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Nanoscopic length scale dependence of hydrogen bonded molecular associates' dynamics in methanol

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In a recent paper [C. E. Bertrand *et al.*, J. Chem. Phys. **145**, 014502 (2016)], we have shown that the collective dynamics of methanol shows a fast relaxation process related to the standard density-fluctuation heat mode and a slow non-Fickian mode originating from the hydrogen bonded molecular associates. Here we report on the length scale dependence of this slow relaxation process. Using quasielastic neutron scattering and molecular dynamics simulations, we show that the dynamics of the slow process is affected by the structuring of the associates, which is accessible through polarized neutron diffraction experiments. Using a series of partially deuterated samples, the dynamics of the associates is investigated and is found to have a similar time scale to the lifetime of hydrogen bonding in the system. Both the structural relaxation and the dynamics of the associates are thermally activated by the breaking of hydrogen bonding. [http://dx.doi.org/10.1063/1.4983179]

I. INTRODUCTION

The fact that many liquids, although homogeneous at the macroscopic level, present significant structuring at the nanoscopic scale is attracting increasing attention.¹ Such behavior can be investigated by determining the structure factor of the system through a measurement, using X-rays or neutrons, of the static scattered intensity as a function of the scattering wavevector, Q. The existence of structuring is particularly evident in hydrogen bonding liquids. In the case of alcohols and other glass forming liquids, the existence of nanoscopic supramolecular ordering is put in evidence by a prepeak in the structure factor at Q values smaller than the First Sharp Diffraction Peak (FSDP), indicating ordering at length scales larger than the inter-molecular distance.

Methanol can be considered as the simplest alcohol and, because of its structural form comprised of a hydrophilic hydroxyl group and a hydrophobic methyl group, the simplest surfactant. Because of these characteristics, together with its relevance in many industrial processes, it is an important model system.² In the past, liquid methanol was investigated extensively using, among other methods, Molecular Dynamics (MD)^{3,4} simulations and different experimental techniques including X-ray⁵⁻⁹ and neutron scattering,¹⁰⁻¹⁵ Dielectric Relaxation (DR) spectroscopy,^{16–19} and Nuclear Magnetic Resonance (NMR).²⁰ The presence of associated molecular structures has been proposed on the basis of early scattering results^{5,6} and molecular dynamics simulations¹³ and is still under investigation.⁷ The dynamics of liquid methanol has been investigated through spectroscopic techniques such as DR,¹⁶⁻¹⁹ NMR,²⁰ and QuasiElastic

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Neutron Scattering (QENS).²¹ Previous QENS investigations on liquid methanol²¹ focused on the accurate description of the measured linewidth as well as on the proper separation of the collective and single particle dynamic signals. However, the relaxational dynamics of the H-bonded associates in methanol have not been investigated.

QENS²² is a technique that measures the characteristic relaxation times of neutron scattering length density fluctuations over specific length scales in the range from Ångstroms to several nanometers. Among scattering techniques, it is unique in its ability to probe relaxation processes taking place over time scales ranging from picoseconds to tens of nanoseconds over the above mentioned nanoscopic length scale. As a result of the way neutrons are scattered by nuclei, the neutron scattering signal can be divided into a coherent component determined by the relative positions and motions of the different atoms, i.e., the collective dynamics; and an incoherent component, which does not provide any structural information, and is determined by the single particle dynamics of the scattering atoms. In contrast, X-ray and light scattering techniques only provide a coherent contribution. The relative weights of the coherent and incoherent neutron scattering signals vary with the scattering wavevector and also depend on the isotopic composition of the system. Coherent and incoherent scattering also affect the spin of a scattered neutron in different ways, so that, using appropriate polarized neutron techniques, it is possible to separate the coherent and incoherent contributions. Hydrogen atoms have a very large incoherent scattering cross section; in fact, QENS has been extensively used to probe the single particle dynamics of hydrogen atoms in several molecular liquids. In contrast, only a handful of QENS investigations focused on the collective dynamics of supramolecular aggregates can be found. In a study of the prototypical fragile glass former m-toluidine,²³ it was found that the H-bonded associates are short lived, with their existence being determined

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by the single particle dynamics of the molecules forming the cluster. On the other hand, investigation²⁴ carried out on 1-propanol has shown that in this case (and most likely in all alcohols), the structures are longlived. In general, there are only a few QENS studies²⁵ of the collective dynamics and there is a need for further development of the theory, especially at length scales approaching the mesoscale.²⁶ In a recent paper,^{27,28} we have used QENS and MD simulations to show that molecular association in methanol gives rise, together with the thermal diffusive dynamics, to a slow, non-Fickian, relaxational process. This slow dynamics is observed in QENS data on perdeuterated methanol and should be considered a signature of molecular association.

Using a combination of neutron scattering techniques and MD simulations, the work reported here addresses the detailed Q dependence of the additional slow relaxation process and establishes its relation to the molecular motions of the associates. In Sec. II, the details of the experimental setup, the principles of neutron scattering measurements, and the parameters of the computer simulations will be reviewed. Sec. III lists and discusses within the framework of current research of the obtained results, from MD simulations as well as from polarized diffraction and QENS measurements. Sec. IV summarizes the main results of the work.

II. MATERIALS AND METHODS

A. Samples

Hydrogenated (CH₃OH), fully deuterated (CD₃OD, D 99.8% purity) and hydroxyl partially deuterated (CH₃OD, D 99.5% purity) methanol were purchased from Sigma-Aldrich.²⁹ Methyl partially deuterated methanol (CD₃OH, D 99.8% purity) was purchased from CDN isotopes.²⁹ The liquids were used without further purification.

B. Instrumentation

We report the results of polarized diffraction measurements performed using a Neutron Spin-Echo (NSE) spectrometer and QENS measurements performed using a Time-of-Flight instrument.

For all experiments, the samples were arranged in an annular geometry and contained in aluminum cans sealed with indium. Polarized diffraction measurements were performed using a sample thickness of 1 mm. For the QENS measurements, the sample thickness was 0.08 mm in order to limit multiple scattering to an acceptable level.

Polarized diffraction measurements were performed at room temperature whereas for the QENS experiment, the temperature was controlled using a closed cycle refrigerator in the range from 290 K to 180 K, with an accuracy of ≈ 1 K.

All neutron scattering measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). Polarized diffraction measurements were carried out using the NSE spectrometer on neutron guide NG-A,³⁰ and the QENS measurements were performed using the Disk Chopper Spectrometer (DCS) on NG-4.³¹

The DCS instrument was operated in its low resolution configuration using 5 Å incoming neutrons. In this configuration, the instrumental energy resolution approximates a Gaussian function with a Full Width at Half Maximum (FWHM) of $\approx 100 \ \mu eV$. A measurement of a standard vanadium sample was used to determine detector efficiencies and the instrumental energy resolution. Data were corrected for the scattering of the sample container, taking into account selfshielding effects through the samples' transmission. The NSE measurements were performed with an incoming wavelength of 5 Å and $\Delta \lambda / \lambda \approx 20\%$. Data were reduced and analyzed using routines available in the Data Analysis and Visualization Environment (DAVE) software.³²

C. Neutron scattering measurements

In a dynamic neutron scattering experiment,²² the relevant measured quantity is the dynamic structure factor, S(Q,E), which is the sum of a coherent term, $S_{coh}(Q,E)$, and an incoherent term, $S_{inc}(Q,E)$,²²

$$S(Q, E) = S_{coh}(Q, E) + S_{inc}(Q, E),$$

where the wavevector (a scalar for amorphous samples) and energy transfer, $Q = |\mathbf{k}_i - \mathbf{k}_f|$ and $E = E_i - E_f$, respectively, are defined by the differences between the initial and final wavevectors, \mathbf{k}_i and \mathbf{k}_f , and energies, E_i and E_f , of the neutrons.

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 ,

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

where N is the total number of atoms, b_{α}^{coh} is the coherent scattering length of the α atoms, and the dynamic structure factors are defined as Fourier transforms of the corresponding Intermediate Scattering Functions (ISFs),

$$S^{\alpha\beta}(\mathbf{Q}, E) = \frac{1}{2\pi\sqrt{N_{\alpha}N_{\beta}}} \sum_{i_{\alpha}=1}^{N_{\alpha}} \sum_{i_{\beta}=1}^{N_{\beta}} \int_{-\infty}^{\infty} I^{\alpha\beta}(Q, t) e^{(-i\frac{E}{\hbar}t)} dt, \quad (1)$$
$$I^{\alpha\beta}(Q, t) = \langle e^{\{i\left[\mathbf{Q}\cdot\mathbf{R}_{i_{\alpha}}(t)-\mathbf{Q}\cdot\mathbf{R}_{i_{\beta}}(0)\right]\}} \rangle, \quad (2)$$

 N_{α} being the number of atoms of the α species in the sample and $\langle \cdots \rangle$ indicates an ensemble average.

In general, the collective ISF, I_{coll} , can be defined as an appropriately weighted sum of the various $I^{\alpha\beta}(Q, t)$, (the weights depending, for example, on the different scattering cross sections for different techniques).

The incoherent term is given by the sum of the single particle (self) dynamic structure factor of each atomic species

$$S_{inc}(Q, E) = \sum_{i_{\alpha}=1}^{N_{\alpha}} \frac{1}{N_{\alpha}} (b_{\alpha}^{inc})^2 S_{self}^{\alpha}(Q, E),$$

where b_{α}^{inc} is the incoherent scattering length of the α atoms and

$$S_{self}^{\alpha}(Q,E) = \frac{1}{2\pi N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \int_{-\infty}^{\infty} I_{self}^{\alpha}(Q,t) e^{(-i\frac{E}{\hbar}t)} dt, \quad (3)$$

$$I_{self}^{\alpha}(Q,t) = \langle e^{\{i [\mathbf{Q} \cdot \mathbf{R}_{i_{\alpha}}(t) - \mathbf{Q} \cdot \mathbf{R}_{i_{\alpha}}(0)]\}} \rangle, \tag{4}$$

where $\mathbf{R}_{i_{\alpha}}$ is the position of the i-th α atom.

In methanol only three atomic species are present, namely, C, O, and H/D. Since the three hydrogen atoms of the methyl group are equivalent, ten partial structure factors, $S^{\alpha\beta}(Q, E)$, can be defined. In the present case, α and β could be M (methyl group hydrogens), C, O, and H (hydroxyl hydrogen).

In a static neutron scattering experiment, data are collected without being analyzed in terms of their energy. The extracted quantity is the structure factor

$$S(Q) = \int_{-\infty}^{\infty} S(Q, E) dE.$$
 (5)

This quantity is the Fourier transform of the instantaneous spatial atomic correlations in the system.

Experimentally, the integral reported in Eq. (5) can be obtained only approximately because the incoming neutron energy determines the upper limit of the integral. The incoming wavelength distribution and energy detector efficiency are also experimental factors that have not been taken into account in the present analysis. Nevertheless these experimental approximations do not seem to significantly alter the results as indicated in the following by the agreement with MD simulations, which determine S(Q) as the Fourier transform of the radial distribution function, g(r).

D. Polarization analysis

In general, neutron diffraction experiments are sensitive to the sum of the coherent and incoherent structure factors, $S(Q) = S_{coh}(Q) + S_{inc}(Q)$. However, using polarized neutrons, it is possible to separate the coherent and incoherent contributions.³³ In fact, coherent scattering does not flip the spin of the scattered neutrons whereas incoherent scattering has 1/3 and 2/3 probability of not flipping and flipping the spins of the scattered neutrons, respectively. Neutron polarization analysis measurements are performed using a polarized incoming beam and an analyzer that allows only one spin state of the scattered neutrons to reach the detector. A π flipper is located in front of the sample. Two measurements are performed, with the π flipper off (NSF) and on (SF), respectively. The ratio of the intensities, $R = I^{NSF}/I^{SF}$, for a purely coherent scatterer is called the flipping ratio and can be used to account for instrumental parameters such as incoming beam polarization, analyzer, and π flipper efficiencies. Taking these factors into account, the coherent and incoherent structure factors are obtained as

$$S^{coh}(Q) = \frac{1+2R}{2(R-1)}I^{NSF}(Q) - \frac{2+R}{2(R-1)}I^{SF}(Q),$$

$$S^{inc}(Q) = \frac{3}{2(R-1)}\left[R I^{SF}(Q) - I^{NSF}(Q)\right].$$
(6)

E. Molecular dynamics simulations

The experimental QENS spectra were modeled at the atomic level using data from molecular dynamics simulations. These simulations were performed with Gromacs 4.6.3³⁴ using the leap frog integrator and a 2 fs time step. The OPLS-AA³⁵ force field was used to model (protiated) methanol. The simulations were performed in the *NPT* ensemble (P = 100 kPa = 1 bar) using a Nosé-Hoover thermostat ($\tau_T = 0.5$ ps) and a

Parrinello-Rahman barostat ($\tau_P = 2.5$ ps). The periodic simulation box contained N = 2048 molecules. Lennard-Jones and Coulomb interactions were truncated at 1.1 nm and the Particle-Mesh Ewald method was used to account for longrange electrostatic interactions. The system was equilibrated for 5 ns at each condition and data were collected for an additional 5 ns. Experimentally accessible correlation functions were calculated using the scattering length of deuterium rather than hydrogen.

III. RESULTS AND DISCUSSION

The existence of a prepeak in methanol, similar to what was observed in higher molecular weight monohydroxy alcohols,^{2,5} has been reported by several authors on the basis of diffraction experiments and MD simulations.^{5,6,13,36} Its presence suggests the existence of a relevant length scale, larger than the interparticle distance, related to H-bonded molecular associates. These structures can be directly put in evidence experimentally using neutron scattering with partial deuteration, as suggested by MD simulation results in the following way. The neutron coherent structure factor for a perdeuterated sample, CD₃OD, is calculated from the MD trajectories and shown in Fig. 1(a) for T = 290 K. In agreement with previous results, it shows the FSDP at $\approx 17 \text{ nm}^{-1}$. Inspecting the partial static structure factors weighted by the coherent scattering lengths shown in Fig. 1(c), it can be understood that the FSDP directly relates to the distance between the methyl groups. In fact, the C-C, M-M, and C-M partial static structure factors all have a peak at $\approx 17 \text{ nm}^{-1}$. We can also notice that the static structure factors of the hydroxyl group atoms, namely, O–O, H–H, and H–O, all have a peak at ≈ 13 nm⁻¹; however, their contribution is canceled out by the M–H and M–O static structure factors. Fig. 1(b) shows the static structure factor for a partially deuterated methanol sample, CH₃OD. In this case, $S^{coh}(Q)$ has its maximum between 12 nm⁻¹ and 14 nm^{-1} . Now, with reference to Fig. 1(d), due to the particular values of the coherent scattering lengths of H and D (positive and negative, respectively), the hydroxyl group structuring is emphasized because the C-M partial static structure factor tends to cancel out the contributions of the C-C and M-M partial static structure factors. Moreover, the partial static structure factors M-H and M-O do not cancel but reinforce the contributions from the hydroxyl partial static structure factors, H–H, O–O, and H–O. In summary, the peak in S^{coh}(Q) of CH₃OD relates to the distance between the hydroxyl groups. In fact, the relevant length scale associated to this peak, which can be estimated as $\approx \frac{2\pi}{Q_{cH_3OD}^{CH_3OD}} = \frac{2\pi}{13}$ nm = 0.48 nm, roughly coincides with the second neighbor shell peak of the radial distribution function of the oxygen atoms. Incidentally, as shown in the supplementary material, MD results predict that CH₃OH has a negligible coherent scattering signal in this Q range and that the CD₃OH coherent static structure factor peaks at the FSDP.

Using polarized neutron diffraction, it was indeed possible to show that the coherent structure factor of CH₃OD has a prominent feature at $\approx 12 \text{ nm}^{-1}$ as shown in Fig. 1(e), in agreement with the MD results. Because this peak is located at a Q value smaller than the FSDP, in what follows this feature will



FIG. 1. (a) and (b) MD calculated neutron coherent structure factors at T = 290 K for CD₃OD and CH₃OD, respectively. (c) and (d) The partial static structure factors at T = 290 K, weighted by the coherent scattering length for the isotopic composition of CD₃OD and CH₃OD, respectively. Partial structure factors involving methyl group atoms only (C-C, C-M, and M-M) are shown with lines and solid symbols; those involving hydroxyl group atoms only (H-H, H-O, and O-O) are shown with lines and open symbols. Notice that in CD₃OD, the methyl groups partial structure factors all contribute positively to the FSDP; on the other hand, in CH3OD C-M tends to cancel the contributions from C-C and M-M at the FSDP. For CD₃OD, at the prepeak, the contributions from H-H, H-O, and O-O are canceled out by M-H and M-O; in CH₃OD all the contributions in the Q range of the prepeak are positive. (e) The coherent static structure factors of CD₃OD and CH₃OD measured with polarized neutron diffraction at room temperature.³⁷

be referred to as a prepeak. As expected, in CD₃OD, polarized neutron diffraction data reveal the signature of the FSDP. Liquid methanol has been extensively investigated in the past using X-rays^{5,6} and neutron diffraction with deuterium substitution.^{10–14} The paper⁵ by Narten and Habenschuss on their x-ray diffraction work on methanol and ethanol points out a shoulder, at $Q \approx 10 \text{ nm}^{-1}$, on the FSDP of methanol which develops into a peak near 8 nm⁻¹ for ethanol. Moreover, the MD work by Perera et al.³⁶ reported the existence of a prepeak at $\approx 10 \text{ nm}^{-1}$. However, to the best of our knowledge, this is the first time that this prepeak in methanol has been observed experimentally. In fact, this structural feature could only be observed so clearly with the use of polarized neutrons because the total scattering pattern for CH₃OD (reported in the supplementary material) is dominated by incoherent scattering. It is not the focus of this paper to address structural details of molecular association in methanol, already discussed extensively in the literature;^{5–7,10–14,36} however, the above proposed results support the picture of the presence of significant H-bond associates in methanol.

In the rest of this study, the effect of molecular association on the collective dynamics is investigated through QENS measurements on a methanol sample that was perdeuterated in order to minimize the incoherent scattering contribution. As reported in our previous work,²⁷ the spectra were analyzed in terms of a Lorentzian function convoluted with the experimental resolution function, R(Q,E), plus a constant background, $BKG_0(Q)$,

$$S(Q,E) = \frac{A(Q)}{\pi} \frac{\Gamma(Q)}{E^2 + \Gamma(Q)^2} \otimes R(Q,E) + BKG_0(Q), \quad (7)$$

where Γ is the Half Width at Half Maximum (HWHM) of the Lorentzian curve. The background takes into account dynamical processes too fast to fall within the experimental window of the present experiment, namely faster than ≈ 1 ps, such as thermal diffusivity.^{27,38,39}

The *Q* dependence of the coherent dynamics is often discussed in terms of the empirical Skold equation, $\frac{I_{coll}(Q,t)}{I_{coll}(Q)}$ = $I_{self} \left[\frac{Q}{\sqrt{S(Q)}}, t \right]$, where I_{coll} and I_{self} represent the collective and single particle ISFs, respectively. Alternatively, using a formalism widely employed for colloidal solutions, the extracted HWHM values can be analyzed in terms of an effective diffusion coefficient, $D_{eff} = \Gamma/Q^2$.

 D_{eff} can be expressed as $D_{eff} = D_0 \frac{H(Q)}{S(Q)}$, in terms of a microscopic diffusion coefficient D_0 , the hydrodynamic function, H(Q), and the structure factor, S(Q). Both this and the Skold equation predict that a peak in S(Q) will result in slowing

down of the dynamics at the corresponding Q, often referred to as de Gennes narrowing,⁴⁰ which indicates slowing down of the relaxational dynamics for length scales associated with relevant structures in the sample.

Fig. 2 reports the Q dependence of D_{eff} as a function of temperature, where symbols and continuous lines represent the QENS and MD results, respectively. These are the results reported in our previous publication.^{27,28} In that case, we reported the relaxation rate Γ as a function of Q because the observed process is not Fickian; however, we are now reporting D_{eff} to better highlight the details of its Q dependence. The experimental data reveal a modulation of the effective diffusion coefficient with shallow minima (indicated by arrows) in the Q ranges from 11 nm^{-1} to 13 nm^{-1} and from 18 nm^{-1} to 19 nm⁻¹, depending on temperature (at low temperature, these features appear as points of inflection). These minima occur in the same Q ranges of the FSDP and the prepeak, which noteworthily cannot be observed in CD₃OD, and can be understood as de Gennes narrowings. The results are consistent with those of previous QENS measurements on hydrogenated and deuterated methanol by Bermejo and co-workers,²¹ even though the analysis method was significantly different. Panel (b) in Fig. 2 of the paper by Bermejo et al.,²¹ also shows the signature of a narrowing of the quasielastic broadening at Q values $\approx 11 \text{ nm}^{-1}$ in agreement with the present results. This finding was not discussed further in the paper by Bermejo et al.,²¹ as it was not the focus of their work.

MD trajectories were analyzed to obtain all $I^{\alpha\beta}(Q, t)$ as well as the collective ISF of the center of mass of methanol. The intermediate scattering function as observable by neutron scattering for CD₃OD was also calculated. The extracted ISFs curve could be fitted with the sum of two exponential decays as shown in our previous publication²⁷

$$\frac{I^{zzz}(Q,t)}{I^{zzz}(Q,0)} = I_0 \left[(1-x)e^{-zt} + x e^{(-\Gamma t)} \right],$$
(8)



FIG. 2. Effective diffusion coefficient for deuterated liquid methanol as a function of Q at the investigated temperatures. Symbols and continuous lines represent the QENS and MD results, respectively. The arrows indicate the approximate positions of the local minima in the experimental D_{eff} data. The vertical dashed lines indicate the position of the prepeak and FSDP as determined at room temperature from the polarized diffraction measurements.³⁷

where *zzz* could be CD₃OD, the Center of Mass (CoM), the methyl group hydrogen to methyl group hydrogen (M–M) distance, the methyl group hydrogen to hydroxyl group hydrogen (M–H) distance, etc. The short time dynamics is of the order of a fraction of a picosecond and is outside the time window explored in the present QENS experiments. Here the slow dynamics relaxation rate, Γ , coincides with the HWHM in Eq. (7) as obtained by QENS measurements. The effective diffusion coefficient corresponding to the slower relaxation process was obtained as Γ/Q^2 .

The comparison with experiment of D_{eff} as obtained from the MD trajectories is reported in Fig. 2. MD data agree well with the experimental results at T = 260 K but the agreement is poorer at T = 290 K and especially at T = 220 K. MD simulations also reveal the existence of D_{eff} minima in the Q ranges of the prepeak and the FSDP. The minima at $\approx 18 \text{ nm}^{-1}$, the Q value of the FSDP, is well reproduced by both the experimental and the MD results. There is instead a discrepancy in the location of the first D_{eff} minima between the QENS and computer results, the latter identifying a de Gennes narrowing centered at slightly higher Qvalues.

At low temperatures, the modulation of D_{eff} with Q, as obtained by QENS, is less pronounced. This finding could be attributed to the fact that as the temperature goes down, the dynamics of all molecular configurations, not only those related to a favoured structure, are significantly slowed down. However, at the moment it could not be ruled out that the instrumental resolution is limiting the accuracy with which such modulations are measured at low temperature. In fact, the MD data would indicate an increased slowing down of the dynamics at the prepeak on lowering the temperature.

Both the experimental and MD data reported in Fig. 2 indicate a de Gennes narrowing at the Q value of the prepeak. A significant slowing down of the dynamics at the prepeak with respect to the FSDP has already been observed for 1propanol²⁴ and some ionic liquids.^{41,42} However, for methanol, we are able to observe such slowing down as a function of Qin the range from the mesoscopic scale to the FSDP, clearly identifying an effect on the dynamics from the associates. Such behavior was not observed for m-toluidine²³ where the clusters originating the prepeak are believed to be small and short-lived.

Fig. 3 reports the obtained D_{eff} results for some other quantities of relevance (the corresponding $\Gamma vs Q^2$ results are reported in the supplementary material). Fig. 3(a) compares the dynamics of the center of mass to the CD₃OD dynamics accessible by neutron scattering measurements. In Fig. 3(a), we note that the de Gennes narrowing observed experimentally for CD₃OD at the prepeak and at the FSDP is also present in the center of mass dynamics, confirming that this behavior is related to the translational dynamics of the molecules. In the Q range reported, the center of mass dynamics is slightly slower but has a similar Q dependence as compared with the dynamics of CD₃OD. Fig. 3(b) shows that in the Q range of the FSDP, the dynamics probed by neutron scattering on CD₃OD coincides with the carbon-carbon collective dynamics. We note here that at 290 K, in panel (a) the high Qbehavior of the $CoM D_{eff}$ differs from that corresponding to the experimentally accessible CD₃OD; similarly, in panel (b),



FIG. 3. (a) The effective diffusion coefficient calculated from the MD trajectories for the collective slow dynamics of the center of mass (solid symbols) and the dynamics of CD₃OD as measured by neutrons (open symbols). (b) The effective diffusion coefficient calculated from the MD trajectories for the dynamics of CD₃OD as measured by neutrons (open symbols), and the carbon-carbon correlation (solid symbols), at three temperatures. (c) The effective diffusion coefficient calculated from the MD trajectories for the dynamics of the methyl hydrogen to hydroxyl hydrogen (M–H, solid symbol), hydroxyl hydrogen to hydroxyl hydrogen (M–H, solid symbol), hydroxyl nydrogen to hydroxyl hydrogen (M–H, solid symbol), squares, circles, and triangles report data at T = 290 K, 260 K, and 220 K, respectively. The vertical dashed lines indicate the position of the prepeak and FSDP as determined at room temperature from the polarized diffraction measurements.

in the high Q region, the data for CD₃OD do not coincide with those for the C–C partial dynamic structure factor. This is contrary to what was just asserted; however, in view of the results for the other temperatures, it is attributed to artifacts in the fitting scheme when it is difficult to separate the fast and slow dynamics branches. Finally, Fig. 3(c) compares the dynamics of the methyl hydrogens with respect to the hydroxyl hydrogens (M–H) to the collective dynamics of the atoms involved in hydrogen bonding, namely, H and O. The quantity $-S^{M-H}(Q)$ is zero away from the prepeak and so data are available in a limited Q range only (this is a consequence of the fact that in this case the collective dynamics only comprises a distinct component without any self contribution). In the Q range of the prepeak, the three datasets reported in Fig. 3(c) have the same relaxational dynamics. Hence, probing the M-H correlation is equivalent to probing the hydrogen bonding dynamics. This will be relevant in the following for a deeper understanding of the molecular dynamics at this length scale.

The dynamics observed experimentally at the FSDP, which is directly linked to the interparticle distance, is related to the relative motion of the first neighboring molecules and is considered the molecular structural relaxation of the system. In methanol, at this Q value, the signal is dominated by the coherent scattering associated with the methyl groups collective dynamics. In CD₃OD, at the prepeak, multiple partial dynamic structure factors contribute to the signal; moreover, about 40% of the scattering is incoherent, hence reflecting the single particle dynamics. These factors prevent a straightforward understanding of the results in terms of the dynamics at the molecular level. In order to overcome this issue, a deuteration technique used to investigate the prepeak dynamics in *m*-toluidine²³ can be applied. The prepeak signal is often stronger in partially deuterated samples; by combining the four methanol samples differing in their hydrogen isotopic composition, the incoherent signal can be completely eliminated,

$$-S^{M-H}(Q, E) = \left[S^{CD_{3}OH}(Q, E) + S^{CH_{3}OD}(Q, E)\right] - \left[S^{CH_{3}OH}(Q, E) + S^{CH_{3}OH}(Q, E)\right].$$
(9)

The combination of dynamic structure factors defined in Eq. (9) results in the negative of the partial dynamic structure factor from the correlation between the hydrogen atoms of the methyl (M) and hydroxyl groups (H). Further experimental details on the determination of $-S^{M-H}(Q,E)$ using Eq. (9) can be found in the supplementary material.

Fig. 4(a) shows a three dimensional plot of the experimentally determined dynamic structure factor defined in Eq. (9), $-S^{M-H}(Q,E)$, at T = 220 K, as an example. The signal is concentrated in the area around $Q = 11 \text{ nm}^{-1}$. MD simulations confirm that this Q value corresponds to a valley in the methyl hydroxyl partial structure factor (see Fig. 4(b)).

The data for $-S^{M-H}(Q,E)$ have been analyzed using Eq. (7) with satisfactory accuracy. Panels (c)–(f) of Fig. 4 show some of the fitted spectra as examples. The results indicate that the methyl hydroxyl correlation is longlived at the length scales of the prepeak as compared with the interparticle structural relaxation. In fact, as shown in Fig. 3(c), at the *Q* values around the prepeak, the M–H dynamics coincides with that of the hydroxyl hydrogen and oxygen atoms, O–O and H–H. Hence, it can be argued that the methyl hydroxyl dynamics probed at the prepeak reflects the dynamics of the H-bonding hydroxyl groups.

The analysis of the temperature dependence of the dynamics gives indications as to the mechanism underlying the molecular motions. Fig. 5(a) is an Arrhenius plot of the effective diffusion coefficients as measured at the Q values



FIG. 4. (a) Methyl-hydroxyl partial dynamic structure factor for methanol at T = 220 K obtained by combining the measurement from four methanol liquid samples differing for their isotopic composition according to Eq. (9). (b) MD calculated partial structure factor for the methyl hydrogens and hydroxyl hydrogens. (c)–(f) Fit of $-S^{M-H}(Q, E)$ according to Eq. (7) at $Q = 11 \text{ nm}^{-1}$ and at the four temperatures investigated. The circles are experimental data, the continuous black line is the fit, the red dashed, and blue dotted lines represent the Lorentzian function and linear background, respectively. The continuous green line is the height normalized resolution function.³⁷

corresponding to the prepeak and the FSDP. In the investigated temperature range, the data follow an Arrhenius law

$$D = D_0^{Arrh} \exp\left[-\frac{E_A}{k_B T}\right],\tag{10}$$

where E_A is the activation energy for the diffusive motion, k_B is the Boltzmann constant, and D_0^{Arrh} is a microscopic parameter linked to the frequency of occurrence of the activated motion. The fitting results are reported in Table I. Within experimental uncertainties, the activation energies for the diffusive dynamics in the CD₃OD sample measured at $Q = 18 \text{ nm}^{-1}$ and for $-\text{S}^{\text{M}-\text{H}}$ at $Q = 11 \text{ nm}^{-1}$ are the same. The activation energy for the CD₃OD sample measured at $Q = 11 \text{ nm}^{-1}$ is slightly lower but the presence of incoherent scattering contributions increases the uncertainty in this value significantly, so that it will not be discussed further. Both these dynamics are likely regulated by breaking and formation of hydrogen bonds which rationalize the finding that E_A is the same for the two processes, with a value of (9.3 ± 0.4) kJ/mol in the range of energies of the hydrogen bond.

In Fig. 5, a comparison with previous results from other experimental techniques, namely, Pulsed Gradient Spin Echo (PGSE) NMR and DR, is also carried out. It should be pointed out that DR does not provide information on the length scale of the observed dynamics, whereas PGSE NMR probes longer length scales than QENS, in general of the order of a micrometer.

Fig. 5(a) shows the comparison of D_{eff} with the self diffusion coefficient, D^s, measured by PGSE NMR.²⁰ D^s follows a super-Arrhenius behavior. Around room temperature, the collective and single particle dynamics have similar time scales; however, as the temperature is lowered approaching the freezing point, the single particle dynamics slows down significantly more than the structural relaxation: a decoupling of the single particle and collective dynamics is observed. As can be seen from Fig. 5(a), the viscosity⁴³ of liquid methanol follows the Arrhenius law (Eq. (10)), with an activation energy similar to those observed for the structural relaxation. This is in agreement with what is seen in 1-propanol,²⁴ where the time scale of the dynamics probed by neutrons at the FSDP coincides with the Maxwell relaxation time, $\tau_{\eta} = \eta/G_{\infty}$, η being the viscosity and G_{∞} the (slightly temperature dependent) high-frequency shear modulus.

Fig. 5(b) carries out the comparison between the relaxation time, $\tau = 1/\Gamma$, from the present QENS data and the results from other spectroscopic techniques. The dashed lines with black solid hexagons and diamonds report the early DR results from Denney and Cole¹⁶ and Bertolini and co-workers,¹⁷ respectively. These data identify a relaxation process about one order of magnitude slower than what was measured for the



FIG. 5. (a) Arrhenius plot of the effective diffusion coefficient measured for deuterated methanol at the FSDP and at the prepeak, together with the results obtained at $Q = 11 \text{ nm}^{-1}$ for the methyl-hydroxyl partial structure factor, -S^{M-H}. Error bars are smaller than the symbol size and are not shown.³⁷ The black, red, and blue dotted lines represent the fit of the data to an Arrhenius law (Eq. (10)). Continuous and dashed black lines represent the parametrized form of the self diffusion coefficient as obtained using PGSE NMR for CH₃OH and CH₃OD, respectively.²⁰ A comparison with the inverse of the viscosity⁴³ (right axis scale) is carried out as well. (b) Relaxation times for deuterated methanol at the FSDP and the methyl-hydroxyl partial structure factor, $-\mathrm{S}^{M-H}$ at the prepeak. Error bars are smaller than the symbol size and are not shown.³⁷ Data are compared with the dielectric relaxation results (black dashed line plus diamond;¹⁷ black dashed line plus hexagons;¹⁶ purple top semisolid symbols;¹⁸ and green bottom semisolid symbols¹⁹) and NMR spin lattice relaxation time measurements (the black short dashed line and the black dotted line plus pentagons represent results for CD₃OD ²H T₁⁴⁴ and CD₃OH ¹H T_1 ,⁴⁵ respectively). The green dashed line represents the viscosity (right axis scale).43

methyl hydroxyl correlation. However, the investigation of the THz region of the dielectric spectra has indicated the necessity to consider three Debye relaxational processes. The purple and green semi-solid symbols report the data by Barthel and co-workers¹⁸ (solid top) and Kindt and Schmuttenmaer¹⁹ (solid bottom), respectively. These latter measurements have been performed around room temperature only; however, the time

TABLE I. Results of the Arrhenius analysis of the measured effective diffusion coefficients. $^{37}\,$

Sample	$\begin{array}{c} Q \\ (\text{\AA}^{-1}) \end{array}$	D_0^{Arrh} (10 ⁻⁹ m ² /s)	E _A (kJ/mol)
CD ₃ OD	1.1	44.6 ± 4.5	7.2 ± 0.2
CD ₃ OD	1.8	108.4 ± 9.4	9.2 ± 0.1
-S ^{M-H}	1.1	69.4 ± 3.5	9.3 ± 0.4

scales of the processes observed by Barthel and co-workers¹⁸ agree with the collective QENS data for the dynamics at the prepeak for $-S^{M-H}$ and the dynamics at the FSDP in CD₃OD. Moreover, the lifetime values of the hydrogen bond, τ^{OH} , as measured from T_1 spin-lattice NMR relaxation in CD₃OH (¹H $(T_1)^{44}$ and CD₃OD $(^{2}H T_1)$,⁴⁵ are close to the relaxation times of the methyl-hydroxyl correlation over the whole temperature range investigated. This finding establishes the connection between the dynamics of molecular associates in methanol and the H-bond lifetime. The results indicate that these structures are longlived having a dynamics slower than that of the individual particles. However, the fact that neutron scattering measures the time scale of H-bonding indicates that the breaking of the associates is their main dynamical process, as opposed to their diffusion, over these length scales. In systems with stronger bonding within the associates, these structures would diffuse as a whole.

According to the Transient Chain Model (TCM),⁴⁶ three dielectric active processes can be identified in alcohols forming chain-like associates through hydrogen bonding: (i) the reorientational dynamics of the whole chain originates the Debye process; (ii) the association and dissociation of the individual molecules in the chain can be measured using ${}^{1}\text{H} T_{1}$ NMR; and (iii) the structural relaxation which can be investigated using DR spectroscopy and other techniques. Although methanol is not known to manifest a Debye process, the results reported here are in agreement with the TCM picture of three dynamical processes, two of which can be probed at different length scales by QENS: (i) the relaxation observed at the FSDP is the structural relaxation; (ii) the dynamics of the methyl-hydroxyl correlation at the Q value of the prepeak relates to the intra-associate dynamics as can also be investigated by NMR. This is similar to what was observed in 1-propanol²⁴ where the α -relaxation as measured by DR coincides with the dynamics measured by OENS at the FSDP; the lifetime of the hydrogen bond as extracted from ¹H T_1 NMR data coincides with the time scales measured by QENS at the prepeak; and the Debye process measured by DR is one order of magnitude slower than the hydrogen bond lifetime. In the liquid temperature range, the α -relaxation, τ^{OH} , and the Debye process have been found to have similar temperature dependences in n-butanol⁴⁶ and 1-propanol²⁴ because they are all activated through the hydrogen bond dynamics. This scenario seems to be valid here as well, although it might break down⁴⁷ on approaching the glass transition temperature, $T_g = 103 \text{ K.}^{48}$

Within the framework of mode coupling theory,⁴⁹ the intermediate scattering function can be related to the zero-frequency shear viscosity.¹³ Hence, the appearance of an additional relaxational process in associating liquids is likely to be relevant for the macroscopic properties of the system. It can be shown that the most relevant contributions arise from the fluctuations over length scales matching the FSDP and the prepeak. In this light, the results reported here using neutron scattering techniques provide a unique insight at the molecular level into the dynamical processes which determine the properties of associating liquids. This work should also stimulate new theoretical studies to improve the modeling of collective dynamics at the nanoscale.^{26,38}

IV. CONCLUSIONS

In summary, (i) the use of polarized diffraction has put in evidence the existence of a structural feature, a prepeak, associated with the molecular arrangement of the hydroxyl groups in liquid methanol, as also supported by MD results; (ii) the collective dynamics of the liquid studied by OENS shows a slowing down (de Gennes narrowing) at the length scales of structural relevance, i.e., both at the prepeak and the FSDP; (iii) the collective dynamics is thermally activated, likely by hydrogen bond formation and breaking; (iv) the dynamics at the prepeak is linked to the lifetime of the nanoscopic molecular associates and of the hydrogen bonds. These features are likely common to monohydroxy alcohols forming chainlike associates and possibly to a larger subset of hydrogen bonding liquids. The present results highlight how the structure imposed by hydrogen bonding of the hydroxyl groups affects the density fluctuations of the liquid, even at length scales larger than the intermolecular distance. Further study is required to establish the link between the dynamics observed over different length scales and the macroscopic, specifically rheological, properties of the system.⁵⁰

SUPPLEMENTARY MATERIAL

See supplementary material for polarized diffraction results, MD calculated coherent static structure factors of CH₃OH and CD₃OH, MD calculated relaxation rates of CoM, CD₃OD, C–C, M–H, H–H, and O–O, and for experimental details of the determination of $-S^{M-H}(Q,E)$.

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