Determining the relaxation time from a temperature-dependent scan of the neutron spin-echo signal amplitude

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Abstract. Temperature-dependent scans of the neutron scattering intensity are commonly employed in high energy-resolution quasielastic measurements. Besides serving as a useful diagnostic tool for identifying the temperature range that could give rise to a measurable relaxation signal, such scans of the "elastic" (resolution-defined) intensity could be employed for determining the temperature at which the relaxation time in the system becomes equal to the resolution-defined characteristic time of the spectrometer measurement. This is a model-independent alternative to the "traditional" approach, when, at a given measurement temperature, the relaxation time in the system is obtained from fitting the full dynamic spectra with a model scattering function. Here we introduce the temperature-dependent scan of the neutron spin-echo signal amplitude. Using a well-characterized system with a complex relaxation pattern, we demonstrate that the relaxation time obtained from the approach proposed herein maps well on the previous "traditionally" measured relaxation times. Thus, despite monitoring a different variable (neutron spin-echo signal amplitude vs. neutron scattering intensity), the benefits of the model-free temperature-dependent scan approach, traditionally utilized in neutron time-of-flight and backscattering experiments, can be extended to measurements of the very slow relaxations assessable only by high-resolution neutron spin-echo.

1 Introduction

High energy-resolution neutron scattering is a powerful technique for studying relaxational dynamics. Despite its unique advantages, such as weak interaction with the sample, H/D selectivity, and the spatial information on the motion accessible via the momentum transfer (Q) signal dependence, neutron scattering, especially when utilized in the high energy-resolution mode, is intensity limited. In quasielastic neutron scattering (QENS) [1], particularly, backscattering, which has very high energy resolution, second only to neutron spin echo (NSE) [2, 3], the severe intensity limitations in measurements of the small samples have prompted numerous attempts to circumvent the problem by measuring only the resolution-defined [stronger] "elastic" line instead of the whole dynamic spectrum with the [weaker] "wings".

It was proposed 20 years ago [4, 5] that measurements of small samples may benefit from "elastic resolution spectroscopy", when the relaxation function (traditionally obtained from the full range dynamic measurement) is reconstructed from the "elastic" incoherent scattering intensity. As originally proposed, this approach relied on the variable energy resolution easily possible with QENS-capable time-of-flight (TOF) neutron spectrometers. More recently this approach was adopted to the data collection from various backscattering spectrometers [6]. The main assumption of the "elastic resolution spectroscopy" approach is that the relaxation mechanism remains continuous when the temperature is changed [6].

An alternative approach, "resolution elastic neutron scattering", proposed [7, 8] that the relaxation time becomes equal to the resolution time of the spectrometer when an inflection point occurs, either in the temperature dependence of the "elastic" incoherent intensity (at a given resolution), or the resolution dependence of the "elastic" incoherent intensity (at a given temperature). The assumption of the "resolution elastic neutron scattering" approach is that the resolution function of the spectrometer is a Gaussian, and the relaxation function to be measured has a simple functional form (e.g., of Lorentz-type).

A newer method to assess the system dynamics by measuring the resolution-dependent "elastic" scattered intensity was proposed and extensively discussed more recently [9-11]. Nevertheless, the approach using an inflection point in the temperature dependence of the "elastic" incoherent scattering intensity at a few resolution settings of a neutron backscattering spectrometer [12] has been validated experimentally [13]. The relaxation times extracted from such analysis of the temperature dependence of the "elastic" neutron scattering intensity were successfully mapped onto the relaxation times previously obtained via the traditional QENS analysis of the same system [14]. The relaxation time mapping was successful even though the relaxation function for the measured system was non-Lorentzian, with a temperature-dependent stretch parameter [14, 15], and the spectrometer's resolution function was not a Gaussian, thus suggesting general applicability of this method of the temperature-dependent "elastic" scattering intensity scans.

In the current work, we would like to investigate possible extension of this approach to the longer

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relaxation times, beyond those measurable with neutron backscattering spectrometers using QENS. NSE spectroscopy is a neutron scattering technique where the very high energy resolution is attained by harnessing neutron Larmor precession in a magnetic field [2, 3]. Since a detailed description of the NSE principles and practice are beyond the scope of this short paper, the reader is kindly referred to the available literature, e.g. [2, 3, 16].

Here we explore how the measurement time per a temperature point (in the course of a temperature-dependent scan) can be dramatically shortened to produce a variable whose temperature dependence can be used to identify the temperature at which the relaxation time in the sample becomes equal to the resolution time of the NSE spectrometer.

2 Methods

The preparation of the sample, an aqueous solution, $(H_2O)_{0.88}(LiCl)_{0.12}$, followed the previously described procedure [14] using deionized distilled water and anhydrous, ultra-dry lithium chloride powder (99.995 % purity) purchased from Alfa Aesar. The sample was loaded into a flat plate aluminum sample holder, 50 mm tall, 30 mm wide, and 0.25 mm thick, which was placed in a Janis SHI-950 (Janis, Woburn, MA, USA) closed cycle refrigerator connected to a LakeShore 336 (LakeShore, Westerville, OH, USA) temperature controller.

The NSE measurements (of the predominantly incoherent scattering signal from the protiated sample) were carried out at the SNS-NSE spectrometer [17] at the Oak Ridge National Laboratory. We chose neutron wavelength band $\Delta\lambda$ = 3-6 Å, the NSE field integral, $J = \int B\, dl$, was set to 0.01971 Tm (corresponding to τ = 0.45 ns at λ = 5 Å), and the scattering angle was 2θ=39.1°. That allowed us to cover the scattering vector Q from approximately 0.7 to 1.4 Å^{-1}.

The measurement outline was as follows:

1. Cooled the sample down to 4 K and measured a "full" echo establishing the symmetry phase (see Fig. 1).
2. Warmed up the sample to 300 K, again measured the full echo (confirmed that the echo "disappeared").
3. Gradually cooling the sample at the average rate of 0.1 K/min, while keeping all the precession currents constant and turning on/off only the flipper currents, we measured three neutron count rates:
    a. U - with all flippers turned off (I~1/3 incoherent, no spin-flip)
    b. D - only π −flipper turned on (I~2/3 incoherent, spin flip)
    c. E - all flippers turned on ("echo" condition).

The data reduction was carried out as follows:

1. Selected pixels with 0.3 ns ≤ τ ≤ 0.6 ns and 0.8 Å^{-1} ≤ Q ≤ 1.0 Å^{-1}
    a. $\langle\tau\rangle$ = (0.45 ± 0.09) ns
    b. $\langle Q\rangle$ = (0.88 ± 0.05) Å^{-1}
2. For the pixels with these values of $\langle\tau\rangle$ and $\langle Q\rangle$:
    a. Calculated the scattering function:

$$F(Q,\tau) = \frac{2(E-\langle A\rangle)}{U-D}$$

    b. Here $\langle A\rangle = \frac{U+D}{2}$
3. Plotted F as a function of temperature, T (see Fig. 2).

Notes:

- Due to the time-of-flight and multipixel nature of the SNS-NSE, we cover a range of scattering angles, Q's, and τ.
- We take advantage of the mu-metal shielding of the spectrometer that allows excellent magnetic field (and, hence, echo phase) stability; see Fig. 3.
- Since this was a non-standard experiment, the data have been reduced and analysed using custom software created by one of the authors (P. Z.).

3 Results and discussion

Fig. 1 illustrates the standard NSE measurement and reduction [16]:

- Measure "full" echo, polarization (U,D)
- Determine the echo (symmetry) phase and echo amplitude A_{ECHO} by fitting a "convoluted cosine"
- Compute $F = \frac{2A_{ECHO}}{U-D}$

While the "traditional" approach relies on the measurement of the full echo at each chosen Fourier time, here instead we determined the echo amplitude at the symmetry phase. Importantly, this approach, bypassing the measurement of the full echo signal, was made possible by never changing the electric currents of the precession coils. Only the flipper currents were turned on and off.

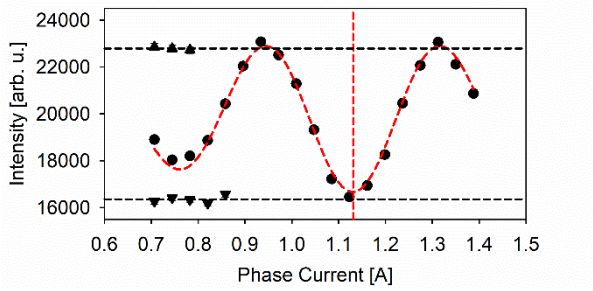

Fig. 1. Illustration of the standard measurement of the neutron spin-echo amplitude at a given temperature.

Fig. 2 shows the temperature dependence of the scattering function. The data (symbols) were fitted to the following expression (analogous to the approach adopted in [13]):

$$F(T) = \left[1 - \frac{1}{1+\exp(-G(T-T_0))}\right](a - bT) \quad (1)$$

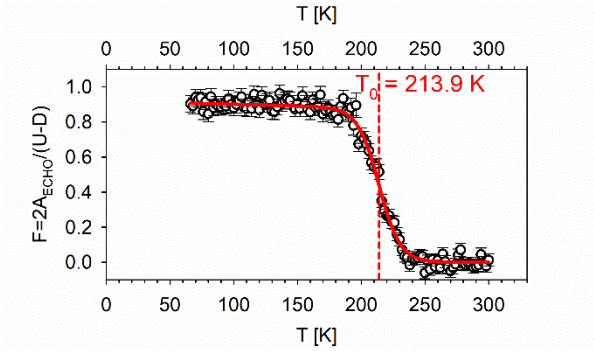

Fig. 2. Illustration of how the inflection temperature point was obtained.

That is, at T_0 (the inflection point), the resolution time measured in the sample is expected to become equal to $\langle\tau\rangle = (0.45 \pm 0.09)$ ns (for $\langle Q\rangle = (0.88 \pm 0.05)$ Å^{-1}). The parameter obtained from the fit with Equation 1 are presented in Table 1.

Table 1. Parameters of the fit shown as the red line in Fig. 2.

Parameter	Value
T_0	(213.9 ± 0.5) K
G	(0.120 ± 0.006) K^{-1}
a	(0.92 ± 0.02)
b	(19 ± 14) 10^{-5} K^{-1}
χ^2	0.69

As mentioned above, the excellent stability of the magnetic field at the sample position, as illustrated by the data presented in Fig. 3, is important for the measurement approach described herein.

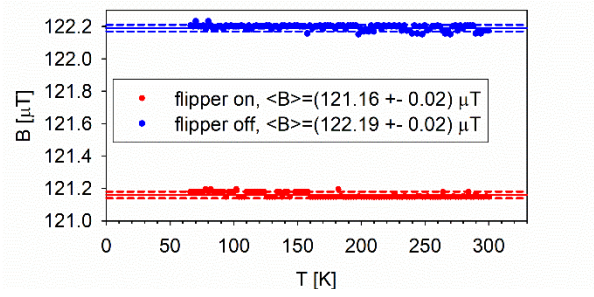

Fig. 3. Magnetic field at the sample position as a function of sample temperature. The field was stable to better than 2·10^{-2} μT (or 0.2 mG).

Finally, this newly determined at $T_0 = (213.9 \pm 0.5)$ K ($\langle\tau\rangle = (0.45 \pm 0.09)$ ns, $\langle Q\rangle = (0.88 \pm 0.05)$ Å^{-1}) point in the (T, τ, Q) space has been added to the previously measured relaxation time map for this sample, as presented in Fig. 4. The data previously measured by neutron backscattering in the "traditional" way [14] show the relaxation times at preset temperatures. Conversely, the data previously measured by neutron backscattering from the elastic intensity temperature scans [13] show the temperatures at which the preset relaxation times are observed in the sample. Likewise, the data point obtained in the current NSE experiment shows the temperature (213.9 K) at which the preset relaxation time (0.45 ns) is observed in the sample. As one can see, the newly measured relaxation time maps well onto the previously measured relaxation times.

At a cooling rate of 0.1 K/min, it took about 2300 minutes, or 38 hours, to obtain the the (T, τ, Q) point of interest. It should be noted that the sample studied herein scatters predominantly incoherently, which necessitates long measurement times with "traditional" NSE measurements. Further, as one can infer from Fig. 2, the number of measured temperature points could have been decreased dramatically, because the 4-parameter fit with Equation 1 of the sigmoidal data set is robust and does not need many data points, especially at the extremes of the temperature range. Therefore, even though we conservatively allowed long measurements in the current proof-of-principle experiment, the measurement time necessary to obtain a (T, τ, Q) point using the approach described herein could be shortened dramatically. We expect that the biggest time saving using the proposed approach compared to the traditional NSE approach could be realized in measurements with the longest preset relaxation times, where not having to collect the full spin-echo spectra could be highly benefitial for shortening the experiment.

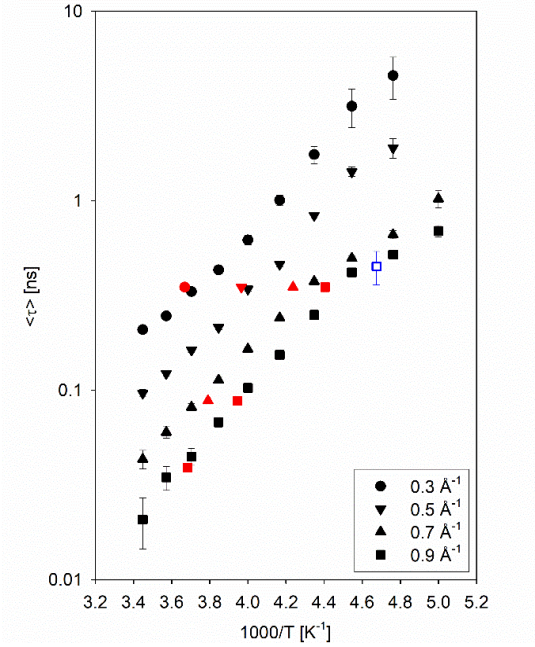

Fig. 4. Filled black symbols from neutron backscattering spectrometer [12] measurements: average relaxation times previously measured in the "traditional" way from QENS data [14] for $(H_2O)_{0.88}(LiCl)_{0.12}$. Filled red symbols from neutron backscattering spectrometer [12] measurements: average relaxation times obtained from the analysis of the temperature-dependent scans as described in [13]. Open blue symbol from SNS-NSE [17] measurements: average relaxation time s obtained in the current work. For the red and blue symbols, the uncertainties in the temperature points are shown with the horizontal bars (when they exceed the size of the symbols).

4 Conclusion

The traditional method of obtaining the relaxation times from NSE data involves fitting the spin-echo spectra measured at variable Fourier times and subsequent fitting with a model relaxation function of the $I(t)$ points resulting from the fitted amplitudes of the spin-echo spectra. In this work we demonstrate an alternative approach that relies of measuring the temperature dependence of the spin echo amplitude. Somewhat analogous to the temperature-dependent "elastic" intensity scans traditionally utilized in neutron time-of-flight and backscattering experiments, the proposed approach provides the benefit of the model-free analysis while greatly extending the measurable relaxation time range, to the energy/time domain inaccessible by any neutron scattering technique other than NSE. Remarkably, this approach is verified for a sample with a non-Lorentzian relaxation function, whose stretch parameter itself is a function of temperature. The method demonstrated in the present work thus holds a promise for time-efficient measurements of long relaxation times in the samples that may not be amenable to traditional full analysis of the NSE signal.

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References

1. M. Bee, Quasielastic Neutron Scattering, Principles and Applications in Solid State Chemistry, Biology and Materials Science, CRC Press (1988)
2. F. Mezei (ed.), Neutron Spin Echo, Lecture Notes in Physics, Vol. 128, Springer Verlag (1980)
3. F. Mezei, C. Pappas, T. Gutberlet (eds.), Neutron Spin Echo Spectroscopy - Basics, Trends and Applications, Lecture Notes in Physics, Vol. 601, Springer Verlag (2003)
4. W. Doster, M. Diehl, W. Petry, M. Ferrand, Physica B **301**, 65-68 (2001)
5. W. Doster, M. Diehl, R. Gebhardt, R.E. Lechner, J. Pieper, Chem. Phys. **292**, 487-494 (2003)
6. W. Doster, H. Nakagawa, M.S. Appavou, J. Chem. Phys. **139**, 045105 (2013)
7. S. Magazù, F. Migliardo, A. Benedetto, Rev. Sci. Inst. **82**, 105115 (2011)
8. S. Magazù, F. Migliardo, M.T. Caccamo, Adv. Mater. Sci. Eng. **2**, 695405-695411 (2013)
9. A. Benedetto, G. J. Kearley, Sci. Rep. **9**, 11284 (2019)
10. A. Benedetto, G. J. Kearley, Sci. Rep. **10**, 6350 (2020)
11. A. Benedetto, G. J. Kearley, Sci. Rep. **11**, 14093 (2021)
12. E. Mamontov, K.W. Herwig, Rev. Sci. Inst. **82**, 085109 (2011)
13. E. Mamontov, Nucl. Inst. Methods Phys. Res. A **949**, 162534 (2020)
14. E. Mamontov, J. Phys. Chem. B **113**, 14073-14078 (2009)
15. M. Nakanishi, P. Griffin, E. Mamontov, A. P. Sokolov, J. Chem. Phys. **136**, 124512 (2012)
16. P.A. Zolnierczuk, O. Holderer, S. Pasini, T. Kozielewski, L.R. Stingaciu, M. Monkenbusch, J. Appl. Cryst., **52**, 1022-1034 (2019)
17. M. Ohl, M. Monkenbusch, N. Arend, T. Kozielewski, G. Vehres, C. Tiemann, M. Butzek, H. Soltner, U. Giesen, R. Achten, H. Stelzer, B. Lindenau, A. Budwig, H. Kleines, M. Drochner, P. Kaemmerling, M. Wagener, R. Moller, E.B. Iverson, M. Sharp, D. Richter, Nucl. Inst. Methods Phys. Res. A **696**, 85-99 (2012)