

Supplementary Information: Dynamics of Molecular Associates in Methanol Water Mixtures

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I. PARTIAL DYNAMIC STRUCTURE FACTORS

The neutron coherent dynamic structure factor is defined as the sum of the dynamic structure factors of all pairs of atomic species α and β :

$$S_{coh}(Q, E) = \frac{1}{N} \sum_{\alpha=1}^n \sum_{\beta=1}^n b_{\alpha}^{coh} b_{\beta}^{coh} \sqrt{N_{\alpha} N_{\beta}} S^{\alpha\beta}(Q, E) \quad (S1)$$

where N is the total number of atoms, b_{α}^{coh} is the coherent scattering length of the α atoms, and:

$$S^{\alpha\beta}(Q, E) = \frac{1}{\hbar \sqrt{N_{\alpha} N_{\beta}}} \sum_{i_{\alpha}=1}^{N_{\alpha}} \sum_{i_{\beta}=1}^{N_{\beta}} \int_0^{\infty} \langle e^{i[\mathbf{Q} \cdot \mathbf{R}_{i_{\alpha}}(t) - \mathbf{Q} \cdot \mathbf{R}_{i_{\beta}}(0)]} \rangle e^{-i \frac{Et}{\hbar}} dt \quad (S2)$$

$$= \mathcal{F} \left\{ \frac{1}{\sqrt{N_{\alpha} N_{\beta}}} \sum_{i_{\alpha}=1}^{N_{\alpha}} \sum_{i_{\beta}=1}^{N_{\beta}} \langle e^{i[\mathbf{Q} \cdot \mathbf{R}_{i_{\alpha}}(t) - \mathbf{Q} \cdot \mathbf{R}_{i_{\beta}}(0)]} \rangle \right\} \quad (S3)$$

$$= \mathcal{F} \{ I^{\alpha\beta}(Q, t) \} \quad (S4)$$

N_{α} being the number of atoms of the α species in the sample, $\mathcal{F} \{ \}$ indicates a Fourier transform, and $I^{\alpha\beta}(Q, t)$ is the coherent Intermediate Scattering Function (ISF) for the couple of atoms α and β .

The incoherent dynamic structure factor is given by the sum of the incoherent dynamic structure factor of each atomic species:

$$S_{inc}(Q, E) = \sum_{i_{\alpha}=1}^{N_{\alpha}} N_{\alpha} \frac{\sigma_{\alpha}^{inc}}{4\pi} S_{inc}^{\alpha}(Q, E) \quad (S5)$$

where σ_{α}^{inc} is the incoherent scattering cross-section of the α atoms and:

$$\begin{aligned} S_{inc}^{\alpha}(Q, E) &= \frac{1}{\hbar N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \int_0^{\infty} \langle e^{i[\mathbf{Q} \cdot \mathbf{R}_{i_{\alpha}}(t) - \mathbf{Q} \cdot \mathbf{R}_{i_{\alpha}}(0)]} \rangle e^{-i \frac{Et}{\hbar}} dt \\ &= \mathcal{F} \left\{ \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \langle e^{i[\mathbf{Q} \cdot \mathbf{R}_{i_{\alpha}}(t) - \mathbf{Q} \cdot \mathbf{R}_{i_{\alpha}}(0)]} \rangle \right\} \\ &= \mathcal{F} \{ I_{inc}^{\alpha}(Q, t) \} \end{aligned} \quad (S6)$$

$\mathbf{R}_{i_{\alpha}}$ being the position of the i -th α atom and $I_{inc}^{\alpha}(Q, t)$ the self ISF for the atomic species α .

II. DISCUSSION ON THE UNCERTAINTIES IN THE EXPERIMENTAL PROCEDURE

It is worth discussing the uncertainty related to the isotopic substitution method employed in this work, resulting in Eq. 1. First of all, it should be noted that, if present, any correlation between MM, WH, and MH is weak as no dominant contribution can be identified in the structure factors of the four samples investigated. In fact, as it will be seen later, the intensity of $S^C(Q)$ (I^C) is only a fraction of the intensity of the most intense scattering sample, S4. Moreover, because the determination of $S^C(Q)$ (I^C) requires the combination of the scattering from samples S1-S4, it is crucial that the four samples are consistent with each other. As noticed above, extra care was taken to make sure that the composition of the four samples was the same with sufficient accuracy. In a coherent neutron scattering experiment multiple scattering effects are usually not critical. This is because multiple scattering arises mostly from the incoherent scattering and contributes to a flat background which can usually be neglected in the Q ranges where the coherent scattering is dominant. Of course, extra care should be taken to make sure that double scattered neutrons from a particularly strong coherent feature in the sample will not produce artifacts. In order to minimize the multiple scattering intensity below that of $S^C(Q)$ (I^C) the sample thickness was chosen as to ensure $\approx 90\%$ transmission in the S4 sample. It should be kept in mind that, assuming that the multiple scattering arises mostly from double incoherent scattering events from the hydrogen atoms, in calculating $S^C(Q)$ (I^C), 50% of the multiple scattering is automatically subtracted: only the multiple scattering coming from neutrons scattered first by the MM (WH or MH) and then by WH or MH (MM) are not accounted for. In order to keep the scattering geometry the same for all samples and reduce the uncertainty on the scattering volume all samples had the same thickness. Given the small amount of sample illuminated by the beam, small differences originate significant errors. To minimize this uncertainty, SANS measurements were performed on three specimens for each of the S1-S4 samples. The obtained scattering for each triplet was averaged out. The individual scattering for each sample measured on the other spectrometer was normalized to the SANS results before $S^C(Q)$ (I^C) was determined (see Fig. S1). Consistency among the data sets obtained from different instrument was thus achieved.

The method is based on the assumption that the properties of the system are not affected by the isotopic substitution. In the past, it has been shown that the isotopic substitution can have a significant impact on the phase diagram of systems where a delicate balance of hydrogen bonding and hydrophobic forces are at play.[1, 2] In the case of methanol the effect of substituting H with D has been addressed both for the structure and the dynamics. The effect is of the order of 10%, [3, 4] although at low temperatures it might be larger.[4] Keeping this in mind, $S^C(Q, E)$ and $I^C(Q, t)$ should be considered a weighted sum of the correlation functions corresponding to the methyl hydroxyl correlations according to eq. 1 and eq. 2, with the methyl atoms being hydrogenated and the hydroxyl atom deuterated and vice-versa.

III. HYDRODYNAMIC LIMIT OF THE PARTIAL DYNAMIC STRUCTURE FACTORS OF A BINARY LIQUID MIXTURE

This section summarises, for the reader convenience, the expression of the partial intermediate scattering functions, $I^{CM_M-CM_M}(Q, t)$ and $I^{CM_M-CM_W}(Q, t)$, in the hydrodynamic limit obtained from the derivation by Bathia, Thornton, and March for a fluid binary mixture.[5]

In the hydrodynamic limit these partial intermediate scattering functions are the sum of two diffusive exponential decays:

$$I^{CM_M-CM_M}(Q \rightarrow 0, t) = A_1^{MM} \exp[-D_1 Q^2 t] + A_2^{MM} \exp[-D_2 Q^2 t] \quad (S7)$$

$$I^{CM_M-CM_W}(Q \rightarrow 0, t) = A_1^{MW} \exp[-D_1 Q^2 t] + A_2^{MW} \exp[-D_2 Q^2 t] \quad (S8)$$

where:

$$D_1 = \frac{1}{2} \{ (\chi + D) + \sqrt{(\chi + D)^2 - 4\chi D^M} \}$$

$$D_2 = \frac{1}{2} \{ (\chi + D) - \sqrt{(\chi + D)^2 - 4\chi D^M} \} \quad (S9)$$

$$D = D^M \left[1 + \frac{k_T^2 Z}{TC_P} \right] \quad (S10)$$

$$Z = \left[\frac{\partial \mu_c}{\partial c} \right]_{P,T,N} = \left[\frac{\partial^2 G}{\partial c^2} \right]_{P,T,N} \quad (S11)$$

$$A_1^{MM} = \frac{2N k_B T x_M \left(\frac{\alpha_T D k_T}{C_P} + \frac{\delta(D-D_2)}{Z} \right)}{-D_1 + D_2} + \frac{(1-\gamma) \kappa_T N k_B T x_M^2 \left(D - \frac{2D\delta k_T}{\alpha_T T} - D_1 + \frac{C_P \delta^2 (-D+D_2)}{\alpha_T^2 T Z} \right)}{\gamma V (D_1 - D_2)} + \frac{N k_B T (-D + D_2)}{(-D_1 + D_2) Z} \quad (S12)$$

$$A_2^{MM} = \frac{2N k_B T x_M \left(\frac{\alpha_T D k_T}{C_P} + \frac{\delta(D-D_1)}{Z} \right)}{D_1 - D_2} - \frac{(1-\gamma) \kappa_T N k_B T x_M^2 \left(D - \frac{2D\delta k_T}{\alpha_T T} - D_2 + \frac{C_P \delta^2 (-D+D_2)}{\alpha_T^2 T Z} \right)}{\gamma V (D_1 - D_2)} + \frac{N k_B T (-D + D_1)}{(D_1 - D_2) Z} \quad (S13)$$

$$A_1^{MW} = \frac{N k_B T (1 - 2x_M) \left(\frac{\alpha_T D k_T}{C_P} + \frac{\delta(D-D_2)}{Z} \right)}{-D_1 + D_2} + \frac{(1-\gamma) \kappa_T N k_B T (1 - x_M) x_M \left(D - \frac{2D\delta k_T}{\alpha_T T} - D_1 + \frac{C_P \delta^2 (-D+D_2)}{\alpha_T^2 T Z} \right)}{\gamma V (D_1 - D_2)} \quad (S14)$$

$$- \frac{N k_B T (-D + D_2)}{(-D_1 + D_2) Z}$$

$$A_2^{MW} = \frac{2N k_B T (1 - 2x_M) \left(\frac{\alpha_T D k_T}{C_P} + \frac{\delta(D-D_1)}{Z} \right)}{D_1 - D_2} - \frac{(1-\gamma) \kappa_T N k_B T (1 - x_M) x_M \left(D - \frac{2D\delta k_T}{\alpha_T T} - D_2 + \frac{C_P \delta^2 (-D+D_2)}{\alpha_T^2 T Z} \right)}{\gamma V (D_1 - D_2)} \quad (S15)$$

$$- \frac{N k_B T (-D + D_1)}{(D_1 - D_2) Z}$$

Here, N is the number of molecules; V is the volume; T is the absolute temperature; k_B is the Boltzmann constant; x_M still represents the methanol mole fraction; κ_T is the isothermal compressibility; k_T is the thermal diffusion ratio; δ represents the fractional change in the volume of the mixture with concentration; $\gamma = C_P/C_V$ is the ratio of the heat capacities at constant pressure, C_P , and volume, C_V ; α_T is the coefficient of thermal expansion; $\chi = \frac{V\lambda}{C_P}$, is the thermal diffusivity, where λ is the coefficient of thermal conductivity; α_T is the coefficient of thermal expansion; D^M is the coefficient of mutual diffusion, k_T is the thermal diffusion ratio, and $\mu_c = N(\mu_M - \mu_W)$, where $\mu_\alpha = \left[\frac{\partial G}{\partial N_\alpha} \right]_{P,T,N_\beta}$ is the chemical potential per atom of type α (i.e. Methanol, M, or Water, W), G being the Gibb's free energy.

For methanol/water mixtures at 290 K, from reported data,[6–8] it can be seen that $D \approx D^M$, so that $D_1 = \chi$ and $D_2 = D^M$. The thermal diffusivity can be estimated [8–10] to be of the order of 10^{-7} m²/s, which is too fast to be measured with the experimental window. Moreover, with reference to Eqs. S7, the weight of its contribution is about two orders of magnitude smaller than the one associated with the mutual diffusion.[11, 12]

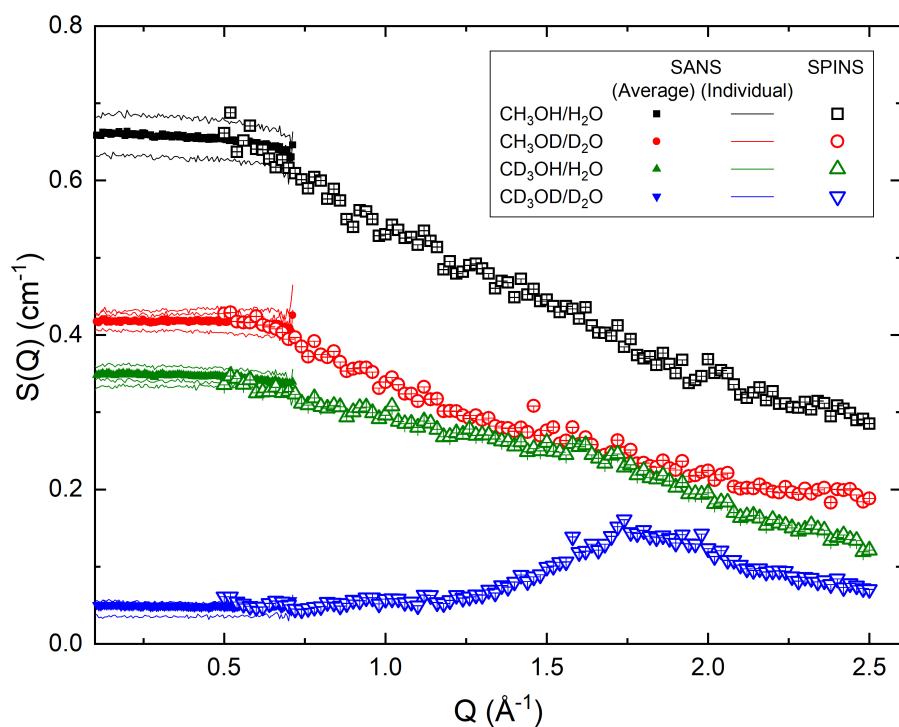


FIG. S1. a) The static structure factor measured for S1-S4 samples using SANS and SPINS. For the SANS measurements, for each sample three sets of data (individual) were collected using different specimens. For each sample the three sets of data give an indication of the reproducibility of the data with respect to the sample thickness. The points represent the average of the sum of the three samples. The statistical error of the measurement is smaller than the symbol size. Open symbols are the results obtained using SPINS for Q values larger than those which can be accessed by SANS. The SPINS data have been normalized to overlap in the low Q region with the SANS data.

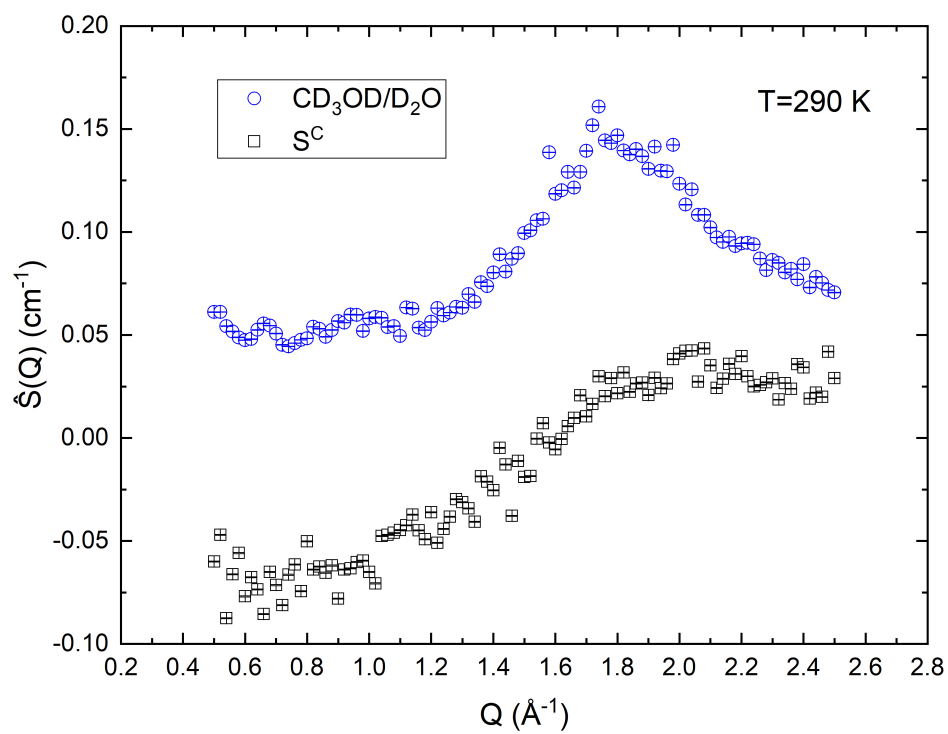


FIG. S2. Comparison of the structure factors measured at $T = 290$ K on SPINS for the perdeuterated sample and as obtained from Eq. 1, i.e. $S^C(Q)$. The methanol mole fraction was $x_M = 0.54$.

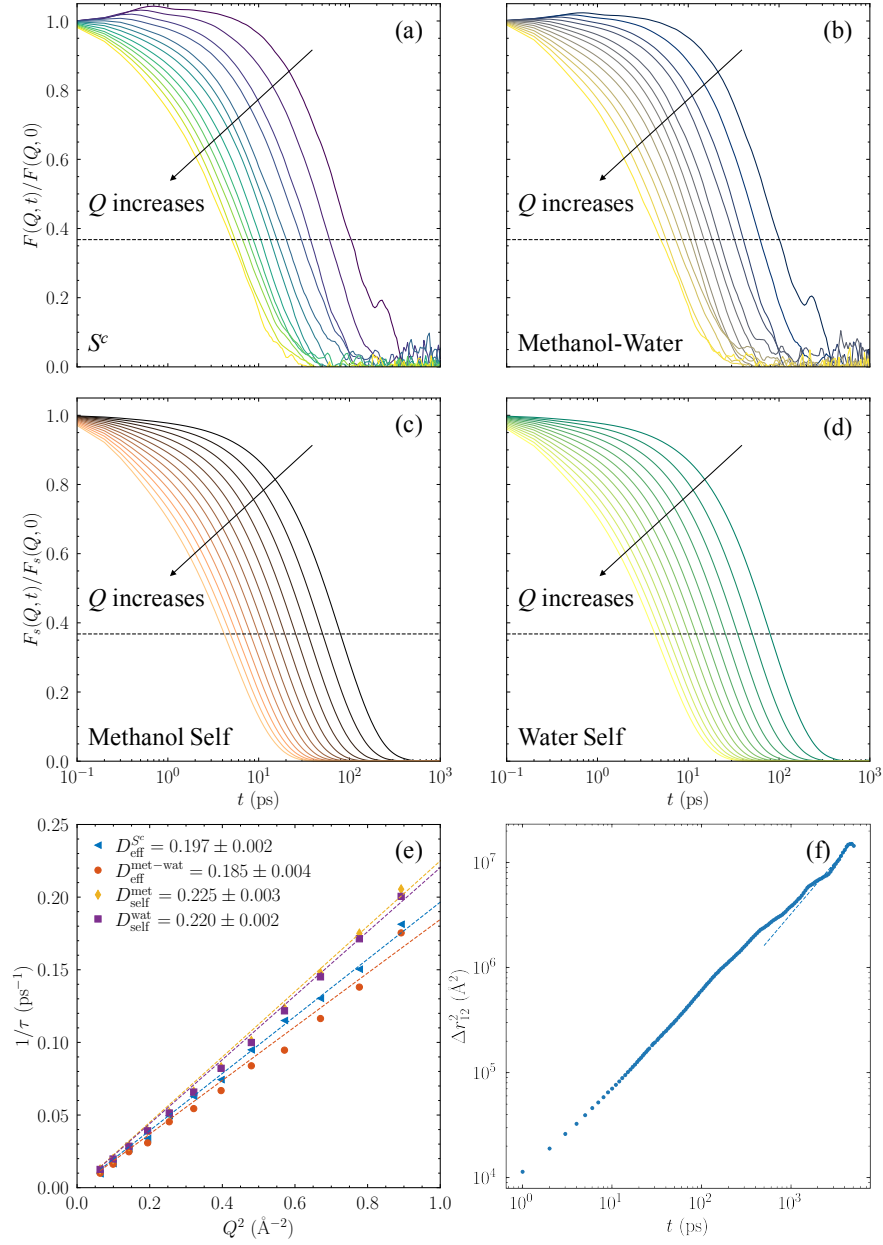


FIG. S3. Collective intermediate scattering functions of (a) S^c and (b) methanol-water mixture with $x^M = 0.54$, and self intermediate scattering functions of (c) methanol and (d) water. (e) A fitting of relaxation times defined as the time for intermediate scattering to decay to $1/e$ as functions of Q , which provides diffusion coefficients. (f) Mutual mean squared displacement of methanol-water mixture with $x_M = 0.54$. The fitting for $t > 100$ ps is shown as the dash line.

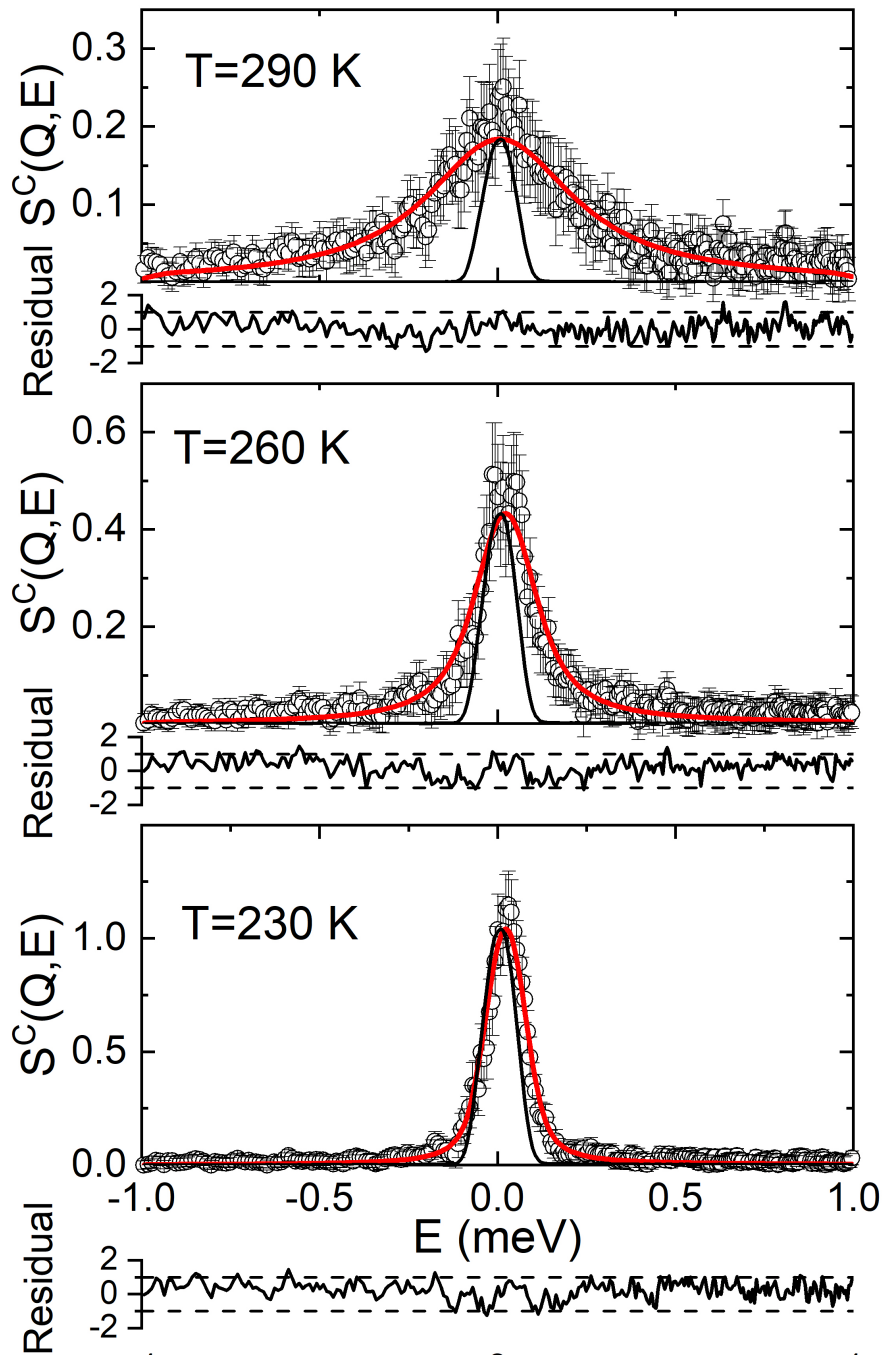


FIG. S4. Fitting of the QENS data for $S^C(Q, E)$ at $Q = 1.8^{-1}$, $x_M = 0.54$, using Eq. 11. The thick red line represents the fitting curve whereas the black line is the instrumental resolution. The normalized residuals, defined as $\frac{\text{exp. data} - \text{fitting}}{\text{error}}$, are shown as well.

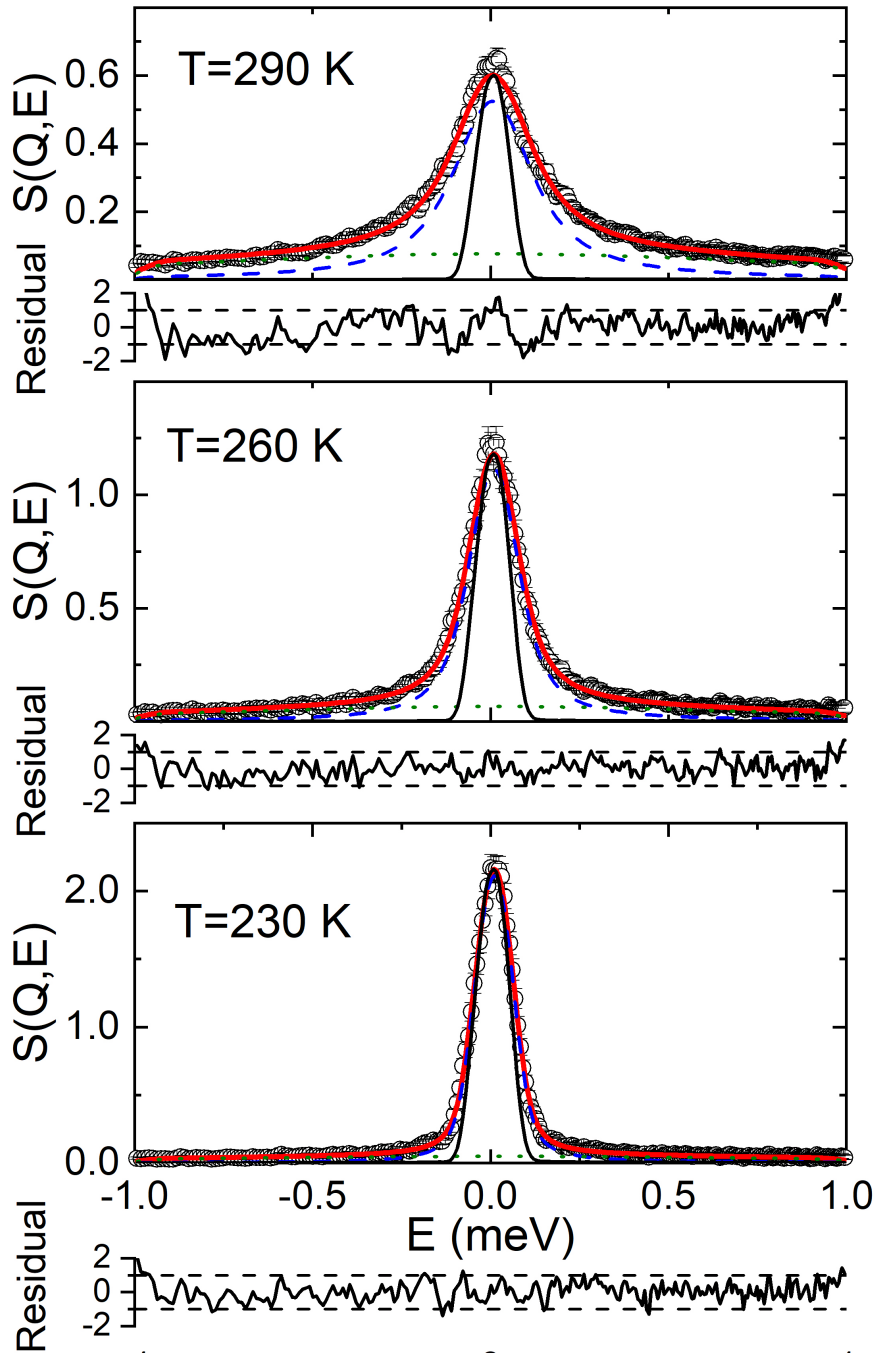


FIG. S5. Fitting of the QENS data for perdeuterated sample at the main structure factor peak, $Q = 1.8^{-1}$, $x_M = 0.54$, using Eq. 16. The thick red line represents the fitting curve whereas the black line is the instrumental resolution. Other lines indicate the two individual Lorentzian components. The normalized residuals, defined as $\frac{\text{exp. data} - \text{fitting}}{\text{error}}$, are shown as well.

DISCLAIMER

Uncertainties and error bars throughout the SI represent the confidence interval of one standard deviation.

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