Neutron scattering in molecular liquids:
Influence of orientational degrees of freedom and the prepeak in a fragile glass former

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The intermediate scattering function $S_n(q,t)$ for neutron-scattering is expanded with respect to a complete set of correlation functions which describe the dynamical correlations in a molecular liquid. For the static $n$–structure factor $S_n(q)$ of a system of diatomic molecules the results of the expansion are compared with the exact results from a MD–simulation and it is shown that the Sears–expansion, which is commonly used to interpret such data, fails in the supercooled regime. The representation for $S_n(q)$ is used to draw conclusions about the $q$–dependence and especially the origin of the prepeak.

PACS numbers: 61.12.-q, 61.20.-p, 61.25.Em

Neutron scattering is one of the most important tools to determine the structure and dynamics of condensed matter. For instance, it has been applied widely in the study of supercooled liquids and the glass–transition, (see e.g. ref. and for more recent work ) where it has been of great value to test theories such as the mode–coupling–theory (see e.g. ). One of the major advantages of neutron scattering is that the neutron as an electrically neutral probe is not influenced by the electron cloud of the target atoms but interacts only with the nucleus. Consequently neutron scattering can be directly interpreted in terms of the atomic motion. However, if one wants to examine a molecular system not only with respect to the motion of the constituent atoms but in terms of the molecular units some care has to be taken. Since the superposition of scattering from atomic sites is in general not equivalent to scattering from the molecular center of mass, neutron scattering from molecular liquids is sensitive to orientational as well as translational correlations in the system. Attempts to account for this fact in the analysis of $ns$–data include the expansion into “partial waves” proposed by Sears . Originally conceived for liquids with negligible correlations between rotational and translational motion it was shown recently to describe well the incoherent scattering in supercooled water . The expansion proposed in the present Letter is closely related to that of Sears but does not make any assumptions on the strength of the coupling between rotation and translation. As a consequence it is able to describe well also the coherent scattering in the supercooled regime. In addition it offers interesting new aspects for the interpretation of the $q$–dependence of the static $ns$–structurefactor $S_n(q)$.

A feature of special interest in supercooled liquids and glasses is the appearance of a prepeak in the static $ns$–structure factor at a $q$–value that corresponds to distances larger than the average nearest–neighbour distance. As a sign of intermediate range order prepeaks have been studied in a variety of systems (see e.g. ). Mostly they have been attributed to the network structure of strong liquids but as our present analysis of a system of rigid diatomic molecules shows prepeaks can appear even in the most simple molecular systems.

We consider a set of $N$ rigid molecules of identical geometry each consisting of $s$ atoms. The assumption of rigidity is one that is commonly used as well in the theoretical analysis as in computer simulations of the liquid state. It is justified on the ground that at the temperature of the liquid only the lowest vibrational states are populated. The starting point of our analysis is the following site–site representation of the intermediate scattering function (cf. )

$$S_n(q,t) = \frac{1}{N s} \sum_{j,j'} \sum_{\nu,\nu'=1}^s \sum_{l_1 l_2} \times$$

$$\times \left( a_{\nu}^{j'} a_{\nu}^{j} + a_{\nu}^{inc} \delta_{jj'} \delta_{\nu\nu'} \right) \left< e^{i q \cdot (R_{\nu}(t) - R_{\nu}(t'))} \right>$$

where $a_{\nu}^{j}$ ($a_{\nu}^{inc}$) is the coherent (incoherent) scattering length and $R_{\nu}(t)$ the position at time $t$ of atom $\nu$ in molecule $j$. The brackets $\langle \cdots \rangle$ denote the canonical average over initial conditions. Unlike the geometry which is identical for all molecules the scattering lengths are allowed to differ from molecule to molecule. This assumption is quite realistic since the chemical structure is independent of the isotopic composition whereas the scattering lengths are. The translational and orientational motion are separated by introducing center of mass $R_j(t)$ and relative coordinates $r_{\nu}(t)$, i.e. $R_{\nu}(t) = R_j(t) + r_{\nu}(t)$. Analogously to Sears we use the Rayleigh-expansion of the plane waves

$$e^{i q \cdot r_{\nu}(t)} = \sum_{l_1} [4 \pi (2l + 1)]^{1/2} l^l \times$$

$$\times j_l (qr_{\nu}) Y^m_l (\theta_{\nu}, \phi_{\nu}) D_{l_1}^{l_1} (\Omega_j(t))$$

to express the relative coordinates $r_{\nu}(t)$ by the polar coordinates $(r_{\nu}, \theta_{\nu}, \phi_{\nu})$ of atom $\nu$ with respect to a body fixed frame with origin at the center of mass of molecule $j$ and by the Euler–angles $\Omega_j(t)$ denoting the orientation of the body–fixed system with respect to the laboratory frame.
Without loss of generality the $z$-axis of the laboratory system has been chosen to point in direction of $\mathbf{q}$. The special functions appearing in eq. (3) are the spherical Bessel functions $j_l$, the spherical harmonics $Y^m_l$, and the Wigner functions $D^m_{ll'}$. Conventions are chosen according to the textbook of Gray and Gubbins [13]. The range of indices is $l, l' = 0, 1, 2, \ldots$; $-l \leq m, n \leq l$; $-l' \leq m', n' \leq l'$. Thus we establish a connection between the intermediate scattering function $S_n(q,t)$ of neutron scattering and the set of functions

$$\begin{align*}
S^{n}_{l,n',n'}(q,t) &= \frac{i^{l'-l}}{(2l+1)(2l'+1)} [2l+1] \frac{1}{N} \sum_{j,j'} \times \text{ (3)} \\
&\times \left\{ e^{-i(qR'_{j}(t)-R'_{j'}(t))} D^{l}_{mn}(\Omega_{j}(t)) D^{l'}_{m'n'}(\Omega_{j'}(t)) \right\}
\end{align*}$$

which can be split up into self ($j = j'$) and distinct part ($j \neq j'$) giving

$$S^{m}_{l,n',n'}(q,t) = S^{m(s)}_{l,n',n'}(q,t) + S^{m(d)}_{l,n',n'}(q,t). \quad \text{(4)}$$

This set of correlation functions is the generalization to arbitrary molecules of the correlators recently introduced for a single linear molecule in an isotropic liquid [13] and for molecular liquids of linear molecules [14]. Similar correlation functions have been used previously in the study of molecular liquids [12, 15]. The tensors (3) have a number of symmetry properties which are discussed in refs. [14, 15]. We just want to point out that $S^{0}_{0,0,0}(q,t)$ is the usual intermediate scattering function for the center of mass whereas $S^{m}_{l,n',n'}(q,t)$ for $l$ or $l'$ different from one reflect correlations between higher "multipoles" of the microscopic density.

Inserting eq. (3) into (1) one obtains with (3) the final result:

$$\begin{align*}
S_n(q,t) &= \sum_{l'} \sum_{n'} b^{inc}_{l',n'}(q,t) S^{0(s)}_{l',n'}(q,t) + S^{0(d)}_{l',n'}(q,t) \text{ (5)} \\
&\quad + b^{coh}_{l',n'}(q,t) S^{d(s)}_{l',n'}(q,t) + S^{d(d)}_{l',n'}(q,t)
\end{align*}$$

with the coefficients

$$\begin{align*}
b^{inc}_{l',n'}(q) &= -\frac{1}{4} \sum_{j,j'} 4 \pi j_l(q) j_{l'}(q) X_{l}^{m'}(\Omega_{j}') \times \text{ (6)} \\
Y^{m*}_{l}(\theta, \phi) Y^{m'}_{l'}(\theta', \phi) \left[ a_{coh}^{m} a_{coh}^{m'} + a_{inc}^{m} \delta_{m,m'} \right] \\
b^{coh}_{l',n'}(q) &= -\frac{1}{4} \sum_{j,j'} 4 \pi j_l(q) j_{l'}(q) X_{l}^{m'}(\Omega_{j}') \times \text{ (7)} \\
Y^{m*}_{l}(\theta, \phi) Y^{m'}_{l'}(\theta', \phi) a_{coh}^{m} a_{coh}^{m'}.
\end{align*}$$

Here $\tau = 1/N \sum_j x^j$ denotes the average over molecules. A similar result for diluted linear molecules in an isotropic liquid is given in ref. [13]. In contrast to the original approach by Sears we will not invoke factorization of correlations between (i) all translational and rotational motion and (ii) the orientational degrees of freedom of different molecules. This assumption which is quite common in the analysis of neutron as well as light-scattering turns out to be not quite satisfactory in the supercooled regime as we will demonstrate in the following. The expansion (3) has a number of interesting properties. Immediately obvious is that eq. (3) can be Fourier-transformed to give a corresponding relation between the spectra or susceptibilities. Further, we notice that only correlators with $m = 0$ enter into $S_n(q,t)$ (which is a consequence of the isotropy of the fluid) and that the coefficients $b^{inc}_{l',n'}(q)$ are completely determined by the geometry of the molecule via $(r_{j}, \theta_{j}, \phi_{j})$ and averages of the scattering length of the constituent atoms. The dependence on the wavevector $q$ enters through the spherical Bessel functions $j_l(qr_{j})$ and is thus connected to the radii $r_{j}$ and the value of $l$. This connection between $q$ and $l$ will be very useful to justify the cutoff of the summations over $l$ in eq. (3) and to analyse the $s$-structure factor.

To demonstrate the quality of expansion (3) we consider the special case of diatomic rigid molecules. From a recent MD-simulation [17] we have taken the static molecular correlation functions according to eq. (3) and we have evaluated the exact result for the static $s$-structure factor using eq. (3). In that simulation a system of 500 molecules was considered each consisting of two atoms labeled A and B. The molecular interaction was represented as the superposition of Lennard–Jones potentials between the atoms. The molecular bond length was fixed at $d = 0.5$ in units of the Lennard–Jones radius of the A-atoms which we will use throughout this Letter. Further details about the simulation can be found in references [17]. Since for linear molecules the third Euler-angle $\chi$ doesn’t play a role the distinct parts of the molecular correlation functions are nonzero for $n = n' = 0$ only and the summations over $n, n'$ can be carried out for the self part. Therefore we will skip the indices $n, n'$ as well as the superscript $m = 0$ in the following. The static correlation functions $S_{ll'}(q)$ evaluated up to $l, l' \leq l_{coh} = 2$ are shown in Figure 1 for the lowest temperature of the simulation. For $l, l' \geq l_{coh}$ only the self part $S^{s(s)}_{ll'}(q) = \delta_{ll'}$
is considered in the following calculations. Specializing to linear diatomic molecules and the static case eqn. (8) simplify to:

\[ S_n(q) \cong \sum_{l,l' \leq l_{co}} b_{ll'}^{coh}(q) S_{ll'}(q) + b_{inc}(q) \]  

\[ b_{ll'}^{coh}(q) = [(2l + 1)(2l' + 1)]^{\frac{1}{2}} j_l(qd) j_{l'}(qd) \times \]

\[ \times \frac{1}{2} \left( a_{coh}^{A} + (-1)^{l} a_{coh}^{B} \right) \left( a_{coh}^{A} + (-1)^{l'} a_{coh}^{B} \right) \]

\[ b_{inc}(q) = \frac{1}{2} \left( a_{inc}^{A} + a_{inc}^{B} \right) \left( a_{inc}^{A} + a_{inc}^{B} \right) \]

The reader should notice that \( l_{co} = 0 \) just yields the usual Sears–expansion with the molecular structure factor \( b_{inc}(q) \) and the intermolecular form factor \( b_{coh}(q) \) for uncorrelated rotation. In Figure 2 we show the comparison between the exact \( S_n(q) \) and the expansion (8) for \( l_{co} = 0 \) (Sears), \( l_{co} = 1 \) and 2 at the lowest temperature of the simulation. The expansion for \( l_{co} = 2 \) is in perfect agreement with the exact \( S_n(q) \) up to \( q \approx 9 \) and in qualitative agreement up to almost \( q \approx 18 \) whereas the Sears–expansion shows hardly more than qualitative agreement up to \( q \approx 8 \). If the scattering length of A– and B–atoms are equal it follows from (9) that only even and \( l' \) contribute to \( S_n(q) \). Hence \( S_n(q) \) from (8) with \( l_{co} = 1 \) is identical to the Sears–result. If neutron–scattering can distinguish between A– and B–atoms the \( l_{co} = 1 \)–result is still not much better than the Sears–expansion (cf. Fig. 2) except for the prepeak at \( q \approx 3 \) which does not show up in the latter (see inset of Fig. 1 [2]). This failure of the Sears–expansion clearly shows that in the supercooled regime the assumption of uncorrelated rotation of different molecules does not hold. Upon increasing the temperature these correlations become weaker and we find that the contributions coming from \( S_{\ell \ell'}(q) \) with \( l, l' \) different from 0 get less important. Whereas usual ways to account for orientational correlations are restricted to assuming specific orientational models like in the analysis of Dore et al. [18] or to fitting the data under the assumption of a preferred orientation our approach is an exact expansion (provided \( l_{co} = \infty \)) that makes no ad hoc assumptions about orientational correlations. Of course the calculation of \( S_{\ell \ell', \ell' \ell} \) (can not be done exactly, but requires either approximation schemes [12,15] or simulational methods. In the case of the time–dependent correlators \( S_{\ell \ell', \ell' \ell} \) one may use the results following from the molecular mode coupling theory [1].

Comparing the \( \ell \)–dependence of the input–data in Figure 1 with that of \( S_n(q) \) reveals the origin of the different peaks in the ns–data. Whereas the position of the prepeak coincides with the first peak in \( S_{11}(q) \) the main peak has its origin in the center of mass correlations \( S_{00}(q) \) though it is slightly shifted to higher \( q \) due to the contributions from \( S_{22}(q) \) and \( S_{22}(q) \). The peaks at \( q \approx 13 \) and \( q \approx 18 \) are easily recognized as stemming mainly from the corresponding ones in the correlator \( S_{22}(q) \).

These obvious identifications are supported even more by a closer inspection of the coefficients \( b_{ll'}^{coh}(q) \) which will also explain why the structure in \( S_n(q) \) at \( q \geq 18 \) is missed by the cut–off we have chosen. As stated in the discussion of the general result (4) the \( q \)–dependence of \( b_{ll'}(q) \) is closely related to the values of \( l \) and \( l' \) through the Bessel functions \( j_{\frac{l+1}{2}}(q) \). These are oscillating functions that decay to zero for increasing argument [20]. Whereas \( j_{\frac{l+1}{2}}(x) \) has a maximum at \( x = 0 \) the functions \( j_{\frac{l+1}{2}}(x) \) with \( l \geq 1 \) start at zero and the position of the first maximum shifts to higher \( x \) with increasing \( l \). This property is inherited by the coefficients \( b_{ll'}^{coh}(q) \) and leads to the consequence that correlators with small \( l \) give a contribution at low \( q \) whereas big \( l \) determine the behaviour at high \( q \) (apart from the incoherent contribution from \( b_{inc}(q) \)). This is also the reason why the expansion with \( l_{co} = 2 \) works less good for \( q \geq 9 \) and particularly for \( q \geq 18 \) since higher values of \( l \) and \( l' \) would be needed. A quantitative analysis of the coefficients at the position \( q \approx 3 \) of the prepeak shows that about 80% of the prepeak amplitude originates from \( S_{11}(q) \). Therefore the appearance of the prepeak will depend sensitively on the ratio of the scattering lengths, as demonstrated in Figure 2.

In the final part of this Letter we want to analyse further the appearance of a prepeak in \( S_n(q) \) for diatomic LJ–molecules. As we have already pointed out in the discussion of the \( q \)–dependence of \( S_n(q) \) the prepeak is connected with the main maximum of the correlator \( S_{11}(q) \). The center of mass correlations show no structure at all at \( q \approx 3 \) which is a remarkable contrast to the situation encountered in supercooled water where the intermediate range order shows up as a prepeak in \( S_{00}(q) \) [21]. This indicates that different mechanisms are responsible for its existence in the present fragile glassformer and the network–former. Taking into account the shape of the spherical harmonic function \( Y_{\ell \ell}^{0} \propto D_{\ell \ell}^{0} \) one can conclude that \( S_{11}(q) \) can be viewed as the correlations between molecules with parallel orientation (of next nearest neighbours). Thus the connection of intermediate range order...
with \( S_{11}(q) \) is in good agreement with the findings of Misawa\(^{[11]} \) who proposed a staggered parallel orientation as the preferred orientation of nearest neighbours in liquid halogenes. In another paper Misawa\(^{[9]} \) showed that the existence of a preferred orientation can give rise to a prepeak depending on the ratio of interatomic spacing and bond length.

![Graph](image)

**FIG. 3.** Dependence of the prepeak amplitude on the ratio of coherent scattering lengths of A– and B–atoms.

In conclusion we can say that the proposed expansion for the intermediate scattering function of neutron-scattering offers a general way of describing orientational correlation effects. It indicates interesting connections between the \( q \)-dependence of \( S_n(q) \), the orientational correlations for different \( l \) and the molecular geometry which are useful in the interpretation of neutron-scattering results for molecular liquids. In particular, we have shown that orientational correlations play a crucial role in the supercooled regime. This is consistent with the recent results by Bermejo et al.\(^{[22]} \). These correlations are also responsible for the existence of a prepeak, whose intensity depends both on the scattering lengths and the temperature.

**Acknowledgement:** We thank E.Bartsch for pointing out some of the references given below and we are grateful for the financial support by SFB–262.

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