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Written by Edgar McCarroll, 14 July 2012 19:59

Quasielastic small-angle neutron scattering from heavy water solutions of cyclodextrins

André Kusmin,^{1,a)} Rued E. Lechner,^{2,b)} and Wolfram Saenger^{1,c)}

¹*Institute for Chemistry and Biochemistry/Crystallography, Freie Universität Berlin, Taku Str. 6, 14195 Berlin, Germany*

²*Guest at Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany*

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We present a model for quasielastic neutron scattering (QENS) by an aqueous solution of compact and inflexible molecules. This model accounts for time-dependent spatial pair correlations between the atoms of the same as well as of distinct molecules and includes all coherent and incoherent neutron scattering contributions. The extension of the static theory of the excluded volume effect [A. K. Soper, *J. Phys.: Condens. Matter* **9**, 2399 (1997)] to the time-dependent (dynamic) case allows us to obtain simplified model expressions for QENS spectra in the low Q region in the uniform fluid approximation. The resulting expressions describe the quasielastic small-angle neutron scattering (QESANS) spectra of D₂O solutions of native and methylated cyclodextrins well, yielding in particular translational and rotational diffusion coefficients of these compounds in aqueous solution. Finally, we discuss the full potential of the QESANS analysis (that is, beyond the uniform fluid approximation), in particular, the information on solute–solvent interactions (e.g., hydration shell properties) that such an analysis can provide, in principle. © 2011 American Institute of Physics. [doi:10.1063/1.3518367]

I. INTRODUCTION

The relative significance of coherent and incoherent neutron scattering depends on the nuclear composition of the sample, the size of the particles or structures present in the sample, and on the range of neutron wave vector transfer (Q) accessed in an experiment. In a small-angle neutron scattering (SANS) experiment Q values are small, and, given a sufficient scattering contrast, coherent scattering from large objects dominates the scattering pattern even when these objects have many hydrogen nuclei (which have a high incoherent scattering cross section). With increasing Q , coherent scattering drops fast (following for instance Guinier's Law) and often becomes much smaller than the incoherent component. Relative to SANS, in a conventional quasielastic neutron scattering (QENS) experiment the Q values are high ($>0.2 \text{ \AA}^{-1}$, typically $>0.5 \text{ \AA}^{-1}$), the molecules are often small, and the hydrogen content is high enough to reduce the coherent scattering contribution to a few percent and less. This is why an analysis of QENS experiments often accounts for incoherent scattering only (see, for instance, Refs. 1–3).

In a SANS diffraction experiment, incoherent scattering is just a flat background, whereas coherent scattering is a source of structural information. In QENS, incoherent scattering informs us about the single molecule motion, and the motions of individual functional groups within the molecule, while coherent scattering gives us information about the motion of molecules (and their parts) relative to each other.

Hence, coherent QENS is more difficult to analyze than incoherent. First, the dependence of the line shape of the coherent QENS spectra on structural properties of the sample is more intricate; consequently, much of the structural information (e.g., the solute's crystal structure, radial distribution functions in solution) is required as a model input. Second, it is in general much more difficult to model the collective motion of a system of particles, than the motion of a single particle.

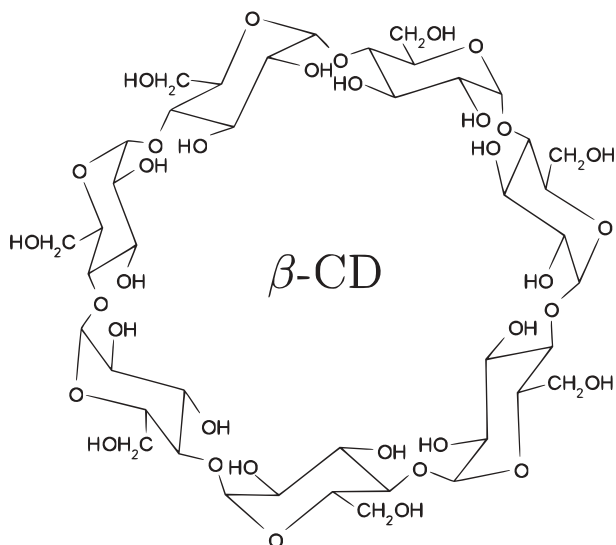
Neutron sources and instrumentation have been and are being improved continuously, so that now a QENS experiment in the low Q region (using longer incident neutron wavelengths) takes a much shorter time than in the past. QENS is increasingly often applied to study proteins and other large molecules. Thus, the neglect of coherent scattering in today's QENS experiments is no longer “automatically” warranted. This neglect must be properly justified (e.g., a small contribution of coherent scattering to the total scattering cross section does not rule out the dominance of coherent scattering in a certain Q region), hence a way to calculate (or at least estimate) the coherent scattering contribution is required. Even more importantly, an analysis of the coherent QENS spectra may provide unique details on the dynamics of intermolecular interactions (e.g., solute–water) and intramolecular interactions (e.g., internal dynamics of proteins⁴).

We know few QENS studies on solutions where coherent scattering was accounted for to some extent.⁵ Neutron spin echo spectroscopy (NSE) delivers, in principle, the same information as QENS does (although in the time and not in the frequency domain). However, intrinsically, NSE is more suitable for the study of coherent rather than incoherent scattering and, relative to QENS, considerably more attention was paid to the analysis of the former, see, e.g., Refs. 4 and 6.

^{a)}Electronic mail: a.kusmin@fz-juelich.de. Present address: Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany.

^{b)}Electronic mail: rued.lechner@gmail.com. Also at: International Graduate College, Freie Universität Berlin, Taku Str. 3, 14195 Berlin, Germany.

^{c)}Electronic mail: saenger@chemie.fu-berlin.de.

FIG. 1. Chemical structure of β -cyclodextrin.

Our QENS investigations^{7,8} that included a partial account for coherent scattering were on D₂O solutions of cyclodextrins (CDs) and their methylated derivatives (mCDs). The CDs are macrocycles consisting of 6, 7, or 8 D-glucose units, and are called α -, β -, and γ -CDs, respectively,⁹ see Fig. 1. The mCDs that we studied were β -CD per-methylated at all 2, 6 hydroxyl groups (DIMEB) and γ -CD per-methylated at all 2, 3, 6 hydroxyl groups (TRIMEG). While the solubility of CDs in water rises upon increasing temperature, the opposite is true for mCDs: mCDs are well soluble in cold water but crystallize upon heating. This makes CDs and mCDs good model systems for the study of the hydrophobic effect and of hydration.¹⁰ In the analysis of QENS spectra of mCD and CD solutions we calculated the coherent scattering by a single solute molecule from atomic coordinates known from x-ray or neutron diffraction crystal structures, and took into account the intermolecular coherent scattering from solutes. Nevertheless, with these ingredients alone we could not explain an observed excess of QENS intensity towards low Q values in the spectra of mCDs dissolved in D₂O. We were, however, successful in explaining this with a phenomenological model that includes an additional coherent scattering contribution from the hydration shell of mCDs.^{7,8} In this model two approximations were made: the coherent scattering due to solute–D₂O spatial correlations was neglected, and both coherent and incoherent D₂O scattering in solution were described by the same parameter values as used for the description of the scattering by pure D₂O.

In this paper we develop a model for the analysis of QENS spectra of aqueous solutions of molecules which are relatively compact and inflexible compared to polymer chains. Most significant (but not strictly necessary) assumptions of this model are (i) hydration water is structurally and dynamically equivalent to bulk water, (ii) scattering contributions from motions of functional groups within the solute molecule can be neglected, and (iii) the scattering function for the collective translational motion can be calculated using Vineyard's convolution approximation.¹¹ The first two as-

sumptions are valid for dilute solutions and $Q < 0.5\text{--}1\text{ \AA}^{-1}$; the last one is used solely for practical purposes. The model accounts for the time-dependent spatial correlations between all atoms and renders a description of all the coherent and incoherent scattering contributions. We then extend the static theory of the excluded volume effect¹² to the time-dependent case, develop simplified model expressions suitable for the QENS spectra recorded at sufficiently low Q values, and show that these expressions are compatible with the concept of scattering contrast. Simplified model expressions adequately describe our QENS spectra proving that an ad hoc assumption about the scattering by the hydration shell made before is not absolutely necessary (although a contribution of this kind cannot be excluded). Finally, we discuss the possibility to study the dynamics of solute–solvent interactions by QENS.

II. THEORY

To help the reader in following the formulae, we have given a list of symbols at the end of the paper, before the Appendices.

A. The scattering function for an aqueous solution

The scattering function, $S(Q, \omega)$, is the time-Fourier transform of the intermediate scattering function, $I(Q, t)$,

$$S(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} I(Q, t) dt, \quad (1)$$

where Q is the wave vector transfer ($Q = k - k_0$), $\hbar Q$ and $\hbar\omega$ are the neutron momentum and energy transfer, respectively ($\hbar\omega = E - E_0$). For an aqueous solution, $I(Q, t)$ can be written as (see, e.g., Ref. 13)

$$I(Q, t) = \sum_{i=1}^{N_w+N_{\text{sol}}} \sum_{\mu=1}^{N_w+N_{\text{sol}}} \sum_{j=1}^{N_w+N_{\text{sol}}} \sum_{\nu=1}^{N_w+N_{\text{sol}}} b_{i\mu} b_{j\nu} \langle e^{-iQ(R_{i\mu}(0) - R_{j\nu}(t))} \rangle, \quad (2)$$

where $R_{i\mu}$ is the vector giving the position of the μ th nucleus in the i th molecule, $b_{i\mu}$ is the neutron scattering length of this nucleus. N_w and N_{sol} denote the number of water and solute molecules, respectively. The angle brackets denote the statistical average.

$I(Q, t)$ can be represented as a sum of three terms depending on solute–solute, solute–water, and water–water space- and time-dependent correlations: $I_{\text{sol}}(Q, t)$, $I_{\text{cross}}(Q, t)$, and $I_w(Q, t)$, respectively. Its time-Fourier transform, the scattering function for an aqueous solution, is the corresponding sum,

$$S(Q, \omega) = S_{\text{sol}}(Q, \omega) + S_{\text{cross}}(Q, \omega) + S_w(Q, \omega). \quad (3)$$

$S_{\text{sol}}(Q, \omega)$ accounts for the intermolecular coherent scattering (due to the time-dependent pair correlations between the positions and orientations of two distinct solute molecules) and for the intramolecular scattering (due to self-correlations between the positions and orientations the single solute molecule takes on at different times). The latter generally is a sum of coherent and incoherent scattering. Likewise, $S_w(Q, \omega)$ accounts for

the intermolecular coherent scattering, and the intramolecular (coherent and incoherent) scattering from water molecules. Finally, $S_{\text{cross}}(Q, \omega)$ accounts for the intermolecular coherent scattering due to solute–water time-dependent spatial correlations (there is no incoherent scattering contribution here because the correlations are between different molecules).

For the solute molecules that are relatively compact and inflexible (as opposed to linear polymers, alkanes, etc.) and just as well for bulk water molecules, the model given in Appendix A can be used to calculate the scattering functions, i.e., $S_{\text{sol}}(Q, \omega)$ and $S_w(Q, \omega)$, respectively. This model was originally developed for molecular liquids, and the motion of an atom located in a molecule is described by the convolution of the center-of-mass (CM) diffusion of the molecule and an isotropic rotational diffusion. The shape of the molecule does not have to be spherical, it should just not be too anisotropic. For flexible molecules other models should be used (e.g., for polymers: CM diffusion and the Rouse model). In the following we write down, as an example, the detailed expression for $S_w(Q, \omega)$; the formally completely analogous expression for $S_{\text{sol}}(Q, \omega)$ can then be obtained simply when replacing everywhere the subscript w by the subscript sol .

For the moment, we assume that hydration water and bulk water are structurally and dynamically equivalent. Consequently, the expressions from Appendix A [Eqs. (A1)–(A3)] can be used for $S_w(Q, \omega)$. Explicitly, $S_w(Q, \omega)$ is

$$S_w(Q, \omega) = n_w \text{DWF}_w \sum_{l=0}^{\infty} S_w^l(Q, \omega), \quad (4a)$$

$$S_w^0(Q, \omega) = A_w^{0\text{coh}}(Q) S_{\text{tr}w}^{\text{coh}}(Q, \omega) + A_w^{0\text{inc}}(Q) S_{\text{tr}w}^{\text{inc}}(Q, \omega) \quad l = 0, \quad (4b)$$

$$S_w^l(Q, \omega) = (2l + 1) [A_w^{l\text{coh}}(Q) + A_w^{l\text{inc}}(Q)] S_{\text{tr}w}^{\text{inc}}(Q, \omega) \otimes \text{Lor}[l(l + 1)D_{rw}, \omega] \quad l \neq 0, \quad (4c)$$

where n_w is the number density of water molecules in solution, DWF_w is the Debye–Waller factor, \otimes is the convolution operator, and D_{rw} is the rotational diffusion coefficient of a water molecule. The coefficients $A_w^l(Q)$ are given by Eq. (A4), $\text{Lor}(x, \omega)$ stands for a Lorentzian function with ω and x being the argument and the parameter (half-width at half maximum), respectively. $S_{\text{tr}w}^{\text{coh}}(Q, \omega)$ and $S_{\text{tr}w}^{\text{inc}}(Q, \omega)$ are the coherent and incoherent translational scattering functions for the CM of water molecules (corresponding to collective diffusion and self-diffusion of water molecules, respectively).

The expression for $S_{\text{cross}}(Q, \omega)$ can be written as (see Appendix B)

$$S_{\text{cross}}(Q, \omega) = 2n_{\text{sol}}b_{\text{sol}}(Q)b_w(Q)S_{\text{tr sol-w}}(Q, \omega), \quad (5)$$

where n_{sol} is the solute number density, $b_{\text{sol}}(Q)$ and $b_w(Q)$ are the effective scattering lengths [see Eq. (A8)] of solute and water molecules, respectively. $S_{\text{tr sol-w}}(Q, \omega)$ is the (coherent) scattering function for the translational motion of water molecules relative to solute molecules.

We made one standard, difficult to avoid, assumption: the rotational and translational motions of a molecule, as well as rotational motions of two distinct molecules, are not coupled

(weak hindering approximation¹³). Throughout the paper we will also assume that, because of the low Q region of our experiment, rotational motions of water molecules and motions of functional groups within the solute molecule contribute to the QENS spectra to a negligible extent. Although this is not strictly true, we make this assumption because our primary goal is to consider the intermolecular coherent scattering, which is only observable in the low Q region ($Q < 0.5\text{--}1 \text{ \AA}^{-1}$).

There exist a number of theoretical expressions for the incoherent translational scattering function, but none for the coherent one. That is, there are no expressions for $S_{\text{tr sol}}^{\text{coh}}(Q, \omega)$, $S_{\text{tr}w}^{\text{coh}}(Q, \omega)$ and $S_{\text{tr sol-w}}(Q, \omega)$, but we need them to use Eq. (3). For our present practical purpose, since we do not have a fully valid theory at our disposal, we proceed by applying Vineyard's convolution approximation.¹¹ Although this approximation has no profound theoretical justification, it is a means of constructing an at least phenomenologically approximate coherent scattering function $S_{\text{app}}^{\text{coh}}(Q, \omega)$ from an incoherent translational scattering function $S^{\text{inc}}(Q, \omega)$ by multiplying the latter with the known Q -dependent integral $S(Q)$ of $S^{\text{coh}}(Q, \omega)$. By doing this, the 0th moment of $S_{\text{app}}^{\text{coh}}(Q, \omega)$ becomes correct, which does, however, not imply the correctness of the higher moments of $S_{\text{app}}^{\text{coh}}(Q, \omega)$; (see also Refs. 14 and 15 for some more information about this). In Vineyard's approximation we have

$$S_{\text{tr sol}}^{\text{coh}}(Q, \omega) = S_{\text{cm sol}}(Q)S_{\text{tr sol}}^{\text{inc}}(Q, \omega), \quad (6)$$

$$S_{\text{tr}w}^{\text{coh}}(Q, \omega) = S_{\text{cm}w}(Q)S_{\text{tr}w}^{\text{inc}}(Q, \omega), \quad (7)$$

$$S_{\text{tr sol-w}}(Q, \omega) \approx S_{\text{sol-w}}(Q)S_{\text{tr}w}^{\text{inc}}(Q, \omega), \quad (8)$$

where $S_{\text{cm sol}}(Q)$, $S_{\text{cm}w}(Q)$, and $S_{\text{sol-w}}(Q)$ are the solute–solute, water–water, and solute–water intermolecular CM structure factors in solution (hereafter, structure factors). The solute–solute structure factor can be obtained from a small-angle neutron, x-ray or light diffraction experiment or can be calculated (see, e.g., Refs. 16 and 17). The solute–water and water–water structure factors can, in principle, be obtained from neutron diffraction experiments.¹⁸ The solute–water structure factor can also be calculated; a way to do this is shown in Appendix C. Note an approximate equality in Eq. (8); this is explained in Appendix C, too.

Above we assumed that hydration water and bulk water are structurally and dynamically equivalent. If the structure of hydration water differs from the bulk, three additional structure factors are required for the correlations: [hydration water–bulk water], [hydration water–solute], and [hydration water–hydration water]. Fortunately, at Q values where intermolecular coherent scattering is important, a (slight) difference in the hydration water structure is likely to have no influence on the scattering from solution. Only a (slightly) different number density of water molecules in the hydration shell may have to be taken into account [via n_w in Eq. (4a)]. On the other hand, the dynamics of hydration water may be substantially different from that of bulk water. Still, $S_w(Q, \omega)$ from Eqs. (4a) to (4c), and $S_{\text{cross}}(Q, \omega)$ from Eq. (5) will remain applicable, if we use the convolution approximation and take for $S_{\text{tr}w}^{\text{inc}}(Q, \omega)$ a two state model, e.g., the

model of Singwi and Sjölander.¹⁹ In a two state model, both translational and rotational dynamics could be described by two sets of parameters, for the bulk and for the hydration water, respectively. Note that although the rotational dynamics of the hydration water is different from that of the bulk water, in our Q region the effect of using somewhat different rotational diffusion coefficients is small (the terms for $l > 0$ are negligible).

Thus, the framework described above makes it possible to account for the coherent scattering.

B. Uniform fluid approximation

In general, for a practical application of the approach described above all three structure factors from Eqs. (6) to (8) have to be known. However, when Q values are sufficiently small, one can use the approximation of the solvent by a uniform continuum (hereafter: the uniform fluid approximation or the UFA); in this case, $S_{cmw}(Q)$ and $S_{sol-w}(Q)$ are not required. Below we derive the corresponding $S_{trw}^{coh}(Q, \omega)$ - and $S_{tr sol-w}(Q, \omega)$ expressions and show that they depend only on the solute structure and dynamics.

The intermediate scattering function, $I(Q, t)$, is the space-Fourier transform of the time-dependent pair correlation function, $G(r, t)$,

$$I(Q, t) = \int_V e^{iQr} G(r, t) dr. \quad (9)$$

Using the uniform fluid approximation, Soper derived the expressions for the static pair correlation functions in solutions, $G_{HH}(r)$, $G_{XX}(r)$ and $G_{XH}(r)$, where H is a hydrogen atom in a solvent molecule and X is any atom in a solute molecule.^{12,20} For our purposes we derived similar expressions by taking the CM of a water molecule as H and the CM of a solute molecule as X. We further extended Soper's approach to obtain the expressions for the time-dependent translational water–water and solute–water pair correlation functions, $G_{trw}(r, t)$ and $G_{tr sol-w}(r, t)$ [hereafter, $G_w(r, t)$ and $G_{sol-w}(r, t)$], respectively (see Appendices D 1–D 2). The expressions for $S_{trw}^{coh}(Q, \omega)$ and $S_{tr sol-w}(Q, \omega)$ follow from the time-Fourier transformation of the intermediate scattering functions [$I_{trw}^{coh}(Q, t)$ and $I_{tr sol-w}(Q, t)$, respectively] that are given in Appendix D 3.

In the UFA $G_w(r, t)$ reflects the time-dependent spatial pair correlations between two (infinitesimal) volume elements of the solvent, and $G_{sol-w}(r, t)$ reflects such correlations between the CM of the solute molecule and the solvent volume element. These correlations depend on the translational motion of the solute molecules relative to each other, described by $G_{sol}(r, t)$, and, if the solute molecules do not have a spherical shape, on their rotational motion described by $G_{sol}^{dist(p)}(r, t)$ and $G_{sol}^{self(p)}(r, t)$. The superscript (p) indicates the function's relation to the volume element inside a particle (in our case, inside a solute molecule). Specifically, $G_{sol}^{dist(p)}(r, t)$ describes the orientational correlation of the volume element of the solute molecule with another volume element of a distinct solute molecule at a different time; $G_{sol}^{self(p)}(r, t)$ describes the orien-

tational correlations between the volume elements of the same solute molecule.

$S_{trw}^{coh}(Q, \omega)$ is the time-Fourier transform of $I_{trw}^{coh}(Q, t)$ defined by Eqs. (D20) and (D21),

$$S_{trw}^{coh}(Q, \omega) = \frac{n_{sol}}{n_w} \sum_{l=0}^{\infty} S^{l(p)}(Q, \omega), \quad (10a)$$

$$S^{0(p)}(Q, \omega) = A^{0(p)}(Q) S_{tr sol}^{coh}(Q, \omega) \quad l = 0, \quad (10b)$$

$$S^{l(p)}(Q, \omega) = (2l + 1) A^{l(p)}(Q) S_{tr sol}^{inc}(Q, \omega) \otimes \text{Lor}[l(l + 1) D_r \text{sol}, \omega] \quad l \neq 0, \quad (10c)$$

where the coefficients $A^{l(p)}(Q)$ are given by Eq. (D22).

$S_{tr sol-w}(Q, \omega)$ is the time-Fourier transform of $I_{tr sol-w}(Q, t)$ given by Eq. (D23),

$$S_{tr sol-w}(Q, \omega) = -N^{(p)}(Q) S_{tr sol}^{coh}(Q, \omega), \quad (11)$$

where $N^{(p)}(Q)$ is given by Eq. (D24).

In Eqs. (10a)–(10c) and (11) the quasielastic broadening depends on the solute structure and dynamics only. Furthermore, the $S_{trw}^{coh}(Q, \omega)$ -expression is similar to that for $S_{sol}(Q, \omega)$ (see Appendix A). This is a consequence of the uniform fluid approximation: the solvent has no structure, and therefore solvent volume elements effectively do not move themselves.

Now that $S_{trw}^{coh}(Q, \omega)$ and $S_{tr sol-w}(Q, \omega)$ are derived, the scattering function for an aqueous solution is fully defined by Eqs. (3)–(5). For a practical application, we still need some means to calculate the coherent translational solute scattering function in Eqs. (10b) and (11); here we use Eq. (6).

While the uniform fluid approximation neither affects the calculation of incoherent scattering, nor that of the coherent scattering for $l = 1, 2, \dots$ in Eq. (4c), it underestimates the term for coherent scattering for $l = 0$ in Eq. (4b). This term accounts for the intermolecular coherent scattering of water molecules in solution and reads

$$S_w^{inter}(Q, \omega) = A_w^{0coh}(Q) S_{trw}^{coh}(Q, \omega). \quad (12)$$

In the UFA, $S_{trw}^{coh}(Q, \omega)$ is given by Eq. (10a); it does not depend on the local water structure and water dynamics, but it *does* depend on the change in the water structure caused by the volume excluded by solute molecules. Without the UFA, Eq. (12) can be rewritten (using Vineyard's convolution approximation) as

$$S_w^{inter}(Q, \omega) = S_{cmw}(Q) A_w^{0coh}(Q) S_{trw}^{inc}(Q, \omega). \quad (13)$$

In Eq. (13) $S_{cmw}(Q)$ depends on both the local water structure and the presence of solute molecules; the line broadening of $S_w^{inter}(Q, \omega)$ depends on water dynamics. Thus, we see that the UFA does not account for the broad coherent scattering component due to translational water dynamics. The intensity of this component can be estimated from the coherent scattering of pure water in the low Q region; as known from experiment, in many cases it is negligible compared to all other scattering contributions, especially for nondilute solutions.

TABLE I. Parameter values for the D₂O scattering model: D_{trw} = translational diffusion coefficient of water molecules; τ_{trw} = translational diffusion correlation time in this model; $\langle u^2 \rangle_w$ = mean-square displacement; D_{rw} = rotational diffusion coefficient of water molecules; these parameter values were taken from the literature, see Sec. III B for details.

	T (K)	D_{trw} (10^{-5} cm ² /s)	τ_{trw} (ps)	$\langle u^2 \rangle_w$ (\AA^2)	D_{rw} (μeV)
$\lambda_0 = 10 \text{ \AA}$	288	1.389	0.75	0.077	88.96
	285.5	1.294	0.827	0.077	86.47
$\lambda_0 = 15.3 \text{ \AA}$	301	1.970	0.502	0.077	102.3
	317.7	2.958	0.400	0.077	120.4

C. Low Q limit and scattering contrast

Even in the uniform fluid approximation the expression for the total scattering function for an aqueous solution is quite involved. Let us find a simplified expression in the limit of very low Q values and without the incoherent scattering contribution.

Qualitatively, one expects rotational and vibrational motions to have little effect in QENS spectra at low Q values. Specifically, at $Q < 0.5 \text{ \AA}^{-1}$, the $A_w^l(Q)$ -coefficients for $l \neq 0$ are negligible and $DWF_w \approx 1$, so Eq. (4a) can be written as

$$S_w(Q, \omega) = n_w b_w^2(Q) S_{trw}^{\text{coh}}(Q, \omega), \quad (14)$$

where $b_w(Q)$ is defined by Eqs. (A8) and (A9). Likewise, at a sufficiently low Q value (which depends on the size of the solute molecule) $A_{\text{sol}}^l(Q)$ and $A_{\text{sol}}^{(p)}(Q)$ for $l \neq 0$ are negligible, too. Therefore, Eqs. (A2), (A9), and (10a) yield

$$S_{\text{sol}}(Q, \omega) = n_{\text{sol}} b_{\text{sol}}^2(Q) S_{tr\text{sol}}^{\text{coh}}(Q, \omega), \quad (15)$$

$$S_{trw}^{\text{coh}}(Q, \omega) = \frac{n_{\text{sol}}}{n_w} A_0^{(p)}(Q) S_{tr\text{sol}}^{\text{coh}}(Q, \omega). \quad (16)$$

Thus, the coherent QENS scattering from solution is

$$S^{\text{coh}}(Q, \omega) = n_{\text{sol}} [b_{\text{sol}}^2(Q) - 2b_{\text{sol}}(Q)b_w(Q)N^{(p)}(Q) + A_0^{(p)}(Q)b_w^2(Q)] S_{tr\text{sol}}^{\text{coh}}(Q, \omega). \quad (17)$$

At low Q , $N^{(p)}(Q)$ is just the number of water molecules excluded from the solution by one solute molecule, and $A_0^{(p)}(Q)$ is equal to the square of this number, as follows from Eqs. (D22) and (D24). Thus, Eq. (17) yields (after applying the convolution approximation)

$$S^{\text{coh}}(Q, \omega) = n_{\text{sol}} [b_{\text{sol}}(Q) - b_w(Q)N^{(p)}(Q)]^2 \times S_{\text{cm sol}}(Q) S_{tr\text{sol}}^{\text{inc}}(Q, \omega). \quad (18)$$

While Eq. (18) is already simple enough for a practical application, it can be simplified further to make its meaning more transparent. Let ρ_{sol} and ρ_w be the solute and water coherent scattering length densities [in general, $\rho_{\text{mol}} = b_{\text{mol}}(Q \rightarrow 0)/V_{\text{mol}}$]. Then $\rho_{\text{sol}} - \rho_w$ is the scattering contrast and Eq. (18) can be written as

$$S^{\text{coh}}(Q, \omega) = n_{\text{sol}} (v^{(p)})^2 (\rho_{\text{sol}} - \rho_w)^2 S_{\text{cm sol}}(Q) \times S_{tr\text{sol}}^{\text{inc}}(Q, \omega), \quad (19)$$

where $v^{(p)}$ is the volume excluded by the solute molecule. As follows from Eq. (1), an integration of Eq. (19) over en-

ergy transfer gives the small-angle scattering intensity, $I(Q, t = 0)$. Because $\int S_{tr\text{sol}}^{\text{inc}}(Q, \omega) d\omega \equiv 1$, we get an equation that is well-known in the field of small-angle neutron and x-ray scattering,

$$I^{\text{coh}}(Q, t = 0) = n_{\text{sol}} (v^{(p)})^2 (\rho_{\text{sol}} - \rho_w)^2 S_{\text{cm sol}}(Q). \quad (20)$$

This result demonstrates that the model framework presented in this paper is, generally speaking, an account for the scattering-contrast in the time-dependent case.

III. EXPERIMENT

A. Experimental details

D₂O 99.9% pure, DIMEB and TRIMEG (>95%, Cyclo-Lab), γ -CD (>98%, ROTH) were used without further purification. In our calculations the density of the solutions was taken to be equal to the density of pure D₂O because the solute concentrations were low.

QENS spectra of D₂O and of solutions of DIMEB (50 mg/ml), TRIMEG (61.4 mg/ml) and γ -CD (48.7 mg/ml) in D₂O, were recorded with the time-of-flight (TOF) spectrometer NEAT at BENSC, Hahn-Meitner-Institut (HMI, Berlin) by one of us (R.E.L.). The sample containers were circular slabs with thicknesses of 1.6 or 2.5 mm, the sample transmission was >0.85 (with the beam perpendicular to the slab).

In one experiment the spectra were recorded with an energy resolution (ΔE), full width at half-maximum, of $\approx 10 \mu\text{eV}$. The incident neutron wavelength (λ_0) was 10.0 \AA , sample angle²¹ (α) = 90°, the range of the Q values for zero energy transfer (Q range, hereafter) was from 0.16 to 1.2 \AA^{-1} . In another experiment, the spectra were recorded with $\Delta E \approx 10 \mu\text{eV}$, $\lambda_0 = 15.3 \text{ \AA}$, $\alpha = 60^\circ$, the Q range was from 0.10 to 0.75 \AA^{-1} . For the QENS analysis the Q range was limited by a maximum value of $\approx 0.6 \text{ \AA}^{-1}$, in order to remain in the low Q region. The sample temperatures are given in Tables I and II.

B. Data analysis

Data reduction of the raw QENS spectra was carried out using the program FITMO.²² The energy resolution function was determined by fitting a Gaussian function to the vanadium spectra. The expression fitted to the sample spectra reads

$$S_{FIT}(Q, \omega) = F_{sc}(\phi) e^{-\hbar\omega/2k_B T} S(Q, \omega) \otimes R(\phi, \omega), \quad (21)$$

TABLE II. Solute translational [$D_{\text{tr sol}}$ (10^{-5} cm²/s)] and rotational [$D_{\text{r sol}}$ (μeV)] diffusion coefficients in D₂O solutions. The values with uncertainties were obtained by fitting the model to the QENS spectra.

	Sample	T (K)	$D_{\text{tr sol}}^{\text{a}}$	$D_{\text{tr sol}}^{\text{b}}$	$D_{\text{tr sol}}^{\text{c}}$	$D_{\text{r sol}}^{\text{d}}$
$\lambda_0 = 10 \text{ \AA}$	γ -CD	303.6	0.268	0.504 ± 0.016	0.393 ± 0.016	0.55 ± 0.03
	TRIMEG	308	0.280	0.458 ± 0.012	0.383 ± 0.011	0.56 ± 0.03
	DIMEB	303	0.184	0.240 ± 0.008	0.180 ± 0.009	0.32 ± 0.03
	γ -CD	285.5	0.144	0.367 ± 0.015	0.263 ± 0.014	0.59 ± 0.04
		301	0.246	0.465 ± 0.016	0.362 ± 0.016	0.59 ± 0.05
		317.7	0.416	0.506 ± 0.021	0.408 ± 0.021	0.28 ± 0.06
$\lambda_0 = 15.3 \text{ \AA}$	TRIMEG	285.5	0.118	0.140 ± 0.005	0.087 ± 0.004	0.13 ± 0.02
		300.8	0.216	0.204 ± 0.004	0.150 ± 0.004	0.009 ± 0.02
	DIMEB	278.1	0.083	0.106 ± 0.005	0.062 ± 0.005	0.25 ± 0.03
		290.8	0.126	0.120 ± 0.006	0.081 ± 0.006	0.17 ± 0.03
		303.7	0.186	0.148 ± 0.006	0.108 ± 0.006	0.05 ± 0.04
		317	0.268	0.287 ± 0.008	0.226 ± 0.008	0.29 ± 0.05

^aFrom the literature, see Sec. III B.^bFitted with $D_{\text{r sol}}$ fixed at 0.^cFitted with $D_{\text{r sol}}$ fixed at $0.25 \mu\text{eV}$.^dFitted with $D_{\text{tr sol}}$ fixed at the values from column 4.

where ϕ is the scattering angle, $R(\phi, \omega)$, the slightly angle-dependent energy resolution function, $e^{-\hbar\omega/2k_B T}$ the detailed balance factor, k_B the Boltzmann constant, T the absolute temperature, $F_{\text{sc}}(\phi)$ the scaling factor and $S(Q, \omega)$ the theoretical scattering function in the classical approximation.

The $S(Q, \omega)$ -expression fitted to the QENS spectra of pure D₂O, as well as the $S_{\text{sol}}(Q, \omega)$ expression describing the scattering by solute molecules are defined in Appendix A. In the spectra analyzed here, $Q < 0.6 \text{ \AA}^{-1}$; for this low Q range, (i) the DWF of the solute can be approximated by unity (for water, taking $\langle u^2 \rangle_w$ from Ref. 23, the DWF decays to 0.97 at $Q = 0.6 \text{ \AA}^{-1}$, and it is reasonable to expect a significantly smaller value of $\langle u^2 \rangle_{\text{sol}}$), (ii) the influence of the $\tau_{\text{tr sol}}$ value on the translational diffusion linewidth given by Eq. (A7) is negligible. Consequently, for the contribution of translational diffusion to $S_{\text{sol}}(Q, \omega)$ we used [instead of Eqs. (A6) and (A7)]

$$S_{\text{tr sol}}^{\text{inc}}(Q, \omega) = \text{Lor}(D_{\text{tr sol}} Q^2, \omega) \quad (22)$$

which is the well-known form of expression (A6) in the low Q limit.

The literature sources for pure-D₂O parameter values were: Refs. 24–26 for $D_{\text{tr w}}$, Ref. 8 for $\tau_{\text{tr w}}$; $D_{\text{tr w}}$ and $\langle u^2 \rangle_w$ originate from studies on H₂O.²³ See Table I for the values actually used in fits to the QENS spectra of pure D₂O and D₂O solutions. $S_{\text{cm w}}(Q)$ was calculated in the “static approximation” [see, e.g., Eq. (14) in Ref. 13] from the D₂O data [O–D bond length, D–O–D angle and the intermolecular function $D_M(Q)$] taken from neutron diffraction.²⁷ Because in our solutions the solute volume fraction was less than 0.05, we neglected the change in the D₂O diffusion coefficient compared to that of pure D₂O. From the crystal structures of γ -CD, DIMEB, and TRIMEG (Refs. 28–30) we computed the $A_{\text{sol}}^l(Q)$ -coefficients and, using the cube method,³¹ the functions $N^{(p)}(Q)$ and $A^{(p)}(Q)$. Van der Waals (vdW) radii were taken as 1.75, 1.58, and 1.1 \AA for C, O, and H

atoms, respectively.³² To account for the difference between the molecule’s vdW volume and the volume excluded by the molecule, a shell of thickness Δ around the vdW volume was used ($\Delta = 0.1, 0.26$, and 0.33 \AA for γ -CD, DIMEB and TRIMEG, respectively³³). More details on our implementation of the cube method are given elsewhere.³³ A multiple scattering calculation was carried out at every iteration of the nonlinear least squares fitting procedure as previously described.⁸

The $D_{\text{tr sol}}$ values of γ -CD, DIMEB, and TRIMEG (Refs. 34–36) were corrected for the differences in viscosity of H₂O relative to D₂O.³⁷ The $D_{\text{tr sol}}$ data used here (Table II, column 4) were found by inter- and extrapolation of the literature values using the Arrhenius Law for the temperature dependence and an analogous exponential law for the concentration dependence. From NMR results, for β -CD in D₂O at 25 °C, the rotational correlation time $\tau_{\text{r sol}}$ is 220 ps,³⁸ corresponding to $D_{\text{r sol}} = 0.5 \mu\text{eV}$ [according to $D_{\text{r sol}}(\text{meV}) = 0.6583/6\tau_{\text{r sol}}(\text{ps})$]. Since molecules we studied are larger than β -CD, smaller $D_{\text{r sol}}$ are expected. Therefore, the $D_{\text{r sol}}$ values, if not fitted, were kept at $0.25 \mu\text{eV}$, $0.1 \mu\text{eV}$ or $0 \mu\text{eV}$; the quality of the fits differed negligibly.

To calculate $S_{\text{cm sol}}(Q)$, we extended Debye’s approach for the calculation of $S_{\text{cm sol}}(Q)$ for hard spheres to the case of hard bodies of an arbitrary shape. We assumed that given a molecule with an orientation Ω_1 and its center-of-mass (CM) at the origin, the probability to find the CM of another molecule with an orientation Ω_2 at a distance r is equal to the mean solute number density everywhere, as long as molecular volumes do not overlap, and zero otherwise. The static CM pair correlation function $G_{\text{cm sol}}(r, \Omega_1, \Omega_2)$ was calculated using the cube method, averaged over all possible orientations Ω_1 and Ω_2 , and Fourier transformed to yield $S_{\text{cm sol}}(Q)$. Although the so-obtained $S_{\text{cm sol}}(Q)$ accounts for the two-body interactions only, it is adequate given the low solute volume fraction in the studied solutions (see, e.g., Ref. 16).

If the correction procedure for the angle-dependent attenuation of the incident beam and of the sample scattering is accurate, and the spectra were normalized to the scattering by vanadium, the scaling factor $F_{sc}(\phi)$ is just a constant that can be calculated from the sample thickness and the properties of the calibration standard.³⁹ However, due to the approximations used in the correction procedure, $F_{sc}(\phi)$ usually deviates from the expected value. To compensate for those small, but non-negligible deviations in the fitting procedure of the model expressions to the spectra, $F_{sc}(\phi)$ was employed as a free but ϕ -dependent fitting parameter.

Since the UFA does not account for the intermolecular coherent scattering due to a finite size of water molecules, $S_w^{inter}(Q, \omega)$ from Eq. (12) lacks a broad scattering component which we call $S_w^{corr}(Q, \omega)$. We estimate the magnitude of this component by the intermolecular coherent scattering from pure water, which is [see Eq. (13)]

$$S_w^{corr}(Q, \omega) = S_{cm D_2O}(Q) A_w^{0coh}(Q) S_{trw}^{inc}(Q, \omega), \quad (23)$$

where $S_{cm D_2O}(Q)$ is the structure factor for pure D₂O. At low Q , where only the first term in the infinite series (4a) needs to be considered, the ratio of the energy-integrated function $S_w^{corr}(Q, \omega)$ to the energy-integrated incoherent water scattering [see Eq. (4b)] is $S_{cmw}(Q) A_w^{0coh}(Q) / A_w^{0inc}(Q) = 0.79$.⁴⁰ Therefore, we decided that for the dilute solutions (as in our case) it was better to add $S_w^{corr}(Q, \omega)$ to the model expression given by the UFA than to neglect it entirely. Hence, in fitting of the QENS spectra a modified version of Eq. (4b) was used

$$S_w^0(Q, \omega) = A_w^{0coh}(Q) S_{trw}^{coh}(Q, \omega) + A_w^{0inc}(Q) S_{trw}^{inc}(Q, \omega) + S_w^{corr}(Q, \omega). \quad (24)$$

IV. RESULTS

The model fitted to all QENS spectra of CD and mCD solutions is represented by Eq. (3) containing the sum of the three terms $S_w(Q, \omega)$, $S_{cross}(Q, \omega)$, and $S_{sol}(Q, \omega)$. The function $S_w(Q, \omega)$ is given by Eqs. (4a)–(4c), where Eq. (24) is replacing Eq. (4b), and by Eqs. (10a)–(10c); $S_{cross}(Q, \omega)$ is given by Eqs. (5) and (11), while $S_{sol}(Q, \omega)$ is given by Eqs. (4a)–(4c) (with superscript “sol” instead of “w”), Eqs. (6) and (22).

Examples of the fit results are shown in Fig. 2 for the elastic wave vector transfer $Q = 0.14 \text{ \AA}^{-1}$, and in Fig. 3 for $Q = 0.5 \text{ \AA}^{-1}$. To see if there is any observable broadening at all, the widths of the separately plotted components of Eq. (3) should be compared to the width of the energy resolution function. In Fig. 2, both $S_{sol}(Q, \omega)$ and $S_w(Q, \omega)$ have widths similar to the resolution width [we had to scale down $R(\phi, \omega)$ so that the curves would not entirely overlap]. The $S_{cross}(Q, \omega)$ width is the same as that of $S_{tr sol-w}(Q, \omega)$ [see Eq. (11)], and thus, because at low Q the rotational QENS contribution is negligible, is similar to that of $S_{sol}(Q, \omega)$. In Fig. 3, at a higher Q value, the widths of both $S_{sol}(Q, \omega)$ and $S_w(Q, \omega)$ are clearly greater than the resolution width, and the $S_{cross}(Q, \omega)$ -term has a negligible intensity.

The broadening of the quasielastic peak due to translational diffusion, taken as the full width at half-maximum

(FWHM) can be calculated from Eq. (22) and Eq. (A7) for the solute and water molecules, respectively [multiply FWHM (ps^{-1}) by 0.6583 to convert it to meV units]. At $Q = 0.14 \text{ \AA}^{-1}$ and 301 K, FWHMs for γ -CD and D₂O are 0.63 \mu eV and 5.1 \mu eV , respectively (see Tables I and II for the input values). Because the resolution width is $\approx 10 \text{ \mu eV}$, it is clear why the $S_{sol}(Q, \omega)$ -broadening can hardly be seen in Fig. 2. Also not seen is the broad contribution due to D₂O dynamics (with FWHM of 5.1 \mu eV) in the $S_w(Q, \omega)$ shown in Fig. 2, because at low Q values the greatest fraction of the $S_w(Q, \omega)$ -intensity is its coherent part which has the width of the $S_{sol}(Q, \omega)$ -component [see Eqs. (24), (10a)–(10c)]. At higher Q , the $S_w(Q, \omega)$ -broadening is greater than that of $S_{sol}(Q, \omega)$, see Fig. 3, because the effect of the excluded volume becomes negligible, and the intramolecular scattering from D₂O dominates $S_w(Q, \omega)$.

The strong decrease of the intensity with increasing Q , both for $S_w(Q, \omega)$ and for $S_{cross}(Q, \omega)$, (compare Figs. 2 and 3) is due to a steep decrease of the effective scattering length, $b(Q)$, for water and solute molecules. The negative sign of $S_{cross}(Q, \omega)$ is, technically, the consequence of the definition of the number density by Eq. (D13). Simply put, this is because the solute molecules are dispersed not in vacuum, but in a medium with a non zero neutron coherent scattering length, and this leads to a destructive interference.

Since the uniform fluid approximation does not account for the intermolecular D₂O scattering arising due to a finite size of D₂O molecules, we approximated it by the corresponding contribution to the pure D₂O scattering [$S_w^{corr}(Q, \omega)$ in Eq. (24)]. In the low Q region, this approximation improved the fit quality for γ -CD, and slightly worsened the fit quality for TRIMEG and DIMEB [as opposed to the fits with neglecting $S_w^{corr}(Q, \omega)$ entirely, see the example of such a fit for DIMEB in Fig. 4]. Since $S_w^{corr}(Q, \omega)$ has about the same intensity as the D₂O-incoherent scattering (see Sec. III B), it can be neglected whenever the total scattering is much more intense than the D₂O-incoherent scattering. As seen from Fig. 2, this is the case for DIMEB and TRIMEG, but not for γ -CD. Thus, the use of $S_w^{corr}(Q, \omega)$ is expected to improve the fit quality to a lesser extent for mCDs than for γ -CD. The reasons for a slightly better fit quality for mCDs when the intermolecular D₂O scattering is neglected altogether are difficult to pursue as we can not at present calculate or measure the exact value of $S_w^{corr}(Q, \omega)$.

At low Q the coherent QENS intensity is proportional to the squares of the contrast and of the excluded volume [Eq. (19)]. The scattering contrasts ($10^{-12} \text{ cm}^3/\text{\AA}^3$) for solutions in D₂O and the solute molecule's excluded volumes (\AA^3) are: -0.0249 and 1302 (γ -CD), -0.0525 and 2125 (TRIMEG), -0.0455 and 1575 (DIMEB).³³ The low contrast for γ -CD is the main reason why at low Q the QENS intensity of the γ -CD spectra is substantially weaker than that of the mCDs spectra.

As shown above, the quasielastic broadening due to the translational diffusion of a solute molecule is about 5% of the resolution width at $Q = 0.14 \text{ \AA}^{-1}$. This broadening quickly rises with increasing Q , thus allowing us to determine $D_{tr sol}$ by fitting. The so-obtained $D_{tr sol}$ values depend on the value at which the rotational diffusion coefficient, $D_{r sol}$, was fixed

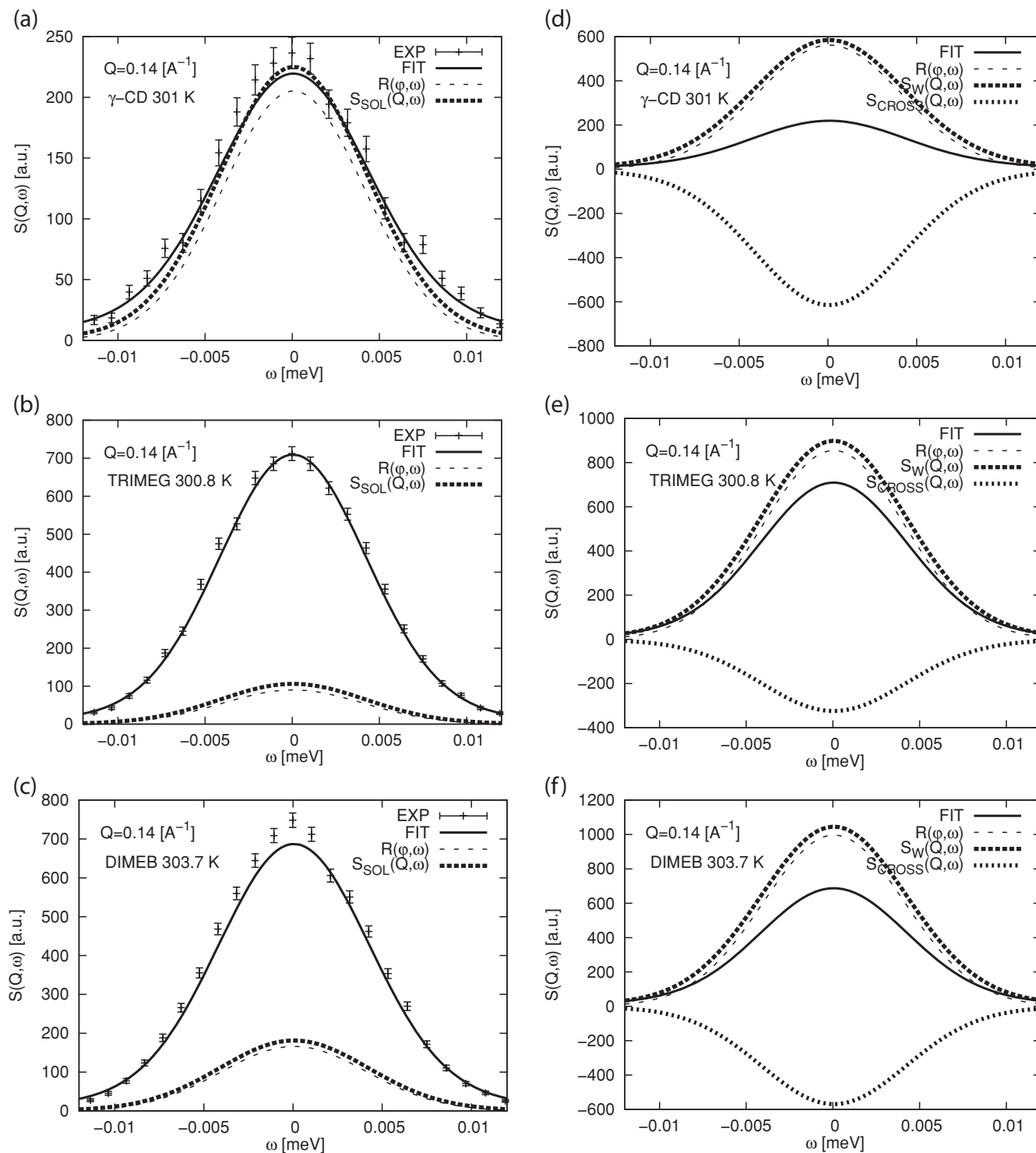


FIG. 2. Examples of fitting of the model to the QENS spectra of cyclodextrins dissolved in D_2O , for the experiment with $\lambda_0 = 15.3 \text{ \AA}$. “EXP” and “FIT” stand for experimental data and the fitted curve, respectively; the “FIT”-curve is the same in both columns. $S_{\text{sol}}(Q, \omega)$ and $S_w(Q, \omega)$ are the solute and D_2O scattering, respectively (both coherent plus incoherent); $S_{\text{cross}}(Q, \omega)$ is the coherent scattering due to D_2O -solute time-dependent spatial correlations. The energy resolution function, $R(\phi, \omega)$, is plotted for the comparison of instrumental broadening with the broadening of the separate scattering contributions. For the theoretical origin of the scattering functions $S_w(Q, \omega)$, $S_{\text{cross}}(Q, \omega)$, and $S_{\text{sol}}(Q, \omega)$, see the beginning of this section.

(see Table II). This is not surprising: the radius of a cyclodextrin molecule is about 10 \AA , therefore, the rotational broadening is non negligible already at $Q = 0.2 \text{ \AA}^{-1}$ [i.e., for $l > 0$, the coefficients $A^l(Q)$ in Eq. (A4) are comparable to or greater than $A^0(Q)$]. Thus, the more we increase $D_{\text{r sol}}$, the smaller $D_{\text{tr sol}}$ values we get. For DIMEB and TRIMEB

the $D_{\text{tr sol}}$ values obtained with $D_{\text{r sol}} = 0$ are fairly close to the ones from the literature, while for γ -CD they differ substantially. This may have to do with a smaller QESANS intensity from γ -CD-solutions, or a greater rotational diffusion coefficient. However, the comparison of the $D_{\text{tr sol}}$ values from different sources must be made with caution. Since at low

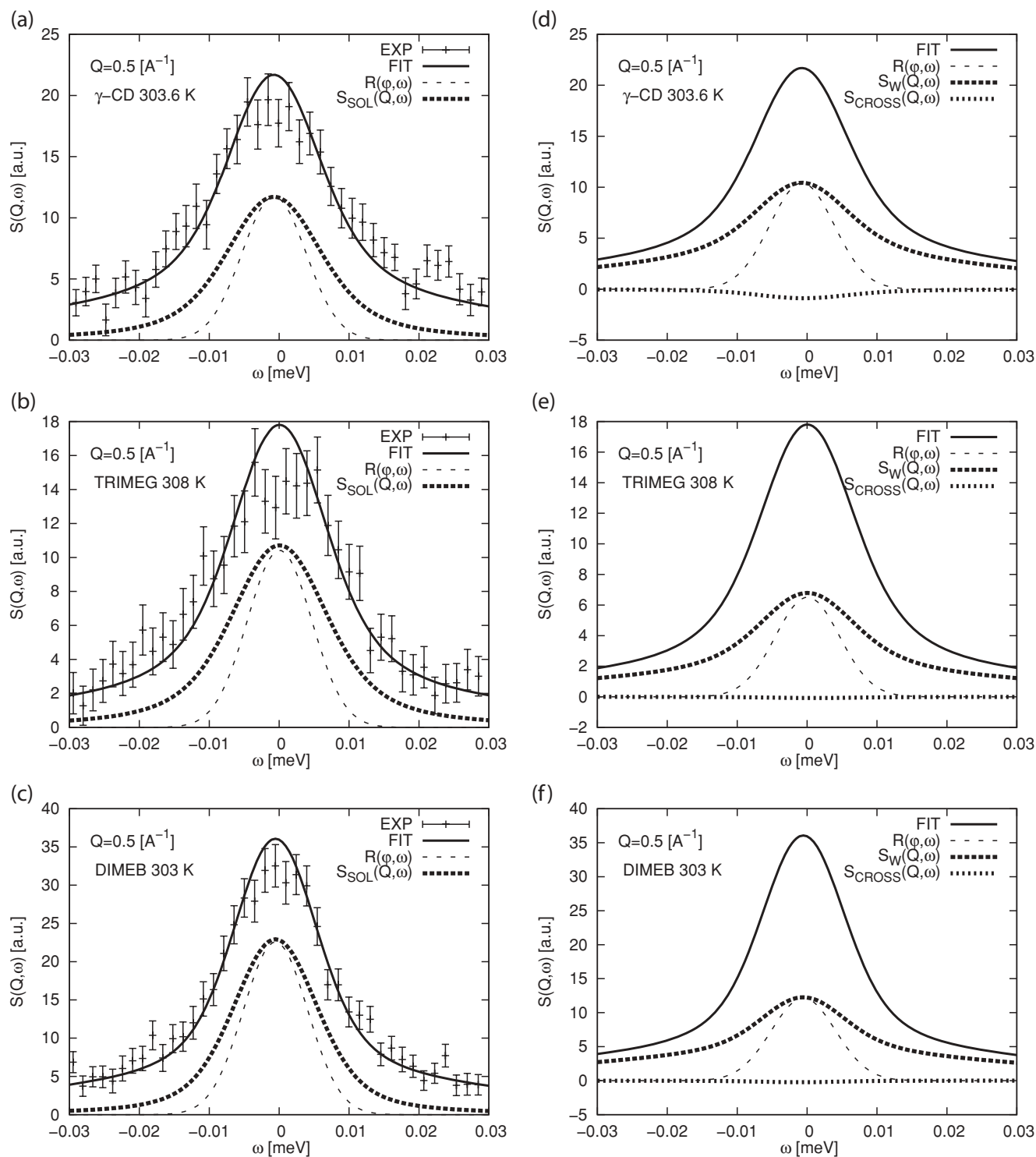


FIG. 3. Examples of fitting of the model to the QENS spectra of cyclodextrins dissolved in D₂O, for the experiment with $\lambda_0 = 10 \text{ \AA}$. The notations are the same as in Fig. 2. As compared to Fig. 2, (i) the broadening of the $S_{\text{sol}}(Q, \omega)$ and $S_w(Q, \omega)$ -terms is clearly observable; (ii) the intensity of the $S_{\text{cross}}(Q, \omega)$ -term is negligible. The scattering is due to $S_{\text{sol}}(Q, \omega)$ and due to the scattering from D₂O that is practically the same as the pure D₂O scattering.

Q most of the scattering is coherent, the fitted $D_{\text{tr sol}}$ value will depend on how the solute intermolecular structure factor and hydrodynamic interactions were taken into account (see, e.g., Ref. 6), while from a PFG-NMR experiment a true self-diffusion coefficient is obtained. For DIMEB at $\approx 303 \text{ K}$ the $D_{\text{tr sol}}$ values obtained for $\lambda_0 = 10 \text{ \AA}$ are substantially higher than for $\lambda_0 = 15.3 \text{ \AA}$. This is in accord with a greater weight

of the low Q region for $\lambda_0 = 15.3 \text{ \AA}$: at smaller Q a greater fraction of the scattering is coherent, and therefore the weight of the collective diffusion coefficient is greater, too.

The fitted $D_{\text{r sol}}$ values (with $D_{\text{tr sol}}$ kept fixed) are in a qualitative agreement with the available data (from Ref. 38 or from the Debye–Stokes–Einstein relation for a sphere: $D_r = k_B T / 6\eta V_{\text{sphere}}$). Having a wider Q range or a

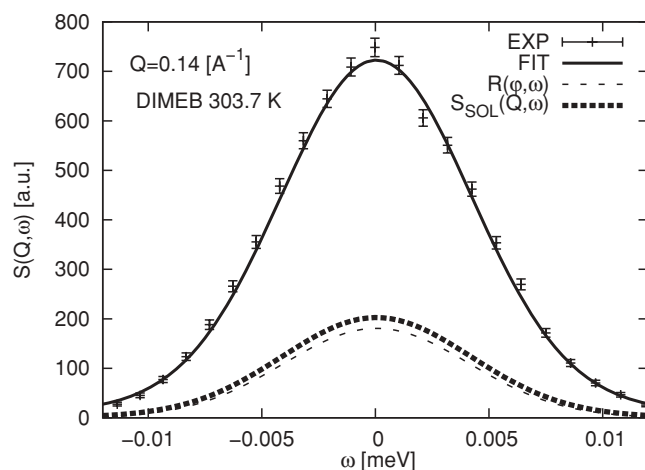


FIG. 4. Fit of the same model to the same spectrum as shown in Fig. 2 for DIMEB, the only difference is that the intermolecular D₂O scattering due to a finite size of water molecules was not approximated by the corresponding term for pure D₂O [i.e., Eq. (4b) was used instead of Eq. (24)]. The notations are the same as in Fig. 2. For reasons why the fit quality is somewhat better, see text.

higher energy resolution or both should help to determine $D_{r\text{sol}}$ with a better precision; this could also allow the simultaneous determination of $D_{tr\text{sol}}$ and $D_{r\text{sol}}$ values.

The fits shown in Figs. 2, 3, 4 are satisfactory; however, approximately the same fit quality could be obtained with the model we used previously^{7,8}

$$S(Q, \omega) = S_{\text{sol}}(Q, \omega) + S_w(Q, \omega), \quad (25)$$

where water scattering was calculated from Eqs. (4a) to (4c) using the structure factor of pure D₂O, and solute scattering was calculated just as it was done here. Moreover, the solute translational diffusion coefficients that were obtained were similar to the values obtained in this work. The reason why Eq. (25) “worked” is the following: at low Q val-

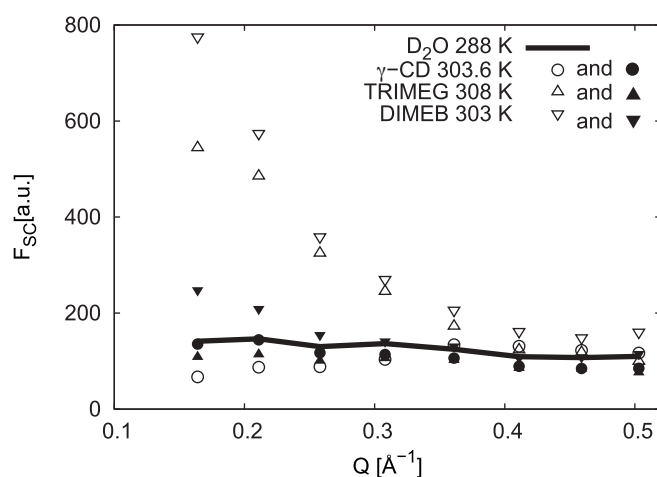


FIG. 5. Curves of the experimental scaling factor $F_{\text{sc}}(\phi)$ obtained in fitting of QENS spectra from the experiment carried out with $\lambda_0 = 10$ Å. The approximately correct $F_{\text{sc}}(\phi)$ -curve (which should ideally be a horizontal straight line) is given by $F_{\text{sc}}(\phi)$ of D₂O. The filled and empty symbols give the $F_{\text{sc}}(\phi)$ values obtained with and without detailed consideration of intermolecular D₂O–D₂O and D₂O–solute coherent scattering, respectively. This corresponds to using Eq. (3) and Eq. (25), respectively.

ues the uniform fluid model is a good approximation and thus the QENS line shape is governed by the solute dynamics alone. However, with Eq. (25), the fitted $F_{\text{sc}}(\phi)$ values for DIMEB and TRIMEG (Fig. 5, open symbols) are up to 8 times higher (at low Q) than they should be [as suggested by the curve of the experimental scaling factor for pure D₂O, Fig. 5]. Fitting of the model developed in this work results in the reasonable $F_{\text{sc}}(\phi)$ -curves for γ -CD and TRIMEG (Fig. 5, filled symbols). As for DIMEB, $S_{\text{cm sol}}(Q)$ that we used accounts for hard body solute–solute interactions only, and solute–solute interactions in DIMEB solutions are substantially attractive.³³ In fact, the excess in the $F_{\text{sc}}(\phi)$ of DIMEB, (increasing toward low Q), is in semiquantitative agreement with experimental $S_{\text{cm sol}}(Q)$ data.³³ Thus, the model developed in the present paper provides a good description not only for the line shape, but for the intensity of the QENS spectra as well.

V. DISCUSSION

The basic goal of this paper is to develop model expressions allowing an explicit consideration of the QENS contributions due to time-dependent spatial pair correlations between all atoms in aqueous solutions of one molecular species. In Sec. II A we showed how one could realize this in general. In Sec. II B we applied an extension of Soper’s theory of the excluded volume effect to derive the simplified QENS model expressions valid in the low Q region. In Sec. II C these model expressions were shown to be compatible with the concept of scattering contrast. Finally, we demonstrated that our model can adequately explain the QENS spectra of cyclodextrins dissolved in heavy water.

An adequate description, in our opinion, comprises not only an adequate fitting quality (that is, a sufficiently good line shape description), but an adequate reproduction of QENS intensities as well. As shown above, a criterion for the latter could be the scattering-angle dependence which results from the fit of the scaling factor $F_{\text{sc}}(\phi)$. Whenever this scaling factor is strongly ϕ -dependent this means that the coherent scattering from the sample was not accounted for properly. Even if one is interested in the dynamics only, e.g., in the rotational and translational diffusion coefficients, the correct coherent scattering intensity matters, because this intensity gives the weight of collective diffusion versus self-diffusion, and the weight of the purely translational QENS component relative to the components that also contain rotational broadening. Thus, a wrong evaluation of the coherent scattering intensity results in wrong $D_{tr\text{sol}}$ and $D_{r\text{sol}}$ values. At somewhat larger Q , when diffusive translational water dynamics becomes increasingly important, an incorrect evaluation of a (still substantial) coherent scattering contribution distorts the mutual proportion of the scattering due to water and solute dynamics. This, too, leads to wrong values of dynamical parameters, even when the fit quality is good. Note that the determination of $D_{tr\text{sol}}$ and $D_{r\text{sol}}$ values from the QENS spectra at higher Q (when incoherent scattering dominates) is far less trivial because in this case intramolecular solute (and solvent) dynamics contributes to the overall broadening to a much larger extent.

We assumed that the differences (i) between dynamical parameters of a single bulk water molecule in solution and in pure water and (ii) between the structure and dynamics of hydration water and bulk water, are negligible. The first assumption is justified for such dilute solutions as used here (solute volume fraction <0.05) but is not required. Instead of keeping $D_{\text{tr}w}$, D_{rw} , etc. fixed to the corresponding values found for pure D₂O or H₂O, we could adjust them, or even make them free fitting parameters. In fact, we tried to determine $D_{\text{tr}w}$ in our solutions by fitting; the obtained values differed from those for pure D₂O to a negligible extent. The second assumption (previously discussed in Sec. II A) is fully justified for dilute solutions, because only a small fraction of water molecules belongs to the hydration shell, and because any change (relative to the bulk water) in the single molecule dynamics of hydration water has a small contribution to $S_w(Q, \omega)$ in the low Q region. With increasing solute concentration the fraction of hydration water increases, and both assumptions mentioned above become inapplicable. In case of crowded solutions, however, there is no bulk water at all; hence, one set of dynamical parameters (different from such for pure water) may be sufficient to satisfactorily describe $S_w(Q, \omega)$.

Using Vineyard's convolution approximation to calculate the scattering function for the collective translational diffusion has little theoretical foundation and is known to fail at very low Q (in the hydrodynamic limit), and in the high Q -region¹⁴ (the start of which is approximately given by the position of the first peak of the intermolecular structure factor). We stress that this approximation is used for practical purposes only. Furthermore, for cyclodextrin solutions, the high Q -region starts from 0.4 to 0.5 Å⁻¹ (Ref. 33), therefore, all analyzed Q values lie in the Q region where the convolution approximation may be acceptable.

With the model presented in Sec. II B it is straightforward to obtain the translational and rotational diffusion coefficients of the solute molecules from quasielastic small-angle neutron scattering (QESANS) experiments. The obvious requirement is a sufficiently high energy resolution [i.e., sufficiently narrow FWHM of $R(\phi, \omega)$], in order to observe the translational or rotational broadening, or both. For cyclodextrins, the resolution used in this work ($\Delta E \approx 10 \mu\text{eV}$) is already high enough, but additional measurements with the resolution of the backscattering spectrometers ($\Delta E \approx 1 \mu\text{eV}$) would be rather beneficial. To profit from the simplicity associated with the uniform fluid approximation, the scattering contrast should be high, and the measurements should be done in the Q region where the QESANS intensity dominates.

It is important to note that the incoherent scattering by the solvent is less of a problem in QESANS than it is in SANS, because the broadening due to solvent dynamics is larger than that of the QESANS component, and a clear separation between both (given a sufficient energy resolution) is easy. Thus, even QESANS measurements of H₂O solutions (despite a high incoherent scattering contribution) would be perfectly feasible. The incoherent solute scattering is obviously not a problem either, except for the fact that it depends on the translational self diffusion, while the line shape of the

QESANS component is governed by the collective translational diffusion.

The uniform fluid approximation is a convenient way to study solute dynamics without the need to bother with water–water [$S_{\text{cm}w}(Q)$] and solute–water [$S_{\text{sol}w}(Q)$] structure factors {to obtain the solute–solute structure factor [$S_{\text{cm} \text{sol}}(Q)$] is relatively easy}. On the other hand, this approximation is limited to the region of low Q values, and it does not allow to extract any information on the motion of water molecules relative to the solute molecules [i.e., $I_{\text{tr} \text{sol}w}(Q, t)$ or $S_{\text{tr} \text{sol}w}(Q, \omega)$]. This approximation is not strictly necessary: the framework presented in Sec. II A is fairly general. However, to use this framework in the QENS analysis, one would require to model (or measure) both $S_{\text{cm}w}(Q)$ and $S_{\text{sol}w}(Q)$.

As an example of what can be learned, consider the hydration shell: it is the layer where significant time-dependent spatial correlations between the solute and water molecules exist, and these correlations contribute to the intermolecular coherent scattering [$S_{\text{cross}}(Q, \omega)$ in Eq. (3)]. Thus, as seen from Eq. (5), to learn about the hydration shell we need an expression for $S_{\text{tr} \text{sol}w}(Q, \omega)$. This expression can be taken from Eq. (8), but an even more simple approach (which does not rely on Vineyard's approximation) could be to write

$$S_{\text{tr} \text{sol}w}(Q, \omega) = S_{\text{sol}w}(Q) \text{Lor}(D_{\text{tr} \text{sol}w} Q^2, \omega), \quad (26)$$

where $S_{\text{sol}w}(Q)$ is given by Eq. (C3). Here the Q^2 -dependent width of the conjectured Lorentzian is controlled by an apparent collective diffusion coefficient, $D_{\text{tr} \text{sol}w}$, which would be analogous to collective diffusion coefficients defined for one molecular species, but would originate exclusively from the diffusive motion of solute and solvent molecules relative to each other. This coefficient will depend on the strength of the interactions between the two different molecules, just as for instance in the case of solute–solute collective diffusion (see Refs. 6 and 41). Therefore the $D_{\text{tr} \text{sol}w}$ value could serve as a measure of solute–water interactions and would be related to the time spent by a water molecule in the hydration shell. If $S_{\text{cm}w}(Q)$ and $S_{\text{sol}w}(Q)$ were known or could be modeled, then, given an energy resolution is sufficiently high to see the change of the QENS line shape due to $S_{\text{cross}}(Q, \omega)$, the experimental determination of $D_{\text{tr} \text{sol}w}$ would be possible.

At present it is not easy to obtain $S_{\text{cm}w}(Q)$ and $S_{\text{sol}w}(Q)$ from a QENS experiment. Indeed, the QENS line shape depends on the Q -dependent intensities of three separate components: $S_{\text{sol}}(Q, \omega)$, $S_{\text{cross}}(Q, \omega)$, and $S_w(Q, \omega)$; these intensities depend on the structure factors $S_{\text{cm} \text{sol}}(Q)$, $S_{\text{sol}w}(Q)$, and $S_{\text{cm}w}(Q)$. If the scaling factor, $F_{\text{sc}}(\phi)$, would result from the fit as an angle-independent constant (as expected in the error-free ideal case), both $S_{\text{sol}w}(Q)$, and $S_{\text{cm}w}(Q)$ could be obtained from fitting the model to the QENS spectra, and then compared to theoretical models. If this were true in the present work, then $F_{\text{sc}}(\phi)$ would be ϕ -independent for the case of pure D₂O but, as seen in Fig. 5, the corresponding $F_{\text{sc}}(\phi)$ curve is still not entirely flat. This is mainly because of the multiple scattering and the attenuation of the incident and singly scattered beams in the sample (in case when the sample container is a plain slab the attenuation is especially ϕ -dependent). The

corrections for these two effects depend on a number of different factors (sample size, macroscopic scattering and absorption cross sections of the sample, scattering angle, sample orientation, etc.) and, to be exact, require a numerical integration of multiple integrals. If the sample container is a hollow cylinder, the attenuation of single scattering is independent on the scattering angle and the multiple scattering is less important; hence, a flatter $F_{sc}(\phi)$ -curve can be expected. Then, one can keep F_{sc} as a ϕ -independent fit parameter and obtain Q -dependent structure factors from the fit to the QENS spectra.

In conclusion, we presented a model accounting for both coherent and incoherent quasielastic neutron scattering from an aqueous solution, and demonstrated how this model together with an extension of Soper's theory of the excluded volume effect¹² to the time-dependent case can reproduce the experimental QENS spectral line shapes and intensities. The model explained the quasielastic small-angle neutron scattering spectra of D₂O solutions of cyclodextrins without an ad hoc assumption on the scattering by the hydration shell made earlier.^{7,8} While the model potentially allows the characterization of the hydration shell, this was not possible with our present QENS spectra. But this may be feasible in the future with better measurement conditions: better statistics, higher energy resolution, and if the QESANS experiment is performed with much stricter observation of conditions of accuracy at low scattering angles, than has been standard in the past mainly in large-angle scattering experiments. This accuracy requirement concerns the precision of our knowledge of the sample container geometry, sample size, scattering angles, sample orientation, etc.

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NOMENCLATURE

$A_w^{l\text{coh}}(Q)$ and $A_w^{l\text{inc}}(Q)$ [$A_{\text{sol}}^{l\text{coh}}(Q)$ and $A_{\text{sol}}^{l\text{inc}}(Q)$]: coefficients in Sears's expansion of the rotational correlation function of a water (solute) molecule.

$A^{(p)}(Q)$: coefficients in Sears's expansion of the rotational correlation function of a solute excluded volume.

$b_w(Q)$ [$b_{\text{sol}}(Q)$]: the effective scattering length of a water (solute) molecule.

$G_w(r, t)$, $G_{\text{sol}}(r, t)$, and $G_{\text{sol-w}}(r, t)$: time-dependent translational water–water, solute–solute, and solute–water pair correlation functions.

$G_{\text{sol}}^{\text{dist}(p)}(r, t)$ [$G_{\text{sol}}^{\text{self}(p)}(r, t)$]: the orientational correlation function for volume elements which belong to two distinct solute molecules (the same solute molecule).

$N^{(p)}(Q)$: an analog of $b(Q)$ for a solute excluded volume.

N_w (N_{sol}): the number of water (solute) molecules in solution.

n_w (n_{sol}): the number density of water (solute) molecules in solution.

$v^{(p)}$ [$V^{(p)}$]: the volume excluded by a single (all) solute molecule(s) in solution.

$S_w(Q, \omega)$, $S_{\text{sol}}(Q, \omega)$, $S_{\text{cross}}(Q, \omega)$: scattering functions originating from water–water, solute–solute and solute–water pair correlations, respectively.

$S_{\text{cm sol}}(Q)$, $S_{\text{cm w}}(Q)$, and $S_{\text{sol-w}}(Q)$: solute–solute, water–water, and solute–water intermolecular CM structure factors in solution.

$S_w^l(Q, \omega)$ [$S_{\text{sol}}^l(Q, \omega)$]: the l th scattering function component in Sears's expansion of the rotational correlation function of a water (solute) molecule.

$S_w^{l(p)}(Q, \omega)$: the l th scattering function component in Sears's expansion of the rotational correlation function of a solute excluded volume.

$S_{\text{tr w}}^{\text{coh}}(Q, \omega)$ and $S_{\text{tr w}}^{\text{inc}}(Q, \omega)$ [$S_{\text{tr sol}}^{\text{coh}}(Q, \omega)$ and $S_{\text{tr sol}}^{\text{inc}}(Q, \omega)$]: the coherent and incoherent translational scattering functions for the CM of water (solute) molecules.

$S_{\text{tr sol-w}}(Q, \omega)$: the (coherent) scattering function for the translational motion of water molecules relative to the solute molecules.

APPENDIX A: QENS MODEL FOR ONE MOLECULAR SPECIES

In Sec. II A the scattering by solute and water molecules, $S_{\text{sol}}(Q, \omega)$ and $S_w(Q, \omega)$, respectively, was expressed using a model developed by Sears.¹³ In the following we show the deduction of this result in more detail.

The scattering function for molecules of one particular species in a liquid solution is,

$$S(Q, \omega) = n \text{DWF} \sum_{l=0}^{\infty} S^l(Q, \omega), \quad (\text{A1})$$

where n is the number density of the molecules. The Debye–Waller factor, $\text{DWF} = e^{-\langle u^2 \rangle Q^2}$, accounts for the Q -dependent decrease (caused by vibrational motions) of the quasielastic intensity, $\langle u^2 \rangle$ is the mean square vibrational amplitude of a molecule. In writing Eq. (A1) we used the model of continuous rotational diffusion on a spherical surface,¹³ thus

$$S^0(Q, \omega) = A^{0\text{coh}}(Q) S_{\text{tr}}^{\text{coh}}(Q, \omega) + A^{0\text{inc}}(Q) S_{\text{tr}}^{\text{inc}}(Q, \omega) \quad l = 0, \quad (\text{A2})$$

$$S^l(Q, \omega) = (2l + 1) A^l(Q) S_{\text{tr}}^{\text{inc}}(Q, \omega) \otimes \text{Lor}[l(l + 1) D_r, \omega] \quad l \neq 0, \quad (\text{A3})$$

where D_r is the rotational diffusion coefficient of the molecule. The coefficients $A^l(Q)$ account for the molecule's coherent and incoherent scattering and are given by

$$A^l(Q) = A^{l\text{coh}}(Q) + A^{l\text{inc}}(Q) = \sum_{\mu, \nu=1}^{m, m} \left[\langle b_{\mu} \rangle \langle b_{\nu} \rangle + \frac{\sigma_{\mu}^{\text{inc}} \delta_{\mu\nu}}{4\pi} \right] j_l(Q r_{\mu}) j_l(Q r_{\nu}) \times P_l(\cos \theta_{\mu\nu}), \quad (\text{A4})$$

where m is the number of nuclei in the molecule, $\langle b_\mu \rangle$ is the neutron coherent scattering length of the μ th nucleus, the vectors \mathbf{r}_μ and \mathbf{r}_ν point from the CM to the μ th and ν th atoms, $\theta_{\mu\nu}$ is the angle between \mathbf{r}_μ and \mathbf{r}_ν , P_l is the Legendre polynomial of degree l , σ_{inc} is the incoherent scattering cross section. Note that for $l \neq 0$, because of the assumption that rotational motions of different molecules are not correlated with each other,¹³ only $S_{\text{tr}}^{\text{inc}}(\mathbf{Q}, \omega)$ appears in Eq. (A3).

For $l = 0$, in Vineyard's convolution approximation,¹¹

$$S^0(\mathbf{Q}, \omega) = (A^{\text{coh}}(\mathbf{Q})S_{\text{cm}}(\mathbf{Q}) + A^{\text{inc}}(\mathbf{Q}))S_{\text{tr}}^{\text{inc}}(\mathbf{Q}, \omega). \quad (\text{A5})$$

The function $S_{\text{cm}}(\mathbf{Q})$ is the intermolecular center-of-mass (CM) structure factor of the molecules.

The incoherent translational scattering function, $S_{\text{tr}}^{\text{inc}}(\mathbf{Q}, \omega)$, is a Lorentzian,

$$S_{\text{tr}}^{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{\pi} \frac{f_{\text{tr}}}{f_{\text{tr}}^2(\mathbf{Q}) + \omega^2} = \text{Lor}(f_{\text{tr}}(\mathbf{Q}), \omega). \quad (\text{A6})$$

In the frame of the isotropic jump-diffusion model⁴²

$$f_{\text{tr}}(\mathbf{Q}) = D_{\text{tr}}Q^2/(1 + \tau_{\text{tr}}D_{\text{tr}}Q^2), \quad (\text{A7})$$

where D_{tr} and τ_{tr} are the molecule's translational diffusion coefficient and correlation time, respectively.

We define the effective scattering length of the molecule, $b(\mathbf{Q})$,

$$b(\mathbf{Q}) = \sum_{\mu=1}^m \langle b_\mu \rangle \frac{\sin \mathbf{Q} \cdot \mathbf{r}_\mu}{Qr_\mu}. \quad (\text{A8})$$

Note that,

$$A^{\text{coh}}(\mathbf{Q}) = b^2(\mathbf{Q}). \quad (\text{A9})$$

The model defined above is applied in Sec. II A to express the scattering by solute and water molecules, $S_{\text{sol}}(\mathbf{Q}, \omega)$ and $S_{\text{w}}(\mathbf{Q}, \omega)$, respectively.

APPENDIX B: INTERMEDIATE SCATTERING FUNCTION FOR SOLUTE-WATER PAIR CORRELATIONS

In the following we show how the term $S_{\text{cross}}(\mathbf{Q}, \omega)$ appearing in Eq. (3) leads to Eq. (5). The contribution of water-solute cross-correlations to Eq. (2) can be written as

$$I_{\text{cross}}(\mathbf{Q}, t) = \sum_{\mu=1}^m \langle b_\mu \rangle \langle e^{-i\mathbf{Q} \cdot \mathbf{r}_\mu} \rangle \times \sum_{\nu=1}^m \langle b_\nu \rangle \langle e^{i\mathbf{Q} \cdot \mathbf{r}_\nu(t)} \rangle I_{\text{tr cross}}(\mathbf{Q}, t), \quad (\text{B1})$$

where the summations over μ and over ν are taken over the nuclei in the solute and in the water molecule, respectively, and $\langle b_\mu \rangle$ is the neutron coherent scattering length of the μ th nucleus. We assumed that (i) the rotational motions of a water molecule, as well as of a solute molecule are uncorrelated with their translational motions; (ii) the rotational motion of a water molecule is uncorrelated with the rotational motion of a solute molecule. The translational contribution, $I_{\text{tr cross}}(\mathbf{Q}, t)$,

reads

$$I_{\text{tr cross}}(\mathbf{Q}, t) = \sum_{i=1}^{N_{\text{sol}}} \sum_{j=1}^{N_{\text{w}}} \langle e^{-i\mathbf{Q}(\mathbf{R}_i - \mathbf{R}_j(t))} \rangle + \sum_{i=1}^{N_{\text{w}}} \sum_{j=1}^{N_{\text{sol}}} \langle e^{-i\mathbf{Q}(\mathbf{R}_i - \mathbf{R}_j(t))} \rangle. \quad (\text{B2})$$

Note that in the first double sum the index i refers to the CM of a solute molecule and j to the CM of a water molecule, while in the second double sum the order is opposite.

Since $I(\mathbf{Q}, t)$ (and $S(\mathbf{Q}, \omega)$) measured in the experiment are the averages over the measurement time (t_m), and because all solute and water molecules are equivalent, Eq. (B2) can be written as

$$I_{\text{tr cross}}(\mathbf{Q}, t) = \frac{1}{t_m - t} \int_0^{t_m - t} dt_0 \times \left\{ N_{\text{sol}} \sum_{j=1}^{N_{\text{w}}} e^{-i\mathbf{Q}[\mathbf{R}_{\text{sol}}(t_0) - \mathbf{R}_j(t+t_0)]} + N_{\text{w}} \sum_{j=1}^{N_{\text{sol}}} e^{-i\mathbf{Q}[\mathbf{R}_{\text{w}}(t_0) - \mathbf{R}_j(t+t_0)]} \right\}. \quad (\text{B3})$$

Henceforth, since $t \ll t_m$, we approximate $t - t_m$ by t_m . By introducing $G_{\text{sol-w}}(\mathbf{r}, t, t_0)$ and $G_{\text{w-sol}}(\mathbf{r}, t, t_0)$ which are solute-water and water-solute time-dependent pair correlation functions, respectively, and by presenting the sums as integrals of these functions, Eq. (B3) can be written as

$$I_{\text{tr cross}}(\mathbf{Q}, t) = \frac{1}{t_m} \int_0^{t_m} dt_0 \int_V e^{i\mathbf{Q} \cdot \mathbf{r}} [N_{\text{sol}} G_{\text{sol-w}}(\mathbf{r}, t, t_0) + N_{\text{w}} G_{\text{w-sol}}(\mathbf{r}, t, t_0)] d\mathbf{r}, \quad (\text{B4})$$

where V is the volume of the sample. Note that $G_{\text{sol-w}}(\mathbf{r}, t, t_0)$ and $G_{\text{w-sol}}(\mathbf{r}, t, t_0)$ are averages over initial positions of the solute and water molecule, respectively.

To introduce the dependence on the spatial origin \mathbf{r}_0 via time-dependent local number densities,^{43,44} $n(\mathbf{r}, t)$ [for the definition see Eqs. (D1)–(D2)], we define

$$G_{\text{sol-w}}(\mathbf{r}, t, t_0) = \frac{1}{N_{\text{sol}}} \int n_{\text{sol}}(\mathbf{r}_0, t_0) n_{\text{w}}(\mathbf{r}_0 + \mathbf{r}, t + t_0) d\mathbf{r}_0, \quad (\text{B5})$$

$$G_{\text{w-sol}}(\mathbf{r}, t, t_0) = \frac{1}{N_{\text{w}}} \int n_{\text{w}}(\mathbf{r}_0, t_0) n_{\text{sol}}(\mathbf{r}_0 + \mathbf{r}, t + t_0) d\mathbf{r}_0. \quad (\text{B6})$$

Equation (B4) can now be written as

$$I_{\text{tr cross}}(\mathbf{Q}, t) = \frac{1}{t_m} \int_0^{t_m} dt_0 \int_V e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{r} \times \int_V n_{\text{sol}}(\mathbf{r}_0, t_0) n_{\text{w}}(\mathbf{r} + \mathbf{r}_0, t + t_0) d\mathbf{r}_0 + \frac{1}{t_m} \int_0^{t_m} dt_0 \int_V e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{r} \times \int_V n_{\text{w}}(\mathbf{r}_0, t_0) n_{\text{sol}}(\mathbf{r} + \mathbf{r}_0, t + t_0) d\mathbf{r}_0. \quad (\text{B7})$$

In principle, Eq. (B7) is just an expanded version of Eq. (B2) with averaging over initial positions and times shown explicitly. Since the functions $n_w(\mathbf{r}, t)$ and $n_{\text{sol}}(\mathbf{r}, t)$ are real valued, the two terms at the right-hand side of Eq. (B7) are identical. Thus, one can see that $I_{\text{tr cross}}(\mathbf{Q}, t)$, and, consequently, the cross-term $I_{\text{cross}}(\mathbf{Q}, t)$ is controlled by the relative motion of a water molecule with respect to a solute molecule, and *vice versa*. For the reason given in Appendix C, from the two possible denominations [$G_{\text{sol-w}}(\mathbf{r}, t)$ and $G_{w-\text{sol}}(\mathbf{r}, t)$] we will use the first one, i.e., $G_{\text{sol-w}}(\mathbf{r}, t)$ and its Fourier transforms.

From the above, after averaging over all \mathbf{Q} -orientations and using Eq. (A8), Eq. (B1) can be written as

$$I_{\text{cross}}(\mathbf{Q}, t) = 2n_{\text{sol}}b_{\text{sol}}(\mathbf{Q})b_w(\mathbf{Q})I_{\text{tr sol-w}}(\mathbf{Q}, t), \quad (\text{B8})$$

where n_{sol} is the solute number density, and $I_{\text{tr sol-w}}(\mathbf{Q}, t)$ is the space-Fourier transform of Eq. (B5). The time-Fourier transformation of Eq. (B8) yields Eq. (5).

APPENDIX C: SOLUTE-WATER PAIR CORRELATIONS

In Sec. II A we related the scattering contribution from the time-dependent water-solute pair correlations, $S_{\text{cross}}(\mathbf{Q}, \omega)$, to $S_{\text{tr sol-w}}(\mathbf{Q}, \omega)$, which, using Vineyard's convolution approximation, was approximated by the product of the solute-water structure factor $S_{\text{sol-w}}(\mathbf{Q})$ and the water incoherent translational scattering function $S_{\text{tr w}}^{\text{inc}}(\mathbf{Q}, \omega)$ [see Eq. (8)]. The explanation is as follows: As it was said in Appendix B, both $S_{\text{tr sol-w}}(\mathbf{Q}, \omega)$ and $S_{\text{tr w-sol}}(\mathbf{Q}, \omega)$ can be used. In Vineyard's approximation one can write

$$S_{\text{tr sol-w}}(\mathbf{Q}, \omega) = S_{\text{sol-w}}(\mathbf{Q})S_{\text{tr w}}^{(\text{sol})\text{inc}}(\mathbf{Q}, \omega), \quad (\text{C1})$$

$$S_{\text{tr w-sol}}(\mathbf{Q}, \omega) = S_{w-\text{sol}}(\mathbf{Q})S_{\text{tr sol}}^{(w)\text{inc}}(\mathbf{Q}, \omega). \quad (\text{C2})$$

In Eq. (C1) $S_{\text{tr w}}^{(\text{sol})\text{inc}}(\mathbf{Q}, \omega)$ depends on the self-diffusion of a water molecule in the coordinate system which has its origin at a solute molecule. Similarly, in Eq. (C2) $S_{\text{tr sol}}^{(w)\text{inc}}(\mathbf{Q}, \omega)$ depends on the self-diffusion of a solute molecule in the coordinate system with the origin at a water molecule. Both equations are correct but neither can be directly used. While, in general, $S_{\text{cross}}(\mathbf{Q}, \omega)$ must depend on both water and solute dynamics, since a water molecule diffuses much faster than a cyclodextrin molecule, in the first approximation one could neglect the translational diffusion of a solute molecule altogether. Thus, Eq. (C1) leads to Eq. (8).

The solute-water structure factor is

$$S_{\text{sol-w}}(\mathbf{Q}) = \int e^{i\mathbf{Q}\cdot\mathbf{r}} (G_{\text{sol-w}}(\mathbf{r}) - n_w) d\mathbf{r}, \quad (\text{C3})$$

where by writing $G_{\text{sol-w}}(\mathbf{r}) - n_w$ instead of $G_{\text{sol-w}}(\mathbf{r})$ we neglect the scattering that cannot be observed in practice (at $\mathbf{Q} \approx 0$), n_w is the mean number density of water in solution. For dilute solutions $G_{\text{sol-w}}(\mathbf{r})$ can be modeled as follows: $G_{\text{sol-w}}(\mathbf{r})$ is n_w if water and solute molecules do not overlap and 0 otherwise. [A similar approach was already used in QENS analysis (Sec. 2.12 in Ref. 5)]. Equation (C3) becomes an integral over the volume which is somewhat larger than the excluded volume of the solute molecule (to account for the finite size of the water molecule). Note that $G_{\text{sol-w}}(\mathbf{r})$ does not have to be spherically symmetric. After averaging over all \mathbf{Q}

orientations, the resulting $S_{\text{sol-w}}(\mathbf{Q})$ can be used to calculate $S_{\text{tr sol-w}}(\mathbf{Q}, \omega)$ in Eq. (8).

APPENDIX D: UNIFORM FLUID APPROXIMATION (UFA) IN QENS

1. General formalism

In order to derive the scattering functions given by Eqs. (10a)–(10c) and Eq. (11) in Sec. II B, we give here an extension of Soper's (static) theory of the excluded volume effect¹² to the dynamical case implying time-dependent correlation functions, while the static theory obviously is restricted to $t = 0$. Equations from the original paper are referred to as Eqs. (S1), (S2), etc. We abbreviate terms $\mathbf{R}_i(t = 0)$ by \mathbf{R}_i , $n(\mathbf{r}, t = 0)$ by $n(\mathbf{r})$, and so on.

Instead of the static local number density, $n(\mathbf{r})$ used in Ref. 12, the function relevant in our case is the time-dependent local number density, $n(\mathbf{r}, t)$, which for N atoms in a volume V is

$$n(\mathbf{r}, t) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{R}_j(t)), \quad (\text{D1})$$

where $\mathbf{R}_j(t)$ is the vector giving the position of j th atom at time t . The expression for the time-dependent pair correlation function, $G(\mathbf{r}, t)$, reads

$$G(\mathbf{r}, t) = \frac{1}{N} \int n(\mathbf{r}')n(\mathbf{r}' + \mathbf{r}, t) d\mathbf{r}'. \quad (\text{D2})$$

$G(\mathbf{r}, t)$ can be presented as the sum of the self and distinct time-dependent correlation functions, $G^{\text{self}}(\mathbf{r}, t)$ and $G^{\text{dist}}(\mathbf{r}, t)$,

$$G(\mathbf{r}, t) = G^{\text{self}}(\mathbf{r}, t) + G^{\text{dist}}(\mathbf{r}, t), \quad (\text{D3})$$

$$G^{\text{self}}(\mathbf{r}, t) = \frac{1}{N} \sum_{i=1}^N \delta(\mathbf{r} + \mathbf{R}_i - \mathbf{R}_i(t)), \quad (\text{D4})$$

$$G^{\text{dist}}(\mathbf{r}, t) = \frac{1}{N} \sum_{i \neq j=1}^{N,N} \delta(\mathbf{r} + \mathbf{R}_i - \mathbf{R}_j(t)).$$

Given that there are N_{cm} molecules, M atoms per molecule, $N = N_{\text{cm}}M$, the functions $n_{\text{cm}}(\mathbf{r}, t)$, and $G_{\text{cm}}(\mathbf{r}, t)$ are defined as above except that they refer to the CM of the molecules. Introducing the internal atomic number density, $n^{(p)}(\mathbf{r}, t)$ (which is zero outside the volume of the molecule), $n(\mathbf{r}, t)$ can be presented as

$$n(\mathbf{r}, t) = \int n_{\text{cm}}(\mathbf{r}', t)n^{(p)}(\mathbf{r} - \mathbf{r}', t) d\mathbf{r}'. \quad (\text{D5})$$

The $G(\mathbf{r}, t)$ expression defined by Eq. (D2) can be rewritten using Eq. (D5) as

$$G(\mathbf{r}, t) = \frac{1}{N} \int d\mathbf{r}' \int n_{\text{cm}}(\mathbf{r}'')n^{(p)}(\mathbf{r}' - \mathbf{r}'') d\mathbf{r}'' \times \int n_{\text{cm}}(\mathbf{r}''', t)n^{(p)}(\mathbf{r} + \mathbf{r}' - \mathbf{r}''', t) d\mathbf{r}'''. \quad (\text{D6})$$

Substituting $\mathbf{u}' = \mathbf{r}' - \mathbf{r}''$ and $\mathbf{u}'' = \mathbf{r} + \mathbf{r}' - \mathbf{r}''$ we get

$$G(\mathbf{r}, t) = \frac{1}{N} \int d\mathbf{r}' \int n_{\text{cm}}(\mathbf{r}' - \mathbf{u}') n^{(p)}(\mathbf{u}') d\mathbf{u}' \times \int n_{\text{cm}}(\mathbf{r} + \mathbf{r}' - \mathbf{u}'', t) n^{(p)}(\mathbf{u}'', t) d\mathbf{u}''. \quad (\text{D7})$$

The substitutions $\mathbf{u} = \mathbf{u}'' - \mathbf{u}'$ and $\mathbf{r}' = \mathbf{r}'' + \mathbf{u}'$ yield [compare with Eqs. (S8) and (S9)],

$$G(\mathbf{r}, t) = \frac{1}{N} \int d\mathbf{u} \int d\mathbf{r}'' n_{\text{cm}}(\mathbf{r}'') n_{\text{cm}}(\mathbf{r}'' + \mathbf{r} - \mathbf{u}, t) \times \int d\mathbf{u}' \langle n^{(p)}(\mathbf{u}') n^{(p)}(\mathbf{u}' + \mathbf{u}, t) \rangle_{\Omega}. \quad (\text{D8})$$

The self and distinct internal correlation functions, $G^{\text{self}(p)}(\mathbf{u}, t)$ and $G^{\text{dist}(p)}(\mathbf{u}, t)$, respectively, are

$$G^{\text{self}(p)}(\mathbf{u}, t) = \frac{1}{M} \int \langle n^{(p)}(\mathbf{u}') n^{(p)}(\mathbf{u}' + \mathbf{u}, t) \rangle_{\Omega} d\mathbf{u}', \quad (\text{D9})$$

$$G^{\text{dist}(p)}(\mathbf{u}, t) = \frac{1}{M} \int \langle n^{(p)}(\mathbf{u}') \rangle_{\Omega} \langle n^{(p)}(\mathbf{u}' + \mathbf{u}, t) \rangle_{\Omega} d\mathbf{u}', \quad (\text{D10})$$

where $\langle \cdots \rangle_{\Omega}$ stands for orientational average. The integrals of $G^{\text{self}(p)}(\mathbf{u}, t)$ and $G^{\text{dist}(p)}(\mathbf{u}, t)$ over the volume of the molecule are equal to 1 and $M - 1$, respectively. It follows from the above,

$$G(\mathbf{r}, t) = \int G^{\text{self}(p)}(\mathbf{u}, t) G_{\text{cm}}^{\text{self}}(\mathbf{r} - \mathbf{u}, t) d\mathbf{u} + \int G^{\text{dist}(p)}(\mathbf{u}, t) G_{\text{cm}}^{\text{dist}}(\mathbf{r} - \mathbf{u}, t) d\mathbf{u}. \quad (\text{D11})$$

For $t = 0$, Eq. (D11) is identical to Eq. (S10).

2. Application of the UFA to water–water and solute–water pair correlations

Let us have N_{sol} solute molecules in a volume V , the mean solute number density is n_{sol} , $n_{\text{sol}} = N_{\text{sol}}/V$. In solution each solute molecule excludes a volume $v^{(p)}$, called the excluded volume in the following; the total excluded volume is $V^{(p)}$, $V^{(p)} = v^{(p)} N_{\text{sol}}$. The water number densities in pure water and solution are n_0 and n_w , respectively [$n_w = N_w/V = n_0(V - V^{(p)})/V$]. The number of water molecules excluded by one solute molecule is M , $M = v^{(p)} n_0$. Let us express N_w as

$$N_w = n_w V = n_0 \left[1 - \frac{V^{(p)}}{V} \right] V = M N_{\text{sol}} \left[1 - \frac{V^{(p)}}{V} \right] \frac{V}{V^{(p)}}. \quad (\text{D12})$$

The local number density of water molecules in solution, $n_w(\mathbf{r}, t)$, is defined like in Eq. (S16),

$$n_w(\mathbf{r}, t) = n_0 - \int n_{\text{sol}}(\mathbf{r}', t) n_w^{(p)}(\mathbf{r} - \mathbf{r}', t) d\mathbf{r}', \quad (\text{D13})$$

where $n_w^{(p)}(\mathbf{r}, t)$ is equal to n_0 if \mathbf{r} lies within the excluded volume and zero otherwise. According to Eq. (D13), $n_w(\mathbf{r}, t)$

is zero inside the excluded volume. The water–water pair correlation function, $G_w(\mathbf{r}, t)$, is

$$G_w(\mathbf{r}, t) = \frac{1}{N_w} \int n_w(\mathbf{r}') n_w(\mathbf{r}' + \mathbf{r}, t) d\mathbf{r}'. \quad (\text{D14})$$

The substitution of Eq. (D13) into Eq. (D14) yields

$$G_w(\mathbf{r}, t) = n_0^2/n_w + \left[2n_0 \left(1 - \frac{n_0}{n_w} \right) \right] + \frac{M N_{\text{sol}}}{N_w} \int G_{\text{sol}}^{\text{self}(p)}(\mathbf{u}, t) G_{\text{sol}}^{\text{self}}(\mathbf{r} - \mathbf{u}, t) d\mathbf{u} + \int G_{\text{sol}}^{\text{dist}(p)}(\mathbf{u}, t) G_{\text{sol}}^{\text{dist}}(\mathbf{r} - \mathbf{u}, t) d\mathbf{u}. \quad (\text{D15})$$

The functions $G_{\text{sol}}^{\text{self}(p)}(\mathbf{u}, t)$ and $G_{\text{sol}}^{\text{dist}(p)}(\mathbf{u}, t)$ are defined as in Eqs. (D9) and (D10), but they describe the time-dependent correlations between the infinitesimal volume elements of the excluded volumes (i.e., between the CMs of water molecules, if the excluded volumes were filled with water). It follows [see Eq. (D12)]

$$G_w(\mathbf{r}, t) = \frac{n_0^2}{n_w} \left[1 - \frac{2V^{(p)}}{V} + \frac{v^{(p)} n_{\text{sol}}}{n_0} \times \int G_{\text{sol}}^{\text{self}(p)}(\mathbf{u}, t) G_{\text{sol}}^{\text{self}}(\mathbf{r} - \mathbf{u}, t) d\mathbf{u} + \frac{v^{(p)} n_{\text{sol}}}{n_0} \int G_{\text{sol}}^{\text{dist}(p)}(\mathbf{u}, t) G_{\text{sol}}^{\text{dist}}(\mathbf{r} - \mathbf{u}, t) d\mathbf{u} \right]. \quad (\text{D16})$$

The solute–water time-dependent pair correlation function, $G_{\text{sol-w}}(\mathbf{r}, t)$, is

$$G_{\text{sol-w}}(\mathbf{r}, t) = \frac{1}{N_{\text{sol}}} \int n_{\text{sol}}(\mathbf{r}') n_w(\mathbf{r} + \mathbf{r}', t) d\mathbf{r}', \quad (\text{D17})$$

where $n_{\text{sol}}(\mathbf{r}, t)$ is the local time-dependent number density of the CM's of solute molecules. Putting Eq. (D13) into Eq. (D17) and substituting $\mathbf{u} = \mathbf{r} + \mathbf{r}' - \mathbf{r}''$, yields

$$G_{\text{sol-w}}(\mathbf{r}, t) = n_0 - \frac{1}{N_{\text{sol}}} \int d\mathbf{u} \langle n_w^{(p)}(\mathbf{u}, t) \rangle_{\Omega} \times \int d\mathbf{r}'' n_{\text{sol}}(\mathbf{r}'', t) n_{\text{sol}}(\mathbf{u} - \mathbf{r} + \mathbf{r}''). \quad (\text{D18})$$

It follows from Eq. (D2),

$$G_{\text{sol-w}}(\mathbf{r}, t) = n_0 - \int \langle n_w^{(p)}(\mathbf{u}, t) \rangle_{\Omega} G_{\text{sol}}(\mathbf{r} - \mathbf{u}, t) d\mathbf{u}. \quad (\text{D19})$$

3. Water–water and solute–water intermediate scattering functions in the UFA

Applying the convolution theorem of Fourier transformation to $G_w(\mathbf{r}, t)$ given by Eq. (D16) and to $G_{\text{sol-w}}(\mathbf{r}, t)$ given by Eq. (D19), after averaging over \mathbf{Q} -orientations, we get the corresponding intermediate scattering functions, $I_{\text{tr w}}^{\text{coh}}(\mathbf{Q}, t)$ and $I_{\text{tr sol-w}}(\mathbf{Q}, t)$, respectively. Specifically, $I_{\text{tr w}}^{\text{coh}}(\mathbf{Q}, t)$ is [omitting the term containing $\delta(\mathbf{Q})$],

$$I_{\text{tr w}}^{\text{coh}}(\mathbf{Q}, t) = \frac{n_{\text{sol}}}{n_w} [A^{0(p)}(\mathbf{Q}) I_{\text{tr sol}}^{\text{dist}}(\mathbf{Q}, t) + \xi^{(p)}(\mathbf{Q}, t) I_{\text{tr sol}}^{\text{self}}(\mathbf{Q}, t)]. \quad (\text{D20})$$

Apart from the factor n_{sol}/n_w , Eq. (D20) is the same as Eq. (6) in Sears's paper on the scattering by molecules in liquids¹³ [except that coherent scattering lengths and cross sections will not appear in the formulas for $A^{(p)}(Q)$]. Indeed, the time-dependent spatial correlations between the nuclei in a reorienting polyatomic molecule are analogous to the correlations between the infinitesimal volume elements in the volume excluded by a reorienting solute molecule. The model of continuous rotational diffusion yields $\xi^{(p)}(Q, t)$,¹³

$$\xi^{(p)}(Q, t) = \sum_{l=0}^{\infty} (2l+1) A^{(p)}(Q) e^{-l(l+1)D_r \text{sol} t} \quad (\text{D21})$$

and the coefficients $A^{(p)}(Q)$ are [see Eq. (A4) for notations]

$$A^{(p)}(Q) = \int \int j_l(Qr_1) j_l(Qr_2) P_l(\cos \theta_{12}) n_w^{(p)}(\mathbf{r}_1) \times n_w^{(p)}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (\text{D22})$$

where $n_w^{(p)}(\mathbf{r})$ is equal to the pure water number density (n_0) if \mathbf{r} lies inside the excluded volume and zero otherwise.

$I_{\text{tr sol-w}}(Q, t)$ is [omitting the term containing $\delta(Q)$],

$$I_{\text{tr sol-w}}(Q, t) = -N^{(p)}(Q) I_{\text{tr sol}}^{\text{coh}}(Q, t), \quad (\text{D23})$$

where $N^{(p)}(Q)$ is

$$N^{(p)}(Q) = \int \frac{\sin(Qr)}{Qr} n_w^{(p)}(\mathbf{r}) d\mathbf{r}. \quad (\text{D24})$$

From Eq. (D20) and Eq. (D23) the scattering functions given by Eqs. (10a)–(10c) and Eq. (11), respectively, are obtained by Fourier transformation.

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