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Molecular correlations in a supercooled liquid

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We present static and dynamic properties of molecular correlation functions $S_{lmn,l'm'n'}(\vec{q},t)$ in a simulated supercooled liquid of water molecules, as a preliminary effort in the direction of solving the molecular mode-coupling theory (MMCT) equations for supercooled molecular liquids. The temperature and time dependence of various molecular correlation functions, calculated from 250 ns long molecular dynamics simulations, show the characteristic patterns predicted by MMCT and shed light on the driving mechanism responsible for the slowing down of the molecular dynamics. We also discuss the symmetry properties of the molecular correlation functions that can be predicted on the basis of the C_{2v} symmetry of the molecule. Analysis of the molecular dynamics results for the static correlators $S_{lmn,l'm'n'}(\vec{q})$ reveals that additional relationships between correlators with different signs of n and n' exist. We prove that for molecules with C_{rv} symmetry this unexpected result becomes exact at least for high temperatures.

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I. INTRODUCTION

In recent years, significant progress has been made in the understanding of the slow dynamics in supercooled liquids [1]. Theoretical [2–5], experimental (see, e.g., [6–10]), and simulation efforts (see, e.g., [11–14]) have highlighted the role played by the ideal-glass transition temperature T_c, first predicted by mode-coupling theory (MCT) for *simple* liquids [15,16] and in a schematic model [17], and identified the different dynamical mechanisms above and below this temperature. This work has clarified the strong interplay between liquid structure and liquid dynamics above T_c as well as the universal aspect of the decorrelation process—which close to T_c is predicted to become independent of the correlation function as well as the q vector that is probed [18]. For colloidal systems MCT has been tested both on a semiquantitative level [6], i.e., the validity of the scaling laws was investigated, and also on a quantitative level where it has been demonstrated that the time-dependent density correlator for a liquid of hard spheres (which is a good model for neutral colloids) obtained from MCT describes the corresponding experimental result over three decades in time by using *only one* fit parameter (for the time scale) [19,20]. All the other experimental tests were semiquantitative and were exclusively restricted to molecular systems, like OTP, salol, glycerol, etc. (for more details, see Refs. [2,3,7–10,21] and references therein). At a first glance the reasonably good agreement between the predictions of MCT for simple liquids and many of the experimental data for the molecular glass forming liquids seems to be surprising, since the orientational degrees of freedom do not appear in the original version of MCT [18]. To do a quantitative comparison between theory and experiment or simulation and especially to describe the molecular correlations (including orientational degrees of freedom) it is necessary to extend MCT to molecular liquids. In particular, a molecular mode-coupling theory (MMCT) allows one to study the role of the coupling between the translational degrees of freedom and orientational degrees of freedom. Such an extension has recently been performed for a single dumbbell molecule in an isotropic liquid [22] and for a liquid of diatomic molecules [23–25]. References [24] and [25] even treat general molecules.

MMCT is also conceptually based on the hypothesis that the liquid structure is controlling the long-time dynamical evolution of the system. Structural information is used as input in the theory via generalization of the density-density structure factor including the angular degrees of freedom. Such quantities, although they are difficult to determine experimentally, can be evaluated from molecular dynamics trajectories and used to test the quality of the recently proposed MMCT. For the case of a liquid of diatomic molecules, the molecular structure factors have been evaluated [26] and a first quantitative test of MMCT has been presented in Refs. [27,28]. Furthermore, the temperature dependence of the molecular correlation functions can give hints regarding the leading mechanism for the slowing down of the dynamics.

The asymptotic predictions of MCT continue to be valid within the MMCT scheme. Also in MMCT [22,23] (i) there exists a β-relaxation regime where the factorization of the time or frequency dependence of the correlators or susceptibilities from the space and angular dependence holds generically and the time dependence is given by the β correlator, which fulfills the *first scaling law* [18], and (ii) there exists an α-relaxation regime in which the *second scaling law* [18] holds, i.e., the time-temperature superposition principle is fulfilled [29]. These two results underline the universality of the ideal structural glass transition based on a bifurcation scenario described by a fold singularity [18]. However, calculation of the various exponents (entering the scaling laws), and of the critical nonergodicity parameter, the critical amplitudes, the transition temperature T_c, and particularly of the molecular correlation functions themselves, requires the solution of the MMCT equations.

In this article we present the temperature and q-vector

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dependence of the generalized structure factors required by the MMCT for the case of the single point charge extended (SPC/E) potential [30]. This potential, which describes the molecule as a rigid planar body and models the pair interactions as a sum of electrostatic and Lennard Jones terms, has been studied in detail and has been shown to reproduce qualitatively the characteristic properties of liquid water—a liquid where the slowing down of the dynamics on cooling is not related to packing constraints but to the formation of a tetrahedral network of highly directional hydrogen bonds [31,32]. Previous numerical studies on the SPC/E system, focused on the center of mass self [33] and collective properties [34], have shown on a semiquantitative level that the center of mass dynamics is well described by MCT, with an estimated critical temperature of about $T_c = 200 \pm 3$ K. It has been shown that orientational degrees of freedom are crucial in strongly enhancing the slowing down of the dynamical processes on supercooling. This has led to the introduction of a semischematic MCT model [35], where the coupling to the orientational degrees of freedom is accounted for phenomenologically by the introduction of a parameter $\chi_R \geqslant 1$ by which the coupling of the center of mass density modes is enhanced. This semischematic approach, recently tested also for the case of a supercooled liquid of diatomic molecules [36], focuses only on the center of mass translational degrees of freedom and is by construction unable to describe the time evolution of the orientational degrees of freedom and to indicate which orientational degrees of freedom are responsible for the slowing down of the center of mass and orientational dynamics. A MMCT description is required to fully describe these important dynamical aspects.

The generalized structure factors presented in this article are a first step in the direction of solving the MMCT for a molecular system. In Sec. II we motivate the introduction of an infinite-dimensional correlation matrix $S_{lmn,l'm'n'}(\vec{q},t)$ where $l = 0,1,2,\ldots,\quad -l \leqslant m \leqslant l,\quad -l \leqslant n \leqslant l$, and corresponding relations for the primed quantities. As already mentioned above, MMCT requires the static correlators $S_{lmn,l'm'n'}(\vec{q})$ as an input. In Sec. III we discuss the relations between the $S_{lmn,l'm'n'}(\vec{q},t)$ correlation functions arising from the symmetries characteristic of isotropic liquids and the symmetries characteristic of C_{rv} molecules. These relations reduce drastically the number of independent $S_{lmn,l'm'n'}(\vec{q},t)$ correlation functions and support the feasibility of a full MMCT calculation for this class of liquids. Finally, in Sec. IV we present the time evolution of the generalized angular correlation functions for the SPC/E case and interpret their behavior in the general MCT framework. The qualitative and semiquantitative agreement between numerical data and asymptotic MCT theoretical predictions strongly suggests performing a full MMCT comparison.

II. MOLECULAR CORRELATION FUNCTIONS

To describe a molecular liquid it is necessary to introduce, besides information on the position of the molecule's center of mass, information on the orientation of the molecules. The microscopic density, defined for simple (atomic) liquids [37] as $\rho(\vec{x},t) = \Sigma_{j=1}^{N} \delta(\vec{x} - \vec{x}_j(t))$, is generalized to

$$\rho(\vec{x},\Omega,t) = \sum_{j=1}^{N} \delta(\vec{x} - \vec{x}_j(t))\,\delta(\Omega - \Omega_j(t)), \tag{1}$$

where the sum runs over the N molecules of the liquid, and $\vec{x}_j(t)$ and $\Omega_j(t) = (\phi_j(t), \theta_j(t), \chi_j(t))$ are, respectively, the position of the center of mass and the Euler angles of the jth molecule at time t.

Any function $f(\vec{x},\Omega)$ can be expanded with respect to plane waves and to generalized spherical harmonics $D^l_{mn}(\Omega) = e^{-im\phi} d^l_{mn}(\theta) e^{-in\chi}$ (see Ref. [38]) as

$$f(\vec{x},\Omega) = \frac{1}{8\pi^2 V} \sum_{q} \sum_{lmn} (-i)^l \times (2l+1)^{1/2} f_{lmn}(\vec{q}) e^{-i\vec{q}\cdot\vec{x}} D^l_{mn}(\Omega), \tag{2}$$

where the coefficients $f_{lmn}(\vec{q})$ are given by

$$f_{lmn}(\vec{q}) = i^l (2l+1)^{1/2} \int d^3x \int d\Omega\, f(\vec{x},\Omega) e^{i\vec{q}\cdot\vec{x}} D^{l*}_{mn}(\Omega). \tag{3}$$

Here $l \geqslant 0,\quad -l \leqslant m \leqslant l,\quad -l \leqslant n \leqslant l$. Application of Eq. (3) to $\rho(\vec{x},\Omega,t)$ yields the tensorial one-particle density:

$$\rho_{lmn}(\vec{q},t) = i^l (2l+1)^{1/2} \sum_{j=1}^{N} e^{i\vec{q}\cdot\vec{x}_j(t)} D^{l*}_{mn}(\Omega_j(t)). \tag{4}$$

The prefactor in Eq. (4) is chosen for technical convenience, e.g., the factor i^l makes the molecular correlators real for $n = n'$. As will be shown below, this choice produces real correlators also for n and $n' \neq 0$ at high temperature. Now we can introduce the time-dependent *molecular* correlation functions

$$S_{lmn,l'm'n'}(\vec{q},t) = \frac{1}{N} \langle \rho^*_{lmn}(\vec{q},t) \rho_{l'm'n'}(\vec{q},0) \rangle, \tag{5}$$

where the angular brackets denote the canonical average over the initial point in phase space. Substitution of Eq. (4) into Eq. (5) yields

$$S_{lmn,l'm'n'}(\vec{q},t) = S^{(d)}_{lmn,l'm'n'}(\vec{q},t) + S^{(s)}_{lmn,l'm'n'}(\vec{q},t) \tag{6}$$

with the *distinct part*

$$S^{(d)}_{lmn,l'm'n'}(\vec{q},t) = i^{l'-l} [(2l+1)(2l'+1)]^{1/2} \frac{1}{N} \times \sum_{j \neq j'} \langle e^{-i\vec{q}\cdot[\vec{x}_j(t) - \vec{x}_{j'}]} D^l_{mn}(\Omega_j(t)) \times D^{l'*}_{m'n'}(\Omega_{j'}) \rangle \tag{7}$$

and the *self part*

$$S^{(s)}_{lmn,l'm'n'}(\vec{q},t)=i^{l'-l}[(2l+1)(2l'+1)]^{1/2}\frac{1}{N}\times\sum_j\langle e^{-i\vec{q}\cdot[\vec{x}_j(t)-\vec{x}_j]}D^l_{mn}(\Omega_j(t))\times D^{l'*}_{m'n'}(\Omega_j)\rangle. \tag{8}$$

The reader should note that these correlation functions involve both translational degrees of freedom and orientational degrees of freedom. They form a complete set for any two-point correlation function of an arbitrary molecular liquid and they are also the main entities entering MMCT [24]. Specialization to $n=n'=0$ yields the corresponding correlators used in Ref. [23] for linear molecules. Although their introduction is enforced by theoretical reasons since homogeneity and isotropy of the liquid is accounted for directly by the Fourier transformation to $\vec{q}$ space and their tensorial nature, only very few of them can be measured experimentally. For instance, $S_{1mn,1mn}(\vec{q}=0,t)$ and $S^{(s)}_{2mn,2mn}(\vec{q}=0,t)$ can be obtained from dielectric measurement and NMR, respectively. Information on the center of mass correlator $S_{000,000}(\vec{q},t)$ follows from light scattering, provided that the contribution of the orientational correlators can be neglected [39]. The neutron scattering cross section is a linear superposition of *all* of these correlators (see, e.g., [40]), from which information on the individual correlators can be obtained by choosing different scattering lengths of the atomic units. On the other hand, it is a great advantage of a molecular dynamics (MD) simulation, which really determines the trajectories $\{\vec{x}_j(t),\Omega_j(t)\}$, that these correlation functions can be calculated. This of course can only be done for l and l' smaller than a cutoff value l_{co}, which will in the analysis of the SPC/E data be chosen as $l_{co}=2$.

III. SYMMETRY PROPERTIES

In this section we will discuss the general properties of the correlators (6), (7), and (8) which follow from symmetry. Similar discussions have been given for an expansion into rotational invariants [38] and in real space [41]. The properties presented in the following will be of great importance for discussion of the results of the simulation and especially to reduce the effort needed for solution of the MMCT equations, which we will present in a subsequent paper. Concerning symmetry, we have to distinguish between global and local symmetries, where the latter are related to the geometry of a single (rigid) molecule.

A. Global symmetry

The global symmetries arise from the invariance of the molecular interactions under the simultaneous translation or rotation of all molecules, provided that the external potentials are zero. Similarly, the absence of a time-dependent external force implies time translational and time reversal symmetry, which are the same as for simple liquids and therefore will not be discussed here. The invariance under translations in space has already been accounted for by the transformation into $\vec{q}$ space, i.e., what remains is the discussion of the transformation of the molecular correlators under rotations and reflections [42].

Let us start with the proper transformations $R(\alpha,\beta,\gamma)\in SO(3)$. From the transformation of $D^l_{mn}(\Omega)$ under R [38], the transformation law for the molecular correlators follow immediately:

$$S_{lmn,l'm'n'}(\vec{q}\,',t)=\sum_{m'',m'''}D^{l*}_{m''m}(R)D^{l'}_{m'''m'}\times(R)S_{lm''n,l'm'''n'}(\vec{q},t), \tag{9}$$

where $\vec{q}\,'=R\vec{q}$. The choice of the q frame, i.e., the laboratory frame of reference oriented such that $\vec{q}$ lies along the z axis, $\vec{q}=\vec{q}_0\equiv(0,0,q)$, leads to a simplification of the molecular correlators. For a rotation $R_z(\alpha)=R(\alpha,0,0)$ around the z axis for which $\vec{q}\,'=R_z\vec{q}_0=\vec{q}_0$, Eq. (9) implies

$$S_{lmn,l'm'n'}(\vec{q}_0,t)=e^{-i(m-m')\alpha}S_{lmn,l'm'n'}(\vec{q}_0,t), \tag{10}$$

where $D^l_{mm'}(R_z(\alpha))=e^{-im\alpha}\delta_{mm'}$ [38] has been used. Since Eq. (10) is valid for all α, the correlators in the q frame must be diagonal in m and m':

$$S_{lmn,l'm'n'}(\vec{q}_0,t)=S^m_{ln,l'n'}(q,t)\,\delta_{mm'}, \tag{11}$$

where $q=|\vec{q}_0|$. Since Eq. (9) is also true for $S^{(d)}_{lmn,l'm'n'}(\vec{q},t)$ and $S^{(s)}_{lmn,l'm'n'}(\vec{q},t)$, the m diagonality also holds for these quantities. A further relationship follows from Eq. (9) by choosing a rotation $R_y(\pi)=R(0,\pi,0)$ by π around the y axis:

$$S_{lmn,l'm'n'}(-\vec{q}_0,t)=(-1)^{l+m+l'+m'}S_{l\underline{m}n,l'\underline{m}'n'}(\vec{q}_0,t). \tag{12}$$

Here we considered that $R_y(\pi)\vec{q}_0=-\vec{q}_0$, $D^l_{mn}(R_y(\pi))=(-1)^{l+m}\delta_{mn}$ [38], and $\bar{m}$ (or $\bar{n}$) denotes $-m$ (or $-n$).

Next we investigate the inversion P for which $D^l_{mn}(P\Omega)=(-1)^{l+n}D^l_{m\underline{n}}(\Omega)$ [38]. Then Eq. (9) yields

$$S_{lmn,l'm'n'}(-\vec{q},t)=(-1)^{l+n+l'+n'}S_{lm\underline{n},l'm'\underline{n}'}(\vec{q},t), \tag{13}$$

which is valid for arbitrary $\vec{q}$.

A further useful relation is obtained by taking the complex conjugate of $S_{lmn,l'm'n'}(\vec{q},t)$ and applying the equality $D^{l*}_{mn}(\Omega)=(-1)^{m+n}D^l_{\underline{mn}}(\Omega)$ [38]:

$$[S_{lmn,l'm'n'}(\vec{q},t)]^*=(-1)^{l+l'+m+m'+n+n'}\times S_{l\underline{mn},l'\underline{m}'\underline{n}'}(-\vec{q},t). \tag{14}$$

Combining Eq. (14) with Eq. (12), and Eq. (13), respectively we have the final relations

$$[S_{lmn,l'm'n'}(\vec{q},t)]^*=(-1)^{m+m'}S_{l\underline{m}n,l'\underline{m}'n'}(\vec{q},t), \tag{15}$$

$$[S_{lmn,l'm'n'}(\vec{q},t)]^*=(-1)^{n+n'}S_{lm\underline{n},l'm'\underline{n}'}(\vec{q},t), \tag{16}$$

or in the q frame, due to the diagonality in m,

$$[S^{m}_{ln,l'n'}(\vec{q}_0,t)]^{*}=S^{m}_{\overline{ln},l'n'}(\vec{q}_0,t), \tag{17}$$

$$[S^{m}_{ln,l'n'}(\vec{q}_0,t)]^{*}=(-1)^{n+n'}S^{m}_{l\underline{n},l'\underline{n}'}(\vec{q}_0,t). \tag{18}$$

We will show in the following section that, in the case of molecules with C_{2v} symmetry, like water, $n+n'$ must be even and, thus, it holds the symmetry

$$[S^{m}_{ln,l'n'}(\vec{q}_0,t)]^{*}=S^{m}_{l\underline{n},l'\underline{n}'}(\vec{q}_0,t). \tag{19}$$

B. Local symmetry

In the case that a molecule has point symmetry we can derive additional identities for $S_{lmn,l'm'n'}(\vec{q},t)$. Since we have water in mind, which has a C_{2v} symmetry, we will discuss molecules with C_{rv} symmetry (see, e.g., [43]). To avoid confusion with the n index of the rotation matrices D^{l}_{mn}, we deviate from the conventional notation C_{nv}. This symmetry means that the molecule possesses an r-fold rotational axis and r planes of reflection symmetry, which contain the rotational axis. It is obvious that application of the local symmetry operations to any single molecule must leave the interaction invariant. Let us begin with the r-fold rotational symmetry. Without restriction of generality we choose the body-fixed z axes along the r-fold symmetry axis. In that case the r-fold symmetry affects only the third Euler angle χ. The transformation

$$\chi_j\rightarrow\chi_j+\nu\frac{2\pi}{r} \tag{20}$$

for ν an integer and fixed j implies that

$$\chi_j(t)\rightarrow\chi_j(t)+\nu\frac{2\pi}{r}. \tag{21}$$

Since $D^{l}_{mn}(\Omega_j(t))=e^{-im\phi_j(t)}d^{l}_{mn}(\theta_j(t))e^{-in\chi_j(t)}$ [38], it follows with the separate use of Eqs. (20) and (21) in the distinct part Eq. (7) that

$$e^{i\nu(2\pi/r)n}=1 \quad \text{and} \quad e^{-\nu(2\pi/r)n'}=1 \tag{22}$$

for all integers ν. This restricts n and n' to integer multiples of r, i.e.,

$$S^{(d)}_{lmn,l'm'n'}(\vec{q},t)=\begin{cases}\neq 0 & \text{for} \quad n,n'\in\{0,\pm r,\pm 2r,\dots\}\\ 0 & \text{otherwise.}\end{cases} \tag{23}$$

For the self part [Eq. (8)], we have to use Eqs. (20) and (21) simultaneously, leading to

$$e^{i\nu(2\pi/r)(n-n')}=1 \tag{24}$$

for all integers ν, which is fulfilled for $n'=n(\mathrm{mod}\,r)$, i.e.,

$$S^{(s)}_{lmn,l'm'n'}(\vec{q},t)=\begin{cases}\neq 0 & \text{for} \quad (n-n')\in\{0,\pm r,\pm 2r,\dots\}\\ 0 & \text{otherwise.}\end{cases} \tag{25}$$

According to these results the total correlator $S_{lmn,l'm'n'}(\vec{q},t)$ [Eq. (6)] reduces to its self part for n or n' not equal to an integer multiple of r. For the case of water $(r=2)$, Eq. (24) requires $n+n'$ to be even, a condition that simplifies Eq. (18) further.

What remains to be discussed is the role of the reflection symmetry. Here we restrict ourselves to the static correlators. It will be shown in the Appendix that for their distinct part it implies

$$S^{(d)}_{lmn,l'm'n'}(\vec{q})\rightarrow S^{(d)}_{lm|n|,l'm'|n'|}(\vec{q}), \quad T\rightarrow\infty, \tag{26}$$

i.e., it does not depend on the sign of n and n'.

We close this section with a discussion of the implications following from the results in both subsections. It will be crucial that we consider the correlators in the q frame. The correlators in an arbitrary reference frame are easily obtained from Eq. (9). Since the identities derived in Sec. III A also hold for $S^{(s)}_{lmn,l'm'n'}(\vec{q},t)$ and $S^{(d)}_{lmn,l'm'n'}(\vec{q},t)$, we get from Eqs. (11)–(14) with Eqs. (23) and (26) for static correlators in the case of high temperatures

$$(S^{(d)m}_{ln,l'n'}(q))^{*}\cong S^{(d)m}_{ln,l'n'}(q)\cong S^{(d)m}_{ln,\overline{l'}n'}(q), \tag{27}$$

i.e., the static distinct part is real and does not depend on the sign of m. Since the static self part fulfills

$$S^{(s)m}_{ln,l'n'}(q)=\delta_{ll'}\delta_{nn'}, \tag{28}$$

it follows from Eqs. (6), (26), and (28) for high temperatures that

$$S^{m}_{ln,l'n'}(q)\cong\begin{cases}S^{(d)m}_{l|n|,l'|n'|}(q), & n\neq n'\\ 1+S^{(d)m}_{l|n|,l'|n'|}(q), & n=n',\end{cases} \tag{29}$$

i.e., $S^{m}_{ln,l'n'}(q)$ is approximately determined by $S^{(d)m}_{l|n|,l'|n'|}(q)$ and in addition it is real and does not depend on the sign of m, due to Eq. (27).

IV. RESULTS

In this section we present a detailed analysis of the static and dynamic rotational correlators as calculated from a molecular dynamics simulation of a molecular network-forming liquid. The system is a liquid of 216 rigid molecules whose geometric parameters are chosen in such a way as to mimic water molecules. The intermolecular interactions are described by the SPC/E potential [30], which has been shown to be able to describe most of the thermodynamic properties of supercooled liquid water. We will not report here the details of the simulation, which can be found in Refs. [33,34].

The low T simulations were run for more than 50^{8} integration time steps, corresponding to 50 ns. Each of the simulation runs requests several months of CPU time on one 400 MHz alpha-processor for equilibration and more than one year of computer time to generate the configuration ensemble studied. In this situation, equilibrium runs for much larger systems at low temperature are very time consuming. Since periodic boundary conditions may introduce distortions in angular properties near the boundaries, since—as will be shown in the following—some of the molecular correlators present unexpected peaks at wave vectors smaller than the center of mass peak position, corresponding to a distance of about three molecular diameters, and since the amplitude of these peaks grows at low temperature, we have made the additional effort to equilibrate a system made of 1728 molecules at $T=207$ K to make sure that no finite-size effects show up in the molecular correlators for the system size considered.

In order to calculate the Euler angles of each molecule the molecular reference frame has been chosen in such a way that the z axis of the body-fixed frame has the same direction as the dipole of the molecule and the y axis lies along the line connecting the two hydrogen atoms. The x axis is therefore determined to be orthogonal to the molecular plane. With this choice of the molecular axes the structure factors Eq. (5) reduce, in the limit $|\vec{q}|\rightarrow 0$ and for $n=n'=0$, to

$$S_{lm0,l'm'0}(0,t)=C_l(t)\,\delta_{ll'}\,\delta_{mm'}\,, \tag{30}$$

where

$$C_l(t)=\frac{1}{N}\sum_{i,j}\,\langle P_l(\vec{e}_i(t)\cdot\vec{e}_j(0))\rangle \tag{31}$$

are the orientational correlation functions of the dipolar moments $\vec{\mu}_i(t)=\mu\vec{e}_i(t)$. In Eq. (31) P_l is the Legendre polynomial of order l and μ is the dipole strength. These q-independent rotational correlation functions can be experimentally measured for some values of l (see above). A complete analysis of the self part of $C_l(t)$ for the system under investigation is treated in Ref. [44]. In what follows the discussion will be extended to the generalized correlators $S^m_{ln,l'n'}(q,t)$ in the q frame.

In the first subsection we will discuss the static correlators and in the second subsection we will turn to the detailed analysis of the dynamic behavior of the correlation functions defined in Eq. (5) as calculated from the MD data. We will discuss the numerical results by comparing them to the qualitative and quantitative predictions of MCT or MMCT.

A. Static properties

We have calculated all the static structure factors as defined in Eq. (5) up to $l=2$. The q-vector range has been chosen in such a way as to include all the meaningful structure of each correlation function, i.e., the value of q ranges from 3.3 nm^{-1}, which is the lower bound imposed by the finite size, up to around 110 nm^{-1}, a value at which all the structure factors have essentially reached their asymptotic values. The grid spacing has been fixed to $\Delta q=1.11$ nm^{-1} which allows all the peaks in the correlators to be well resolved.

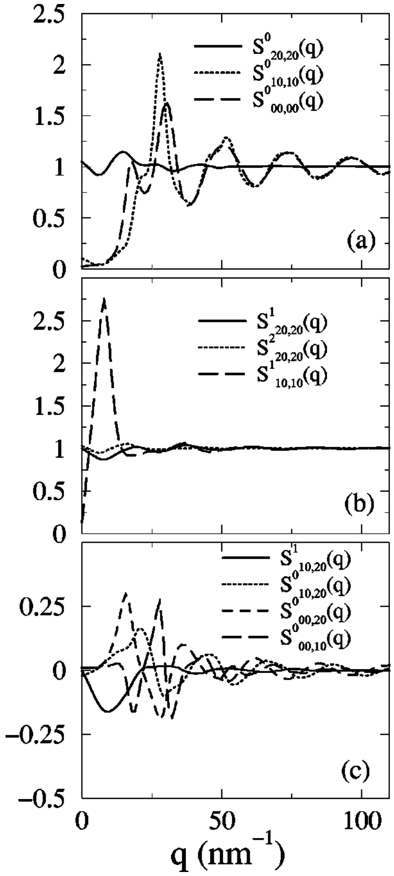

FIG. 1. Static structure factors $S^m_{ln,l'n'}(q)$. Diagonal correlation functions with $n=n'=0$ are shown in (a) and (b). Off-diagonal correlation functions with $n=n'=0$ are shown in (c).

In order to obtain more significant statistics, the static structure factors have been calculated, for each configuration, for several directions of the q vectors with respect to the fixed laboratory frame. The different results are averaged after performing a suitable rotation which brings the q vector along the z axis of the laboratory frame [Eq. (9)]. Furthermore, the resulting correlation functions have been averaged over several configurations extracted from a time evolution that extends up to 250 ns. The global symmetries described in Sec. III, which are all fulfilled within the numerical error by the numerical correlators, allow a further average of the static correlators. In this way the numerical noise is reduced to its lowest possible value. The resulting structure factors are shown in Figs. 1 and 2 for the lowest simulated temperature $T=207$ K. We found that within the numerical error all correlators are real.

Some of the static correlators shown in Figs. 1 and 2 are characterized by large amplitude peaks at q vectors corresponding to distances of the order of three molecular diameters. This is exactly the distance where finite-size effects could be expected for a system composed of 6^3 molecules. To check if the results are real or simply artifacts of the simulation conditions, we report in Fig. 3 the static structure factors for the 6^3 and 12^3 molecule systems. We perform the check at the lowest studied temperature, where the angular correlations are enhanced. Although the statistic for the large system is poorer, as expected from the shorter simulation time, both position and amplitude of the peaks are unaffected. Data in Fig. 3 confirm that the angular correlations do persist longer than the center of mass correlations and that the static molecular correlators, i.e., the quantities that are requested as input by the molecular mode-coupling theory, are not affected by the size of the system studied.

The different figures list the static correlation functions in terms of progressive angular complexity. Figures 1(a) and 1(b) include all the diagonal correlators (i.e., $l=l'$) with $n=n'=0$. In Fig. 1(c) n and n' are still fixed to zero but the

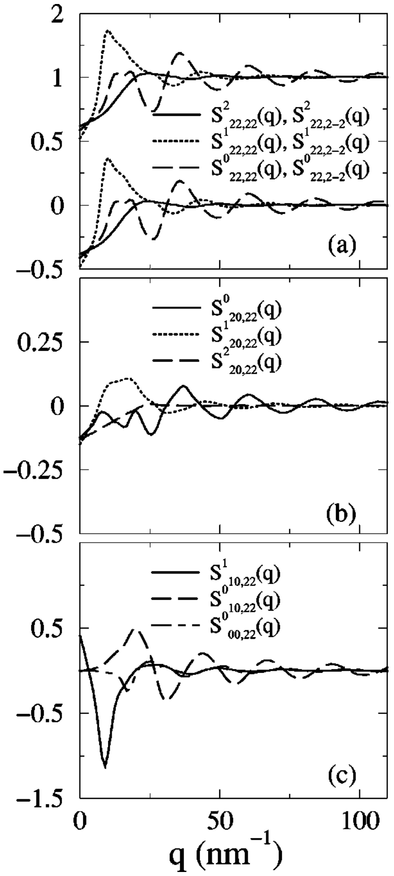

FIG. 2. Static structure factors $S^m_{ln,l'n'}(q)$ with n and/or $n' \neq 0$. (a) demonstrates the validity of Eq. (29). The three upper lines refer to the case $n=n'$ while the lower ones represent $n=-n'$.

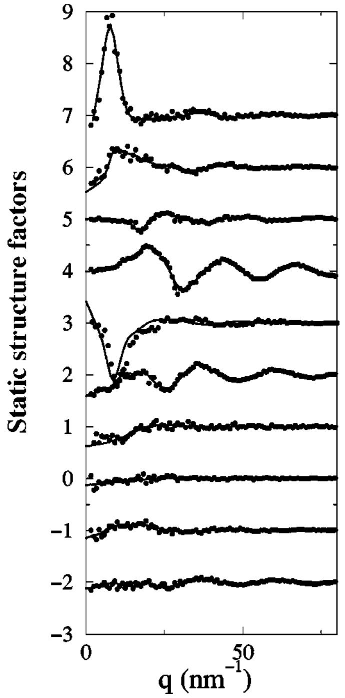

FIG. 3. Comparison of the static structure factors $S^m_{ln,l'n'}(q)$ at $T=207$ K between the 6^3 (solid lines) and the 12^3 (symbols) molecule systems. The comparison is presented for several $S^m_{ln,l'n'}(q)$, which have been arbitrarily shifted along the y-axis to improve the quality of the figure. From top to bottom: $S^1_{10,10}$, $S^1_{22,22}$, $S^0_{00,22}$, $S^0_{10,22}$, $S^1_{10,22}$, $S^0_{22,22}$, $S^2_{22,22}$, $S^2_{20,22}$, $S^1_{20,22}$, $S^0_{20,22}$. The molecular correlators that have a peak at small q vectors are shown, to highlight the absence of finite-size effects even in the worst case where the molecular correlation extends over about three molecular diameters.

diagonality in l and l' is now relaxed. In Fig. 2 the correlators with n and/or n' different from zero are reported. Figures 1 and 2 show that several molecular correlators are comparable in intensity to the center of mass correlation function. Furthermore, some of them present completely new features, i.e., the q dependence of the molecular correlations with l and l' different from zero is completely different from the center of mass structure factor. Some of the $S^m_{ln,l'n'}(q)$ display peaks and minima at q-vector values where the center of mass structure factor is rather structureless. The generalized spherical harmonics $D^l_{mn}(\Omega_j)$ in Eqs. (7) and (8) can be viewed as weights that ''single out'' molecules with certain orientations Ω_j. The differences in the q dependence of the generalized orientational correlators show that looking at molecules with ''selected'' orientation reveals characteristic length scales of the system that are different from the center of mass ones. This can result in the shift of a peak as in the case of the main peak of $S^0_{10,10}(q)$ compared to $S^0_{00,00}(q)$ [see Fig. 1(a)]. The ''proper choice'' of orientations can also reveal order on scales that are longer than the typical intermolecular distance and that is not visible in the center of mass correlators. For example, the most significant peak in $S^1_{10,20}(q)$ and $S^1_{10,10}(q)$ is located around $q=6.5\ \mathrm{nm}^{-1}$, a q vector much smaller than the center of mass structure factor first peak. The $q=6.5\ \mathrm{nm}^{-1}$ peak, which appears in correlators with l or l' equal to 1 and $n=n'=0$, may reflect the strong dipolar interactions characteristic of water. At distances of the order of $2\pi/6.5$ nm, about three molecular diameters, the SPC/E potential is equivalent to the potential generated by an electrostatic dipole with the same dipole moment as in the SPC/E model. Thus, the data in Figs. 1 and 2 suggest that in water angular correlations persist over distances much longer than the center of mass correlations. We also point out that the correlators in Fig. 1(c) have an intensity more than three times smaller than the ones reported in Fig. 1(a) [for the latter one has to use as intensity $S^m_{l0,l0}(q)-1$]. This suggests that the diagonal static correlation function could provide a good starting approximation for a MMCT description of the slowing down of dynamics in SPC/E water. We recall that this is at odds with the case of a liquid of Lennard-Jones dumbbells [26] where the off-diagonal terms have a large amplitude.

Correlators with n different from zero (see Fig. 2) carry information about the planar shape of the molecule ($n=n'=0$ is equivalent to assuming that the Euler angle χ is always zero), i.e., on the absence of cylindrical symmetry. Figure 2(a) demonstrates the validity of the property (29). Data in Fig. 2 show that a few of these correlators describe a significant amount of angular correlation. Again, the largest amplitude is observed for the case in which l or l' is 1, i.e., for $S^1_{10,22}(q)$.

Figure 2 also exhibits the $n \to -n$ (or $n' \to -n'$) symmetry as given by Eq. (29). Although this symmetry becomes exact at least at high temperatures (see the Appendix), it

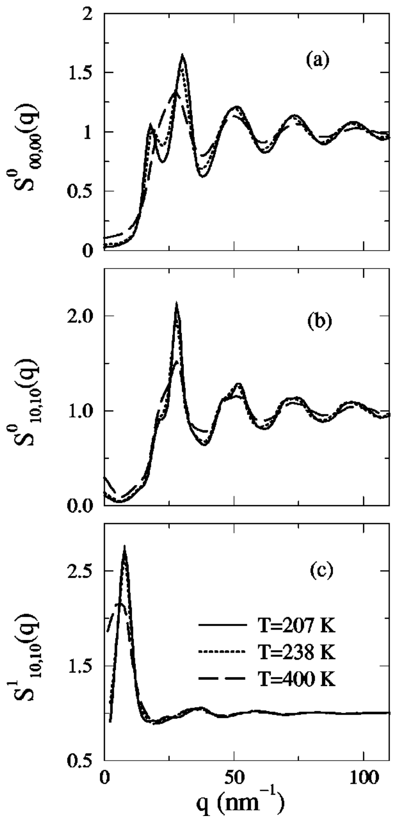

FIG. 4. Temperature dependence of the diagonal static structure factors with $l=0,1$ and $n=n'=0$.

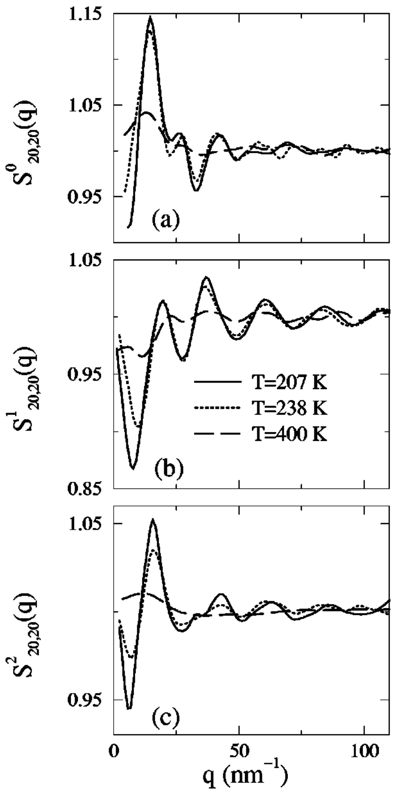

FIG. 5. Temperature dependence of the diagonal static structure factor with $l=2$ and $n=n'=0$.

seems to be valid within the numerical error even at $T=207$ K, which is not high anymore. Although in the Appendix it is shown that for *any* temperature contributions to the distinct part exist for which this symmetry is still exact, it is not obvious to us why their weight is so large.

Figures 4–7 show the temperature dependence of the static structure factors $S^m_{ln,l'n'}(q)$. In order to analyze the relative variation of the correlators on varying T we report three different temperatures, i.e., $T=207$ K, $T=238$ K, and $T=400$ K. Figures 4 and 5 report the diagonal $S^m_{l0,l0}(q)$. Figure 6 reports the off-diagonal terms with $n=n'=0$, while Fig. 7 reports some correlation functions with $n\neq 0$. From these figures we see that the behavior of $S^m_{ln,l'n'}(q)$ on changing T is strongly correlator dependent. The static structure factor $S^0_{00,00}(q)$ (center of mass) shows a significant increase of the resolution of the peaks, which become sharper as T is lowered, especially at small q vectors. The diagonal correlators with $l=l'=1$ are less temperature, dependent. They remain almost unchanged at low temperatures on changing T by 30 K, from $T=238$ K to $T=207$ K, i.e., in the region where the molecular diffusivity decreases by more than two orders of magnitude [33]. Thus, while these correlators have a large amplitude, which implies that they might contribute substantially to the MMCT vertices, the dynamical transition may not be controlled by them. The off-diagonal terms shown in Fig. 6 as well as the static correlation functions with n and/or $n'\neq 0$ (Fig. 7) also do not show significant temperature variation at low temperatures. This suggests that a small set of diagonal correlators may play the relevant role in the slowing down of the molecular dynamics on supercooling. Of course, only a full MMCT calculation can confirm such a hypothesis and provide definitive answers on which modifications of the angular correlations drive the ideal-glass transition.

B. Dynamic properties

In this section we discuss the time evolution of the molecular structure factors with $l,l'\leq 2$ at different q-vector values. We present the results of the calculation in the per-

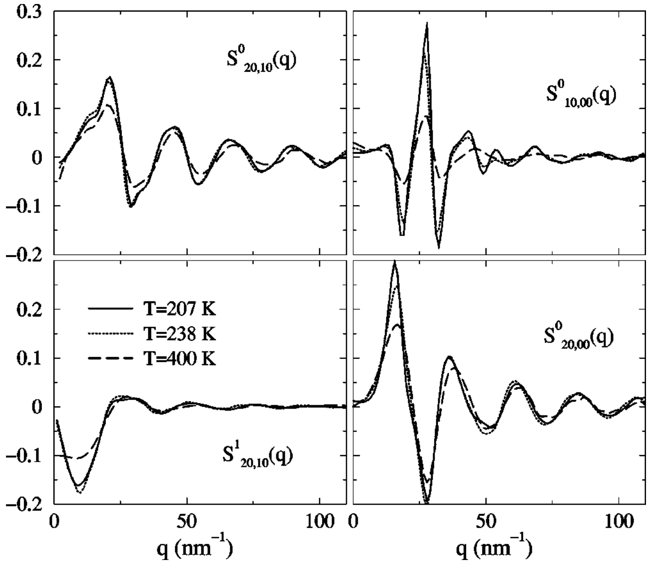

FIG. 6. Temperature dependence of the off-diagonal static structure factor with $n=n'=0$.

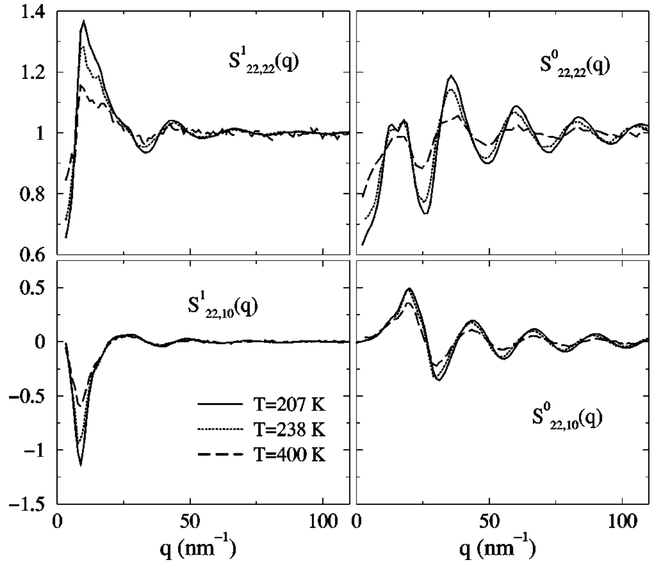

FIG. 7. Temperature dependence of some static structure factors with n and/or $n' \neq 0$.

spective of testing how far the mode-coupling framework can describe the behavior of $S^m_{ln,l'n'}(q,t)$. Since the complete MMCT equations have not yet been solved for the complete dynamic evolution of the correlators, we mostly keep our discussion to a qualitative level. We show that most of the universal predictions (see the Introduction) for the slow relaxation in supercooled liquids are excellently satisfied by the numerical data.

One of the strongest predictions of MCT is the validity of the so-called time-temperature superposition principle in the α-relaxation region (see the Introduction). The time-temperature superposition principle states that in a wide range of temperatures above the MCT critical point (which will be defined in the following) it is possible to scale the same correlator evaluated at different T on a single master curve through a rescaling of the time, i.e.,

$$\phi(t) = \tilde{\phi}(t/\tau(T)). \tag{32}$$

In Eq. (32) $\phi(t)$ indicates any dynamic structure factor, $\tilde{\phi}(\tilde{t})$ is the master function, and $\tau(T)$ is a temperature-dependent time scale that is characteristic of the chosen correlator. The temperature dependence of the time scale is also predicted by MCT or MMCT. In leading order $\tau(T)$ is a power law diverging at the critical transition temperature:

$$\tau(T) \sim |T - T_c|^{-\gamma}. \tag{33}$$

Equation (33) is one of the possible operative definitions of the mode-coupling critical temperature T_c. T_c is the temperature at which the characteristic time scales diverge, i.e., the point at which the dynamic of the liquid is completely frozen. Thus T_c defines a kinetic transition from an ergodic to a nonergodic dynamic. This is a purely kinetic transition which does not have a thermodynamic counterpart. In real liquids no sharp transition is observed and close to T_c the system switches to a different dynamic where hopping phenomena become dominant. Thus T_c assumes the meaning of a crossover temperature. The transition temperature T_c and the scaling exponent γ are not universal quantities since they strongly depend on the physical system under investigation and on the volume and pressure conditions, but they have a sort of ‘‘universality’’ in the sense that they are predicted to be correlator independent. Indeed, T_c and γ are predicted to have the same value for all correlation functions that couple to each other. In the case of molecular liquids, their values can be obtained from MMCT. In previous papers [33,34,44] it has been shown that in the case of SPC/E, the time-temperature superposition principle is satisfied by the self and collective center of mass correlators and also by the q-independent rotational correlation functions. It has also been shown that $T_c = 200 \pm 3$ and the critical exponent $\gamma = 2.7$ are the same for all examined correlators within the numerical error. Here we generalize this conclusion, showing that the time-temperature superposition principle also holds for all the molecular collective correlators up to $l = 2$. We show here only two representative correlators. In Fig. 8 we have reported $S^0_{10,10}(q,t)$ at the different temperatures normalized to its static value $S^0_{10,10}(q)$. We have rescaled each curve choosing as $\tau(T)$ the time at which the correlator has decayed to the value $1/e$. The different curves overlap perfectly in the α region, confirming the validity of the time-temperature superposition principle. The small graph shows as a reference the static structure factor; an arrow is pointing to the q value for which the analysis is performed. In Fig. 9 we show the test of the time-temperature superposition principle for the same correlator but for a different value of q, while Fig. 10 shows the same analysis for a different correlator, $S^1_{10,10}(q,t)$. These results, and similar analysis for other correlators (not reported in this article), lead to the conclusion that the time-temperature superposition principle is satisfied for all examined $S^m_{ln,l'n'}(q)$.

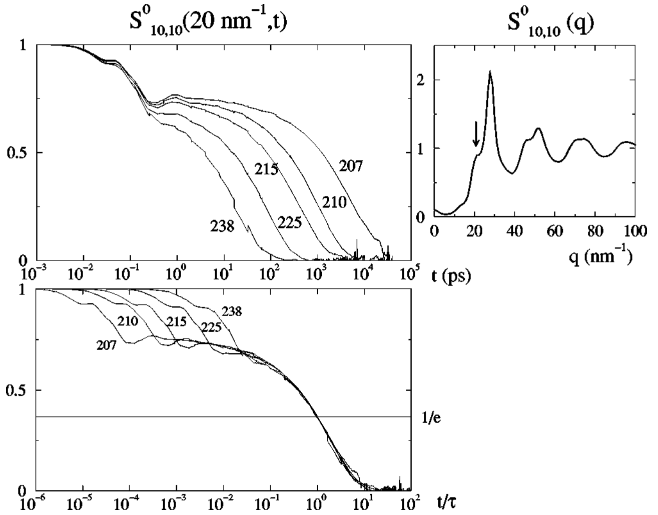

FIG. 8. Time dependence of $S^m_{ln,l'n'}(q,t)/S^m_{ln,l'n'}(q)$ for different temperatures (top) and the corresponding time-temperature scaling representation (bottom). The small inset shows the corresponding static structure factor with an indication of the chosen q vector (see arrow). This figure refers to $S^0_{10,10}(q = 20\ \mathrm{nm}^{-1},t)$.

In order to verify the validity of the scaling law for the time scale $\tau(T)$ and the ‘‘universality’’ of the exponent γ, we represent in Fig. 11 $\tau^{-1/\gamma}$, for $\gamma = 2.7$, as a function of T. The two figures are at two different values of the q vector,

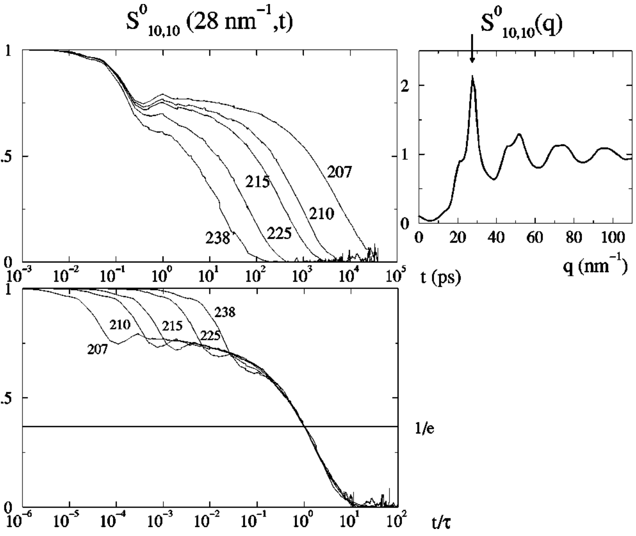

FIG. 9. Same as Fig. 8 for $S^0_{10,10}(q=28\ \text{nm}^{-1},t)$.

i.e., $q=18\ \text{nm}^{-1}$ and $q=28\ \text{nm}^{-1}$ and in each figure $\tau^{-1/\gamma}(T)$ is shown for all examined correlation functions (i.e., $l\leqslant 2$, $-l\leqslant m\leqslant l$, and $-l\leqslant n\leqslant l$). Data in Fig. 11 suggest that, as previously observed for the center of mass and q-independent rotational correlators, the power law (33) is well satisfied with the same ''universal'' values of the critical exponent $\gamma=2.7$ and of the critical temperature $T_c=200\pm 3$. We also note that the time scales for fixed T vary by about one decade as can be observed from the rather different slopes. This analysis strongly confirms the MCT and MMCT prediction of the existence of a unique critical temperature T_c at which both translational and rotational degrees of freedom cross from an ergodic to a nonergodic dynamics following a power law behavior ruled by an ''universal'' exponent γ. Thus, MMCT seems to be a good framework in order to describe qualitatively and semiquantitatively the temperature dependence of the structural correlations in a supercooled molecular liquid in a wide range of temperatures above a critical T_c, as defined by Eq. (33).

Data in Figs. 8, 9, and 10 show oscillations at short times connected with the librational and vibrational dynamics of the water molecules. These motions (with a characteristic time scale of the order of 0.1 ps) modulate the approach to the plateau and may interfere with the universal dynamics characteristic of the β region [45]. If the temperature is lowered very close to T_c, MCT provides quantitative predictions for the time evolution of the correlation function. We stress again that these predictions are the same for MMCT.

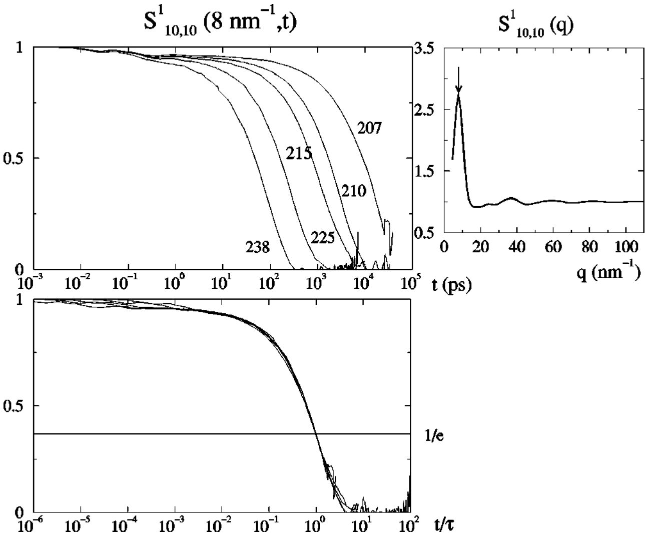

FIG. 10. Same as Fig. 8 for $S^1_{10,10}(q=8\ \text{nm}^{-1},t)$.

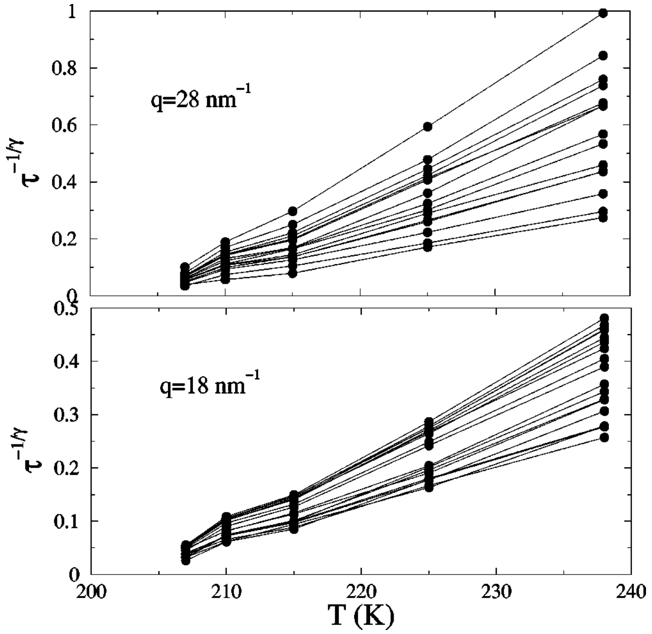

FIG. 11. α-relaxation time to the power $-1/\gamma$ for all correlation functions with $l\leqslant 2$, $-l\leqslant m\leqslant l$, and $-l\leqslant n\leqslant l$ at two different q-vector values. Lines are drawn to guide the eyes.

In the region of the first scaling law MMCT predicts for $S^m_{ln,l'n'}(q,t)$ the factorization of the time dependence from the dependence on q,l,n,l',n', and m, i.e., near to T_c its time dependence is given by the so-called β correlator $G(t)$, which describes the dynamics close to the plateau on a time scale $t_\sigma(T)$(β regime). The equation for $G(t)$ does not depend on q, l, n, l', n', and m; it involves only the exponent parameter λ. This equation, which is the same for MCT and MMCT, can be solved exactly in the asymptotic limits $t\ll t_\sigma$ and $t\gg t_\sigma$, yielding for both cases a power law dependence with exponent a (critical law) and exponent b (von Schweidler law), respectively. The first one describes the relaxation onto and the second one from the plateau.

The two exponents are both functions of λ according to [46]

$$\lambda=\frac{\Gamma(1-a)^2}{\Gamma(1-2a)}=\frac{\Gamma(1+b)^2}{\Gamma(1+2b)}, \tag{34}$$

where Γ is the Euler gamma function, and they are connected to the relaxation time exponent γ by the relation

$$\gamma=\frac{1}{2a}+\frac{1}{2b}. \tag{35}$$

MMCT provides an explicit expression for λ which contains the static molecular correlators at T_c [28].

The von Schweidler law, which also describes the early α-relaxation regime, is given by

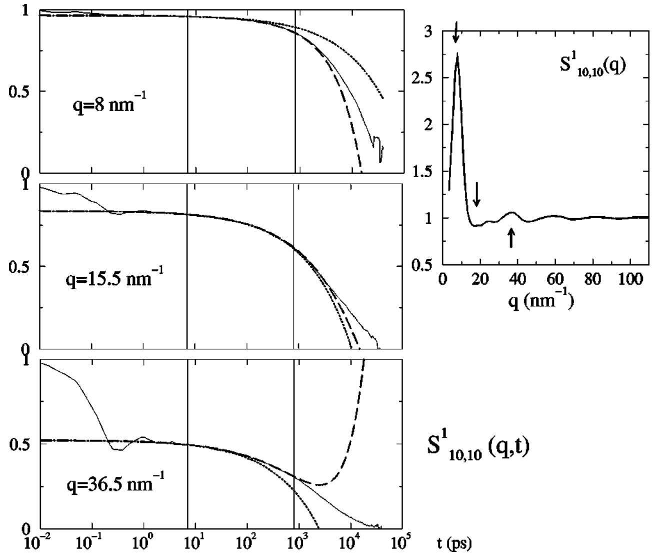

FIG. 12. Fit to Eq. (36) of the time dependence of $S^m_{ln,l'n'}(q,t)/S^m_{ln,l'n'}(q)$ for different q-vector values. The solid line represents the MD data whereas the dashed line and the dotted line are fits to the von Schweidler law with and without second order correction, respectively. The inset shows the corresponding static structure factor with an indication of the chosen q vectors (see arrows). This figure refers to $S^1_{10,10}(q,t)$.

$$S^m_{ln,l'n'}(q,t)-F^{m,c}_{ln,l'n'}(q)\cong -H^{(1)m}_{ln,l'n'}(q)\hat{t}^b+H^{(2)m}_{ln,l'n'}(q)\hat{t}^{2b}+O(\hat{t}^{3b}), \qquad (36)$$

where $F^{m,c}_{ln,l'n'}(q), H^{(1)m}_{ln,l'n'}(q)$, and $H^{(2)m}_{ln,l'n'}(q)$ are, respectively, the critical nonergodicity parameter, the critical amplitude, and the amplitude of the next to leading order correction for the unnormalized correlators. An explicit expression for $h^{(2)}(q)=H^{(2)}(q)/S(q)$ for simple liquids has recently been derived [47]. The time window in which the asymptotic power law $\hat{t}^b$ holds is strongly correlator and q dependent. Hence, to perform a careful MCT analysis it is always necessary to take into account the second order corrections also. This has previously been found for the center of mass correlator for water [34] and for the molecular correlators for diatomic molecules [26]. In order to test the validity of the von Schweidler law and the relevance of the second order corrections, we have fitted the time evolution of our correlators according to Eq. (36) for the lowest simulated temperature $T=207$ K, which is a few degrees above the critical temperature. In Figs. 12–15 we show the fits with Eq. (36) performed for some representative normalized diagonal correlators. The vertical lines indicate the time window selected for the fit, which has been chosen consistently with the previous fits for translational and q-independent correlators, i.e., t covers a range of two orders of magnitude, from 7 ps up to 800 ps. Figure 12 represents the fit with Eq. (36) using the value $b=0.5$ as previously found in the MCT study of the time dependence of self and collective center of mass correlators. We show the correlator $S^1_{10,10}(q,t)$ for three different values of the q vector, marked by arrows in the small graph representing the static $S^1_{10,10}(q)$. The solid line is the numerical curve, while the dashed line is the result of the fit.

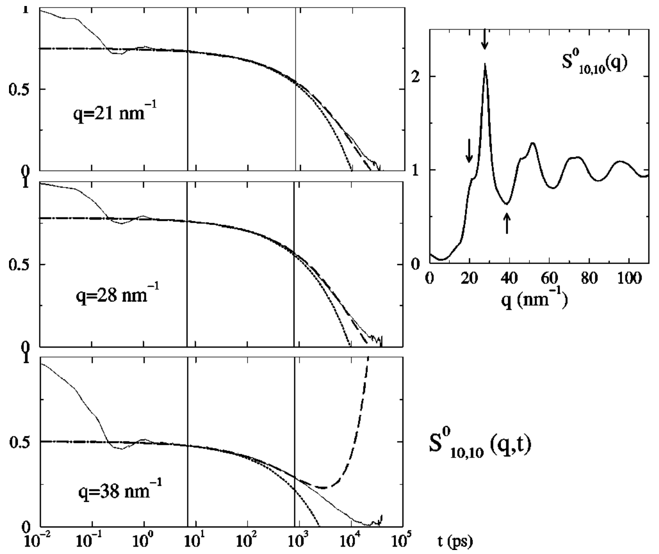

FIG. 13. Same as Fig. 12 for $S^0_{10,10}(q,t)$.

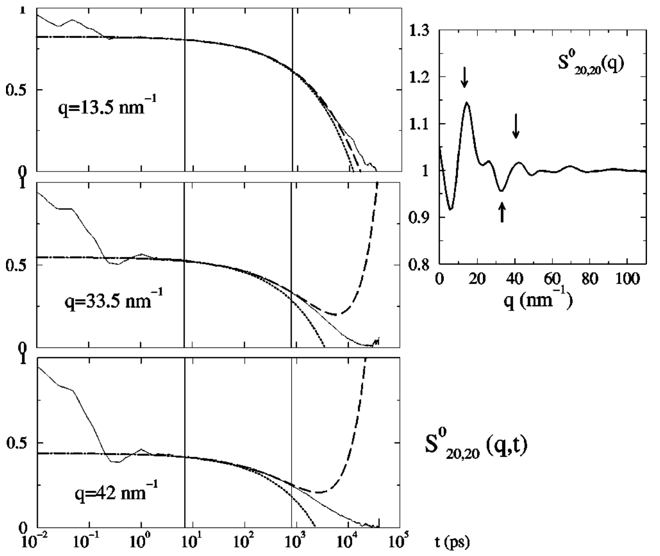

FIG. 14. Same as Fig. 12 for $S^0_{20,20}(q,t)$.

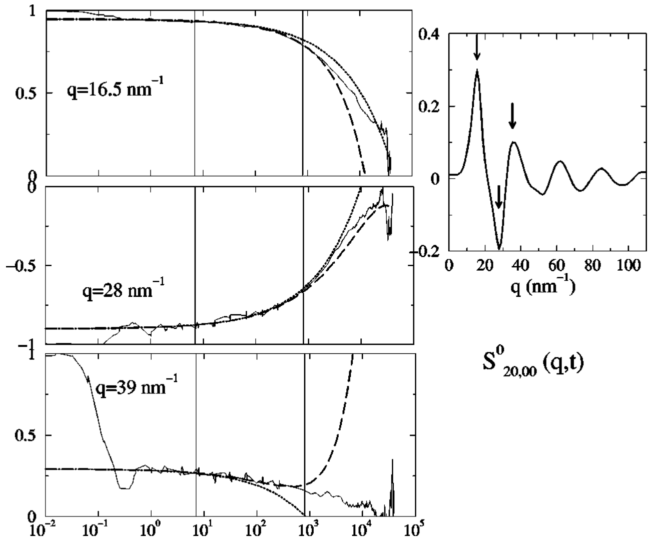

FIG. 15. Same as Fig. 12 for $S^0_{20,00}(q,t)$.

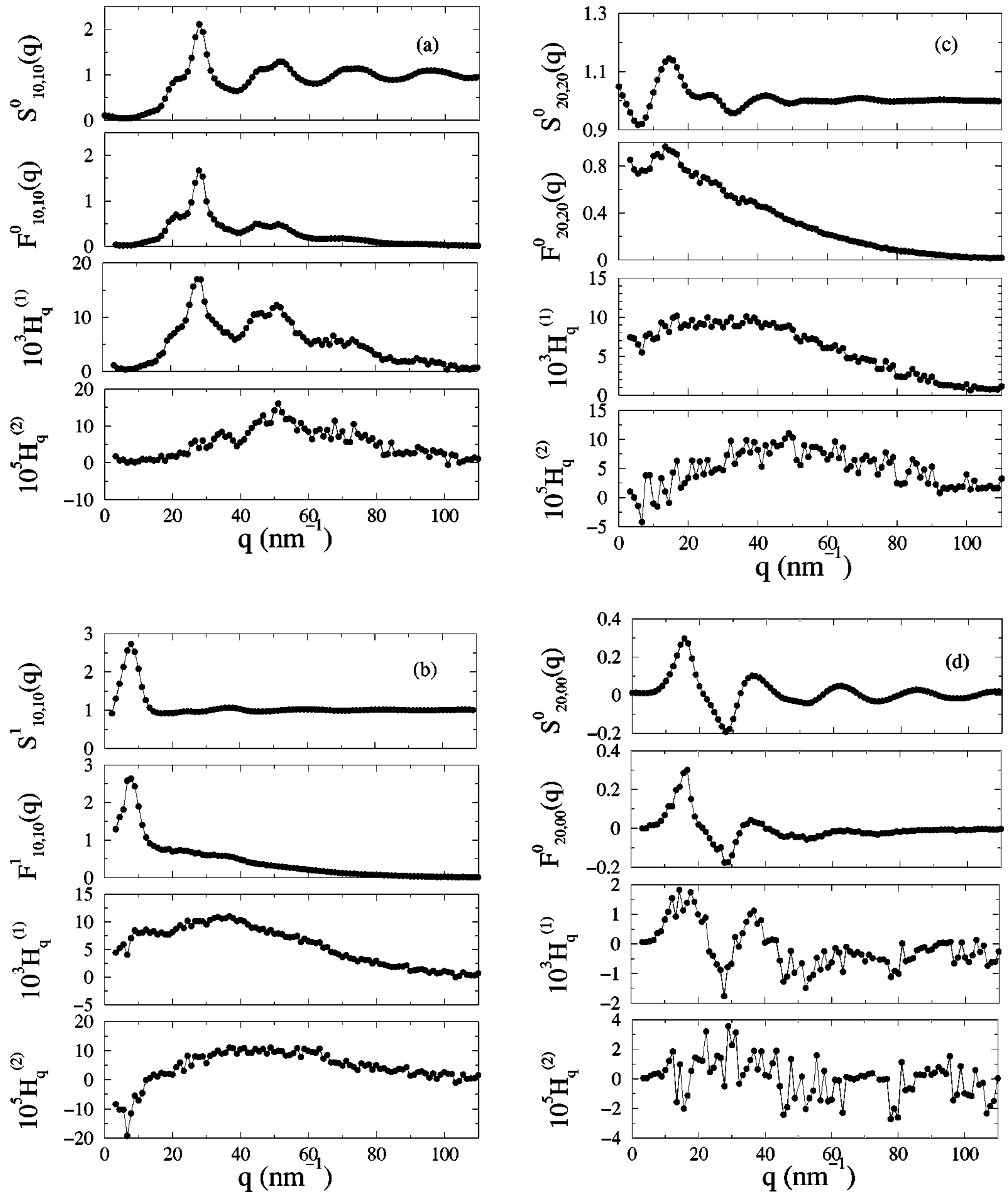

FIG. 16. Parameters of the fits shown in Figs. 12–15. The parameters refer to a fit of the unnormalized $S^m_{ln,l'n'}(q,t)$. Note that the statistical noise is large when the amplitude of the α relaxation is rather small.

The quality of the fit is remarkably good. The q dependence of the validity of the fit is evident, noting that for $q = 8\ \text{nm}^{-1}$ and $q = 15.5\ \text{nm}^{-1}$ the fitted von Schweidler law holds far above the fitting range, while for $q = 36.5\ \text{nm}^{-1}$ the two curves separate out of the fit window. To clarify the importance of the second order corrections we have also reported in the figure the curve obtained keeping only the term $\hat{t}^b$ (dotted line). We see that while in the case $q = 15.5\ \text{nm}^{-1}$ the first power law fit alone extends to almost three orders of magnitude, for the other values of q the second order corrections are necessary. The fitting parameters obtained, F, $H^{(1)}$, and $H^{(2)}$, are shown in Fig. 16 as functions of q together with the static structure factors. Analytic expressions for the calculation of these quantities are provided by MMCT (for the amplitude $H^{(2)}$ no explicit expression for the molecular system has been derived yet), so that they can be, in principle, calculated using the molecular static structure factors. For diatomic molecules this has been done for F and $H^{(1)}$ [28].

The fits to other correlators show similar behaviors. We want to stress that, according to MCT and MMCT predictions, in all the fits to Eq. (36) the same exponent b has turned out to be satisfactory. The independence of the power law exponent b of the chosen correlator and of the q value is a strong argument in favor of MMCT as a framework to describe the slow relaxation in supercooled molecular liquids. We also stress that the two independently calculated exponents b and γ satisfy the theoretical prediction of Eq. (35).

In view of a future comparison with the full time dependence of the MMCT correlations, we report in Fig. 17 the parameters of the fit to the numerical correlation function according to a stretched exponential form,

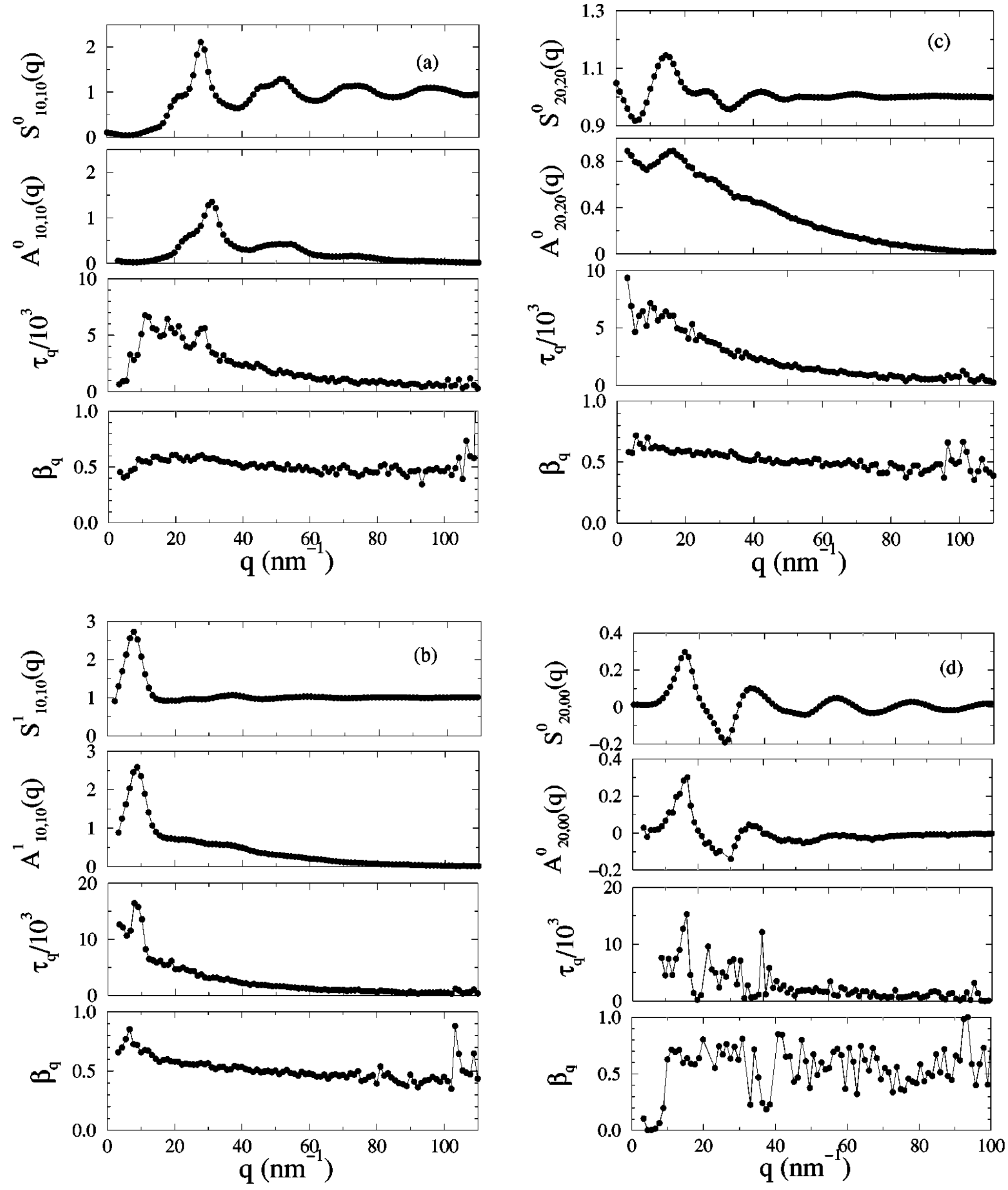

FIG. 17. Parameters of the fits to a stretched exponential function of the same correlators shown in Figs. 12–15. The parameters refer to a fit of the unnormalized $S^m_{ln,l'n'}(q,t)$. Note that the statistical noise is large when the amplitude of the α relaxation is rather small.

$$S^m_{ln,l'n'}(q,t)=A^m_{ln,l'n'}(q)\exp\left[-\left(\frac{t}{\tau^m_{ln,l'n'}(q,T)}\right)^{\beta^m_{ln,l'n'}(q)}\right]. \tag{37}$$

We note that in all cases examined the large-q-vector limit of the stretching parameter β is about 0.5, i.e., equal to the value of b. Such equivalence is predicted by MCT [48].

V. SUMMARY AND CONCLUSIONS

In this paper we have analyzed the slow relaxation properties of a supercooled liquid of planar rigid molecules described by means of a MD simulation. The parameters of the simulation have been chosen in such a way as to mimic the thermodynamic and dynamic properties of liquid water, a molecular liquid characterized by a network structure at low temperatures. Starting from the set of MD data we have calculated all the static and dynamic molecular structure factors $S^m_{ln,l'n'}(q,t)$ up to $l=2$ in the q frame. These correlators present a variety of features which open a deeper insight into the structural properties of the liquid. For example, the symmetries of the rotational correlators reflect the geometrical properties of the water molecules, while the peak distribution describes the intermolecular interactions. It becomes clear from an overview of the complete set of correlators that a theory able to describe the relaxational properties of a supercooled molecular liquid cannot neglect the molecular correlators with $l,l'\neq 0$ and their coupling to the center of mass correlator. For the static distinct part, at least at high temperatures, we have proved that it is independent of the sign of n and n' for molecules with C_{rv} symmetry. The MD results indicate that the independence even holds at lower temperatures (down to 207 K) within the numerical error.

In this article we argue that MCT in its molecular formulation is a good candidate to be the correct framework for the description of the slow dynamics in supercooled molecular liquids. In order to support this view we have compared the properties of our MD liquid to the universal predictions of MCT (or MMCT), which are independent of the molecular nature of the liquid. Even if the complete set of MMCT equations has not yet been solved, thus preventing a rigorous comparison between theory and simulation, we have tested several asymptotic MCT predictions. We have shown that the temperature and time dependence of our MD correlators perfectly obeys the time-temperature superposition principle predicted by MCT and MMCT, and we have found the MMCT ''universality,'' i.e., the critical temperature T_c and the exponents b and γ (and therefore also a) do not depend on q, l, n, l', n', and m.

Close to T_c, where the asymptotic β-correlator behavior is reinforced, we have compared the numerical correlator with the predicted von Schweidler law plus second order corrections in the early α region. We have shown good quality fits consistent with what was previously found for the self and collective dynamics of the center of mass alone and of the q-independent angular correlators. Again, the predicted relation (35) between the von Schweidler exponent and the relaxation time exponent is fulfilled, as well as the large-q-vector limit of the stretching exponent $\beta^{m}_{ln,l'n'}(q)$.

ACKNOWLEDGMENTS

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APPENDIX MOLECULES WITH C_{rv}–SYMMETRY

In this appendix we will investigate the validity of the $n \to -n$ symmetry for the *static* distinct part of the correlators [cf. Eq. (26)] for molecules with C_{rv} symmetry.

We consider a liquid of N identical, rigid molecules. Each molecule is made up of N_α atoms of type α, $\alpha=1,2,\ldots$. The position of atom ν_α of type α in the jth molecule is denoted by $\vec{x}^{(\alpha)}_{j,\nu_\alpha}$, $j=1,2,\ldots,N$, $\nu_\alpha=1,2,\ldots,N_\alpha$. Then, in a site-site representation the total potential energy V is given by

$$V(\{\vec{x}^{(\alpha)}_{j,\nu_\alpha}\})=\frac{1}{2}\sum_{j\neq j'}\sum_{\alpha,\alpha'}\sum_{\nu_\alpha,\nu'_{\alpha'}} v_{\alpha\alpha'}(|\vec{x}^{(\alpha)}_{j,\nu_\alpha}-\vec{x}^{(\alpha')}_{j',\nu'_{\alpha'}}|), \tag{A1}$$

where we restrict ourselves to two-body interactions with pair potential $v_{\alpha\alpha'}(\vec{x})$ between atoms of type α and α'. Introducing the microscopic molecular density for atoms of type α in molecule j,

$$\rho^{(\alpha)}_j(\vec{x})=\sum_{\nu_\alpha=1}^{N_\alpha}\delta(\vec{x}-\vec{x}^{(\alpha)}_{j,\nu_\alpha}), \tag{A2}$$

and its Fourier transform,

$$\rho^{(\alpha)}_j(\vec{q})=\sum_{\nu_\alpha=1}^{N_\alpha} e^{i\vec{q}\cdot\vec{x}^{(\alpha)}_{j,\nu_\alpha}}, \tag{A3}$$

we can rewrite Eq. (A1) as follows:

$$V(\{\vec{x}^{(\alpha)}_{j,\nu_\alpha}\})=\frac{1}{2}\sum_{j\neq j'}\sum_{\alpha,\alpha'}\int_V d^3x\int_V d^3x'\,\rho^{(\alpha)}_j(\vec{x})v_{\alpha\alpha'}\times(\vec{x}-\vec{x}')\rho^{(\alpha')}_{j'}(\vec{x}'), \tag{A4}$$

or by use of Eq. (A3)

$$V(\{\vec{x}^{(\alpha)}_{j,\nu_\alpha}\})=\frac{1}{2}\sum_{j\neq j'}\sum_{\alpha,\alpha'}\frac{1}{V}\sum_{\vec{q}}\rho^{(\alpha)*}_j(\vec{q})\tilde{v}_{\alpha\alpha'}(\vec{q})\rho^{(\alpha')}_{j'}(\vec{q}), \tag{A5}$$

with $\tilde{v}_{\alpha\alpha'}(\vec{q})=\int d^3x v_{\alpha\alpha'}(\vec{x})e^{i\vec{q}\cdot\vec{x}}$, the Fourier transform of the pair potential which depends on $q=|\vec{q}|$ and the volume V of the system only.

Instead of the site-site coordinates we introduce center of mass and relative coordinates:

$$\vec{x}_j=\left(\sum_\alpha m_\alpha\sum_{\nu_\alpha=1}^{N_\alpha}\vec{x}^{(\alpha)}_{j,\nu_\alpha}\right)\Bigg/\sum_\alpha N_\alpha m_\alpha \tag{A6}$$

and

$$\vec{r}^{(\alpha)}_{j,\nu_\alpha}=\vec{x}^{(\alpha)}_{j,\nu_\alpha}-\vec{x}_j, \tag{A7}$$

respectively. m_α is the mass of atoms of type α. Next we substitute Eqs. (A6) and (A7) into Eq. (A3), which leads to

$$\rho^{(\alpha)}_j(\vec{q})=e^{i\vec{q}\cdot\vec{x}_j}\tilde{\rho}^{(\alpha)}_j(\vec{q}) \tag{A8}$$

where

$$\tilde{\rho}^{(\alpha)}_j(\vec{q})=\sum_{\nu_\alpha=1}^{N_\alpha} e^{i\vec{q}\cdot\vec{r}^{(\alpha)}_{j,\nu_\alpha}}. \tag{A9}$$

Now, let $\{\vec{R}^{(\alpha)}_{\nu_\alpha}\}$ be the relative vectors in the body-fixed frame and $\Omega_j=(\phi_j,\theta_j,\chi_j)$ the Euler angles between the laboratory and the body-fixed frame. Then

$$\vec{r}^{(\alpha)}_{j,\nu_\alpha}=R^{-1}(\Omega_j)\vec{R}^{(\alpha)}_{\nu_\alpha} \tag{A10}$$

with $R(\Omega)\in \mathrm{SO}(3)$. Substitution of Eq. (A10) into Eq. (A9) and making use of the Rayleigh expansion [38], we arrive at

$$\tilde{\rho}^{(\alpha)}_j(\vec{q},\Omega_j)=4\pi\sum_{lm} i^l j_l(qR_\alpha)Y^*_{lm}(R(\Omega_j)\vec{e}_q)\sum_{\nu_\alpha=1}^{N_\alpha} Y_{lm}(\vec{e}^{(\alpha)}_{\nu_\alpha}), \tag{A11}$$

and with the transformation of the spherical harmonics under $R\in \mathrm{SO}(3)$ [38]

$$\tilde{\rho}^{(\alpha)}_j(\vec{q},\Omega_j)=4\pi\sum_{lm} i^l j_l(qR_\alpha)D^{l*}_{m'm}(\Omega_j)Y^*_{lm}(\vec{e}_q)\times\sum_{\nu_\alpha=1}^{N_\alpha} Y_{lm}(\vec{e}^{(\alpha)}_{\nu_\alpha}). \tag{A12}$$

$j_l(r)$ are the spherical Bessel functions, $D^{l}_{m'm}(\Omega)$ are Wigner's rotation matrices, $R_\alpha=|\vec{R}^{(\alpha)}_{\nu_\alpha}|$ for all ν_α, $\vec{e}^{(\alpha)}_{\nu_\alpha}$

$=\vec{R}^{(\alpha)}_{\nu_\alpha}/R_\alpha$, and $\vec{e}_q=\vec{q}/q$. The substitution of $\rho^{(\alpha)}_j(\vec{q})$ [Eq. (A8)] with $\tilde{\rho}^{(\alpha)}_j(\vec{q},\Omega_j)$ from Eq. (A12) into Eq. (A5) yields the center of mass angular representation of V:

$$V(\{\vec{x}^{(\alpha)}_{j,\nu_\alpha}\})\equiv V(\vec{x}_1,\ldots,\vec{x}_N;\Omega_1,\ldots,\Omega_N)$$
$$=\frac{1}{2}\sum_{j\neq j'}\frac{1}{V}\sum_{\vec{q}}\sum_{\substack{lmn\\ l'm'n'}}\tilde{v}_{lmn,l'm'n'}(\vec{q})$$
$$\times e^{-i\vec{q}\cdot(\vec{x}_j-\vec{x}_{j'})}D^l_{mn}(\Omega_j)D^{l'*}_{m'n'}(\Omega_{j'}), \tag{A13}$$

with the transformed pair potential

$$\tilde{v}_{lmn,l'm'n'}(\vec{q})=(4\pi)^2 i^{l'-l}Y_{lm}(\vec{e}_q)Y^*_{l'm'}(\vec{e}_q)$$
$$\times\sum_{\alpha\alpha'}\tilde{v}_{\alpha\alpha'}(q)j_l(qR_\alpha)j_{l'}(qR_{\alpha'})$$
$$\times\left(\sum_{\nu_\alpha=1}^{N_\alpha}Y_{ln}(\vec{e}^{(\alpha)}_{\nu_\alpha})\right)\left(\sum_{\nu'_{\alpha'}=1}^{N_\alpha}Y_{l'n'}(\vec{e}^{(\alpha')}_{\nu'_{\alpha'}})\right). \tag{A14}$$

The representation of V by Eq. (A13) is quite obvious, since the interaction potential $V_0(\vec{x},\Omega,\Omega')$ between two molecules with center of mass separation $\vec{x}$ and orientation Ω and Ω' can be expanded with respect to the complete set of functions $e^{i\vec{q}\cdot\vec{x}}D^l_{mn}(\Omega)D^{l'*}_{m'n'}(\Omega')$.

All the local molecular symmetry is contained in the coefficients $\tilde{v}_{lmn,l'm'n'}(\vec{q})$ through the entity

$$y^{(\alpha)}_{ln}=\sum_{\nu_\alpha=1}^{N_\alpha}Y_{ln}(\vec{e}^{(\alpha)}_{\nu_\alpha}), \tag{A15}$$

which will be discussed for C_{rv} symmetry. In the following we choose the body-fixed z axis along the molecular r-fold symmetry axes. First of all we note that the *r-fold rotational symmetry* implies

$$y^{(\alpha)}_{ln}=\begin{cases}\neq 0, & n\in\{0,\pm r,\pm 2r,\ldots\}\\ =0 & \text{otherwise.}\end{cases} \tag{A16}$$

Here we have assumed that all types of atoms $\alpha=1,2,\ldots$ have exactly an r-fold rotational symmetry. This is not necessary for a molecule with r-fold axes. There may be some types of atoms that have a $2r$-, $3r$-, fold, etc., symmetry. For such α, $y^{(\alpha)}_{ln}\neq 0$ for $n=\mu^{(\alpha)}r$ where $\mu^{(\alpha)}=2,3,\ldots$. Nevertheless, Eq. (A16) remains true since $\mu=\min_\alpha\mu^{(\alpha)}=1$, by assumption.

Now let us turn to the *reflection symmetry*. With $(\phi^{(\alpha)}_{\nu_\alpha},\theta^{(\alpha)})$ (where $\theta^{(\alpha)}$ does not depend on ν_α, due to the C_{rv} symmetry and the appropriate choice of the body-fixed z axis), we denote the azimuthal and polar angles of $\vec{e}^{(\alpha)}_{\nu_\alpha}$. For r even and fixed α the angles $\phi^{(\alpha)}_{\nu_\alpha}$ can be chosen such that the reflection symmetry with respect to the $(x$-$z)$ plane implies

$$\phi^{(\alpha)}_{N_\alpha-\nu_\alpha+1}=\pi-\phi^{(\alpha)}_{\nu_\alpha}+\lambda_{\nu_\alpha}2\pi \tag{A17}$$

for $\nu_\alpha=1,2,\ldots,N_\alpha$. The integer λ_{ν_α} may depend on ν_α. Using the explicit (ϕ,θ) dependence of $Y_{ln}(\vec{e})\equiv Y_{ln}(\theta,\phi)=c_{ln}P_{ln}(\theta)e^{in\phi}$ [38], we get from Eq. (A15) with Eq. (A17)

$$y^{(\alpha)}_{ln}=c_{ln}P_{ln}(\theta^{(\alpha)})\sum_{\nu_\alpha=1}^{N_\alpha}e^{in\phi^{(\alpha)}_{\nu_\alpha}}$$
$$=c_{ln}P_{ln}(\theta^{(\alpha)})(-1)^n\sum_{\nu_\alpha=1}^{N_\alpha}e^{-in\phi^{(\alpha)}_{N_\alpha-\nu_\alpha+1}}$$
$$=(-1)^n c_{ln}P_{ln}(\theta^{(\alpha)})\sum_{\nu_\alpha=1}^{N_\alpha}e^{-in\phi^{(\alpha)}_{\nu_\alpha}}$$
$$=\sum_{\nu_\alpha=1}^{N_\alpha}Y_{l\underline{n}}(\phi^{(\alpha)}_{\nu_\alpha},\theta^{(\alpha)})=y^{(\alpha)}_{l\underline{n}}, \tag{A18}$$

where $n=-n$. In the case that r is odd a similar choice of $\phi^{(\alpha)}_{\nu_\alpha}$ can be made, such that Eq. (A18) holds. Due to Eq. (A18) we find that the coefficients $\tilde{v}_{lmn,l'm'n'}(\vec{q})$ do not depend on the sign of n and n'. Therefore Eq. (A13) can also be rewritten as follows:

$$V(\vec{x}_1,\ldots,\vec{x}_N;\Omega_1,\ldots,\Omega_N)$$
$$=\frac{1}{8}\sum_{j\neq j'}\frac{1}{V}\sum_q\sum_{\kappa\kappa'}v_{\kappa\kappa'}(\vec{q})e^{-i\vec{q}\cdot(\vec{x}_j-\vec{x}_{j'})}[D_\kappa(\Omega_j)$$
$$+D_{\underline{\kappa}}(\Omega_j)][D_{\kappa'}(\Omega_{j'})+D_{\underline{\kappa}'}(\Omega_{j'})]^*, \tag{A19}$$

where $\kappa=(l,m,n),\kappa=(l,m,n)$, and $D_\kappa=D^l_{mn}$ has been used as a shorthand notation. Equation (A19) is the basic result that allows us to study the $n\rightarrow -n$ symmetry for the static distinct part of the correlators. From Eq. (A6) we get for $t=0$

$$S^{(d)}_{\kappa,\kappa'}(\vec{q})=i^{l'-l}[(2l+1)(2l'+1)]^{1/2}\frac{1}{N}$$
$$\times\sum_{k\neq k'}\frac{1}{Z_c}\int\prod_{j=1}^{N}(d^3x_j d\Omega_j)$$
$$\times e^{-i\vec{q}\cdot(\vec{x}_k-\vec{x}_{k'})}D_\kappa(\Omega_k)D^*_{\kappa'}(\Omega_{k'})$$
$$\times e^{-\beta V(\vec{x}_1,\ldots,\vec{x}_N;\Omega_1,\ldots,\Omega_N)}, \tag{A20}$$

where Z_c is the configurational partition function. Now we expand $\exp(-\beta V)$ into a power series. The zeroth order term of $S^{(d)}_{\kappa,\kappa'}(\vec{q})$ is proportional to $\delta_{n0}\delta_{n'0}$, which in a trivial sense is invariant under n or n' into $-n$ or $-n'$, for arbitrary $\vec{q}$, l, m, l', and m'. For the first order term we find with Eq. (A19)

$$(S^{(d)}_{\kappa,\kappa'}(\vec{q}))_{1.\text{order}}\propto\tilde{v}_{\kappa,\kappa'}(\vec{q}), \tag{A21}$$

where the factor of proportionality is independent of m, m', n, and n'. Since $\tilde{v}_{\kappa,\kappa'}$ does not depend on the sign of n and n' for all $\vec{q}$, l, m, l', and m', the same is true for $S^{(d)}_{\kappa,\kappa'}(\vec{q})$ in first order. In second and higher order, products of the rotation matrices occur. In the μth order contributions of type

$$\frac{1}{V^{\nu}}\sum_{q_1,\ldots,q_\nu}\sum_{\substack{\kappa_1,\ldots,\kappa_\nu\\ \kappa_1',\ldots,\kappa_\nu'}}\tilde{v}_{\kappa_1,\kappa_1'}(\vec{q}_1)\cdots\tilde{v}_{\kappa_\nu,\kappa_\nu'}(\vec{q}_\nu)$$
$$\times e^{-i(\vec{q}_1+\cdots+\vec{q}_\nu)(\vec{x}_j-\vec{x}_{j'})}D_{\kappa_1}(\Omega_j)\cdots D_{\kappa_\nu}(\Omega_j)$$
$$\times D^{*}_{\kappa_1'}(\Omega_{j'})\ldots D^{*}_{\kappa_\nu'}(\Omega_{j'}) \qquad \text{(A22)}$$

occur with $\nu\leqslant\mu$. For $\nu=1$ this coincides with the first order contribution. Using the product rule for the D's, we get for $\nu=2$ a contribution to $S^{(d)}_{\kappa,\kappa'}(\vec{q})$ that is proportional to

$$A^{(2)}_{\kappa\kappa'}(\vec{q})\equiv\frac{1}{V}\sum_{q_1q_2}{}'\sum_{\substack{\kappa_1\kappa_1'\\ \kappa_2\kappa_2'}}\mathcal{C}(\kappa_1\kappa_2\kappa)\mathcal{C}(\kappa_1'\kappa_2'\kappa')$$
$$\times\tilde{v}_{\kappa_1\kappa_1'}(\vec{q}_1)\tilde{v}_{\kappa_2\kappa_2'}(\vec{q}_2), \qquad \text{(A23)}$$

where $\Sigma'_{q_1q_2}$ denotes summation over $\vec{q}_1$ and $\vec{q}_2$ such that $\vec{q}_1+\vec{q}_2=\vec{q}$, and

$$\mathcal{C}(\kappa_1\kappa_2\kappa)=C(l_1l_2l;m_1m_2m)C(l_1l_2l;n_1n_2n) \qquad \text{(A24)}$$

is a product of Clebsch-Gordan coefficients. Then it follows from Eq. (A23) with the properties of $C(l_1l_2l;n_1n_2n)$ [38] that

$$A^{(2)}_{\underline{\kappa}\kappa'}(\vec{q})\equiv\frac{1}{V}\sum_{q_1q_2}{}'\sum_{\substack{\kappa_1\kappa_1'\\ \kappa_2\kappa_2'}}(-1)^{l_1+l_2+l}\mathcal{C}(\kappa_1\kappa_2\kappa)\mathcal{C}(\kappa_1'\kappa_2'\kappa')$$
$$\times\tilde{v}_{\kappa_1\kappa_1'}(\vec{q}_1)\tilde{v}_{\kappa_2\kappa_2'}(\vec{q}_2), \qquad \text{(A25)}$$

where we have used the independence of $\tilde{v}_{\kappa_1\kappa_1'}$ and $\tilde{v}_{\kappa_2\kappa_2'}$ of the sign of n_1 and n_2. First of all, we observe that all terms in the sum of Eq. (A25) with l_1+l_2+l even coincide with the corresponding terms in Eq. (A23), independent of $\vec{q}$, m_1, and m_2. Hence for those terms the $n\to-n$ symmetry holds for arbitrary $\vec{q}$, l_1, m_1, l_2, and m_2, provided l_1+l_2+l is even. On the other hand, choosing $m=0$ and $\vec{q}=\vec{q}_0=(0,0,q)$($q$ frame) and changing $m_1\to-m_1$, $m_2\to-m_2$, we find

$$A^{(2)}_{\underline{\kappa}\kappa'}(\vec{q})=\frac{1}{V}\sum_{q_1q_2}{}'\sum_{\substack{\kappa_1\kappa_1'\\ \kappa_2\kappa_2'}}\mathcal{C}(\kappa_1\kappa_2\kappa)\mathcal{C}(\kappa_1'\kappa_2'\kappa')$$
$$\times\tilde{v}_{\overline{\kappa}_1\kappa_1'}(\vec{q}_1)\tilde{v}_{\overline{\kappa}_2\kappa_2'}(\vec{q}_2), \qquad \text{(A26)}$$

where $\overline{\kappa}=(l,m,n)$. The $(\vec{q}_1m_1,\vec{q}_2m_2)$ dependence of $\tilde{v}_{\overline{\kappa}_1\kappa_1'}(\vec{q}_1)\tilde{v}_{\overline{\kappa}_2\kappa_2'}(\vec{q}_2)$ is given by [cf. Eq. (A14)],

$$Y_{l_1\underline{m}_1}(\vec{e}_{q_1})Y_{l_2\underline{m}_2}(\vec{e}_{q_2})\propto e^{-i(m_1\phi_1+m_2\phi_2)}=e^{im_1(\phi_2-\phi_1)} \qquad \text{(A27)}$$

where $0=m=m_1+m_2$ has been used. The azimuthal angles ϕ_1 and ϕ_2 of $\vec{e}_{q_1}$ and $\vec{e}_{q_2}$ fulfill $\phi_2-\phi_1=\pi$ due to $\vec{q}_0\vec{e}_{q_1}+\vec{q}_0\vec{e}_{q_2}=0$, i.e., the right-hand side of Eq. (A27) equals $(-1)^{m_1}$, which does not depend on the sign of m_1. Therefore we find that $Y_{l_1\underline{m}_1}(\vec{e}_{q_1})Y_{l_2\underline{m}_2}(\vec{e}_{q_2})=Y_{l_1m_1}(\vec{e}_{q_1})Y_{l_2m_2}(\vec{e}_{q_2})$ and accordingly that

$$\tilde{v}_{\overline{\kappa}_1\kappa_1'}(\vec{q}_1)\tilde{v}_{\overline{\kappa}_2\kappa_2'}(\vec{q}_2)=\tilde{v}_{\kappa_1\kappa_1'}(\vec{q}_1)\tilde{v}_{\kappa_2\kappa_2'}(\vec{q}_2). \qquad \text{(A28)}$$

Making use of Eq. (A28), we get from Eq. (A26) that

$$A^{(2)}_{\kappa\kappa'}(\vec{q}_0)=A^{(2)}_{\underline{\kappa}\kappa'}(\vec{q}_0) \qquad \text{(A29)}$$

for all κ' and κ with $m=0$. We see that the $n\to-n$ (or $n'\to-n'$) symmetry of all the second order contributions holds only in the q frame and for $m=m'=0$.

Besides $A^{(2)}_{\kappa\kappa'}(\vec{q})$, in third order there also exist contributions of type

$$A^{(3)}_{\kappa\kappa'}(\vec{q})=\frac{1}{V^2}\sum_{q_1q_2q_3}{}''\sum_{\substack{\kappa_1\kappa_2\kappa_3\\ \kappa_1'\kappa_2'\kappa_3'}}(\cdots)\tilde{v}_{\kappa_1\kappa_1'}(\vec{q}_1)$$
$$\times\tilde{v}_{\kappa_2\kappa_2'}(\vec{q}_2)\tilde{v}_{\kappa_3\kappa_3'}(\vec{q}_3), \qquad \text{(A30)}$$

where $(\cdots)$ contains products of $\mathcal{C}$'s, and the sum over $\vec{q}_1,\vec{q}_2$, and $\vec{q}_3$ is restricted to $\vec{q}_1+\vec{q}_2+\vec{q}_3=\vec{q}$. For $\vec{q}=\vec{q}_0$ and $m=0$ the same procedure as for $\nu=2$ can be used in order to prove that the $n\to-n$ symmetry will be true if the threefold product of the $\tilde{v}$'s in Eq. (A29) is invariant under $m_i\to-m_i$, $i=1,2,3$. This requires that (in analogy to the $\nu=2$ case)

$$e^{-i(m_1\phi_1+m_2\phi_2+m_3\phi_3)}=e^{i(m_1\phi_1+m_2\phi_2+m_3\phi_3)}. \qquad \text{(A31)}$$

Although $0=m=m_1+m_2+m_3$, the azimuthal angles ϕ_i of $\vec{e}_{q_i}$ (in contrast to $\nu=2$) are not restricted because $\Sigma_{i=1}^{3}\vec{q}_0\cdot\vec{q}_i=0$ does not fix ϕ_3 if ϕ_1 and ϕ_2 are given. Therefore the generic case for $\vec{q}_i$ obeying $\Sigma_{i=1}^{3}\vec{q}_0\cdot\vec{q}_i=0$ will not satisfy Eq. (A30). But, similar to the $\nu=2$ case, there is a subset of terms in the sum of Eq. (A29) that will be invariant under $n\to-n$ (or $n'\to-n'$) for *all* $\vec{q}$, l, m, l', and m'.

The results show that the invariance of $S^{(d)}_{lmn,l'm'n'}(\vec{q})$ for arbitrary $(\vec{q},l,m,l',m')$ and for $(\vec{q}=\vec{q}_0,l,l',m=m'=0)$ only holds up to, respectively, the first and second orders in $1/k_BT$.

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