Test of mode coupling theory for a supercooled liquid of diatomic molecules.
II. q-dependent orientational correlators

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Using molecular-dynamics computer simulations, we study the dynamics of a molecular liquid by means of a general class of time-dependent correlators $S_{ll'}^m(q,t)$, which explicitly involve translational (TDOF) and orientational degrees of freedom (ODOF). The system is composed of rigid, linear molecules with Lennard-Jones interactions. The q dependence of the static correlators $S_{ll'}^m(q)$ strongly depends on l, l', and m. The time-dependent correlators are calculated for $l=l'$. A test of some of the predictions of mode coupling theory (MCT) is performed for $S_{ll}^m(q,t)$ for $l=1,2$ and its self-part $S_{ll}^{(s)m}(q,t)$, for $l=1,\ldots,6$. We find a clear signature for the existence of a single temperature T_c, at which the nature of the dynamics changes significantly. In the first scaling law regime of MCT it is found that the various correlators can be fitted with the β correlator $G(t)$, with the exception of those with $l=1$. Since this is true for the same exponent parameter λ as obtained for the TDOF, we thus find that MCT gives a consistent description of the dynamics of the TDOF as well as the one of the ODOF, with the exception of $l=1$. This different behavior for $l\neq1$ and $l=1$ can also be seen from the corresponding susceptibilities $(\chi'')_{ll}^m(q,\omega)$, which exhibit a minimum at about the same frequency $\omega_{\min}$ for all q and all $l\neq1$, in contrast to $(\chi'')_{11}^m(q,\omega)$ for which $\omega'_{\min}\approx10\omega_{\min}$. The asymptotic regime, for which the first scaling law holds, shrinks with increasing l. The second scaling law of MCT (time-temperature superposition principle) is reasonably fulfilled for $l\neq1$ but not for $l=1$. Furthermore, we show that the q and (l,m) dependence of the self-part approximately factorizes, i.e., $S_{ll}^{(s)m}(q,t) \cong C_l^{(s)}(t)F_s(q,t)$ for all m. [S1063-651X(98)02808-6]

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I. INTRODUCTION

In the past few years quite a few papers were published in which computer simulations were used to study the time dependence of the *translational* degrees of freedom (TDOF) in supercooled liquids. On the other hand, the *orientational* degrees of freedom (ODOF) were so far investigated in much less detail since the simulation and data analysis of systems in which the particles are molecules are quite a bit more involved than the ones in which the particles have no structure. However, since most real materials are of molecular nature and since experimental methods such as light scattering or dielectric measurements probe also the ODOF, it is important to understand how the dynamics of the TDOF and the ODOF are related to each other. Only by understanding this relationship will it be possible to make a correct interpretation of the experimental measurements and to gain insight into the nature of the glass transition, i.e., the dramatic slowing down of the relaxation dynamics of supercooled liquids upon approaching the glass transition temperature. A more thorough discussion of these connections can be found, e.g., in Ref. [1], where we also review some of the other work in this field.

Very recently we have carried out a molecular-dynamics computer simulation of a simple molecular system in order to make a detailed comparison between the dynamics of the TDOF and the ODOF [1]. Each molecule in this system is dumb-bell shaped and consists of two Lennard-Jones particles that are separated by a fixed distance d. More details on the system and the simulation can be found in Ref. [1]. In that paper we studied the time and temperature dependence

of the orientational correlation functions

$$C_l(t)=\frac{1}{N}\sum_{n,n'}\langle P_l(\vec{u}_n(0)\cdot\vec{u}_{n'}(t))\rangle, \quad l\geq1, \tag{1}$$

and the self-part $C_l^{(s)}(t)$. Here, $\vec{u}_n(t)$ is the unit vector pointing along the molecular symmetry axis of molecule n and $P_l(x)$ is the lth Legendre polynomial. The relevance of these types of correlation functions is given by the fact that they can be measured in experiments. The main results of that paper were that the temperature dependence of the relaxation times of C_l, $C_l^{(s)}$ and the diffusion constant D were given by a power law with the same critical temperature T_c but with critical exponents that depend on the observable. In addition, we showed that the so-called time temperature superposition principle works well for $C_l^{(s)}$, if $l>2$. Thus we concluded that many of the predictions of mode coupling theory (MCT) [2,3] hold for these correlation functions, although certain discrepancies are present.

In the preceding paper, subsequently called KKS-I, we have investigated the time and temperature dependence of the *translational* degrees of freedom by studying quantities such as the van Hove correlation function $G_s(r,t)$ and the intermediate scattering function $F(q,t)$ [4]. The main conclusion of that paper was that MCT is able to give also a good description for the time and temperature dependence of these correlation functions.

As we will demonstrate below, the intermediate scattering function $F(q,t)$ and the orientational correlation functions $C_l(t)$ are just a special case of a more general type of correlation function, which involves the translational as well as

the orientational degrees of freedom at finite wave vector $\vec{q}$, i.e., $|\vec{q}|>0$. The goal of the *present* paper is therefore to investigate the time and temperature dependence of these more general correlation functions, since it is these correlators that are needed for a more detailed description of the dynamics of a molecular system. In addition, these correlation functions can also be calculated directly within the framework of MCT (although such a calculation might in practice be quite involved) thus allowing to perform a more stringent test of whether MCT is able to give a correct description of the dynamics of the system investigated.

Our paper is organized as follows: In the next section we will introduce the mentioned generalized correlation functions and will discuss some of their properties. Section III presents the results and the MCT analysis and the final section contains a summary and our main conclusions.

II. CORRELATION FUNCTIONS

We introduce a set of correlators that involves the one-particle density and the angular dependence for a molecular liquid of rigid, axially symmetric molecules:

$$\rho(\vec{x},\Omega,t)=\sum_{n=1}^{N}\delta(\vec{x}-\vec{x}_n(t))\delta(\Omega,\Omega_n(t)), \qquad (2)$$

where $\vec{x}_n(t)$ and $\Omega_n(t)\equiv(\theta_n(t),\phi_n(t))$ denote the center of mass position and the orientation of the nth molecule at time t, respectively. Due to the non-Euclidean metric for the angles θ and ϕ, one must use the invariant delta function $\delta(\Omega,\Omega')$. For this and other details of the theoretical description of molecular liquids, the reader is referred to the textbook by Gray and Gubbins [5]. Expansion of $\rho(\vec{x},\Omega,t)$ with respect to a product of plane waves and spherical harmonics $Y_{lm}(\Omega)$ leads to the tensorial density modes

$$\rho_{lm}(\vec{q},t)=i^l\sqrt{4\pi}\sum_{n=1}^{N}e^{i\vec{q}\cdot\vec{x}_n(t)}Y_{lm}(\Omega_n(t)), \qquad (3)$$

where $l=0,1,2,\dots$ and $-l\leq m\leq l$. The factor $\sqrt{4\pi}$ is used so that $\rho_{00}(\vec{q},t)$ equals the definition of $\rho(\vec{q},t)$ for simple liquids and i^l is introduced for convenience (see below). The corresponding correlators

$$S_{lm,l'm'}(\vec{q},t)=\frac{1}{N}\langle\delta\rho_{lm}^*(\vec{q},t)\delta\rho_{l'm'}(\vec{q},0)\rangle \qquad (4)$$

of the fluctuation $\delta\rho_{lm}(\vec{q},t)=\rho_{lm}(\vec{q},t)-\langle\rho_{lm}(\vec{q},t)\rangle$ vanish for $(q,l,m)=(0,0,0)$, and are otherwise given by

$$S_{lm,l'm'}(\vec{q},t)=\frac{4\pi}{N}i^{l'-l}\sum_{n,n'}\langle\exp\{-i\vec{q}\cdot[\vec{x}_n(t)-\vec{x}_{n'}(0)]\}$$
$$\times Y_{lm}^*(\Omega_n(t))Y_{l'm'}(\Omega_{n'}(0))\rangle, \qquad (5)$$

which shows the explicit dependence on both the TDOF and the ODOF. Its corresponding self-part $S_{lm,l'm'}^{(s)}(\vec{q},t)$ is obvious.

Taking into account that $Y_{00}=1/\sqrt{4\pi}$, one obtains from Eq. (5)

$$\frac{S_{00,00}(\vec{q},t)}{S_{00,00}(\vec{q})}=F(q,t), \qquad (6)$$

i.e., the normalized density correlator for the center of mass positions, which was studied in KKS-I. On the other hand, we find from Eq. (5) for $\vec{q}=0$,

$$S_{lm,l'm'}(0,t)=C_l(t)\delta_{mm'}\delta_{ll'}. \qquad (7)$$

Here the addition theorem for the spherical harmonics [5] and the isotropy have been used. As already mentioned in the Introduction, this special case was investigated in Ref. [1]. Equations (6) and (7) hold for the corresponding self-part as well.

Although it is not obvious how these correlators for $l,l' \neq 0$ can be measured in real experiments for $\vec{q}\neq0$, they are the basic quantities that enter the MCT for a molecule in a simple liquid [6] and for molecular liquids [7–11]. To our knowledge, there exists only one computer simulation that considers q-dependent orientational correlators [12]. But the experimental relevance of the correlators considered in Ref. [12] is unclear. The correlators given in Eq. (5) simplify a bit, if one uses the q frame [5], i.e., $\vec{q}=\vec{q}_0\equiv(0,0,q)$. In that case one obtains [8]

$$S_{lm,l'm'}(\vec{q}_0,t)\equiv S_{ll'}^m(q,t)\delta_{mm'}, \qquad (8)$$

which differ from zero only for $0\leq|m|\leq\min(l,l')$. Since $S_{ll'}^m(q,t)=S_{ll'}^{-m}(q,t)$, one can restrict oneself to $m\geq0$. The introduction of i^l in Eq. (3) makes $S_{ll'}^m(q,t)$ a real quantity. The same properties hold for the self-part as well. In the following we will present all results in the q frame.

Some of the equations that we will subsequently make use of have been given in KKS-I and are not reproduced here. We will refer to Eq. (n) of that paper by (I-n).

III. RESULTS

This section is subdivided into two parts. The first part contains the results for the static correlators $S_{ll'}^m(q)$, and the second one presents the dynamical correlators $S_{ll'}^m(q,t)$ and $S_{ll'}^{(s)m}(q,t)$. In the following we restrict the values of l and l' to 0, 1, and 2.

A. Static properties

The static correlators are shown in Figs. 1–3 for $T=0.477$, the lowest investigated temperature. First of all, it becomes obvious from these figures that $S_{ll'}^m(q=0)$ is m-independent and diagonal in l and l', as it should be due to isotropy. A comparison of the various diagonal correlators in Figs. 1 and 2 with each other shows that the correlators $S_{ll}^0(q)$ for $l=1$ and 2 possess a significant q dependence similar to that of $S(q)\equiv F(q,0)$, in contrast to those for $m\neq0$. The same behavior was found for a system of dipolar hard spheres [8], although for that system the most prominent peak occurs for $S_{ll}^1(q)$ at $q=0$. In contrast to $S(q)$ and $S_{11}^0(q)$, the correlator $S_{22}^0(q)$ has a rather broad maximum at $q=0$ with a height that is comparable to that at $q'_{max}\approx7.3$,
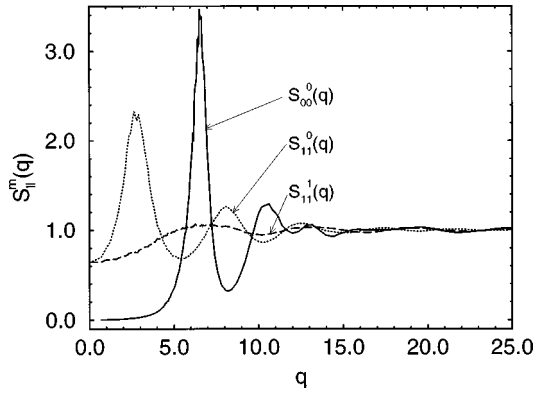
FIG. 1. Wave-vector dependence of static correlation functions for $T=0.477$. $S(q) \equiv S_{00}^0(q)$ (solid line), $S_{11}^m(q)$ for $m=0$ (dotted line), and $m=1$ (dashed line).

the location of the main peak in $S_{22}^0(q)$. In Fig. 3 we present the nondiagonal correlators $S_{ll'}^m(q)$ with $l \neq l'$. First of all one recognizes that $S_{02}^0(q)$ is much larger than $S_{01}^0(q)$ and $S_{12}^m(q)$. This can easily be understood. If the molecules had "head-tail" symmetry, then it can be shown that $S_{ll'}^m(q) \equiv 0$, for l,l' such that $l+l'$ is odd. Since for our molecules this symmetry is only slightly broken, we expect $S_{ll'}^m(q)$ to be much smaller for $l+l'$ odd than for $l+l'$ even.

The second point one recognizes from this figure is that the nondiagonal correlators $S_{ll'}^m(q)$ can have the same magnitude as the diagonal ones. Hence, there is no reason why the former should be neglected in analytical calculations. For example, since the solutions of the MCT equations for the time-dependent correlators $S_{ll'}^m(q,t)$ are determined by the static correlators $S_{ll'}^m(q)$ [8], it might not be a good approximation to consider $l=l'$, only.

B. Dynamical properties

We have investigated both the self-correlators for $l=l' = 0,1,\ldots,6$ and the collective correlators for $l=l' = 0, 1,$ and 2. Let us start with the self-part $S_{ll}^{(s)m}(q,t)$. Often it is assumed (see, e.g., Ref. [13]) that the q and (l,m) dependence (where $l=l'$) factorizes, i.e.,

$$S_{ll}^{(s)m}(q,t) \cong C_l^{(s)}(t) F_s(q,t) \qquad (9)$$
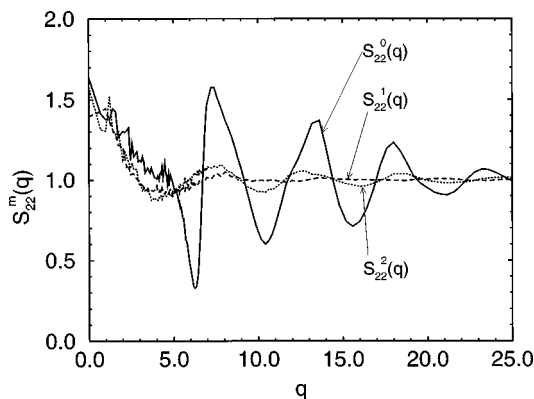

FIG. 2. $S_{22}^m(q)$ versus q for $T=0.477$ and $m=0$ (solid line), $m=1$ (dashed line), and $m=2$ (dotted line).
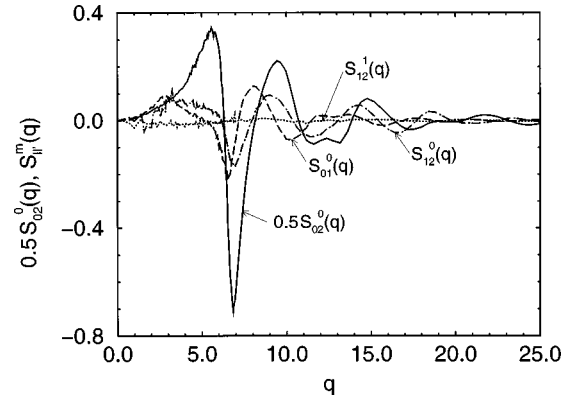

FIG. 3. $0.5 S_{02}^0(q)$ (solid line), $S_{01}^0(q)$ (dashed line), $S_{12}^0(q)$ (dashed dotted line), and $S_{12}^1(q)$ (dotted line) versus q for $T = 0.477$.

with $C_l^{(s)}(t)$ the self-part of Eq. (1) and $F_s(q,t) \equiv S_{00}^{(s)0}(q,t)$ the self-part of Eq. (6). The reader should note that Eq. (9) is assumed to hold for all m, and that the factorization is trivial for $q=0$. To check the validity of Eq. (9) for $q>0$, we show $S_{ll}^{(s)m}(q,t)$ and $C_l^{(s)}(t)F_s(q,t)$ in Fig. 4 ($l=1$) and Fig. 5 ($l=2$) for three different q values and $T=0.477$. Although the factorization becomes worse with increasing q, it is still a reasonable approximation, even for $q=10.6$. Furthermore, the quality of the factorization is better in the β-relaxation than in the α-relaxation regime (at least for $l=2$), and it also becomes better with increasing temperature.

This approximate factorization does not necessarily mean that the coupling between the TDOF and ODOF is very weak. The comparison of $C_l^{(s)}(t)$ with $F_s(q,t)$ in Fig. 4 and Fig. 5 reveals the reason why $S_{ll}^{(s)m}(q,t)$ can be approximately factorized. For instance, $C_1^{(s)}(t)$ has decayed to 0.1 for $t \cong 2 \times 10^4$, whereas at this time the value of $F_s(q=2.8,t)$ is still around 0.85, i.e., the ODOF relax much faster than the TDOF. This is consistent with our observation that in the time span of the orientational correlation time, as deduced from $C_1^{(s)}(t)$ at the lowest temperature, the average center of mass positions change only a fraction (about 30%) of the mean distance between the molecular centers. We stress that this is different from the MD simulation of supercooled water. There, $F_s(q,t)$ and $C_l(t)$ relax on approximately the same time scale [14].

We now turn to the test of the various MCT predictions (see KKS-I). We find [15] that $S_{11}^{(s)m}(q,t)$ do not obey the second scaling law, i.e., the time-temperature superposition principle. This observation has already been made for the case $q=0$ [1], which shows that this type of correlation function does not follow the predictions of MCT. This situation is different for the correlation function $S_{ll}^{(s)m}(q,t)$ with $l \geq 2$, for which the second scaling law holds reasonably well. The critical exponents (which are practically independent of q) for the divergence of the relaxation time, $\gamma_1^{(s)}$ and $\gamma_2^{(s)}$, are 1.8 and 2.45, respectively, where the latter value is fairly close to the one found for the TDOF, $F_s(q,t)$, which was 2.56 [4]. The exceptional role for the correlators with $l=1$ is due to the existence of 180° jumps of the molecular axis [1], since the Legendre polynomial $P_1(\cos\theta)$ is sensitive on reorientations by 180°. The same is true for all $P_l(\cos\theta)$ with l odd. But the weight of $P_l(\cos\theta)$ for $\theta \approx 0°$ and $\theta \approx 180°$
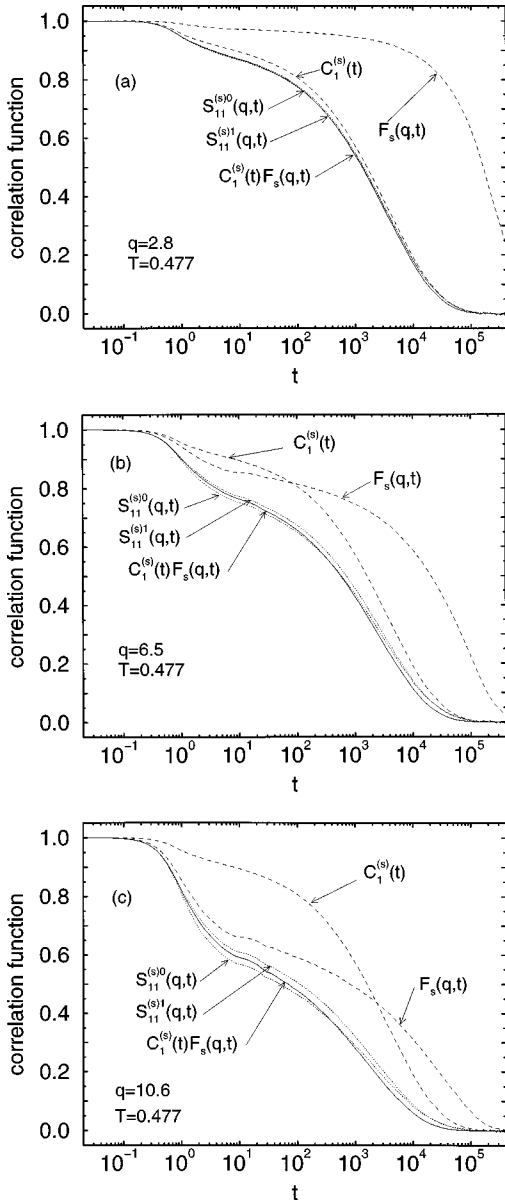
FIG. 4. $S_{11}^{(s)m}(q,t)$ for $m=0,1$ (dotted lines), $C_1^{(s)}(t)$ and $F_s(q,t)$ (dashed lines), and $C_1^{(s)}(t)F_s(q,t)$ (solid line) versus t for $T=0.477$ and (a) $q=2.8$, (b) $q=6.5$, (c) $q=10.6$.
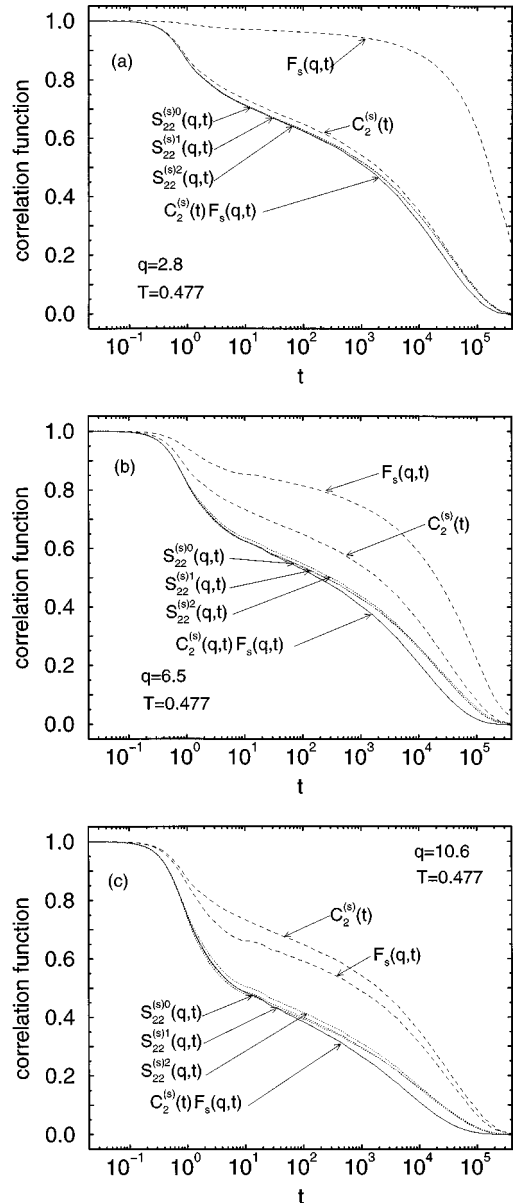
FIG. 5. $S_{22}^{(s)m}(q,t)$ for $m=0,1,2$ (dotted lines), $C_2^{(s)}(t)$ and $F_s(q,t)$ (dashed lines), and $C_2^{(s)}(t)F_s(q,t)$ (solid line) versus t for $T=0.477$ and (a) $q=2.8$, (b) $q=6.5$, (c) $q=10.6$.

decreases with increasing l. Since the second scaling law holds for $l \neq 1$, we can restrict ourselves in the following to the analysis of the correlation functions at the *lowest* temperature.

In Fig. 6 we investigate the validity of the first scaling law [Eq. (I-4)]. This is done for $q=0$ by fitting $C_l^{(s)}(t)$ with the critical correlator $G(t)$. We remind the reader that this fit is performed for *fixed* values $\lambda=0.76$ and $t_\sigma=69$ as obtained from the similar fit of $F(q_{max},t)$. More details on this analysis can be found in Sec. IV C of the preceding paper [4]. For $l \geq 2$ (Fig. 6) the critical correlator fits the data very well over about two decades in time. This range, however, becomes smaller with increasing l, which may indicate that corrections to the asymptotic law become more important for large l. If one uses λ and t_σ [cf. (I-4)] as free fit parameters, the resulting fits follow the data longer by an additional one to two orders of magnitude in time. [We note that even

$C_1^{(s)}(t)$ can be fitted reasonably well with $G(t)$. Since we have shown in Ref. [1] that for this correlation function the first scaling law does not hold, one might argue that it does not make sense to analyze $C_1^{(s)}$ in the way proposed by MCT. However, we find that the violation of the second scaling law is only weak and therefore it is not unreasonable to make such an analysis.] The so-obtained values for λ increase towards unity with increasing l and reach, e.g., 0.97 for $l=6$. We also mention that we do not observe a critical law, Eq. (I-6), *in its pure form*, the reason for which is likely the strong influence of the microscopic dynamics on the early β-relaxation regime. However, the gentle approach of the curves to their inflection points (see Fig. 6) is a clear indication that a contribution of this form is important.

We have found that these results do not change significantly for $S_{ll}^{(s)m}(q,t)$ if $q>0$. From the fit with the von Schweidler law plus corrections, Eq. (I-9) (not shown in Fig.
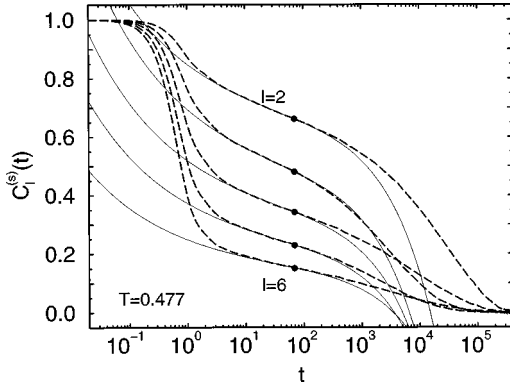
FIG. 6. Time dependence of $C_l^{(s)}(t)$ for $l=2,3,\ldots,6$ (bold dashed lines). Thin lines: β correlator with $\lambda=0.76$. The circles indicate the position of the inflection point.

6), one can deduce the critical nonergodicity parameter $f_{ll}^{(s,c)m}(q)$, the critical amplitude $\tilde{h}_{ll}^{(s)m}(q)$, and the correction $\tilde{h}_{ll}^{(s,2)m}(q)$, which are shown in Fig. 7 for $l=1$, 2, and 6, for the case $m=0$ [see KKS-I for the difference between $(h(q),$ $h^{(2)}(q))$ and $(\tilde{h}(q),\tilde{h}^{(2)}(q))$]. We note that the result for $l=1$ was obtained for $\lambda=0.76$ and a shift of the time scale to $t'_\sigma=10$. Due to the approximate factorization property, the q dependence of $f_{ll}^{(s,c)m}(q)$ is given by that of $f^{(s,c)}(q)$ $\equiv f_{00}^{(s,c)0}(q)$. The functions $f_{ll}^{(s,c)m}(q)$ decrease with increasing l, as expected from Fig. 6. The variation of the critical amplitude $\tilde{h}_{ll}^{(s)m}(q)$ and the correction $\tilde{h}_{ll}^{(s,2)m}(q)$ with q is similar to that for $l=l'=0$ (cf. Fig. 13 of KKS-I) with the exception that these quantities do not vanish for $q\to 0$.

The α, β, and the microscopic time scale can be better visualized from the imaginary part $(\chi^{(s)''})_{ll}^m(q,\omega)$ of the dynamical susceptibility as a function of ω, which is shown for $m=0$ in Fig. 8 for $q=q_{max}$, $l=0$ and $q=0$, $l=1,2$. The microscopic peak is at about $\omega=1$ for all these values of l. Whereas the position of the α peak and the location of the minimum (for low temperatures) are approximately the same for $l=0$ and $l=2$, these positions are shifted to higher frequencies by about one decade for $l=1$. We believe that this shift relates to the 180° jumps of the molecules (see Ref. [1]), because these jumps do not affect the correlators with even l, but those with odd value of l, and particularly those with $l=1$.

The rest of this section is devoted to the discussion of the collective correlators $S_{ll}^m(q,t)$, which are presented in Fig. 9 for $q=2.8$ [the position of the main peak of $S_{11}^0(q)$ (cf. Fig. 1)] and in Fig. 10 for $q=6.5$ [the location of the main peak of $S(q)=S_{00}^0(q)$ (cf. Fig. 1)]. Note, that, due to symmetry (cf. Sec. II), there are only two and three independent correlators for $l=1$ and $l=2$, respectively. These correlators exhibit a strong m dependence, in contrast to $S_{ll}^{(s)m}(q,t)$. The reader should also note that $S_{11}^1(q,t)<S_{11}^0(q,t)$ for $q=2.8$, whereas $S_{11}^1(q,t)>S_{11}^0(q,t)$ for $q=6.5$. These inequalities are related to the fact that $S_{11}^0(q)$ has its main peak at $q\cong 2.8$, where $S_{11}^1(q)$ does not have a maximum, whereas $S_{11}^1(q)$ has its main peak at $q\cong 6.5$, where $S_{11}^0(q)$ is close to a minimum. Similar considerations hold for the m and q
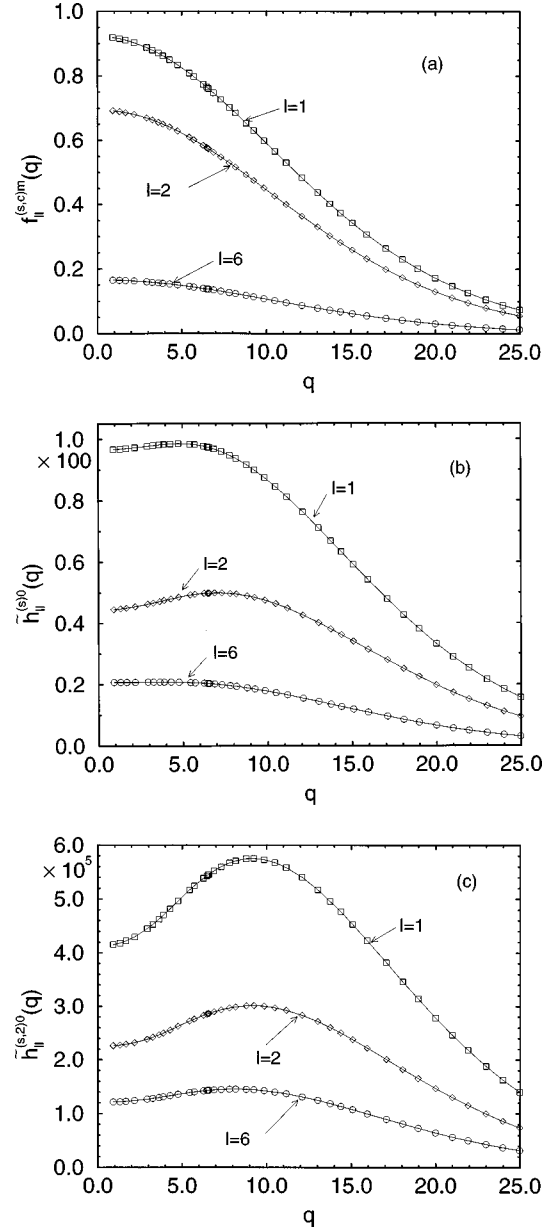

FIG. 7. Wave-vector dependence of $f_{ll}^{(s,c)0}$ (a), $\tilde{h}_{ll}^{(s)0}$ (b), and $\tilde{h}_{ll}^{(s,2)0}$ (c) for $l=2$ and $l=6$.

dependence of $S_{22}^m(q,t)$. These observations make it obvious that a factorization [cf. Eq. (9)] does not work for the collective correlators.

The test of the second scaling law is shown in Fig. 11 for $q=2.8$, $m=0$, and $l=1,2$. As already found for $C_l^{(s)}(t)$ and $C_l(t)$, i.e., the correlation functions for $q=0$, this scaling law holds for $l=2$ but not for $l=1$. We define the α-relaxation time $\tau_{lm,q}(T)$ as the time it takes $S_{ll}^m(q,\tau_{lm,q})$ to decay to the value of $1/e$. The temperature dependence of $\tau_{lm,q}(T)$ is shown in Fig. 12. Fixing $T_c=0.475$, the α-relaxation times obey a power law (I-10) over about two to three decades in time. For the corresponding exponent γ one obtains approximately 1.9 for $l=1$ and 2.5 for $l=2$ with no significant q dependence. Again the γ values for $l=2$ (and the same remains true for $l=3,\ldots,6$) fit with that for $l=0$, which was around 2.55 (see KKS-I), whereas the value of γ for $l=1$ is quite different.
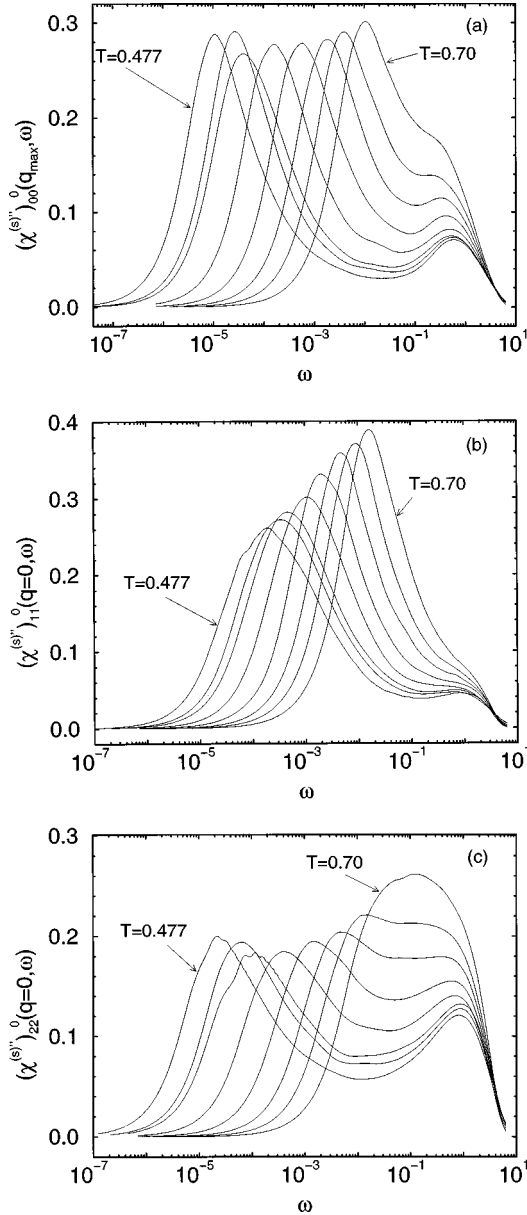
FIG. 8. Imaginary part $(\chi^{(s)''})^0_{ll}(q,\omega)$ versus ω for the lowest investigated temperatures $(0.477 \leqslant T \leqslant 0.7)$; (a) $q=6.5$ and $l=0$, (b) $q=0$ and $l=1$, (c) $q=0$ and $l=2$.

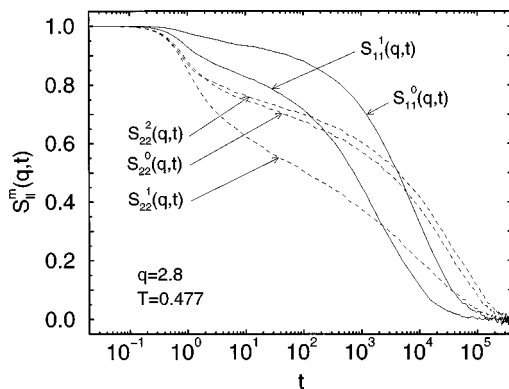FIG. 9. Time dependence of the collective correlators $S^m_{ll}(q,t)$ for $q=2.8$, $T=0.477$, and $l=1$ (solid lines), $l=2$ (dashed lines).
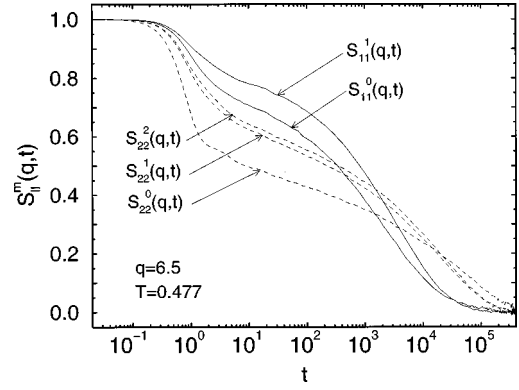

FIG. 10. Time dependence of the collective correlators $S^m_{ll}(q,t)$ for $q=6.5$, $T=0.477$, and $l=1$ (solid lines), $l=2$ (dashed lines).

The test of the first scaling law by fitting the time dependence of $S^m_{ll}(q,t)$ with the β correlator is done in Fig. 13 for $l=2$, $m=0$. This fit (again with $\lambda=0.76$ and $t_\sigma=69$) works well for different values of q. From the fit with the von Schweidler law plus correction, Eq. (I-9) (not shown in Fig. 13), we compute the critical nonergodicity parameter $f^{c,m}_{ll}(q)$, the critical amplitude $\tilde{h}^m_{ll}(q)$, and the correction $\tilde{h}^{(2)m}_{ll}(q)$, shown in Figs. 14 and 15 for, respectively, $l=1$ and $l=2$. Although we have seen that $l=1$ is rather special, we have analyzed the corresponding correlators at the lowest temperature and have included its result. For reference we also show in Figs. 14 and 15 the static correlator $S^m_{ll}(q)$ and the α-relaxation time $\tau_{lm,q}(T)$ for $T=0.477$. These quanti-
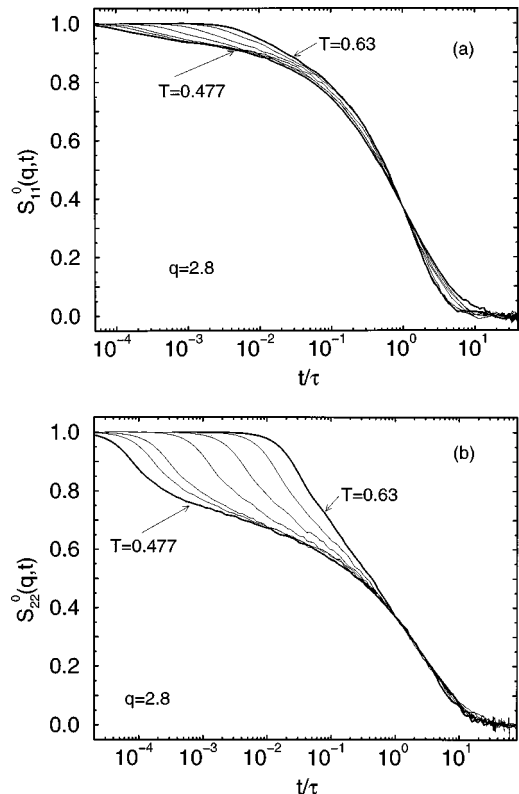

FIG. 11. $S^m_{ll}(q,t)$ versus rescaled time for $q=2.8$, $m=0$, and (a) $l=1$, (b) $l=2$ for the seven lowest temperatures. The bold lines indicate the lowest and highest of these temperatures.
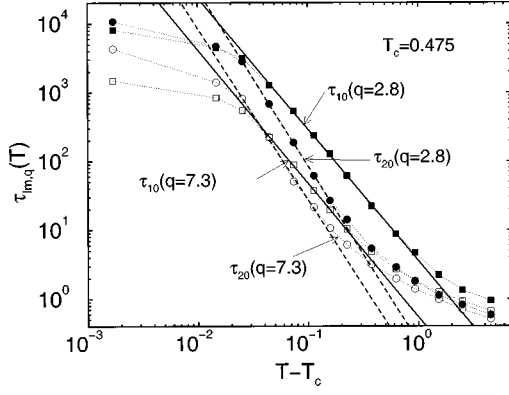
FIG. 12. Relaxation times $\tau_{lm,q}(T)$ versus $T-T_c$ for $m=0$ and $q=2.8$, $l=1$ (filled squares); $q=2.8$, $l=2$ (filled circles); $q=7.3$, $l=1$ (open squares); $q=7.3$, $l=2$ (open circles). $T_c=0.475$. The bold lines represent power laws and the thin lines are a guide to the eye.

ties possess the same characteristic q dependence already found for the corresponding quantities of the TDOF, i.e., for $l=l'=m=m'=0$ (cf. Figs. 13 and 14 of KKS-I). This means that (i) $\tau_{lm,q}$ and $f_{ll}^{c,m}(q)$ are in phase and $\tilde{h}_{ll}^m(q)$ and $\tilde{h}_{ll}^{(2)m}(q)$ are in antiphase with $S_{ll}^m(q)$ and (ii) the correction $\tilde{h}_{ll}^{(2)m}(q)$ is smallest at that q where $S_{ll}^m(q)$ has its main peak. This latter fact is well pronounced for $(l,m)=(1,0)$ and $(l,m)=(2,0)$ and less for the others, because there also the q dependence of $S_{ll}^m(q)$ is less pronounced.

IV. DISCUSSION AND CONCLUSIONS

For a system of diatomic and rigid molecules interacting via Lennard-Jones potentials we have investigated by means of a MD simulation the time and temperature dependence of a general class of $\vec{q}$-, (l,m)-, and (l',m')-dependent correlators. These correlators $S_{lm,l'm'}(\vec{q},t)$ contain the TDOF and ODOF explicitly.

The static correlators $S_{ll'}^m(q)$ in the q frame are not diagonal in l and l'. Whereas those with $l+l'$ odd are smaller than $S(q)\equiv S_{00}^0(q)$ by about one order of magnitude, this is not true for $S_{02}^0(q)$, where $l+l'$ is even. This different be-
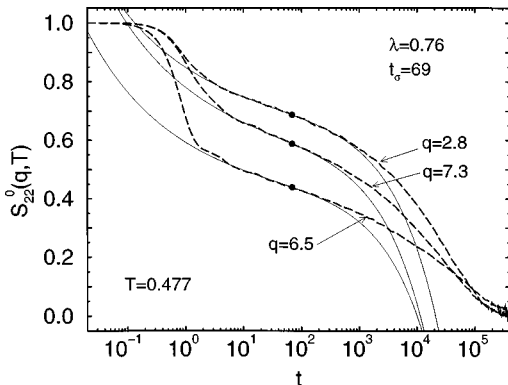

FIG. 13. $S_{22}^0(q,t)$ (bold dashed lines) versus t for $q=2.8$, 6.5, and 7.3 for the lowest temperature and the critical correlator (thin solid lines) with $\lambda=0.76$ and a time scale $t_\sigma=69$. The circles indicate the position of the inflection point.
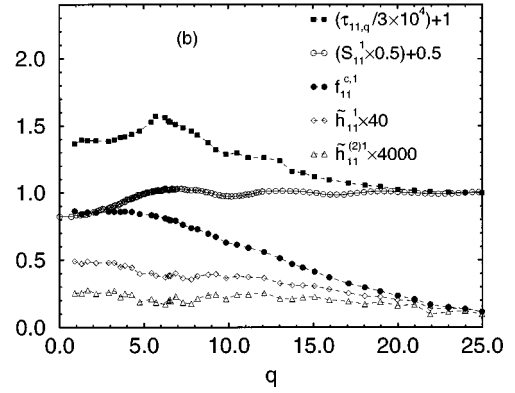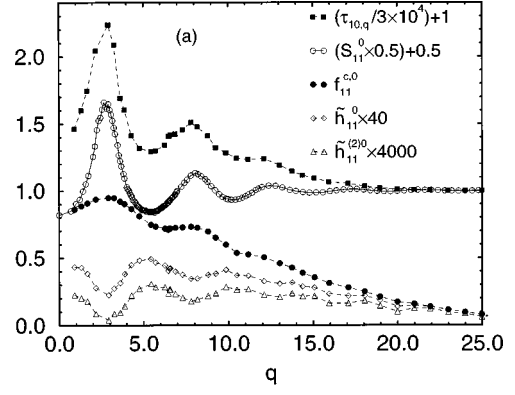

FIG. 14. $f_{11}^{c,m}(q)$ (filled circles), $\tilde{h}_{11}^m(q)$ (open diamonds), $\tilde{h}_{11}^{(2)m}(q)$ (open triangles), $S_{11}^m(q)$ (open circles), and $\tau_{1m,q}(T)$ (filled squares) versus q for $T=0.477$; (a) $m=0$ and (b) $m=1$.

havior results from a head-tail symmetry that is only slightly broken for our molecules.

Our main concern has been the investigation of the time-dependent correlators (collective and self-part) and a test of the predictions of mode coupling theory (MCT). This has been restricted to the diagonal correlators $(l=l')$. As a by-product we have found that the q and (l,m) dependence of the self-correlators $S_{ll}^{(s)m}(q,t)$ approximately factorizes, which was demonstrated for $l=1,2$ and for q up to 10.6. The reason for this factorization is based on a faster relaxation of the ODOF, compared to that of TDOF.

Concerning the MCT predictions, we first studied the existence of a single transition temperature T_c. For the (q,l,m)-dependent α-relaxation times $\tau_{lm,q}(T)$ we have found that they can be fitted with a power law (I-10) with $T_c=0.475\pm0.01$. Thus from the numerous correlators we have investigated, one unique temperature T_c can be located, at which the dynamics of TDOF and ODOF crosses over from an ergodic to a quasinonergodic behavior. This temperature also agrees with that obtained from the translational diffusion constant $D(T)$. This indicates that the TDOF and the ODOF are strongly coupled. Values for γ and the corresponding exponent parameter λ are given in Table I for the translational diffusion constant and a selection of correlators. From this table we observe that γ is approximately constant (within the statistical error) with only two exceptions. The γ values for all the correlators with $l\neq1$ correspond to $\lambda=0.76\pm0.03$ and are essentially independent of q and independent of whether the collective or self-correlator is considered. A deviation from this value occurs for γ_D, the expo-
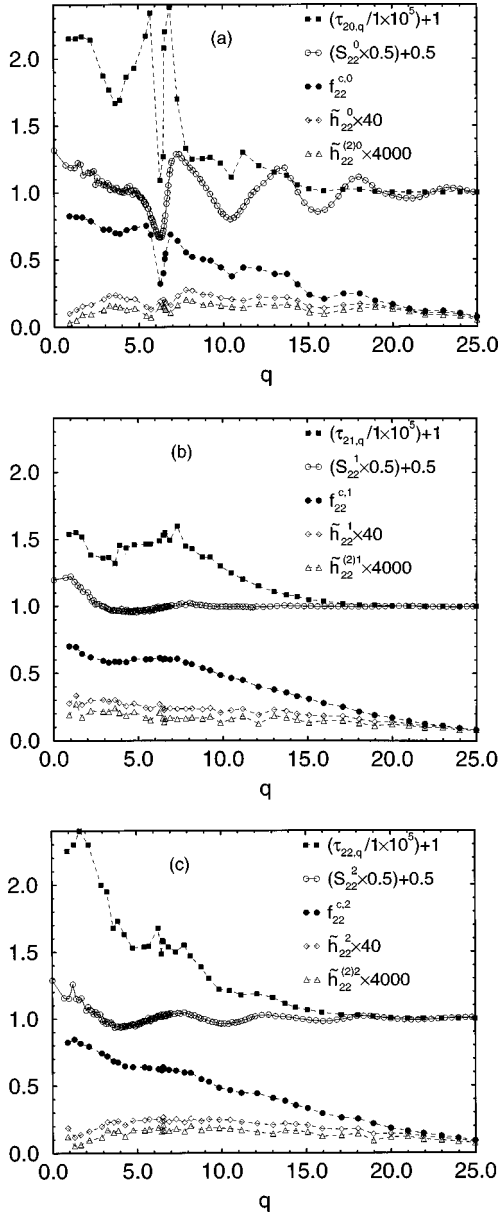
FIG. 15. $f_{22}^{c,m}(q)$ (filled circles), $\tilde{h}_{22}^m(q)$ (open diamonds), $\tilde{h}_{22}^{(2)m}(q)$ (open triangles), $S_{22}^m(q)$ (open circles), and $\tau_{2m,q}(T)$ (filled squares) versus q for $T=0.477$; (a) $m=0$, (b) $m=1$, and (c) $m=2$.
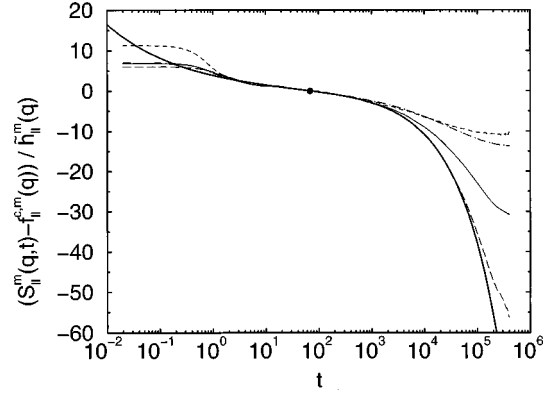

FIG. 16. Time dependence of various correlators for $T=0.477$ shifted by the corresponding nonergodicity parameter $f_{ll}^{c;m}(q)$ and subsequently divided by the critical amplitude $\tilde{h}_{ll}^m(q)$. $T=0.477$. $F_s(q_{max},t)$ (solid line), $F(q_{max},t)$ (long dashed line), $F(q_{min},t)$ (short dashed line), and $C_2^{(s)}(t)$ (dashed-dotted line). The bold line is the critical correlator $G(t)$ for $\lambda=0.76$ and $t_\sigma=69$.

nent for the diffusion constant, and even a stronger one for all correlators with $l=1$. A similar discrepancy between γ_D and the exponent for the $l=0$ relaxation time has been reported before [16].

This exceptional role of the ($l=1$) correlators is also observed for the first and second scaling law of ideal MCT. A

TABLE I. The γ exponent and the corresponding exponent parameter λ [from (I-7) and (I-11)] for the translational diffusion constant D and various correlators.

	D	$C_1^{(s)}$	$C_2^{(s)}$	$C_6^{(s)}$	$F_s(q_{max})$	$F(q_{min})$	$F(q_{max})$
γ	2.20	1.66	2.42	2.80	2.56	2.47	2.57
λ	0.67	<0.5	0.73	0.79	0.76	0.74	0.76

consistent picture within ideal MCT emerges for all q,l,m with $l\neq 1$. The situation is illustrated in Fig. 16 for an exponent parameter $\lambda=0.76$. There we plot $[S_{ll}^m(q,t)-f_{ll}^{c,m}(q)]/\tilde{h}_{ll}^m(q)$ versus t, which should in the first scaling regime be equal to the critical correlator $G(t)$. All the correlators shown follow the "universal" time dependence of the critical correlator $G(t)$ for $\lambda=0.76$. Such a behavior was also found by Wahnström and Lewis [17] for a simple model for orthoterphenyl. The time range for which the correlators can be fitted by $G(t)$ depends on q, l, and m and varies between one and a half decade [for $C_2^{(s)}(t)\equiv S_{22}^{(s)m}(0,t)$] and three decades [for $F(q_{max},t)\equiv S_{00}^0(q_{max},t)$]. Although this time range increases significantly by taking λ and the β-relaxation time scale t_σ as free parameters, we believe that the different time ranges relate to the (q,l,m) dependence of the size of the asymptotic regime. This has been demonstrated earlier for the TDOF of supercooled water [18] and for the TDOF for our molecular system in KKS-I. That the asymptotic regime depends on q has recently been shown by the analytical calculation of the next order corrections for a system of hard spheres [6]. We also find that for the correlators with $l=l'\geq0$ (with the exception of $l=l'=1$) the asymptotic regime is largest for $q_{max}^{(l)}$, the main peak of the static correlator $S_{ll}^m(q)$. This is in variance with the result for water [19]. There it has been found that the corrections are smallest for $q=q_{FSDP}$, where q_{FSDP} is the position of the first sharp diffraction peak and not that of the main peak of $S(q)$. This difference probably relates to the different types of glass forming liquids. Water is a network former due to covalent bonding mechanism, which is absent for our model liquid. The role of this correction to the asymptotic laws is also supported by the fact that the (q,l,m) dependence of the critical nonergodicity parameters, shown in Fig. 15, is only consistent with that of $f_{ll}^{c,m}(q)$ obtained from the molecular MCT [20] for the present liquid of diatomic molecules, if the next order correction to the von Schweidler law [cf. Eq. (I-9)] is taken into account.

The existence of a *stretched* relaxation onto a more or less pronounced plateau can be observed for most of the correla-

tors $S_{ll}^m(q,t)$. It is even more visible for the susceptibilities $(\chi^{(s)''})_{ll}^m(q,\omega)$ (cf. Fig. 8), since the high frequency wing of the β relaxation, i.e., the part on the right of the minimum, is strongly enhanced in comparison to a white noise behavior $(\chi^{(s)''})_{ll}^m(q,\omega)\sim\omega$. The existence of such an anomalous spectrum, which has also been observed in several experiments (e.g., Refs. [22–25]), is one of the important predictions of MCT. A fit of $(\chi^{(s)''})_{ll}^m(q,\omega)$ with a critical law $\omega^{0.3}$, where $a=0.3$ follows from Eq. (I-6) for $b=0.55$, works, but again the time span is at most one decade.

The result shown in Fig. 16 also demonstrates the validity of the factorization of the (q,l,m) and t dependence of the various correlators on the time scale of t_σ. For simple liquids, i.e., for $l=m=0$, this is a prediction of MCT [2,3]. There it has been shown that the vertices of the mode coupling terms are positive for a simple, one-component liquid, which, however, is not true anymore for molecular liquids [8]. Since the factorization theorem only requires that the largest eigenvalue of a certain stability matrix (see Ref. [3]) is nondegenerate, for which the positivity of the vertices is sufficient but not necessary, we still believe that this nondegeneracy is generic and that therefore the factorization theorem holds for molecular liquids as well. In the case that a system exhibits a type-B transition [3], this nondegeneracy and hence the factorization is guaranteed.

The exceptional behavior for the correlators with $l=1$ has also been observed in the susceptibility (cf. Fig. 8). The position of the minimum between α and the microscopic peak of $(\chi^{(s)''})_{ll}^m(q,\omega)$ is approximately the same for $l=0$ and $l=2$, but not for $l=1$. For the latter it is shifted to higher frequencies by about one order of magnitude. It is interesting that this result resembles the experimental results for some glass forming liquids. For instance, it has been stressed by Cummins *et al.* [21] that light scattering data that may include contributions from both $l=0$ and $l=2$ are consistent with the spectra obtained from neutron scattering (which is only $l=0$), but not with those from dielectric measurements. This is nicely demonstrated for glycerol by Lunkenheimer *et al.* [24,25]. The situation illustrated in Fig. 2 of Ref. [25] is exactly what we have found in Fig. 8 for our system. The reader should also note that even the relative weight between the intensity of α and microscopic peaks has the same qualitative behavior in both cases, i.e., it is significantly larger for $l=1$ than for $l=0$ and $l=2$. A similar result has been recently found from a MD simulation of CKN, where the ori-

entational dynamics (self part) of the NO_3^- ion was studied for $l=1$ and $l=2$ [26]. In that paper, and also for the collective dynamics of dipolar hard spheres [7,8], it has been concluded that the different weights of the α and microscopic peaks relate to the different numerical values for the critical nonergodicity parameters. For $q=0$ is has been argued that $f_{l+1,l+1}^{(s,c)m}<f_{ll}^{(s,c)m}$ (due to $q=0$, no m dependence exists) [26]. Since $f_{ll}^{(s,c)m}(q=0)$ is the α-relaxation strength of the corresponding susceptibility and $(\chi^{(s)''})_{ll}^m(q=0)$ fulfills a sum rule (on a logarithmic frequency scale), it becomes obvious that the ratio between the α-relaxation strength and the area under the microscopic peak is larger for $l=1$ than for $l=2$. Whether this agreement between the susceptibilities of glycerol and that for our diatomic molecular liquid is merely accidental or not is, however, not obvious. One has to keep in mind (i) that dielectric spectroscopy and light scattering measures the collective dynamics and not their self-part and (ii) glycerol has a permanent dipolar moment, in contrast to our diatomic molecules. How far the dipolar interaction would change our MD results is not clear. In addition, we believe that the special role of $l=1$ relates to the 180° jumps of the molecules [1]. Whether these jumps exist for glycerol also and whether they really cause a shift of the minimum is uncertain.

To summarize, we may say that the results obtained in Refs. [1] and [4] and in the present paper are consistent with MCT. There is strong evidence for a single transition temperature, as is predicted from molecular MCT [8] and for the validity of the two scaling laws, with the exception of the correlators with $l=1$. Regarding the second scaling regime we have found that the γ exponent is essentially independent of the quantity studied, with the exception of $l=1$ and the diffusion constant D. It will be a challenge to clarify this remaining discrepancy for the γ values. The critical law, which is part of the first scaling regime, could *in its pure form* not be observed. However, we found strong indirect evidence that such a law is indeed present and is just masked by the strong interference with the microscopic dynamics.

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