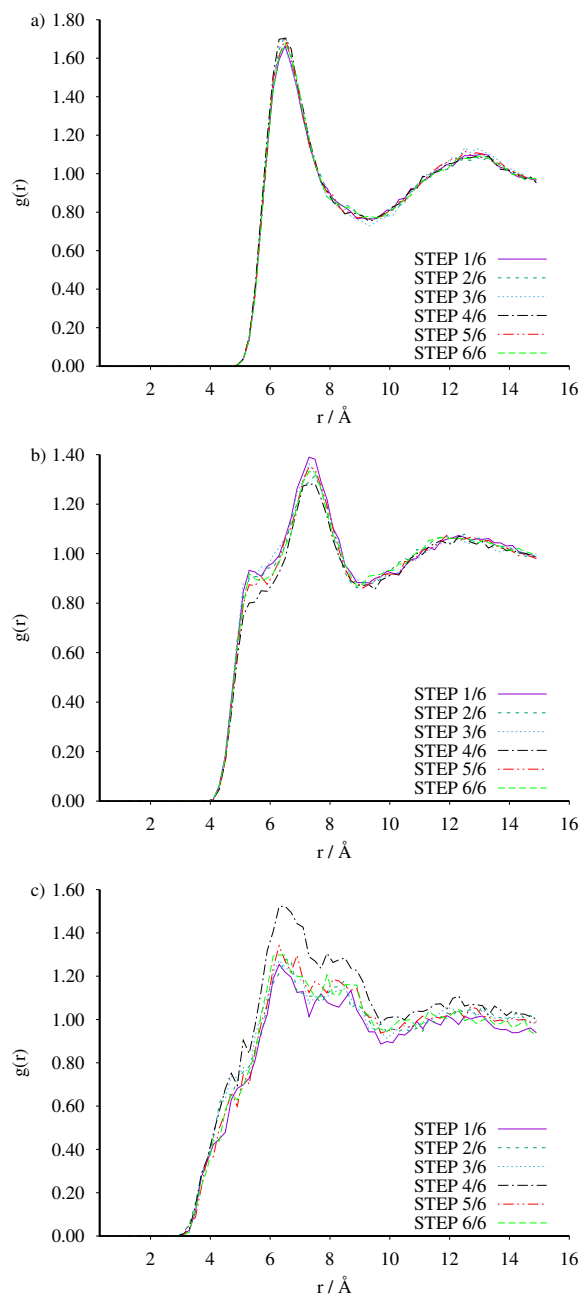


Figure A.5: Example of the radial distribution functions for the annealing step for a) DGEBA-DGEBA, b) DGEBA-MXDA, c) MXDA-MXDA. In all cases for DGEBA the quaternary carbon is used, whilst for MXDA the carbon in the aromatic ring between the two amines is used.

Bond formation

The bonds in these simulations are represented with a harmonic bond given by

$$U(r) = k(r - r_0)^2 \quad (\text{A.1})$$

All steps in the bond relaxation (STEP 2) are run for 20ps at 500K at *NVT* unless otherwise specified.

	$k / \text{kcal mol}^{-1} \text{\AA}^{-2}$	$r_0 / \text{\AA}$
i.	1	3.00
ii.	10	2.75
iii.	50	2.50
iv.	100	2.25
v.	200	2.00
vi.	250	1.75
vii.	300	1.50
viii.	382	1.448
ix.	<i>NPT</i> at 1 atm for 20ps, with k, r_0 from viii.	

Table A.4: Bond constant and equilibrium values used in the bond relaxation step (STEP 2)

A.2.3 Density on water removal

In this Figure A.6 water is deleted from the simulation box and a NPT simulation to equilibrate the system. This confirms that adding the water prior to the cross-links does not alter the properties. In all cases above 400K, the density of the system returned to that of the dry state.

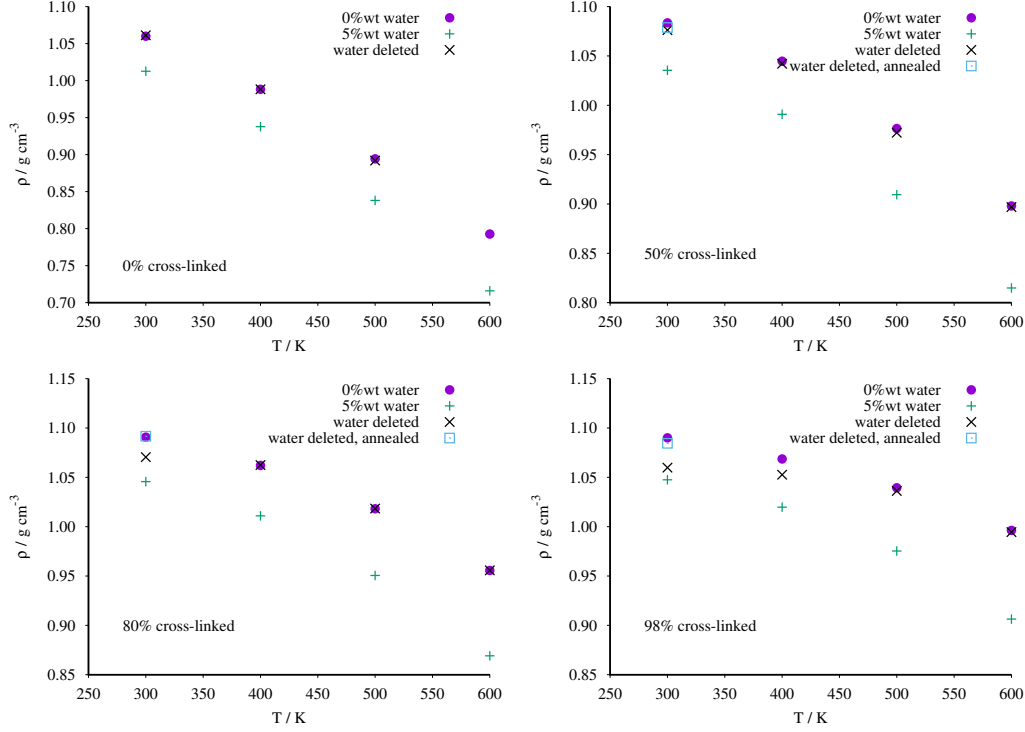


Figure A.6: Densities of the dry system (purple circles), with 5%wt water (green plus) and after the water is removed from the 5%wt system (black crosses). Also shown for some are after the water is removed and the system is annealed (blue square).

A.2.4 Glass transition temperature

The T_g was calculated from the $\rho(T)$ curve (Fig A.7 left) [5–8]. Above and below the T_g , corresponding to the rubbery and glassy regions respectively, have different gradients for $\rho(T)$. The T_g can be as the intersection between linear fits to the high and low temperature regions. Here we use an automated piece-wise linear fitting routine which optimises the fit and break points between two linear regions (glassy and rubbery regions, shown in green and red) and a quadratic region (intermediate temperatures, shown in blue) and identify the T_g . By using an automated procedure it eliminates errors from arbitrarily assigning the fitting ranges used.

However, it is known that the calculated T_g is highly dependent on the cooling rate [5, 9], with higher cooling rates leading to higher T_g values [10]. This can be corrected using the well-known Williams-Landel-Ferry (WLF) equation [11, 12] which describes the connection between the temperatures and relaxation time of a polymeric material by

$$\log_{10} a_T = \log_{10} \frac{\tau}{\tau_g} = \frac{-C_1 (T - T_g)}{C_2 + T - T_g} \quad (\text{A.2})$$

where a_T is the shift factor, τ and τ_g are the values of the relaxation time at T and T_g respectively. C_1 and C_2 are constants. Equation A.2 can be rewritten by considering that at $T = T_g$ the relaxation time of the polymer is equal to the time scale of the measurement leading to

$$\log_{10} \frac{q_{(exp)}}{q_{(sim)}} = \log_{10} \frac{\tau_{g(exp)}}{\tau_{g(sim)}} = \frac{-C_1 (T_{g(sim)} - T_{g(exp)})}{C_2 + T_{g(sim)} - T_{g(exp)}} \quad (\text{A.3})$$

where q is the cooling rate. This can then be used to give

$$\Delta T_g = T_{g(sim)} - T_{g(exp)} = \frac{-C_2 \log_{10} \frac{q_{(exp)}}{q_{(sim)}}}{C_1 + \log_{10} \frac{q_{(exp)}}{q_{(sim)}}} \quad (\text{A.4})$$

Núñez *et al* [13] calculate the T_g for a comparable system of DGEBA and MXDA with $q_{(exp)} = 5\text{K/min}$. Here we use the “universal” values [11] $C_1 = 17.44$ and $C_2 = 51.6\text{K}$ which gives $\Delta T_g = 97\text{K}$. When the WLF correction is included, we observe the correct trend with crosslinking and find good agreement with experimental results. The deviations from experimental results are likely to derive from the small system sizes inherent with MD simulations.

References

- (1) Jorgensen, W. L.; Tirado-Rives, J. *Proceedings of the National Academy of Sciences* **2005**, *102*, 6665–6670.
- (2) Dodda, L. S.; Cabeza de Vaca, I.; Tirado-Rives, J.; Jorgensen, W. L. *Nucleic Acids Research* **2017**, *45*, W331–W336.

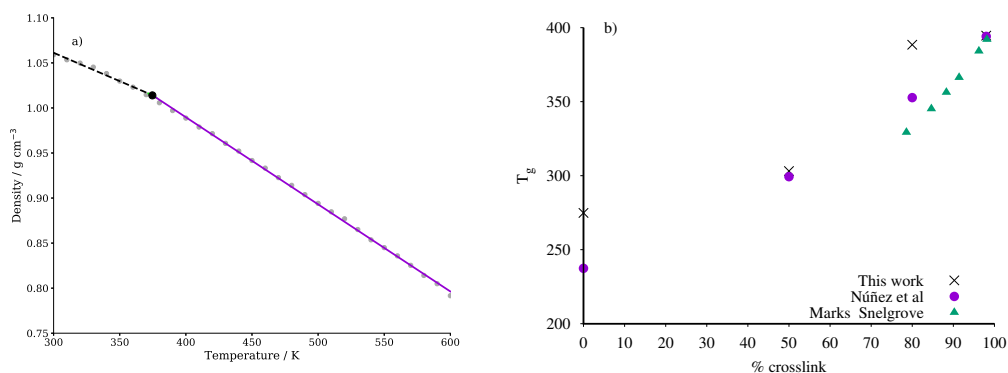
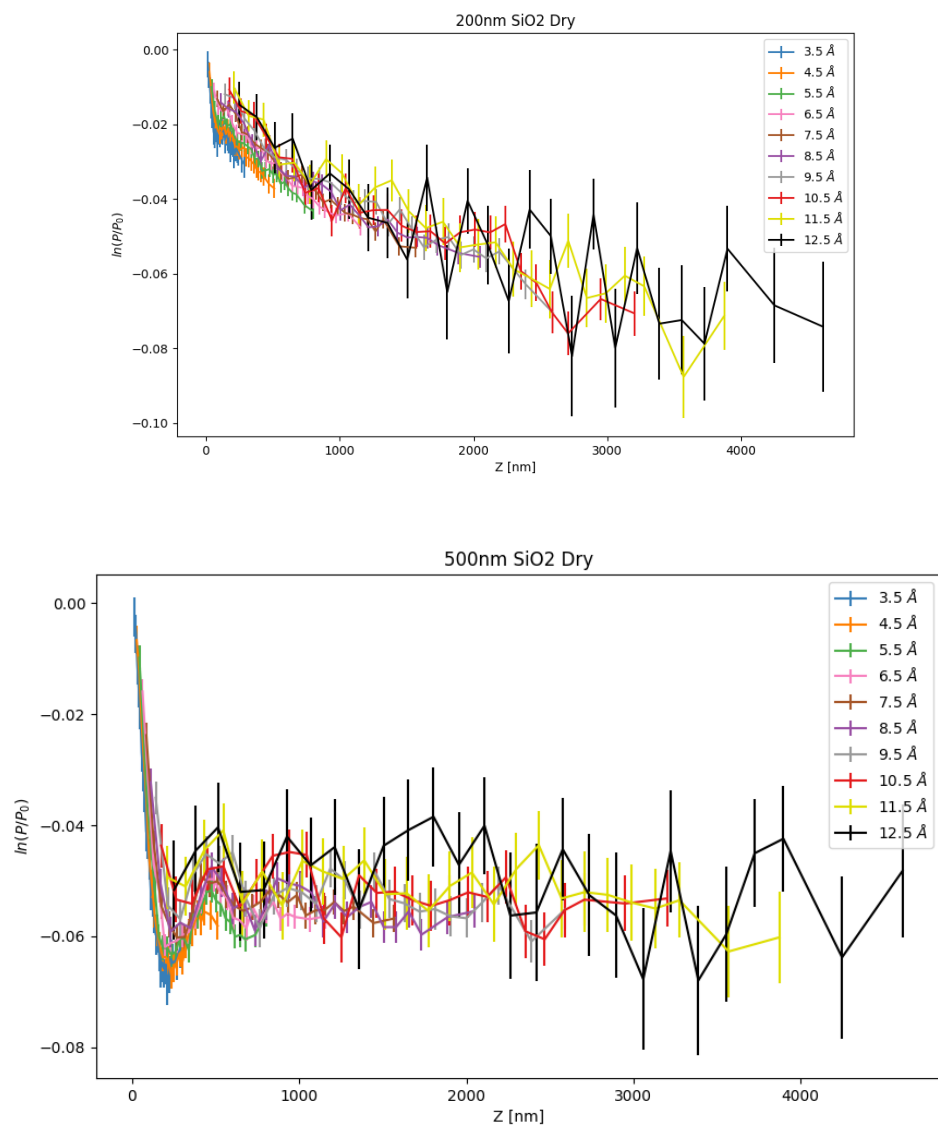
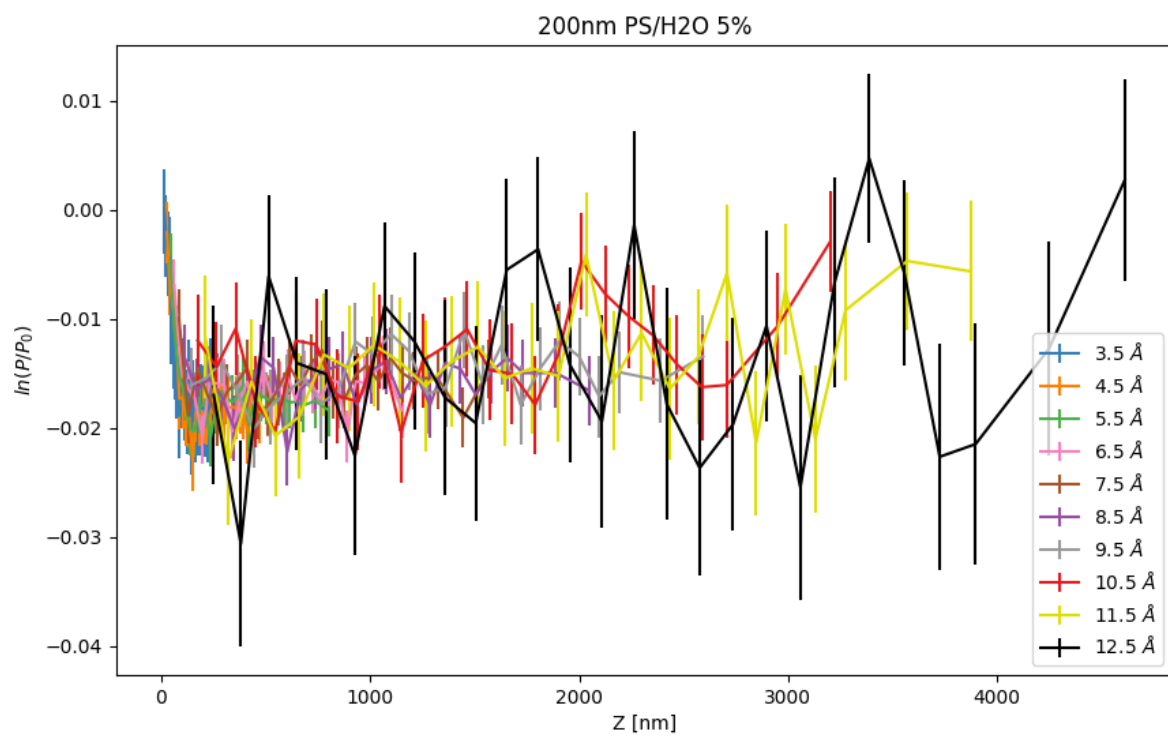
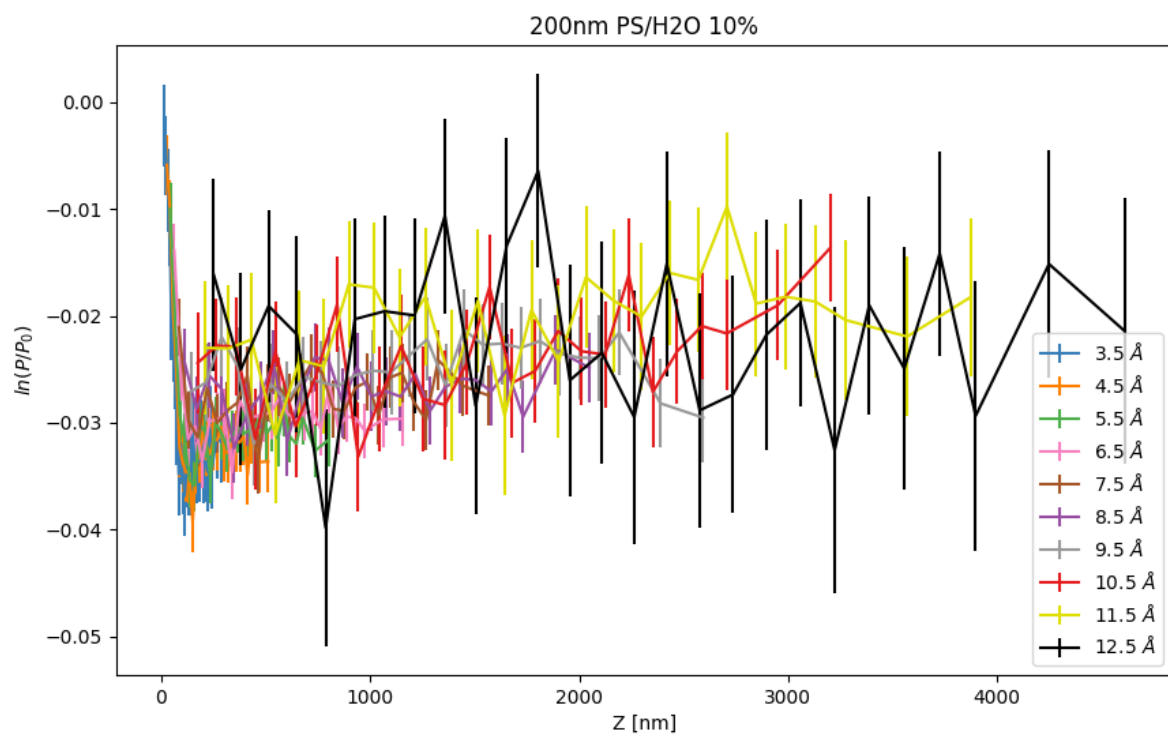


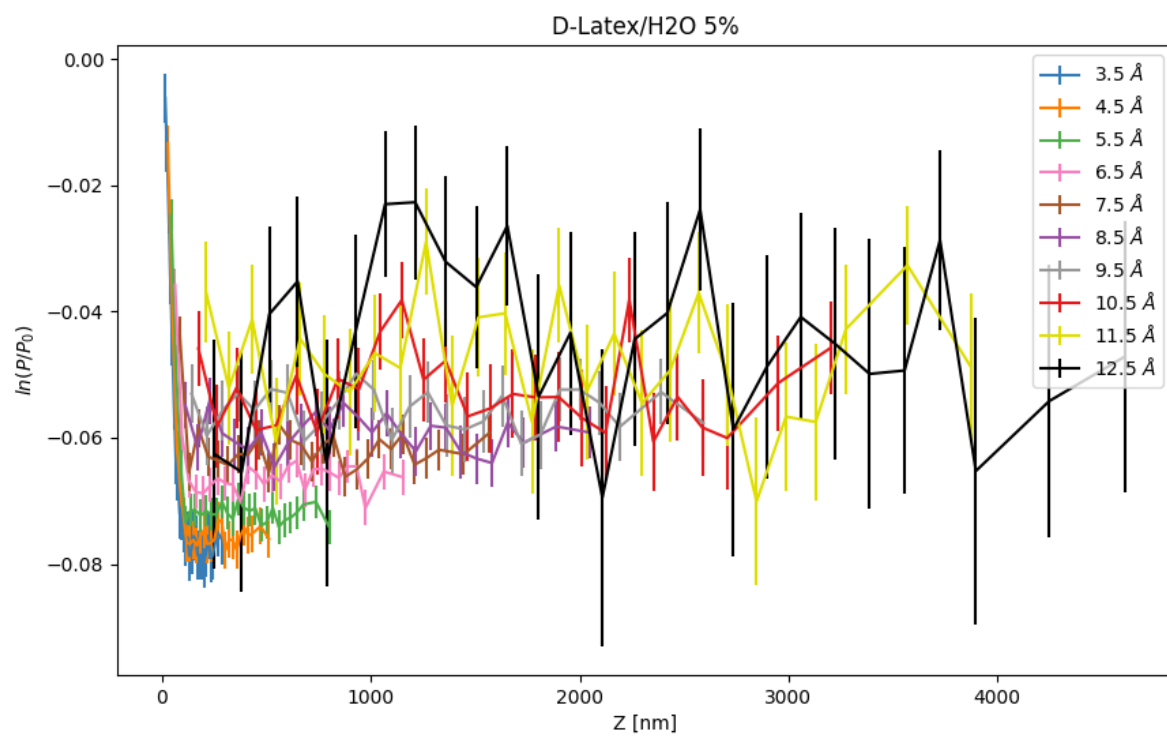
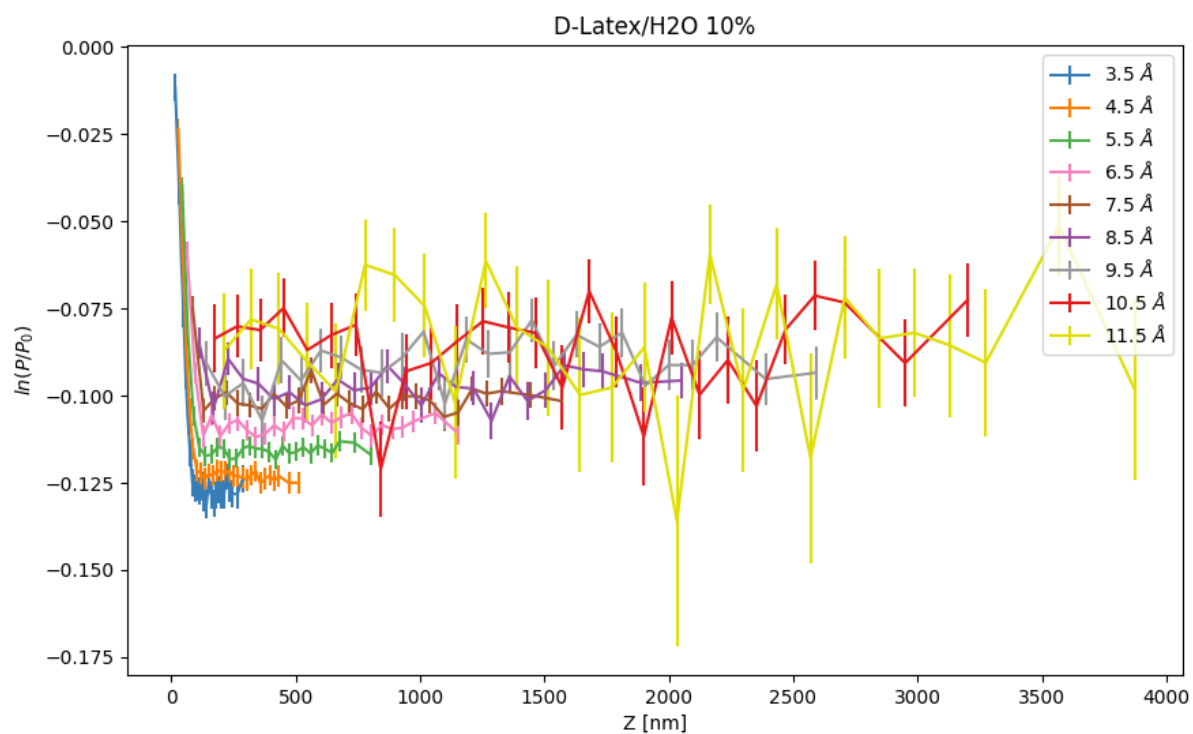
Figure A.7: Left: Example fit for T_g calculation for 0%wt water, 0% crosslinking. Right: Graph showing the calculated glass transition temperature including the WLF correction due to different heating/cooling rates. Experimental results are from Núñez *et al* [13] and Marks and Snelgrove [14]

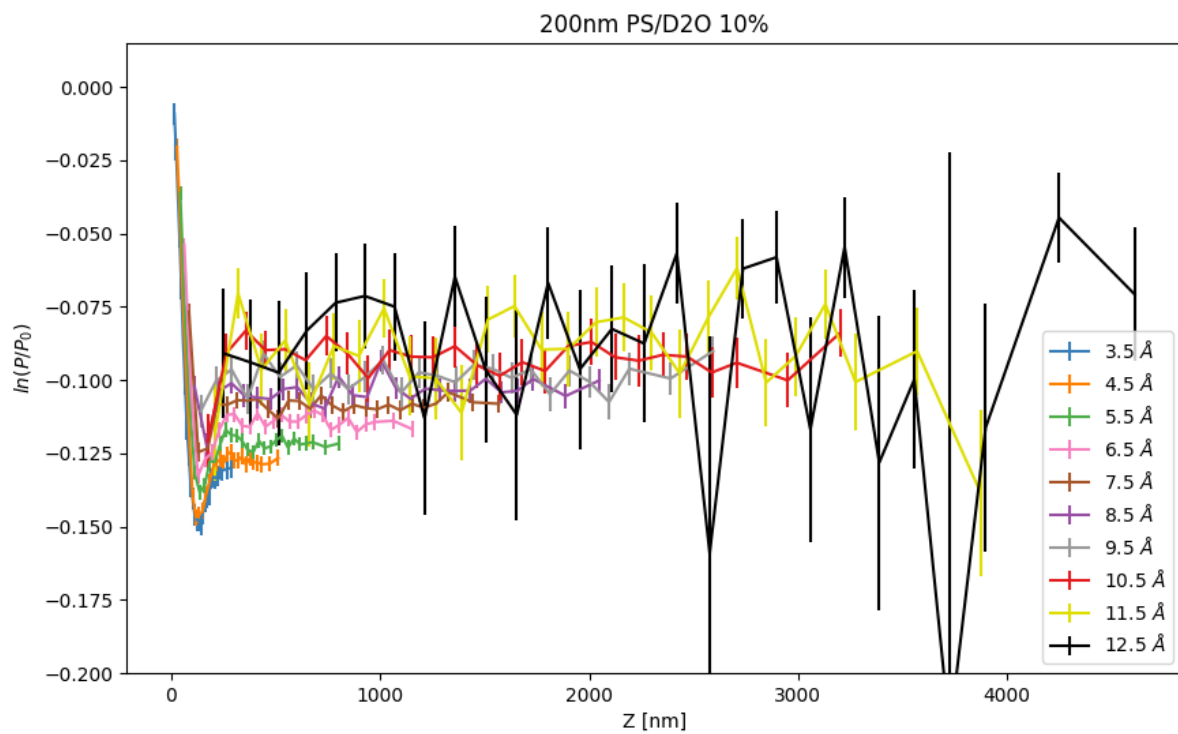
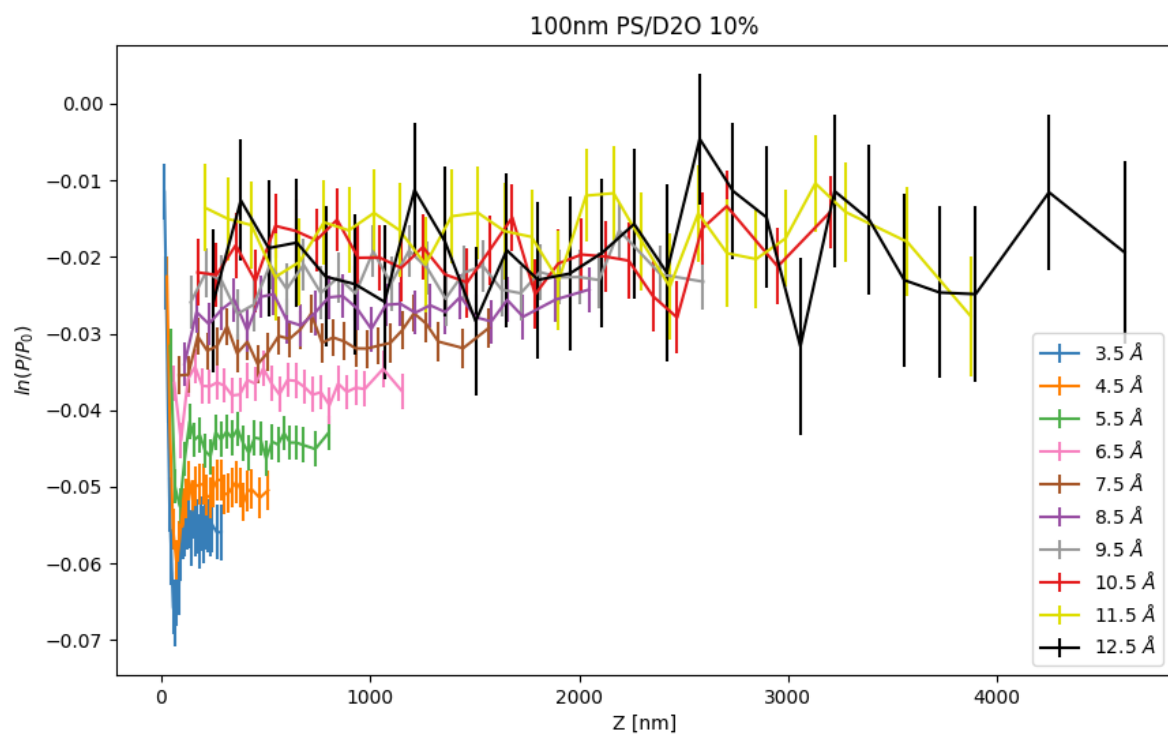
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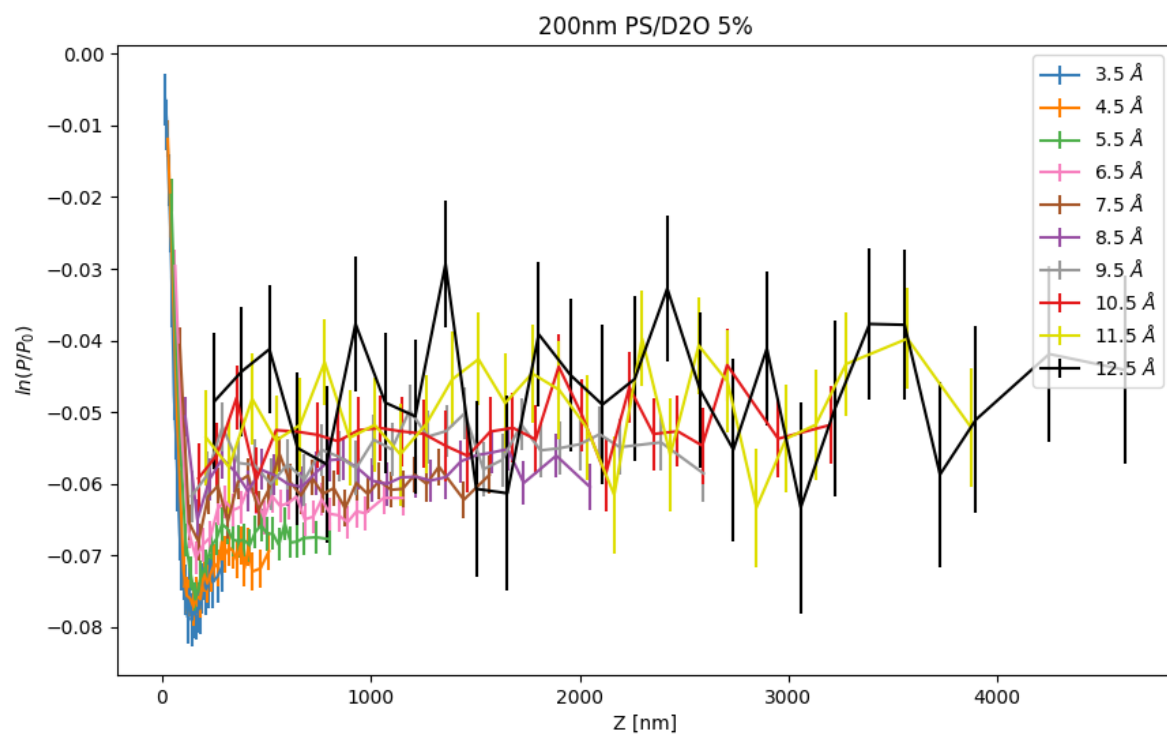
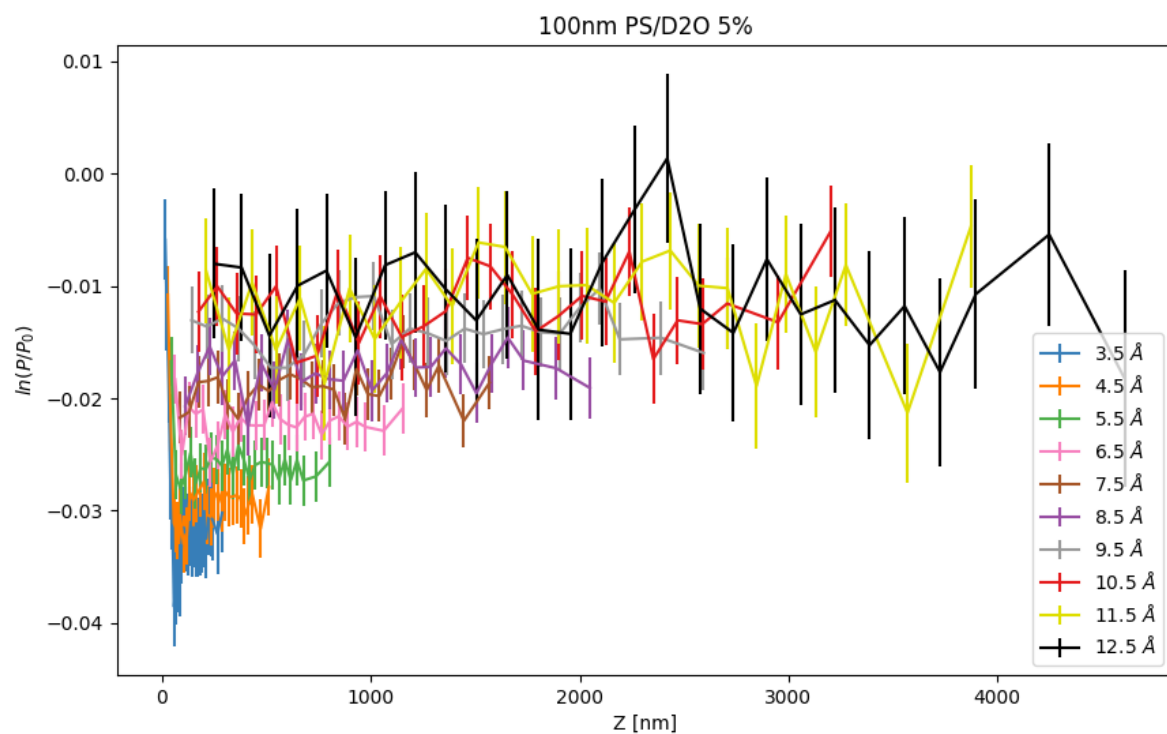
A.3 Monosians











A.3.1 Virtual Larmor McStas Instrument

```
DEFINE INSTRUMENT MONOSESANS_larmor(L0=2.165, DL=0.02, By=4.68e-3, foilthick = 3.0)
```

```
DECLARE
```

```
{
```

```
}
```

```
INITIALIZE
```

```
{
```

```
}
```

```
TRACE
```

```
COMPONENT origin = Progress_bar()
```

```
AT (0, 0, 0) RELATIVE ABSOLUTE
```

```
// insert components here (e.g. Insert -> Source -> ...)
```

```
COMPONENT src = Source_simple(
```

```
  yheight=0.01,
```

```
  xwidth=0.01,
```

```
  dist=2.25,
```

```
  focus_xw=0.01,
```

```
  focus_yh=0.01,
```

```
  lambda0=L0,
```

```
  dlambd=DL,
```

```
  gauss=1)
```

```
AT (0, 0, 0) RELATIVE PREVIOUS
```

```
COMPONENT set_pol = Set_pol(
```

```
  px=1)
```

```
AT (0, 0, 0.1) RELATIVE PREVIOUS
```

```
COMPONENT px1 = PolLambda_monitor(
```

```
  restore_neutron=1, Lmin=L0-DL, Lmax=L0+DL, nL=501,
```

```
  mx=1,filename="pxAfterAnalyser")
```

```
AT (0, 0, 0.01) RELATIVE PREVIOUS
```

```
/*
```

```
COMPONENT py1 = PolLambda_monitor(
```

```
  restore_neutron=1, Lmin=L0-DL, Lmax=L0+DL, nL=501,
```

```
  my=1,filename="py1")
```

```
AT (0, 0, 0.01) RELATIVE PREVIOUS
```

```
*/
```

```

COMPONENT f1 = Foil_flipper_magnet2(
  xwidth=0.1,
  yheight=0.1,
  zdepth=0.3,
  phi=0.095993,
  foilthick=foilthick,
  Bx=0,
  By=By,
  Bz=0,
  foil_in=1, verbose=0)
AT (0, 0, 0.5) RELATIVE src

COMPONENT px2 = COPY(px1)(filename="pxAfterFirstFoil")
AT (0, 0, 0.16) RELATIVE PREVIOUS

/*
COMPONENT py2 = COPY(py1)(filename="py2")
AT (0, 0, 0.01) RELATIVE PREVIOUS
*/

COMPONENT f2 = COPY(f1)(By=By)
AT(0,0,2.0) RELATIVE src

COMPONENT px3 = COPY(px1)(filename="pxAfterSecondFoil")
AT (0, 0, 0.16) RELATIVE PREVIOUS

/*
COMPONENT py3 = COPY(py1)(filename="py3")
AT (0, 0, 0.01) RELATIVE PREVIOUS
*/

COMPONENT sans_spheres = SANS_spheres2(xwidth=0.02,
  yheight=0.02,
  zthick=0.001,
  dsdw_inc=0.02,
  sc_aim=0.8,
  sans_aim=0.95,
  R=1000,
  phi=0.1,
  singlesp=0,
  Qmind = 0.00003,
  Qmaxd = 0.001)
WHEN (1==1) AT (0, 0, 2.25) RELATIVE src

/*
COMPONENT px4 = COPY(px1)(filename="px4")
AT (0, 0, 0.01) RELATIVE PREVIOUS

```

```

COMPONENT f3 = COPY(f1)(By=-By)
AT(0,0,2.5) RELATIVE src

/*
COMPONENT px5 = COPY(px1)(filename="px5")
AT (0, 0, 0.16) RELATIVE PREVIOUS

COMPONENT py5 = COPY(py1)(filename="py5")
AT (0, 0, 0.01) RELATIVE PREVIOUS
*/

COMPONENT f4 = COPY(f1)(By=-By)
AT(0,0,4.0) RELATIVE src

COMPONENT px6 = COPY(px1)(filename="px6")
AT (0, 0, 0.16) RELATIVE PREVIOUS

/*
COMPONENT py6 = COPY(py1)(filename="py6")
AT (0, 0, 0.01) RELATIVE PREVIOUS
*/

COMPONENT ana = PolAnalyser_ideal(mx=1)
AT(0,0,4.4) RELATIVE src

/*Alanis det*/
COMPONENT det = PSD_monitor(xwidth=0.0385, yheight=0.035, filename="det",ny=60, nx=64)
AT(0,0,6.65) RELATIVE src
/*
COMPONENT trick = Arm()
AT(0,0,4.4) RELATIVE src
EXTEND
%{
  RESTORE_NEUTRON(INDEX_CURRENT_COMP-2,x,y,z,vx,vy,vz,t,sx,sy,sz,p);
%}

COMPONENT ana2 = PolAnalyser_ideal(mx=-1)
AT(0,0,4.4) RELATIVE src

COMPONENT det2 = PSD_monitor(xwidth=0.011, yheight=0.011, filename="det2",ny=101, nx=101)
AT(0,0,4.5) RELATIVE src
*/

FINALLY
%{
%}

END

```