The Interfacial Dynamics of Amorphous Materials as Revealed by β -NMR Measurements and Molecular Simulations

by

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The Interfacial Dynamics of Amorphous Materials as Revealed by β -NMR Measurements and Molecular Simulations

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Abstract

The free surface is important for developing a fundamental understanding of dynamical length scales in glasses. We first investigate the relaxation of freestanding atactic polystyrene (aPS) thin films with molecular dynamics simulations. As in previous coarse-grained simulations, the surface modification on the relaxation times for backbone segments and phenyl rings may be expressed as a power law relation, wherein the bulk dynamics fully encapsulate the temperature-dependence. Variation of the coupling exponent with distance from the surface is consistent with depth-dependent activation barriers. We also quantify a reduction of dynamical heterogeneity, transient spatial fluctuations of the dynamics, at the interface which can be interpreted in the framework of cooperative models for glassy dynamics.

Capable of depth-resolved measurements near the surface, implantedion β -detected nuclear magnetic resonance (β -NMR) has been a powerful technique for the study of dynamics in aPS thin films. We have completed and commissioned an upgrade to the β -NMR spectrometer, extending the accessible upper temperature, and enabling a direct comparison between this experimental technique and the molecular dynamics simulations. We demonstrate that the modified spectrometer is now capable of operation to at least 400 K, an improvement of more than 80 K.

We also demonstrate the application of β -NMR as a probe of ionic liquid molecular dynamics through the measurement of ⁸Li spin-lattice relaxation (SLR) and resonance in 1-ethyl-3-methylimidazolium acetate. The motional narrowing of the resonance, and the local maxima in the SLR rate, $1/T_1$, imply a sensitivity to sub-nanosecond Li⁺ solvation dynamics. From an analysis of $1/T_1$, we extract an activation energy and Vogel-Fulcher-Tammann constant in agreement with the dynamic viscosity of the bulk solvent. Near the melting point, the lineshape is broad and intense, and the form of the relaxation is non-exponential, reflective of our sensitivity to heterogeneous dynamics near the glass transition. We also employ the depth resolution capabilities of this technique to probe the subsurface dynamics with nanometer resolution. We show modified dynamics near the surface in, and above, the glassy state.

Lay Summary

Glasses are a fascinating category of materials. Solid by our everyday measure, the configuration of their molecules is nearly indistinguishable from a liquid. The primary difference between the two is that the molecules in glasses move unbelievably slowly. Important clues for understanding these amorphous materials may lie in how the surface affects motion of their molecules. We contribute to 25 years of active research on this question by studying two very different materials: a polymer and an ionic liquid. The former are materials composed of long molecular chains, whereas the latter are mixtures of two charged components, half positive and half negative. We use experiments employing a beam of radioactive lithium and, separately, molecular-scale simulations to reveal how the surface modifies the rate of molecular rearrangement with nanometer resolution.

Preface

Part of this work is based on classical molecular dynamics simulations, and part on experiments which were the result of a collaboration between the University of British Columbia and the TRIUMF laboratory. Chapter 4 is based on the former technique which resulted in the publication:

D. Fujimoto, W.A. MacFarlane, and J. Rottler, J. Chem. Phys. 153, 154901 (2020).

These simulations were conceived by my supervisors J. Rottler, W.A MacFarlane, and R.F. Kiefl. I wrote all the code for both the simulations, which was executed within an external package, and performed the analysis. J. Rottler and I wrote the manuscript in close collaboration.

Experiments at TRIUMF are conducted in a manner very common across other accelerator facilities. Limited access to the radioactive beam requires experiments to be run 24 h a day for weeks at a time, necessitating that data collection be a collaborative effort. Furthermore, the apparatus depends on a complex set of supporting systems which requires several teams of researchers and scientists to operate and maintain.

The β -NMR data presented in Chapter 5 is unpublished, and was the logical progression of the work of McKenzie et al.,¹ which was also the catalyst for the above simulations. The data was collected by me and I. McKenzie. I performed the analysis independently with my own code.

The design of the new forward detector was suggested by R.F. Kiefl and facility scientists G.D. Morris and R. Abasalti. I conceived and designed the RF coaxial connector assembly and the split thermometer holders. With my direction, all technical drawings were made by engineer M. McLay, the TRIUMF machine shop produced all metallic components, and D. Vyas fabricated the Vespel components. The scintillator and light guide were manufactured by the scintillator shop at TRIUMF. With some help and guidance from G.D. Morris, I disassembled and reassembled the UHV-exposed components of the spectrometer, and assembled the new forward detector. I conceived and wrote the simulations for the detector efficacy. I conceived and conducted the temperature tests of the new RF assembly with the guidance of G.D. Morris.

Chapter 6 is largely based on the following published work:

D. Fujimoto, R.M.L. McFadden, M.H. Dehn, Y. Petel, A. Chatzichristos, L. Hemmingsen, V.L. Karner, R.F. Kiefl, C.D.P. Levy, I. McKenzie, C.A. Michal, G.D. Morris, M.R. Pearson, D. Szunyogh, J.O. Ticknor, M. Stachura, and W.A. MacFarlane, Chem. Mater. 31, 9346 (2019).

The data in this paper was opportunistically taken during the experiment of Szunyogh et al.,² in which I also participated in the data collection. M. Stachura produced all of the ionic liquid samples. The published analysis was first performed by R.M.L. McFadden. R.M.L. McFadden and W.A. Mac-Farlane wrote a partial first draft before I was involved. Subsequent drafts and the final manuscript were written by me, in collaboration with W.A. Mac-Farlane. PFG NMR measurements were performed and analyzed by Y. Petel and C.A. Michal, with my direction. All of the data which followed this publication is unpublished, and was taken as a result of experiments which I conceived, designed, proposed, and analyzed with my own code.

The simulations in Appendix A.3 were written by me, in consultation with M. Dehn. I conceived, designed, and wrote the software presented in Appendix D; although many features are the result of constructive feedback from the group.

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Acronyms

$[\mathrm{Si-MIm}][\mathrm{Bf}_4]$	1-methyl-3-trimethylsilylmethylimidazolium
EMIM-Ac	1-ethyl-3-methylimidazolium acetate iii, xii, xiii, xv, 4, 10–14, 34–36, 38, 83, 85–87, 89–92, 94–103, 106–111, 113–115, 159–161
ACF API	autocorrelation function 56–58, 61 application programming interface 165, 167–171
aPS	atactic polystyrene iii, xii–xv, 4–11, 13, 14, 16, 17, 21, 34, 35, 44, 49, 50, 54, 55, 59, 64, 66–68, 78, 79, 82, 83, 92, 105–107, 111–114, 157, 158, 168
β -NMR	β -detected nuclear magnetic resonance iii, vi, ix, x, xii–xv, xxv, 1, 5, 7, 8, 10, 13, 14, 21, 31–33, 36, 37, 39, 44, 50, 67–73, 79, 81–83, 85–88, 92–94, 97, 99–101, 109–115, 148, 156, 157, 163, 165, 167, 169, 170
β -NQR	$\beta\text{-}detected$ nuclear quadrupole resonance 167, 169, 170
BMIM BMIM-BMSF	1-butyl-3-methylimidazolium xvii, 14 1-butyl-3-methylimidazolium bis(trifluoro- methane sulphonate)imide 12

BMIM-Cl	1-butyl-3-methylimidazolium chloride 12									
$BMIM-PF_6$	1-butyl-3-methylimidazolium hexafluoro-									
	phosphate 12, 14, 108, 109									
BMIM-TFSA	1-butyl-3-methylimidazolium bis(trifluoro-									
	methanesulfonyl)amide 14									
BPP	Bloembergen-Purcell-Pound 29, 68, 69, 82, 85,									
	89, 90, 96, 99–101, 104, 112–114									
CCD	charge-coupled device 37, 169									
CKN	$2Ca(NO_3)_2$ -3KNO ₃ 12									
CW	continuous wave 86, 93, 97									
DAC	digital to analog converter 169									
DEME	N, N-diethyl-N-methyl-N-(2-methoxyethyl)-									
	ammonium 97									
DFT	density functional theory 17, 19, 114									
ECNLE	elastically collective nonlinear Langevin equa-									
	tion 50, 52, 59–62, 64									
EFG	electric field gradient 27–30, 86, 90, 93, 96,									
	148-150, 153									
FITS	flexible image transport system 169									
FSA	bis(fluorosulfonyl)amide 97									
FWHM	full width at half maximum 47, 163									
GPL-3.0 License	GNU General Public License v3.0 166, 167,									
	170									
GUI	graphical user interface xv, 167–171									
IL	ionic liquid x, 10, 159									
KWW	Kohlrausch-Williams-Watts 158									

LJ	Lennard-Jones potential xxii, xxiii, 18
MC	Monte Carlo xiv, 35, 47, 48, 68, 77, 79, 101,
MD	molecular dynamics vii–viv 1 3 8 10 14
MD	16-21 49 50 55 64 66-69 71 84 96 101
	$107 \ 111 \ 112 \ 114 \ 156-158$
MUD	muon data 165-167 169
uSB	muon spin rotation relaxation and resonance
μοι	5, 7, 8, 165, 166
NMR	nuclear magnetic resonance vii, x, xii, xiv, 5,
	13, 14, 21-23, 28, 29, 31, 32, 44, 66-69, 84, 85,
	87, 90, 93, 94, 97–100, 103, 112–114, 148, 156,
	157, 160
PEEK	Polyether ether ketone 74, 76
PEO	poly(ethylene oxide) 105, 106
PFG	pulsed field gradient vii, 87, 97, 103, 160
PMT	photo multiplier tube 71
\mathbf{PS}	polystyrene 56–58
PVT	polyvinyl toluene 77
PyPI	python package index 166, 167, 170
RF	radio frequency vi, vii, xiv, 23, 44, 46, 47, 70,
	72, 74-76, 81, 86, 95, 97, 98, 113, 154, 162,
	169
RTIL	room temperature ionic liquid xii, xiii, 1, 4,
	$10-14,\ 83-85,\ 96,\ 97,\ 99,\ 102,\ 107-109,\ 111,$
	112, 115, 157, 160, 162

SLR	spin-lattice relaxation iii, ix, xiii, xv, xxii, 24,
	$26, \ 28{-}31, \ 44{-}46, \ 66{-}68, \ 84{-}86, \ 88{-}90, \ 93,$
	95, 96, 98–103, 105–109, 113, 115, 148, 149,
	157-164
SRIM	Stopping and Range of Ions in Matter xii, xiii,
	34, 35, 88, 101, 103, 106
SWR	standing wave ratio xiv, 74–76
TFSA	bis(trifluoromethanesulfonyl)amide xvii, 14, 97
UHV	ultra-high vacuum vii, 10, 13, 36, 70, 71, 73, 74, 79, 81, 108
VFT	Vogel-Fulcher-Tammann iv, xii, xxi, xxiii, 5, 6, 11, 12, 51, 57–60, 64, 91, 92, 104, 109, 113, 160, 161

Symbols

- $B_0 \qquad \mbox{Magnitude of static magnetic field [T] 23, 24,} \\ 77-79, \, 90, \, 154, \, 155$
- B_1 Magnitude of fluctuating magnetic field (Equation 3.1.6) [T] 23, 24, 47, 93, 155
- $B_{\rm eff}$ Magnitude of $\mathbf{B}_{\rm eff}$ [T] 154, 155
- C_2 Autocorrelation function within second Legendre polynomial 21, 56, 61
- *I* Nuclear spin xiii, 26–30, 32, 38, 66, 68, 92, 149, 150
- M_n Number average of the molecular weight 66
- M Nuclear magnetization 25, 26, 29
- N(t) The total number of ⁸Li in the sample at time t > t' 39, 45
- Q Nuclear quadrupole moment. Often quoted in units of barns, where a factor of e is dropped. The quantity eQ has the proper units [Cm²] 27, 32, 92, 109, 113, 149, 150
- R_0 Implantation rate into sample [s⁻¹] 39–41, 45
- R_B Detection rate by backward detector [s⁻¹] 40–43
- R_F Detection rate by forward detector [s⁻¹] 40–43

- T_2 Exponential spin-spin relaxation time of transverse magnetization: Equation 3.1.13 [s] 26
- $\begin{array}{ll} T_{\rm VFT} & {\rm Vogel-Fulcher-Tammann \ temperature \ [K] \ 5, \ 6,} \\ & 12, \ 51, \ 57, \ 58, \ 92, \ 93, \ 96 \end{array}$
- $\begin{array}{ll} T_{\rm g} & \mbox{Glass transition temperature [K] xii, xiv, 2, 3,} \\ & \mbox{6-9, 11-13, 49, 55, 56, 58, 68, 82-84, 86-90,} \\ & \mbox{95, 97-102, 104, 108, 113, 114} \end{array}$
- $\begin{array}{ll} T_{\rm m} & \mbox{ Melting temperature [K] 2, 3, 14, 84, 90, 95,} \\ & \mbox{ 99, 102, 105, 106, 108, 109} \end{array}$
- $V \qquad \text{Electric field gradient component (Equation 3.1.14)} [V/m²] 27, 28, 92, 109, 113$
- $\begin{array}{ll} W(\theta) & \mbox{Probability density of beta emission angle θ} \\ & 38 \end{array}$
- $\Delta \mathcal{A}$ Helicity-averaged two-counter asymmetry 41–43
- Δ Beam on pulse duration [s] 45
- α Ratio of detector count rates without polarization xxii, 41–44
- $\beta \qquad {\rm Ratio \ of \ detector \ initial \ asymmetries \ without} \\ {\rm polarization \ 43, \ 44}$
- β Stretching exponent in stretched exponential (Equation 3.2.27). xv, 45, 84, 85, 88–90, 92, 93, 99, 104–108, 110, 114, 158
- χ^2 Chi squared, least-squares measure of best fit 89, 103, 157, 169

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LJ potential scaling prefactor 18
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- σ LJ potential distance constant 18

- $\begin{array}{ll} \mathbf{B}_{\mathrm{eff}} & \mbox{ Effective magnetic field due to } \mathbf{B}_0 \mbox{ and } \mathbf{B}_1 \mbox{ in the rotating reference frame (Equation 3.1.8)} \\ & \mbox{ [T] xiii, xx, 24, 25, 154, 155} \end{array}$
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- **J** Total angular momentum $[\text{kg m}^2/\text{s}]$ 22, 23, 26
- μ Nuclear magnetic moment [Am²] xiii, 22, 24–26
- τ' Equal to $1/\tau + 1/T_1)^{-1}$ [s] 45

$ au_c$	Microscopic molecular correlation time [s] xiii,
	xiv, 6, 9, 12, 29–31, 47, 49, 51, 52, 54, 56, 57,
	$59-61,\ 64,\ 68,\ 69,\ 90,\ 92,\ 98,\ 112,\ 149,\ 150,$
	154, 155

- $\tau_{\rm bulk} \quad \mbox{Microscopic molecular correlation time in the} \\ \mbox{bulk [s] 49, 51, 53, 54, 59, 60}$
- $\tau_{\rm onset}$ $\,$ Microscopic molecular correlation time in the bulk 53 $\,$
- au Nuclear lifetime [s] xxiii, 32, 39, 40, 42, 45, 162, 163
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- a_B Initial asymmetry of backward detector 40, 41, 43, 44
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- f Coupling exponent containing the depth dependence near the surface interface. $f(z) \in [0, 1]$. 49–54, 59–62
- $\begin{array}{ll} k_B & \mbox{ Boltzmann constant 6, 12, 51, 52, 54, 92, 160,} \\ & 163 \end{array}$
- r_c Cyclotron radius 77
- $\begin{array}{ll} t' & \mbox{ Nuclear implantation time [s] 39, 40, 88, 159,} \\ & \mbox{ 162} \end{array}$
- v Velocity of emitted e^- in nuclear decay [m/s] 38

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Chapter 1

Introduction

Humans have been making glasses for millennia and they form an integral part of our daily lives. Despite this, the underlying physics of glasses is not fully understood. In this work, we study the molecular dynamics (MD) in the near-surface region of two glass-forming materials: a polymer and a room temperature ionic liquid (RTIL). This work was accomplished through the application of both computational MD simulations and experiments, employing implanted-ion β -detected nuclear magnetic resonance (β -NMR).

1.1 What is a glass?

From an early age, we are taught that the difference between a liquid and a solid is that a liquid will flow, taking the shape of its container, and a solid will not. Most solids derive this behaviour from the arrangement of their atoms. The structure is that of a crystalline lattice, in which no one atom can move without the participation of a great many other atoms. This long-range periodic order is responsible for the characteristic rigidity of solid materials. Glassy materials, on the other hand, are amorphous: they have no regular periodic structure, and consequently, no long-range order; yet they share the rigidity of solids. An instantaneous snapshot of a glassy molecular arrangement is indistinguishable from that of a liquid.

Supercooled liquids and glasses have three primary defining features:³



Figure 1.1.1: The transition to a glass is continuous and occurs below the crystallization temperature $(T_{\rm g} < T_{\rm m})$, if the cooling rate is fast enough to avoid crystallization. Faster cooling rates result in earlier glass formation $(\dot{T}_{\rm glass~2} > \dot{T}_{\rm glass~1})$.

firstly, as the material is cooled it undergoes a smooth transition from a fluid to a solid glass, characterized by the temperature T_g . Secondly, during the glass transition, a dearth of accessible molecular configurations (configurational entropy) results in the glass falling out of equilibrium.⁴ and the timescales for cooperative motion quickly become immeasurably long. This effectively traps the configuration in a metastable liquid state, slowing the decrease in thermal entropy. As shown in Figure 1.1.1, if the trend in the liquid entropy were to continue unabated, it would eventually become lower than that of the crystalline state, which would be unphysical. As a result, its properties become time-dependent as the glass slowly ages. The third feature is the emergence of dynamic heterogeneity, or spatially heterogeneous dynamics. At temperatures approaching the glass transition, non-trivial fluctuations in the rate of molecular rearrangement become resolved in both time and space. The local dynamics of these spatial regions may vary up to several orders of magnitude, even if they are only a few nanometers apart,^{3,5} and are seemingly disconnected from fluctuations in density. Furthermore, these dynamics evolve in time such that all particles eventually participate in both fast and slow rearrangement.

The most common method of vitrification is to cool rapidly enough that the material falls out of equilibrium and becomes trapped in an non-ideal (amorphous) configuration before a crystalline structure is achieved. This transition to an amorphous solid state is notably not a true thermodynamic phase transition.⁶ Unlike a first-order liquid-solid transition, the glass transition is primarily a dynamical phenomenon. The transition is continuous and dependent on the cooling rate. This is exemplified in Figure 1.1.1, showing the typical signature of the glass transition, occurring below the melting point $T_{\rm m}$. Figure 1.1.1 also demonstrates a standard method for calculating $T_{\rm g}$: from the intersection of the extrapolation of the linear regions of some quantity, such as volume or enthalpy. This definition is hardly fundamental, as the glassy state itself lacks a formal definition. however a truly rigorous definition has yet to be elucidated.

Since both entropic⁴ and simple free-volume^{7,8} models have enjoyed success in predicting bulk behaviour,^{9,10} the dynamics near an interface should intuitively be connected to variations in the local molecular structure. However, structural indicators consistently fail to be good predictors of dynamical behaviour in the near-surface region, where dynamics are greatly enhanced.^{11–13} For example, it is well known from MD simulations of thin films that the length scales associated with dynamical gradients are much greater than those of the density.^{14,15} Furthermore, a machine learning approach has shown that surface-modified dynamics can be factored into a depth-independent component dictated in part by molecular structure, and a depth-sensitive component which has no correlation with structure.¹¹ This region of dynamical enhancement increases in size at lower temperatures¹⁶ and is cooling-rate dependent, with slower cooling rates resulting in a larger surface effect.^{17,18} In polymeric glasses, the size surface effect is independent of chain length, except in the cases of very long chains or very thin freestanding thin films.^{19–21} While some theoretical progress has been made, for example by combining free volume ideas with those of dynamical heterogeneity²² or string-like cooperative rearrangement,²³ the origin for the effect of the surface on the dynamics has remained an open question over the past 25 years.¹⁹

This work contributes to the effort of understanding the surface effect



Figure 1.2.1: Structure of the styrene monomer. Atactic polystyrene is formed by the random up/down combinations of this monomer, connected via the tail extended from the benzene-like phenyl ring.

by examining two glass-forming materials: atactic polystyrene (aPS), a polymer; and 1-ethyl-3-methylimidazolium acetate (EMIM-Ac), a RTIL. We use computational and experimental methods to study the dynamical gradient directly, without specifying a sharply defined surface layer^{24,25} or using film-averaged properties.^{26,27} We now give an overview of the material, bulk, and surface properties of these glass-formers.

1.2 Polystyrene

1.2.1 Bulk properties

Atactic polystyrene (aPS) can be considered as the prototypical glass-former and is easily the best-studied polymer in the field of glasses. It is formed from long chains of the styrene monomer, depicted in Figure 1.2.1, making it both chemically and geometrically simple. The random tacticity (spatial orientations of the monomers in the chain) of aPS prevents crystallization by avoiding the possibility of achieving translational invariance. These features make aPS an ideal candidate for the study of polymetric glasses.

Because vitrification is fundamentally a dynamical phenomenon, measurements of the molecular dynamics in the resulting glass are extremely important. A compilation of experimentally determined dynamical relaxation times in bulk aPS are presented in Figure 1.2.2, revealing trends identified by their dielectric peak. Each trend corresponds to a different mechanism



Figure 1.2.2: A compilation of correlation times from bulk aPS reveals several different relaxation mechanisms. Data compiled from a number of techniques: mechanical (blue): $\bullet,^{32} \odot,^{33}$, $\bullet,^{34}$, $\Box,^{35}$, $\bullet,^{36}$, $\Delta,^{37}$, $\bullet,^{38}$, $\delta,^{39}$, $O,^{40}$, $\bullet,^{41}$, $\star,^{42}$, $\bullet,^{43}$, $\bullet,^{44}$ dielectric (orange): $\bullet,^{45}$, $O,^{46}$, $\bullet,^{38}$, $\Box,^{47}$, $\bullet,^{48(a)}$, $\Delta,^{49}$, $\bullet,^{44}$ NMR (green): $\bullet,^{50}$, $O,^{51}$, $\bullet,^{29}$, $\Box,^{53}$, $\Delta,^{54}$, $\bullet,^{28}$ neutron scattering (red): $\bullet,^{55}$, β -NMR (purple): $\bullet,^{31}$ optical photobleaching (brown): $\bullet,^{56}$ and μ SR (pink): $\bullet,^{57}$ Dashed lines are Arrhenius fits with activation energies 1.26(3) eV (β), 0.28(1) eV (γ), and 0.080(3) eV (δ), with the exception of the α process, which was fit with the VFT relation, resulting in an activation energy of 0.14(3) eV and $T_{\rm VFT}$ of 324(7) K.

^a As cited by Frosini and Woodward.³⁴

of relaxation, overall spanning over 15 orders of magnitude. The α branch corresponds to relaxation requiring the cooperative motion of large portions of the backbone chain, and is primarily responsible for the calorimetric glass transition. The other processes are all attributed to phenyl side group motion: β involves a coupling to the backbone motion,^{28,29} γ relaxation is attributed to cooperative phenyl motion,^{29,30} and the δ process is thought to be due to torsional waggling.³¹ Other than the α process, all of the processes are well-described by the Arrhenius equation,

$$\tau_c = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right),\tag{1.2.1}$$

where τ_c is the microscopic correlation time; τ_0 is an exponential prefactor, often interpreted as the time between attempts; k_B is Boltzmann's constant; T is the absolute temperature; and ΔE is the activation energy, found for β , γ , and δ to be 1.26(3) eV, 0.28(1) eV, and 0.080(3) eV respectively. The α process was found to follow a Vogel-Fulcher-Tammann (VFT) relationship,

$$\tau_c = \tau_0 \exp\left(\frac{\Delta E}{k_B (T - T_{\rm VFT})}\right), \qquad (1.2.2)$$

where the activation energy was 0.14(3) eV and the constant T_{VFT} was 324(7) K. The observed scatter is likely due to the differences in polymer molecular weight, thermal history, and other treatments (exposure to oxygen, for example). In this work we will probe the ring dynamics, most likely attributed to the γ process.

Another method of calculating $T_{\rm g}$ is to take the temperature at which $\tau_c \gtrsim 100 \,\mathrm{s.}$ From Figure 1.2.2, the α process crosses this threshold at $T = 374 \,\mathrm{K}$, a typical calorimetric $T_{\rm g}$ for aPS.⁵⁸ The other processes cross this threshold at $287 \,\mathrm{K}$ (β), 109 K (γ), and 31 K (δ); indicative of the approximate temperatures at which each processes undergoes its own glass transition. In constrained systems, such as near an interface, $T_{\rm g}$ will acquire a spatial dependence, in addition to other contributing factors such as chain length and cooling rate.

1.2.2 Surface properties

The first comprehensive study of glasses in confined geometries was that of Jackson and McKenna⁵⁹ in 1991. They showed that the $T_{\rm g}$ of an organic liquid was reduced when the liquid was confined to nanometer-scale pores, and that $T_{\rm g}$ was further reduced with the pore size. It was not long before the first study of polymer films was published, with the film height acting as

the confining dimension.²⁶ This early work used ellipsometry to extract $T_{\rm g}$ from the temperature dependence of the film height for thin films of varying starting thicknesses. They clearly showed two important details:

- 1. $T_{\rm g}$ is reduced in a PS films thinner than ${\sim}100\,{\rm nm},$ and
- 2. in films thicker than ${\sim}100\,{\rm nm},\,T_{\rm g}$ is constant.

This effect has now been attributed to a region of enhanced molecular mobility in the near-surface region. 19,60

Probing this nanoscale surface region is difficult experimentally. Techniques such as ellipsometery or dielectric spectroscopy infer the enhancement of surface dynamics from a change in $T_{\rm g}$ as a function of film thickness. $^{60-63}$ As a result, they do not have the spatial resolution to directly measure the surface effect. An optical photobleaching technique has been able to improve on this method by inferring the mobile layer size (7 nm at 374 K) from the fraction of their signal which decayed below T_g .⁵⁶ Direct depth resolution can be achieved by burying a tagged layer a known distance from the surface and picking out the dynamics from the buried layer using neutron scattering^{64,65} or by measuring fluorescent dopants.⁶⁶ While these types of measurements benefit from measuring dynamics at a well-determined depth, they are also heavily reliant on the inference of dynamics from $T_{\rm g}$. Additionally, in the latter, the molecular dopants used were quite massive and would have greatly perturbed the local dynamics. It is not yet known how to extract a relaxation time from $T_{\rm g}$, if such a task is possible. Observing the fill rate of indentations formed by gold nanoparticles, allows for the direct measurement of relaxation times, however the method fundamentally does not allow for measurements deeper than directly at the surface.^{67,68} Additionally, in most of these experiments, multiple films must be prepared to vary the measured depth, introducing a source of uncertainty.

Experimental techniques capable of directly measuring the dynamics with depth resolution in a single polymer film include muon spin rotation, relaxation, and resonance (μ SR);⁶⁹ and the implanted-ion β -NMR method^{1,31} used in this work. In both, spin-polarized radioactive probe ions are implanted into the sample at low energy and the local magnetic and electronic structure are measured via the relaxation of the polarization. In ⁸Li β -NMR, the binding energy of the implanted ions to the phenyl rings is large, suggesting that under the measured conditions, the probes don't appreciably move from their site of implantation.³¹ Similarly, it is expected that the μ SR muon will bind to the carbons of the phenyl rings in the form of muonium (a $\bar{\mu} - e$ pair, behaving similarly to H), and be likewise sensitive to the ring motion.⁵⁷ While β -NMR is most likely a probe of γ relaxation below T_{g} ,³¹ μ SR has been shown to be sensitive to this mechanism only above T_{σ} .⁵⁷ In agreement with the optical photobleaching measurement, the surface effect on dynamics was measured in the glassy state to be $5 \,\mathrm{nm}$ to $10 \,\mathrm{nm}$ using β -NMR.¹ In contrast, early μ SR measurements show a layer of enhanced dynamics spanning $\sim 35 \text{ nm}^{69}$ below the surface; however, there is good reason to question this result. The dynamical gradient in this case spans a distance that is inconsistent with both simulations and the aforementioned experiments. This may be attributed to the fact that these measurements were taken with zero applied magnetic field, inappropriate for this material.⁷⁰ Furthermore, these measurements were taken well below $T_{\rm g}$, where the mechanism responsible for the μ SR signal has not vet been identified.

 β -NMR has also been used to measure the effect of annealing and surface treatment, both of which produced an overall shift of dynamics but with no significant change to the length scale associated with enhancement of surface dynamics.³¹ Furthermore, β -NMR results in a bilayer film show a dramatic enhancement of dynamics in the vicinity of the buried aPS/aPS interface, suggesting that the above multilayer experiments are likely to have overestimated the size of the mobile layer.³¹

Experimental work has been greatly supported and supplemented by MD simulations. As a virtual experiment, the molecular configuration in simulation is exactly known, allowing for a great deal of insight of the mechanisms controlling glassy dynamics, particularly when nanoscale precision is needed with regards to the surface. Results of both highly coarse-grained¹⁴ and more chemically accurate⁷¹ simulations show a surface region of enhanced dynamics on the order of ~ 5 nm. In an additional confirmation that whole-film measurements were affected by a mobile surface layer, the film thickness-



Figure 1.2.3: Film density as a function of the normalized correlation time for ring dynamics, with depth implicit. Clearly, there is a low degree of correlation between these two quantities. Simulation details presented in Chapter 4.

dependence of $T_{\rm g}$ has been reproduced, and the $T_{\rm g}$ of the surface and middle layers were reported to be each relatively thickness-independent.^{24,25} One important contribution of simulations to the understanding of aPS surface effects has been the elimination of density as a predicting factor of the interfacial dynamics. Using data from our simulated films, which will be presented in detail during Chapter 4, Figure 1.2.3 clearly shows a lack of correlation between the density and the dynamical correlation times. Here, the distance from the surface is implicit, with measurements closer to the surface attributed to the points with the shortest correlation times. This lack of correlation prompts a need for more sophisticated theories of molecular dynamics when modified by the free surface.

Figure 1.2.2 shows that the bulk dynamics of aPS vary according to an Arrhenius relationship, where the relaxation times, τ_c , are exponentially related to the inverse temperature. However, the presence of the surface introduces a depth dependence to τ_c . In Chapter 4 we investigate a power-law decoupling of the temperature and depth dependencies in the context of MD simulations of an aPS thin film. In this description, the temperature dependence is fully dictated by the bulk and the surface effect is contained in the temperature-independent exponent. This functional form can be shown to arise by introducing a position-sensitive Arrhenius activation barrier;¹³ or by considering string-like cooperative molecular rearrangements,²³ similar to the cooperative rearranging region famously introduced by Adam and Gibbs.⁴

Simulations have also provided insight not easily measurable in the lab, for example, showing that surface dynamic enhancement does not arise from local molecular structure.¹¹ They have also provided evidence for the presence of dynamic heterogeneity,^{6,72–74} a quantity not easily measured experimentally, although it is possible.^{75,76} β -NMR is one such technique, and Chapter 6 demonstrates how β -NMR can be used to observe the emergence of dynamical heterogeneity in an imidazolium RTIL. Like aPS, these RTILs readily vitrify upon cooling, although this property arises from size differences and asymmetry in the composite ions, rather than the tacticity and entanglement of polymer chains. We now turn to a description of the bulk and surface properties of EMIM–Ac, the RTIL studied in this work.

1.3 1-ethyl-3-methylimidazolium acetate

1.3.1 Bulk properties

Depicted in Figure 1.3.1, 1-ethyl-3-methylimidazolium acetate (EMIM-Ac) is a RTIL, a material similar to high-temperature molten salts. Ionic liquids (ILs) are composed of two charged components and, like polymers, are highly tunable both chemically and mechanically. They have many applications in energy production and storage, including: electrolytes in Li-ion batteries⁷⁷⁻⁷⁹ and supercapacitors,⁸⁰ iontronics,⁸¹ thermo-electrochemical cells, and solar cells.⁸² A negligible vapour pressure opens avenues towards applications in chemistry under ultra-high vacuum (UHV),⁸³ and lubrication;^{83,84} notably by NASA who, under simulated space conditions, showed that RTILs perform comparably well or better than other commonly used space oils.⁸⁵ In addition,
EMIM-Ac also has potential use in biorefinery, being one of the few solvents capable of the dissolution of cellulose.^{86–88}



Figure 1.3.1: Structure of the EMIM cation (left) and Ac anion (right).

The strong Coulomb interactions between the two species is the source of their many interesting properties; even in the liquid state the ions remain quasi-ordered, with an alternating-charge structure.^{89–91} Many RTILs are notoriously difficult to crystallize, easily supercooling and eventually freezing into a glassy state.⁹² The $T_{\rm g}$ is dependent on the interionic spacing, achieved through a balance between attractive Coulomb and van der Waals forces and Pauli repulsion.⁹³ The potential well associated with pairs of oppositely charged ions results in a $T_{\rm g}$ minimum as a function of ionic spacing, as quantified by the radius sum of the two ionic species.⁹³

Unfortunately, the study of the dynamics of these ionic glasses is very much in its infancy and, as of this writing, no RTIL has been singled out as a focus point for the study of glass physics. En lieu, a compilation of several imidazolium-based RTILs can be made, scaling the temperature by $T_{\rm g}$ for a reasonable collapse of the data as shown in Figure 1.3.2. This compilation from the literature aggregates many experimental methods, as well as RTILs. The scatter in the figure is likely due to both chemical differences in the various RTILs, and in experimental method. As with aPS, these RTILs can be seen to have at least one confirmed secondary dielectric relaxation,⁹⁴ and one author appears to have tentatively found a third (cautiously labelled here as γ).⁹⁵ Unlike aPS, there is not yet enough confidence to assign a relaxation mechanism to each dielectric peak. When the γ and β relaxation modes are fit with an Arrhenius equation (Equation 1.2.1) or, in the case of α , the VFT

			α	β	γ
ΔE	General	$(k_B T_g)$	6.0(5)	23(1)	12.2(7)
	$\mathrm{EMIM}\mathrm{-Ac}$	(eV)	0.10(1)	0.40(2)	0.21(1)
$T_{\rm g}$	General	$(T_{\rm g})$	0.99	0.61	0.38
	$\mathrm{EMIM}\mathrm{-Ac}$	(\breve{K})	195.7	120.6	75.1

Table 1.3.1: Activation energies from the fits in Figure 1.3.2 and the anticipated $T_{\rm g}$ based on $\tau_c > 100 \, {\rm s}$, for general imidazolium RTILs and converting for EMIM–Ac, where $T_{\rm g} = 197.65 \, {\rm K}.^{100}$ The $T_{\rm VFT}$ for the α process was $0.79(1) \, T_{\rm g}$.



Figure 1.3.2: A reasonable collapse of correlation times from several bulk RTILs reveals at least two different relaxation mechanisms. Data compiled from a number of RTILs: BMIM-BMSF (blue): \bigcirc ,⁹⁵ BMIM-Cl (orange): \bigcirc ,⁹⁵ BMIM-PF₆ (green): \bigcirc ,⁹⁵ \square ,¹⁰¹ \triangle ,¹⁰² [Si-MIm][Bf₄] (red): \diamondsuit ,⁹⁴ and EMIM-Ac (purple): \blacktriangle .¹⁰³ Dashed lines are VFT (α) or Arrhenius (β , γ) fits.

equation (Equation 1.2.2), we are able to extract the ΔE and $T_{\rm g}$ seen in Table 1.3.1. A similar treatment with the molten salt 2Ca(NO₃)₂-3KNO₃ (CKN) shows similar secondary relaxation processes, albeit at much longer correlation times.^{96–99}

EMIM–Ac is particularly well-suited for the β -NMR spectrometer at TRIUMF. Implanted-ion β -NMR must be conducted in a UHV environment to avoid the buildup of condensed gases on the sample surface at cryogenic temperatures, and samples must be mounted in an upright orientation such that the face is exposed to the ion beam. The high viscosity at $T \leq 320$ K allows EMIM–Ac to be mounted in the proper orientation. As a RTIL, its $T_{\rm g}$ is quite low and the full phase space is accessible within the spectrometer, unlike aPS whose $T_{\rm g}$ lies slightly above the spectrometer's maximum temperature. Thus, vitrification takes place in situ, and the thermal history of the EMIM–Ac glass is fully controlled and accounted for in our implementation of β -NMR.

Prior measurements of β -NMR in EMIM–Ac show nuclear magnetic resonance (NMR) spectra which compare favourably with conventional NMR, and allow for the distinction of coordination with different species.² This indicates that the coordination occurs within the lifetime of the probe, which in this case was ³¹Mg (236 ms). The probe used in this work was ⁸Li, which lives about five times longer, and we expect the ⁸Li dynamics to be fully correlated with those of the host ions.

1.3.2 Surface properties

Interfacial properties of RTILs are extremely important to the design of electrodes when the RTIL is used as a electrolyte. As the simplest possible interface, the surface of a number of imidazoluim-based RTILs have been investigated, from which some common observations can be made.

While neither ion species appears to be enriched at the surface,^{104–108} an ordering of the cation orientation emerges at the surface. In many studies, the preferred orientation has the imidazolium rings perpendicular to the surface plane, with alkyl chains extended out from the liquid,^{108–112} however both orientations of the rings are possible.^{107,113} In hydrophobic RTILs, the ring orientation is dependent on the water concentration, with the orientation parallel to the surface plane at water vapour pressures less than 10^{-4} Torr.^{114,115} As a hydrophilic RTIL, the orientation of EMIM–Ac

cations should be unaffected by the presence of water.

It has been proposed that short alkyl chains have a tendency to extend out from the liquid, whereas longer chains fold over and lie on the surface, explaining the increasing surface coverage of longer alkyl chains.^{106,108,116} The packing at the surface was found to be dominated by steric effects, with smaller anions having more efficient packing at the surface.^{106,112} Perhaps due to this ordering, the first ~1 nm below the surface of these RTILs exhibits a 20% to 30% increase in density.^{105,109,113,116,117}

A few peculiar cases should be highlighted as well. Firstly, in 1-butyl-3methylimidazolium hexafluorophosphate (BMIM-PF₆), nanoscale crystalline regions were observed using x-ray diffraction nearly 40 K above $T_{\rm m}$.¹¹⁸ In mono-layer supported films of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (BMIM-TFSA), apparently solid and layered structures up to 50 nm were formed.¹¹⁹ Lastly, in supported thin films of imidazolium RTILs, dynamics were seen to slow with increasing alkyl chain length¹²⁰ and decreasing film thickness;¹²¹ an effect apparently related to the substrate surface functionalization.¹²² Unlike aPS, no depth-resolved study, independent of substrate effects, has been conducted.

1.4 Thesis scope

The work presented in this thesis pertains to the investigation of the molecular dynamics of the supercooled and glassy states of both aPS thin films and EMIM–Ac droplets, using a combination of MD simulations and β -NMR experiments. Chapter 2 briefly describes the simulation methods used. Chapter 3 presents an overview of the basics of NMR theory and specifics related to the implanted-ion β -NMR technique. In Chapter 4, MD simulations are used to show that the relaxation times of backbone segments and phenyl rings of aPS thin films are related to the bulk relaxation time by a power-law coupling. In Chapter 5, the simulation results are compared to β -NMR measurements and changes to the spectrometer, allowing for operation at higher temperatures, are detailed. Chapter 6 concerns the measurement of the bulk and surface of EMIM–Ac, an RTIL, above and below the glass

transition. Concluding remarks are then made in Chapter 7.

Chapter 2

The Principles of Molecular Dynamics Simulations

Classical molecular dynamics (MD) simulation is a widely used technique to understand physical and chemical processes at atomic and molecular scales. Simply put, the method works by constructing a computational model with simplified atomic interactions and forces, and uses classical equations of motion to progress the model through time. Done properly, the result is a virtual representation of the internal motion of the atoms and molecules of the material in question, from which the quantities of interest can be calculated. In Chapter 4, MD simulations are used to model a freestanding atactic polystyrene (aPS) thin film in order to understand the depth dependence of the dynamics. This chapter covers the basics of the technique and its implementation.

2.1 Motivation

While MD simulations have seen widespread popularity in the field of material science, the technique is used across a wide variety of fields, such as biochemistry and biophysics in advancing the problem of protein folding.¹²³ As applied to amorphous materials, MD simulations have been used to model a wide variety of systems and phenomena, such as residual stress distributions during plastic flow,¹²⁴ the design of smart polymers,¹²⁵ thermal transport,¹²⁶ and of course, polymer thin films.^{71,73} In this thesis, we use MD simulation to study the effect of the free surface on the dynamics in a free standing aPS thin film.

Classical MD simulations are able to simulate molecules with varying degrees of coarse-graining. The all-atom scenario is the most chemically accurate, with each atom realized.¹²⁷ In many cases, chemical accuracy is not needed, for example when the motions of H atoms do not significantly contribute to the overall dynamics of the system. In this case, the H atoms can be combined with their bonded counterparts, for example the C atoms, and the force field is modified to account for the resulting united-atom structure.¹²⁸ One can also strip all chemical details for a greater degree of abstraction, such as bead-spring polymer models, which allow for more general observations.¹² Increasing the degree of coarse-graining does not necessarily result in a less-accurate simulation.¹²⁹ Simulations which include a large amount of chemical detail run much slower, as each atom introduces many additional forces which must be calculated at each time step. Additionally, accurate results depend on a small in-simulation time step to account for fast thermal fluctuations. For chemically realistic systems, the time step must be in the range of 1 fs to 10 fs. For most applications, this restricts the total simulation duration to the order of $\sim 1 \, \mu s$ or less. As a rule, systems with a greater degree of coarse-graining can have larger time steps without introducing significant error in the propagation of atomic configurations. Highly coarse-grained simulations are then able to simulate longer times and collect more statistics than those which have a greater level of detail.

The flexibility accorded to classical MD simulations by the level of coarsegraining allows MD simulations to span a particularly large range length and time scales, from 10^{-9} to 10^{-3} meters¹³⁰ (or seconds¹³¹). This is in contrast to <u>ab inito</u> methods, such as density functional theory (DFT) or DFT-based hybrid methods such as <u>ab inito</u> MD,¹³² which uses DFT to calculate the interatomic forces and MD to propagate the system through time. DFT is an extremely powerful method capable of calculating the static electronic structure with quantum mechanical rigor.¹³³ While recent progress has greatly expanded the scale at which <u>ab inito</u> MD can be applied,¹³⁴ the computational cost of electronically accurate calculations remains prohibitively expensive for the large-scale scenarios regularly modelled by classical MD simulation methods, which may often be composed of millions of particles.¹³⁵ Since the dynamics of glasses can be slow, span a large range of timescales, and are largely a classical phenomenon; classical MD is extremely well suited to this field of study.

2.2 Theory

The inputs for classical MD simulations consist solely of the atomic positions and velocities, as well as the rules for calculating the forces on each particle. Simply put, the method works by applying the following two steps:

- 1. Calculate the forces to which each particle is subject.
- 2. Propagate the system under these forces for a short period of time, and repeat.

Classical MD simulations substitute computationally expensive quantum mechanically-accurate calculations for simple analytical forms of the atomic forces. The equations and parameters of these forces are then carefully chosen for each system to properly replicate the interatomic interactions. For example, pairwise interactions in amorphous systems are commonly modelled with the Lennard-Jones potential (LJ) potential,

$$E_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \qquad (2.2.1)$$

where ϵ sets the energy scale, σ sets the distance scale, and r denotes the distance between the two interacting particles.¹³⁶ The repulsive (first) term phenomenologically describes Pauli repulsion at short distances, whereas the attractive (second) term arises from a van der Waals attraction. The result is a potential well whose minimum is slightly more than one σ from r = 0, with a large repulsive barrier preventing collapse, and tending to zero as $r \to \infty$.

In addition to the Coulomb force, other phenomenological forces may be



Figure 2.2.1: Common force schemes allocated to groups of atoms connected by chemical bonds.

added to describe the effects of atomic bonding. As depicted in Figure 2.2.1, these may describe changes to the bond length, angle, or twisting through the dihedral angle. Complex molecules, such as polymers, can be accurately modelled with the appropriate application of these simple forces. In Chapter 4, the bond distances and angles are described with a harmonic function,

$$E = K(x - x_0)^2, (2.2.2)$$

where K sets the energy scale and $x \in \{r, \theta\}$ as appropriate; whereas the dihedral and other dihedral-like potentials are described by

$$E = [1 + d\cos(n\phi)].$$
(2.2.3)

While classical simulations are effective on length scales where the electron orbitals can be replaced by simple analytical forces, such as the aforementioned, any MD simulation model must first be validated before meaningful results can be obtained. This validation is to ensure that the force fields used in the model will accurately describe the system before it is employed. This can be done either in comparison to a more fundamental calculation, such as DFT,¹²⁷ or to experiment.¹²⁸ In this work, the parameters used in Equations 2.2.2 and 2.2.3 were reproduced from Vorselaars et al.,¹³⁷ which were validated against X-ray scattering measurements.¹³⁸

At each time step, the simulation must be propagated forward in time. A popular algorithm for this task is the Velocity Verlet algorithm.¹³⁹ The algorithm can be understood in three steps: first, calculate the new positions, $\boldsymbol{r}_i(t + \Delta t)$, of each atom using the velocities, \boldsymbol{v}_i , and forces, \boldsymbol{f}_i , at the current timestep, t. Second, find the new resulting forces at the next timestep, $t + \Delta t$, based on the new positions. Lastly, average the forces at time t and $t + \Delta t$ to find the velocity at time $t + \Delta t$. This can be written more succinctly as:¹²⁹

$$\begin{aligned} \boldsymbol{r}_{i}(t+\Delta t) &= \boldsymbol{r}_{i}(t) + (\Delta t)\boldsymbol{v}_{i} + (\Delta t)^{2}\frac{\boldsymbol{f}_{i}(t)}{2m_{i}}, \\ \boldsymbol{v}_{i}(t+\Delta t) &= \boldsymbol{v}_{i}(t) + (\Delta t)\frac{\boldsymbol{f}_{i}(t) + \boldsymbol{f}_{i}(t+\Delta t)}{2m_{i}}. \end{aligned} \tag{2.2.4}$$

This formulation has the system evolving within the microcanonical ensemble, commonly labelled as NVE since the particle number, volume, and energy are all fixed. Other ensembles, such as the NVT (T = temperature) canonical or isothermal ensemble, and the isobaric ensemble, or NPT (P = pressure), are also possible with an appropriate thermo or barostat.

While several thermostat algorithms exist, one of the most accurate and widely used methods is that developed by Nosé,^{140,141} later refined by Hoover.¹⁴² Importantly, the Nosé-Hoover thermostat preserves the canonical ensemble, whereas some others, such as the Berendsen thermostat, do not. Nosé's central idea was to write a temperature-dependent Hamiltonian by controlling the momentum of the particles via a time-scaling parameter, representative of a coupling to a heat bath. The magnitude of the coupling is determined by a coefficient which follows a feedback equation, allowing control over the kinetic energy. Hoover later re-cast Nosé's equations of motion without the scaling variable, instead introducing a phenomenological relaxation time for which the kinetic energy approaches the required time-averaged kinetic energy for the given temperature. Non-Hamiltonian procedures are possible as well, such as that of Tuckerman et al.,¹⁴³ which acts as both a thermostat and barostat.

While many specifics are needed for each application, a great deal of commonality exists in the implementation of each MD simulation. To facilitate this work, popular general-purpose MD simulation codes have been written to provide a framework within which to set up and run the simulation. Examples of such codes are GROMACS¹⁴⁴ and LAMMPS.¹⁴⁵ Both exhibit a high degree of optimization in algorithm design and the use of hardware, particularly with regards to the parallelization necessary to run large simulations in a reasonable time. The simulations in this work leverage the LAMMPS code.

We are interested in the relaxation times associated with the molecular dynamics of glasses, particularly aPS. In practice, the relaxation time is determined from the decay of the autocorrelation function. For some normalized vector $\hat{\boldsymbol{v}}$, the autocorrelation of the vector orientation may be calculated as

$$C_2(t) = \frac{3}{2} \left\langle [\hat{\boldsymbol{v}}(t') \cdot \hat{\boldsymbol{v}}(t'-t)]^2 \right\rangle_{t'} - \frac{1}{2}, \qquad (2.2.5)$$

where t' is the duration over which the correlation is calculated. We encapsulate the correlation in the second Legendre polynomial to introduce a rotational symmetry. For example, if a phenyl ring rotates by π , it is identical to the un-rotated ring. The vector $\hat{\boldsymbol{v}}$ may be indicative of the orientation of the ring, chain segment, or the location of a coarse-grained sphere.

While MD simulations have long been compared to experiments,^{128,146} they are particularly well-suited for the comparison with nuclear magnetic resonance (NMR) experiments.¹⁴⁷ Unlike many measurements, the processes driving NMR relaxation operate on timescales accessible in MD simulations, potentially allowing for a direct comparison.¹⁴⁸ We now explain the basics of NMR and our implanted-ion variant, β -detected nuclear magnetic resonance (β -NMR).

Chapter 3

The Principles of Nuclear Magnetic Resonance

3.1 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a technique sensitive to local magnetic and electric properties of a material by measuring the precession of nuclear spins in a magnetic field. This chapter presents a summary of how these spins interact with magnetic and electric fields, following the canonical text of Slichter.¹⁴⁹

3.1.1 Static field

Consider an isolated nucleus in an external magnetic field **B**. The (Zeeman) Hamiltonian for this interaction is

$$\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{B},\tag{3.1.1}$$

where μ is the nuclear magnetic moment, and is proportional to the total angular momentum by a factor of γ , the gyromagnetic ratio:

$$\boldsymbol{\mu} = \gamma \mathbf{J}.\tag{3.1.2}$$

The magnetic moment therefore points in the same direction as the spin. In a typical NMR experiment, a large static magnetic field is used, usually defined to be aligned along \hat{z} , with magnitude B_0 . The Zeeman Hamiltonian for a spin in this field is

$$\mathcal{H}_0 = -\gamma B_0 J_z, \qquad (3.1.3)$$

where J_z is the operator for the \hat{z} component of **J**. Hamilton's equations easily show that the interaction with \mathbf{B}_0 results in a rotation about \hat{z} with frequency ν_L , where

$$\nu_L = \gamma B_0. \tag{3.1.4}$$

This frequency is called the Larmor frequency, and is specific to both the nuclear species (via γ) and the magnitude of the external magnetic field.

3.1.2 Time-dependent magnetic fields

NMR experiments make heavy use of a time-dependent magnetic field, denoted \mathbf{B}_1 . This field is applied perpendicularly to \mathbf{B}_0 , and oscillates at radio frequencies (RF). We define the applied magnetic field to be along \hat{x} ,

$$\boldsymbol{B}_x(t) = B_x \cos(\omega t) \hat{\boldsymbol{x}}.$$
(3.1.5)

As shown by Slichter,¹⁴⁹ $\boldsymbol{B}_x(t)$ can be written as the sum of two counterrotating components,

$$\mathbf{B}_1 = B_1 \left(\hat{x} \cos(\omega t) \pm \hat{y} \sin(\omega t) \right), \tag{3.1.6}$$

corresponding to angular velocities $\pm \omega$, depending on the sense of the rotation (clockwise or counter-clockwise).

The Hamiltonian for the motion of the spin in these conditions is most intuitive in the rotating reference frame, a frame which rotates about \hat{z} in the same direction as the spin itself. When the frame is rotating near resonance, the counterrotating component of Equation 3.1.6 will be negligible. The lab frame unit vectors $(\hat{x}, \hat{y}, \text{ and } \hat{z})$ and those of the rotating reference frame $(\hat{i},$ \hat{j} , and \hat{k}) are related by the following set of transformations:

$$\hat{\imath} = \hat{x}\cos(\omega t) + \hat{y}\sin(\omega t),$$

$$\hat{\jmath} = \hat{x}\cos(\omega t) - \hat{y}\sin(\omega t),$$

$$\hat{k} = \hat{z}.$$
(3.1.7)

If the rotating reference frame has the same angular velocity as \mathbf{B}_1 , then \mathbf{B}_1 is a constant given by $B_1\hat{\imath}$; however, due to the rotation of the frame, the nuclear precession due to B_0 is reduced to $\omega_L - \omega$. In the rotating reference frame, the nuclear spin precesses about an effective magnetic field given by

$$\mathbf{B}_{\rm eff} = \left(B_0 - \frac{\omega}{\gamma}\right)\hat{k} + B_1\hat{\imath}.$$
 (3.1.8)

The effective field is shown schematically in Figure 3.1.1.

By Equation 3.1.1, the Hamiltonian in this reference frame is

$$\mathcal{H}_{\rm eff} = -\hbar\gamma \Big\{ \left(B_0 - \frac{\omega}{\gamma} \right) I_z + B_1 I_x \Big\}, \tag{3.1.9}$$

where I_i are the dimensionless angular momentum operators $I_i \equiv J_i/\hbar$ for $i \in \{x, y, z\}$. This is exactly the Hamiltonian one obtains from a quantum mechanical treatment of the rotating reference frame.¹⁴⁹ When the rotating reference frame is on resonance ($\omega = \omega_L$), the amplitude of the $\mu \cdot \hat{k}$ oscillations are maximal. In the lab frame, this results in a nutation of the nuclear magnetic moments.

3.1.3 Spin-Lattice Relaxation

Spin-lattice relaxation (SLR) is the process through which a polarized ensemble of nuclear spins returns to equilibrium, via thermal energy exchange with the surrounding medium (i.e., the lattice, used as a shorthand for all other degrees of freedom, regardless of atomic structure). The characteristic relaxation time for exponential SLR is denoted by T_1 , as demonstrated by the Bloch Equations.

The Bloch Equations are a useful phenomenological description of the



Figure 3.1.1: The magnetic moments μ rotate about $\mathbf{B}_{\rm eff}$ in the rotating reference frame. This emerges as a nutation in the lab frame. Reproduced from Slichter.¹⁴⁹

time dependence of the nuclear magnetization. They can be derived by considering a simple two-state model with populations N_+ and N_- . By thermal exchange with a reservoir, the nuclei are able to change their state. Let W_{\uparrow} be the probability per unit time of a transition from - to +, and W_{\downarrow} for the inverse transition. The state populations then follow the "master equations", a coupled set of rate equations:

$$\frac{dN_+}{dt} = N_- W_{\uparrow} - N_+ W_{\downarrow} \quad \text{and} \quad \frac{dN_-}{dt} = N_+ W_{\downarrow} - N_- W_{\uparrow}. \tag{3.1.10}$$

Using $N \equiv N_+ + N_-$ and $n \equiv N_+ - N_-$, we can combine the master equations as

$$\frac{dn}{dt} = \underbrace{(W_{\downarrow} + W_{\uparrow})}_{1/T_1} \left[\underbrace{N\left(\frac{W_{\downarrow} - W_{\uparrow}}{W_{\downarrow} + W_{\uparrow}}\right)}_{n_0} - n \right].$$
(3.1.11)

Making the identified substitutions, the difference in the state populations decays exponentially to the constant value n_0 , with characteristic time T_1 . Given that the magnetization along the z-axis, M_z , is proportional to n, it is reasonable to conclude that

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}.$$
(3.1.12)

Accounting for the additional rate due to the torque caused by the magnetic field $\left(\frac{d\mathbf{J}}{dt} = \frac{1}{\gamma}\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times \mathbf{B}\right)$, the rate of change of the magnetization is

$$\frac{dM_z}{dt} = \gamma (\mathbf{M} \times \mathbf{B})_z + \frac{M_0 - M_z}{T_1}.$$
(3.1.13a)

Since the field has a tendency to align with \hat{z} , the x- and y-components must vanish at long times, and for these components $M_0 = 0$:

$$\frac{dM_x}{dt} = \gamma (\mathbf{M} \times \mathbf{B})_x - \frac{M_x}{T_2}$$
(3.1.13b)

$$\frac{dM_y}{dt} = \gamma (\mathbf{M} \times \mathbf{B})_y - \frac{M_y}{T_2}.$$
(3.1.13c)

For the transverse magnetization we have defined a new time constant, T_2 . This is the spin-spin relaxation time constant and describes the decay of phase coherence among the probe nuclei, where typically in solids $T_2 \ll T_1$, and in liquids $T_2 \approx T_1$. Equations 3.1.13 are known as the Bloch Equations.

The full quantum description of the density matrix master equation results in a much more complex treatment, as addressed by Slichter¹⁴⁹ and Abragam.¹⁵⁰ Outside of two level systems, this exponential evolution of the magnetization is obtained only in a few specific instances. Many systems, especially those dominated by quadrupolar interactions, show a time evolution of the magnetization that is multi-exponential.^{151–153} In Appendix A.1 we show when these quadrupolar interactions, which are highly relevant to this thesis, result in single exponential SLR. In the case of amorphous materials, molecular motion in the disordered material results in a distribution of T_1 relaxation times, which may be described by a stretched exponential function.^{154–156}

3.1.4 Electric Quadrupole Interactions

Only nuclei with $I > \frac{1}{2}$ have a preferential orientation due to electrostatic interactions. Nuclei with I = 0 lack any spin orientation and are unaffected. The two possible spin orientations of $I = \frac{1}{2}$ nuclei, differing only by spin



Figure 3.1.2: An asymmetric (elliptical) nucleus in a field of four point charges. The orientation (b) will be energetically preferential as the positive nucleus is closest to the negative charges.

inversion, have the same effective nuclear charge distribution.¹⁵¹ This corresponds to a 180° rotation of the nucleus in Figure 3.1.2, where it is easy to see that these states are degenerate. Figure 3.1.2 also makes it clear that a non-spherical nucleus, corresponding to all other nuclear spins, have an orientational dependence to their energy state. These spins are coupled with the electric field gradient (EFG) through a quadrupolar interaction, including the I = 2 nuclei used in this thesis. The dipole term in the electrostatic potential expansion vanishes because the center of charge and center of mass are coincident.¹⁴⁹ The EFG is a 2-tensor whose elements are defined as the second partial derivative of the electric potential:¹⁵¹

$$V_{\alpha\beta} = \frac{\partial^2 V}{\partial \alpha \partial \beta},\tag{3.1.14}$$

where $\alpha, \beta \in \{x, y, z\}$. The Hamiltonian describing this interaction is^{149,150}

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} \sum_m V^{(-m)} A^{(m)}(I), \qquad (3.1.15)$$

where Q is the nuclear quadrupole moment, e is the electron charge, and I is the nuclear spin. The functions $V^{(m)}$ describe the EFG and its time

dependence, whereas the $A^{(m)}$ operators depend only on the time-independent spin terms:

$$\begin{split} V^{(0)} &= V_{zz} & A^{(0)}(I) = 3I_z^2 - I(I+1) \\ V^{(\pm 1)} &= V_{zx} \pm i V_{zy} & A^{(\pm 1)}(I) = I_z I_\pm + I_\pm I_z \\ V^{(\pm 2)} &= \frac{1}{2}(V_{xx} - V_{yy}) \pm i V_{xy} & A^{(\pm 2)}(I) = I_\pm^2, \end{split}$$
(3.1.16)

where $I_{\pm} = I_x \pm i I_y$, and the I_{α} are the dimensionless total nuclear spin operators.

There always exists a Principal Axis reference frame wherein the EFG is diagonal, such that $|V_{zz}| \ge |V_{yy}| \ge |V_{xx}|$ and $\sum_{\alpha} V_{\alpha\alpha} = 0$. In this frame it is sufficient to specify only the following two quantities:¹⁵¹

$$eq = V_{zz} \tag{3.1.17}$$

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}},\tag{3.1.18}$$

where eq is the magnitude of the gradient (its principle component) and $\eta \in [0, 1]$ is its asymmetry, where $\eta = 0$ at axisymmetric sites. In this frame, and in the case of $\eta = 0$, \mathcal{H}_Q contains only the magnitude term (V_{zz}) , which is greatly affected by the presence of closed-shell electrons. Outside the shell radius, the effect is constant and given by

$$V_{zz} = V_{zz}^0 [1 - \gamma_\infty], \qquad (3.1.19)$$

where γ_{∞} is called the Sternheimer antishielding factor.¹⁵⁷ For ⁸Li, the correction is typically relatively small, for example in LiF, $|1 - \gamma_{\infty}| = 3.4$.¹⁵⁸

Coupling to the EFG has an impact on both the resonance and SLR. In amorphous systems, because each probe experiences a unique local environment, coupling with the EFG simply produces a static time-averaged broadening. If a large portion of the NMR probes experience identical local environments, one would observe a hyperfine splitting of the Zeeman interaction, as may be observed in crystalline materials.¹⁵⁹

With regards to the SLR, fluctuations in the electric quadrupole interac-

tion provides an additional source of relaxation which, in many nonmagnetic cases, dominates the magnetic relaxation. Unlike the relaxation described by the Bloch equations (Equation 3.1.13), the magnetization for spins of I > 1 do not evolve exponentially with time, unless fluctuations of the EFG are extremely fast relative to $1/\omega_L$ (the fast fluctuation limit). The single exponential cases are addressed in Appendix A.1. The NMR probe in this work is ⁸Li which has a nuclear spin of I = 2. The resulting SLR relaxation from a I = 2 coupling to the EFG is bi-exponential:^{151–153,160}

$$M_z \propto c_1 e^{-t/T_1^{(1)}} + c_2 e^{-t/T_1^{(2)}}, \qquad (3.1.20)$$

where c_1 and c_2 are the relative weights for each contribution. The c_i and $T_1^{(i)}$ in Equation 3.1.20 are fully determined by the spectral density of the EFG,

$$\mathcal{J}_m(\omega) = \int_{-\infty}^{\infty} dt \, \left\langle V^{(m)}(\tau) V^{(-m)}(t+\tau) \right\rangle_{\tau} e^{-i\omega t}, \tag{3.1.21}$$

as described by Becker.¹⁵² For the case of isotropic dynamics, the Debye equation serves as a sufficient approximation,

$$\mathcal{J}_m(\omega) = C_m \frac{2\tau_c}{1 + \omega^2 {\tau_c}^2}, \qquad (3.1.22)$$

where the C_m constant prefactors related to the magnitude of Equation 3.1.21. The $T_1^{(i)}$ and c_i in Equation 3.1.20 are therefore fully determined by the microscopic correlation times associated with EFG fluctuations.

Figure 3.1.3 shows the $T_1^{(i)}$ and c_1 for the case of I = 2, as solved by Becker.¹⁵² The SLR rates go through a maximum at $\tau_c \approx 1/\omega_L$, often referred to as a Bloembergen-Purcell-Pound (BPP) peak. At this point, EFG fluctuations are most effective at coupling to the spins and the fastest relaxation will occur at this point. All other fluctuation rates must necessarily produce longer T_1 values. Finding the peak is a useful strategy for measuring τ_c .^{161,162}

In the fast fluctuation limit, Figure 3.1.3 shows that the ⁸Li SLR becomes single exponential with $T_1 \propto 1/\tau_c$. Outside of this limit, while the functional



Figure 3.1.3: The bi-exponential SLR times and weights, as solved by Becker¹⁵² for I = 2, with all coupling constants set to 1, and using the Debye spectral density. In the slow or fast fluctuation limits, the dependence is nearly linear. In the fast fluctuating limit, the relaxation is single exponential. Note that $c_1 + c_2 = 1$.

form is bi-exponential, 96 % of the relaxation is due to a single component at the high fields used in this work (6.55 T).^{152,163} The relaxation can therefore be approximated with single relaxation rate given by^{31,103}

$$\frac{1}{T_1} = K \Big(\mathcal{J}(\omega_L) + 4 \mathcal{J}(2\omega_L) \Big), \qquad (3.1.23)$$

which is the relation for I = 1 (see Appendix A.1), albeit with a different EFG coupling coefficient K. Figure 3.1.4 shows the difference between the weighted average of the SLR rates found in Equation 3.1.20 and the single relaxation rate described by Equation 3.1.23, with an appropriately chosen value for K. This minuscule difference would be extremely hard to detect in amorphous systems, where each probe has a unique environment and the



Figure 3.1.4: The difference between the weighted average of the SLR rates of Equation 3.1.20 and the single rate of Equation 3.1.23, denoted in the following as $T_1^{(\alpha)}$: $\Delta\lambda = (c_1/T_1^{(1)} + c_2/T_1^{(2)})/(c_1 + c_2) - \alpha/T_1^{(\alpha)}$. The factor α was found to be 8.40(7).

relaxation may be heavily affected by effects such as dynamic heterogeneity.

We use an implanted-ion variant of conventional NMR, called β -detected nuclear magnetic resonance (β -NMR). While β -NMR shares the fundamental physics underpinning the NMR technique, its implementation is radically different. In the next Section, we will introduce how the β -NMR experiment is implemented at TRIUMF, Canada, and examine how the spin-polarization of the ensemble of implanted ions is measured.

3.2 Beta-Detected Nuclear Magnetic Resonance

A variant of conventional NMR, β -NMR uses the anisotropic beta-decay of spin-polarized radionuclei to detect polarization. First performed in 1959 by Connor,¹⁶⁴ β -NMR can be implemented using neutron activation or through the direct implantation of the probe ions. Relative to conventional NMR, β -NMR requires far fewer nuclei for a desirable signal to noise ratio ($\sim 10^8$ vs $\sim 10^{18}$). This permits measurements in low-volume materials, such

Table 3.2.1: Properties of $^{8}\mathrm{Li},$ the nuclear probe used in this implementation of $\beta\text{-NMR}.^{173}$

Lifetime	au	$1.21\mathrm{s}$
Gyromagnetic ratio	γ	$6.3015\mathrm{MHz/T}$
Nuclear spin	Ι	2
Quadrupole moment	Q	$31.4\mathrm{mb}$

as thin films, which are inaccessible to conventional NMR. By its nature, implanted-ion β -NMR may also perform depth-resolved studies by varying the implantation energy, which has been used to investigate the effects of surfaces^{1,31,165} or heterostructures.^{166,167} The technique also has an initial polarization orders of magnitude larger, as the ions are spin-polarized in-flight.^{168,169}

3.2.1 From Beam to β -NMR

The data in this work was taken with the implanted-ion β -NMR spectrometer in the ISAC facility at TRIUMF, Vancouver, Canada. The spectrometer has been used to successfully measure β -NMR signals using a host of radionuclei, including ⁹Li,^{170,171} ¹¹Li,¹⁷² ³¹Mg,² and ¹¹Be; however the vast majority of measurements (including all of those in this work) use a ⁸Li probe. The ⁸Li nucleus is a particularly good probe for β -NMR; in addition to its availability from a host of production targets, the beta-decay from this short-lived nucleus is particularly asymmetric, and results in no daughters which would then contaminate the signal and the sample. Relevant β -NMR properties of this nucleus can be found in Table 3.2.1.

Ion production is the result of the interaction of a 520 MeV proton beam from the main TRIUMF cyclotron with a production target. The incident beams in this work had a typical flux of $\sim 10^6$ ions/s. Since 2007, targets for the production of ⁸Li⁺ have included tantalum, zirconium carbide, silicon carbide, and a uranium dioxide surface ion source. Upon impact, the target produces a host of isotopes species, the desired species is selected via a mass separator magnet, and the nuclei are transported at 20 keV to 30 keV to the polarizer¹⁷⁴ (Figure 3.2.1).



Figure 3.2.1: Schematic of the beamline heading to the β -NMR high-field spectrometer in the ISAC hall at TRIUMF, Vancouver, Canada. Reproduced from Kiefl et al.¹⁷⁵

The polarizer consists of a collection of beamline elements immediately upstream from the spectrometer. These elements neutralize, spin-polarize, and lastly re-ionize the radioactive beam. The first element, neutralizing the beam, is a Rb vapour jet cell. In Figure 3.2.1 it is listed as the Na cell, but has since been replaced. Electrostatic deflection plates then remove the unneutralized ions from the beam. Over the next 1.9 m, a ~2 mT longitudinal magnetic field is applied, and the neutral beam interacts with circularly polarized laser light travelling down the center of the beam pipe. The beam velocity is fine-tuned such that the laser light is Doppler shifted near 673 nm. The laser thus excites the D₁ transition in the $\pm \Delta m$ direction, depending on the sense of the circular polarization. Repeated excitation leaves the electrons in a spin state of maximum |m|, which is then transferred to the nucleus by spin exchange.¹⁷⁶ This collinear optical pumping scheme yields a nuclear spin polarization of ~70%.¹⁷⁴ After polarization, the beam is re-ionized in a He vapour cell. Thereafter, transport to the spectrometer is achieved with electrostatic elements, preserving the spin polarization, and isolating the ionized component of the beam in the process. The discarded neutral beam is measured as a sample-independent diagnostic of the polarization.

The implantation energy is controlled by applying a voltage to the experimental platform, allowing for implantation energies down to ~0.1 keV. The implantation depth profile is sample-dependent, but may be simulated with Monte-Carlo codes such as Stopping and Range of Ions in Matter (SRIM).¹⁷⁷ SRIM is a heavily used software package which allows for the simulation of ion stopping profiles in materials and compounds. It is based on the binary collision approximation, where interactions are treated as two-body collisions and the path of the implanted ion is unimpeded between collisions. A universal screening potential is used in calculating the atomic interaction.¹⁷⁷ Figure 3.2.2 shows the implantation profiles for 1-ethyl-3-methylimidazolium acetate (EMIM-Ac). For both EMIM-Ac and atactic polystyrene (aPS), the distribution of ions implanted at low-energy is quite narrow, broadening as the energy increases. For both materials, the distributions are phenomenologically well-described by a skew-normal distribution,

$$\Pr(x) = \frac{A}{2} \exp\left(-\frac{1}{2} \left(\frac{x - x_0}{\sigma}\right)^2\right) \left(1 + \operatorname{erf}\left(\eta \frac{x - x_0}{\sqrt{2}\sigma}\right)\right), \quad (3.2.1)$$

where A, x_0 , σ , and η are parameters controlling the amplitude, peak position, width, and asymmetry respectively. The energy dependence of the implantation mean and straggle (standard deviation) for these materials are reported in Table 3.2.2. The figure inset shows, as a function of implantation energy, the fraction of backscattered ions: a reflection of the particles at the material surface due to low implantation energy. Note that this estimate does not account for surface phenomenon in these amorphous materials, such as reduced density (as is the case for aPS) or the ion charges (in the case of EMIM–Ac).

While the amount of heating due to this ion implantation is a complex relationship between the energy deposited by the beam and the energy radiated and conducted out of the sample,¹⁷⁸ an upper bound can be estimated simply by neglecting all terms associated with energy dispersion out of the



Figure 3.2.2: Implantation profiles in EMIM–Ac as calculated by the Monte Carlo code SRIM, fit with a skew-normal distribution (Equation 3.2.1). Inset shows the calculated fraction of backscattered ions as a function of implantation energy, for both EMIM–Ac and aPS.

Table 3.2.2: Implantation energy (in keV) to depth (in nm) conversion for the ion stopping distribution mean and straggle, as calculated by SRIM.

aPS
Mean
$$x = (12.6 \pm 0.2)E^{(0.962\pm0.007)}$$

Straggle $x = (6.3 \pm 0.2)E^{(0.73\pm0.01)}$
EMIM-Ac
Mean $x = (11.63 \pm 0.04)E + (0.7 \pm 0.3)$
Straggle $x = (6.2 \pm 0.3)E^{(0.78\pm0.01)} + (-0.3 \pm 0.3)$

sample. In this case, the change in temperature can be estimated by

$$\Delta T(t,E) = \frac{RE}{c} \left(\rho \pi r^2 \int dx \Pr(x;E) \right)$$
(3.2.2)

where c is the specific heat capacity of the sample, ρ is the density, $\Pr(x; E)$ is the implantation distribution given by Equation 3.2.1, r is the radius of the implanted region (~1.5 mm), R is the implantation rate (~1 × 10⁷ s⁻¹), and E is the kinetic energy of each incident ion. For polystyrene, which has a density¹⁷⁹ of 1048 kg/m³ and a specific heat capacity¹⁸⁰ of 1.287 J g⁻¹ K⁻¹

at room temperature, the relationship between the temperature change per second and implantation energy is linear: $\Delta T(E)/t = (9 \times 10^{-28})E - (4.5 \times 10^{-26})$. Thus, implanting the beam continuously at an energy of 25 keV for 100 years would result in only a 10^{-15} K change in temperature, at most. Given the similar thermophysical properties of EMIM-Ac,¹⁸¹ it too undergoes a similarly negligible amount of heating due to ion implantation.

3.2.2 Spectrometer Description

The necessary components of the β -NMR spectrometer are as follows:

- A cold-finger cryostat manufactured by Oxford instruments allows for temperature control within a ultra-high vacuum (UHV) chamber at pressures on the order of 10^{-10} Torr. While the cryostat itself is operable between temperatures of 2 K to 500 K, other elements placed about the sample position are not capable of withstanding such high temperatures.
- A superconducting solenoid magnet, also manufactured by Oxford instruments, provides \mathbf{B}_0 along the beam axis, up to a maximum magnetic field of 9 T. It has a 101.7 mm UHV warm bore. The radial and axial homogeneity over the central $10 \times 10 \text{ mm}$ region is 20 ppm and 9 ppm respectively.
- A split Helmholtz coil, manufactured in-house, applies the oscillating B₁ at the sample position, with magnitudes on the order of 1 G.
- Two plastic scintillating detectors with conventional photomultiplier tubes detect the beta-decays from the implanted probe. They are arranged in the forward and backward directions (relative to the beam momentum) as depicted in Figure 3.2.3. These can operate to rates of about 10^6 counts/s without count rate distortions.

The cryostat design, along with the split coil about the sample position, limits samples to sizes of 8×10 mm and thicknesses of ~ 2 mm. Beam spots are visible due to scintillation in the sample or substrate; the latter, when



Figure 3.2.3: Schematic of the β -NMR spectrometer. The spin-polarized beam of ⁸Li⁺ is implanted to the position marked in red, indicating the (+) helicity orientation of the spin. The scintillating detectors count the beta-decays of the probe.

made of an impure sapphire (as is typical), scintillates particularly well. As shown in Figure 3.2.4, the beam spot can be viewed by imaging the scintillation with a charge-coupled device (CCD) camera (a cooled Starlight Xpress MX516 with a Sony ICX055AL CCD chip), capable of viewing the sample position through a mirror. Images can be taken with LED lights on or off, to view the sample and beam spot respectively. This imaging capability is used to facilitate the alignment of the beam spot to the sample by adjusting the upstream steering beam line elements.

3.2.3 Detecting Polarization

Beta decay

The parity-violating weak interaction responsible for nuclear beta decay correlates the direction of emission with the nuclear spin orientation, providing a mechanism through which the spin polarization can be measured. The probe used in this work decays as ⁸Li $\rightarrow e^- + \nu + 2\alpha$, which is intermediated



(a) EMIM-Ac sample (b) Beam spot at high field (c) Superposition of \underline{a} and holder \underline{b} , magnified

Figure 3.2.4: (Left) EMIM-Ac sample holder: an aluminum plate with a 3 mm dimple in the center. (Center) Scintillation from the beam impacting sapphire. (Right) Superposition of the left and center images showing the position of the beam relative to the sample. Images were produced using the bccd program described in Appendix D.4.

by the fast ${}^{8}\text{Be} \rightarrow 2\alpha$ decay.¹⁸² The probability distribution function of the beta emission angle, relative to the ${}^{8}\text{Li}$ nuclear spin direction, is described by

$$W(\theta) = 1 + \frac{v}{c} P A \cos(\theta), \qquad (3.2.3)$$

where P is the polarization of the nuclear ensemble; θ is the angle between the momentum of the e^- at the moment of emission and the spin of the host nucleus; v is the speed of the emitted e^- ; c is the speed of light; and |A| < 1is an asymmetry parameter.^{183–185} For ⁸Li, $A = -\frac{1}{3}$, as calculated from the pure Gamow-Teller transitions of ⁸Li.¹⁸⁶ The polarization is defined by

$$P = \frac{1}{I} \sum_{m=-I}^{+I} p_m m, \qquad (3.2.4)$$

where p_m is the normalized occupancy of the $m^{\rm th}$ state. In principle, a single polarization may arise from many distributions of state populations. Attempts to deduce the state populations from the quadrupole splitting in bismuth show that, while the dominant population is in the $m = \pm 2$ states, all of the states provide non-negligible contributions to the overall polarization.¹⁸⁷

Polarization from asymmetry

We now show that the polarization of the implanted population is proportional to the asymmetry of the beta-decay, based on the (unpublished) work of Kiefl.¹⁸⁸ This relationship is central to all β -NMR measurements.

For this treatment, we consider a simplified beam which has an assumed constant ion implantation rate of R_0 , and is switched on discontinuously at t' = 0. Let t' be the time of implantation such that N(t', t)dt' is the number of ions which arrive in the interval (t', t' + dt'), and survive until time t. The expected total number of probes in the sample at time t > t' is then

$$\begin{split} N(t) &= \int_0^t N(t,t') dt' \\ &= \int_0^t R_0 \underbrace{\exp[-(t-t')/\tau]}_{\text{nuclear decay}} dt' \\ &= R_0 \tau [1 - \exp(-t/\tau)], \end{split} \tag{3.2.5}$$

where τ is the nuclear lifetime.¹⁸⁸

We are interested in knowing the time-evolution of the polarization, p(t',t), of the probes at the moment of their decay, which occurs at time t > t'. The simplest case is when p(t',t) is exponential, however in general it may be any function of t and t'. Because the polarization decay only begins after the moment of implantation (at time t'), and since the probes are implanted continuously, the measured signal will necessarily be a sum over all arrival times. Thus, we calculate the average polarization:

$$\begin{aligned} \mathcal{P}(t) &= \frac{1}{N(t)} \int_0^t p(t',t) N(t,t') dt' \\ &= \frac{\int_0^t \exp[-(t-t')/\tau] p(t',t) dt'}{\tau [1-\exp(-t/\tau)]}. \end{aligned} (3.2.6)$$

In β -NMR, $\mathcal{P}(t)$ is measured by counting the betas emitted from the implanted probes in the forward (F) and backward (B) directions, as shown in Figure 3.2.3, and constructing an asymmetry. We now derive the expressions for the measured number of counts in each detector, accounting for the

continuously varying implantation times. To do this, we first define f(t', t)dt'as the number of betas detected in detector F throughout the implantation time interval (t', t' + dt'). These betas arise from a population of probes numbering N(t', t)dt' and, assuming perfect detectors which capture all beta emissions, can be written as

$$f(t',t)dt' = \frac{1}{2}N(t',t)[1+ap(t-t')]dt', \qquad (3.2.7)$$

where p(t - t') is again the polarization of the probes at the moment of their decay. The parameter a is a proportionality constant relating the asymmetry to the polarization, which is in part determined by the decay properties of the probe. Sensibly, when p(t - t') = 0 (no polarization), then $f(t',t) = \frac{1}{2}N(t',t)$. As before, we integrate over the implantation times to find the average number of betas arriving in detector F in the interval (t, t + dt):

$$\begin{split} \mathcal{F}(t) &= \int_0^t f(t',t) dt' \\ &= \frac{R_0}{2} \int_0^t \exp[-(t-t')/\tau] \left\{ 1 + ap(t-t') \right\} dt' \\ &= \frac{R_0}{2} \tau [1 - \exp(-t/\tau)] \left(1 + a \frac{\int_0^t \exp[-(t-t')/\tau] p(t-t') dt'}{\tau [1 - \exp(-t/\tau)]} \right). \end{split}$$

We then substitute Equation 3.2.6 to show that

$$\mathcal{F}(t) = \frac{R_0}{2}\tau[1-\exp(-t/\tau)](1+a\mathcal{P}(t)),$$

and similarly for the B detector. In practice, the detection rates and proportionality constants of the two detectors will be different, such that:

$$\mathcal{F}(t) = R_F \tau [1 - \exp(-t/\tau)] (1 + a_F \mathcal{P}(t)), \, \text{and} \tag{3.2.8}$$

$$\mathcal{B}(t) = R_B \tau [1 - \exp(-t/\tau)] (1 - a_B \mathcal{P}(t)), \qquad (3.2.9)$$

where $R_F(R_B)$ is the detection rate in the F(B) detector in the absence of polarization. This rate depends on the effective solid angle subtended by the

detector, the incoming beam rate and various other instrumental variables such as light collection efficiency or signal discrimination. The proportionality constant between the polarization and detector asymmetry $a_F(a_B)$ may, in general, also depend on the effective solid angle, but this relationship may be more complex than that of $R_F(R_B)$. In the ideal situation, when $R_F = R_B = R_0/2$ and $a_F = a_B = a$, the asymmetry between the F and B detector rates, measured at time t, is proportional to the average polarization at time t:

$$\mathcal{A}(t) \equiv \frac{\mathcal{F}(t) - \mathcal{B}(t)}{\mathcal{F}(t) + \mathcal{B}(t)} = a\mathcal{P}(t). \tag{3.2.10}$$

The effect of α

In the prior section we made the assumption that if a beta is emitted, then it is necessarily detected by either the forward or backward detector. In practice this is not true, and the effective detection rate (in the absence of polarization) for each detector may differ: $R_F \neq R_B$. Defining

$$\alpha \equiv \frac{R_F}{R_B},\tag{3.2.11}$$

Equation 3.2.10 evaluates to

$$\mathcal{A}(t) = \frac{\alpha(1+a\mathcal{P}(t)) - (1-a\mathcal{P}(t))}{\alpha(1+a\mathcal{P}(t)) + (1-a\mathcal{P}(t))}$$
$$= \frac{(\alpha-1) + (\alpha+1)\mathcal{P}(t)}{(\alpha+1) + (\alpha-1)\mathcal{P}(t)}$$
$$= \frac{\delta + a\mathcal{P}(t)}{1+\delta a\mathcal{P}(t)}$$
(3.2.12)

where $\delta = \frac{\alpha - 1}{\alpha + 1}$. The effect of $\alpha \neq 1$ is reduced by combining the asymmetry with that of the inverted spin polarization state, achieved by reversing the helicity of the polarizing laser,

$$\Delta \mathcal{A}(t) = \frac{\mathcal{A}^{+}(t) - \mathcal{A}^{-}(t)}{2} = \frac{a\mathcal{P}(t)(1 - \delta^{2})}{1 - [\delta a \mathcal{P}(t)]^{2}},$$
(3.2.13)

where the initial asymmetries corresponding to the two helicities are equal in absolute magnitude, but different in sign: $a_+ = -a_-$. The reduced dependence on α is more clearly seen in the limit where $\alpha \to 1$ (i.e., $\delta \to 0$):

$$\mathcal{A}(t) = a\mathcal{P}(t) + \left(1 - [a\mathcal{P}(t)]^2\right)\delta + \left([a\mathcal{P}(t)]^3 - a\mathcal{P}(t)\right)\delta^2 + \dots \quad (3.2.14)$$

$$\Delta \mathcal{A}(t) = a\mathcal{P}(t) \qquad \qquad + \Big([a\mathcal{P}(t)]^3 - a\mathcal{P}(t) \Big) \delta^2 + \dots \quad (3.2.15)$$

The 4-counter asymmetry

The dependence on α may be completely eliminated by noting that if the spins are pointed at detector F in the (+) helicity state, then in the (-) state they are pointed at detector B. Therefore, in the scenario of ideal and identical detectors, $\mathcal{F}^{\pm} = \mathcal{B}^{\mp}$. This observation serves as the justification for taking the geometric means of these pairings to form a 4-counter asymmetry,

$$\mathcal{A}_4(t) = \frac{\sqrt{\mathcal{F}^+ \mathcal{B}^-} - \sqrt{\mathcal{F}^- \mathcal{B}^+}}{\sqrt{\mathcal{F}^+ \mathcal{B}^-} + \sqrt{\mathcal{F}^- \mathcal{B}^+}}, \qquad (3.2.16)$$

which is often written $as^{189,190}$

$$\mathcal{A}_4(t) = \frac{r-1}{r+1}, \text{ where } r = \sqrt{\frac{\mathcal{F}^+(t)\mathcal{B}^-(t)}{\mathcal{F}^-(t)\mathcal{B}^+(t)}}. \tag{3.2.17}$$

To show the advantage of this formulation we see that the terms

$$\begin{split} \sqrt{\mathcal{F}^{+}\mathcal{B}^{-}} &= \sqrt{R_{F}R_{B}}\tau \Big(1 - \exp(-t/\tau)\Big) \Big(1 + a\mathcal{P}(t)\Big),\\ \sqrt{\mathcal{F}^{-}\mathcal{B}^{+}} &= \sqrt{R_{F}R_{B}}\tau \Big(1 - \exp(-t/\tau)\Big) \Big(1 - a\mathcal{P}(t)\Big) \end{split} \tag{3.2.18}$$

share the factor $\sqrt{R_F R_B}$ which easily cancels in Equation 3.2.16, eliminating any dependence on the detection rate. The 4-counter asymmetry is also proportional to the polarization, with the same scaling factor as Equation 3.2.10.

The effect of β

We now consider the case where the asymmetry proportionality constants $(a_F \text{ and } a_B \text{ in Equations } 3.2.8 \text{ and } 3.2.9)$ associated with the two detectors also differ, that is:

$$\beta \equiv \frac{a_F}{a_B} \neq 1. \tag{3.2.19}$$

As shown in Equations 3.2.8 and 3.2.9, these proportionality constants also affect the detector count rate when there is nuclear polarization. On the other hand, R_F and R_B are the detector rates without nuclear polarization and are proportional to the effective solid angle of each detector. It may be noted that a_F and a_B are also affected by solid angle but are not directly proportional as in the case of R_F and R_B . With very similar algebra as before, the $\beta \neq 0$ equivalent of Equation 3.2.13 is

$$\begin{split} \Delta \mathcal{A}(t) &= \frac{1}{2} \left\{ \frac{\frac{\alpha - 1}{\alpha + 1} + \delta_{+} a_{B} \mathcal{P}(t)}{1 + \delta_{-} a_{B} \mathcal{P}(t)} - \frac{\frac{\alpha - 1}{\alpha + 1} - \delta_{+} a_{B} \mathcal{P}(t)}{1 - \delta_{-} a_{B} \mathcal{P}(t)} \right\} \\ &= \delta_{+} a_{B} \mathcal{P}(t) \frac{1 - \frac{\delta_{-}}{\delta_{+}} \left(\frac{\alpha - 1}{\alpha + 1}\right)}{1 - \left(\delta_{-} a_{B} \mathcal{P}(t)\right)^{2}} \end{split}$$
(3.2.20)

where $\delta_{\pm} \equiv \frac{\alpha \beta \pm 1}{\alpha + 1}$. In the limit where $\beta \to 1$ and $\alpha \to 1$, to second order in β and α ,

$$\begin{split} \Delta \mathcal{A}(t) &\approx \ \frac{1}{2} \Big[(\beta+1) - (\alpha-1)^2 \Big] a_B \mathcal{P}(t) + \\ &\qquad \frac{1}{2} \Big[(\beta-1) + (\alpha-1) \Big]^2 \Big(a_B \mathcal{P}(t) \Big)^3. \end{split} \tag{3.2.21}$$

In contrast, if this generalization of β is accounted for in Equation 3.2.16, we find that the dependence on α again is exactly cancelled, however the dependence on β remains. To second order in β , as $\beta \to 1$,

$$\mathcal{A}_4(t) \approx \left(\frac{\beta+1}{2}\right) a_B \mathcal{P}(t) + \left(\frac{\beta-1}{2}\right)^2 \frac{[a_B \mathcal{P}(t)]^3}{[a_B \mathcal{P}(t)]^2 - 1}.$$
 (3.2.22)



Figure 3.2.5: Spin-lattice relaxation data with stretched exponential fit, binned by a factor of 5 for clarity.

With respect to $a_B \mathcal{P}(t)$, in comparison to Equation 3.2.21, Equation 3.2.22 has the same first order dependence on β , if in the former $\alpha = 1$.

3.2.4 Measuring SLR

SLR measurements use a pulsed beam. The transient decay of spin-polarization is monitored both during and following pulses of duration Δ (in this work four seconds), where the polarization approaches a steady-state value during the pulse, and relaxes to ~0 afterwards. The effect is a pronounced kink at the end of the beam pulse, characteristic of β -NMR SLR data. The SLR in an aPS thin film is shown in Figure 3.2.5. No RF magnetic field is required for these SLR measurements, as the probe nuclei are implanted in a spin state already far from thermal equilibrium. This type of relaxation measurement has no spectral resolution, unlike conventional NMR, and reflects the spin relaxation of all the ⁸Li.

Modelling this curve must account for the implantation process, which results in a piecewise-defined function. Following the derivation of Equation 3.2.5, the number of ions in the sample which survive until time t, is given by

$$N(t) = \begin{cases} R_0 \tau [1 - \exp(-t/\tau)], & 0 < t \le \Delta \\ R_0 \tau \exp(-t/\tau) [\exp(\Delta/\tau) - 1], & \Delta < t. \end{cases}$$
(3.2.23)

The polarization during and after the pulse is then

$$\mathcal{P}(t) = \begin{cases} \frac{R_0}{N(t)} \int_0^t \exp[-(t-t')/\tau] p(t-t') dt', & 0 < t \le \Delta; \\ \frac{R_0}{N(t)} \int_0^\Delta \exp[-(t-t')/\tau] p(t-t') dt', & \Delta < t. \end{cases}$$
(3.2.24)

If the relaxation is exponential, we set

$$p(t,t') = p_0 \exp[-(t-t')/T_1], \qquad (3.2.25)$$

where the characteristic decay rate $1/T_1$ is equivalent to the SLR rate discussed in Section 3.1.3, and p_0 is a constant amplitude. In this case we can find a closed form solution for the polarization. Setting $1/\tau' = 1/\tau + 1/T_1$, the polarization is

$$\mathcal{P}(t) = \begin{cases} p_0\left(\frac{\tau'}{\tau}\right) \left(\frac{1 - \exp(-t/\tau')}{1 - \exp(-t/\tau)}\right), & 0 < t \le \Delta; \\ p_0\left(\frac{\tau'}{\tau}\right) \left(\frac{\exp(-t/T_1)[\exp(\Delta/\tau') - 1]}{\exp(\Delta/\tau) - 1}\right), & \Delta < t. \end{cases}$$
(3.2.26)

For stretched exponential relaxation,

$$p(t-t') = p_0 \exp\left[-\left(\frac{t-t'}{T_1}\right)^{\beta}\right], \qquad (3.2.27)$$

the integrals must be computed numerically. This is best accomplished with the double exponential integration method, which is robust when the derivative diverges near t = 0, a region where other common integrators fail.¹⁹¹ The fit in Figure 3.2.5 is the result of the numerical integration of Equation 3.2.24, plugging in Equation 3.2.27. Typical settings for pulsed measurements can be found in Table 3.2.3. Table 3.2.3: Typical settings for pulsed SLR measurements. A dwell time is the binning duration in the histogram shown in Figure 3.2.5. Some dwell times are taken prior to beam on as a measure of the background. These are later discarded in the analysis and are not shown. Some time is spent waiting for the laser polarization to stabilize before taking data, this is the helicity flip sleep time.

Dwell time (bin size)	$10\mathrm{ms}$
Number of Prebeam dwell times	50
Number of Beam On dwell times	400
Number of Beam Off dwell times	1200
Helicity Flip Sleep	$3000\mathrm{ms}$

3.2.5 Measuring resonances

With a continuous beam, the asymmetry will be in a state of dynamic equilibrium, similar to the asymmetry near t = 4 s in Figure 3.2.5. If a transverse RF \mathbf{B}_1 is introduced, it will cause any on-resonance probes to be rapidly nutated, destroying the spin polarization of this subpopulation. When the RF is slowly stepped through a range of frequencies about the Larmor frequency, a distribution such as the one in Figure 3.2.6 is observed.



Figure 3.2.6: Resonance data in MgO, our reference material, with two-Lorentzian fit (Equation 3.2.28) sharing the peak value.
For ⁸Li, the integration time at any given RF is typically 1 s, and B_1 is on the order of a Gauss. If the integration time is too long, the measurement will become extremely sensitive to fluctuations in the baseline. These fluctuations are often slow, occurring on the timescale of minutes to hours, and may be attributed to a myriad of factors such as beam drift due to changes to the proton target or temperature. If the integration time is too short, a significant "bleed-over" effect will be introduced wherein a significant portion of the probe population will have been depolarized by the prior RF step during the scan of the frequency range. To help reduce this distortion, the RF is swept across the specified frequency range in both directions (increasing and decreasing frequency), such that the effect from the previous frequency step is averaged and reduced. The result is a distribution which may see some modification to the linewidth, but not the peak location.

Resonance lines are typically fit well with the superposition of Lorentzian functions:

$$\mathcal{P}(\nu) = p_0 \frac{\frac{1}{4}\sigma^2}{(\nu - \bar{\nu})^2 + \frac{1}{4}\sigma^2},$$
(3.2.28)

where $\bar{\nu}$ is the mean, σ is the full width at half maximum (FWHM), and p_0 is the amplitude; noting that Equation 3.2.28 is normalized to have unity height when $p_0 = 1$. When normalized to have unity area, $p_0 = 2/(\pi\sigma)$.

The Larmor frequency is largely set by \mathbf{B}_0 , however, local magnetic fields and quadrupole couplings will shift the peak. Measuring these shifts can be used as a means of determining the coordination of the probe with the host material.² The line width may be affected by the dynamics. Given a local field which fluctuates randomly with some average correlation time τ_c , the linewidth narrows with smaller τ_c . Figure 3.2.7 shows a Monte Carlo (MC) simulation exhibiting this motional narrowing using the theory presented in Section 3.1.2 for a local field with standard deviation $\gamma \Delta B_{\text{local}} = 6 \text{ kHz}$. Simulation details are presented in Appendix A.3.



Figure 3.2.7: MC simulations based on the classical theory of a fluctuating magnetic field (Section 3.1.2) show the effect of motional narrowing. Dashed lines show the off-resonance baseline for each of the spectra. Probe decay rates match those of ⁸Li.

Chapter 4

Molecular Dynamics in Polystyrene Thin Films

4.1 Introduction

In this Chapter we employ molecular dynamics (MD) simulations to study the dynamics of atactic polystyrene (aPS) thin films. Polymers like aPS have a high degree of mechanical and chemical tunability, making them extremely versatile materials. Upon cooling, many vitrify rather than crystallizing. Long before a crystal forms, molecular motion becomes frozen and dynamical timescales quickly surpass those accessible in experiments. Boundary conditions have a strong impact on these relaxation dynamics in glassy polymers.¹⁹ In freestanding films with a vacuum interface, the glass transition temperature, $T_{\rm g}$, is reduced as the thickness decreases.^{58,192} Moreover, the layer-resolved segmental (relaxation) dynamics accelerates substantially as the depth z below the free interface decreases.^{1,16,31,56} Recent evidence from MD¹⁹³ and theoretical arguments¹³ suggest that the molecular relaxation time $\tau_c(z, T)$ near the surface is coupled to the bulk relaxation time $\tau_{\rm bulk}(T)$ via a power-law relation

$$\tau_c(z,T) \sim \tau_{\text{bulk}}(T)^{f(z)},\tag{4.1.1}$$

with a "coupling exponent" $f(z) \in [0, 1]$ capturing the dependence on depth z. The origin of this power-law form, as explained below, lies in the exponential dependence of the relaxation time on an energetic barrier for activated motion.

Several theoretical pictures have been proposed that arrive at the same functional form as Equation 4.1.1, but differ in their interpretation of the coupling exponent. The elastically collective nonlinear Langevin equation (ECNLE) theory of Schweizer and co-workers,¹⁹⁴ for instance, proposes a reduction of the activation barrier via modified local caging constraints due to loss of neighbors as well as truncation of long range elastic interactions.^{195–198} Another picture asserts that the coupling exponent reflects a temperature and distance-dependent reduction of the size of string-like cooperative mobile regions as the major driver of interfacial relaxation.²³ A recent study by Zhang et al.,¹⁹⁹ however, indicates that the length of such mobile strings varies only weakly near the interface, although the dynamical scale of this layer¹⁵ is proportional to the length of mobile strings.^{200,201} Gaps thus remain in our understanding of interfacial dynamics of glass-forming materials.

The present study presents MD simulations of freestanding aPS films at the united-atom level. It builds on previous results of Zhou and Milner,⁷¹ who computed the layer-resolved segmental relaxation times in aPS-films of up to 28 nm thickness by monitoring the angular displacement along the polymer backbone (see Figure 4.2.1). Here we focus additionally on the rotational dynamics of the phenyl side groups that reflect (slightly faster) γ -relaxation processes.¹³⁷ The phenyl ring motion is particularly important for the interpretation of β -detected nuclear magnetic resonance (β -NMR) experiments, because the ⁸Li⁺-ions are expected to be bound between such rings.^{1,202} We determine the coupling exponent that describes the dynamics at the surface, and show that its functional form is consistent with an average activation barrier that varies with depth. We also compute, as one measure of cooperativity, the dynamical four-point susceptibility $\chi_4(T, z, t)$, and find that it decreases strongly at the surface. A coupling exponent based on this parameter can therefore also describe the observed variation of relaxation times with depth.

4.2 Descriptions of interfacial dynamics

4.2.1 Distance dependent energy barrier

In polymeric glass formers, the temperature dependence of the bulk relaxation time typically exhibits thermally activated behaviour, which is well-described over some range of T by the Vogel-Fulcher-Tammann (VFT) equation, given by Equation 1.2.2. In a film, it is reasonable to expect that the barrier for activated motion, as well as the exponential prefactor, become explicitly dependent on the depth z, such that the VFT equation reads

$$\tau_c(z,T) = \tau_0(z) \exp\left[\frac{\Delta E(z)}{k_B(T-T_{\rm VFT})}\right], \eqno(4.2.1)$$

where $T_{\rm VFT}$ denotes the Vogel temperature, and the effective activation energy barrier $\Delta E(z)$ reflects an average over a distribution of local energy barriers for molecular motion. To avoid overparameterizing the model, we assume a depth-independent $T_{\rm VFT}$ and show below that such a model provides an excellent fit to the simulation data. The bulk relaxation time is $\tau_{\rm bulk}(T) = \tau_c(\infty, T)$. After dividing by $\tau_{\rm bulk}(T)$, Equation 4.2.1 can be rearranged as

$$\frac{\ln\left(\tau_c(z,T)/\tau_0(z)\right)}{\ln\left(\tau_{\text{bulk}}(T)/\tau_0\right)} = \frac{\Delta E(z)}{\Delta E_{\infty}} = f(z), \qquad (4.2.2)$$

or alternatively

$$\frac{\tau_c(T,z)}{\tau_0(z)} = \left(\frac{\tau_{\text{bulk}}(T)}{\tau_0}\right)^{f(z)}.$$
(4.2.3)

This simple heuristic derivation yields a coupling relation between bulk and surface dynamics with a temperature-independent coupling exponent as introduced by Diaz-Vela et al..¹⁹³ It can be expected to hold below an onset temperature where $\tau_{\text{bulk}}(T) \gg \tau_0 \equiv \tau_0(\infty)$ and the interfacial dynamics "decouples" from the bulk and becomes faster. At higher temperatures, however, the coupling exponent $f(z) \simeq 1$ and the interfacial dynamics is strongly coupled to the bulk. Simulations for vacuum interfaces suggest that below the onset temperature the coupling exponent is temperature-independent and has an exponential depth-dependence, $f(z)=1-\epsilon_0\exp(-z/\xi_{\Delta E})$ with $\xi_{\Delta E}$ an interfacial length scale.¹⁹³

4.2.2 ECNLE theory

In the above empirical treatment, the energy barrier factorization $\Delta E(z) = \Delta E_{\infty} f(z)$ is in some sense a consequence of the assumption of a z-independent Vogel temperature. The factorization property and the resultant (de)coupling relation can be justified with much more rigour in the microscopic ECNLE theory.^{195–198} Here, the central object is a dynamic free energy barrier $F_{\rm dyn}(T,r,z)$, where r denotes the displacement from a particle or segment from a local equilibrium position. Several physical mechanisms are included to capture the influence of an interface on this barrier: (i) loss of nearest neighbours immediately at the surface, (ii) a transfer mechanism by which the less constrained surface particles in turn provide fewer caging constraints in the layers below and (iii) a modification of collective, long ranged elastic contributions via lowering and truncation of displacement field amplitudes.¹³ Based on this physical picture, the theory is able to predict a factorization of the dynamical free energy into separate dependencies on distance and temperature/density,¹⁹⁶

$$F_{\text{total}}^{\text{film}}(T, z) \approx F_{\text{total}}^{\text{bulk}}(T) f(z).$$
 (4.2.4)

If one furthermore assumes activated dynamics for barrier crossing, $\tau_c(z,T) \sim \exp\left[F_{\text{total}}^{\text{film}}(T,z)/k_BT\right]$, a coupling relationship of the type of Equation 4.1.1 immediately follows. Moreover, as a result of mechanism (ii) mentioned above, the coupling exponent is predicted to have an exponential depth dependence with a short characteristic length of ~1.4 particle diameters. All of the temperature dependence is carried by the behaviour of the bulk material. As a result, the coupling exponent can ultimately be related to the gradient of the glass transition temperature. The theory has recently been extended beyond a description of the mean relaxation time by including barrier fluctuations via Gaussian distributions of local volume fractions.^{203,204}

These changes also extended the applicability of the theory, previously limited to the glassy regime, to the deeply supercooled liquid regime.²⁰⁴

4.2.3 Cooperative strings

An alternative approach posits that the origin of the enhanced surface relaxation is a reduction of the number of particles involved collectively in a structural relaxation event. It builds on the observation (mainly from simulations) that mobile particles in glasses organize themselves in a stringlike form such that $N^*(T)$ particles have to relax for one particle to escape from a local cage. Salez et al.²³ start from a free volume picture and write the probability for an *N*-particle relaxation process along a string in the bulk:

$$P_N(T) \sim \frac{1}{\lambda^3 \tau_{\text{onset}}} \epsilon^{N-1} (1-\epsilon) \theta(N-N^*(T)), \tag{4.2.5}$$

where τ_{onset} is an 'onset' timescale, λ an average intermolecular distance, and $\epsilon = \tau_0 / \tau_{\text{onset}} \ll 1$ is an elementary 'coherence probability'. Since particles in a cooperative string need to move in phase, one expects the probability to decrease exponentially with the string length. The total probability for relaxation,

$$P(T) = \sum_{N=N^*}^{\infty} P_N(T) \sim \frac{1}{\lambda^3 \tau_{\text{onset}}} \epsilon^{N^* - 1}, \qquad (4.2.6)$$

is dominated by the threshold string length N^* . Defining the bulk relaxation time as $\tau_{\text{bulk}}(T) \sim 1/P(T)$, one obtains

$$\frac{\tau_{\text{bulk}}(T)}{\tau_0} \sim \left(\frac{\tau_{\text{onset}}}{\tau_0}\right)^{N^*(T)}.$$
(4.2.7)

Salez et al.²³ now generalize this expression for the bulk relaxation time to free interfaces by replacing $N^*(T)$ with $N^*(z,T) = N^*(T)f(z/\xi_{\text{bulk}}(T))$ where $f(z/\xi_{\text{bulk}}(T)) \leq 1$ reflects a reduction of the length of the cooperative string near the surface. This reduction can be expected to occur over a scale set by the temperature-dependent bulk cooperative length scale $\xi_{\text{bulk}}(T)$. Interestingly, this yields a formula for the relaxation times near free interfaces that has the same form as Equation 4.2.3,

$$\frac{\tau_c(T,z)}{\tau_0} = \left(\frac{\tau_{\text{bulk}}(T)}{\tau_0}\right)^{f(z,T)},\tag{4.2.8}$$

but the coupling exponent now reads

$$f(z,T) = \frac{N^*(z,T)}{N^*(T)}$$
(4.2.9)

and depends explicitly on temperature. Moreover, τ_0 is assumed to be independent of position and just reflects a microscopic timescale. The fact that the same functional form arises in two seemingly independent derivations can be traced to the exponential dependence of the probability for relaxation on the size of the cooperative region. The model thus embodies the central tenet of the Adam-Gibbs argument, namely that the activation barrier is proportional to the number of particles in the cooperatively rearranging region. The string model of (bulk) glassy dynamics²⁰⁵ makes this explicit,

$$\tau_c(T) \propto \left[\exp(\Delta\mu/k_B T)\right]^{f(T)} \tag{4.2.10}$$

with $f(T) = L(T)/L(T_A)$, where L(T) is the length of the cooperative string and $\Delta \mu$ is the activation barrier at an onset temperature T_A . The relevance of these string-like excitations has, however, been called into question by a recent computer simulation study.²⁰⁶

4.3 Simulation methods

A united atom model of aPS, introduced previously by Vorselaars et al.,¹³⁷ was used to simulate free standing films $\sim 30 \text{ nm}$ thick. The force field parameters were faithfully reproduced from this earlier work, and a snapshot of the resulting configuration at 200 K is shown in Figure 4.2.1. The $\sim 4 \times 10^4$ atom simulation was composed of 500 polymer chains, each 10 monomer units in length. Molecular dynamics simulations were carried out using the LAMMPS package¹⁴⁵ in an NVT ensemble with a Nosé-Hoover thermostat. The equations of motion were integrated with a time step of 2 fs in a velocity-Verlet scheme. Periodic boundaries were used along both \hat{x} and \hat{y} , and



Figure 4.2.1: Snapshot of a simulated free-standing atactic polystyrene film at T = 200 K. The distance between the two surfaces is about 31 nm. Vectors connecting ortho-atoms and adjacent CH₂ united atoms on the backbone are used to measure the polymer dynamics.

reflective walls were used along \hat{z} , with final box dimensions fixed to $5.5 \times 5.5 \times 40$ nm. To prevent drift, the center of mass linear momentum was re-scaled to zero at every time step.

The film was generated by placing the polymer chains in a $40 \times 40 \times 40$ mm simulation box and equilibrating at 600 K for 5 ns, accommodating for placement overlap by limiting atomic motion to 0.1 Å for the first 10 ps. The box was then compressed to a cube of side length 5.5 nm over 10 ns. After another 5 ns, the reflective walls along \hat{z} were relaxed to their initial positions over the course of 10 ns, and an additional 5 ns was allowed to pass. The film was then cooled at 0.01 K ps⁻¹, which is a typical rate used in MD.^{71,137} The glass transition temperature $T_{\rm g}$ of the film was found to be 390(5) K using the average film density, and 404(7) K using the film height (Figure 4.3.1), where the film edge was defined by the Gibbs dividing surface as illustrated by Hudzinskyy et al..²⁵ These values are within a few degrees from those reported by Zhou and Milner⁷¹ for an aPS film also composed of 10mers of comparable thickness. From 600 K to 100 K, the film height decreased from



Figure 4.3.1: Average film density and film height (inset) as functions of temperature during cooling of the PS-film. The glass transition temperature, $T_{\rm g}$ was found by fitting the linear regions (fitted points indicated by the filled symbols). Film edges were defined by the Gibbs dividing surface.²⁵

35.7 nm to 31.0 nm, and the density increased from 0.80 g/cm^3 to 0.93 g/cm^3 .

The motion of the two local structure vectors v(t) connecting the ortho atoms in the phenyl rings (adjacent to the tethering bond between the ring and the backbone) as well as adjacent CH_2 united atoms on the backbone were considered as indicators of polymer dynamics, as depicted in Figure 4.2.1. The former vector was chosen to measure the torsional motion of the rings, and the ortho atoms were used in the place of the meta atoms to reduce the effect of non-tortional motion on the correlation function. The latter vector was chosen to exclude connections with the phenyl rings in order to decouple, as much as possible, rings and backbone motion. The autocorrelation function (ACF) of the second Legendre polynomial of the normalized vectors,

$$C_2(t) = \frac{3}{2} \left\langle [\hat{\boldsymbol{v}}(t') \cdot \hat{\boldsymbol{v}}(t'-t)]^2 \right\rangle_{t'} - \frac{1}{2}, \qquad (2.2.5)$$

was used to determine the relaxation time, $\tau_c(z,T)$, defined to be the time it takes for the average ACF to decay by a factor of 1/e. The ACF was averaged by grouping each vector into 1 nm thick parallel laminae by distance



Figure 4.4.1: Distance from surface (left) and temperature (right) dependence of the time of the autocorrelation function given by Equation 2.2.5 to decay to 1/e, corresponding to the rotational motion of the polystyrene phenyl rings. Also shown are VFT fits to Equation 4.2.1 with a global VFT-temperature $T_{\rm VFT} = 292(1)$ K. The inset shows that the preexponential factor and activation barrier follow the Meyer-Neldel rule.

to the nearest free surface.

4.4 Results

The left plots of Figures 4.4.1 and 4.4.2 present the layer-resolved rotational relaxation time of the phenyl rings and backbones for temperatures $400 \text{ K} \leq T \leq 500 \text{ K}$. The data represents an average over three independent trajectories of 0.5 µs to 1 µs duration. The relaxation times decrease significantly in layers less than 5 nm from the free surface, converging quickly with increasing depth to a temperature-dependent bulk value. The depth dependence was fit with the phenomenological form $\log \tau_c = c_0 + c_1 \text{erf}(z/z_0)$, as in Zhou and Milner,⁷¹ but with shared z_0 across all temperatures, yielding dynamical length scales of $z_0 = 3.23(2) \text{ nm}$ and $z_0 = 2.85(4) \text{ nm}$ for the rings and backbones, respectively. In our model, a freely varying z_0 produced length scales which did not vary appreciably in the temperature range studied. The length scales are comparable to that reported by Zhou and Milner⁷¹ for the interfacial backbone relaxation and those found in bead-spring model simulations.^{11,15,16,201}



Figure 4.4.2: Distance from surface (left) and temperature (right) dependence of the time of the autocorrelation function given by Equation 2.2.5 to decay to 1/e, corresponding to the relaxation of the polystyrene backbone segments. Also shown are VFT fits to Equation 4.2.1 with a global VFT-temperature $T_{\rm VFT} = 294(4)$ K. The inset shows that the preexponential factor and activation barrier follow the Meyer-Neldel rule.

The right panels replot the same data in an Arrhenius representation and also show VFT fits, where the activation barrier and pre-exponential factors were allowed to vary with z but a single value of the VFT temperature $T_{\rm VFT}$ was used over the entire data set. With a depth-dependent $T_{\rm VFT}$, the model was overparametrized, resulting in artificial variability of the fit parameters. The VFT fits were performed only for $T \geq 410$ K, since the behaviour has been observed to cross over to a purely Arrhenius temperature dependence at temperatures near and below $T_{\rm g}$.²⁰⁷ In the supercooled regime, the data follows the VFT form reasonably well. The inset shows that the logarithm of the pre-exponential timescale $\tau_0(z)$ is proportional to the activation barrier $\Delta E(z)$, a behaviour often referred to as the Meyer-Neldel rule.^{208,209} This can be interpreted as an entropy-enthalpy compensation effect and has also been observed in bead-spring models.²⁰⁰ Results for the backbone motion mirror the behaviour of the rings with longer relaxation times.

In order to test the validity of the explanations for near-surface relaxation,



Figure 4.4.3: Coupling exponent given by the logarithmic ratio of relaxation times $\log(\tau_c(T, z)/\tau_0(z))/\log(\tau_{\text{bulk}}(T)/\tau_0)$ (coloured, open) and ratio of activation barriers $\Delta E(z)/\Delta E_{\infty}$ (black, filled) from the VFT fits found in Figures 4.4.1 and 4.4.2 for rings (left) and backbones (right). The insets show the relaxation times vs bulk relaxation time. The dashed line indicates an exponential fit, as calculated from the relaxation times.

we plot in Figure 4.4.3 our data for aPS films in the form

$$\frac{\ln\left(\tau_c(T,z)/\tau_0(z)\right)}{\ln\left(\tau_{\rm bulk}(T)/\tau_0\right)} \ {\rm vs} \ z$$

as suggested by Equation 4.2.2, where the value of τ_{bulk} is obtained from the depth-independent film center. This representation collapses curves for different T onto a master curve and thus reveals a temperature independent coupling exponent f(z). A fit to an exponential form suggests a short interfacial length scale $\xi \simeq 1.5$ nm. As a reference, the average distance between two CH₂-groups along the backbone is 0.27 nm. The insets show $\tau_c(z,T)/\tau_0(z)$ vs. $\tau_{\text{bulk}}(T)$ in double-logarithmic form, so that the slope of the curves is the coupling exponent. Obtaining straight lines, we conclude that f(z) depends only on z and not on T. Our results are thus consistent with the proposal of Diaz-Vela et al.¹⁹³ and the predictions of ECNLE theory^{195,196} that the activation barrier at distance z factorizes into distinct temperature-



Figure 4.4.4: Coupling exponent given by the logarithmic ratio of relaxation times $\log(\tau_c(T, z)/\tau_0)/\log(\tau_{\text{bulk}}(T)/\tau_0)$ for rings (left) and backbones (right) where the normalization τ_0 is taken as the bulk value and independent of z. Fits are to the exponential form as in Figure 4.4.3, with the characteristic length scale ξ fixed to the same as the corresponding fits in Figure 4.4.3. The inset shows the temperature dependence of the coupling exponent at z = 0.

and depth-dependent parts,

$$\Delta E(z) = f(z)\Delta E_{\infty}, \qquad (4.4.1)$$

As a further check of this relation, we can compare directly with the z-dependence of the activation barrier extracted from the VFT fits. The ratio $\Delta E(z)/\Delta E_{\infty}$ agrees strongly with the relaxation time data, and thus the form proposed in Equation 4.2.3, as shown in Figure 4.4.3.

The above results clearly support the picture of a depth-dependent activation barrier driving the interfacial relaxation dynamics.¹³ In Figure 4.4.4 we examine the same data using a z-independent microscopic timescale τ_0 , which is assumed in the cooperative strings model and also in ECNLE theory. In this representation, the curves do not fully collapse but include a residual temperature dependence that is captured by exponential fits using the temperature independent length scales found in Figure 4.4.3 (1.54 nm or 1.48 nm), but allowing for temperature-dependent prefactors. As a result, the temperature dependence is carried by a variation of the coupling exponent 0.6 < f(0) < 0.9 at the surface (see insets). This result is at variance with

the cooperative string model that anticipates complete decoupling at the interface,²³ i.e. $f(0) \sim 0$. Our simulations cover the regime of weak to moderate supercooling, in which the assumed scaling form for the coupling exponent $f(z,T) = f(z/\xi_{\text{bulk}}(T))$ might not yet apply. The absence of complete decoupling at the surface is however entirely compatible with ECNLE theory.¹³

In order to probe the role of cooperativity more directly, we need a measure of the scale of dynamical heterogeneity. One possibility is to consider the layer-resolved variance of the autocorrelation function or four-point dynamical susceptibility^{5,210}

$$\chi_4(T, z, t) = N_{\upsilon}(z) N_{\tau_c}(t) \Big[\left\langle \bar{C}_2(z, t)^2 \right\rangle - \left\langle \bar{C}_2(z, t) \right\rangle^2 \Big], \tag{4.4.2}$$

where C_2 is the ACF of an individual ring (backbone) vector as given by Equation 2.2.5, the overbar denotes an average over $N_{\boldsymbol{v}}(z)$ ring (backbone) vectors in a given layer, $\langle \rangle$ an average over 100 simulation instances and $N_{\tau}(t)$ the number of time slices used in the calculation of the ACF for a given lag time t. $\chi_4(T,z,t)$ measures the fluctuations of the total molecular mobility as given by the backbone or phenyl ring dynamics. It can also be viewed as a (spatial) integral over a four-point correlation function that measures how the dynamics at locations r_1 and r_2 over a time interval $t=t_1-t_2$ are spatially correlated over a distance ${\pmb r}={\pmb r}_1-{\pmb r}_2.$ This function is shown for layers at different depths in the top panel of Figure 4.4.5 at temperature $T = 450 \,\mathrm{K}$ as a function of time. All curves at different layers z exhibit maxima at times that coincide with the layer-resolved relaxation times. The peak height can be interpreted as a correlation volume and thus proportional to the number of particles involved in a cooperative relaxation event. The middle panel plots this peak height $\chi_4^{\max}(T)$ normalized by the bulk value in the center of the film vs distance from the surface. While the data at 500 K does not exhibit any trend, we clearly see a reduction of cooperativity at the lower temperatures 475 K and 450 K.

Reduced dynamical heterogeneity at the interface could for instance arise from a reduced collective barrier for activated processes as envisioned by ECNLE theory.^{203,204} It could also accompany smaller cooperatively rearranging regions, i.e. shorter strings. A comparison with the cooperative string model is facilitated by rescaling z by the bulk cooperativity length $\xi_{\text{bulk}}(T)$, see Equation 4.2.7. In principle, this length scale could be extracted from the spatial decay of a four-point dynamical correlation function.²¹⁰ Here, we use instead a simple estimate $\xi_{\text{bulk}}(T) \propto [\chi_4^{\max}(T)]^{1/3}$, which is supported by simulations of a Lennard-Jones glass former.²¹¹ This may also help eliminate the known system size effects on χ_4 which, given the density profile, may account for changes in the surface-most layer only.⁷⁴ The bottom panel of Figure 4.4.5 shows that plotting the normalized $\chi_4^{\text{max}}(T)$ data against $z/[\chi_4^{\max}(T)]^{1/3}$ leads to a reasonable collapse of our (limited) data set. The form of this master curve is overall consistent with the behaviour of the coupling exponent f(z) computed in Figure 4.4.3 from the relaxation times (solid lines). This is reasonable given recent experimental correlations between the length scales associated with the dynamic heterogeneity and interfacial effects in nanocomposites.^{212,213}



Figure 4.4.5: (Top) Dynamical susceptibility $\chi_4(T = 450 \text{ K}, z, t)$ for the phenyl rings, at various depths from the free surface. (Center) Maximum of $\chi_4(T, z, t)$ vs. distance z from the free surface normalized by χ_4^{bulk} , which is computed as an average of the 5 layers furthest away from the surface. (Bottom) For comparison with the string model, we re-scale by $\chi_4^{1/3}(T)$, an estimate for $\xi_{\text{bulk}}(T)$. The surface point of the 500 K data (~1.8) was omitted for clarity. Black lines are produced from the fits in Figure 4.4.3.

4.5 Conclusions

The relaxation times of backbone segments and phenyl rings at the surface of a freestanding aPS film were examined with molecular dynamics simulations. The times τ_c are coupled to the bulk relaxation times via a power law relation with a temperature independent coupling exponent. These results extend previous bead-spring level simulations to a more detailed united atom model. The coupling exponent agrees well with the ratio of energy barriers extracted from VFT-fits, giving strong support to the notion that changes in the interfacial dynamics should be understood from interfacial changes in the activation free energy barrier. Moreover, the preexponential factors obey a Meyer-Neldel rule and thus exhibit considerable variation with depth below the free surface.

The near-exponential variation of the coupling exponent with distance, the short and temperature independent characteristic length scale of ~ 1.5 nm and the absence of complete decoupling at the surface are all observations entirely consistent with the predictions of ECNLE theory. Our calculations also reveal a significant decrease of the dynamical four-point susceptibility near the surface, but cannot pinpoint the mechanism that is ultimately responsible for this behaviour. One measure which may be useful in further understanding this phenomenon is the four-point correlation function. Calculating the characteristic length scale associated with dynamical heterogeneity arising from specific aspects of the dynamics (for example the torsional ring motion, separate from the backbone motion) may reveal in greater detail how the heterogeneity is affected by the surface.

If one accepts this measure of dynamical heterogeneity as a good characterization of cooperative motion, one can reconcile the coupling exponent with a normalized $\chi_4^{\max}(z,T)$ ratio. This does not prove, however, that varying string size controls the changes in relaxation times. Our results can be compared to a recent simulation study of the length L of mobile strings in supported bead-spring polymer films.¹⁹⁹ This work did not find any strong variation of L across the film except very close to the free surface, and concluded that collective motion does not vary spatially in any strong manner. It must be noted, however, that the characteristic string time that maximizes the dynamical string length is shorter than the alpha-relaxation time that marks the peak of $\chi_4(t,T)$. For this reason, the $\chi_4^{\max}(z,T)$ parameter is more sensitive to slow particles as explained by Starr et al..²¹⁴ Future work could clarify the relationship between different measures of cooperativity.

Chapter 5

High-Temperature Spectrometer Operation

5.1 Introduction

One of the major challenges in comparing molecular dynamics (MD) simulations to experiments is the timescales accessible by each method. Processes responsible for the glass transition occur on the order of seconds, well past the upper limit of chemically realistic simulations, which are typically no more than a few microseconds. Fortunately, the Larmor frequency dictates the relevant timescale for nuclear magnetic resonance (NMR) measurements, which may be chosen such that the measured processes are observable in simulation. This makes NMR a prime candidate for direct comparison with simulation.

Such a comparison was made by He et al.¹⁴⁸ in 2004, using a number of fully deuterated atactic polystyrene (aPS) samples, two of which were labelled d₈PS-2 and d₈PS-11. In this notation, d₈ denotes the number of H atoms replaced by ²H (i.e., all of them), and the numerical suffix denotes the molecular weight: $M_n = 2.1 \text{ kg/mol}$ and 10.9 kg/mol respectively. The comparison was made by converting the simulated correlation times to the ²H NMR spin-lattice relaxation (SLR) rate through the use of Equation 3.1.23 (see Equation A.1.7 for the I = 1 constants needed for ²H).



Figure 5.1.1: A comparison of the MD simulation data presented in Chapter 4 to the NMR data measured by He et al..¹⁴⁸ Symbol shape differentiates between field magnitude (labelled by Larmor frequency), and the inset shows the sample with the smaller molecular weight. The simulation data was averaged over depths 10 nm and larger. Small translations in T_1 and temperature were needed (see Appendix B.1). In all cases, the agreement is quite good.

In Chapter 4, we presented a series of depth-resolved MD simulations which may be converted to an NMR T_1 using the same methods implemented by He et al..¹⁴⁸ Using our simulated spectral density and the known coupling constants for ²H,¹⁴⁸ we are able to compare the two methods and validate the simulations. The comparison was made after the simulation data was averaged over $z \ge 10$ nm and small translations were made in both temperature and T_1 (see Appendix B.1 for details) to correct for the differences between simulation and experiment. As shown in Figure 5.1.1, we achieve an extraordinarily good agreement between the simulation and ²H SLR. This confirms that the ²H NMR and the simulations converge on a consistent picture of the relevant fluctuations.

One advantage of implanted-ion β -detected nuclear magnetic resonance (β -NMR) over its conventional counterpart is the ability to conduct depthresolved measurements. This has been used already to characterize the free surface effect in supported aPS films.^{1,31} However, because the Li ions are nonnative, there is some uncertainty as to how they couple to the polymer, and which dynamics are measured. In contrast, ²H NMR is selectively sensitive to the C–²H bond reorientation, and partial deuteration can be used to identify the dynamics of particular structures with certainty. Furthermore, it is not known how well the relaxation of the β -NMR probes reflect the molecular dynamics of the polymer. Agreement with MD simulations would support the conjecture that the ⁸Li SLR is a measure of the intrinsic molecular dynamics, and would help identify the nature of the dynamics measured.^{1,31}

The translation from NMR T_1 to microscopic τ_c for the I = 2 ⁸Li may be done in a similar manner as the I = 1 ²H, as shown in Figure 3.1.4. Unfortunately, as no measurement of the quadrupole coupling has been made, we estimate it by comparison to the correlation times in other measurements in aPS, as described in McKenzie et al..³¹ This introduces a significant source of systematic uncertainty to the conversion. The comparison is also complicated by the fact that as the beam energy is increased to implant deeper in the material, the corresponding width of the stopping distribution also increases (Figure 3.2.2). To account for this, the fits to the depth-resolved simulation results (Figure 4.4.1a) were weighted by the distribution of implantation depths, as calculated by the SRIM Monte Carlo (MC) program.¹⁷⁷ Figure 5.1.2 shows the results of these treatments on the measurements, detailed in Appendix B.2.

The comparison in this case is exceedingly difficult. Most obviously, there is a large separation in temperature such that one method is measuring the glass phase and the other the melt. The β -NMR spectrometer was not capable of reaching temperatures above 317 K, well below the $T_{\rm g}$ of aPS. This upper temperature bound also introduced a severe limitation on how well the quadrupolar coupling could be determined, as the Bloembergen-Purcell-Pound (BPP) peak has yet to be observed. Changes to this coupling constant would result in a global vertical shift of the β -NMR measurements, and the high degree of uncertainty in this value would allow for the correlation times to lengthen by up to order of magnitude in size. In contrast, MD simulations are extremely limited below $T_{\rm g}$, as relaxation times quickly grow immeasurably large. Given that continuous particle trajectories are needed, the timescale problem in simulation is quite fundamental.²¹⁵ In contrast, the



Figure 5.1.2: A comparison of β -NMR and MD simulation data. The measured β -NMR T_1 values have been converted to a microscopic τ_c using the method outlined in McKenzie et al..³¹ The simulated τ_c have been weighted by the β -NMR implantation profiles to account for distribution width increasing with implantation energy. The depths indicated are the mean implantation depths. The inset shows the original unweighted simulation results, corresponding to evenly distributed 1 nm thick layers.

limitation in β -NMR is one of implementation.

Extending the upper temperature bound would expand the scope of the overall β -NMR research program at TRIUMF. Radiation damage at high temperature is more apt to thermally heal. The result would be narrower lines and more certainty about the ⁸Li stopping site. It would also enable ⁸Li to be used in characterizing structural and magnetic phase transitions above room temperature. The β -NMR study of ⁸Li diffusion, which is of interest in several materials, ^{161,162,216} would also benefit from an extended temperature range, permitting the study of materials where the interstitial Li becomes mobile not far above 300 K. For our purposes, measuring within the temperature range of the MD simulations would allow for a direct comparison, similar to that of the ²H NMR.¹⁴⁸ An observation of the BPP peak, which occurs above room temperature, would also provide a reliable estimate of the magnitude of the quadrupole coupling. It is also of interest to directly observe the effects of the glass transition on the depth dependence dynamics

near the free surface interface.

While temperatures up to 500 K have always been achievable by the β -NMR cryostat, a number of modifications and components specific to β -NMR limit the temperature range of the spectrometer. The design challenge of this upgrade was to extend the upper temperature range while maintaining performance at low temperature (in the vicinity of 3.5 K), subject to the highly restrictive pressure and space constraints imposed by the spectrometer. The spectrometer is open to a ultra-high vacuum (UHV) beam line, which severely limits which materials may be used and the design of components. High temperatures are also adversarial to operation in UHV, as the vapour pressure of heated material grows in an activated manner. This is the means by which UHV chambers typically remove water and other contaminants prior to operation. The cryostat also imposes significant spatial constraints on design. The prior construction is housed within a heat shield with millimetres of tolerance for the replacement with larger components. In this Chapter, we detail the changes which were needed to extend the temperature range of the TRIUMF β -NMR spectrometer, and the resulting spectrometer performance.

5.2 Spectrometer upgrade details

5.2.1 Detailed spectrometer description

The β -NMR sample position is located at the end of the coldfinger cryostat (Oxford Instruments) shown in Figure 5.2.1. The cryostat is encased in a gold-plated copper heat shield (removed in the figure), is rated for operation from 2 K to 500 K, and is limited in size by the magnet bore. The heat shield is held concentrically about the cryostat by a Teflon spacer (item 6 of Figure 5.2.1). Three 50 Ω semi-rigid spline dielectric coaxial cables run the length of the cryostat to the sample position. Two of the cables (item 1) supply power to the split Helmholtz coil which provides the radio frequency (RF) magnetic field **B**₁. The third cable (item 2) is connected to a pickup antenna which measures this field. These cables make a 90° bend in order to enter the sample block housing these components (item 3). A pair of

symmetrically positioned GaAlAs thermometers (Lakeshore) measure the temperature of the copper sample block. Small teflon pieces, pinned under copper plates (item 4), are used to hold the thermometers in place. The sample is assumed to be in thermal equilibrium with this structure, and great care is taken to ensure that thermal contact is well established between the needed components. The entire apparatus is pumped down to UHV conditions.

The environment near the sample location is shown in Figure 5.2.2, with the front covering removed. Threading into a copper mounting block at the top (item 1 of Figure 5.2.2), the sample holder is positioned such that the sample hangs within the split Helmholtz coil facing the beam (item 2 marks the sample position). The coil itself is composed of a copper wrapping (item 3) under tension about a Sharpal ceramic core. The core is held in place by a set of anodized Al clamps, and the characteristic impedance of the coil can be adjusted by varying the capacitance through a set of adjustable Al plates (item 6). The antenna is visible below the coil (item 5).

The forward detector is housed inside the re-entrant tube, a steel sleeve which sits within the body of the cryostat, isolating the detector from the UHV. The end of the re-entrant tube has a 25.4 µm thick stainless steel "window" to hold the vacuum and let the high-energy electrons emitted from the implanted probes reach the detector. The forward detector is composed of a plastic scintillator on the end of a light guide leading to a photo multiplier tube (PMT) well outside of the large static magnetic field. The scintillator and re-entrant tube window both sit $\sim 5 \,\mathrm{cm}$ downstream from the sample location.

With the goal of connecting the data from the MD simulations to those from the β -NMR spectrometer, the spectrometer was modified for hightemperature operation. The components which were modified or substituted include the grease used on the sample holder, the components near the sample location which contained Teflon, and the plastic forward detector. We now detail the changes made, and how the operation of the spectrometer was impacted.



Figure 5.2.1: Photo of β -NMR coldfinger cryostat prior to modification. Components: (1) Coaxial cable for the RF Helmholtz coil, connected by stainless steel SMA connectors in the center of the photo. (2) Coaxial cable from the readback antenna. (3) Weld for the 90° bend of the cable towards the coil. (4) Thermometer beneath a protective copper plate. (5) Threaded sample holder mounting block. (6) White Teflon concentricity spacer. (7) Heat shield (partially removed). Components 1, 3, and 4 are symmetrically mirrored on the far side. The beam enters from the left.



Figure 5.2.2: End-on view of the β -NMR spectrometer prior to modification. Components: (1) Threaded sample mounting block (sample inserted through here, hanging downwards). (2) Sample location upon mounting. (3) Split Helmholtz coil (copper wrapping about a Sharpal ceramic core). (4) Symmetric pins from the coaxial cables supplying power to the Helmholtz coil. (5) Aluminum plates for adjusting the capacitance of the coil. (6) \mathbf{B}_1 readback antenna. (7) Sample thermometers mounting locations. The beam direction is into the page.

5.2.2 Lubricant

The copper sample holder is threaded into a copper mounting block, shown at the top of Figure 5.2.2 (item 1), to maintain a good thermal connection between the sample holder and the cryostat. UHV-compatible L grease (Apiezon) was used to prevent the cold-welding of the two pieces, however L grease is intended for operation near 300 K and migrates at much higher temperatures. Eventually it will decompose and contribute to the total outgassing near the sample position. A tungsten disulphide (WS_2) powder (Lower Friction), shown applied to these threaded parts in Figure 5.2.3, was chosen to be its replacement on the recommendation of R. Sutarto at the Canadian Light Source, where it is used in a UHV X-ray scattering spectrometer. As a layered transition metal dichalcogenide, the triatomic layers are only weakly bound to one another by van der Waals interactions, analogous to the monatomic graphene layers in graphite (another well-known dry lubricant). As a result, its coefficient of friction is extremely low, and responds linearly with temperature; dropping from 0.02 at 303 K to the ultra-low friction regime of 0.005 at 143 K.²¹⁷ When applied to stainless steel, WS_2 was found by NASA to have a wear life of 50,000 passes in UHV. 218 For the purposes of β -NMR, the powder is best applied dry through the application of friction. Since frequent reapplication is unnecessary, the use of WS_2 lubricant does not affect operation in any way.

5.2.3 Teflon components

Teflon blocks were used as a concentricity spacer, as mounting blocks for the sample thermometers, and as spacers in the spline dielectric coaxial cables. At elevated temperatures, Teflon may soften, resulting in deformation. This is particularly a concern for the coaxial cable, as a strict 50Ω impedance depends on the concentricity of the center conductor. Both the spacer and the mounting blocks were replaced with creep-resistant Vespel (DuPont) high temperature polyimide equivalents, as shown in Figure 5.2.4. Vespel has a maximum service temperature of about 561 K. The thermometer mounts were also redesigned to ease the installation of the thermometers and reduce



Figure 5.2.3: The WS_2 coating applied to the copper threaded sample holder and mounting block. The powder bonds to the metal, leaving it a matte grey colour with no visible particulate residue. The coating was applied through friction, with best results (as shown) from power tools.

the chance of damage to the fragile leads.

The old 50 Ω cable was a semi-rigid copper spline dielectric, with the center conductor held in place by Teflon spacers. The center conductor was welded to a pin which was then fed to the RF coil, as shown in Figure 5.2.4a. This rigid construction was replaced by a flexible UHV-compatible coaxial cable (Accu-Glass). The cable is Kapton-shielded with stainless steel conductors, a solid Polyether ether ketone (PEEK) dielectric, and gold-plated copper SMA connectors. The bend towards the RF coil was also redesigned to be soldered rather than welded, as shown in Figure 5.2.5. A copper pin was soldered to the center conduction of the coaxial cable, which was stripped to reveal each of the layers. The cable was then clamped by the grounding mesh to prevent tension from being applied to the solder joint, and to provide an electrical connection to ground. A PEEK dielectric was used to center the pin. Both the coaxial cable and 90° bend assembly have a characteristic impedance of 50 Ω .

The standing wave ratio (SWR) is a measure used to quantify the impedance matching in circuits of RF signals. A mismatched impedance results in a reflected wave, and loss in the circuit. The SWR is defined as $|V_{\text{max}}|/|V_{\text{min}}|$, where V_{max} and V_{min} are the maximum and minimum voltage amplitudes of the RF envelope. An Agilent 8714ET RF Network Analyzer, was used to find the SWR of the RF coil and coaxial cables assembly. At



(a) Teflon components (b) Vespel components

Figure 5.2.4: (Left) Teflon components act as thermometer mounts and spacers for the coaxial RF voltage cable. The old 90° bend to the RF coil is shown near the bottom. (Right) Replacement Vespel parts, including the concentricity spacer, and a new split design for the thermometer mounts. The new 90° bend is also visible near the bottom.

room temperature, the circuit through the RF coil using the semi-rigid coaxial cables had a SWR of 1 – 1.15 at 42.005 MHz, whereas the new cables produced the higher SWR of 1.296. While the amplitude of the reflected signal has increased by a factor of two, the power transmitted to the RF coil is still high, 98%, a decrease of only $\sim 1\%$ from the old construction. Figure 5.2.6 shows the SWR of the new circuit as a function of temperature on two consecutive days. On the second day, a discontinuous change in the SWR near 375 K was observed, which also changed the temperature dependence of the SWR. This is attributed to the thermally enabled, and possibly irreversible, movement of the wrapped copper coils or capacitance plates in the RF coil (Figure 5.2.2).



Figure 5.2.5: Schematic of the pin and connector assembly for the 90° bend in the RF coaxial cable. (Left) Assembly of connector plate with pin and PEEK dielectric. The clamp both physically secures the coaxial cable and ensures a connection to the grounding mesh. (Top right) The pin allows for the 90° conduction of the RF signal. The center conduction is inserted from the left, and the holes on the side allow for the insertion of solder. (Bottom right) The coaxial cable stripped to reveal the layers: Kapton outer shielding, grounding mesh, PEEK dielectric, and center conductor inserted in the 90° pin. Solder was then applied and the assembly was clamped in the connector plate.



Figure 5.2.6: SWR of the updated RF coil circuit as a function of temperature, on two consecutive days. During the second iteration, a discontinuous change in the SWR was observed, and is attributed to a change in the RF coil wrapping.

5.2.4 Forward detector

The danger at high temperature to the forward detector was the softening and resulting deformation of both the light guide and the scintillator. The scintillator was replaced by a cross-linked plastic scintillator from Eljen Technology (EJ-248M). This material is a variant of conventional polyvinyl toluene (PVT) scintillators, specially modified to have a softening point 20 K higher, or 373 K. The cross-linking extends the scintillator lifetime if it is used above its softening point for an extended duration. To further reduce the thermal load on the detector, a 10 cm spacer was introduced to displace the re-entrant tube from the sample position. As shown in Figure 5.2.7, the light guide was redesigned to have a flat on two opposing sides to create space for thermometry wiring and piping for cooling N_2 gas flow. The DT-670 silicon diode thermometer (Lakeshore) was taped to the inside of the end cap, and a thin copper tube was run along the opposing flat to the scintillator a the front of th detector. Operation of the new design is largely similar to the old setup, although the new configuration had twice the light output. The primary advantages of this setup were the ability to measure and control the temperature of the forward detector.

Retracting the forward detector by 10 cm reduces the detector's effective solid angle, as it pertains to the detection of beta emitted from the sample location. The consequential reduction in detection efficiency can be determined via a rudimentary MC simulation. The cyclotron radius in a magnetic field $\mathbf{B}_0(z)$ is

$$r_{c}(z) = \frac{cp_{\perp}}{eB_{0}(z)},$$
 (5.2.1)

where c is the speed of light, $B_0(z)$ is the magnitude of the magnetic field at distance z from the magnet center, e is the electron charge, and $p_{\perp} = ||\mathbf{p} - \mathbf{p} \cdot \mathbf{B}/B||$ is the electron momentum perpendicular to \mathbf{B}_0 and is independent of z. The total relativistic electron momentum is given by $\mathbf{p} = \gamma m_e \dot{\mathbf{x}}$, where the electron end-point energy of 13 MeV¹⁸⁵ determines the velocity magnitude, and Equation 3.2.3 determines the direction. The Lorentz factor is written here as γ . The detection probability can be determined from the number of electrons which have $r_c \leq r_{\text{detector}}$ once they arrive at the detector, where



Figure 5.2.7: Schematic of the redesigned forward detector. Components: (1) Aluminum end cap, held in place with set screws, secures the plastic scintillator to the light guide. (2) Plastic light guide, with two flat sides to make space for thermometry wiring and piping for active cooling. (3) A 10 cm spacer to move the re-entrant tube back from the sample position. (4) Housing for ports (from left to right): thermometry wiring pinout, a KF flange, and a port for gas inflow.

 $r_{\text{detector}} = 19.05 \text{ mm}$. As shown in Figure 5.2.8, the reduction in detection probability by the addition of 10 cm is at most 40 %, and is clearly unchanged at high field ($B_0 > 3 \text{ T}$). Given the neglected off-axial fringe fields, this is likely a rough estimate at best.

5.3 Commissioning and performance summary

In Fall of 2020, two experiments were run to high temperature with the new setup: a study of the wide gap semiconductor ZnO (TRIUMF experiment M1828), and an aPS thin film (M1892). Figure 5.3.1 demonstrates that the temperature of the new forward detector lags that at the sample position. At this stage, this is largely a proof of concept. The cooling gas was sourced from the boil-off vapour in a dewar of liquid N_2 with unquantified and manual flow control. As the vapour is removed to the detector, the pressure is reduced



Figure 5.2.8: MC simulation of beta detection at two detector positions as a function of field. While there is a slight reduction in detection at $B_0 < 3 \,\mathrm{T}$, at high field there is no expected difference.

and the flow rate is reduced as well. To account for this, the flow rate was manually adjusted throughout both experiments.

During these experiments, it was observed that the vacuum near the sample position spiked during temperatures changes (see Figure 5.3.2). The increased vapour pressure in the beamline reduced the maximum voltage attainable by the β -NMR platform, subsequently increasing the minimum implantation depth. Above ~340 K, the 12 kV needed for bulk aPS implantation was not possible. Due to its low mass, the sample was not the likely source of the outgassing. Rather it is more likely that the outgassing source was the cryostat and surfaces immediately surrounding the sample, which have not been baked in nearly 20 years of operation. We also note that, should the issues with the platform bias not be resolved easily, a thicker sample of aPS may also be used for bulk measurements at high temperature.

Unlike the prior setup, which was under a rough vacuum, the new detector was open directly to atmosphere. As a result, the detector cavity could have had a non-negligible quantity of water vapour which would condense and freeze at low temperature. Other experiments in this period employed the old forward detector. Since the detector cavity is not at UHV, exchanging the detector is a process completed in ~ 10 min. This is an extremely fast process in comparison to routine sample changes, which may take up to an hour



Figure 5.3.1: The temperature of the forward detector (red) lags the temperature at the sample position (black) in two separate experiments. Throughout both experiments, the detector had a variable amount of N_2 flow providing active cooling. Data is the run-averaged temperature as monitored through normal operation.



Figure 5.3.2: Spikes in the vacuum near the sample position were recorded when the temperature was increased during the measurement of ZnO. The steady state vacuum also increased with temperature.

Table 5.3.1: Temperature limits of components in β -NMR spectrometer. The upper limit on the RF coil has not been determined, but the coil was safely operated at 400 K. The temperature of the forward detector elements is monitored separately and has an active cooling element.

	Max Operating Temperature (K)
WS_2	1589
Vespel	561
Solder	553
RF coaxial cables	532
Cryostat	500
GaAlAs thermometers	500
Si diode thermometers	500
RF coil	≥ 400
Forward detector scintillator	373
Forward detector light guide	323

to complete. The condensation issue may also be resolved by pumping the detector cavity to a rough vacuum. The pump would then remove moisture, provide a means of controlling the N₂ flow, and act as a light seal to the otherwise open vent; allowing the new forward detector to be utilized at both low and high temperatures. In future refinements, the N₂ flow should also be better controlled by drawing liquid N₂ with a flow controller, and vaporizing it before its introduction to the detector cavity. With an improved cooling system, the maximum operating temperature of the upgraded β -NMR cryostat should be ~500 K (see Table 5.3.1). The remaining limitation is primarily the RF coil, whose reliability under thermal cycling to high temperature is unknown.

Some minor additional testing and modification of the upgraded system is needed. Most importantly, the cryostat should be baked to remove any residual contaminants and water, as is done with most UHV systems. The detector outflow should be sealed with roughing pump, and the inflow of N_2 should be properly controlled and logged. Finally, the RF coil should be tested more thoroughly to determine the upper limit of its operating temperature. With these issues resolved, the upgraded spectrometer will have an operating temperature range of 3.5 K to 400 K or more, well above the $T_{\rm g}$ of aPS. Not only would this close the gap in Figure 5.1.2, but it may lead to an observation of the BPP peak which would allow for a determination of the quadrupolar coupling constant, and a rigorous conversion to a microscopic correlation time. It is also expected that this upgrade will enable many other β -NMR experiments which were not previously possible.
Chapter 6

Supercooled and Glassy Ionic Liquids

6.1 Introduction

The crystalline state is absent in atactic polystyrene (aPS) due to the random chain tacticity. In contrast, 1-ethyl-3-methylimidazolium acetate (EMIM-Ac) is a binary molecular glass, and for it, the contrasting size and shapes of the constituent ions prevent crystallization. Since the $T_{\rm g}$ of this room temperature ionic liquid (RTIL) is well below ambient temperatures, and the β -detected nuclear magnetic resonance (β -NMR) spectrometer has a lower temperature bound of ~3 K, vitrification of EMIM-Ac is easily accomplished in situ. We can then use β -NMR to observe the signature of the glass transition in these materials, and how this is perturbed by the presence of the surface.

RTILs are a fascinating class of amorphous materials with many practical applications,^{82,219} such as lubrication in space applications and other low-pressure environments.⁷⁹ As in high temperature molten salts, strong Coulomb forces yield a liquid with significant structure. Pair distribution functions from scattering experiments reveal an ion arrangement of alternating charges,^{89–91} resulting in a large and strongly temperature dependent viscosity η . In contrast to simple salts, RTILs consist of large, low-symmetry molecular ions and they remain liquid at ambient temperature. Many RTILs are notoriously difficult to crystallize. Rather, they are easily supercooled, eventually freezing into a glassy state at the glass transition temperature $T_{\rm g}$ far below the thermodynamic melting point, $T_{\rm m}$.⁹²

A key feature of supercooled liquids and glasses is dynamic heterogeneity.^{3,220,221} Distinct from homogeneous liquid or crystalline phases, the local molecular dynamics (MD) exhibit fluctuations which are transient in both time and space. These non-trivial fluctuations are found to be stronger closer to the glassy phase, and are characterized by an increasing dynamical correlation length as the temperature is reduced.⁵ An understanding of dynamic heterogeneity may be central to a fundamental theoretical description of glass formation.

With highly localized probes in the form of nuclear spins, nuclear magnetic resonance (NMR) is one of the few methods with the spatial and temporal resolution to quantify this heterogeneity and reveal its characteristics.^{221–223} The degree of heterogeneity in the NMR signal can be modelled by the "stretching" of an exponential nuclear spin-lattice relaxation (SLR), exp $\{-[(\lambda t)^{\beta}]\}$, where $\lambda = 1/T_1$ is the SLR rate and β is the stretching exponent. Single exponential relaxation ($\beta = 1$), corresponds to homogeneous relaxation, whereas $\beta < 1$ describes a broad distribution of exponentials,¹⁵⁵ the case where each probe nucleus relaxes at a different rate. The breadth of the distribution of rates is determined by β , with $\beta = 1$ corresponding to a delta function.

While it has been clearly demonstrated that dynamical heterogeneities result in stretched exponential relaxation,^{224,225} it is worth considering whether it instead results from a population which homogeneously relaxes in an intrinsically stretched manner. To this point, MD simulations of a supercooled model binary liquid have shown β to be independent of scale, at least down to a few hundred atoms.²²⁶ This implies that the stretching is intrinsic and homogeneous; however, the NMR nuclei are each coupled to far fewer atoms, and are capable of identifying dynamical heterogeneity.^{222,223} This sensitivity is clearly demonstrated by 4D exchange NMR, where subsets of nuclei in supercooled polyvinyl acetate were tracked by their local relaxation rate, revealing a broad distribution of relaxation times.⁷⁶ Furthermore, dynamical heterogeneities have been theoretically shown to be a prerequisite for stretched exponential relaxation in dynamically frustrated systems, such as supercooled liquids.²²⁷ A reduction of β below one is a signature of dynamic heterogeneity.

Potential applications of the RTIL EMIM-Ac, with ions depicted in Figure 1.3.1, have motivated detailed studies of its properties, including neutron scattering measurements of its liquid structure,⁹¹ its bulk physical properties,²²⁸⁻²³⁷ and its ability to dissolve cellulosic material.^{86,88} Here, we use implanted-ion β -NMR to study the development of dynamic heterogeneity and ionic mobility of implanted ⁸Li⁺ in supercooled EMIM-Ac. The β -NMR signal is due to the anisotropic β -decay of a radioactive NMR nucleus,²³⁸⁻²⁴⁰ similar to muon spin rotation. The probe in our case is the short-lived ⁸Li, produced as a low-energy spin-polarized ion beam and implanted into the sample.¹⁷³ At any time during the measurement, the ⁸Li⁺ are present in the sample at ultratrace (10⁻¹³ M) concentration. Implanted-ion β -NMR has been developed primarily for studying solids, particularly thin films. It is not easily amenable to liquids, since the sample must be mounted in the beamline vacuum, yet the exceptionally low vapour pressure of RTILs makes the present measurements feasible.²

We have measured the strong temperature dependence of the SLR $(1/T_1)$ and resonance of ⁸Li in EMIM–Ac, as shown in Figures 6.3.1 and 6.3.5. The relaxation shows a characteristic Bloembergen-Purcell-Pound (BPP) peak at 298 K, coinciding with the emergence of dynamical heterogeneity, indicated by stretched exponential relaxation. The surface has a clear modification of the SLR. Resonance measurements clearly demonstrate motional narrowing as the RTIL is heated out of the supercooled regime. Our findings show that β -NMR could provide a new way to study depth-resolved dynamics in thin films of RTILs.¹²¹

6.2 Experiment

 β -NMR experiments were performed at TRIUMF's ISAC facility in Vancouver, Canada. A highly polarized beam of ⁸Li⁺ was implanted into the sample in the high-field β -NMR spectrometer with static field $B_0 = 6.55 \text{ T}.^{165,169}$ Implantation depth profiles are shown in Figure 3.2.2, but well above T_g the solvent diffusion (see Section 6.3.3) modifies this initial implantation profile significantly during the ⁸Li lifetime. The nuclear properties of the ⁸Li probe are listed in Table 3.2.1. The nuclear spin-polarization of ⁸Li is monitored through its anisotropic β -decay, using the combined asymmetry of both polarization states as described in Section 3.2.3.

Similar to other quadrupolar (I > 1/2) nuclei in nonmagnetic materials, the strongest interaction between the ⁸Li nuclear spin and its surroundings, after the Zeeman interaction, is typically the electric quadrupolar interaction, even when the time average of this interaction is zero. In EMIM–Ac, it is very likely that the spin relaxation is due primarily to fluctuations in the local electric field gradient (EFG) at the position of the ⁸Li nucleus. As described in Sections 3.2.4 and 3.2.5, SLR measurements used a pulsed ⁸Li⁺ beam with no transverse field, whereas resonances were acquired by stepping a continuous wave (CW) transverse radio frequency (RF) magnetic field slowly through the ⁸Li Larmor frequency, with a continuous ⁸Li⁺ beam. The spin of any on-resonance ⁸Li is rapidly nutated by the RF field, resulting in a loss in time-averaged asymmetry.

The sample consisted of a EMIM-Ac solution (Sigma-Aldrich). To avoid the response being dominated by trace-level Li-trapping impurities, we introduced a stable isotope "carrier" (LiCl) at 25 mM, a low but macroscopic concentration to saturate impurity Li⁺ binding sites. Additional characterization of a similar solution, prepared in the same manner, can be found in the supplementary information of Szunyogh et al..² The solution was kept in a dry-pumped rough vacuum (~10 mTorr) for 12 h to 48 h prior to the measurement. A ~3 µL droplet was placed in a 3 mm diameter blank hole set 0.5 mm into a 1 mm thick aluminum plate, as shown in Figure 6.2.1. The Al plate was then bolted vertically into the ultrahigh vacuum (10^{-10} Torr)



Figure 6.2.1: The β -NMR sample holder with Al plate. The 3 mm blank impression contains 3 µL of EMIM–Ac, and is mounted in a vertical orientation (shown horizontal).

coldfinger liquid He cryostat. The viscosity was sufficient to prevent the liquid from flowing out of the holder during the experiment. Sample mounting involved a few minutes exposure to air, followed by pumping for 30 min in the spectrometer's load lock. To account for the size of the droplet, the beam spot was maintained at less than $\sim 2 \text{ mm}$ in diameter.

Independent sets of measurements in bulk EMIM–Ac were taken in 2017, 2019, and 2020. In both 2019 and 2020, the temperature was first reduced to well below $T_{\rm g}$ at a constant rate of 1 K/min. In 2019, measurements were taken as the temperature was changed, with each point integrating over 10 K, whereas in 2020 the temperature was first stabilized during warming. In both years, the temperature was varied monotonically, other than the necessary reversal to warm back to room temperature.

Separately, we determined the self-diffusion coefficients of the LiCl EMIM–Ac solution using conventional bi-polar pulsed field gradient (PFG) NMR. This technique can be described as a spin-echo measurement wherein the magnetic field pulses have a macroscopic spatial gradient. Because the phase imparted on the nuclear spin precession is now position dependent, the intensity of the echo can be used as a measure of the diffusion along the gradient axis. An in-house probe²⁴¹ and spectrometer²⁴² were used at 8.4 T and room temperature, and a gradient pulse of $\delta = 3.2$ ms was applied in varying strength, g, from 50 G cm⁻¹ to 1200 G cm⁻¹. The probe frequency was set to either ¹H or ⁷Li, and the diffusion time Δ was varied between

100 ms to 450 ms, according to the species diffusion rate. A delay of 30 ms allowed eddy currents to decay before acquisition. Diffusion coefficients were extracted by fitting the resulting Gaussian to the Stejkal-Tanner diffusion equation.²⁴³ These diffusion coefficients were $D_{\rm Li} = 3.46(11) \times 10^{-10} \,\mathrm{m^2 s^{-1}}$ and $D_{\rm H} = 3.61(7) \times 10^{-10} \,\mathrm{m^2 s^{-1}}$.

6.3 Bulk measurements

Implanting ${}^{8}\text{Li}^{+}$ at ~19 keV, we first consider the data which, according to the Stopping and Range of Ions in Matter (SRIM) program, has a mean implantation depth of 200 nm. We assume that the SLR and resonance will then reflect characteristics primarily attributed to the bulk dynamics.

6.3.1 Relaxation results

Typical ⁸Li β -NMR SLR measurements are shown in Figure 6.3.1. Below $T_{\rm g}$, both T_1 and β are effectively constant, a sharp contrast to the strong temperature dependence once above $T_{\rm g}$. There is a minimum in λ near $T_{\rm g}$. At higher temperatures, the rate increases rapidly with temperature, revealing a maximum near room temperature. Besides the rate, the form of the relaxation also evolves with temperature. At low temperature it is highly non-exponential, but gradually steps up throughout the supercooled regime to become nearly exponential at room temperature. The SLR is well-described by a stretched exponential:

$$p(t,t') = \exp\left\{-\left[\lambda \left(t - t'\right)\right]^{\beta}\right\}.$$
 (3.2.27)

A very small fraction, less than 3 % of the SLR signal can be attributed to $^{8}\text{Li}^{+}$ stopping in the sample holder. While this background signal is nearly negligible, it is accounted for with an additive bi-exponential signal, tightly constrained from a set of control measurements in the empty holder (see Appendix C.1).

The SLR time series at all T were fit simultaneously with a common initial asymmetry and background fraction. To find the global least-squares



Figure 6.3.1: The β -decay asymmetry of ⁸Li in EMIM–Ac, with stretched exponential fits from 2017. The SLR is strongly temperature-dependent, and is well described by Equation 3.2.27 convoluted with the square beam pulse, as evidenced by $\tilde{\chi}^2_{\text{global}} \approx 0.99$. The data have been binned by a factor of 20 for clarity.

fit, we used a Python3 code leveraging the MINUIT²⁴⁴ minimization routines wrapped by iminuit,²⁴⁵ accounting for the strongly time-dependent statistical uncertainties in the data (see Appendix D for details). The fitting quality was excellent, with $\chi^2_{\rm global} \approx 0.99$ in all three data sets.

As shown in Figure 6.3.2, the change in $1/T_1$ over the measured ~200 K range is remarkable, varying over 3 orders of magnitude. These changes coincide with the relaxation converging to monoexponentiality with increasing temperature, as evidenced by $\beta \rightarrow 1$ (upper panel). The temperature dependence of $1/T_1$ is, however, not monotonic; the rate clearly has a minimum near $T_{\rm g}$ and is maximized at room temperature, the latter corresponding to a BPP peak.²⁴⁶ At this temperature, the characteristic fluctuation rate of



Figure 6.3.2: The stretched exponential parameters from fits to the SLR in EMIM–Ac (refer to Figure 6.3.1 for fit curves). For the rate $(1/T_1)$, the line denotes a fit using Equations 3.1.22, 6.3.1 and 6.3.2, as detailed in the text, omitting 150 K < T < 250 K from the fit. Both T_1 and β are highly temperature dependent with a $1/T_1$ BPP²⁴⁶ peak at 298 K, above which $\beta \approx 1$. The shading gradient approximately indicates the departure of dynamical characteristics from that of the liquid phase, with supercooling developing between $T_{\rm g}$ and $T_{\rm m}$.

the dynamics responsible for the SLR (τ_c^{-1}) matches the probe's Larmor frequency $(\omega_L = \gamma B_0)$, i.e., $\tau_c \omega_L \approx 1$. The SLR due to a fluctuating EFG can be described by the following simple model:¹⁵⁰

$$\frac{1}{T_1} = a \left[\mathcal{J}(\omega_L) + 4 \mathcal{J}(2\omega_L) \right] + b, \tag{6.3.1}$$

where a is a coupling constant related to the strength of the EFG, b is a small phenomenological temperature-independent relaxation rate important at low T,¹⁶⁸ and \mathcal{J} is the NMR fluctuation spectral density function. If the



Figure 6.3.3: The dynamic viscosity (η) from the literature,^{86,88,228–237} fitted with a VFT model (see Equation 1.2.2). EMIM-Ac is a fragile glass former, as evidenced by a super-Arrhenius η .



Figure 6.3.4: The resonance linewidth as a function of $\eta(T)/T$, where η is the dynamic viscosity from the literature as shown in Figure 6.3.3. The red line is a linear fit for $T \geq 250$ K. This linear scaling is expected from the Stokes-Einstein relation.

local dynamics relax exponentially, the spectral density is described by the Debye expression (Equation 3.1.22).

Local fluctuations may be related to other macroscopic properties of the liquid such as the viscosity. Using values from the literature, $^{86,88,228-237}_{\rm }$

Figure 6.3.3 shows that the dynamic viscosity $\eta(T)$ of EMIM-Ac is non-Arrhenius, characteristic of a fragile glass-former, and can be described with the phenomenological Vogel-Fulcher-Tammann (VFT) model (Equation 1.2.2). Figure 6.3.4 shows that the linewidth is proportional to η/T , consistent with the Stokes-Einstein relation, $D = k_B T/6\pi\eta a$, and Equation 48 of Bloembergen et al.:²⁴⁶ $\tau = r^2/6D$; where D is the diffusion constant, a is the distance of closest approach of two particles, and r is the distance travelled in time τ . Outside of the region neighbouring the minimum (approximately 150 K < T < 250 K), which may be a technique-related phenomenon, we assume that τ_c is proportional to η/T , as suggested by the viscosity dependence of the linewidth. This choice is further justified and discussed in Section 6.3.3. Since the viscosity is well-described by the VFT equation, τ_c will have the following functional form:

$$\tau_c = \frac{c}{T} \exp\left[\frac{\Delta E}{k_B \left(T - T_{\rm VFT}\right)}\right]. \tag{6.3.2}$$

In Equation 6.3.2, c is a prefactor, ΔE is the activation energy, k_B is the Boltzmann constant, T is the absolute temperature, and $T_{\rm VFT}$ is a constant. Together, Equations 3.1.22, 6.3.1 and 6.3.2 encapsulate the temperature and frequency dependence of the ⁸Li $1/T_1$ in the supercooled ionic liquid. A fit of this model to the data is shown in Figure 6.3.2, and parameter values can be found in Table 6.3.1. From the value of the *a* parameter and the constant prefactors for $I = 2,^{31}$ we can establish that the upper bound on magnitude of the quadrupole coupling constant $eQV_{zz}/h \leq 67.8(4)$ kHz, about a factor of two larger than in $aPS.^{31}$ The correlation times from 220 K to $315 \,\mathrm{K}$ are on the order of nanoseconds. The choice of Equation 3.1.22assumes that the $\beta < 1$ stretching arises from a population of exponential relaxing environments with a broad distribution of τ_c . As mentioned, this assumption is likely good for the ⁸Li β -NMR probe; especially since the basic local relaxation of ⁸Li due to quadrupolar coupling is not intrinsically stretched, independent of the dynamical fluctuation spectrum.¹⁵² Therefore the departure from $\beta = 1$ in the supercooled regime is consistent with the emergence of dynamical heterogeneity.

Table 6.3.1: Fit parameters for $1/T_1$ (β -NMR) and η (literature). Parameters are defined in Equations 6.3.1 and 6.3.2, substituting $c/T \leftrightarrow \eta_0$ in the latter. Corresponding curves are shown in Figures 6.3.2 and 6.3.3.

		$1/T_1(T)$	$oldsymbol{\eta}(oldsymbol{T})$
c	(nK s)	1.3(4)	
η_0	$(\mu Pa s)$		59(4)
ΔE	(meV)	68(4)	81.7(13)
$T_{\rm VFT}$	(K)	172(3)	175.8(9)
a	(s^{-2})	$1.59(2) \times 10^9$	
b	(s^{-1})	0.106(2)	

Despite providing a clear indication of the presence of dynamical heterogeneity, β provides limited information as to its nature. Such nonexponentiality may be brought about by changes to the dynamical rate which may occur on a wide range of timescales, spanning from MHz to Hz. Even if temporal fluctuations in the rate of molecular motion occur slowly enough to be effectively constant, averaging over spatial variation in the rate will result in non-exponential relaxation of the polarization. Furthermore, if fluctuations to the dynamical rate are fast relative to $1/\omega_L$, they may be averaged out to result in a single exponential signal. In this case, such as that in the liquid state, we claim only that such dynamical heterogeneities must occur on timescales equal to, or faster than the dynamics to which we are coupled.

6.3.2 Resonance results

Typical ⁸Li resonances are shown in Figure 6.3.5. Similar to the SLR, they show a strong temperature dependence. At low *T*, the resonance is broad with a typical solid-state linewidth on the order of 10 kHz. The lack of resolved quadrupolar splitting reflects the absence of a single well-defined EFG; the width likely represents an inhomogeneous distribution of static, or partially averaged, EFGs giving a broad "powder pattern" lineshape convoluted with the CW NMR excitation, a Lorentzian of width γB_1 , where $B_1 \approx 0.1$ G. This inhomogeneous quadrupolar broadening is qualitatively



Figure 6.3.5: The ⁸Li resonance in EMIM–Ac, shifted by the Larmor frequency ($\nu_L \approx 41.27 \,\mathrm{MHz}$), with Lorentzian fit. The line narrows and increases in height as the temperature is raised, with a peak in the latter near 260 K (see Figure 6.3.6). The vertical scale is the same for all spectra, which have been offset for clarity. Spectra are inverted for consistency with the presentation in conventional NMR.

consistent with the heterogeneity in the dynamics implied by the stretched exponential relaxation.

The resonances are well-described by a simple Lorentzian (Equation 3.2.28). The baseline (time-integrated) asymmetry is also strongly temperature dependent due to the temperature dependence of $1/T_1$. The shift of the resonance relative to a single crystal of MgO (our conventional frequency standard, see Figure 3.2.6) is about -9 ppm. Unlike conventional NMR, where the magnetic field is maintained with high precision for many years at a time, the β -NMR magnet is ramped down to zero field between experimental periods to facilitate the beam tuning process. The measurement of small chemical shifts is therefore reliant on the comparison to a reference material. In this case, a slow drift of the magnetic field over the course of the experiment prevented a more accurate determination or a reliable measurement of any slight T dependence. The other fit parameters extracted from this analysis; the linewidth, peak height, and intensity (area of normalized spectra); are



Figure 6.3.6: The Lorentzian fit parameters and the intensity of the ⁸Li resonance in EMIM–Ac, illustrated in Figure 6.3.5, with lines to guide the eye. Narrowing of the line suggests an onset of solvent molecular motion above the melting point. The corresponding drop in intensity (area of the normalized spectra), and the non-monotonic peak height suggests inhomogeneous broadening at low temperature, and slow spectral dynamics occurring on the scale of 1 s, the integration time at each frequency. Shading indicates the supercooled region between $T_{\rm m}$ and $T_{\rm g}$ (off scale). All measurements were conducted with the same RF power.

shown in Figure 6.3.6.

As anticipated from the most striking features in Figure 6.3.5, the linewidth and peak height evolve considerably with temperature. Note that the peak height in Figure 6.3.6 is measured from the baseline, and is normalized to be in units of the baseline, accounting for changes in the SLR. With this normalization, a height of one indicates a complete destruction of the polarization on-resonance, and a height of zero indicates that the peak is indistinguishable from the off-resonance baseline. Reduction in the linewidth by several orders of magnitude is expected from motional narrowing, where rapid molecular motion averages out static inhomogeneous broadening. Also, the saturation of the narrowing by room temperature^{*} with an onset far below the $1/T_1$ maximum is consistent with the BPP interpretation of the SLR peak.²⁴⁶ At this peak, the timescale for molecular dynamics approaches ω_L^{-1} , and it would be expected that the ensuing spectral dynamics (the evolution of each probe's Larmor frequency) would be sufficiently fast well below this temperature to narrow the line.

6.3.3 Discussion

Mediated by a strong Coulomb interaction, RTILs are known to contain a significant amount of structure. One might expect pairing of anions and cations, but calculations based on a simplified ion interaction model suggest that such pairs are short-lived.⁷⁸ Dielectric relaxation experiments confirm this, placing a 100 ps upper bound on their lifetime at room temperature, rendering them a poor description of the average ionic structure.²⁴⁷ Rather, the arrangement can be described as two interpenetrating ionic networks. As revealed by neutron scattering,^{89–91} each network forms cages about the other that are highly anisotropic due to the tendency for EMIM rings to stack.⁹¹ In fragile glass formers, such as EMIM–Ac, MD simulations indicate that the motion of the caged ion and the center of mass motion of the cage are correlated.²⁴⁸ Presumably, in our case, the small ⁸Li⁺ cation is coordinated by several acetates and a similar correlation will exist for the ⁸Li⁺ in the absence of independent long-range diffusion.

Naturally, the motion of the surrounding ionic solvent cage will cause the local EFG to fluctuate, and a strong temperature dependence is reasonable since these same fluctuations have a role in determining the strongly temperature dependent viscosity $\eta(T)$ shown in Figure 6.3.3. While a direct relation between the specific motions sensed by ⁸Li and the bulk η is complex and unclear,²⁴⁹ one may anticipate a consistency between their kinetics should a single mechanism govern both. The similarity of both ΔE and $T_{\rm VFT}$ with those found from the viscosity of the pure EMIM–Ac suggests that this is

^{*} The high temperature linewidth (~ 1.6 ppm) is compatible with the limit imposed by the homogeneity of the magnet at its center (~ 10 ppm over a cubic centimeter).

the case and provides further justification for the choice of Equation 6.3.2.

Figure 6.3.4 shows that motional narrowing causes the resonance linewidths to scale as η/T in the liquid state above $T_{\rm g},$ a situation also observed in DEME-TFSA [DEME = N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium; and TFSA = bis(trifluoromethanesulfonyl)amide] with solute ⁷Li NMR.²⁵⁰ That this relationship holds for ⁸Li is surprising; our β -NMR signal is due to the dynamics of a population of implanted local probes, for which solvent self-diffusion and probe tracer-diffusion are not differentiated, whereas the viscosity is a bulk property. If ⁸Li⁺ is diffusing, it implies that the diffusion is controlled by the solvent dynamics. In the limiting case of a solid, interstitial diffusion can be fast, yet the viscosity infinite, and the decoupling of diffusion and the host viscosity is self-evident. Many RTILs violate the Stokes-Einstein relation that linearly relates self-diffusivity D to T/η , and its violation at low T in Figure 6.3.4 shows that ionic diffusion in supercooled RTILs may contain some of the character expected from a solid. At 295 K however, our ⁷Li PFG NMR in EMIM–Ac with 30 m M LiCl shows that the diffusion is not significantly larger than the solvent, demonstrating that the ⁸Li is primarily sensing the mobility of its surrounding solvent cage.

Relatively little is known about Li^+ as a solute in EMIM-Ac, compared to other imidazolium-based RTILs, which have been explored as electrolytes for lithium-ion batteries.^{250,251} Their properties should be qualitatively comparable, but the details certainly differ as both anion size and shape play a role in the diffusivity.²⁵² Shown to compare favourably with implanted-ion β -NMR,² conventional NMR can provide a comparison to some closely related RTILs: EMIM-TFSA and EMIM-FSA [FSA = bis(fluorosulfonyl)amide]. In both cases, the diffusion of ⁷Li was similar to that of the solvent ions.²⁵³ Differences in the tracer diffusion are reflected in the activation barrier for ⁷Li hopping: 222(6) meV and 187(2) meV, respectively.²⁵³ This correlates well with anion molecular weight, 280 g mol⁻¹ and 180 g mol⁻¹, and with the barrier we report for ⁸Li: 68(4) meV for acetate of 59 g mol⁻¹. This further emphasizes the probe sensitivity to the solvent dynamics.

The motional narrowing immediately apparent in Figure 6.3.6 is analogous to conventional pulsed RF NMR, but the use of CW RF modifies the detailed description significantly. While the details are beyond the scope of this thesis, we now give a qualitative description. In the slow fluctuation regime, the line is broadened relative to the static limit at T = 0 due to slow spectral dynamics occurring over the second-long integration time at each RF frequency. Both the peak height and the intensity (area of the normalized curve) are increased through the resulting double counting of spins at multiple RF frequencies, although this effect on the peak height is small relative to that when fluctuations are fast. In this fast fluctuation limit, the time spent with a given local environment is small and the RF is relatively ineffective at nutating off-resonance spins. Unlike the slow fluctuation limit, transverse coherence is now needed to destroy polarization. Coherence is maintained only in a small range about the Larmor frequency, narrowing as the fluctuation rate increases. The intensity (area) is also reduced from the preservation of off-resonance polarization.

The local maximum in the peak height is explicable from a small relatively slowly relaxing background component. When the RF is applied on-resonance, the signal from the sample is partially eliminated and, in the case of saturation, the asymmetry becomes independent of the SLR. Increasing the SLR rate will, however, reduce the off-resonance asymmetry and results in a reduction in the fraction of destroyed polarization. This competes with the increase in peak height from motional narrowing and produces the local maximum in Figure 6.3.6. This competition is described in detail in Appendix C.3.

The increase in the SLR rate as the temperature is cooled above and near $T_{\rm g}$ (Figure 6.3.2) is of unknown origin. The naïve assumption of $\lambda \propto \tau_c$, normally valid in the slow fluctuation limit (see Figure 3.1.3), would imply that the dynamics slightly above $T_{\rm g}$ are slower than deep in the glassy state. If true, this would have profound implications on our understanding of glass physics. However, the explanation is likely far more mundane. Preliminary measurements using conventional ⁷Li NMR in EMIM–Ac with 25 mM LiCl do not exhibit this phenomenon, however a similar increase can be observed in the proton SLR. This suggests that the nature of the increase is related to the dynamics of the ¹H. One plausible scenario is that, because the ⁸Li is implanted, the time to coordinate with the host ions increases drastically near $T_{\rm g}$. As the RTIL passes into the glassy phase, this time becomes longer than the ⁸Li lifetime. This would then change the effective coordination of the probe ions to those from the host material. Alternatively, Figure 1.3.2 suggests the existence of secondary relaxations which diverge from the primary relaxations at a temperature slightly above $T_{\rm g}$. If the $1/T_1$ increase were due to the BPP peak of a secondary process, the peak would be extremely broad. Measurement of the SLR temperature dependence at a different static NMR field is likely provide strong evidence for or against the attribution of this phenomenon to secondary relaxation processes.

The 2019 SLR data shown in Figure 6.3.2 has some discrepancy from the rest of the data, particularly in β . These measurements were acquired as the temperature was changed, and it is likely that this introduced an overall temperature lag. The differences between the warming and cooling curves, and the temperature-stable data sets support this hypothesis.

The development of dynamic heterogeneity at the nanosecond timescale (ω_L^{-1}) is demonstrated by the stretched exponential SLR, as shown in Figure 6.3.2. Concurrently, the line broadening shows that this heterogeneity reaches down to the static timescale. There are no definitive measurements of the melting point of EMIM-Ac, since it has not yet been crystallized, but $T_{\rm m}$ is no larger than $250\,{\rm K}.^{87}$ In contrast, a calorimetric glass transition has been observed at about $\sim 198 \,\mathrm{K}$.¹⁰⁰ Thus, the dynamic inhomogeneity develops in a range of T that corresponds well to the region of supercooling, indicated by the shading in Figure 6.3.2. Stretched exponential relaxation, reflecting dynamic heterogeneity, is a well-known feature of NMR in disordered solids.^{254,255} In some cases, diffusive spin dynamics, driven by mutual spin flips of identical near-neighbour nuclei, can act to wash out such heterogeneity. Such spin diffusion may be quenched by static inhomogeneities that render the nuclei non-resonant with their neighbours.²⁵⁶ However, a unique feature of β -NMR is that spin diffusion is absent: even in homogeneous systems, the probe isotope is always distinct (as an NMR species) from the stable host isotopes, and the β -NMR nuclei are, themselves, always isolated from one another. In the absence of spin diffusion, on quite general grounds, it has been shown^{168,257} that the stretching exponent β should be 0.5. Our data in

Figure 6.3.2 appear to be approaching this value at the lowest temperatures. While stretched exponential relaxation is very likely a consequence of microscopic inhomogeneity, unequivocal confirmation requires more sophisticated measurements such as spectral resolution of the SLR or the pulse sequences employed by techniques such as reduced 4D-NMR.⁷⁶ One possibility, which should be tested by further investigation, is whether dynamic heterogeneity is present at all temperatures. In the liquid state, these heterogeneities may occur on short enough timescales to be averaged out during the probe lifetime, thereby resulting in an single exponential relaxation. The apparent emergence of dynamical heterogeneity in this scenario would be brought about by a slowing of the dynamics, resulting in an increased sensitivity of the ⁸Li probe to the spatial and temporal differences in the molecular dynamics.

Based on the non-Arrhenius behaviour of $\eta(T)$, EMIM–Ac is a reasonably fragile glass former, comparable to toluene which has been studied in some detail using ²H NMR,^{254,258} providing us with a useful point of comparison to a non-ionic liquid. Like ⁸Li, ²H should exhibit primarily quadrupolar relaxation. Toluene is supercooled between its melting point 178 K and glass transition ~117 K, though it shows stretched exponential relaxation only below about 1.1 $T_{\rm g}$, considerably deeper into the supercooled regime than in our case, with an onset near 1.25 $T_{\rm g}$, likely due to the stronger tendency to order in the ionic liquid.

The closest analogue to our experiment is, perhaps, an early (neutron activated) ⁸Li β -NMR study in LiCl \cdot 7 D₂O.^{168,259} There, the observed temperature dependence of the SLR is qualitatively similar (see Figure 9 of Heitjans et al.¹⁶⁸): at low temperatures, the relaxation is nearly temperature independent, followed by a rapid increase above the glass transition, leading eventually to the BPP peak at higher temperatures. This behaviour was interpreted as the onset of molecular motion above ~80 K, whose characteristic correlation times reflect the diffusion and orientational fluctuations in D₂O. This is consistent with the picture outlined here, although in our more limited temperature range the relaxation can be ascribed to a single dynamical process.

At present, there are few examples of ⁸Li β -NMR in organic materials, as this application is in its infancy. Nevertheless, several trends from these early investigations have emerged, which serve as an important point of comparison. From an initial survey of organic polymers,²⁶⁰ it was remarked that resonances were generally broad and unshifted, with little or no temperature dependence. In contrast, the SLR was typically fast and independent of the proton density, implying a quadrupolar mechanism caused by the MD of the host atoms. These dynamics turned out to be strongly depth dependent, increasing on approach to a free surface¹ or buried interface.³¹ In addition to dynamics of the polymer backbone, certain structures admitted Li⁺ diffusion,²⁰² whose mobility was found to depend on the ionicity of the anion of the dissolved Li salt.²⁶¹ A few small molecular glasses have also been investigated, where the relaxation is similarly fast.²⁶²

Common to all of these studies is the non-exponential decay of the ⁸Li spin-polarization, which is well described by a stretched exponential. In these disordered materials, the "stretched" behaviour is compatible with the interpretation of a distribution of local environments, leading to an inhomogeneous SLR. Due to their high $T_{\rm g}$, the dynamics did not homogenize below the spectrometer's maximum temperature of ~315 K, unlike EMIM–Ac. This work is an important first example where the liquid state is attainable to a degree where we recover simple exponential SLR, accompanied by motional narrowing and a BPP peak.

6.4 Depth-Resolved Measurements

Depth resolved measurements are achieved in implanted-ion β -NMR by varying the incident beam energy. Collisions in the target material impact how far the implanted ⁸Li⁺ ions penetrate. This process can be modelled with a Monte Carlo (MC) simulation, for example the SRIM software.¹⁷⁷ We now focus on how varying the implantation energy modifies the bulk behaviour.



Figure 6.4.1: Temperature- and depth-resolved stretched exponential fit parameters in EMIM-Ac. (a) and (b) The stretching exponent indicates a higher degree of dynamic heterogeneity near the surface in the liquid state. Below $T_{\rm g}$ there is no significant difference. (c) and (d) Below $T_{\rm m}$, the SLR rate is faster near the surface. As a liquid, T_1 is relatively depth independent, except near the surface. The depression near $T_{\rm g}$ remains present at all depths. The data at 220 nm is the 2020 bulk data shown in Figure 6.3.2. Dashed lines are a linear interpolation to guide the eye. Solid lines are lines of best fit for Equation 6.4.1, with the corresponding data indicated with filled markers.

6.4.1 Relaxation results

As shown in Figure 6.2.1, the sample was a small droplet set into an Al plate. While the surface of this configuration has not been characterized, we may make some inferences from other RTILs. As a liquid, the surface roughness is negligible if it is similar to other imidazolium-based RTILs, where the roughness has been measured to be $\sim 3 \text{ Å}$.¹¹⁷ In the absence of surface crystallization, we do not expect this roughness to vary much. Despite its high

viscosity, the EMIM–Ac surface is surely also distorted as a result of being mounted vertically in the spectrometer. These considerations may result in distortions of the simulated implantation profiles shown in Figure 3.2.2. Additionally, the diffusion in the liquid state means that these profiles are not likely to reflect the distribution of the ⁸Li at the moment of decay, 1.21 s after implantation.¹⁷³ Over this lifetime, our PFG NMR measurements have shown that the Li displacement in the bulk is ~50 µm at 295 K. The temperature dependence of the diffusion length can be estimated with the additional consideration of the viscosity (Figure 6.3.3) and the Stokes-Einstein equation (see Appendix C.2). At temperatures below ~208 K, the diffusion length is less than 1 nm and the implantation profiles are much more likely to be accurate. Above ~214 K the diffusion length surpasses 10 nm, and depth-resolved measurements start to become a more tentative prospect.

With these caveats in mind, the spectrometer was biased to high positive potential in order to vary the beam energy from 19 keV to 0.16 keV, probing the depth dependence of the SLR in EMIM-Ac. Slight imperfections in the beam alignment, introduces a momentum transverse to the strong static magnetic field, and forces the ions to follow a circular path in the transverse plane. Varying the longitudinal momentum causes the plane of the sample to intersect the beam at different locations in this circular path, resulting in the region of implantation (the beam spot) spiralling as a function of the beam energy. The analysis of these data was the same as described in Section 6.3.1, with each implantation energy treated independently to account for a varying background component, resulting from drift in the beam spot position. The average background fraction was 4(1) %, with an average χ^2_{global} of 1.021(4). The stretched exponential fit parameters are shown in Figure 6.4.1, where the indicated depths are the mean depths as modelled by SRIM.¹⁷⁷ It is clear that varying the implantation energy introduces a large modification to both the SLR rate and the stretching exponent.

As shown in Figure 6.4.1d, the dynamics at 150 K slow as the implantation energy was lowered. Otherwise, the supercooled and glassy EMIM–Ac had a faster $1/T_1$ near the surface, on average ~15 times larger than the bulk and at most a factor of 45 larger. Surprisingly, a dependence with implantation



Figure 6.4.2: The depth-resolved fits in Figure 6.4.1 (<u>b</u> and <u>d</u>), show an increase in the length scale (x_0) attributed to the presence of the free surface as the temperature decreases. The bulk behaviour (b) traces direct measurements in the bulk, as shown in Figure 6.3.2. The surface value is reflected in a. Red curves are fits to β and those in black are for $1/T_1$.

energy was observed in the liquid phase. At these temperatures, the bulk diffusion length is an order of magnitude longer than the largest implantation depth so no depth dependence was expected. Figure 6.4.1c shows that the increase of $1/T_1$ on cooling above $T_{\rm g}$ is less apparent closer to the surface.

The temperature and implantation energy dependence of the stretching exponent, β , is shown in Figures 6.4.1a and 6.4.1b. In the former, as the implantation energy decreased, the step-like emergence of dynamical heterogeneity was less pronounced as β became small (~0.5) and surprisingly temperature-independent near the surface. In the latter figure, β decreases near the surface at all temperatures when possible: at 215 K and below, the bulk value of β approximately equalled the surface value of ~0.5.

Poor resolution about the BPP peak prohibited a well-defined fit of the VFT model which was applied to the bulk temperature dependence in Section 6.3. Our data collection strategy focused on the depth-dependence of $1/T_1$ and β , which were each modelled with an exponential weighted by the implantation profile:

$$f(E) = \frac{\int dx \left(a \exp(x/x_0) + b\right) \Pr(E, x)}{\int dx \Pr(E, x)},$$
(6.4.1)

where $\Pr(E, x)$ is a skew normal best fit to the implantation depth profile for initial beam energy E (see Equation 3.2.1 and Figure 3.2.2). In the absence of post-implantation diffusion, this weighting would account for the increasing width of the implantation profile at larger energies (see Figure 3.2.2). The free fit parameters were a, b, and x_0 . Fits to β excluded temperatures at which the trend is mostly flat (low temperature); and fits to $1/T_1$ excluded the temperatures above $T_{\rm m}$, which had amplitudes whose absolute magnitude was incredibly large, likely due to a small plateau region near the surface. The resulting fits are indicated in Figure 6.4.1 as the solid lines, and the fitted data by solid markers. The parameters of the exponential depth-dependence are drawn in Figure 6.4.2.

As expected, the parameter b in Equation 6.4.1 simply traces the bulk values shown in Figure 6.3.2. The x_0 of both fit parameters shows an increase in the length scale attributed to the free surface below $T_{\rm m}$. In the liquid state, $x_0^{(\beta)}$ is tentatively constant. Curiously, the surface effect on β persists for nearly a order of magnitude further than that of the SLR rate. In summation with b, the parameter a indicates the value of T_1 or β at the surface. The surface value of $1/T_1$ is large and decreases with temperature. In contrast, the surface value of β is unphysically negative. This is attributed to the small near-surface region where β is constant, which was also omitted from the fit.

Implanting to 2.5 nm (not shown) shows markedly different behaviour from the rest of the near-surface measurements. At this depth, the SLR more closely resembles the SLR in the bulk than other measurements near the surface. Despite the experiments in aPS and poly(ethylene oxide) (PEO), materials of similar density, which showed that backscatter (a reflection of the particles at the material surface due to low implantation energy) should be negligible, even at this implantation energy,³¹ the SRIM simulations in Figure 3.2.2 suggest that this may not be the case for the lowest implantation energies in EMIM–Ac. While the backscatter at larger implantation energies (i.e., those presented) results in significantly less backscatter, at a level comparable to aPS, it may nonetheless be a contributing factor in the other depth-resolved measurements as well. Given the difficulty of these low-energy measurements, and the complicated surface of the EMIM–Ac droplet, further inquiry is needed to confirm the location of the ⁸Li at the moment of decay.

6.4.2 Discussion

At the two temperatures above $T_{\rm m}$, both the stretching exponent and SLR rate show a clear modification near the surface (Figures 6.4.1b and 6.4.1d). Given that the EMIM–Ac was in the liquid state and diffusion was fast, this is extremely surprising. These trends in $1/T_1$ and β are clear and reproducible as functions of implantation energy at nearby temperatures. Similarly, the temperature dependence of these quantities is clearly an evolution of other neighbouring implantation depths. Regardless of the beam energy, the diffusion in the liquid state should ensure that the ⁸Li⁺ samples the entire scanned depth (and more) before it decays. This case is exemplified in the Lithium-ion conductor PEO, where no depth dependence was found.^{31,202} In contrast, here we observe that β is affected nearly 50 nm from the surface, and a slight depth dependence to T_1 as well.

There are a number of possible explanations for this. One such hypothesis is that diffusion is slowed near the surface. We can estimate the effect of the surface on the measured dynamics by considering that Figure 6.4.1c shows a significant distinction emerging in the depth-resolved SLR rates below T = 250 K. If surface mobility were slowed by an equivalent amount, such that one would expect some depth resolution in the liquid state, one would expect an order of magnitude decease in $1/T_1$ (corresponding to a factor of 60 reduction in the bulk microscopic correlation time). While the observed decrease in Figure 6.4.1c is merely a factor of two, there is some precedent for this hypothesis in the literature. Two-dimensional infrared spectroscopy measurements in RTILs thin films showed that dynamics become slower with decreasing film thickness.¹²¹ They also found that the correlation length for these dynamics is 28(5) nm, a similar length scale to that of the stretching exponent in Figure 6.4.2. While it was later found that these dynamics were likely dominated by interactions with the functionalized substrate,¹²² they still observed slower-than-bulk dynamics with a neutral substrate. In their thickest film $(278 \,\mathrm{nm})$, the depression of the dynamics was a factor of 2–3 slower than the bulk,¹²¹ and the surface dynamics would need be to much slower to achieve this film-averaged effect. Although the thinner films employed by Nishida et al.¹²¹ (> 14 nm) show a sufficient decrease of dynamics to account for the change in diffusion, it is not clear how much of this must be attributed to the strongly interacting substrate, rather than the surface. Despite this, it may not be unreasonable to suggest that the surface induces slower dynamics in the liquid state. This may also be inferred from MD simulations which show a region of enhanced density within $\sim 1 \text{ nm}$ of the surface.^{105,109,113} As a function of temperature, β near the surface is nearly constant, with a magnitude similar to the glassy state, and the relaxation rate is reduced, yet clearly faster than glassy dynamics. The origin for such dynamical slowing and heterogeneity may be the molecular orientational ordering at the surface.¹⁰⁸⁻¹¹²

Another possibility is that dynamics are uniform throughout the liquid state and the apparent relationship with implantation energy is a techniquerelated phenomenon. The simulations in Figure 3.2.2 predict that the degree of backscattering in EMIM–Ac is comparable to aPS, even at the lowest energies presented in Figure 6.4.1. However, if this were the case, one might expect that the length scales attributed to β and T_1 would be similar, as is the case in aPS.¹ Furthermore, this phenomenon was not observed at lower temperatures, where the increase in $1/T_1$ is smooth and β is largely depth-independent. The resonance linewidth and shift may prove to be very insightful to identify the source of the implantation energy dependence. If the narrow resonance peak in EMIM–Ac can be traced to the surface, we can be confident that the SLR signal is a result of EMIM–Ac dynamics.

A small plateau, approximately 15 nm thick, is present in both T_1 and β

near the surface in the liquid state (Figure 6.4.1b). While X-ray diffraction patterns in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) show evidence of incomplete surface crystallization well above $T_{\rm g}$,¹¹⁸ it is not clear whether these nanocrystalline domains would form in EMIM–Ac; these structures were only observed after annealing in a dry environment. It is, however, possible that some crystalline domains may emerge after surface exposure to ultra-high vacuum (UHV) and thermal cycling. In BMIM-PF₆, it was observed that four layers of these quasi-two-dimensional crystals formed at the surface, each ~1 nm thick (the size of one imidazolium ring and one PF₆-anion). It was proposed that butyl chains fill the interstitial space between the layers.¹¹⁸ The ethyl chains in EMIM–Ac are slightly shorter, and the Ac anion smaller, so any quasi-two-dimensional crystalline formations would presumably have a closer packing of thinner layers.

Figure 6.4.1d shows that the SLR rate at temperatures in the range of 185 K to 240 K was faster near the surface. These are all below the estimated $T_{\rm m},$ and are either in the glass or supercooled liquid state. Below ~ 210 K, diffusion is reasonably slow enough to be confident that the ⁸Li⁺ remains at its stopping site after implantation, $\pm 1 \,\mathrm{nm}$. At 240 K however, the expected diffusion is on the scale of a micrometer. Despite this longrange diffusion, the depth dependence of $1/T_1$ at this temperature is similar to that at 185 K, which has negligible diffusion. This suggests that the Stokes-Einstein extrapolation must underestimate the reduction of diffusion in EMIM-Ac with temperature. If this is the case, the deviation at 240 K would be large, with a difference of nearly three orders of magnitude. The significance of this discrepancy must diminish as the temperature is lowered and diffusion drops well below the 1 nm threshold. In contrast to the SLR rate, Figure 6.4.1b shows that β at 240 K is almost identical to the higher temperature measurements. This shows that as the RTIL is cooled, dynamics are slowed first and dynamical heterogeneity emerges second, and that the temperature lag between these two signatures is large. This temperature lag is also evident from Figures 6.4.1a and 6.4.1c, if much less obvious at first glance. Enhanced surface dynamics in the supercooled and glassy state, and a length scale which increases on cooling towards $T_{\rm g}$ (shown in

Figure 6.4.2), are consistent with well-studied polymer glasses.^{12,15,24} That the opposite appears to be the case at 150 K is remarkable. As with the surface measurements at 300 K, depth-resolved resonance measurements would be extremely important to verify this finding.

An X-ray reflectivity study showed that the surface roughness of two RTILs (including BMIM-PF₆) were well described by capillary wave theory.¹¹⁷ While a continuum theory, it has shown to be a good predictor of the surfaces of many liquids to a molecular level.^{263–265} These capillary waves are highly dependent on the surface tension, which is in turn highly sensitive to the presence of impurities,¹¹⁷ which may in turn indicate that the surface dynamics are highly impurity-sensitive as well. The purification of RTILs is a difficult process,²⁶⁶ and future studies of surface dynamics in RTILs may need to control for compositional purity and concentration of the LiCl, which may be considered as an impurity in this regard.

6.5 Conclusion

We report the first measurements of ⁸Li β -NMR in the ionic liquid 1-ethyl-3methylimidazolium acetate. Our results demonstrate that the quadrupolar interaction does not hinder our ability to follow the β -NMR signal through both the liquid and glassy state. We observed clear motional narrowing as the temperature is raised, accompanied by enhanced spin-lattice relaxation, whose rate is maximized at room temperature. From an analysis of the temperature dependent SLR rate, we extract an activation energy and VFT constant for the solvation dynamics, which are in relatively good agreement with the dynamic viscosity of (bulk) EMIM-Ac. We measure an upper bound to the quadrupole coupling constant, $eQV_{zz}/h \leq 67.8(4)$ kHz. At low temperatures near $T_{\rm m}$, the resonance is broad and intense, reflective of our sensitivity to slow heterogeneous dynamics near the glass transition. In this temperature range, the form of the relaxation is well-described by a stretched exponential, again indicative of dynamic heterogeneity. These findings suggest that ⁸Li β -NMR is a good probe of both solvation dynamics and their heterogeneity.

Diffusion at high temperature was expected to eliminate any implantation energy dependence of both T_1 and β . In the liquid state, the observed depth dependence suggests that the surface has inhibited dynamics. While it is possible that this is a technique-related systematic, such as backscattering, the scale over which this effect persists and the lack of observed backscattering present in materials of similar density, not to mention EMIM–Ac in the glassy state, implies that this should be a relatively small effect. Rough estimates of the diffusion from the viscosity suggest that the diffusion is large enough even in the supercooled liquid state that the energy dependence should not be observed. Despite this, the trend at these temperatures is consistent and comparable to those where diffusion is negligible. This implies that a Stokes-Einstein extrapolation overestimates the diffusion in the supercooled liquid state.

These trends show that at low temperature, a region of enhanced shortrange dynamics exists near the free surface, increasing in size as the temperature decreases, as might be expected from the behaviour in polymer glasses. The data presented here would benefit greatly from depth-resolved resonance measurements. Identification of the resonance peak would resolve questions pertaining to backscatter and dynamics near the surface. This would also help verify the inconsistent trend with depth at 150 K. While we were able to make a prediction of the diffusion, a clear measurement of when diffusion becomes negligible is needed. These findings show that β -NMR is a useful probe of surface dynamics in EMIM–Ac, despite the additional work needed to better understand the effect of diffusion on the implantation.

Chapter 7

Concluding Remarks

We have conducted depth-resolved studies of two very different glass-forming materials: atactic polystyrene (aPS), a polymer, and 1-ethyl-3-methylimidazolium acetate (EMIM-Ac), a room temperature ionic liquid (RTIL). In the former we employed molecular dynamics (MD) simulations described in Chapter 4, whereas in the latter we have used implanted-ion ⁸Li⁺ β -detected nuclear magnetic resonance (β -NMR) experiments, as discussed in Chapter 6. In Chapter 5 we described the spectrometer modifications needed to extended its upper temperature limit, enabling future comparison between β -NMR and MD simulations in aPS.

The free surface of glasses has long been a topic of intense study, and has been highlighted as important for developing a complete picture of the physics of glasses. In contrast to MD simulations, which are heavily employed in the study of amorphous materials, and despite its potential to reveal interfacial effects, implanted-ion β -NMR has been greatly underutilized in understanding glassy interfaces. Studying polymer films with this technique was a sensible place to start given the incredible amount of scrutiny directed at these materials in the past quarter century. However, as they are out-of-equilibrium materials, glasses are sensitive to many factors other than chemical makeup. The prior thermal limitations of the β -NMR spectrometer meant that each polymer film studied was vitrified off-site and had a different thermal history, making reproducibility much more difficult. In contrast, RTILs have an extremely low glass transition temperature and in situ vitrification was achievable with the β -NMR cryostat. This enables β -NMR measurements in these materials to result from a tightly controlled and reproducible glassy state. While both materials are amorphous solids at low temperature, the mechanics of their dynamics are necessarily quite different. The dynamics of aPS are heavily modified by inter- and intra-chain interactions, whereas the RTIL dynamics are dominated by long-range Coulomb forces and the low symmetry of the molecular ions. Despite this, we revealed that the free surface modifies the dynamics of both materials on a nanometer scale.

Using a united-atom model of short-chain aPS, our MD simulations have probed the nature of both the backbone and phenyl side group dynamics in a free standing thin film. We showed that the depth-dependence of the correlation time τ_c can be factored into a temperature-independent coupling exponent, and that the temperature dependence is entirely dictated by the bulk behaviour. Such a factorization was justified from a cooperative string model,²³ and from a depth-dependent energy barrier for activated motion.¹³ Both rings and backbones exhibited exponential surface-induced dynamical enhancement, characterized by a temperature-independent length scale of ~1.5 nm. We also calculated the four-point dynamical susceptibility, χ_4 , whose maximum is a measure of dynamical heterogeneity. This showed that dynamical heterogeneity decreases near the free surface on a similar length scale as the dynamical coupling exponent. This work is consistent with other simulations, extending coarse grained models by introducing a greater degree of chemical specificity for aPS.

These MD simulations placeed the phenyl ring dynamics on an appropriate timescale for measurement with β -NMR. While our MD simulations showed an extraordinary agreement with deuterium NMR measurements from the literature, a direct comparison with β -NMR was not possible. Because no observation of the Bloembergen-Purcell-Pound (BPP) peak has been made in aPS for ⁸Li spin lattice relaxation, the NMR coupling constant remains in a state of high uncertainty.

Through a redesign of the forward detector, and the replacement of several components, we have extended the upper temperature range of the of the high field β -NMR spectrometer by at least 80 K. The behaviour of the radio frequency (RF) Helmholtz coil will determine the final maximum temperature. Although some final refinements are needed to ease operation at low temperature, the spectrometer is now operational up to 400 K, while maintaining the lower temperature bound of ~3.5 K. In addition to experiments with aPS, this enables many other experiments above room temperature. This may prove important for the study of magnetism in novel materials or ion diffusion in energy storage candidates.

We also demonstrated the sensitivity of the β -NMR ⁸Li spin-lattice relaxation (SLR) and resonance to the dynamics in a droplet of EMIM–Ac. As the temperature was raised, the resonance linewidth in the bulk was motionally narrowed and bulk SLR rate was increased, clearly consistent with faster dynamics. The stretching of the SLR showed a characteristic signature of the emergence of dynamical heterogeneity on approach to the glass transition. Unlike aPS, we observed a BPP peak at 298 K and were able to determine an upper bound to the NMR coupling constant, $eQV_{zz}/h \leq$ 67.8(4) kHz. From the microscopic correlation times, we extracted a Vogel-Fulcher-Tammann activation barrier and characteristic temperature in good agreement with bulk dynamic viscosity measurements from the literature. This showed that β -NMR is a good probe of both the dynamics and dynamical heterogeneity in EMIM–Ac.

We then use the depth-resolution of β -NMR to make the first characterization of the effect of the free interface on sub-surface dynamics in EMIM-Ac. At temperatures when the diffusion has been sufficiently slowed, we observed enhanced dynamics on the order of 5 nm below the surface, similar to aPS. In contrast, the dynamical heterogeneity, as indicated by the degree of exponential stretching of the SLR, was relatively depth-independent at these temperatures. In the liquid state, a near-surface depression of the SLR stretching exponent was present and reproducible despite the large expected Li diffusion length. Depth-resolved resonances will be important for verifying the results from the SLR. Near $T_{\rm g}$, the SLR rate began to increase with decreasing temperature, eventually reaching a plateau deep in the glassy state. This is clearly inconsistent with all current theories of glass formation, but has been very reproducible over multiple iterations of the experiment. Preliminary measurements of ⁷Li NMR did not show this behaviour, suggesting that this is an artifact of the technique, likely related to the dynamics immediately following ion implantation. In addition to resonance measurements, MD simulations may also prove to be insightful in understanding this phenomenon.

Much of this thesis established the foundations for future study of aPS and EMIM–Ac. Our MD simulations could be extended with a direct calculation of the four-point correlation function. Identifying if there are also lateral modifications to the dynamics may contribute to a better understanding of how the dynamical heterogeneity is modified by the free surface. With the extended temperature range, β -NMR should be used to investigate the surface dynamics of aPS near and above T_g . A search for the BPP peak in aPS is warranted, and certainly necessary for producing an accurate microscopic correlation time which could then be compared with other methods. This is extremely important for the relevance and impact of β -NMR as a technique for understanding polymeric glasses. Together, these two β -NMR studies of aPS may be extremely important for characterizing the free surface interface. Identifying the peak as a function of depth would be a well-defined, although time-consuming, method for identifying depth-resolved dynamics in aPS.¹⁶² Fully atomistic MD, or quantum chemical simulations with the inclusion of ⁸Li⁺, may also be useful in determining how the probe couples with the polymerand firmly identifying the mechanisms to which the β -NMR probe is coupled.. Our current understanding from simple density functional theory (DFT) is that there is a tight binding to pairs of phenyl rings;³¹ however, how well the probe reports local dynamics is yet unknown. This may also reveal how β -NMR is sensitive to dynamics; whether directly or via interaction with the neighbouring rings. In EMIM-Ac, many open questions naturally lead to future iterations on the results presented in this thesis. These include a determination of the temperature-resolved diffusion, important for determining the validity of depth-resolved measurements; identifying the mechanism for the depth dependence of β in the liquid state; and uncovering the reason why $1/T_1$ increases on cooling near $T_{\rm g}.$ Additionally, resonance

measurements are clearly needed to complete the picture which has begun to be unveiled by the SLR. Tracing the chemical shifts has been used to identify the coordination of ³¹Mg in similar RTILs.² Similar shifts, or lack thereof, in EMIM–Ac near the surface may reveal the nature of local ⁸Li environment. Varying the applied magnetic field or the constituent ions of the RTIL may also be important contrasting cases to the presented work. Furthermore, β -NMR may be used as a probe of nanoscale dynamics in RTIL thin films, which would be the first measurement of the dynamical gradient in any RTIL thin film.

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Appendix A

NMR Addendum

In Appendices A.1 and A.2, we expand on some of the details presented by Abragam¹⁵⁰ in order to determine the spin-lattice relaxation (SLR) rate arising from fluctuations of the electric field gradient (EFG) in a liquid or similarly disordered system. Many of the needed parts for this summary are scattered disparately throughout his book, or are not elaborated on entirely, prompting this review.

In Appendix A.3 we describe the Monte Carlo (MC) simulation algorithm used to produce the β -detected nuclear magnetic resonance (β -NMR) linewidths shown in Figure 3.2.7.

A.1 Single exponential electric quadrupole SLR

We will use the density matrix master equation of Slichter,¹⁴⁹

$$\frac{d\rho^*(t)}{dt} = -\frac{1}{\hbar^2} \int_0^t dt' \overline{\left[\left[\rho^*(0), \mathcal{H}_1^*(t')\right], \mathcal{H}_1^*(t)\right]},$$
(A.1.1)

and the quadrupolar Hamiltonian, Equation 3.1.15, to find the cases where the SLR due to quadrupole relaxation in fluids result in a well-defined singleexponential relaxation. The following discussion is an elaboration of the treatment presented in Chapter 8 of Abragam.¹⁵⁰

To preserve the focus of this Appendix, some of the mathematical details have been relegated to Appendix A.2. The first of which is the expectation value of I_z , found by multiplying Equation A.1.1 on the left hand side with I_z and applying the linear and cyclic properties of the trace:

$$\frac{d\langle I_z\rangle}{dt} = -\{\langle D\rangle - \langle D\rangle_0\},\tag{A.1.2}$$

where $\langle D \rangle = \operatorname{tr}(D\rho^*)$, $\langle D \rangle_0 = \operatorname{tr}(D\rho_0)$, and ρ^* is the average density matrix in the interaction representation: $\rho^* = e^{i\mathcal{H}_0 t}\rho e^{-i\mathcal{H}_0 t}$. We wish to write Equation A.1.2 in such a way that it resembles Equation 3.1.12 and solve for D such that we can identify the prefactor with $1/T_1$, thus extracting the single-exponential SLR rate. To do this, we use \mathcal{H}_Q (Equation 3.1.15) in the interaction picture,

$$\begin{split} \mathcal{H}_{Q}^{*}(t) &= e^{i\mathcal{H}_{0}t}\mathcal{H}_{Q}e^{-i\mathcal{H}_{0}t} \\ &= \frac{eQ}{4I(2I-1)\hbar}\sum_{p,m}V^{(-m)}A^{(m)}e^{i\omega_{p}^{(m)}t}, \end{split} \tag{A.1.3}$$

to solve for D, as shown in Appendix A.2:

$$D = \frac{1}{2} \sum_{m} \overline{|V^{(m)}|^2} \mathcal{J}_m(m\omega_0)[A^{(-m)}, [A^{(m)}, I_z]], \tag{A.1.4}$$

where \mathcal{J} is the spectral density of $V^{(m)}$. By definition,

$$\mathcal{J}_m(\omega) = \int_{-\infty}^{\infty} dt \ \langle V^{(m)}(\tau) V^{(-m)}(t+\tau) \rangle_{\tau} e^{-i\omega t}, \tag{3.1.21}$$

however in practice we shall use the Debye equation,

$$\mathcal{J}_m(\omega) = C_m \frac{2\tau_c}{1 + \omega^2 \tau_c^{\ 2}}, \qquad (3.1.22)$$

which corresponds to exponential decorrelation of the EFG components (which is independent of the nature of T_1), characterized by microscopic correlation time constant τ_c . This replacement is reasonable in the case of isotropic dynamics.

In the Principal Axis frame, Equation A.1.4 can be rewritten in the

following way:

$$D = \frac{1}{160} \left(\frac{eQ}{\hbar I (2I-1)} V_{zz} \right)^2 \left(1 + \frac{\eta^2}{3} \right) \sum_m \mathcal{J}(m\omega_L) [A^{(-m)}, [A^{(m)}, I_z]]$$
(A.1.5)

where

$$\begin{split} & [A^{(-1)}, [A^{(1)}, I_z]] = \frac{3}{2} \left\{ 16I_z^3 - I_z[8I(I+1)-2] \right\} \\ & [A^{(-2)}, [A^{(2)}, I_z]] = \frac{3}{2} \left\{ -16I_z^3 + I_z[16I(I+1)-8] \right\}. \end{split} \tag{A.1.6}$$

The comparison with Equation 3.1.12 is only possible upon the elimination of the I_z^3 term. This can be done in the case of I = 1 (when $I_z^3 = I_z$):

$$\frac{1}{T_1} = \frac{3}{80} \left(1 + \frac{\eta^2}{3} \right) \left(\frac{eQ}{\hbar} V_{zz} \right)^2 \left(\mathcal{J}(\omega_L) + 4\mathcal{J}(2\omega_L) \right), \tag{A.1.7}$$

and in the case of extreme motional narrowing, when $\mathcal{J}(\omega)=\mathcal{J}(2\omega)=2\tau_c,$ and the I_z terms cancel:

$$\frac{1}{T_1} = \frac{3}{40} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{eQ}{\hbar} V_{zz}\right)^2 \tau_c.$$
(A.1.8)

A.2 Time dependence of operators

In this Appendix we will show how T_1 is related to the spectral density of the EFG fluctuations. Our goal, in the interaction picture, to find the time dependence of $\langle I_z \rangle$. While we are interested in I_z , note that in principle this discussion is valid for any operator acting on the system governed by Hamiltonian $\mathcal{H}_1(t)$, which varies random in time. We start with density matrix master equation of Equation A.1.1:

$$\frac{d\rho^*}{dt} = -\int_0^\infty d\tau \overline{\left[\mathcal{H}_1^*(t), \left[\mathcal{H}_1^*(t-\tau), \rho^*(t)\right]\right]}$$
(A.2.1)

where we have made the assumption that $\rho^*(0) = \rho^*(t)$, made the replacement $t' \to t - \tau$, and switched both commutators.¹⁵⁰ We then act on the right with operator I_z :

$$\frac{d\rho^*}{dt}I_z = -\int_0^\infty d\tau \overline{[\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t-\tau), \rho^*(t)]]}I_z, \qquad (A.2.2)$$

and take the trace:

$$\operatorname{tr}\left\{\frac{d\rho^*}{dt}I_z\right\} = \operatorname{tr}\left\{-\int_0^\infty d\tau \overline{\left[\mathcal{H}_1^*(t), \left[\mathcal{H}_1^*(t-\tau), \rho^*(t)\right]\right]}I_z\right\}.$$
 (A.2.3)

The left hand side follows simply as

$$\operatorname{tr}\left\{\frac{d\rho^{*}}{dt}I_{z}\right\} = \frac{d}{dt}\operatorname{tr}\left\{\rho^{*}(t)I_{z}\right\}$$
(A.2.4)

$$=\frac{d\langle I_z\rangle}{dt}.\tag{A.2.5}$$

On the right hand side, we first move the trace into the integral, for now neglecting the overline denoting the ensemble average (linearity of the trace permits this):

$$\text{RHS} = -\int_0^\infty d\tau \,\text{tr}\left\{ [\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t-\tau), \rho^*(t)]] I_z \right\}. \tag{A.2.6}$$

Expanding the commutators,

$$= \operatorname{tr} \left\{ \left(\mathcal{H}_{1}^{*}(t) [\mathcal{H}_{1}^{*}(t-\tau), \rho^{*}(t)] - [\mathcal{H}_{1}^{*}(t-\tau), \rho^{*}(t)] \mathcal{H}_{1}^{*}(t) \right) I_{z} \right\}$$
(A.2.7)
$$= \operatorname{tr} \left\{ \mathcal{H}_{1}^{*}(t) \mathcal{H}_{1}^{*}(t-\tau) \rho^{*}(t) I_{z} - \mathcal{H}_{1}^{*}(t) \rho^{*}(t) \mathcal{H}_{1}^{*}(t-\tau) I_{z} \right\}$$

$$= \left\{ \mathcal{H}_{1}(t)\mathcal{H}_{1}(t-\tau)\rho^{*}(t)I_{z} - \mathcal{H}_{1}(t)\rho^{*}(t)\mathcal{H}_{1}(t-\tau)I_{z} - \mathcal{H}_{1}^{*}(t-\tau)\rho^{*}(t)\mathcal{H}_{1}^{*}(t)I_{z} + \rho^{*}(t)\mathcal{H}_{1}^{*}(t-\tau)\mathcal{H}_{1}^{*}(t)I_{z} \right\}$$
(A.2.8)

and applying the cyclic and linear properties of the trace,

$$= \operatorname{tr} \Big\{ I_z \mathcal{H}_1^*(t) \mathcal{H}_1^*(t-\tau) \rho^*(t) - \mathcal{H}_1^*(t-\tau) I_z \mathcal{H}_1^*(t) \rho^*(t) \\ - \mathcal{H}_1^*(t) I_z \mathcal{H}_1^*(t-\tau) \rho^*(t) + \mathcal{H}_1^*(t-\tau) \mathcal{H}_1^*(t) I_z \rho^*(t) \Big\}$$
(A.2.9)

we are able to factor out the density matrix, and combine what's left back into commutator notation:

$$= \operatorname{tr} \left\{ \left(I_{z} \mathcal{H}_{1}^{*}(t) \mathcal{H}_{1}^{*}(t-\tau) - \mathcal{H}_{1}^{*}(t-\tau) I_{z} \mathcal{H}_{1}^{*}(t) - \mathcal{H}_{1}^{*}(t) I_{z} \mathcal{H}_{1}^{*}(t-\tau) + \mathcal{H}_{1}^{*}(t-\tau) \mathcal{H}_{1}^{*}(t) I_{z} \right) \rho^{*}(t) \right\}$$
(A.2.10)

$$= \operatorname{tr}\left\{ \left(I_{z} \mathcal{H}_{1}^{*}(t) - \mathcal{H}_{1}^{*}(t) I_{z} \right) \mathcal{H}_{1}^{*}(t-\tau) - \mathcal{H}_{1}^{*}(t-\tau) \left(I_{z} \mathcal{H}_{1}^{*}(t) - \mathcal{H}_{1}^{*}(t) I_{z} \right) \rho^{*}(t) \right\}$$
(A.2.11)

$$= \operatorname{tr}\left\{\left([I_z, \mathcal{H}_1^*(t)]\mathcal{H}_1^*(t-\tau) - \mathcal{H}_1^*(t-\tau)[I_z, \mathcal{H}_1^*(t)]\right)\rho^*(t)\right\}$$
(A.2.12)

$$= \operatorname{tr} \Big\{ \Big([[I_z, \mathcal{H}_1^*(t)], \mathcal{H}_1^*(t-\tau)] \Big) \rho^*(t) \Big\}.$$
 (A.2.13)

For consistency with Abragam, 150 we again switch the order of both commutators,

$$= \operatorname{tr} \Big\{ [\mathcal{H}_{1}^{*}(t-\tau), [\mathcal{H}_{1}^{*}(t), I_{z}]] \rho^{*}(t) \Big\}.$$
(A.2.14)

Combining the two sides, we have that

$$\frac{d\langle I_z\rangle}{dt} = -\int_0^\infty d\tau \operatorname{tr}\left\{ [\mathcal{H}_1^*(t-\tau), [\mathcal{H}_1^*(t), I_z]]\rho^*(t) \right\}$$
(A.2.15)

$$= -\text{tr}\left\{\int_{0}^{\infty} d\tau \left[\mathcal{H}_{1}^{*}(t-\tau), [\mathcal{H}_{1}^{*}(t), I_{z}]\right]\rho^{*}(t)\right\}$$
(A.2.16)

$$= -\text{tr} \{ D\rho^*(t) \}, \qquad (A.2.17)$$

where, re-introducing the overline which was dropped,

$$D = \int_0^\infty d\tau \ \overline{\left[\mathcal{H}_1^*(t-\tau), \left[\mathcal{H}_1^*(t), I_z\right]\right]}.$$
 (A.2.18)

With the replacement $\rho^*(t) \rightarrow \rho^*(t) - \rho^*(0),$

$$\frac{d\langle I_z\rangle}{dt} = -\Big(\langle D\rangle - \langle D\rangle_0\Big). \tag{A.2.19}$$

If $F^{(q)}(t)$ are functions containing the randomness attributed to \mathcal{H}_1 , and $A^{(q)}$ are stationary operators, then we can write the Hamiltonian as

$$\mathcal{H}_1(t) = \sum_q F^{(q)}(t) A^{(q)}.$$
 (A.2.20)

By comparison with Equation 3.1.15, we note that these $F^{(q)}$ are simply the time dependent EFG terms in Equation 3.1.16. In the interaction picture, this is

$$\mathcal{H}_1^*(t) = e^{i\mathcal{H}_0 t} \mathcal{H}_1 e^{-i\mathcal{H}_0 t}$$
(A.2.21)

$$=\sum_{p,q} F^{(q)}(t) A_p^{(q)} e^{i\omega_p^{(q)}t}.$$
 (A.2.22)

Plugging this into D, yields

$$\begin{split} D &= \int_{0}^{\infty} d\tau \; \overline{[\mathcal{H}_{1}^{*}(t-\tau), [\mathcal{H}_{1}^{*}(t), I_{z}]]} & (A.2.23) \\ &= \int_{0}^{\infty} d\tau \; \overline{\left[\sum_{p,q} F^{(-q)}(t-\tau) A_{p}^{(-q)} e^{i\omega_{p}^{(-q)}(t-\tau)}, \left[\sum_{p,q} F^{(q)}(t) A_{p}^{(q)} e^{i\omega_{p}^{(q)}t}, I_{z}\right]\right]}. \end{split}$$

$$(A.2.24)$$

Factoring and noting that $\omega^{(-q)} = -\omega^{(q)}$,

$$=\sum_{p,q} [A_p^{(-q)}, [A_p^{(q)}, I_z]] \int_0^\infty d\tau \ \overline{F^{(q)}(t)} F^{(-q)}(t-\tau) e^{i\omega_p^{(q)}\tau}, \tag{A.2.25}$$

and recognizing $\mathcal{J}_q(\omega)\equiv\int_{-\infty}^\infty d\tau\ \overline{F^{(q)}(t)F^{(-q)}(t+\tau)}e^{-i\omega\tau}$ as the spectral density,

$$D = \frac{1}{2} \sum_{q} \mathcal{J}_{q}(\omega_{p}^{(q)})[A^{(-q)}, [A^{(q)}, I_{z}]].$$
(A.2.26)

A.3 Simulating linewidths

Here we simulate the motional narrowing due to a randomly fluctuating local field, using the classical theory developed in Section 3.1.2. The MC simulation will follow the simplified model as outlined below:

- In the rotating reference frame, let B₀ be the static field along k̂ and B₁ be the radio frequency (RF) field along î. The frame rotates with angular frequency ω, the frequency of the applied RF.
- The randomly fluctuating local field \mathbf{B}_{ℓ} is constant between discrete fluctuations and is aligned with \hat{z} .
- The duration of each \mathbf{B}_{ℓ} step is distributed exponentially with a mean of τ_c , and the magnitude of the local field is drawn from a Gaussian distribution with width ΔB_{ℓ} and mean of zero.

Therefore, between discrete jumps of \mathbf{B}_{ℓ} , the system propagates as if in the static case, with effective field \mathbf{B}_{eff} , as given by Equation 3.1.8 (where $B_0 \rightarrow B_0 + B_{\ell}$). The polarization as a function of time is therefore given by

$$\mathbf{P}(t) = \begin{cases} R_0 \mathbf{P}_0 & 0 < t < t_1 \\ R_1 R_0 \mathbf{P}_0 & t_1 < t < t_2 \\ \vdots \\ R_i R_{i-1} ... R_0 \mathbf{P}_0 & t_i < t < t_{i+1} \end{cases}$$
(A.3.1)

where R_i is the rotation matrix in the rotating reference frame. Any $R(t, B_{\text{eff}})$ can be found by rotating the frame such that B_{eff} is along \hat{z} , precessing the
spin about $B_{\rm eff},$ then rotating back to the original frame:

$$\begin{split} R(t,B_{\rm eff}) &= \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} \cos(\gamma B_{\rm eff}t) & -\sin(\gamma B_{\rm eff}t) & 0 \\ \sin(\gamma B_{\rm eff}t) & \cos(\gamma B_{\rm eff}t) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \\ & (A.3.2) \end{split} \\ &= \begin{pmatrix} \sin^2\theta + \cos^2\theta\cos(\gamma B_{\rm eff}t) & -\cos\theta\sin(\gamma B_{\rm eff}t) & \cos\theta\sin\theta[1 - \cos(\gamma B_{\rm eff}t)] \\ \cos\theta\sin(\gamma B_{\rm eff}t) & \cos(\gamma B_{\rm eff}t) & -\sin\theta\sin(\gamma B_{\rm eff}t) \\ \cos\theta\sin\theta[1 - \cos(\gamma B_{\rm eff}t)] & \sin\theta\sin(\gamma B_{\rm eff}t) & \cos^2\theta + \sin^2\theta\cos(\gamma B_{\rm eff}t) \end{pmatrix} . \end{split}$$

Here, $\boldsymbol{\theta}$ is the angle between \hat{k} and $\mathbf{B}_{\mathrm{eff}},$ given by

$$\cos \theta = \frac{\left(B_0 + B_\ell - \frac{\omega}{\gamma}\right)}{B_{\text{eff}}} \qquad \sin \theta = \frac{B_1}{B_{\text{eff}}}.$$
 (A.3.4)

The procedure is then as follows:

- 1. Choose values for ΔB_{ℓ} , ω , and τ_c .
- 2. Find the mean trajectory $\langle \mathbf{P}(t) \rangle$ using Equation A.3.1.
- 3. Weight the mean trajectories with the exponential probe decay probability.
- 4. Numerically integrate.

The result is shown in Figure 3.2.7, using $\gamma \Delta B_{\ell} = 6 \text{ kHz}$ and $B_1 = 0.1 \text{ T}$; and integrating over 4 s with a resolution of 0.1 s.

Appendix B

High-Temperature Operation Addendum

In Appendix B.1 we list the translational shifts needed to properly compare our molecular dynamics (MD) simulation results from Chapter 4 to the nuclear magnetic resonance (NMR) literature. In Appendix B.2 we provide a description of the experimental and analysis details for the unpublished β -detected nuclear magnetic resonance (β -NMR) measurements in Chapter 5.

B.1 Comparing MD simulations to literature NMR

In Chapter 5, we compared the simulation results from Chapter 4 to literature NMR measurements taken by He et al.¹⁴⁸ in 2004. Due to differences in sample preparation, resulting quantity (our simulations are on films, the literature data is on a macroscopic quantity), and likely some model inaccuracy, some small translational shifts were needed to make a clean comparison. The resulting translated and shifted MD simulation data are presented in Figure 5.1.1. The translations needed for each of the curves are presented in Table B.1.1.

		Field (MHz)	$\Delta T_1 \ (\mathrm{ms})$	$\Delta T \left(\mathrm{K} \right)$
$\mathrm{d}_8 \; \mathrm{PS-2}$	Ring	46.1	0.7(2)	-23(2)
		76.8	1.4(4)	-26(2)
	Backbone	46.1	1.6(2)	-31(2)
		76.8	2.6(4)	-35(2)
d ₈ PS-11	Ring	46.1	0.5(2)	10(2)
		76.8	0.7(4)	9(2)
	Backbone	46.1	1.2(2)	2(2)
		76.8	2.2(4)	-2(2)

Table B.1.1: A translational shift was needed in both time and temperature for the trend in the MD data to align with the NMR measurements. Shifted MD data from Chapter 4, translated to SLR times are shown in Figure 5.1.1.

B.2 Experimental details of β -NMR measurements in aPS

In Chapter 5, we converted a series of β -NMR spin-lattice relaxation (SLR) measurements in atactic polystyrene (aPS) to a microscopic correlation time in order to compare with MD simulations. The sample used in this case was a fully deuterated 104 kg/mol thin film of aPS (Polymer Source). The film was spin coated 200 nm thick onto a polished Al₂O₃ substrate by the group of J. Forrest at The University of Waterloo approximately one week prior the experiment. The thickness and surface roughness was verified with ellipsometry by the same group. A pulsed beam of 4s was used to measure the SLR at various temperatures and implantation depths. The Rb cell was manually biased to 8.08 kV to lower the beam energy approaching the platform. The platform was then biased to adjust the final beam energy.

Figure B.2.1 shows the SLR at various depths and temperatures. These curves are fit with a stretched exponential, Equation 3.2.27, with a χ^2_{global} of 0.99, although no parameters were shared between runs. The minimization was performed with the Python3 packages described in Appendix D. The effect, especially in comparison to the room temperature ionic liquid (RTIL)



Figure B.2.1: SLR measurements and fits in aPS for <u>(left)</u> constant temperature and <u>(right)</u> constant implantation depth. In both cases the effect is rather subtle and the stretching plays a large role in differentiating the relaxation.

presented in this thesis (see Figure 6.3.1), is rather subtle. The stretching plays a large role in differentiating the curves. Since T_1 and β are highly correlated, and the difference in T_1 between the runs is small, we average T_1 over the Kohlrausch-Williams-Watts (KWW) distribution defined by the stretching exponent β :^{155,267}

$$T_1^{(\text{avg})} = \frac{T_1}{\beta} \Gamma\left(\frac{1}{\beta}\right), \qquad (B.2.1)$$

where Γ is the gamma function. It is this $T_1^{(avg)}$ that is eventually converted to a microscopic correlation time and compared with the MD simulations. This is a valid operation, assuming that the relaxation is fundamentally exponential, with relaxation times distributed according to the KWW distribution.

Appendix C

IL Addendum

In this addendum we elaborate on the analysis details of the sample holder background, which is important for future studies with ionic liquids (Appendix C.1). In Appendix C.2 we show the estimate of the diffusion length of Li in 1-ethyl-3-methylimidazolium acetate (EMIM-Ac) as a function of temperature. Subsection Appendix C.3 shows how the temperature dependence of the resonance peak height may be described as the joint effects of motional narrowing and non-relaxing background component.

C.1 Sample holder background

The temperature dependence of the spin-lattice relaxation (SLR) in the Al sample holder was measured in order to properly account for the signal background. While our prior work assumed a root exponential,¹⁰³ $p_b(t,t') = \exp\left\{-[\lambda_b(t-t')]^{0.5}\right\}$, a phenomenological choice given the disorder in the Al alloy, a bi-exponential fit was shown to produce a better fit:

$$p_b(t,t') = f_{\rm fast} \exp\left\{-\lambda_b^{\rm fast}(t-t')\right\} + (1-f_{\rm fast}) \exp\left\{-\lambda_b^{\rm slow}(t-t')\right\} \ ({\rm C.1.1})$$

where $f_{\rm fast}$ is the fraction of the signal attributed to the fast component and was found to be about 7%. As shown in Figure C.1.1, the slow component was nearly linear with temperature (as expected from the Korringa law: $\lambda \propto T$), but was better described by the power law $10^{-5}T^{1.7} + 0.077$. In



Figure C.1.1: Slow (left) and fast (right) components from a bi-exponential fit to the SLR in the Al sample holder. The fast component comprised only 7% of the background signal.

contrast, the fast component was described by the Korringa law, despite the high degree of scatter in the measurement, noting that this component had an exceedingly small contribution to the final signal. As determined from a shared parameter fit, the signal in the bulk room temperature ionic liquid (RTIL) had background contributions of 2 % in 2017, 3 % in 2019, and ~ 0 % in 2020. These contributions are largely determined by the size and positioning of the beam spot.

C.2 Diffusion lengths

The diffusion coefficients for Li and H in EMIM–Ac with 25 mM of LiCl were measured to be $D_{\rm Li} = 3.46(11) \times 10^{-10} \,\mathrm{m^2 s^{-1}}$ and $D_{\rm H} = 3.61(7) \times 10^{-10} \,\mathrm{m^2 s^{-1}}$ at 295 K by pulsed field gradient (PFG) nuclear magnetic resonance (NMR) in Chapter 6. The diffusion length can be calculated using Equation 48 of Bloembergen et al.:²⁴⁶ $r = \sqrt{6\tau D}$. The Stokes-Einstein equation,

$$D = \frac{k_B T}{6\pi\eta a},\tag{C.2.1}$$

which relates this diffusion coefficient, D, to the viscosity η at temperature T, given some length of closest approach a.²⁴⁶ In Figure 6.3.3, we show a compilation of the viscosity from the literature, and fit it with the Vogel-



Figure C.2.1: Estimated diffusion lengths in EMIM–Ac as a function of temperature. The black dot indicates the measured diffusion, whereas the line indicates the estimated temperature dependence from the viscosity in Figure 6.3.3. Shading indicates the error in this estimation, resulting from conventional uncorrelated error propagation.

Fulcher-Tammann (VFT) equation to determine the temperature dependence. From our above measurements of D at 295 K, and the viscosity VFT fit, we are able to calculate $a_{\rm Li} = 3.7(6)$ pm. This is much smaller than the Li covalent radius of 128(9) pm,²⁶⁸ and also the ionic radius of Li⁺ of 60 pm,²⁶⁹ both measured from crystallographic data. Despite this, we can use this value to make a rough prediction the diffusion lengths in the ⁸Li lifetime, 1.21 s, as shown in Figure C.2.1.

C.3 Reduction in normalized peak height

The reduction of the normalized peak height in Figure 6.3.6 may be described by the competing effects of motional narrowing and a non-relaxing background, attributed to the Al sample holder.

Suppose, first, that the SLR relaxation function is a simple exponential. As shown in Chapter 6, this is not the case, but it is a useful simplifying assumption since the polarization can be solved analytically, whereas the stretched exponential treatment requires a numerical solution. From Equation 3.2.6, if $p(t',t) = p_0 \exp[-(t-t')/T_1]$, then the steady-state implantation-averaged polarization at large times is

$$\lim_{t \to \infty} \mathcal{P}(t) = p_0 \left(\frac{T_1}{\tau + T_1} \right), \tag{C.3.1}$$

where τ is the nuclear lifetime of the probe, T_1 is the SLR relaxation time, p_0 is the initial polarization at the time of implantation. Consider now the measured asymmetry arising from a relaxing signal component due to the RTIL, $A_s(t)$, and a non-relaxing background component, $A_b(t)$, which may attributed to the Al sample holder:

$$A_s(\infty) = A_s(0) \left(\frac{T_1}{\tau + T_1}\right) \tag{C.3.2a}$$

$$A_b(\infty) = A_b(0). \tag{C.3.2b}$$

We now make the further simplifying assumptions that when the applied radio frequency (RF) field is on-resonance, the polarization from the signal fraction is completely destroyed. The remaining signal on-resonance may then be completely attributed to the non-relaxing background. When far off-resonance, both signal and background components are measured:

$$A_{\rm on} = A_b(\infty) \tag{C.3.3a}$$

$$A_{\rm off} = A_s(\infty) + A_b(\infty). \tag{C.3.3b}$$

The normalization applied to the peak height in Figure 6.3.6 is such that the height is one when polarization is fully destroyed, and zero when far off-resonance. Effectively,

$$A_{\text{norm}} = \frac{A_{\text{off}} - A_{\text{on}}}{A_{\text{off}}} = \frac{1}{1 + \frac{A_b(0)}{A_s(0)} \left(1 + \frac{\tau}{T_1}\right)}.$$
 (C.3.4)

The temperature dependence of T_1 can be found from the fits of Equations 3.1.22, 6.3.1 and 6.3.2 to the SLR data in Figure 6.3.2; τ is a fixed property of the probe nucleus; and $A_b(0)/A_s(0)$ is determined by the beam alignment with the sample, and will be treated as a fit parameter.

While this describes changes to the normalized peak height as a consequence of the temperature-dependent T_1 , we must also account for the increase in height due to motional narrowing. The red line in the top panel of Figure 6.3.6, denoted in the main text as a guide to the eye, is the following phenomenological description for the motional narrowing in solids:²⁷⁰

$$\sigma(T) = \frac{c_1}{1 + (\frac{c_1}{c_2} - 1)\exp(-c_3/k_BT)} + c_4, \tag{C.3.5}$$

where σ is the Lorentzian linewidth defined in Equation 3.2.28. The parameters c_1 , c_2 , and c_3 respectively describe the static linewidth, the motionally narrowed linewidth, and the energy required for activated motion. The inclusion of c_4 is a line-broadening term. While the applicability of this formulation is questionable in the case of β -detected nuclear magnetic resonance (β -NMR) and in amorphous materials, as will be evident by poor agreement of the fit values with our expectations, it appears to describe the full width at half maximum (FWHM) qualitatively well. When normalized to unity area, it is clear from Equation 3.2.28 that the Lorentzian height is proportional to $1/\sigma$. We can then use Equation C.3.5 to describe the functional form of the motional narrowing and extract the resulting variation in the peak height.

Normalizing by the high-temperature limit, $\lim_{T\to\infty} \sigma(T) = c_2 + c_4$, we take the product of $1/\sigma$ with Equation C.3.4 to describe the effects of both motional narrowing and a non-relaxing background component. The parameters c_i and the fraction $A_s(0)/A_b(0)$, are all fit parameters. The result of this fit is shown in Figure C.3.1. We find that $c_1 = 5(2)$ kHz, $c_2 =$ 2.89(4) fHz, $c_3 = 336(2)$ meV, $c_4 = 41(4)$ nHz, and $A_s(0)/A_b(0) = 4.41(9)$ %. We note that these parameters are either unreasonable or not what would be expected from Figure 6.3.6, and additionally, the activation energy does not compare favourably with that found from the SLR. In contrast, this treatment resulted in a ~4% non-relaxing background component, which is



Figure C.3.1: The temperature dependence of the normalized peak height may be described as the result of two competing effects: the motional narrowing and a small non-relaxing background component. This background was found to comprise 4% of the measured asymmetry, in good agreement with that found from the SLR (3%).

highly comparable to the $3\,\%$ found from the analysis of the SLR.

Despite these differences, however, the functional form of Equation C.3.5 appears to do a modestly good job of describing the increase in peak height due to motional narrowing, as shown in Figure C.3.1. It might be expected that a more rigorous treatment of this phenomenon would result in a better fit. The modelling of the background fraction, by comparison, appears to produce excellent results.

Appendix D

Software

 β -detected nuclear magnetic resonance (β -NMR) and muon spin rotation, relaxation, and resonance (μ SR) data taken at TRIUMF is saved in the muon data (MUD) file format.²⁷¹ The format was developed in 1994 as an efficient, lightweight, and self-describing means of storing μ SR data. The application programming interface (API) is written in C and FORTRAN. These staticallytyped and compiled languages are known for their computational efficiency, but can be difficult to work with. This is perhaps one of the reasons why scientific computing has, in many communities, shifted to more modern languages such as Python: a dynamically-typed and interpreted language. As a result, Python has amassed a massive library of data analysis tools.^{272,273} The primary advantage of Python is the short development time of programs written in the language. This is particularly important in the context of scientific analysis, which are typically run only a few times by select individuals. As a result, the time taken to write the analysis code is a large part of the program's effective run time. The aim of this work is to bring this rapid prototyping style of analysis to the μ SR and β -NMR communities.

D.1 mudpy

The goal of the mudpy package is to provide a simple and intuitive means of interfacing with MUD files in Python, regardless of their contents. To accom-

plish this, the package primarily describes two main modules: mud_friendly and mdata. The mud_friendly module contains a one-to-one set of low-level Cython²⁷⁴ functions wrapping those in the original mud_friendly distribution, written in C by Jess H. Brewer and Donald Arseneau. The MUD source code is included in mudpy, as it lacks an automated method for distribution. The mdata module describes the mdata object, which automates the reading of the MUD file using the functions in the mud_friendly module. Once the MUD file is read into memory, its attributes are easily accessible.

MUD files store data of five different types: descriptions, histograms, independent variables, scalers, and comments. The description type contains the file metadata and is saved directly as mdata attributes. The remainder are saved in specialized containers and dictionaries provided by the mudpy package. The histograms contain the bulk of the data: counts from the various detectors needed to measure the nuclear spin polarization. The independent variables may contain experiment settings or measurements such as the temperature. The scalers contain information from secondary readouts of the detectors: total number of counts and the most recent reading. Comments are additional notes written by the experimenters.

It should be acknowledged that a large body of analysis software exists to support μ SR workers. Examples include WIMDA,²⁷⁵ an older Windows application; MANTID,²⁷⁶ developed by and for ISIS; and Musrfit,²⁷⁷ maintained by the workers at PSI. Data stored in the MUD format are compatible with Musrfit. These programs are quite powerful,²⁷⁸ but can be cumbersome outside of their intended scope (e.g. when developing new methods²⁷⁹). The mudpy package is very lightweight by comparison, providing a simple interface to any other Python package, which allows for a great deal of flexibility and sophistication.

Like many Python packages, the source code is publicly available under the GNU General Public License v3.0 (GPL-3.0 License) on the python package index (PyPI) (listed as mud-py) or on GitHub at https://github.com/dfujim/mudpy. This trivializes installation and maintenance by installing missing dependencies, updating packages, and providing a consistent method of version tracking. This is in stark contrast to another popularly used framework, ROOT,²⁸⁰ which serves as the basis for Musrfit, and whose set up process can be quite involved.

D.2 bdata

The bdata package augments the mdata object with the specifics of the β -NMR and β -detected nuclear quadrupole resonance (β -NQR) experiments at TRIUMF. In addition to the goals of mudpy, bdata aims to organize the MUD data in a way that is sensible for these experiments, automate fetching data from the online archive, and provide common data manipulations (such as calculating asymmetries or combining scans). The main object in the package is the bdata object, which inherits from mdata. Its attributes standardize the various variable names, which have changed several times over the past two decades of β -NMR operation.

The bdata object calculates asymmetries in several different ways, according to the theory presented in Section 3.2.3, and will detect and account for the peculiarities of all commonly used run modes. bdata also does some data cleaning, including the removal of pre-beam bins, the calculation and correction for detector deadtime, the removal of unwanted bins from resonance scans, the combination of resonance scans, and the averaging of blocks of bins to re-bin the data.

The bdata package also defines two additional objects for combining and appending bdata objects together: bmerged and bjoined respectively. They are useful in the case when a run is interrupted and must be restarted. Finally, the package also defines a dictionary of lifetimes corresponding to the radioactive probes suitable for β -NMR and β -NQR.

The bdata source code is also publicly available under the GPL-3.0 License on the PyPI or on GitHub at https://github.com/dfujim/bdata.

D.3 bfit

The bfit package implements a graphical user interface (GUI) and API for the analysis of β -NMR data. It was written with the goals of providing the means for a quick on-line analysis during measurement, providing an easy-

🙍 🗇 bft: β-NMR and β-NQR Data Analysis (version 4.7.10)							
File Settings Calculate Draw Mode Minimizer Help							
Inspect Fetch Fit							
Year: 2020 🖨 Run Number: 44	1123 🛱 Fetch Draw						
Run Info	PPG Parameters						
Bun: 4012 (2020) Rum Mode: SLR 200 Title: P5:46 42 kg/mol 200 nm thick on sapphire, 6.55 T, 12.0 kV, 286 K, SLR Start: Frisep 22 09:40:29 2020 En: Frisep 23 09:40:29 2020 Start: Start 200 Rum Duration: 328 468 50:30:317 2020 Start: Start 42 kg/mol 200 nm thick on sapphire Orientation: Start: Start 42 kg/mol 200 nm thick on sapphire Orientation: Experiment: 1930 Area: Experiment: IN	Number of Preben Boellines: 30 millines: Number of Bean On Doellines: 400 doellines: Humber of Bean Of Doellines: 200 doellines: PF on Dely: 50 doellines: PF on Dely: 400 ms PF onble: True Frequency: 50001 Hz						
Casp Temperature: 28:35 +/- 0.66 K Medicer Current: 0.72 +/- 0.02 A Magnetic [17:14] 0.324 +/- 0.100 T Cryck Mass Flow: 3.066 +/- 0.144 Total Counts Suple: 37:35 30:022 Fate Sample: 22:35 00:02 Fate Sample: 22:35 00:02 Fate Mode: 1 005 095 (1/5)	Platform Bias: 12.008 +/-0.008 kV Solital Read Bias Initial Read Bia						
Rebin: 1 🕏 <u>Combined Helicity</u> _ = Periodic Redraw							

Figure D.3.1: Screenshot of the bfit GUI displaying some aPS data. The inspect tab (shown) allows the user to read the file headers in detail.

to-use and flexible API with enough sophistication for publication quality analysis, providing an intuitive and user-friendly GUI operable by nonprogrammers, and to be easily maintainable and distributable. A screenshot of the GUI is presented in Figure D.3.1.

The GUI is composed of three tabs. In the Inspect tab, the file headers and description are presented in detail. This is useful for replicating runs, understanding under what conditions the data was taken, and for debugging problems with the spectrometer. The Inspect tab also allows for the drawn data to be updated periodically, such that ongoing measurements can be monitored easily.

The second tab, Fetch, batches of runs can be loaded into memory at once. A syntax is provided to read ranges of runs and to combine runs. Some useful run headers are summarized for quick understanding of which runs are loaded. The Fetch tab will load runs of only a single run mode, and will automatically select those which are already loaded into memory. Runs of different modes must be treated independently and in practice this feature greatly simplifies the run input string. In the third tab, Fit, the user is given a number of useful tools to fit commonly used functions to the data. It allows for parameters to be fixed or shared across runs. Variables may also be defined as functions of the run properties, such as the temperature or field. The resulting fit parameters are drawn from this tab, and may be modelled by a user-defined function. Two χ^2 minimization algorithms are available: the trust region reflective algorithm²⁸¹ included in the SciPy package,²⁷² and the MIGRAD routine which is included in the MINUIT2 library²⁴⁴ employed by ROOT.²⁸² The latter also includes the option to compute robust asymmetric errors on the fit parameters via the MINOS algorithm.

The bfit GUI also features rate corrections for the daughter products of ³¹Mg, the calculation of fit residuals, calculators to convert current to field in the β -NQR magnet, to determine the attenuation in the radio frequency (RF) β -NMR field due to a digital to analog converter (DAC) controlling the input power, and to determine the RF β -NMR field strength from the antenna voltage.

The API provides easy access to all fit functions, including the pulsed functions which account for probe implantation, and the global fitter for χ^2 minimization with shared parameters. Used in conjunction with bdata, nearly any β -NMR analysis should be possible in Python. The GUI may also be used to supplement other analysis methods by exporting the fit parameters to file.

D.4 bccd

Independent of the MUD analysis packages, the bccd package defines a GUI and API for the visualization and analysis of beamspot images in Python. The images are taken with a cooled Starlight Xpress MX516 camera with a Sony ICX055AL charge-coupled device (CCD) chip, and the images are saved using the flexible image transport system (FITS) file format commonly used for astronomical data. The package facilitates the visualization and analysis of these images, and corrects for common distortions. In particular, the GUI was designed to provide an intuitive and documentable means of determining

😣 🖨 🗊 βccd: β-NMR and β-NQR	Beamspot Vie	wer (versio	on 2.7.0)						
File 🗸 Remote Sync 🖌 Draw New With Targets									
Img 1 Img 2									
20200929_1812_Sapphire_LEDon.fits Exposure: 0.001 s 2020-09-29 18:01:41	Draw Style Black Value Alpha (%): Colour Map	: Greysca e: 32768.0 100 : Greys	ale Reset		×				
	Remove	■ Inve Superim	rt Colour Ma pose Draw	ap New					
	Ne	ew Target	Add Image	Add La	st				

Figure D.4.1: Screenshot of the bccd GUI displaying an image of the β -NMR spectrometer with the LED lights on.

beamspot alignment and to correct thermal contraction and expansion in the β -NQR sample rod. The bccd source is available under the GPL-3.0 License on the PyPI or on GitHub at https://github.com/dfujim/bccd.

Both the GUI and API allow the user to remove noise by adjusting the pixel floor, rescale the image to account for the asymmetric pixels, and draw in different modes. The drawing modes are greyscale, contour, gradient (sobel), and edges. Greyscale mode simply draws the pixel values on a linear colour scale. Contour mode draws lines corresponding to evenly spaced constant pixel value, with the number of contours defined by the user. The gradient mode employs a Sobel transformation to calculate a 2D gradient. The image is then drawn in greyscale with the gradient value used as the light intensity. The edges mode first applies a Gaussian filter to remove noise, then computes the gradients, and determines the edge positions based on a threshold. Edge mode is different from the gradient mode in that the edges are binary (either a pixel is an edge or not). bccd makes heavy use of the scikit-image image analysis package.²⁸³

The GUI is shown in Figure D.4.1. In addition to the above, it allows the user to fetch images from the remote experimental machine and load multiple images into memory at once. These images can then be drawn and superimposed in a variety of colour scales and transparencies. The GUI also allows for the drawing of "targets". These simple shapes (circle, square, ellipsis, rectangle) are superimposed on the drawn images and may be graphically modified by the user. The target may then also be superimposed on other images in other windows and are synchronized in real time. This is an alternate and useful method for comparing the positions and sizes of objects in the images, such as beam spots or samples.

The API provides a number of functions not accessible in the GUI. These include automated line and circle detection, masking the image (such that areas are obscured), and a few methods for calculating the center of mass. These methods, useful for quantifying the beamspot position and size, include a direct center of mass calculation, fitting the 1D x and y projections of the pixel values with a Gaussian, or directly fitting the image with a 2D Gaussian.