

Neutron scattering and molecular correlations in a supercooled liquid

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We show that the intermediate scattering function $S_n(q,t)$ for neutron scattering (ns) can be expanded naturally with respect to a set of molecular correlation functions that give a complete description of the translational and orientational two-point correlations in the liquid. The general properties of this expansion are discussed with special focus on the q dependence, and hints for a (partial) determination of the molecular correlation functions from neutron scattering results are given. The resulting representation of the static structure factor $S_n(q)$ is studied in detail for a model system using data from a molecular dynamics simulation of a supercooled liquid of rigid diatomic molecules. The comparison between the exact result for $S_n(q)$ and different approximations that result from a truncation of the series representation demonstrates its good convergence for the given model system. On the other hand it shows explicitly that the coupling between translational and orientational degrees of freedom of each molecule and rotational motion of different molecules cannot be neglected in the supercooled regime. Further we report the existence of a prepeak in the ns static structure factor of the examined fragile glass former, demonstrating that prepeaks can occur even in the most simple molecular liquids. Besides examining the dependence of the prepeak on the scattering length and the temperature we use the expansion of $S_n(q)$ into molecular correlation functions to point out the intermediate range orientational order as its principle origin. [S1063-651X(99)05407-0]

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I. INTRODUCTION

Neutron scattering is one of the most important tools to determine the structure and dynamics of condensed matter. One of its major advantages 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 structure and motion. However, if one wants to examine a molecular system not only with respect to 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.

This was realized many years ago [1–5], and led to different formulations of neutron scattering by molecules. For reasons of simplicity and also because the center of mass correlations were of principle interest, those approaches tried to “correct” for the effect of orientational degrees of freedom. In the work of Sears [4] this was done using the so-called *weak hindering approximation*, i.e., the assumption of the statistical independence of (i) the rotational and translational motion of any molecule, and (ii) the rotational motion of any two different molecules.

In recent years the mode coupling theory of the glass transition (see, e.g., Refs. [6–8]) stimulated many experiments on supercooled liquids. Among other techniques, neutron scattering was used (see, e.g., Ref. [9] and, for more recent work, Refs. [10,11]) to study the static and dynamic properties of glass forming substances, most of which are of molecular nature, like, e.g., glycerol, salol, or orthoterphenyl. In the situation of the dense packed molecular liquid where the motion becomes more and more cooperative, the assumptions of Sears are no longer reasonable, as shown by Chen

et al. [12] for incoherent neutron scattering in simulated supercooled water. Below, in a study of a liquid of diatomic rigid molecules, we will come to the same conclusion for coherent scattering. This raises the question of how neutron scattering data can be analyzed in terms of molecules in this case.

With increasing computer power the simulations of supercooled liquids tend to deal with more realistic model systems [13] like SPC/E water [14] or orthoterphenyl [15]. Thus it has also become feasible to examine in detail the orientational degrees of freedom in the strongly supercooled regime (see, e.g., Refs. [16,17]). In experiments, up to now it has only been possible to measure orientational correlators for $q=0$, i.e., one cannot obtain information about the spatial arrangement of orientationally correlated molecules. On the other hand, this information would be valuable to understand the interaction between translational and orientational degrees of freedom. Therefore, it seems sensible to examine in which way orientational correlations enter into the neutron scattering function.

A feature of special interest in supercooled liquids and glasses is the appearance of a prepeak in the static neutron scattering (ns) structure factor at a q value that corresponds to distances larger than the average nearest neighbor distance. As a sign of intermediate range order, prepeaks have been studied in a variety of systems (see, e.g., Refs. [19–21] and references therein). Mostly these have been attributed to the network structure of strong glasses or charge effects in ionic glass formers. The behavior of prepeaks in molecular systems seems to be quite different, as pointed out recently by Morineau *et al.* [22] in their study of temperature and pressure dependence for *m*-toluidine and *m*-fluoroaniline, which will be discussed in Sec. III C.

We will present results for the ns static structure factor of a liquid of diatomic molecules, i.e., one of the most simple systems in which effects of the molecular nature can be stud-

ied. We will discuss the dependence of the prepeak on temperature and scattering length, and make a comparison to findings for other systems. Using the representation of $S_n(q)$ in terms of the molecular correlation functions, we will also give strong evidence that the existence of the peak is closely connected to orientational degrees of freedom.

The paper is organized as follows. In Sec. II we will briefly summarize the approach of Sears to the intermediate scattering function $S_n(q,t)$ for molecular systems. We will show that dropping the weak hindering approximation leads naturally to a description in terms of molecular correlation functions. Some aspects of the representation for arbitrary molecules are discussed, and hints for an application to experiments are given. Section III presents the results from the molecular dynamics simulation of a system of diatomic molecules. It is divided into three subsections concerning the

molecular correlation functions, the ns static structure factor, and a detailed discussion of the prepeak, respectively. Section IV gives some conclusions.

II. NEUTRON SCATTERING FUNCTION

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 simulation of the liquid state. It is justified on the grounds that at the temperature of the liquid only the lowest vibrational states are populated. The starting point of an analysis of neutron scattering from molecules is the following site-site representation of the intermediate scattering function (see, e.g., Refs. [4,23]):

$$S_n(q,t) = \frac{1}{Ns} \sum_{j,j'=1}^N \sum_{\nu,\nu'=1}^s (a_{\text{coh}}^{j\nu} a_{\text{coh}}^{j'\nu'} + (a_{\text{inc}}^{j\nu})^2 \delta_{jj'} \delta_{\nu\nu'}) \langle e^{i\vec{q} \cdot (\vec{R}_{j\nu}(t) - \vec{R}_{j'\nu'})} \rangle, \quad (1)$$

where $a_{\text{coh}}^{j\nu}$ ($a_{\text{inc}}^{j\nu}$) is the coherent (incoherent) scattering length, and $\vec{R}_{j\nu}(t)$ the position of atom ν in molecule j at time t . The brackets $\langle \dots \rangle$ denote canonical averaging over initial conditions. Unlike the geometry which is supposed to be 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.

Appealing as this site-site description is, it is not very favorable from a molecular view. The rigid molecules are most suitably described by the center of mass coordinates $\vec{R}_j(t)$ and the Euler angles $\Omega_j(t) = (\phi_j(t), \theta_j(t), \chi_j(t))$ giving the orientation of the body fixed system relative to the laboratory frame.

To make a connection between these two different views, Sears [4] introduced center of mass and relative coordinates by $\vec{R}_{j\nu} = \vec{R}_j + \vec{r}_{j\nu}$ and used the Rayleigh expansion of the plane waves

$$e^{i\vec{q} \cdot \vec{r}_{j\nu}(t)} = \sum_{ln} [4\pi(2l+1)]^{1/2} i^l j_l(qr_\nu) Y_l^n(\vartheta_\nu, \varphi_\nu) \mathcal{D}_{0n}^l(\Omega_j(t)), \quad (2)$$

where $(r_\nu, \vartheta_\nu, \varphi_\nu)$ are the polar coordinates of atom ν with respect to the body fixed frame with origin at the center of mass of molecule j . Without loss of generality the z axis of the laboratory frame has been chosen to point in direction of \vec{q} . The special functions appearing in Eq. (2) are the spherical Bessel functions j_l , the spherical harmonics Y_l^n , and the Wigner functions \mathcal{D}_{mn}^l [24,25]. In the summation of Eq. (2) l runs over $0, 1, 2, \dots$, and n is restricted by $-l \leq n \leq l$.

Following this strategy and *not* doing any factorization of translational and rotational motion or of rotational motion of different molecules, one is naturally led to consider correlation functions of the following kind:

$$S_{ln,l'n'}^m(q,t) = i^{l'-l} [(2l+1)(2l'+1)]^{1/2} \frac{1}{N} \sum_{jj'} \langle e^{-iq(R_j^z(t) - R_{j'}^z)} \mathcal{D}_{mn}^l(\Omega_j(t)) \mathcal{D}_{mn'}^{l'*}(\Omega_{j'}) \rangle, \quad (3)$$

which equal $(1/N) \langle \rho_{lmn}^*(q,t) \rho_{l'mn'}(q,0) \rangle$, the correlation function of the tensorial one particle density mode $\rho_{lmn}(q,t)$ [26]. As usual, it is possible to separate them into self ($j = j'$) and distinct terms ($j \neq j'$) giving

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

This set of correlation functions is the generalization to arbitrary molecules of the correlators introduced in mode

coupling theory for a single molecule in an atomic liquid [27] and for liquids of linear molecules [26], and has been used recently to study molecular correlations in supercooled water [28] and diatomic molecules [16]. Similar correlation functions have also been used earlier in the study of molecular liquids [23,25], and go back to the work on statistical mechanics of nonspherical molecules by Steele [29].

At first sight one might be frightened by the large number of indices, and not willing to consider an infinite set of correlation functions. Therefore, we want to stress that due to

the tensorial nature of quantities (3) the symmetry of the molecule may reduce the number of correlators. Second, one can expect that reasonable results can be achieved if one considers only the finite number of correlators with $l, l' \leq l_{\text{co}}$ for small l_{co} . For a system of diatomic molecules, we will see in Sec. III that $l_{\text{co}}=4$ turns out to be sufficient to describe $S_n(q)$ in the q range of interest. Depending on the size and form of the molecules, it might also be necessary to consider larger values for l_{co} . This becomes clear if one looks at the angular dependence of the Wigner functions, since extending the range of l corresponds mainly to improv-

ing the angular resolution. In this argument we have considered the factors $\mathcal{D}_{mn}^l(\Omega)$ in Eq. (3) as ‘‘weights’’ which select molecules within a certain range of orientations for the canonical averaging. While, for instance, $\mathcal{D}_{00}^0(\Omega) \equiv 1$ gives equal weight to all orientations, $\mathcal{D}_{00}^1(\Omega) \propto Y_1^0(\theta, \phi)$ puts emphasis on molecules with $\theta \approx 0$ or $\theta \approx \pi$. This may elucidate a bit more the meaning of the q -dependent orientational correlators.

Having introduced the suitable correlation functions Eqs. (1)–(3) can be easily combined to give

$$S_n(q, t) = \sum_{l'} \sum_{n'} [b_{ln, l'n'}^{\text{inc}}(q) S_{ln, l'n'}^{(s)0}(q, t) + b_{ln, l'n'}^{\text{coh}}(q) S_{ln, l'n'}^{(d)0}(q, t)], \quad (5)$$

with the coefficients

$$b_{ln, l'n'}^{\text{inc}}(q) = \frac{1}{s} \sum_{\nu\nu'} 4\pi j_l(qr_\nu) j_{l'}(qr_{\nu'}) Y_l^{n*}(\vartheta_\nu, \varphi_\nu) Y_{l'}^{n'}(\vartheta_{\nu'}, \varphi_{\nu'}) [\overline{a_{\text{coh}}^\nu a_{\text{coh}}^{\nu'}} + \overline{(a_{\text{inc}}^\nu)^2} \delta_{\nu\nu'}], \quad (6)$$

$$b_{ln, l'n'}^{\text{coh}}(q) = \frac{1}{s} \sum_{\nu\nu'} 4\pi j_l(qr_\nu) j_{l'}(qr_{\nu'}) Y_l^{n*}(\vartheta_\nu, \varphi_\nu) Y_{l'}^{n'}(\vartheta_{\nu'}, \varphi_{\nu'}) \overline{a_{\text{coh}}^\nu a_{\text{coh}}^{\nu'}}. \quad (7)$$

Here $\bar{x} = 1/N \sum_j x^j$ denotes the average over molecules. For the special case of a single linear molecule in an isotropic liquid, a similar result was given by Franosch *et al.* [27].

The representation [Eq. (5)] has a number of interesting properties. Immediately obvious is that it can be Fourier transformed to give a corresponding relation for the spectra or susceptibilities with the same coefficients. 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. From the general expression one can also draw some conclusions about the q dependence of the ns intermediate scattering function. Equation (5) clearly reflects that neutron scattering from molecular liquids is the superposition of two contributions: (i) the correlations within a molecule which are expressed in the incoherent terms involving the self-part of the molecular correlation functions, and (ii) the correlation between molecules which enter the distinct terms. The q dependence of both contributions again has two sources. The coefficients $b_{ln, l'n'}^{\text{inc}}(q)$ and $b_{ln, l'n'}^{\text{coh}}(q)$, which could be termed the *incoherent* and *coherent molecular form factors*, respectively, are completely determined by the molecular geometry and the scattering lengths. Thus they can be calculated exactly if the molecular units are known. Their q dependence is given by the spherical Bessel functions $j_l(qr_\nu)$, and thus connected primarily to the distances r_ν of the atoms from the center of mass of the molecule. We will discuss the q dependence of the molecular form factors in more detail in Sec. III. The more important quantities that enter into the q dependence of $S_n(q, t)$ are of course the molecular correlation functions which give a statistical description of the interactions and the dynamic of the system. We will discuss their q dependence for the above-mentioned model system in Sec. III A.

The coefficients $b_{ln, l'n'}^{\text{coh}}(q)$ and $b_{ln, l'n'}^{\text{inc}}(q)$ represent weighting functions that determine at which q values a given molecular correlation function $S_{ln, l'n'}^0(q, t)$ appreciably contributes to $S_n(q, t)$. In turn, knowledge of the molecular form factors could be used to attribute the structure of the ns intermediate scattering function to some molecular correlation functions. To undertake such an effort one would have to do a series of experiments in which the molecular form factors $b_{ln, l'n'}^{\text{coh}}(q)$ and $b_{ln, l'n'}^{\text{inc}}(q)$ are varied systematically. A common technique to do so would be the use of isotopes of different scattering length, i.e., to combine results obtained with mixtures of different isotopic composition. From the discussion of Eq. (5) given above, we can conclude the following limitations: (i) only molecular correlation functions $S_{ln, l'n'}^0(q, t)$ with $m=0$ are accessible, and (ii) information about the correlator $S_{ln, l'n'}^0(q, t)$ can only be extracted from $S_n(q, t)$ in a q range where the form factor $b_{ln, l'n'}(q)$ is different from zero and not too small compared to the other form factors. Upon changing the scattering lengths one can separate the site-site correlation functions contributing to $S_n(q, t)$. Since these are connected by a linear relation with the functions $S_{ln, l'n'}(q)$ [as a special case of Eqs. (5)–(7)] we also have that (iii) the number of molecular correlation functions that can be determined (for a given q) is restricted by the number of site-site correlators.

Since the molecular form factors depend also on the atomic configuration within the molecule another idea would be to compare results for molecules with similar geometry. To examine the structure of a liquid of diatomic molecules one could for example try to combine results for F_2 , Cl_2 , Br_2 , and I_2 , taking into account the shift in the average nearest neighbor distance due to the difference in

atomic size by rescaling the q values accordingly. In such a way one could change systematically the intramolecular distance d . Although this would offer a way to bypass the limitations given by (iii), changing the geometry will also affect the molecular correlation functions themselves.

In spite of this limitation we think that experimental efforts in the direction of determining molecular correlation functions from neutron scattering are worth considering. Here one has to keep in mind that up to now information about the orientational degrees of freedom is restricted to the few $q=0$ correlation functions that can be measured by dielectric response or NMR. Especially to understand the interaction between rotational and translational degrees of freedom, the q -dependent molecular correlation functions have to be considered.

III. RESULTS

We will now turn to an examination of a special system. On the one hand, this will give us the opportunity to illustrate the molecular correlation functions and the representation of the scattering function introduced in Sec. II. On the other hand, the system shows interesting features which are apparent in the ns static structure factor $S_n(q)$, and give on their own a motivation for a detailed inspection.

We will study a simulated supercooled liquid of 500 diatomic rigid molecules each consisting of two atoms which will be labeled A and B . The atoms have equal masses but the head-tail symmetry is slightly broken by the interactions which are given by a superposition of Lennard-Jones potentials between the atomic sites. 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 paper. Particularly, q is given in units of 2π times the inverse of that radius. For further details about the molecular dynamics simulation and the potential we refer the reader to Ref. [16].

In the following we will concentrate on the static properties of the system. This is done for a number of reasons: (i) To test the convergence of the series representation (5) as function of the l cutoff, it is sensible to consider the worst case. Usually this should be given by the static case as the following argument explains. If one assumes that the relaxation of the orientational degrees of freedom (ODOF) takes place primarily through small angular variations, and that large angular jumps can be neglected the correlators with larger l , i.e., better angular resolution, will decay faster than those with small l . Therefore, one concludes that for $t>0$ terms with larger l are less important than in the static case. (ii) We are primarily interested in the q dependence. Thus it will be necessary to choose a fixed time t and $t=0$ being a natural choice. Readers interested in the dynamics of the studied system, and especially experimentors who are interested in the time scales involved, are referred to the publications of Ref. [16] where these aspects were discussed for translational degrees of freedom (TDOF's) as well as ODOF's.

A. Molecular correlation functions

We will now present molecular correlation functions for the system of diatomic rigid molecules. As already mentioned in Sec. II the number of independent correlators can

be reduced for molecules possessing an intrinsic symmetry. In our case we deal with linear molecules that are invariant under any rotation around the axis connecting atoms A and B . This axis will be chosen as the z axis of the body fixed frame of reference in the following.

Symmetry considerations similar to those carried out in Ref. [28] show that the distinct part of the static correlation functions fulfills

$$S_{ln,l'n'}^{(d)m}(q) = \begin{cases} S_{ll'}^{(d)m}(q) & n=n'=0 \\ 0 & \text{otherwise.} \end{cases} \quad (8)$$

Since the self-part of the static correlation is given simply by $S_{ln,l'n'}^{(s)m}(q) = \delta_{ll'} \delta_{nn'}$, all the important structure is contained in the correlation functions with $n=n'=0$. As pointed out in Sec. II, for neutron scattering only correlators with $m=0$ are relevant. Thus in the following we will only consider the quantities $S_{ll'}(q) \equiv S_{l0,l'0}^0(q)$. We can further restrict ourselves to $l \leq l'$ since the correlation functions $S_{ll'}(q)$ are real and symmetric with respect to l and l' , as can be easily seen from their definition [Eq. (3)].

The correlation functions up to $l, l' \leq l_{co} = 2$ were already presented in Ref. [16]. We want to take the opportunity to point out a minor error in this publication: In order to obtain the correct data which are in accordance with the chosen conventions (ours and theirs) the off-diagonal terms given in Fig. 3 of the second of Refs. [16] have to be multiplied by -1 . The correct graphs for the $m=0$ terms are given in Fig. 1(b).

In addition we have determined all correlators up to $l, l' \leq l_{co} = 4$. Figures 1(c)–1(e) show the $m=0$ terms which are relevant for neutron scattering. In the discussion given below we will only refer to this data although the properties of the $m \neq 0$ terms (not shown here) are quite similar.

All the molecular correlation functions have been evaluated at $T=0.477$ (in units of the Lennard-Jones energy ϵ_{AA} of the A particles), which is the lowest temperature considered in the simulation. This is a temperature located in the supercooled regime very close to the critical temperature $T_c=0.475$ of the mode coupling theory [16].

We will now give a discussion of the molecular correlators $S_{ll'}(q)$ by comparing their q dependences. Thereby we want to point out the similarities and differences between the q -dependent orientational correlators (l and/or l' different from zero) and the better known center of mass correlations ($l=l'=0$). We also mention some features for which a general relation between the q dependence and the values of l and l' seems to exist. Thereby we will substantially enlarge the discussion given in Ref. [16] which focused mainly on the m -dependence and the effects of the approximate head-tail symmetry of the molecule.

The most prominent peak is displayed by the center of mass correlator $S_{00}(q)$. Located at a q value of $q_{\max} \approx 6.6$ it represents the first order of the nearest neighbor peak. Such a peak can also be found at almost exactly the same position for all correlation functions $S_{0l'}(q)$ with $l=0$. Also for the other correlators this nearest neighbor peak exists, but it is usually shifted to a slightly different value than q_{\max} . This shift can easily be understood. Whereas for $S_{00}(q)$ an average over all possible orientations of the molecule is per-

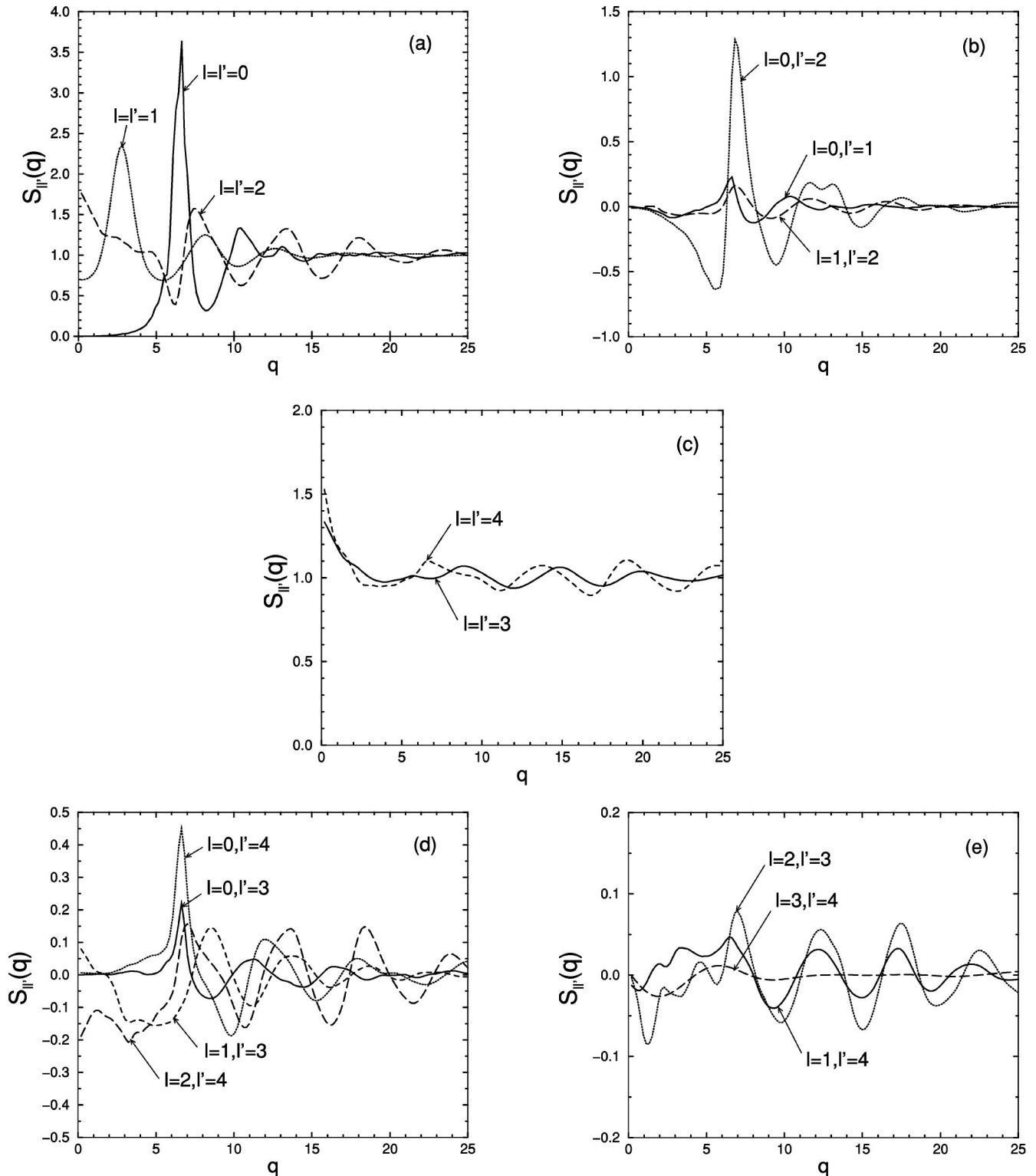


FIG. 1. Molecular static structure factors $S_{ll'}(q)$ for a system of diatomic rigid molecules at the lowest temperature $T=0.477$ of the simulation.

formed, the factor $\mathcal{D}'_{00}(\Omega_j)\mathcal{D}'_{00}(\Omega_{j'})$ in Eq. (3) for l and/or l' unequal to zero “restricts” the average to a certain range of orientations. Since in the supercooled liquid the molecules are very closely packed, the characteristic distance between molecules depends on the choice of orientations Ω_j and $\Omega_{j'}$ simply because of steric hindrance. Thus for different correlators a shift in the position of the peaks is expected. A

strong support for this picture is also that the peak is much less shifted for $S_{0l'}(q)$ as for $S_{ll'}(q)$ with l and l' unequal to zero because an average over all possible *relative* orientations is already done if *one* of the angles Ω_j or $\Omega_{j'}$ is not restricted.

Besides the shift in the peak position, we observe that the peak amplitude also depends strongly on the correlator. One

reason for this, already pointed out in Ref. [16], is the approximate head-tail symmetry of the molecule which results in a smaller amplitude for correlators with $l+l'$ odd. Further we can state that the amplitude of the main peak tends to decrease with increasing l and l' .

Apart from the main maximum the center of mass correlation function $S_{00}(q)$ also shows structure at higher values of q . Clearly perceptible is a double peak at $q \approx 10.5$ and 13.2 . Whereas the peak at $q \approx 13.2$ can be identified as the second order of the nearest neighbor peak the origin of the peak at $q \approx 10.5$ is not quite clear. It could also be the second order of a peak located around $q \approx 5.25$ which is merged with the main peak.

A rich structure at higher values of q is also found in all other molecular correlation functions. If one takes into account possible shifts in the peak position the peaks located at $q \approx 12-14$, $q \approx 16-19$, and $q \approx 23-25$ can be attributed to the higher orders of the nearest neighbor peak. While their principal origin thus seems to be clear, the interesting structure that appears in their shape, which in some cases clearly indicates a double peak, cannot be understood from the present investigation. A further aspect which immediately strikes the eye is that, while the oscillations at higher q are strongly damped for small l and l' , the higher order peaks are comparable to or even larger than the first maximum for the correlators with $l, l' \in \{2, 3, 4\}$.

So far we have considered only the structure of the molecular correlation functions for q values larger than the value of the first maximum corresponding to distances smaller than the average nearest neighbor distance. The center of mass correlator $S_{00}(q)$ for $q \leq 6.6$ resembles the structure also found for simple liquids, which is in strong contrast to the behavior of the molecular correlation functions for $l, l' \neq 0$. The correlator $S_{11}(q)$ exhibits a pronounced maximum at $q \approx 2.8$, a q value corresponding to about twice the average nearest neighbor distance.

A further point worth mentioning is that all diagonal correlators $S_{ll}(q)$ with $l \geq 2$ show a maximum at $q=0$ as was

already found for $S_{22}(q)$ in Ref. [16]. This might indicate a tendency for a *local* nematic order.

To conclude this section we want to point out that a comparison of our findings with an analysis of the system in real space would be very valuable for a better understanding of the molecular correlation functions. It would be especially interesting to connect the shifts in peak positions, the relation between the peak amplitudes of different correlators, and the peak shapes to a microscopic characterization of the system in real space.

B. Neutron scattering function

As mentioned above, the results of Sec. II are best tested for the static case. The molecular correlation functions necessary for an evaluation of the series representation Eq. (5) were presented in Sec. III A for $l, l' \leq l_{\text{co}}=4$. The result of these calculations will be compared to the exact data for neutron scattering as determined according to Eq. (1).

Since we are dealing with the special case of linear molecules and static correlations, Eqs. (5)–(7) can be further simplified. As justified in Sec. III A the indices n and n' can be set to 0 for the coherent terms if the z axis of the body-fixed frame of reference is chosen in direction of the symmetry axis connecting both atoms of the molecule. The polar coordinates of the atoms A and B are given by $(r_A, \vartheta_A, \varphi_A) = (d/2, 0, 0)$ and $(r_B, \vartheta_B, \varphi_B) = (d/2, \pi, 0)$, respectively. This information can be inserted into Eq. (7) for the coherent molecular form factors. Taking into account the trivial expression $S_{ln, l'n'}^{(s)0}(q) = \delta_{ll'} \delta_{nn'}$ for the static self-correlations, and using sum rules for the spherical harmonics and spherical Bessel functions [24], all summations over the incoherent terms can be carried out leaving only one q -dependent function $b^{\text{inc}}(q)$, usually termed the molecular structure factor. We can combine these reformulations to obtain the following result for the ns static structure factor of diatomic rigid molecules:

$$S_n(q) \cong S_n^{(l_{\text{co}})}(q) = \sum_{l, l' \leq l_{\text{co}}} b_{ll'}^{\text{coh}}(q) S_{ll'}^{(d)}(q) + b^{\text{inc}}(q), \quad (9)$$

$$b_{ll'}^{\text{coh}}(q) = [(2l+1)(2l'+1)]^{1/2} j_l\left(\frac{qd}{2}\right) j_{l'}\left(\frac{qd}{2}\right) \frac{1}{2} (\overline{a_{\text{coh}}^A} + (-1)^l \overline{a_{\text{coh}}^B}) (\overline{a_{\text{coh}}^A} + (-1)^{l'} \overline{a_{\text{coh}}^B}), \quad (10)$$

$$b^{\text{inc}}(q) = \frac{1}{2} (\overline{(a_{\text{coh}}^A)^2} + \overline{(a_{\text{coh}}^B)^2} + \overline{(a_{\text{inc}}^A)^2} + \overline{(a_{\text{inc}}^B)^2}) + \overline{a_{\text{coh}}^A a_{\text{coh}}^B} j_0(qd). \quad (11)$$

We want to mention that choosing $l_{\text{co}}=0$ yields the usual Sears expression [4]. This fact demonstrates again that the representation through molecular correlation functions is a natural extension of the approach by Sears.

The molecular structure factor $b^{\text{inc}}(q)$, shown in Fig. 2 for the system of diatomic molecules with a special choice of scattering lengths, has a very simple q dependence. Starting from a maximum at $q=0$, it quickly decays and shows os-

cillations around the asymptotic value for $q \rightarrow \infty$ which is given by the q -independent first term of Eq. (11). In the case of general molecules the q dependence is given by a linear superposition of functions $j_0(qr_{\nu\nu'})$ involving all intramolecular distances $r_{\nu\nu'} = |\vec{r}_{j\nu} - \vec{r}_{j\nu'}|$.

Both the molecular correlation functions $S_{ll'}(q)$ and the coherent form factors $b_{ll'}^{\text{coh}}(q)$ are symmetric with respect to l

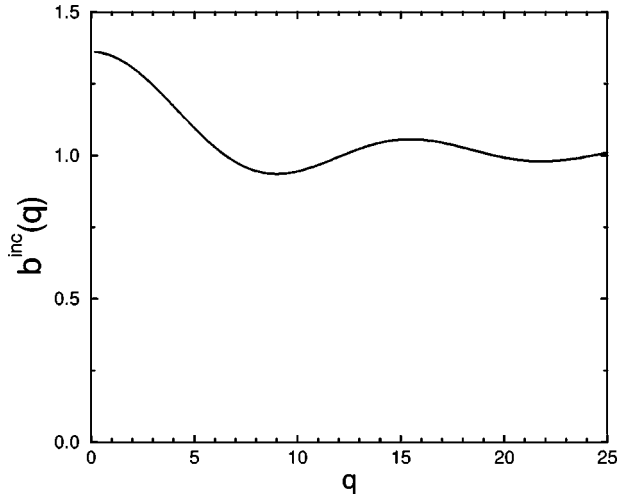


FIG. 2. Molecular structure factor $b^{\text{inc}}(q)$ for a system of diatomic rigid molecules with $a_{\text{coh}}^A=1.4$, $a_{\text{coh}}^B=0.25$, and $a_{\text{inc}}^v=0$ for $v=A$ and B .

and l' . Thus the summation in Eq. (9) can be restricted to $l' \geq l$. If the scattering lengths of A and B atoms are equal, the coherent molecular form factors $b_{ll'}^{\text{coh}}(q)$ vanish unless l and l' are both even, i.e., only molecular correlation functions with l and l' even contribute to $S_n(q)$. This is a specific property of the diatomic linear molecule closely related to head-tail symmetry. In the case of exact head-tail symmetry, the correlators $S_{ll'}^{(d)}(q)$ are zero for l or l' odd. If only the scattering lengths are equal, such correlations may exist but they do not enter $S_n(q)$ since the neutron probe cannot distinguish between A and B atoms.

Apart from this system-specific property, Eq. (10) and the examples of form factors presented in Fig. 3 clarify some properties of the q dependence of $b_{ll'}^{\text{coh}}(q)$ which are quite universal, i.e., also valid in the time-dependent case and for general molecules. In both subfigures one can observe that the weight $b_{ll'}^{\text{coh}}(q)$ of a given correlation function $S_{ll'}(q)$ depends very strongly on the value of q . For instance the center of mass correlations $S_{00}(q)$ are very important for $q \approx 0$ but only of minor relevance for $q > 10$. From the mathematical properties of the spherical Bessel functions, also determining the q dependence of $b_{ll'}^{\text{coh}}(q)$ in the general case given by Eq. (7), one can conclude a systematic relation between the values of l and l' and the range of q values in which the correlator $S_{ll'}(q)$ will have a large weight. This relation is demonstrated in Fig. 3. Figure 3(a) shows the diagonal form factors $b_{ll}^{\text{coh}}(q)$ up to $l=4$. All of them are positive over the entire q range. $b_{00}^{\text{coh}}(q)$ has a maximum for $q=0$ which decays to zero with increasing q , and is followed by further oscillations with a strongly reduced amplitude. The other diagonal correlators also show a pronounced maximum that is followed by smaller oscillations, but the location of this main maximum is shifted to higher values of q . This shift grows monotonously with increasing l . Further we see that the maximum's amplitude decreases and its width becomes larger upon increasing l . We have chosen $a_{\text{coh}}^A=1.4$ different from $a_{\text{coh}}^B=0.25$ in order to have nonvanishing form factors for l or l' odd. Still we can observe that the dependence of $b_{ll'}^{\text{coh}}(q)$ on the scattering lengths leads to smaller

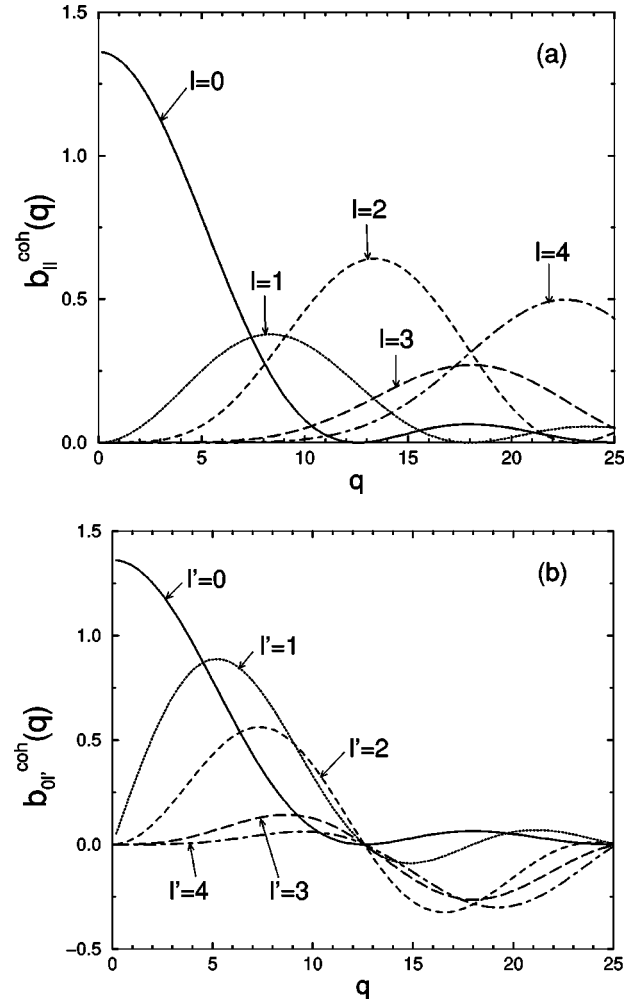


FIG. 3. Molecular form factors $b_{ll'}^{\text{coh}}(q)$ for a system of diatomic rigid molecules with $a_{\text{coh}}^A=1.4$, $a_{\text{coh}}^B=0.25$, and $a_{\text{inc}}^v=0$ for $v=A$ and B . Subfigure (a) shows the progressing shift of the first maximum to higher q for the diagonal form factors $b_{ll}^{\text{coh}}(q)$; subfigure (b) shows the shift and decrease of the first maximum for the form factors $b_{0l'}^{\text{coh}}(q)$ with $l=0$.

amplitudes for odd l . Figure 3(b) also shows the systematic behavior for the off-diagonal form factors $b_{0l'}^{\text{coh}}(q)$ with $l=0$. Upon growing $l'-l$ the amplitude of the first maximum quickly reduces, and the contribution at the second maximum becomes more important. Thus, while the off-diagonal terms cannot be neglected, the relevant range is also shifted to higher values of q for growing l' . The same is true for the nondiagonal terms with $l > 0$.

Consequently the systematic behavior of the weights $b_{ll'}^{\text{coh}}(q)$ can be formulated as a rule of thumb: *The larger the values of l and $l'-l$, the higher the value of q at which the form factor $b_{ll'}^{\text{coh}}(q)$ will become relevant.* We merely note that for the form factors as well as for the molecular correlation functions themselves negative values are possible for the off-diagonal terms.

Having discussed all the relevant terms for the evaluation of the right hand side of Eq. (9), we can now turn to the ns static structure factor itself, and test the convergence of the series representation, i.e., the quality of the different approximations $S_n^{(\text{co})}(q)$, $l_{\text{co}}=0, 1, \dots, 4$. Figure 4(a) shows the ex-

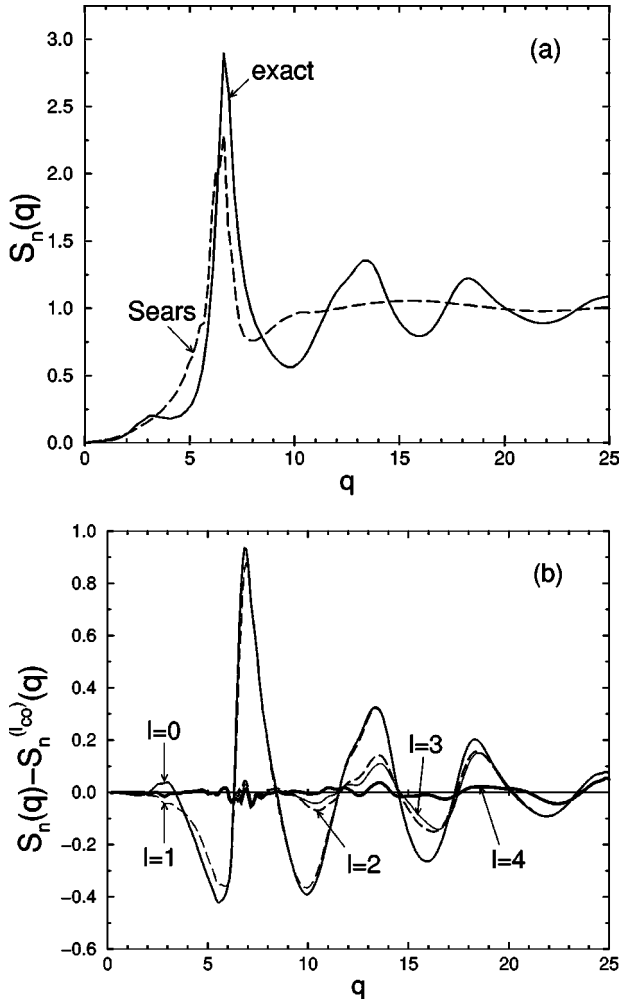


FIG. 4. Static structure factor of neutron scattering and its series representation according to Eq. (9) for different values of the l cutoff. The scattering lengths are chosen as $a_{\text{coh}}^A = 1.4$, $a_{\text{coh}}^B = 0.25$, and $a_{\text{inc}}^{\nu} = 0$ for $\nu = A, B$. (a) Exact and Sears results ($l_{\text{co}} = 0$). (b) Absolute error of the approximation for different values of $l = l_{\text{co}}$.

act result for $S_n(q)$ as evaluated according to Eq. (1). The scattering length have been chosen as $a_{\text{coh}}^A = 1.4$, $a_{\text{coh}}^B = 0.25$, and $a_{\text{inc}}^{\nu} = 0$, where $\nu = A, B$. At $q \approx 3$ the static structure factor exhibits a small but well pronounced prepeak followed by a strong maximum at $q \approx 6.6$, and further maxima at $q \approx 13$, 18, and 25. Thus the q dependence of $S_n(q)$ shows the general structure also found for the molecular correlation functions. Taking a closer look to the various maxima, and taking into account the properties we found for the weights $b_{ll'}^{\text{coh}}(q)$ we can further illuminate their origin. In case of the prepeak this is rather obvious since (i) at $q \approx 3$ only correlators with small l and l' have to be taken into account (see the discussion above), and (ii) only $S_{11}(q)$ possesses a significant peak at $q \approx 3$. Therefore, its origin must be connected to the structure found in the correlation function $S_{11}(q)$. A quantitative analysis of this statement will be given in Sec. III C. From Fig. 3 we can also see that at the position $q \approx 6.6$ of the main peak, correlators with l or l' larger than 2 do not play a large role. Thus the center of mass correlation function $S_{00}(q)$ and the molecular correlation function $S_{02}(q), S_{22}(q)$ as well as $S_{01}(q)$ can be identified as the origin of the main peak in

$S_n(q)$. The latter correlators are responsible for the slight shift of the peak position to higher q in comparison with the center of mass correlations. For peaks at $q \approx 13$ and 18, a number of correlators will be relevant. Using the weights $b_{ll'}^{\text{coh}}(q)$, one can still conclude that $S_{22}(q)$ will be one of the main sources for the peak at $q \approx 13$, and that $S_{24}(q)$ as well as $S_{44}(q)$ will be of great relevance for the structure at $q \approx 18$. From the molecular correlation functions we have determined $S_{44}(q)$ is the one which contributes most to the peak at $q \approx 25$, though correlation functions with $l, l' > 4$ could also be of great importance.

Apart from the exact result for $S_n(q)$, Fig. 4(a) also shows the result of the weak hindering approximation as used by Sears [4]. Except for the limiting values for $q \rightarrow 0$ and $q \rightarrow \infty$, the results of this approximation are rather poor, since almost all of the structure in $S_n(q)$ is missed and even the main peak is not reproduced properly. This finding strongly supports results of Chen *et al.* [12], who observed that a factorization of translational and rotational correlations is not suitable for the description of a supercooled liquid.

Figure 4(b) shows the convergence of the series representation by presenting the dependence of the error $S_n(q) - S_n^{(l_{\text{co}})}(q)$ on l_{co} . The large error of the Sears result corresponding to $l_{\text{co}} = 0$ is already reduced to statistical fluctuations in a range of q up to $q \approx 9$ by choosing $l_{\text{co}} = 2$. For $l_{\text{co}} = 4$ the static structure factor $S_n(q)$ is almost perfectly reproduced for the entire range of q values at least up to $q \approx 20$. Since the q range chosen here compares well to the values accessible in a real neutron scattering experiment, we can conclude that the convergence of the series representation (5) is fast enough to make it attractive for practical purposes. The cutoff of the infinite sum at a relatively small value of l_{co} is well justified, at least for our choice of model. The actual value of l_{co} that is sufficient will depend on the size and form of the molecule as well as their interactions [18]. In accordance with the given rule of thumb increasing the value of l_{co} merely corresponds to an enlargement of the range in which $S_n(q)$ is reproduced.

C. Prepeak

We will now turn to a special feature of the static structure factor. As mentioned in Sec. III B, $S_n(q)$ shows a prepeak at $q \approx 3$. Given that prepeaks or first sharp diffraction peaks have been studied mostly in connection with strong glasses like, e.g., SiO_2 [20] or ionic glass formers [19], this observation is quite surprising. In the system of diatomic rigid molecules studied here we neither find a network structure nor do we have long range electrostatic interactions. Since the proposed explanations for the prepeak usually rely heavily on the network structure and/or the effects of the ionic charges, they cannot be applied to the prepeak in the present system. What, then, could be the mechanism leading to intermediate range order in a system without an extended network or long range interactions?

In the preceding sections we have pointed out the connection between the q dependence of $S_n(q)$ and the contribution of various molecular correlation functions. To understand the mechanism responsible for the formation of a prepeak, it will surely be helpful to analyze in detail which of the relevant molecular correlations contribute at $q_{\text{pp}} \approx 3$. The contribu-

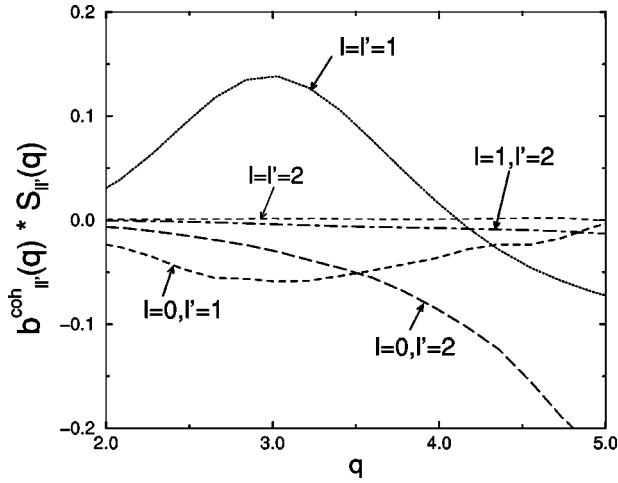


FIG. 5. Contributions of the different molecular correlation functions to the prepeak for $a_{\text{coh}}^A = 1.4$, $a_{\text{coh}}^B = 0.25$, and $a_{\text{inc}}^v = 0$ for $v = A$ and B .

tions of the intramolecular structure factor $b^{\text{inc}}(q)$ and the center of mass correlations $S_{00}^{(d)}(q)$ are of large amplitude, but they contain no structure at all at q_{pp} . Since they have opposite signs they almost cancel each other. Together they give the Sears result which does not exhibit any prepeak [cf. Fig. 4(a)]. The other relevant contributions at q_{pp} are shown in Fig. 5. Thus the importance of the correlator $S_{11}(q)$ for the formation of the prepeak is corroborated by this quantitative analysis. Besides the negative contribution of $S_{01}(q)$, no other term shows any structure at q_{pp} . It may be noted that the negative contributions of $S_{11}(q)$ and $S_{02}(q)$ at $q \approx 5$ induce a better separation between the prepeak and the main peak. In accord with our ‘‘rule of thumb,’’ the terms involving $l, l' > 2$ are even less important than $S_{22}(q)$.

The predominant role of $S_{11}(q)$, and the fact that no structure is observed in the center of mass correlation, strongly suggest that orientational effects are responsible for the prepeak in the studied system. Apart from the evidence given here it seems not too far fetched to consider spatial ordering due to steric hindrance as a mechanism for prepeaks in molecular systems, as close packing [30] and size effect [31] have also been shown to be of great relevance in other systems. The importance of orientational degrees of freedom for the structure of $S_n(q)$ for liquid halogens and the prepeak in the molecular liquid CCl_4 has also been put forward by Misawa [32,33]. Whereas in his work orientational correlations between neighboring molecules had to be introduced as an *assumption*, we have been able to give *direct* evidence for their relevance.

Taking into account the interpretation of the molecular correlation functions (see above), it is also possible to get additional information on the kind of intermediate range order. $\mathcal{D}_{00}^1 \propto Y_1^0$ has the shape of a dumbbell which is, due to the choice of the body fixed frame, aligned to the symmetry axis connecting the atoms of the molecule. Thus the correlations of $S_{11}(q)$ at q_{pp} can be attributed to a preference for a parallel orientation of *next* nearest neighbors. Apart from the geometric effects leading to a parallel alignment of molecules, energetic effects are also important for this ‘‘antiferromagnetic’’ order,

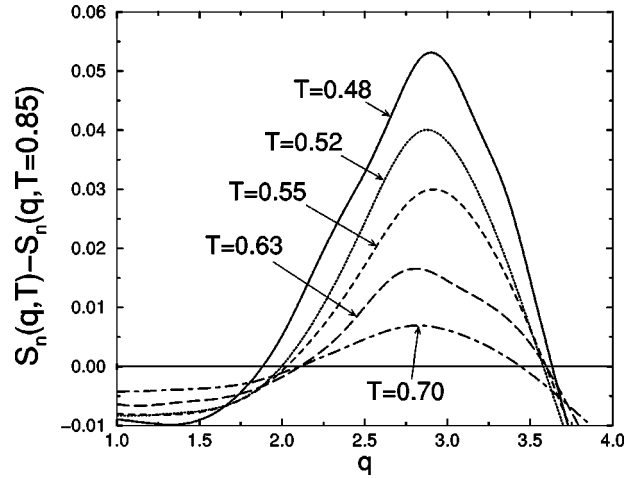


FIG. 6. Temperature dependence of the prepeak for $a_{\text{coh}}^A = 1.4$, $a_{\text{coh}}^B = 0.25$, and $a_{\text{inc}}^v = 0$ for $v = A$ and B .

$$\begin{array}{cccc}
 & A & B & A \\
 \cdots & | & | & | \cdots \\
 & B & A & B
 \end{array} \quad (12)$$

since the vicinity of A and B molecules is favored by the choice of Lennard-Jones energies $\epsilon_{AB} < \epsilon_{AA} = \epsilon_{BB}$.

Prepeaks have often been reported to show special behaviors. In many glassy systems an increase of the prepeak amplitude with increasing temperature is found [20,21], which is quite contrary to the behavior of the other peaks in $S_n(q)$. The amplitude and position was also shown to be affected by the pressure [20] and the composition of the liquid [19]. Therefore, it will be interesting to characterize further the behavior of the prepeak in our system.

Figure 6 shows the temperature dependence of the prepeak in the range $T = 0.48$ – 0.70 . To eliminate the background given by the low q wing of the main peak, we have subtracted $S_n(q)$ at $T = 0.85$. At this temperature the prepeak is not discernible any longer. With increasing temperature the prepeak decreases in amplitude, and the width at half maximum grows. In the given temperature range no shift in the position of the peak can be observed whereas the main peak is shifted downwards by $\Delta q = 0.2$. Although seemingly uncommon for a prepeak, such temperature dependence has been reported before. It has been found for carbon tetrachloride [34] and also in a recent study of *m*-toluol and *m*-fluoranilin by Morineau *et al.* [22]. Like our system these are molecular liquids. Thus one is tempted to infer that this behavior might be typical for such systems.

We are not able to determine the pressure dependence of the prepeak or to study effects of composition, i.e., the influence of atomic size and interactions since this has not been done in the simulation [16]. Still, we want to point out one aspect which is closely related to compositional studies but which, to our knowledge has never been considered before. A substitution of atoms of a certain species in the liquid will not only alter the interactions and the size of the atoms but will also affect the scattering lengths. Figure 7 shows that the observability of the intermediate range order as a prepeak can indeed be influenced. As can also be inferred from Eq. (9) in the case $a_{\text{coh}}^A = a_{\text{coh}}^B$, i.e., $x = a_{\text{coh}}^A / a_{\text{coh}}^B = 1$, the cor-

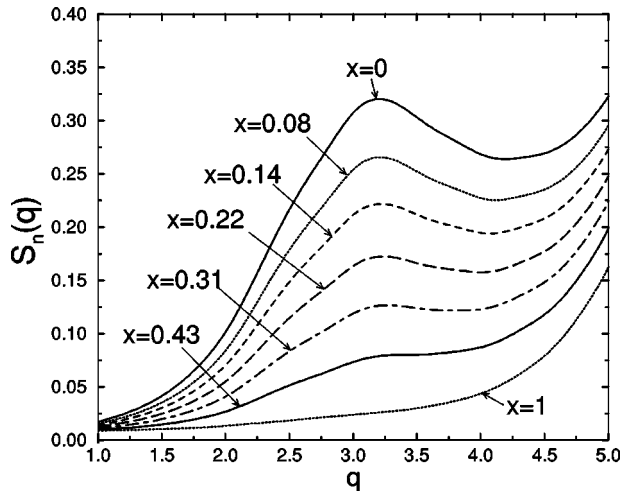


FIG. 7. Dependence of the prepeak amplitude on the choice of the scattering length. $x = a_{\text{coh}}^B / a_{\text{coh}}^A$ denotes the ratio of the coherent scattering lengths. The incoherent scattering lengths are set to zero and a_{coh}^v , and $\nu = A$ and B are chosen in such a way that the large q limit of $S_n(q)$ is constant.

relator $S_{11}(q)$ gives no contribution to $S_n(q)$ and the prepeak vanishes. Keeping the overall normalization constant and increasing the asymmetry in the scattering lengths, the prepeak grows to its maximum value. Since at the small q value of the prepeak position the molecular correlation function with $l=1$ will be the most important one [apart from $S_{00}(q)$], a prepeak in molecular systems will be most easily observed for molecules with *no* head-tail symmetry. Thus it is, for instance, not surprising that in liquid halogens no prepeak is observed, although their liquid structure might be not too different from our system [32].

IV. CONCLUSION

Tackling the problem of neutron scattering in supercooled molecular liquids, we have shown that well known concepts can be generalized naturally to give a concise description including all molecular degrees of freedom. Thus it was pos-

sible to reduce the large discrepancy that was found between the exact result for $S_n(q)$ and a description in terms of the center of mass only. The resulting description of $S_n(q, t)$ in terms of molecular correlation functions $S_{ln, l'n'}^m(q, t)$ was shown to shed light on the q dependence, offering clear relations between the q range and the angular resolution described by the “quantum numbers” l and n . Giving a relation between the intermediate scattering function and the molecular correlations, the representation could be used to extract (partial) information on the correlations of TDOF’s as well as ODOF’s and their interference from neutron scattering experiments. From the general expression we were able to give hints at an effort in this direction. A quantitative test of the formalism for a liquid of diatomic molecules in the “worst case” of static correlations led to a good agreement with exact results for $S_n(q)$ if molecular correlation functions up to $l_{\text{co}}=4$ are taken into account. This analysis also confirmed that a factorization like the weak hindering approximation which leads to a description in terms of the center of mass only is not suitable in the supercooled regime.

In the simulation of a liquid of diatomic Lennard-Jones molecules, we observe a prepeak in the ns static structure factor $S_n(q)$ which could be attributed to intermediate range orientational order. The temperature dependence of this prepeak is in accord with the results found for the molecular liquids CCl_4 , *m*-toluidine and *m*-fluoroaniline, but at variance with the behavior found for most covalent glass formers. The influence of scattering lengths on the observability of intermediate range (orientational) order was examined offering the conclusion that a manifestation as a prepeak may not occur in case of head-tail symmetry of the molecules.

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