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Comment on "Elastic incoherent neutron scattering operating by varying instrumental energy resolution: Principle, simulations, and experiments of the resolution elastic neutron scattering (RENS)" [Rev. Sci. Instrum. 82, 105115 (2011)]

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In a recent contribution to this journal, Magazù, Migliardo, and Benedetto suggest to determine relaxation times from inflection points in the elastic neutron scattering intensity as function of (1) resolution time or (2) temperature. Method (1) can be generalized into a scaling law. Method (2) is only approximately valid; its application to protein data does not back a wavenumber-independent dynamic transition. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4757973]

I. INTRODUCTION

In a recent contribution to this journal,[1] Magazù, Migliardo, and Benedetto (MMB) suggest new ways to extract *dynamic* information from *elastic* neutron scattering experiments by varying the instrumental resolution. Based on a numeric example, they conjecture that sample relaxation times τ_S can be determined from inflection points of the elastic scattering as function of resolution time τ_R or temperature T. Reanalyzing literature data on hydrated protein powder, they support controversial[2] claims[3] that there is a physically meaningful kink in the T dependence of $\log \tau_S$.

In this comment, I will generalize the first conjecture of MMB into a scaling law for the resolution dependence of the elastic signal and suggest a numerically more robust method to determine the T dependence of τ_S; I will show that the second conjecture that relates τ_S to an inflection in the T dependence of the elastic signal does not generally hold; and finally, I will expose problems in the protein data analysis.

II. METHODOLOGY

For brevity, only incoherent scattering shall be considered in this comment, and the wavenumber q will be dropped from the scattering function $S(q, \omega)$. The Fourier transform that connects $S(\omega)$ and the self-correlation function $I(t)$ shall be used in the asymmetric form that is universally accepted in neutron scattering. MMB deviate from this convention (though they cite the classical texts[4–6] that established it), introducing symmetric prefactors $1/\sqrt{2\pi}$. This breaks either the normalization $\int d\omega\, S(\omega) = 1$ or the initial value $I(0) = 1$.[7]

It is advisable to define the instrumental resolution $R(\omega)$ as a probability density normalized to 1 so that the expected experimental signal, the resolution-broadened scattering function, can be written as a convolution integral $S_R(\omega) := \int d\omega'\, R(\omega - \omega')S(\omega')$. Therefore, a prefactor $\tau_{\text{RES}}/\sqrt{2\pi}$ should be inserted in Eq. (8) of Ref. 1. Without this correction,

Eqs. (7) and (11) are dimensionally inconsistent with each other.

In inelastic neutron scattering experiments, an absolute scale can be established by straightforward normalization. For elastic scans, absolute units of $S(\omega = 0)$ are meaningless. Instead, the resolution-broadened elastic scattering intensity is usually normalized to a purely elastic scatterer,

$$F_R = \frac{\int d\omega\, R(-\omega)S(\omega)}{\int d\omega\, R(-\omega)\delta(\omega)} = \frac{\int d\omega\, R(-\omega)S(\omega)}{R(0)}. \qquad (1)$$

This seems to be tacitly done in Figs. 2, 3, and 5, but not in Eq. (6) and Fig. 7 of Ref. 1.

Let $\omega_X \sim 1/\tau_X$ denote a characteristic width of function $X = R, S$, and let us assume with MMB that S is all quasielastic (no phonon scattering, Lamb-Mossbauer factor of 1). Depending on ω_S/ω_R, the measured F_R crosses over from well-resolved elastic scattering $F_R \simeq S(0)$ for $\omega_S \gg \omega_R$ to resolution-dominated $F_R \simeq 1$ for $\omega_S \ll \omega_R$. MMB introduce this "dynamical transition" with a series of didactic figures as if it were a novel and difficult insight, while it is actually well known since the early days of neutron backscattering when the pioneers explained it in few sentences.[8] In 1976, Leadbetter *et al.*[9] communicated a quantitative expression for F_R that contains all the physics of MMB's Eq. (11).

Reference 1 is all based on simulations, and the simulations are all based on a specific choice of $R(\omega)$ and $S(\omega)$, both assumed to be Gaussians. This is an acceptable approximation for R, but not for S. Gaussian scattering functions, characteristic for noninteracting particles with a Maxwell velocity distribution, have little more than didactic interest, being applicable only to dilute gases and to the extreme short-time regime of ballistic motion. Describing a Gaussian S as a "diffusive model" is a misunderstanding: For translational diffusion $I(q, t)$ is Gaussian in q, but not in t.

To defend the choice of an oversimplified model, one could bring up its analytic simplicity: the convolution of two Gaussians yields another Gaussian. However, the convolution of a Gaussian resolution and a Lorentzian scattering function would provide a much more realistic model while still being

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analytically tractable, as Doster *et al.* exploited in their seminal work on elastic resolution spectroscopy.[10,11]

The "main innovation" claimed by MMB [page 2 of Ref. 1] consists in the suggestion to determine τ_S from the inflection point of F_R as function of ω_R,

$$\tau_S = c/\omega_R^{\text{infl}} \tag{2}$$

with $c = 1$. However, this only comes out because S and R have been parametrized in different ways by [Eq. (8) vs. (9) of Ref. 1]. For standard Gaussians, one gets the less suggestive $c = 1/\sqrt{2}$.

Anyway, since S is usually *not* a Gaussian one should better not rely on the numeric value of c. I rather suggest to see the linear dependence of τ_S on τ_R^{infl} as a prototypical scaling result. It can be obtained without specifying any functional form for R and S. It is only necessary to require scaling conditions ensuring that τ_S and τ_R be the only relevant time scales:

$$S(\omega; \tau_S) = \tau_S \tilde{S}(\omega\tau_S), \tag{3}$$

$$R(\omega; \tau_R) = R(0) \tilde{r}(\omega\tau_R) \tag{4}$$

with $\tilde{r}(0) = 1$. Taking into account the normalization of F_R to a purely elastic scatterer (1), one reads off the scaling form

$$F_R(\tau_S, \tau_R) = \int d\omega \tau_S \, \tilde{r}(-\omega\tau_R)\tilde{S}(\omega\tau_S) = \tilde{F}(\tau_R/\tau_S) \tag{5}$$

with the functional form of $\tilde{F}$ depending on that of $\tilde{S}$ and $\tilde{r}$. It is then obvious that an inflection of F_R must be located at

$$\tau_R^{\text{infl}} = \tau_S/\tilde{c} \tag{6}$$

with $\tilde{c}$ depending only on the form of $\tilde{F}$.

It is unlikely that elastic resolution scans will be used to determine *one* relaxation time τ_S on absolute scale. In a more plausible application, one would perform resolution scans at different sample conditions, say at different temperatures T. One could then employ (6) to determine the T dependence of $\tau_S(T)$ while ignoring the numeric value of $\tilde{c}$.

Determining an inflection point from noisy experimental data is impractical. The scaling form (5) suggests a more robust method, namely, an iterative master curve construction: For given T, plot and replot the measured $F_R(\tau_S, \tau_R)$ on reduced time scales τ_R/τ_S until all data points fall onto a common curve. Such an analysis makes full use of the experimental data set, not just of a few points around τ_R^{infl}, and it even works if τ_R^{infl} falls outside the accessible τ_R range.

The second conjecture MMB concerns F_R at constant τ_R as function of T,

$$\tau_S(T^{\text{infl}}) = c\tau_R, \tag{7}$$

where c is subject to the same remarks as before. MMB support their discovery by no more than a numeric example and a graphical analysis, assuming Gaussian R and S as before, and an Arrhenius law $\tau_S = \tau_\infty \exp(A/T)$. This model is analytically tractable up to a transcendental equation for the inflection point T^{infl},

$$\frac{\tau_R}{\tau_\infty} \exp\left(-\frac{A}{T^{\text{infl}}}\right) = \frac{1}{c} \sqrt{\frac{A - T^{\text{infl}}}{A + 2T^{\text{infl}}}}. \tag{8}$$

MMB, by choice of their parameters $\tau_\infty \simeq 0.7$ ps and $A \simeq 1000$ K (infered from Fig. 8(a)) only consider the limiting case $T \ll A$ where the square root is so close to 1 that (7) is approximately fulfilled. For less special parameter values, or for almost all other functions $\tau_S(T)$, Eq. (7) does not hold. Therefore, an inflection in $F_R(T)$ cannot normally be used to determine τ_S.

III. REINTERPRETATION OF PROTEIN DATA

MMB terminate their contribution[1] by an application to a hydrated protein. In Fig. 9 (essentially published before as abstract figure in Ref. 12, critically discussed in Ref. 13), they find outstanding agreement between the inflection times $\tau_S(T^{\text{infl}})$ and relaxation times $\tau_{\text{QENS}}(T)$ from the literature.[3] Those τ_{QENS} originate from model-dependent fits to weak quasielastic scattering in an asymptotic power-law regime where time scale and amplitude are degenerate so that model fits are underdetermined. This may cause the τ_{QENS} to be wrong by orders of magnitude at the lowest T.[2] In the worst case, the *shape* of $S(\omega)$ varies with T,[14] which makes it rigorously impossible to determine relaxation times $\tau_S \gg \tau_R$ from neutron scattering—no matter whether carried out as spectral measurements or as elastic resolution scans.

The protein data analysis of MMB depends crucially on the numeric values of τ_R attributed to the four different spectrometers. From page 9 of Ref. 1, it appears that MMB took their τ_R from nominal resolution widths. However, rough rounding (1 μeV for IN10) and other discrepancies (0.85 μeV for HFBS, where the online documentation has 0.79 μeV; 100 μeV for IN4 where Ref. 12 has 200 μeV) cast a doubt upon the reliability of these data. No justification is given for the conversion formula on page 3, and it has not been uniformly applied: with the fwhm data of page 9 and the τ_R data of page 10, $\tau_R \cdot$ fwhm$/\hbar$ is 3.33 for IN10, but 3.58 for HFBS.

The four spectrometers used in this analysis operate at different neutron wavelengths, and therefore cover different q ranges. These ranges are documented neither in Ref. 1, nor in the preceding experimental paper.[12] From Fig. 9 in Ref. 1, one can infer that MMB assume a simple functional relationship between the elastic scattering F_R and the mean squared displacement $\langle r^2 \rangle$, most likely in the standard form

$$F_R = \exp(-q^2 \langle r^2 \rangle/3). \tag{9}$$

However, Eq. (9) is rarely the full story; there are many possible physical causes for systematic deviations,[6,15,16] with further distortions due to multiple scattering[17,18] and resolution effects.[18–20] A linear dependence of $\ln F_R$ on q^2 can be observed at most for limited q ranges. In consequence, a q independent analysis is justified neither for F_R nor for $\langle r^2 \rangle$, and will result in uncontrolled errors.

Determining an inflection point by differentiation of noisy data can be a difficult undertaking. MMB do not explain how they obtain their T^{infl}. The only pertinent remark is in the caption of Fig. 9 in Ref. 1. Figures 9(a) and 9(b) show $\langle r^2 \rangle$ versus T. A change in slope at 220 K (IN10) or 240 K (IN13) is identified as "dynamical transition." The figure caption then says: "These transition temperatures are equal to the inflection point temperatures shown in the two insets." The

insets show F_R versus T, but no inflection. Also, there is no theoretical reason why a kink in $\langle r^2 \rangle(T)$ should produce an inflection in $F_R(T)$. Similarly, the HFBS studies[3,21] cited by MMB do not support an inflection of $F_R(T)$ at 200 K.

For all these reasons, the data analysis of MMB does not back the claim[3] that there is a q-independent kink in $\ln \tau_S$ vs. T at 220 K. Detecting such a kink from (7) is inconsistent anyway since that equation has been derived assuming a kink-free Arrhenius law for $\tau_S(T)$.

ACKNOWLEDGMENTS

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