The dynamics of liquid 1-ethyl-3-methylimidazolium acetate measured with implanted-ion $^8$Li $\beta$-NMR

Derek Fujimoto,$^{1,2,4}$ Ryan M. L. McFadden,$^{2,3}$ Martin H. Deln,$^{1,2}$ Yael Petel,$^3$ Aris Chatzichristos,$^{1,2}$ Lars Hemmingsen,$^4$ Victoria L. Karner,$^{2,3}$ Robert F. Kiefl,$^{1,2,5}$ C. D. Philip Levy,$^5$ Iain McKenzie,$^{5,6}$ Carl A. Michal,$^1$ Gerald D. Morris,$^5$ Matthew R. Pearson,$^5$ Daniel Szunyogh,$^5$ John O. Ticknor,$^{2,3}$ Monika Stachura,$^{5,1}$ and W. Andrew MacFarlane$^{2,3,5,1}$

$^1$Department of Physics and Astronomy, University of British Columbia, Vancouver, BC V6T 1Z1, Canada
$^2$Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver, BC V6T 2Z4, Canada
$^3$Department of Chemistry, University of British Columbia, Vancouver, BC V6T 2Z1, Canada
$^4$Department of Chemistry, University of Copenhagen, 2100 København Ø, Denmark
$^5$TRIUMF, Vancouver, BC V6T 2A3, Canada
$^6$Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

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We demonstrate the application of implanted-ion $\beta$-detected NMR as a probe of ionic liquid molecular dynamics through the measurement of $^8$Li 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 $E_A = 74.8(15)$ meV and Vogel-Fulcher-Tammann constant $T_{VFT} = 165.8(9)$ K, 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. The depth resolution of this technique may later provide a unique means of studying nanoscale phenomena in ionic liquids.

I. INTRODUCTION

Room temperature ionic liquids (RTILs) are a fascinating class of amorphous materials with many practical applications,$^{1,2}$ such as lubrication in space applications and other low-pressure environments.$^3$ 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,$^{1-6}$ resulting in a large and strongly temperature dependent viscosity $\eta$. 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 $T_g$ far below the therodynamic melting point, $T_m$.$^7$

A key feature of supercooled liquids and glasses is dynamic heterogeneity.$^8-10$ 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 characterized by a growing dynamic correlation length, and are found to be stronger closer to the glassy phase.$^{11}$ 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.$^{10,12,13}$ The degree of heterogeneity can be modelled by the “stretching” of an exponential nuclear spin-lattice relaxation (SLR), $\exp\left\{-(\lambda/\beta) \right\}$, where $\lambda = 1/T_1$ is the SLR rate and $\beta$ is the stretching exponent. Single exponential relaxation ($\beta = 1$), corresponds to homogeneous dynamics, whereas $\beta < 1$ describes a broad distribution of exponentials,$^{14}$ the case where each probe nucleus relaxes at a different rate. The breadth of the distribution of rates is determined by $\beta$, with $\beta = 1$ corresponding to a delta function. While stretched exponential relaxation is suggestive of dynamic heterogeneity, 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 $\beta$ to be independent of scale, at least down to a few hundred atoms.$^{15}$ 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.$^{12,13}$ 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.$^{16}$ Furthermore, dynamical heterogeneities have been theoretically shown to be a prerequisite for stretched exponential relaxation in dynamically frustrated systems, such as supercooled liquids.$^{17}$ A reduction of $\beta$ below one is a signature of dynamic heterogeneity.

Potential applications of the RTIL 1-ethyl-3-methylimidazolium acetate (EMIM–Ac), with ions depicted in Figure 1, have motivated detailed studies of its properties, including neutron scattering measurements of its liquid structure.$^6$ Its bulk physical
properties\textsuperscript{18–27} and its ability to dissolve cellulose material\textsuperscript{28,29} Here, we use implanted-ion \(\beta\)-detected NMR (\(\beta\)-NMR) to study the development of dynamic heterogeneity and ionic mobility of implanted \(^{8}\text{Li}^+\) in supercooled EMIM–Ac. The \(\beta\)-NMR signal is due to the anisotropic \(\beta\)-decay of a radioactive NMR nucleus,\textsuperscript{30–32} similar to muon spin rotation. The probe in our case is the short-lived \(^{8}\text{Li}\), produced as a low-energy spin-polarized ion beam and implanted into the sample.\textsuperscript{33} At any time during the measurement, the \(^{8}\text{Li}^+\) are present in the sample at ultratrace (10\textsuperscript{–13} M) concentration. Implanted-ion \(\beta\)-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 vapor pressure of RTILs makes the present measurements feasible.\textsuperscript{34} We have measured the strong temperature dependence of the SLR (1/\(T_1\)) and resonance of \(^{8}\text{Li}\) in EMIM–Ac. 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. Resonance measurements clearly demonstrate motional narrowing as the RTIL is heated out of the supercooled regime. Our findings show that \(\beta\)-NMR could provide a new way to study depth-resolved dynamics in thin films of RTILs.\textsuperscript{35}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{EMIM.png}
\caption{Structure of the EMIM cation (left) and Ac anion (right).}
\end{figure}

\section{II. EXPERIMENT}

\(\beta\)-NMR experiments were performed at TRIUMF’s ISAC facility in Vancouver, Canada. A highly polarized beam of \(^{8}\text{Li}^+\) was implanted into the sample in the high-field \(\beta\)-NMR spectrometer with static field \(B_0 = 6.55\text{T}\).\textsuperscript{36,37} The incident beam had a typical flux of \(~10^{8}\text{ions/s}\) over a beam spot \(~2\text{mm}\) in diameter. With a beam energy of 19 keV, the average implantation depth was calculated by SRIM\textsuperscript{38} to be \(~200\text{nm}\), but solvent diffusion (see discussion) modifies this initial implantation profile significantly during the \(^{8}\text{Li}\) lifetime. Spin-polarization of the \(^{8}\text{Li}\) nucleus was achieved in-flight by collinear optical pumping with circularly polarized light, yielding a polarization of \(~70\%\).\textsuperscript{39} The \(^{8}\text{Li}\) probe has nuclear spin \(I = 2\), gyromagnetic ratio \(\gamma = 6.3016\text{MHz}\text{T}^{-1}\), nuclear electric quadrupole moment \(Q = +32.6\text{mb}\), and radioactive lifetime \(\tau_\beta = 1.21\text{s}\). The nuclear spin-polarization of \(^{8}\text{Li}\) is monitored through its anisotropic \(\beta\)-decay, where the observed asymmetry of the \(\beta\)-decay is proportional to the average longitudinal nuclear spin-polarization.\textsuperscript{33} The proportionality factor is fixed and is determined by the \(\beta\)-decay properties of \(^{8}\text{Li}\) and the detector geometry. The asymmetry of the \(\beta\)-decay was combined for two opposite polarizations of the \(^{8}\text{Li}\) by alternately flipping the helicity of the pumping laser. This corrects for differences in detector rates and baseline.\textsuperscript{33,40}

Similar to other quadrupolar (\(I > 1/2\)) nuclei in non-magnetic materials, the strongest interaction between the \(^{8}\text{Li}\) nuclear spin and its surroundings 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 \(^{8}\text{Li}\) nucleus. The relaxation of a single \(I = 2\) nucleus is fundamentally bi-exponential, regardless of the functional form of the EFG spectral density, although the bi-exponential is not very evident in high fields where the faster exponential has a small relative amplitude.\textsuperscript{41,42}

SLR measurements used a pulsed \(^{8}\text{Li}^+\) beam. The transient decay of spin-polarization was monitored both during and following the 4 s pulse, where the polarization approaches a steady-state value during the pulse, and relaxes to \(\sim 0\) afterwards. The effect is a pronounced kink at the end of the beam pulse, characteristic of \(\beta\)-NMR SLR data (Figure 2). No radio frequency (RF) magnetic field is required for the SLR measurements, as the probe nuclei were implanted in a spin state already far from thermal equilibrium. Thus, it is typically faster and easier to measure SLR than to measure the resonance spectrum; however, this type of relaxation measurement has no spectral resolution, unlike to conventional NMR, and reflects the spin relaxation of all the \(^{8}\text{Li}\).

Resonances were acquired by stepping a continuous wave (CW) transverse RF magnetic field slowly through the \(^{8}\text{Li}\) Larmor frequency, with a continuous \(^{8}\text{Li}^+\) beam. The spin of any on-resonance \(^{8}\text{Li}\) is rapidly nutated by the RF field, resulting in a loss in time-averaged asymmetry.

The sample consisted of a 1-ethyl-3-methylimidazolium acetate solution (Sigma-Aldrich). To avoid the response being dominated by trace-level Li-trapping impurities, we introduced a stable isotope “carrier” (LiCl) at 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 Ref. 34. The solution was kept in a dry-pumped rough vacuum for approximately 12 h prior to the measurement. A \(\sim 3\mu\text{L}\) droplet was placed in a 3 mm diameter blank hole set 0.5 mm into a 1 mm thick aluminum plate. The Al plate was then bolted vertically into an ultrahigh vacuum (10\textsuperscript{–10} Torr) coldfinger liquid He cryostat and the temperature was varied from 220 K to 315 K. 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.

Separately, we determined the self-diffusion coefficients of the LiCl EMIM–Ac solution using conventional bipolar pulsed field gradient (PFG) NMR with an in-house probe and spectrometer at 8.4 T and room temperature. 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 $^1$H or $^7$Li, and the diffusion time $\Delta$ 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.$^{45}$

III. RESULTS AND ANALYSIS

A. Relaxation

Typical $^8$Li $\beta$-NMR SLR measurements are shown in Figure 2. Clearly, the relaxation shows a strong temperature dependence. At low temperatures it is slow, but its 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 crosses-over to nearly exponential at room temperature. For a $^8$Li$^+$ ion implanted at time $t'$, the spin polarization $P(t, t')$ at time $t > t'$ is well-described by a stretched exponential:

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

(1)

where $t'$ is integrated out as a result of convolution with the 4 s beam pulse.$^{46}$ A very small fraction, about 2%, of the SLR signal can be attributed to $^8$Li$^+$ stopping in the sample holder. While this background signal is nearly negligible, it is accounted for with an additive signal: $P_b(t, t') = \exp \left\{ - [\lambda_b(t - t')]_{0.3} \right\}$, a phenomenological choice given the disorder in the Al alloy. The relaxation rate, $\lambda_b$, was obtained from a separate calibration run at 300 K and was assumed to follow the Korringa law: $\lambda_b \propto T$.

The SLR time series at all $T$ were fit simultaneously with a common initial asymmetry. To find the global least-squares fit, we used C++ code leveraging the MINUIT minimization routines implemented within ROOT, accounting for the strongly time-dependent statistical uncertainties in the data. The fitting quality was excellent, with $\chi^2_{\text{global}} \approx 0.99$.

As shown in Figure 3, the change in $1/T_1$ over the measured 100 K range is remarkable, varying over 3 orders of

FIG. 2. The $\beta$-decay asymmetry of $^8$Li in EMIM–Ac, with stretched exponential fits. The SLR is strongly temperature-dependent, and is well described by Equation (1) convoluted with the square beam pulse, as evidenced by $\chi^2_{\text{global}} \approx 0.99$. The data have been binned by a factor of 20 for clarity.

FIG. 3. The stretched exponential parameters from fits to the SLR in EMIM–Ac (refer to Figure 2 for fit curves). For the rate ($1/T_1$), the line denotes a fit using Equations (2) to (4), as detailed in the text. For the stretching exponent ($\beta$), the line is a guide for the eye. Both are highly temperature dependent, showing a monotonic increase until the $1/T_1$ BPP peak at 298 K, above which $\beta \approx 1$. The shaded region indicates the approximate temperature range of supercooling between $T_g$ and $T_m$. 

$\chi = 1.02 \pm 0.09$ nK s
$E_A = 74.8 \pm 1.5$ meV
$TV_{VT} = 165.8 \pm 0.9$ K

$T_g = 3$ K
$T_m = 300$ K
$T_{VT}$ = 305 K

$\Delta T = 100$ K

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As shown in Figure 3, the change in $1/T_1$ over the measured 100 K range is remarkable, varying over 3 orders of
the phenomenological Vogel-Fulcher-Tammann (VFT) model. The inset shows that the linewidth is proportional to $\eta/T$, consistent with the Stokes-Einstein relation (Equation 48 of Bloembergen et al.\textsuperscript{49}). We then assume that $\tau_c$ is proportional to $\eta/T$:

$$\tau_c = \frac{c}{T} \exp \left[ \frac{E_A}{k_B (T - T_{\text{VFT}})} \right],$$  \hspace{1cm} (4)

where $c$ is a prefactor, $E_A$ is the activation energy, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $T_{\text{VFT}}$ is a constant. Together, Equations (2) to (4) encapsulate the temperature and frequency dependence of the $^8$Li $1/T_1$ in the supercooled ionic liquid. A fit of this model to the data is shown in Figure 3, and parameter values can be found in Table I. The correlation times from 220 K to 315 K are on the order of nanoseconds. The choice of Equation (3) assumes that the $\beta < 1$ stretching arises from a population of exponential relaxing environments with a broad distribution of $\tau_c$. As mentioned, this assumption is likely good for the $^8$Li $\beta$-NMR probe; especially since the basic local relaxation of $^8$Li due to quadrupolar coupling is not intrinsically stretched, independent of the dynamical fluctuation spectrum.\textsuperscript{41} Under this construction, the departure from $\beta = 1$ in the supercooled regime is consistent with the emergence of dynamical heterogeneity.

### B. Resonance

Typical $^8$Li resonances are shown in Figure 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 $\gamma B_1$, where $B_1 \approx 0.1$ G. This inhomogeneous quadrupolar broadening is qualitatively consistent with the heterogeneity in the dynamics implied by the stretched exponential relaxation.

The resonances are well-described by a simple Lorentzian. The baseline (time-integrated) asymmetry

### TABLE I. Fit results for $1/T_1$ ($\beta$-NMR) and $\eta$ (literature). Parameters are defined in Equations (2) and (4), substituting $c/T \leftrightarrow \eta_0$ in the latter. Corresponding curves are shown in Figures 3 and 4.
FIG. 5. The $^8$Li resonance in EMIM–Ac, shifted by the Larmor frequency ($\nu_0 \approx 41.27 \text{ MHz}$), 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). 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.

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) is about $-9 \text{ ppm}$, but a slow drift of the magnetic field prevents 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 shown in Figure 6.

As anticipated from the most striking features in Figure 5, the linewidth and peak height evolve considerably with temperature. Note that the peak height in Figure 6 is measured from the baseline, and is normalized to be in units of the baseline, accounting for changes in the SLR. Reduction in the linewidth by several orders of magnitude is compatible with motional narrowing, where rapid molecular motion averages out static inhomogeneous broadening. 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.

IV. 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. Dielectric relaxation experiments confirm this, placing a 100 ps upper bound on their lifetime, rendering them a poor description of the average ionic structure. Rather, the arrangement can be described as two interpenetrating ionic networks. As revealed by neutron scattering, each network forms cages about the other that are highly anisotropic due to the tendency for EMIM rings to stack. 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. Presumably, in our case, the small $^8$Li$^+$ cation is coordinated by several acetates and a similar correlation will exist for the $^8$Li$^+$ 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 4. While a direct relation between the specific motions sensed by $^8$Li and the bulk $\eta$ is complex and unclear, one may anticipate a consistency between their kinetics should a single mechanism govern both. The similarity
of both $E_A$ and $T_{\text{VT}}$ with those found from the viscosity of the pure EMIM–Ac suggests that this is the case and provides further justification for the choice of Equation (4).

The inset of Figure 4 shows that motional narrowing causes the resonance linewidths to scale as $\eta/T$ in the liquid state above $T_g$, a situation also observed in DEME-TFSA [DEM = N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium; and TFSA = bis(trifluoromethanesulfon)amide] with solute $^8\text{Li}$ NMR. That this relationship holds for $^8\text{Li}$ is surprising; our $\beta$-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 $^8\text{Li}^+$ 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 $T/\eta$, and its violation at low $T$ in the inset of Figure 4 shows that ionic diffusion in supercooled RTILs may contain some of the character expected from a solid. At 295 K however, our $^7\text{Li}$ PFG NMR in EMIM–Ac with 30 mM LiCl shows that the diffusion is not significantly larger than the solvent ($D_{\text{Li}^+} = 3.46(11) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ vs $D_{\text{H}} = 3.61(7) \times 10^{-10} \text{ m}^2\text{s}^{-1}$), demonstrating that the $^8\text{Li}$ is primarily sensing the mobility of its surrounding solvent cage.

Relatively little is known about $\text{Li}^+$ as a solute in EMIM–Ac, compared to other imidazolium-based RTILs, which have been explored as electrolytes for lithium-ion batteries. Their properties should be qualitatively comparable, but the details certainly differ as both anion size and shape play a role in the diffusivity. Shown to compare favorably with implanted-ion $\beta$-NMR, conventional NMR can provide a comparison to some closely related RTILs: EMIM–TFSA and EMIM–FSA [FSA = bis(trifluoromethanesulfon)amide]. In both cases, the diffusion of $^7\text{Li}$ was similar to that of the solvent ions. Differences in the tracer diffusion are reflected in the activation barrier for $^7\text{Li}$ hopping: 222(6) meV and 187(2) meV, respectively. This correlates well with anion molecular weight, 280 g mol$^{-1}$ and 180 g mol$^{-1}$, and with the barrier we report for $^7\text{Li}$: 74.8(15) 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 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 work, and will be clarified at a later date, 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. In the fast fluctuation limit, the time spent with a given local environment is small and the RF is relatively ineffective at nutating the 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, but the peak height is unaffected.

The local maximum in the peak height is explicable from the small slow relaxing background. When the RF is applied on resonance, the signal from the sample is eliminated and the asymmetry is independent of the SLR. Increasing the SLR 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.

The development of dynamic heterogeneity at the nanosecond timescale ($\omega_0^{-1}$) is demonstrated by the stretched exponential SLR, as shown in Figure 3. 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 $T_m$ is no larger than 250 K. In contrast, a calorimetric glass transition has been observed at about $\sim 198$ K. Thus, the dynamic inhomogeneity develops in a range of $T$ that corresponds well to the region of supercooling, indicated by the shading in Figure 3. Stretched exponential relaxation, reflecting dynamic heterogeneity, is a well-known feature of NMR in disordered solids. In some cases, diffusive spin dynamics, driven by mutual spin flips of identical near-neighbor 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 neighbors. However, a unique feature of $\beta$-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 $\beta$-NMR nuclei are, themselves, always isolated from one another. In the absence of spin diffusion, on quite general grounds, it has been shown that the stretching exponent $\beta$ should be 0.5. Our data in Figure 3 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 and reduced 4D-NMR.

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 $^2\text{H}$ NMR, providing us with a useful point of comparison to a nonionic liquid. Like $^8\text{Li}$, $^2\text{H}$ should
exhibit primarily quadrupolar relaxation. Toluene is supercooled between its melting point 178 K and glass transition \( \sim 117 \) K, though it shows stretched exponential relaxation only below about 1.1 \( T_g \), considerably deeper into the supercooled regime than in our case, with an onset near 1.25 \( T_g \), likely due to the stronger tendency to order in the ionic liquid.

The closest analogue to our experiment is, perhaps, an early (neutron activated) \( ^{8} \)Li \( \beta \)-NMR study in LiCl \( \cdot 7 \)D\(_2\)O.\(^{51,68}\) There, the observed temperature dependence of the SLR is qualitatively similar (see Figure 9 of Ref. 51): 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 \( \sim 80 \) K, whose characteristic correlation times reflect the diffusion and orientational fluctuations in D\(_2\)O. 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 \(^{8} \)Li \( \beta \)-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,\(^{69}\) 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. To date, the SLR was typically fast and independent of temperature, in contrast to our observations. The BPP peak is attainable to a degree where we recover simple exponential SLR, accompanied by motional narrowing and a BPP peak.

V. CONCLUSION

We report the first measurements of \(^{8} \)Li \( \beta \)-NMR in the ionic liquid 1-ethyl-3-methylimidazolium acetate. Our results demonstrate that the quadrupolar interaction does not hinder our ability to follow the \( \beta \)-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. At low temperatures near \( T_m \), 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 \( ^{8} \)Li \( \beta \)-NMR is a good probe of both solvation dynamics and their heterogeneity. The depth resolution of ion-implanted \( \beta \)-NMR may provide a unique means of studying nanoscale phenomena in ionic liquids, such as ion behaviour at the liquid-vacuum interface or the dependence of diffusivity on film thickness.\(^{75}\)

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