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Test of mode coupling theory for a supercooled liquid of diatomic molecules. I. Translational degrees of freedom

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A molecular-dynamics simulation is performed for a supercooled liquid of rigid diatomic molecules. The time-dependent self and collective density correlators of the molecular centers of mass are determined and compared with the predictions of the ideal mode coupling theory (MCT) for simple liquids. This is done in real as well as in momentum space. One of the main results is the existence of a unique transition temperature T_c, at which the dynamics crosses over from an ergodic to a quasinonergodic behavior. The value for T_c agrees within the error bars with that found earlier for the orientational dynamics. In the first scaling law regime of MCT, also called the β regime, we find that the correlators in the late stage of the β regime can be fitted well by the von Schweidler law. Although we do not observe the critical decay predicted by MCT for the early β-relaxation regime in its pure form, our relaxation curves suggest that this decay is indeed present. In this first scaling regime, a consistent description within ideal MCT emerges only, if the next order correction to the asymptotic law is taken into account. This correction is almost negligible for $q=q_{\max}$, the position of the main peak in the static structure factor $S(q)$, but becomes important for $q=q_{\min}$, the position of its first minimum. The second scaling law, i.e., the time-temperature superposition principle, holds reasonably well for the self and collective density correlators and different values for q. The α-relaxation times $\tau_q^{(s)}$ and τ_q follow a power law in $T-T_c$ over two to three decades. The corresponding exponent γ is practically q independent and is around 2.55. This value is in agreement with the one predicted by MCT from the value of the von Schweidler exponent but at variance with the corresponding exponent $\gamma \approx 1.6$ obtained for the orientational correlators $C_1^{(s)}(t)$ and $C_1(t)$, studied in a previous paper. [S1063-651X(98)02708-1]

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I. INTRODUCTION

Although several interpretations of the glass transition exist (see, e.g., Ref. [1]), the only microscopic approach leading to a multitude of predictions is based upon the mode coupling theory (MCT). This theory, which was proposed first by Bengtzelius, Götze, and Sjölander [2] and Leutheusser [3], provides an equation of motion for the normalized density correlator

$$F(q,t)=\frac{\langle \delta\rho_q^*(t)\,\delta\rho_q\rangle}{\langle \delta\rho_q^*\,\delta\rho_q\rangle} \tag{1}$$

of a simple liquid. Note that F depends on $q=|\vec{q}|$ only, due to the isotropy of the system. In its idealized version, MCT predicts the existence of a dynamical transition at a critical temperature T_c (or a critical density n_c) from an ergodic to a nonergodic phase, corresponding to a liquid and a glass, respectively. The nonergodicity parameter (NEP)

$$f(q)=\lim_{t\to\infty} F(q,t) \tag{2}$$

serves as an order parameter for that transition. $f(q)$ may change either continuously (type-*A* transition) or discontinuously (type-*B* transition) at T_c. For the structural glass transition only the latter is relevant.

The test of the predictions of the ideal MCT has challenged both experimental work and computer simulations. Most of the experiments have determined the intermediate scattering function $F(q,t)$ or its time-Fourier transform, the dynamical structure factor (coherent and incoherent part). This yields information on the dynamics of the translational degrees of freedom (TDOF) only. Many of these investigations have been reviewed by Götze and Sjögren [4] and in Refs. [5].

Since most of the glass formers are molecular systems, it is also important to study the role of the orientational degrees of freedom (ODOF) and their coupling to the TDOF. A convenient way for this is, e.g., the use of dielectric spectroscopy. Recent results from dielectric measurements [6] are partly consistent with the predictions of MCT for simple liquids. The interpretation of light scattering experiments is not so obvious. Since TDOF and ODOF may both contribute to light scattering, it is not so easy to separate the orientational part (see, e.g., Ref. [7]). Concerning computer simulations, only a few molecular liquids have been studied so far [8–15]. In a recent molecular-dynamics (MD) simulation [16] the present authors have investigated a liquid of diatomic, rigid molecules with Lennard-Jones interactions. Apart from linear molecules with head-tail symmetry, this is the simplest choice for a molecular system. Because dielectric and light scattering measurements yield essentially only information for $q\approx 0$, we restricted ourselves to orientational correlators with $q=0$ and to the translational and rotational diffusion constant D and D_r, respectively [16]. The main result we have found is the existence of a power-law dependence on temperature of all the orientational relaxation times $\tau_l^{(s)}(l=1-6)$, τ_l $(l=1)$, and of D with a single critical temperature $T_c=0.475$, in agreement with ideal MCT. Slightly above T_c, the numerical results for $\tau_l^{(s)}$, τ_l, and D deviate from a power law, due to ergodicity restoring processes. These processes, which are not considered by the ideal MCT, can be accounted for by its extended version [17]. The observation that the temperature dependence of D_r does not fit into this scheme, but bifurcates from D at a temperature significantly above T_c and then obeys an Arrhenius law, rather than a power law, has been a further important result.

The main purpose of the present and the following paper [18] is the extension of our recent results [16] to finite q and to perform a thorough test of the predictions of the ideal MCT. The present paper is restricted to the TDOF only, whereas the following paper [18] considers orientational correlators, which explicitly contain the coupling between ODOF and TDOF. Although our simulation investigates a molecular system, we make a comparison with the predictions of MCT for *simple* liquids. The ideal MCT for simple liquids has been recently extended to a dumbbell molecule in a simple liquid [19] and to molecular liquids of linear [20,21] and arbitrary shaped molecules [22]. So far, the investigations of these molecular MCT equations were restricted to the calculation of the NEP [19,21,22]. For linear molecules without head-tail symmetry, it follows from these equations [21] that the TDOF and ODOF freeze at a single critical temperature T_c, consistent with our recent results for $q=0$ [16]. The investigation of the time-dependent molecular MCT equations, which would allow comparison with our MD results, will be done in the future.

The outline of this paper is as follows. The next section will review those predictions of the ideal MCT (for simple liquids) that will be tested. In Sec. III the model as well as some details of the computer simulation are discussed. In Sec. IV we present our MD results and the final section contains a discussion of these results and our main conclusions.

II. MODE COUPLING THEORY

In this section we will give a short summary of those predictions of the ideal MCT (for simple liquids), which will be compared with our MD results. For details, the reader may consult the review papers [4,5].

Ideal MCT predicts the existence of a dynamical transition at T_c from an ergodic to a nonergodic phase, which is an ideal glass transition. For temperatures close to T_c, MCT predicts the existence of two scaling laws for $F(q,t)$ with time scales t_σ and $\tau(\gg t_\sigma)$, where τ is the α-relaxation time. In the first scaling regime, i.e., for $t_0 \ll t \ll \tau$, the density correlator takes the form

$$F(q,t)=f^c(q)+h(q)G(t) \tag{3}$$

with $f^c(q)$ the NEP at T_c and $h(q)$ the critical amplitude. t_0 is a microscopic time that, for an atomic system, is of the order of 10^{-13} sec. The reader should note that for $T>T_c$ the long time limit of $F(q,t)$ is zero. However, the theory predicts the existence of a time range $t_0 \ll t \ll \tau$ in which $F(q,t)$ exhibits a plateau, when plotted versus the *logarithm* of time. The height of this plateau is equal to the NEP $f^c(q)>0$. Thus the fact that $f^c(q)>0$ does not imply that $\lim_{t\to\infty}F(q,t)>0$. Rather, the time range over which the plateau is observed increases rapidly when the temperature approaches T_c from above and extends up to $t=\infty$ at T_c. Thus at T_c we have $\lim_{t\to\infty}F(q,t)=f^c(q)$ and the system has become nonergodic, since the correlation functions do not decay to zero any more.

The so-called β correlator $G(t)$ in Eq. (3) obeys the first scaling law:

$$G(t)=c_\sigma g_\pm(t/t_\sigma) \tag{4}$$

with the correlation scale $c_\sigma=|\sigma|^{1/2}$ and the separation parameter $\sigma=\sigma_0(T-T_c)$, where $\sigma_0>0$. The σ-independent master functions $g_\pm(\sigma \lessgtr 0)$ are solutions of a certain scaling equation. The corresponding β-relaxation time scale t_σ is given by

$$t_\sigma \propto |T-T_c|^{-1/2a}, \quad T \gtrless T_c. \tag{5}$$

For $g(t)$ one obtains the following asymptotic power laws:

$$g(t)\propto \begin{cases} t^{-a}, & t_0 \ll t \ll t_\sigma \\ -t^b, & t_\sigma \ll t \ll \tau. \end{cases} \tag{6}$$

The critical law, upper part of Eq. (6), holds above and below T_c, whereas the von Schweidler law, lower part of Eq. (6), is valid only above the transition point. Below T_c, $g(t)$ decays to a constant for $t \gg t_\sigma$. Both exponents a and b are related to the exponent parameter λ, with $1/2<\lambda<1$, by

$$\frac{\Gamma(1-a)^2}{\Gamma(1-2a)}=\lambda=\frac{\Gamma(1+b)^2}{\Gamma(1+2b)}, \tag{7}$$

with Γ the Gamma function. From Eq. (7) one gets that $0<a<\frac{1}{2}$ and $0<b\leq 1$. λ is determined by the static correlators at T_c. The result (3), which states that in the first scaling regime the q and t dependence factorizes, is one of the most important predictions of the ideal MCT. (We remind the reader that this prediction holds only on the time scale $t_0 \ll t \ll \tau$.) Due to this factorization, Eq. (3) can easily be transformed to real space:

$$\phi(r,t)=f^c(r)+H(r)G(t), \tag{8}$$

where $\phi(r,t)$, $f^c(r)$, and $H(r)$ are the Fourier transform of $F(q,t)$, $f^c(q)$, and $h(q)$, respectively.

It is important to realize that the result (6) only holds asymptotically for $T\to T_c$. The next order correction to both of these asymptotic laws was recently derived and calculated for a system of hard spheres by Franosch *et al.* [23]. Corrections to the von Schweidler law [24]

$$F(q,t)=f^c(q)-h(q)(t/\tau)^b+h^{(2)}(q)(t/\tau)^{2b}-\cdots \tag{9}$$

have already been studied for hard spheres by Fuchs *et al.* [25]. There it was demonstrated that these corrections may be important. The expansion (9) is valid for $t_\sigma \ll t \ll \tau$, where the α-relaxation time scale τ is given by

$$\tau(T)\propto (T-T_c)^{-\gamma}, \quad T \geq T_c \tag{10}$$

with

$$\gamma=\frac{1}{2a}+\frac{1}{2b}. \tag{11}$$

The translational diffusion constant D is predicted to scale like τ^{-1}. Therefore it is

$$D(T) \propto (T-T_c)^{\gamma}, \quad T \geq T_c. \tag{12}$$

Corrections to the critical law lead to [23]

$$F(q,t) = f^c(q) + h(q)(t/t_0)^{-a} + \overline{h}^{(2)}(q)(t/t_0)^{-2a} + \cdots. \tag{13}$$

In Ref. [23] it was shown that $\overline{h}^{(2)}(q) - h^{(2)}(q)$ is proportional to $h(q)$, which allows thus a further interesting test of MCT. Unfortunately we will not be able to present in the following the outcome of such a check of the theory, since the accuracy of our data for $\overline{h}^{(2)}(q)$ is insufficient.

In the second scaling regime, i.e., for t of the order of τ, a master function $\tilde{F}_q(\tilde{t})$ exists such that

$$F(q,t,T) = \tilde{F}_q(t/\tau(T)). \tag{14}$$

In glass science the result (14) is called time-temperature superposition principle. The expansion of the right-hand side of Eq. (14) with respect to t/τ yields Eq. (9). Equation (14) represents the second scaling law.

Finally we mention that all these MCT results hold for the self-part of the density correlator as well.

III. MODEL AND DETAILS OF THE SIMULATION

The model we investigate is a one-component system of rigid diatomic molecules. Each molecule is composed of two different Lennard-Jones particles, in the following denoted by A and B, which are separated by a distance $d=0.5$ and each of which has the same mass m. The interaction between two molecules is given by the sum of the interaction between the four particles, which is given by the Lennard-Jones potential $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\{(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6\}$, where $\alpha,\beta \in \{A,B\}$. The Lennard-Jones parameters are given by $\sigma_{AA} = \sigma_{AB} = 1.0$, $\sigma_{BB} = 0.95$, $\epsilon_{AA} = \epsilon_{AB} = 1.0$, and $\epsilon_{BB} = 0.8$. In the following we will use reduced units and use σ_{AA} as the unit of length, ϵ_{AA} as the unit of energy (setting $k_B = 1$), and $(\sigma_{AA}^2 m/48\epsilon_{AA})^{1/2}$ as the unit of time. If the atoms are argon-like, this time unit corresponds to approximately 0.3 ps.

In order to make the simulation more realistic, we did it at constant external pressure $p_{\mathrm{ext}} = 1.0$. The length of the equilibration runs always exceeded the typical relaxation time of the system at the temperature considered, which allows us to conclude that in the subsequent production runs we were investigating the *equilibrium* dynamics of the system. The temperatures we investigated are $T = 5.0$, 3.0, 2.0, 1.4, 1.1, 0.85, 0.70, 0.632, 0.588, 0.549, 0.520, 0.500, 0.489, and 0.477. The total number of molecules was 500 and, in order to improve the statistics of the results, we averaged at each temperature over at least eight independent runs. For more details on the simulation see [16].

IV. RESULTS

For a clearer presentation of our results, this section is divided into two subsections, where the first is devoted to the static and the second to the dynamical properties. The latter is divided into two parts again, which are real space and q-space representation.

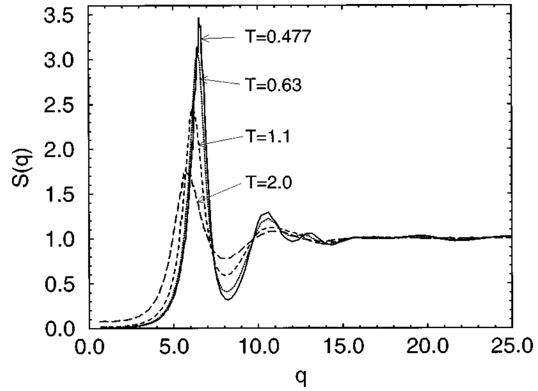

FIG. 1. Wave-vector dependence of the static structure factor $S(q)$ (center of mass) for $T=0.477$, 0.63, 1.1, and 2.0 (at the main peak from top to bottom).

A. Static properties

First of all we remark that thermodynamic quantities such as, e.g., the average density and the enthalpy, do not exhibit any signature of a singular behavior for the full temperature range $0.477 \leq T \leq 5.0$ that we have investigated. From this we conclude that the observed slowing down is probably not related to an approach of the system to a critical point of a second-order phase transition. Furthermore, the regularity of the temperature dependence of the mentioned quantities also gives evidence that the system does not show any sign of the presence of a transition to an ordered phase (crystalline or liquid crystalline) and this fact is also corroborated by investigating snapshots of the configuration of the molecules.

The structural properties are one of the most interesting static features of a supercooled liquid. Figure 1 shows the static structure factor $S(q)$ of the center of mass positions for different temperatures as a function of q. Its q dependence has the typical behavior expected for a liquid [26], with a main peak at $q_{\max} = 6.5$ and a first minimum at $q_{\min} = 8.15$ for the lowest temperature. With increasing temperature the peak positions shift to smaller q values, due to an increase of the average distance between the molecular centers, and the peaks become broader.

A comparison of $S(q)$ for $T = 0.477$ with the partial structure factors $S_{\alpha\beta}(q)$, where α,β refers to atom A and atom B, is given in Fig. 2. Whereas the main peak in $S(q)$ and $S_{\alpha\beta}(q)$ is essentially at the same position, the remaining q dependence is quite different for the various correlators. For the prepeak of $S_{AA}(q)$ and $S_{BB}(q)$ at $q \approx 3.1$, which could indicate a ''medium'' range order, we have not found a conclusive interpretation. Note that the main reason we have presented $S(q)$ is to compare its q dependence with the static correlation functions of the orientational correlators presented in paper II. We already anticipate that this q dependence can be rather different for the various correlators.

B. Dynamical properties: Real space

To start, we discuss the self-motion of a molecule. One of the important transport coefficients is the translational diffusion constant D, which is obtained from the mean squared displacement by

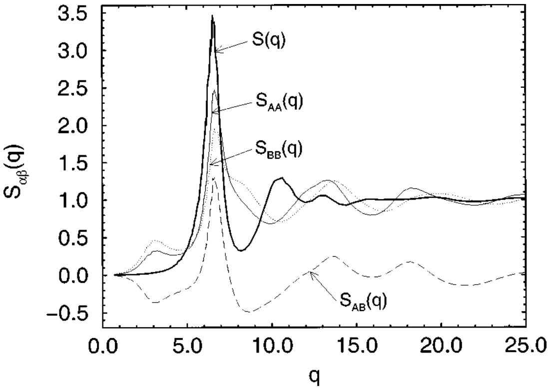

FIG. 2. $S(q)$ (bold solid line) and the partial structure factors $S_{\alpha\beta}$ versus q for $T=0.477$; S_{AA} (solid line), S_{BB} (dotted line), and S_{AB} (dashed line).

$$D=\lim_{t\to\infty}\frac{1}{6tN}\sum_{n=1}^{N}\langle[\vec{x}_n(t)-\vec{x}_n(0)]^2\rangle, \tag{15}$$

where N is the number of molecules. The temperature dependence of D is presented in Fig. 3 on a double-logarithmic scale. The diffusion constant follows a power law, as predicted by ideal MCT [cf. Eq. (12)], over a surprisingly large range of four decades in D. As critical temperature we obtain $T_c=0.475$ and for the corresponding exponent $\gamma_D=2.20$. With use of Eqs. (7) and (11), this yields a von Schweidler exponent $b_D=0.69$, a critical exponent $a_D=0.34$, and an exponent parameter $\lambda_D=0.67$. At the two lowest temperatures the deviations of the numerical values for D from the power law, which has been mentioned in the Introduction, can clearly be seen. The inset of Fig. 3 depicts the time dependence of the mean squared displacement for all temperatures, from which $D(T)$ was deduced.

More detailed information on the self-motion is contained in the self-part of the van Hove correlator:

$$G_s(r,t)=\left\langle\frac{1}{N}\sum_{n=1}^{N}\delta[r-|\vec{x}_n(t)-\vec{x}_n(0)|]\right\rangle. \tag{16}$$

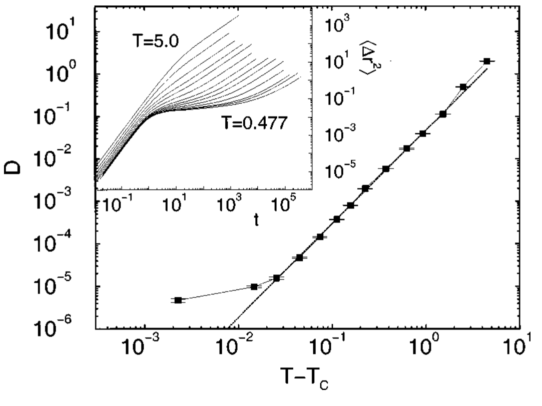

FIG. 3. Temperature dependence of the translational diffusion constant D; numerical data (squares, including error bars), power law (dotted line). The solid line serves as a guide for the eye. Inset: time dependence of the mean squared displacement for all temperatures investigated.

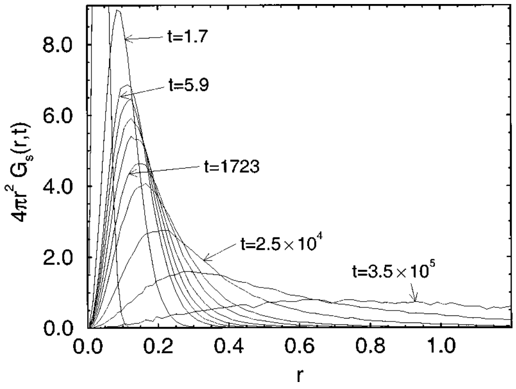

FIG. 4. r dependence of $4\pi r^2 G_s(r,t)$ for $t=0.4$, 1.7, 5.88, 24.3, 101, 416, 1723, 5000, 2.5×10^4, 10^5, and 3.5×10^5 (from top to bottom) and for $T=0.477$.

The r dependence of $G_s(r,t)$ is shown in Fig. 4 for times that are equidistant on a logarithmic time axis and for the lowest temperature. With time, the δ peak at $t=0$ broadens and for $t\to\infty$ and $r\to\infty$, i.e., in the hydrodynamic limit, it approaches a Gaussian distribution:

$$G_s(r,t)\to\frac{1}{(4\pi Dt)^{3/2}}\exp\left(-\frac{r^2}{4Dt}\right)\quad\text{for } t,r\to\infty. \tag{17}$$

In the time span $5.0\leqslant t\leqslant 10^3$, where the mean squared displacement for the lowest temperature exhibits a plateau (cf. the inset of Fig. 3), the *shape* of $G_s(r,t)$ depends only weakly on time.

Another interesting conclusion can be drawn from the r dependence of G_s for the largest time. As can be seen from Fig. 4, at no time is there any indication for the presence of a secondary peak at $r\approx1$, the nearest-neighbor distance. From the absence of such a peak it is usually concluded, see, e.g., Ref. [27], that no hopping processes are present. However, since the temperature dependence of the diffusion constant shows deviations from the power law predicted by the *ideal* MCT (see Fig. 3), i.e., the theory in which no hopping processes are included, we conclude that in our system hopping processes *are* present. Whether these processes are jumps of the molecules or only due by 180° flips of the molecules that are observed at lower temperatures [16] is, however, not clear. Thus we conclude that hopping processes do not necessarily lead to a secondary peak in G_s.

The r dependence of G_s is not Gaussian for a large time regime. The deviation from a Gaussian can be quantified by the non-Gaussian parameters $\alpha_n(t), n=2,3,\ldots$ [28]. Figure 5 shows

$$\alpha_2(t)=\frac{3\langle\vec{r}^4(t)\rangle}{5\langle\vec{r}^2(t)\rangle^2}-1. \tag{18}$$

In the case of a Gaussian process, $\alpha_2(t)$ vanishes. For $t\to0$ and $t\to\infty$, $\alpha_2(t)$ goes to zero. But in between there exists a time regime for all temperatures where α_2 is substantially different from zero. The increasing part of α_2 seems to have a common envelope, as already found earlier [13,27]. This time dependence of α_2 is very reminiscent of the one of the critical law, see Eq. (13), i.e., on the time scale

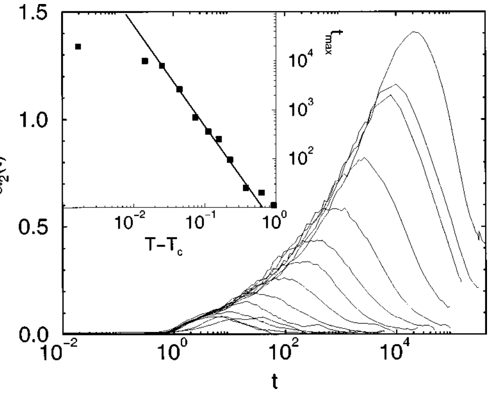

FIG. 5. Non-Gaussian parameter $\alpha_2(t)$ versus time for all temperatures investigated. Inset: the maximum position $t_{\max}$ versus $T-T_c$ with $T_c=0.475$.

$t_0 \ll t \ll \tau$ we have $\alpha_2(t)=\tilde{\alpha}_2(t/t_0)$. Thus it can be expected that the existence of the envelope and the critical decay have a common origin.

The time $t_{\max}(T)$, where $\alpha_2(t)$ attains its maximum [and at which $\alpha_2(t)$ does not fall onto the envelope anymore] obeys a power law $(T-T_c)^{-\gamma_\alpha}$ (see the inset of Fig. 5) with $\gamma_\alpha \approx 2.1$, which coincides with γ_D, derived from $D(T)$, in agreement with the results of Sciortino *et al.* [13]. This suggests that $\alpha_2(t)$ for $t \approx t_{\max}$ is determined by the α relaxation as it follows from ideal MCT. Exactly the same conclusions also hold for $\alpha_3(t)$.

The collective dynamics can be studied by use of the distinct part of the van Hove correlator

$$G_d(r,t)=\left\langle \frac{1}{N-1}\sum_{n\neq m} \delta[r-|\vec{x}_n(t)-\vec{x}_m(0)|] \right\rangle, \qquad (19)$$

which is shown in Fig. 6 for various times and again for the lowest temperature. Its r and t dependence is quite similar to that found for a binary liquid [27] and again in the time span $5.0 \leq t \leq 10^3$ its shape depends only weakly on time.

C. Dynamical properties: *q* space

Although the visualization of local structural properties favors the use of a real space representation of the correlators, most experimental results are obtained in q space. In addition, the translational invariance of the interactions also suggests a theoretical description by use of q-dependent correlators. For instance the memory part of the MCT equation for the density correlator $F(q,t)$ is ‘‘diagonal’’ in q space but involves a convolution in real space.

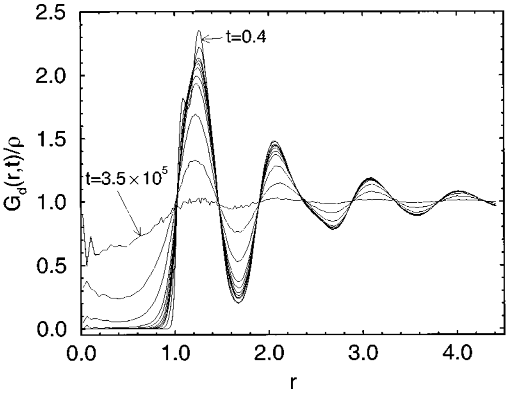

FIG. 6. r dependence of G_d, normalized by the average density ρ, for the same times as in Fig. 5 and for $T=0.477$.

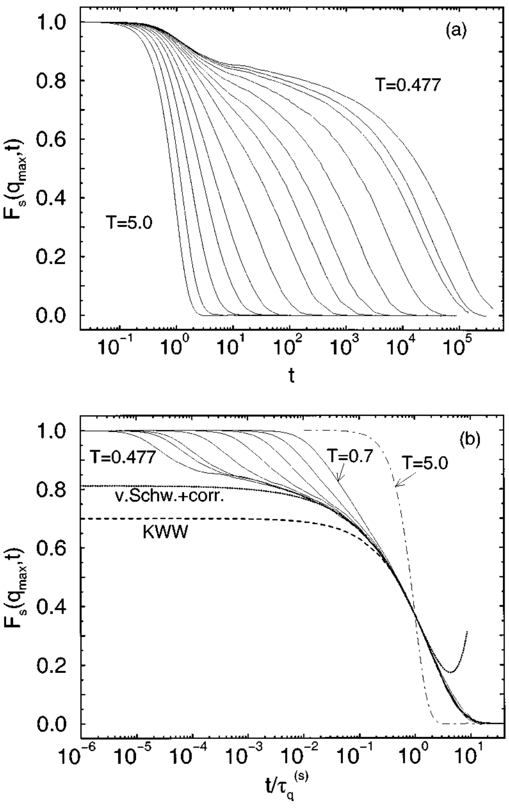

FIG. 7. (a) Time dependence of the self-part F_s for $q=q_{\max}=6.5$ for all temperatures investigated. (b) $F_s(q_{\max},t)$ versus rescaled time. The eight curves (solid lines) on the left refer to the eight lowest investigated temperatures and the one farthest to the right (dashed-dotted curve) corresponds to the highest temperature $T=5.0$. The von Schweidler law including corrections [cf. Eq. (9)] is represented by the dotted line, and a KWW fit is shown dashed.

Let us start with the self-part $F_s(q,t)$ of the collective density correlator $F(q,t)$ [cf. Eq. (1)], which is presented in Fig. 7 for $q=q_{\max}=6.5$, the position of the main peak in $S(q)$ (cf. Fig. 1). We remind the reader that q is measured in units of σ_{AA}. The small bump in $F_s(q,t)$ at $t_s \cong 12$ is due to a sound wave and t_s is the time for the sound wave to traverse the box size of our sample. This effect was also observed by Lewis *et al.* [10] and has recently been shown to be much more pronounced in strong glass formers [29].

For the highest temperature, $T=5.0$, the decay of $F_s(q,t)$ is essentially exponential. With decreasing temperature the relaxation crosses over into a two-step process, as predicted by MCT. The change from the fast exponential relaxation to a much slower one in which a pronounced plateau is found can be interpreted as a crossover of the system from an ergodic to a quasinonergodic behavior, since on the time scale at which the plateau is observed the system is not ergodic. For the lowest temperature, $T=0.477$, a ‘‘quasiplateau’’ can be seen. Its height is a measure of the critical NEP $f_s^c(q)$. The reader should note that for all temperatures $F_s(q_{\max},t)$ decays to zero for large times, indicating that the length of

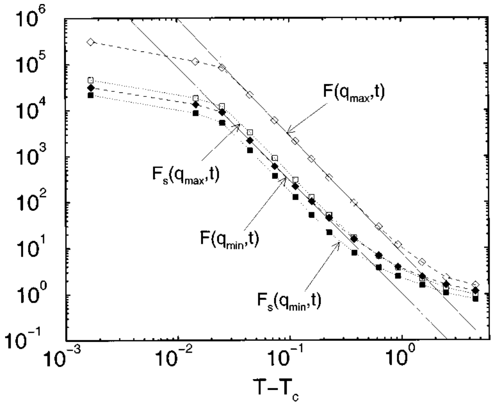

FIG. 8. α relaxation times τ_q versus $T-T_c$: open diamonds from $F(q_{\max},t)$, filled diamonds from $F(q_{\min},t)$, open squares from $F_s(q_{\max},t)$, filled squares from $F_s(q_{\min},t)$. The dashed lines are a guide for the eye and both solid lines represent fits with a power law.

the runs is large enough to equilibrate the system. In order to test MCT, we have determined the α-relaxation times $\tau_q^{(s)}(T)$ from the condition $F_s(q,\tau_q^{(s)})=1/e$. Its temperature dependence is shown in Fig. 8 (squares) for $q=q_{\max}=6.5$ and $q=q_{\min}=8.15$. Using $T_c = 0.475$, as determined from $D(T)$, both relaxation times follow a power law over about three decades. The corresponding γ values are practically the same $\gamma^{(s)}=2.56$, but differ significantly from $\gamma_D=2.20$. Such a discrepancy between γ_D and $\gamma^{(s)}$ has been observed already before [27] and indicates that the MCT prediction that the two exponents should be equal is not valid for these systems. $\gamma^{(s)}=2.56$ yields the von Schweidler exponent $b=0.55$ and the exponent parameter $\lambda=0.76$. We also note that a power-law fit with T_c as a free parameter yields a value for T_c that coincides with $T_c=0.475$ to within 2%.

The relaxation time $\tau_q^{(s)}(T)$ can now be used to rescale time in order to test the validity of the time-temperature superposition principle [Eq. (14)], which is done in Fig. 7(b). We find that the relaxation curves fall indeed onto one master curve for the lowest temperatures. The late stage relaxation can be fitted well by a Kohlrausch-Williams-Watts law (KWW), i.e., $F_s(q,t)=A\exp[-(t/\tau^{(s)})^{\beta}]$, dashed curve. For higher temperatures (cf., e.g., the curve for $T=5.0$) no such scaling exists. We also note that such a scaling was *not* possible for certain types of *orientational* correlation functions [16], which shows that this prediction of MCT is not a trivial one.

Having demonstrated the validity of the second scaling law [Eq. (14)], we can test whether the von Schweidler law, including the next order correction [Eq. (9)], fits the master curve well in the late β-relaxation regime. As can be seen from Fig. 7(b), this type of fit works very well (dotted line). In practice, this has been done for $F_s(q,t)$ at the lowest temperature by keeping b fixed to 0.55 (deduced from $\gamma^{(s)}$). The wave-vector dependence of $f_s^c(q)$, $\tilde{h}^s(q)$, and $\tilde{h}^{(2)s}(q)$ is shown in Fig. 9. Here a comment is in order. The fit of the data with the von Schweidler law including the next order correction yields $\tau^{-b}h^s(q)$ and $\tau^{-2b}h^{(2)s}(q)$ [cf. Eq. (9)]. Since the q-independent α-relaxation time scale $\tau(T)$ can only be determined up to a T-independent factor, the same is true for $h^s(q)$ and $h^{(2)s}(q)$. In Fig. 9 we therefore show $\tilde{h}^s(q)=\tau^{-b}h^s(q)$ and $\tilde{h}^{(2)s}(q)=\tau^{-2b}h_q^{(2)s}(q)$. The q variation of these quantities is quite similar to that for hard spheres [25]. Particularly we also find a zero of $\tilde{h}^{(2)s}(q)$ at a finite q value $q_0\approx 3.5$ with $\tilde{h}^{(2)s}(q)<0$ (>0) for $q<q_0$ $(q>q_0)$. Taking into account that q for the hard sphere system is given in units of the diameter $d^{\mathrm{HS}}=1$, we can deduce $q_0^{\mathrm{HS}}\approx 12$ from Ref. [25]. That this is about three times larger than our value is partly due to a larger effective diameter $d_{\mathrm{eff}}\approx 1.5$ of our molecules, compared to $d^{\mathrm{HS}}=1$.

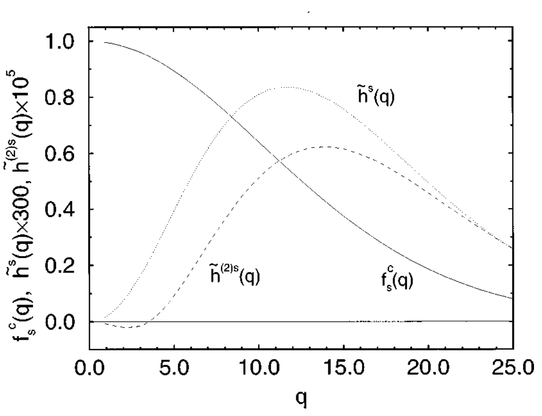

FIG. 9. Wave-vector dependence of $f_s^c(q)$ (solid line), critical amplitude $\tilde{h}^s(q)$ (dotted line), and the correction $\tilde{h}^{(2)s}(q)$ (dashed line).

We now turn to the collective dynamics as obtained from the density correlator $F(q,t)$, which is presented for $q=q_{\max}$ and $q=q_{\min}$ in Figs. 10(a) and 10(b), respectively. The time dependence looks similar to that of $F_s(q,t)$, but the

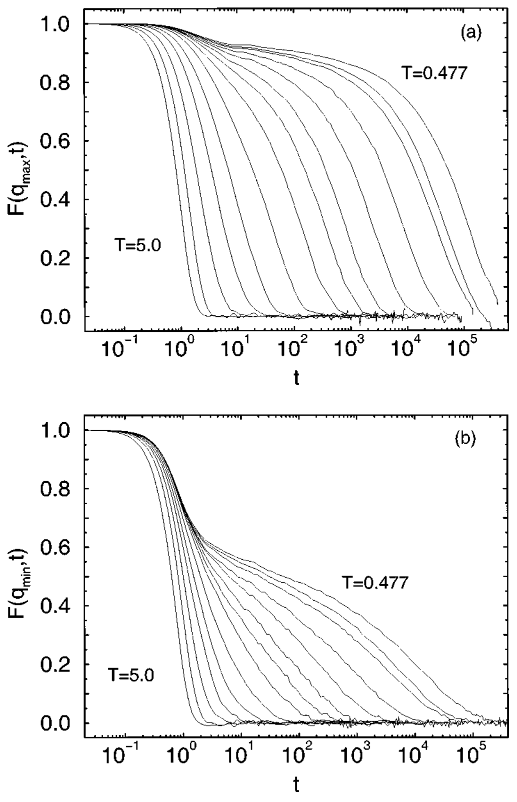

FIG. 10. Time dependence of $F(q,t)$ for all temperatures investigated. (a) $q=q_{\max}=6.5$, (b) $q=q_{\min}=8.15$.

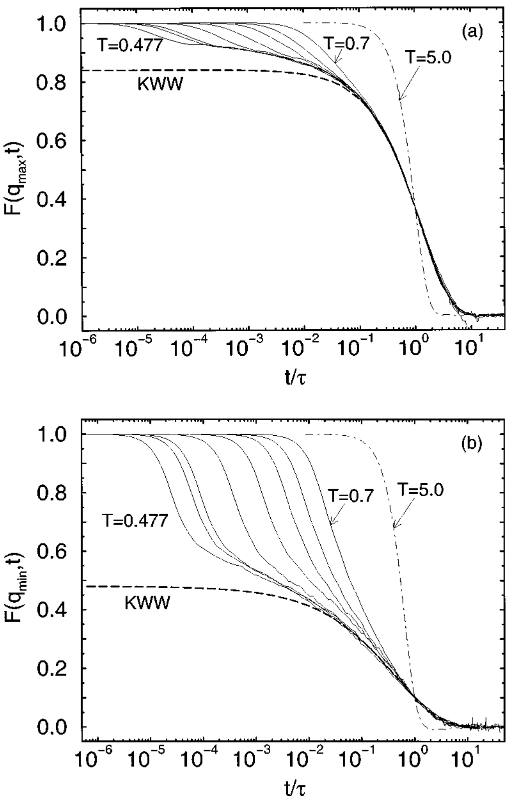

FIG. 11. $F(q_{\max},t)$ (a) and $F(q_{\min},t)$ (b) versus rescaled time. The eight curves (solid lines) on the left refer to the eight lowest temperatures and the one farthest to the right (dashed-dotted curve) corresponds to the highest temperature $T=5.0$. The dashed line is a fit with a KWW law.

height of the ''quasiplateau'' is much lower and the stretching of the relaxation is more pronounced for the case of $q=q_{\min}$. The α-relaxation time $\tau_q(T)$ has been determined from the condition $F(q,\tau_q)=0.1$, since using the e^{-1} definition of τ would lead to an underestimation of the α-relaxation time for $q=q_{\min}$, since the plateau is so low. (We note that choosing e^{-1} instead of 0.1, for the case where both definitions can be used, or even using a KWW fit to deduce $\tau_q(T)$, leads to essentially the same temperature-dependence.) The temperature dependence of τ_q is shown in Fig. 8. Taking again T_c = 0.475 as given, $\tau_q(T)$ obeys a power law, with $\gamma_{q_{\max}}=2.57\approx\gamma^{(s)}$ and $\gamma_{q_{\min}}=2.47$. It is remarkable that the range for the power law for $q=q_{\min}$ is almost one decade less than for $q=q_{\max}$, which shows that different correlators reach the asymptotic regime at different temperatures.

Figure 11 shows that also for these correlation functions the second scaling law holds and that it holds better for $q_{\max}$ than for $q_{\min}$. The reader should also notice that these two correlation functions behave quite similar to the corresponding ones of a hard-sphere system (cf. Fig. 17 in Ref. [23]). The late stage relaxation can again be fitted well by a KWW law (dashed line). Since the curves for the different temperatures fall onto a master curve, it is sufficient to focus on the curve for the lowest temperature in order to test whether the first scaling law holds. The results of our analysis are shown in Figs. 12 for $q=q_{\max}$ and $q=q_{\min}$. Let us discuss $q=q_{\max}$ first. As can be seen from Fig. 12, the von Schweidler law, with $b=0.55$, which corresponds to $\lambda=0.76$, the same value we used to fit the von Schweidler law to $F_s(q,t)$, fits the data over about 2.5 decades in time (long dashed line). Taking into account the next order correction [cf. Eq. (9)] leads to a significant improvement of the fit for $t\geqslant 4\times 10^4$ (solid line). We have also fitted the numerical data with the β correlator with (dotted line) and without (short dashed line) correction. This was done by solving the equation for $g_-(t/t_\sigma)$ (see Ref. [5]) and making use of Eqs. (3) and (4). Here we encounter the same problem as we did for the fit with the von Schweidler law, because the β relaxation time t_σ can only be determined up to a T-independent factor. In order to proceed, we have chosen for t_σ the position of the inflection point of $F(q_{\max},t)$, indicated in Fig. 12 by a filled circle. The optimum values $\lambda=0.76$ and $t_\sigma=69$ stemming from that fit were used for the analogous fits to all the other correlators of the present paper and of Ref. [18], except for the orientational correlators with $l=1$ [18]. From the figure we recognize that in the late β-relaxation regime these fits are identical to the ones of the von Schweidler law, as it should be. In the early β-relaxation regime, however, the β correlator fits the data much better than the von Schweidler law, since part of the approach to the plateau is fitted well also. In this early β-relaxation regime, MCT predicts the critical law [Eq. (13)]. Due to this result the relaxation onto the plateau for T near T_c should be stretched. This stretching can clearly be seen, e.g., in Fig. 11 for $q=q_{\min}$, by noticing how gentle the curves approach the quasiplateau. A further indication of the critical law is the existence of an inflection point on a logarithmic time scale at a time of order t_σ. This inflection point can easily be observed in Fig 11 as well. However, a fit with the critical law t^{-a} or even with the leading and next leading order [Eq. (13)] is possible but extends at most over one decade in time.

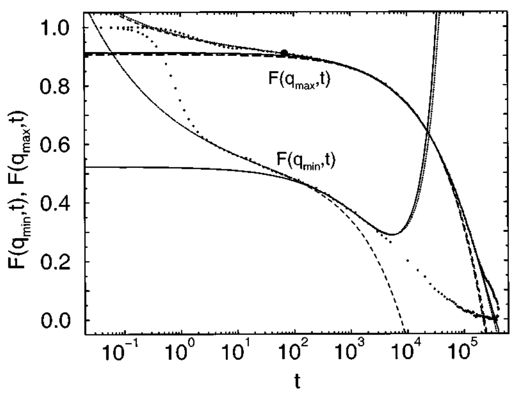

FIG. 12. $F(q,t)$ versus t for $T=0.477$: numerical data (bold dots), β correlator with $\lambda=0.76$ (short dashed line), β correlator with $\lambda=$ 0.76 including the next order corrections in the von Schweidler regime (dotted line), von Schweidler law with $b=0.55$ ($\hat{=}\lambda=0.755$) (long dashed line), von Schweidler law with $b=0.55$ including the next order corrections (solid line).

For $q=q_{\min}$ it is not possible to obtain a good fit with the von Schweidler law alone, if b is kept fixed at 0.55. If b is used as a free parameter, a satisfactory fit is obtained but at the cost of a q-dependent von Schweidler exponent b_q, in contradiction to the spirit of MCT. Since the critical NEP obtained from this fit are rather structureless and do not

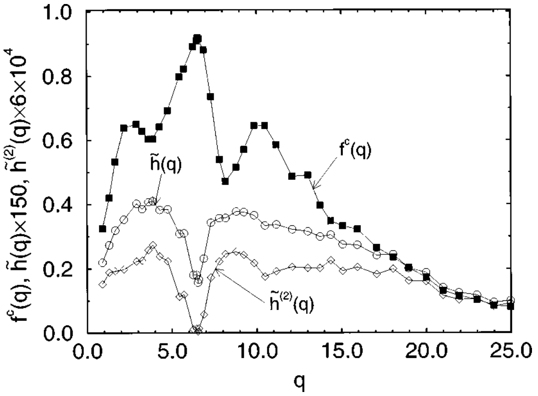

FIG. 13. Wave-vector dependence of $f^c(q)$ (filled squares), $\tilde{h}(q)$ (open circles), and $\tilde{h}^{(2)}(q)$ (open diamonds).

qualitatively agree with the NEP obtained from solving the molecular MCT equations [22], we decided to keep $b=0.55$ (obtained from $\gamma^{(s)}$) fixed and to take the next order correction into account. With this approach we obtained good agreement between all NEP from our MD simulation and those from the MCT equations [22]. But even if the first correction to the von Schweidler law [cf. Eq. (9)] is taken into account, the fit with Eq. (9) works well for only about one decade in time. On the other hand, the critical correlator (with $\lambda=0.76$) including the correction (on the von Schweidler side) fits the data over two decades. Nevertheless, this range is significantly smaller than the one found for $q=q_{\max}$, which shows that corrections to the scaling laws might be more important for $q_{\min}$ than for $q_{\max}$.

The quantities $f^c(q)$, $\tilde{h}(q)$, and $\tilde{h}^{(2)}(q)$, depicted in Fig. 13, were determined in a similar way as for the self-part, i.e., by keeping the value of b fixed to 0.55. Comparing these quantities with $S(q)$ (Fig. 1) we find that $f^c(q)$ is in phase and both $\tilde{h}(q)$ and $\tilde{h}^{(2)}(q)$ in antiphase with $S(q)$. We note that the peak at $q\approx3$ in $f^c(q)$ does not exist for $S(q)$. However, whether this peak is real or just a statistical fluctuation cannot presently be decided for sure. Since the orientational static correlator $S_{11}^0(q)$ has a pronounced maximum at $q\approx3$ (see Ref. [18]), one might be tempted to relate this prepeak of $f^c(q)$ to the translation-rotation coupling.

The variation of $f^c(q)$ and $\tilde{h}(q)$ with q resembles the one found, e.g., for hard spheres [25], for a binary liquid [27,30], and that for water molecules [31]. Interestingly the q dependence of $\tilde{h}^{(2)}(q)$, which is in phase with that of $\tilde{h}(q)$, qualitatively agrees with that found by Fuchs *et al.* for hard spheres [25]. However, in contrast to the hard-sphere system, $\tilde{h}^{(2)}(q)$ does not change sign for the q regime we have studied, but vanishes at $q=q_{\max}$ at which it has a minimum. This fact explains why the (asymptotic) von Schweidler law fits the data rather well for $q=q_{\max}$, where $\tilde{h}^{(2)}(q)\approx0$, but not for $q=q_{\min}$. To conclude, we show in Fig. 14 that also the variation of the α-relaxation time τ_q with q is in phase with $S(q)$, which is in close analogy with, e.g., the hard sphere system [25].

V. DISCUSSION AND CONCLUSIONS

There were two reasons for doing the investigations presented in this paper. On the one hand, we wanted to study how in a *molecular* supercooled liquid the translational degrees of freedom (TDOF) slow down when the temperature of the system is decreased in order to allow a comparison with (i) the corresponding slowing down in atomic systems that have been studied by other investigators and (ii) the slowing down of the orientational degrees of freedom (ODOF) of the same system and which will be presented in the following paper [18]. On the other hand, we wanted to test whether also for this molecular system the dynamics of the TDOF can be described by the ideal version of MCT for simple liquids.

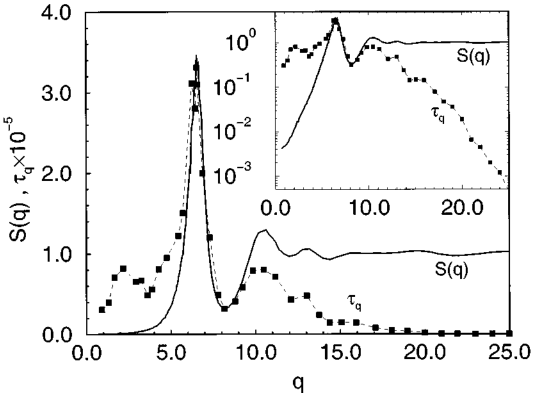

FIG. 14. Comparison of $S(q)$ (solid line) for $T=0.477$ and the α-relaxation time τ_q (filled squares) for $T=0.477$, where τ_q has been multiplied by 10^{-5}. Inset: The same quantities on a logarithmic scale.

The system we have investigated consists of rigid diatomic molecules without head-tail symmetry. The Lennard-Jones interactions we used for the molecular system are not so different from those of the binary liquid [27] with 80% A and 20% B atoms. The main difference between both systems is of course that for the present model the 50% A and 50% B atoms are pairwise connected in order to form diatomic molecules. Therefore, the comparison of the dynamical behavior of both systems allows us to discuss the influence of the ODOF on the TDOF.

Our test was mainly concerned with (i) the existence of a single critical temperature T_c and (ii) the validity of the predictions of the ideal MCT in the two scaling law regimes. The existence of such a single critical temperature indicates a strong coupling between TDOF and ODOF. Although the mathematical structure of the MCT equations for molecular liquids [19–22] differs from the one of simple liquids, we expect that the two scaling laws hold for molecular liquids, too. This belief is based upon the fact that the first scaling law is always valid in a so-called type-B transition (i.e., the NEP changes *discontinuously* at the transition), the type of transition that is relevant for structural glasses [5]. Furthermore, we expect the existence of a *single* transition temperature for linear and arbitrary molecules without additional symmetry, as is the case for simple liquids.

Taking T_c and γ as free parameters, the α relaxation times $\tau_q^{(s)}$ and τ_q for $q=q_{\max}$ and $q=q_{\min}$ can be fitted with a power law. The resulting T_c's differ from $T_c=0.475$ [deduced from $D(T)$] by less than 2%. The same value of T_c was found for the orientational correlation functions in Ref. [16] and we therefore conclude that our data are compatible with the existence of a single transition temperature. The sharp transition at T_c, as predicted by *ideal* MCT, is, however, smeared out, due to ergodicity restoring processes that can be accounted for by the extended MCT [17]. These processes are often associated with a hopping of the atoms or molecules, as it has been demonstrated for a binary simple liquid [32]. One possible piece of evidence for such hopping processes is the occurrence of a second peak in $G_s(r,t)$ at $r \approx 1$ for large times [32]. However, no such peak is observed in our results, even beyond the r range shown in Fig. 4. The absence of hopping processes with respect to the TDOF was also found in the MD simulation of CKN [8]. Therefore, only orientational jumps remain, which indeed have been shown to be present [16]. Comparing the different values of γ, one finds that those determined from $F_s(q,t)$ and $F(q,t)$ fluctuate around 2.55. The same is more or less true for the purely orientational correlators $C_l^{(s)}(t)$ and $C_l(t)$ [17] for $l>1$, but not for $l=1$, where $\gamma_1^{(s)}=1.66$ and $\gamma_1 = 1.52$ was found. Therefore, we can conclude that, apart for the case $l=1$, γ has essentially the same value for all correlators. We also note that in an MD simulation of supercooled water no such exceptional behavior of $l=1$ was observed [13].

For all the correlators related to the TDOF, the second scaling law is reasonably well fulfilled. This is in contrast to our findings for $C_1^{(s)}(t)$ and $C_1(t)$ [16]. Only for relatively large values of l do the $C_l^{(s)}(t)$ show the second scaling law.

Regarding the first scaling law, we can say that it works well for $F_s(q,t)$ and $F(q,t)$. For $q=q_{\min}$ we have demonstrated that the next correction to the von Schweidler law becomes important. We stress that a consistent description of our data in the framework of MCT is only possible by taking this correction into account. If this is not done, a q-dependent *effective* von Schweidler exponent and a rather structureless q variation of the orientational NEP (which will be discussed in the following paper [18]) results. The critical law manifests itself by a stretched relaxation onto the plateau with height $f_s^c(q)$ and $f^c(q)$, respectively. But for our system a convincing *quantitative* proof for the existence of the t^{-a} law is not possible.

In summary, we conclude that, with respect to ideal MCT, the TDOF of our molecular system behave quite similarly to those of a binary simple liquid [27]. Hence, the qualitative features of the dynamics of TDOF are not altered by its coupling to ODOF. Although a single transition temperature for TDOF and ODOF can be specified, part of the orientational dynamics as measured, e.g., by $C_1^{(s)}(t)$, does not fit into the framework of ideal MCT [16]. Whether this is only due to the 180°-reorientational jumps [16] is presently not clear.

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