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A Surrogate for Debye-Waller Factors from Dynamic Stokes Shifts

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Abstract

We show that the short-time behavior of time-resolved fluorescence Stokes shifts (TRSS) are similar to that of the intermediate scattering function obtained from neutron scattering at q near the peak in the static structure factor for glycerol. This allows us to extract a Debye-Waller (DW) factor analog from TRSS data at times as short as 1 ps in a relatively simple way. Using the time-domain relaxation data obtained by this method we show that DW factors evaluated at times ≥ 40 ps can be directly influenced by α relaxation and thus should be used with caution when evaluating relationships between fast and slow dynamics in glassforming systems.

Keywords

Time Resolved Stokes Shifts; Solvation; Debye-Waller factor; Mean-squared-displacement; Alpha relaxation

The Van Hove single particle correlation function, $G_s(\mathbf{r}, t)$ gives the probability of finding a particle at a position $\mathbf{r}$ at time t relative to the position of that particle at time $t=0$. Thus, this function and its Fourier space analog, the incoherent intermediate scattering function, $F_s(q, t)$, contain significant information about dynamics and thermodynamics of solids and

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Supporting Information Available <Fit Parameters for Figure 1>

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gasses¹. A time-weighted average of $F_s(q,t)$, the Debye-Waller (DW) factor is commonly used for characterization of condensed matter systems.

The concept of a Debye-Waller (DW) factor, originally defined as the mean-squared displacement $\langle u^2 \rangle$ of atoms around equilibrium positions in a crystal², has been extended to a harmonic oscillator approximation of motion in amorphous materials, and has emerged as an important parameter in theories of and experiments on supercooled liquids and glass³⁻⁴. DW factors and changes in their behavior have been connected in one way or another to virtually all of the classical characteristics of these systems, including the Kauzmann temperature (T_K), crossover temperature (T_c), glass transition temperature (T_g), viscosity and fragility⁶. This striking relationship between long-time and short-time dynamics seems also to be manifest in the relationship of DW factors to the dynamic coupling between proteins and solvent⁷, between protein function and dynamics⁸ and between host dynamics and stability of proteins encapsulated in sugar-based glass.⁹⁻¹⁰ This latter context is of considerable practical importance, as protein instability accounts for significant losses in the biopharmaceutical industry¹¹. Both gaining a better fundamental understanding of this striking relationship and exploiting it for screening protein-stabilizing glasses requires the ability to routinely and reliably measure DW factors without access to a nuclear reactor or need for Mossbauer-active elements in the sample. Until now, this has not been possible.

DW factors can be obtained from x-ray¹¹ and neutron¹² scattering, as well as from Mossbauer spectroscopy.⁷ Below we show that one can also obtain a surrogate for DW factors in glasses through time resolved fluorescence Stokes shifts (TRSS). Unlike x-ray, neutron, and Mossbauer scattering, Stokes shifts are not sensitive to oscillatory motion *per se*, but respond to the same molecular rearrangements that cause decay of the correlation functions from which $\langle u^2 \rangle$ values are derived.

The TRSS of a probe molecule senses changes in position and orientation of host molecules through their influence on the electric field at the probe. Upon $S1 \leftarrow S0$ photoexcitation of a dye molecule there can be a significant change in dipole moment. Concomitant with this change, nearby host molecules begin to reorganize to accommodate the new local electric field. As this occurs the energy gap between the $S1$ and $S0$ state of the probe becomes smaller, resulting in a time-dependent red shift in the emitted fluorescence. The magnitude and time dependence of the red shift depends on the solvents relative permittivity (ϵ_r) and the timescale for relaxation in the material respectively.¹⁴

TRSS decays presented here were measured in the time-domain subsequent to a sub-ps excitation pulse by spectrally dispersing fluorescence from rhodamine 6G (R6G) onto an 8-channel avalanche photodiode array (*id150 Quantique*)*. Detector output was digitized using a Becker and Hickl SPC 830 module. The convolved time resolution of the detector and digitizer was 54 ps. 515 nm excitation light was generated by pumping a 10 cm length of photonic crystal fiber (Crystal-Fiber) with 10 nJ pulses of ~790 nm, 30 fs from a cavity dumped Ti: Sapphire oscillator (Kapteyn-Murnane Laboratories Inc.). Fluorescence was collected in a 180° geometry, and dispersed onto the detector as eight equally spaced emission bands in the range (533 to 600) nm, covering the major fluorescence peak of R6G. The transmission efficiency of each spectral channel was calibrated against steady-state fluorescence of R6G in glycerol at 300 K. The instantaneous fluorescence energy was calculated as the first moment average of the signal from each detector channel; $\nu(t) = \sum_i \nu_i n_i(t) / \sum_i n_i(t)$, where n is the number of detector counts in time bin t , ν is the average energy

*Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

of the light detected in each channel, and i runs from 1 to 8. Assuming a linear relationship between molecular relaxation and a change in fluorescence energy, a decay function, $\Phi(t)$, was defined in the usual way as¹⁵:

$$\Phi(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (1)$$

where $\nu(\infty)$ is obtained from the slightly temperature-dependent long-time values of $\nu(t)$. In this work, $\nu(\infty)$ obtained at the lowest reliable temperature is used at all lower temperatures. The value of $\nu(0) = 18100 \text{ cm}^{-1}$ is obtained from steady-state Stokes shifts in a series of solvents of decreasing polarity, as described in Ref 16.

Figure 1a shows time-resolved Stokes shifts for R6G in glycerol at temperatures ranging from below T_g to above T_c , and covering times from 13 ps to 20 ns. Dots in Fig. 1b are $\Phi(t)$ values calculated from the TRSS data of Fig 1a. Solid lines are fits to a stretched exponential

function, $\Phi(t) = \Phi_0 \text{Exp} \left[-\left(\frac{t}{\tau_\alpha}\right)^\beta \right]$, the fitting parameters for which are available as supplementary information. The α relaxation times (τ_α) we obtain from these fits are similar to those from dielectric spectroscopy for $T > 250 \text{ K}$ ¹⁷, consistent with observations of Richert et al.¹⁸ Dashed lines are $F_s(q,t)$ from neutron scattering¹⁹ on glycerol. These neutron scattering data, obtained at $q = 1.2 \text{ \AA}^{-1}$ are slightly adjusted to $q = q_{\text{max}} = 1.4 \text{ \AA}^{-1}$ ²⁰, where q_{max} corresponds to the peak of the static structure factor. The data are also interpolated to match temperatures used in this study.

It is clear from Fig. 1b that TRSS data from glycerol correspond to $F_s(q,t)$ from neutron scattering extremely well at times on the order of 10 ps. In order to determine whether $\Phi(t)$ follows $F_s(q,t)$ at longer times, we examine the correspondence between a quantity derived from $F_s(q,t)$, the DW factor, and an analogous quantity derived from Φ . We use DW factors in this comparison for two reasons. One is that direct $F_s(q,t)$ data as a function of time and temperature over the range needed for this comparison would be quite difficult to obtain by neutron scattering, whereas the DW factors can be obtained much more easily²¹. The other is the DW factors themselves are of intrinsic interest, having become an important parameter in many theoretical and experimental studies of condensed matter systems.

Debye-Waller factors can be obtained from neutron scattering under an harmonic oscillator approximation as the q^2 dependence of $\ln(S(q, \omega))$, where $S(q, \omega)$ is averaged over a range of ω corresponding to the width of the energy spread (σ_ω) of the impinging neutron beam. DW factors can also be obtained from $F_s(q, t)$, the Fourier transform of $S(q, \omega)$. The expression relating $\langle u^2 \rangle$ and $F_s(q, t)$ is:

$$\langle u^2 \rangle = -\frac{6}{q^2} \ln \left[\frac{2}{\sigma_t \sqrt{\pi}} \int_0^\infty F(q, t) e^{-\left(\frac{t}{\sigma_t}\right)^2} dt \right] \quad (2)$$

where the coherence time of the neutron beam, σ_t , is related to σ_ω by $\sigma_t = 0.44 / \sigma_\omega$ for a Gaussian energy distribution.

We calculate a surrogate for $\langle u^2 \rangle$ from TRSS decays using an analog of the expression in square brackets of Eq (2),

$$\phi(\sigma_t) = \sum_i \Phi_i e^{-\left(\frac{t_i}{\sigma_t}\right)^2} / e^{-t_i} \quad (3)$$

The exponential term in the denominator accounts for logarithmic time sampling. Eq (3) contains no explicit lengthscale. In analogy to Eq (2), we scale $\ln(\phi)$ by $6/q^2$, using q at which the static structure factor has a maximum.

In Figure 2 we plot DW factors obtained from neutron scattering on several timescales along with values of $\ln(\phi)$ derived from TRSS data in glycerol. Annotation indicating the relevant energy resolution and timescales (σ_ω and σ_t) is included in each panel. Since we do not have experimental TRSS data at 1 ps, we assign $\phi(1 \text{ ps}) = \Phi_0$ from fits to the TRSS data. The 1 ps values of $\langle u^2 \rangle$ from neutron scattering are obtained through Eq. (2) using experimental $F_s(q, t)$ data¹⁹. Consistent with the treatment of time of flight (TOF) data in Fig.1, here we use q_{max} ($q = 1.4 \text{ \AA}^{-1}$) to scale the TRSS data with no further fit parameters and obtain excellent agreement with the neutron scattering data, as shown in Fig. 2.

Agreement between TRSS and DW data is quite good, particularly at low temperatures and short times. This suggests that TRSS might be used as a reliable surrogate for DW factors from neutron scattering on the 1 ps timescale, which are currently obtained by TOF methods, and quite costly to measure compared to DW factors on longer timescales²¹. Disagreement between TRSS and DW data at 322 K in the bottom panel is probably due to significant α relaxation that occurs at this temperature before our measurement time window starts, impairing the quality of Φ_0 estimation in the fit. This is likely not a fundamental limitation; if our detectors were of higher temporal resolution we would catch the earlier decay and better estimate Φ_0 . On the other hand, the slight disagreement between TRSS and DW data in the top panels of Fig. 2, particularly at higher temperatures, seems more likely to arise from fundamental differences between the two measurements. Neutron backscattering data is sensitive to dynamics over the range $(0.36 \leq \xi \leq 1) \text{ nm}$, and the DW factors in the top panels of Fig. 2 are derived from q^2 dependence of scattering intensity over this range, where $\xi = 2\pi/q$. In contrast, analysis of TRSS signal under a continuum approximation suggests that motions on all lengthscales contribute to the signal, including significant contribution from $\xi > 1 \text{ nm}$. Given that α relaxation associated with longer lengthscale (lower q) occurs more slowly¹⁹, one expects the results observed in the top two panels of Fig. 2 that TRSS underestimates the degree of relaxation relative to neutron scattering at long times and high temperatures.

In light of the discrepancy in lengthscales probed, it may seem surprising that the short time and low temperature TRSS data agree so well with the TOF scattering data. There are two possible reasons for the agreement. One possibility is that, in contrast to α relaxation, the fast β relaxation being probed at 1 ps is scale invariant, at least on short and intermediate lengthscales. This does not seem too unreasonable, as it is single particle motion we are interested in, and only local relaxation should occur on these short timescales. This potential explanation is consistent with q -dependent neutron scattering results²⁰ for glycerol. It is also possible that the TRSS response is not entirely scale-invariant in highly viscous media²³, and that motions on an intermediate lengthscale may be sensed preferentially.²⁴ We see from the long-time behavior discussed above that if motions on some lengthscale are sensed preferentially, this lengthscale must be $\xi > 1 \text{ nm}$ for glycerol. It is left for future work to determine the underlying reasons for the striking correspondence between TRSS and neutron scattering at short times and low temperatures.

Having time domain data that reproduces the short-time behavior of the intermediate scattering function, we are in a position to comment on recent treatments of the relationship

between short time and long time dynamics in glassforming liquids. During the past couple of decades several lines of investigation have lead to a number of proposed relationships between DW factors obtained on the ps timescale, and α relaxation that occurs on much longer times^{25–29}. Typically the functional forms used are variations on a proportionality proposed by Hall and Wolynes²⁵ (HW), as $\ln(\tau_\alpha) \propto \alpha^2 \langle u^2 \rangle^{-1}$. This relation obtains if α relaxation is assumed to progress along a potential energy landscape where the energy wells are parabolic and uniformly separated by a distance a ³⁰. This formalism considers $\langle u^2 \rangle$ for the system within the potential wells, so DW factors used in these relationships must be measured in a narrow time window where both the ballistic and the relaxation effects are not present. This time window starts at roughly 1 ps.²⁸

The HW relation assumes uniform separation of potential energy minima, and thus a dynamically homogeneous system. On the other hand, dynamics in supercooled liquids and glasses are known to be spatially heterogeneous³¹. Larini et al.²⁸ have proposed that dynamic heterogeneity can be represented in the HW formalism by a distribution of potential energy minima spacings, and thus have added a quadratic term. They have suggest that this form can universally fit rescaled DW data from the high temperature regime down through T_g .

Here we use our time-resolved relaxation data to comment on conditions under which this expanded HW relationship might be valid. We evaluate the relationship in terms of absolute (rather than rescaled) fit for glycerol. To do so requires only that we add a term to the relation of Larini et al. to account for α relaxation time in the high temperature limit ($\tau_{\alpha,\infty}$):

$$\tau_\alpha = \tau_{\alpha,\infty} \exp \left[\frac{\alpha^2}{2 \langle u^2 \rangle} + \frac{\sigma_{\alpha^2}^2}{8 \langle u^2 \rangle^2} \right] \quad (4)$$

where α^2 and $\sigma_{\alpha^2}^2$ are the average and variance in the square of a molecular displacement required for local structural relaxation.

In Fig. 3 we plot $\log(\tau_\alpha)$ from glycerol against $\langle u^2 \rangle^{-1}$ obtained from neutron scattering on timescales of 2.2 ns, 40 ps or 1 ps as indicated. These data are fitted to Eq. (4) and fit parameters are shown in Table 1. We note that the data clearly fit better to a quadratic form than a linear one at all timescales, but that the fit values for $\sigma_t = 40$ ps and $\sigma_t = 2.2$ ns data are unphysical. Inspection of the time domain data in of Fig. 1b gives us the reason for the unphysical fits parameters; $F_s(q_{\max}, t)$, and thus DW factors derived from it, are directly influenced by slow relaxation processes at almost all temperatures for the 2.2 ns data, and at the highest temperatures for the 40 ps data. DW factors obtained in these regimes become artificially high to an increasing extent as temperature is raised, leading to excessive curvature at low values of $\langle u^2 \rangle^{-1}$. In this vein, Ottochan et al.^{33, 34} have suggested that DW factors acquired on timescales of 5 ns may not be used in Eq. (4) to obtain universal fits. Our results are consistent with theirs, although we show that one obtains reasonable fit values to absolute (rather than rescaled) data only when DW factors on the shortest timescales are considered. We also see that DW factors acquired at times as short as 40 ps can have significant influence due to α relaxation at elevated temperatures, and suggest that these should be used with care, even in a rescaled fit. Within the model of Larini et al.²⁸, the positive value of $\sigma_{\alpha^2}^2$ indicates presence of heterogeneity, and, while we clearly obtain a positive, nonzero value for $\sigma_{\alpha^2}^2$, we note that such curvature could arise independent of heterogeneity if, as proposed by Martinez and Angell³⁵, the glassformers explore potential surfaces of increasing curvature as they are cooled.

We have shown that TRSS data can be used as a surrogate for DW factors in glycerol. We expect this result to be general to the extent that that fast (≈ 1 ps) dynamics are intrinsically local. Further exploration of the correspondence between TRSS and $F_s(q,t)$ at these short times is expected to shed further light on the behavior of supercooled and glassy systems, and perhaps provide insight into the TRSS response. As evidenced by the work presented here, we expect that the ability to extract DW-like factors from TRSS data will facilitate a better understanding of the relationships between $\langle u^2 \rangle$ and longtime phenomena. We also expect that it could form the basis for more widespread and routine use of DW factors in characterization of glasses, such as routine and rapid prediction of protein stability in sugar glasses.¹⁰

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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REFERENCES

1. Van Hove M. Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles. *Phys. Rev.* 1954; 95:249–262.
2. Blackman M. A Note on the Debye-Waller Theory. *Acta Crystallographica.* 1956; 9:734–737.
3. Gotze W, Sjogren L. Relaxation Processes in Supercooled Liquids. *Rep. Prog. Phys.* 1992; 55:241–376.
4. Lewis LJ, Wahnstrom G. Molecular-dynamics Study of Supercooled Ortho-terphenyl. *Phys. Rev. E.* 1994; 50:3865–3877.
5. Sciortino F, Kob W. Debye-Waller Factor of Liquid Silica: Theory and Simulation. *Phys. Rev. Lett.* 2001; 86:648–651. [PubMed: 11177903]
6. Angell CA. Formation of Glasses from Liquids and Biopolymers. *Science.* 1995; 267:1924–1935. [PubMed: 17770101]
7. Frauenfelder H, Chen G, Berendzen J, Fenimore PW, Jansson H, McMahon BH, Stroer IR, Swenson J, Young RD. A Unified Model of Protein Dynamics. *P. Natl. Acad. Sci. USA.* 2009; 106:5129–5134.
8. Zaccai G. How Soft Is a Protein? A Protein Dynamics Force Constant Measured by Neutron Scattering. *Science.* 2000; 288:1604–1607. [PubMed: 10834833]
9. Cicerone MT, Soles CL. Fast dynamics and Stabilization of Proteins: Binary glasses of Trehalose and Glycerol. *Biophys. J.* 2004; 86:3836–3845. [PubMed: 15189880]
10. Wang BQ, Tchessalov S, Cicerone MT, Warne NW, Pikal MJ. Impact of Sucrose Level on Storage Stability of Proteins in Freeze-dried Solids: II. Correlation of Aggregation Rate with Protein Structure and Molecular Mobility. *J Pharm. Sci.-Us.* 2009; 98:3145–3166.
11. Nayar R, Manning MC. High Throughput Formulation: Strategies for Rapid Development of Stable Protein Products. *Pharm. Biotechnol.* 2002; 13:177–198. [PubMed: 11987752]
12. Weiss RJ, Demarco JJ, Weremchuk G, Hastings J, Corliss L. Anisotropic Debye-Waller Factors in Cubic Crystals. *Phys. Rev.* 1954; 94:1420.
13. Bellissent-Funel MC, Filabozzi A, Chen SH. Measurement of Coherent Debye-Waller Factor in In Vivo Deuterated C-phycocyanin by Inelastic Neutron Scattering. *Biophys. J.* 1997; 72:1792–1799. [PubMed: 9083683]
14. Ware WR, Chow P, Lee SK. Time-resolved Nanosecond Emission Spectroscopy: Special Shift Due to Solvent-solute Relaxation. *Chem. Phys. Lett.* 1968; 2:356–358.

15. Bagchi B, Oxtoby DW, Fleming GR. Theory of the Time Development of the Stokes Shift in Polar Media. *Chem. Phys.* 1984; 86:257–267.
16. Fee RS, Maroncelli M. Estimating the Time-Zero Spectrum in Time-Resolved Emission Measurements of Solvation Dynamics. *Chem. Phys.* 1994; 183:235–247.
17. Lunkenheimer P, Loidl A. Dielectric Spectroscopy of Glass-Forming Materials: α -relaxation and Excess Wing. *Chemical Physics*. 2002; 284:205–219.
18. Richert R, Stickel F, Fee RS, Maroncelli M. Solvation Dynamics and the Dielectric Response in a Glass-Forming Solvent: From Picoseconds to Seconds. *Chem. Phys. Lett.* 1994; 229:302–308.
19. Wuttke J, Petry W, Coddens G, Fujara F. Fast Dynamics of Glass-Forming Glycerol. *Phys. Rev. E.* 1995; 52:4026–4034.
20. Wuttke J, Chang I, Randl OG, Fujara F, Petry W. Tagged-Particle Motion in Viscous Glycerol: Diffusion-Relaxation Crossover. *Phys. Rev. E.* 1996; 42:5364–5369.
21. Doster W, Diehl M, Petry W, Ferrand M. Elastic Resolution Spectroscopy: A Method to Study Molecular Motions in Small Biological Samples. *Physica B: Cond. Matt.* 2001; 301:65–68.
22. Gehring PM, Neumann DA. Backscattering Spectroscopy at the NIST Center for Neutron Research. *Physica B.* 1997; 241:64–70.
23. Matyushov DV. On the microscopic theory of polar solvation dynamics. *J. Chem. Phys.* 2005; 122 044502.
24. Sen S, Andreatta D, Ponomarev SY, Beveridge DL, Berg MA. Dynamics of Water and Ions Near DNA: Comparison of Simulation to Time-Resolved Stokes-Shift Experiments. *J. Am. Chem. Soc.* 2009; 131:1724–1735. [PubMed: 19191698]
25. Hall RW, Wolynes PG. The Aperiodic Crystal Picture and Free Energy Barriers in Glasses. *J. Chem. Phys.* 1987; 86:2943–2948.
26. Buchenau U, Zorn R. A Relation between Fast and Slow Motions in Glassy and Liquid Selenium. *Europhys. Lett.* 1992; 18:523–528.
27. Starr FW, Sastry S, Douglas JF, Glotzer SC. What Do We Learn from the Local Geometry of Glass-Forming Liquids? *Phys. Rev. Lett.* 2002; 89 125501.
28. Larini L, Ottochian A, De Michele C, Leporini D. Universal Scaling Between Structural Relaxation and Vibrational Dynamics in Glass-forming Liquids and Polymers. *Nat. Phys.* 2008; 4:42–45.
29. Magazu S, Maisano G, Migliardo F, Mondelli C. Mean-Square Displacement Relationship in Bioprotectant Systems by Elastic Neutron Scattering. *Biophys. J.* 2004; 86:3241–3249. [PubMed: 15111437]
30. Dyre JC. The Glass Transition and Elastic Models of Glass Forming Liquids. *Rev. Mod. Phys.* 2006; 78:953–972.
31. Cicerone MT, Blackburn FR, Ediger MD. Anomalous Diffusion of Probe Molecules in Polystyrene: Evidence for Spatially Heterogeneous Segmental Dynamics. *Macromolecules.* 1995; 28:8224–8232.
32. Lunkenheimer P, Wehn R, Riegger Th, Loidl A. Excess Wing in the Dielectric Loss of Glass Formers: Further Evidence for a β -Relaxation. *J. Non-Cryst. Solids.* 2002; 336:307–310.
33. Ottochian A, Leporini D. Scaling between Structural Relaxation and Caged Dynamics in $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ and Glycerol: Free Volume, Time-scales and Implications for Pressure-energy Correlations. *Philos Mag.* 2011; 91:1786–1795.
34. Ottochian A, De Michele C, Leporini D. Universal divergenceless scaling between structural relaxation and caged dynamics in glass-forming systems. *J. Chem. Phys.* 2011; 131 224517.
35. Martinez L-M, Angell CA. A Thermodynamic Connection to the Fragility of Glass-Forming Liquids. *Nature.* 2001; 410:663–667. [PubMed: 11287947]

Figure 1.

a) Time-resolved Stokes shifts for R6G in glycerol at temperatures (from top down) 169 K, 212 K, 234 K, 256 K, 278 K, 293 K, 300 K, 322 K. b) $\Phi(t)$ from Stokes shift data for R6G in glycerol (blue points) at the same temperatures. Solid black lines are stretched exponential fits to the TRSS data. Dashed red lines are $F_s(q,t)$ at $q = 1.4 \text{ \AA}^{-1}$ from neutron scattering¹⁹.

Figure 2. Neutron scattering measured on NG2²² or IN13 and time-of-flight²⁰ (solid red lines) compared with a DW surrogate (blue symbols), obtained from TRSS using Eq (3) and $q = 1.4 \text{ \AA}^{-1}$. Symbol size indicates uncertainties.

Figure 3.

Inverse DW factors plotted against α relaxation times for glycerol. DW factors were obtained at 2.2 ns (squares), 40 ps (circles), and 1 ps (triangles). Neutron scattering data is from ref. 14 or measured on NG2²² at NCNR and viscosity data is from ref.s20 and 32.

TABLE I

Fit parameters for data in Fig. 3 to Eq. (4).

σ_t	$\log(\tau_{a,\infty})$	$\alpha^2 \left(\frac{q_{max}}{2\pi} \right)^2$	$\sigma_\alpha^2 \left(\frac{q_{max}}{2\pi} \right)^2$
1 ps	-11 ± 0.5	0.4 ± 0.05	1.0 ± 0.1
40 ps	-8.5 ± 0.6	-0.3 ± 0.2	1.8 ± 0.2
2.2 ns	-7.2 ± 0.4	-0.7 ± 0.2	4.0 ± 0.4