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Dynamics of the rotational degrees of freedom in a supercooled liquid of diatomic molecules

Stefan Kämmerer, Walter Kob,* and Rolf Schilling†
Institut für Physik, Johannes-Gutenberg-Universität, Staudinger Weg 7, D-55099 Mainz, Germany

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Using molecular-dynamics computer simulations, we investigate the dynamics of the rotational degrees of freedom in a supercooled system composed of rigid, diatomic molecules. The interaction between the molecules is given by the sum of interaction-site potentials of the Lennard-Jones type. In agreement with mode-coupling theory (MCT), we find that the relaxation times of the orientational time correlation functions $C_1^{(s)}(t)$, $C_2^{(s)}(t)$, and $C_1(t)$ show at low temperatures a power law with the same critical temperature T_c, which is also identical to the critical temperature for the translational degrees of freedom. In contrast to MCT, we find, however, that for these correlators the time-temperature superposition principle does not hold well and also the critical exponent γ depends on the correlator. For $C_l^{(s)}$ with $l=3,\ldots,6$ this principle does hold. We also study the temperature dependence of the rotational diffusion constant D_r and demonstrate that at high temperatures D_r is proportional to the translational diffusion constant D and when the system starts to become supercooled the former shows an Arrhenius behavior, whereas the latter exhibits a power-law dependence. We discuss the origin for the difference in the temperature dependence of D (or the relaxation times of $C_l^{(s)}$) and D_r. Finally, we present results that show that at low temperatures 180° flips of the molecule are an important component of the relaxation dynamics for the orientational degrees of freedom. [S1063-651X(97)03411-9]

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I. INTRODUCTION

In the past ten years mode-coupling theory (MCT) [1–4] has led to a strong interest in the phenomenon of the glass transition since this theory makes detailed predictions on the dynamics of glass formers in the vicinity of the glass transition and thus challenges the experimentalists to test these predictions. Starting from the microscopic equations of motion, MCT derives, by using certain approximations that are believed to be quite reliable for *simple* liquids, an equation of motion for the density correlator. One of the main results of MCT is the existence of a dynamical transition at a temperature T_c, at which, in the so-called idealized version of the theory, the dynamics of the system undergoes a transition from an ergodic ($T>T_c$) to a nonergodic behavior ($T<T_c$) and which can be interpreted as a glass transition. Due to the presence of ergodicity-restoring processes, commonly called ''hopping processes,'' most glass formers show, to a certain extent, deviations from the predictions of the idealized theory since this version of MCT does not take into account these sort of processes. In the extended version of the theory hopping processes are taken care of and one finds that in the vicinity of T_c a crossover in the behavior of the dynamics can still be observed [1,2,4]. Many of the predictions of MCT were confirmed by experiments and in numerical simulations on various glass-forming systems. For reviews the reader is referred to Refs. [1–5].

In the real world most of the good glass formers are *molecular* systems. One of the important differences between molecular systems and simple liquids is that the former have orientational degrees of freedom (ODOF). The dynamics of these ODOF can be measured, e.g., by dielectric spectroscopy, light scattering, and NMR. For the molecular glass former salol, e.g., it has been shown that MCT gives a satisfactory description of the relaxation behavior of this system [6]. This conclusion seems to contradict the outcome of experiments in which the dielectric response of this system was probed [7] because of the following fact: MCT predicts that for all observables that couple to the density fluctuations the imaginary part of the corresponding susceptibility exhibits a minimum at the same frequency $\omega_{\min}$ if one is very close to T_c. Light scattering experiments have shown that in salol this minimum occurs at a frequency of about 7 GHz if $T=290$ K [6]. However, Dixon *et al.* showed that at the same temperature no such minimum is observed in the dielectric function $\epsilon''(\omega)$ for frequencies up to 18 GHz [7], thus seemingly contradicting the conclusions of Ref. [6] that MCT gives a correct description of the dynamics of this system. Similar conclusions were drawn for glycerol. However, in recent extensive dielectric measurements on glycerol this minimum was found and it was shown that the data can be described by the β correlator of MCT for simple liquids [8,9], although in this experiment the location of the minimum is indeed different from the one in the light scattering experiment. This could be due to at least two reasons. First, the MCT equations for *molecular* liquids might be significantly different from those for *simple* liquids, hence leading to different predictions. Second, the predictions of MCT for simple liquids can be used, but corrections to the asymptotic laws of MCT have to be taken into account. These corrections make the reduction theorem invalid and therefore the location of the minimum depends on the observable [10]. We also note that very recently evidence has been given that a minimum exists in $\epsilon''(\omega)$ for salol also [11]. However, its location remains still undetermined

The above discussion shows that the role of the ODOF for the glassy dynamics in the supercooled regime is certainly

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*Electronic address: kob@moses.physik.uni-mainz.de http://www.cond-mat.physik.uni-mainz.de/~kob/home_kob.html

†Electronic address: schillin@einstein.physik.uni-mainz.de

not settled and thus remains an interesting field of research. One possibility to gain some insight into the dynamics of supercooled liquids is to perform molecular-dynamics computer simulations of such systems [12]. Simulations of *simple* liquids have shown that this method can indeed be very useful to understand the dynamics down to temperatures close to T_c [13–15]. For *supercooled* molecular liquids, however, only few numerical simulation have been done so far. Signorini *et al.* investigated the dynamics of the ionic glass former $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN), where the NO_3 unit was treated as a rigid molecule [16] and Sindzingre and Klein studied methanol [17]. Orthoterphenyl (OTP) was investigated by Lewis and Wahnström [18,19], who modeled the molecule with a rigid isoscale triangle of Lennard-Jones particles, and by Kudchadkar and Wiest [20], who used an 18-site, three-ring model. Very recently Sciortino *et al.* presented their results on supercooled H_2O (also taken as a rigid molecule) [21,22]. In these papers a two-step relaxation process, as predicted by MCT, was observed for both the translational and rotational degrees of freedom. But a more quantitative analysis in the framework of MCT was essentially restricted to the translational degrees of freedom (TDOF). In particular, it does not become clear from these studies whether the ODOF freeze at the same temperature as the TDOF do since no detailed analysis with respect to this point was made (although very recently evidence was given that for water the freezing temperatures of the ODOF and the TDOF are very close together [22]). The investigation of this point is one of the major objectives of the present work. For this we will focus on the time scale of the α relaxation and discuss our findings regarding the β relaxation elsewhere [23]. We also mention that in a very recent paper Ma and Lai investigated the dynamics of the translational degrees of freedom for a dumbbell-shaped molecule and argued that the molecular character leads to a decrease of the MCT parameter λ [24].

We note that the role of the ODOF was also studied for quite different types of systems. For the so-called mixed *crystals*, e.g., $KBr_{1-x}K(CN)_x$, where the isotropic bromide is partly substituted by the linear molecule CN, which leads to a *quenched* disorder, an orientational glass transition occurs. For more details the reader may consult the reviews by Höchli *et al.* and Binder and Reger [25]. The reader should note, however, that these *crystalline* systems are very different from the molecular liquids in which we are interested in the present work.

The molecular system we consider consists of molecules in which two different atoms are connected rigidly. Apart from diatomic molecules with head-tail symmetry, this is the *simplest* molecular system one can choose. Although the choice of a linear molecule is of course somewhat special, it is nevertheless interesting to study the dynamics of such a molecular system in the supercooled regime in order to check whether even such a simple system shows the phenomenon of a glass transition. Furthermore, the continuous rotational symmetry around the long axis of the molecules simplifies also the theoretical description of this system, as compared to the molecules studied in Refs. [16–22], and thus allows us to make a more stringent test of the theory. Although the MCT equations for a diatomic molecule in a simple liquid [26] and for molecular liquids have been recently derived [27,28], they have not been analyzed in great detail so far. Since the structure of these equations is not identical to that for simple liquids, it is not obvious whether the predictions derived by Götze and collaborators [1–4,29] for MCT equations that apply to simple liquids are still valid. Thus one of the main motivation of the present work is to test whether these predictions hold also for the molecular system investigated here.

The outline of our paper is as follows. In the next section we define the various correlators and diffusion constants that we will study. In addition, we also summarize those results of MCT whose validity we will check for the present system. In Sec. III the model and the details of the computer simulation are presented. The results are given in Sec. IV and are discussed in Sec. V where we also offer our main conclusions.

II. CORRELATION FUNCTIONS AND PREDICTIONS OF MCT

In this section we define the correlation functions that are studied in this work and recapitulate some of the predictions of MCT. More details on MCT can be found in Refs. [1–4].

To study the static and dynamical properties of macroscopic systems with N particles it is convenient to use correlation functions. For the translational degrees of freedom it is customary to characterize the dynamics with the help of the Van Hove correlation function or its space Fourier transform, the intermediate scattering function. For the rotational degrees of freedom convenient correlation functions are the functions $C_l(t)$ and $C_l^{(s)}(t)$, which are defined as

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

and its self-part

$$C_l^{(s)}(t)=\frac{1}{N}\sum_{n=1}^{N}\langle P_l(\vec{u}_n(t)\cdot\vec{u}_n(0))\rangle,\quad l\geqslant 1. \tag{2}$$

Here $P_l(x)$ is the Legendre polynomial of order l and $\vec{u}_n$ is the normalized orientational vector of the nth molecule. These orientational correlation functions are straightforward generalizations of the intermediate scattering function to the case where also ODOF are present. More details on this point are given in Ref. [23]. The experimental relevance of the functions $C_l(t)$ is given by the fact that for $l=1$ and $l=2$ they can be measured in dielectric and light scattering experiments, respectively. We also note that it is often assumed (cf., e.g., Ref. [30]) that the cross terms in $C_l(t)$ can be neglected. In that case the experiments would also yield information on $C_l^{(s)}$. We will discuss this point below.

In addition to the intermediate scattering function or the correlators given in Eqs. (1) and (2), the dynamics of the system can also be studied by means of the autocorrelation functions of the velocities $\vec{v}_n(t)$ of the particles

$$\Phi(t)=\frac{1}{N}\sum_{n=1}^{N}\langle\vec{v}_n(t)\cdot\vec{v}_n(0)\rangle \tag{3}$$

or the corresponding one of the angular velocities $\vec{\omega}_n(t)$

$$\Psi_l(t)=\frac{1}{N}\sum_{n=1}^{N}\langle P_l(\cos\alpha_n(t))\rangle,\quad l\geq 1,\tag{4}$$

where $\alpha_n(t)$ is the angle between $\vec{\omega}_n(t)$ and $\vec{\omega}_n(0)$. It was recently shown that $\Psi_2(t)$ is particularly useful to study the freezing of the ODOF [31]. Since the translational and rotational diffusion constants D and D_r, respectively, can be obtained by means of a Green-Kubo relation from Eqs. (3) and (4), respectively, the significance of these time correlation functions is obvious.

In the strongly supercooled regime $\Phi(t)$ and $\Psi_1(t)$ exhibit a negative, slowly decaying long time tail. This makes the numerical calculation of D and D_r from the Green-Kubo relation a difficult task if the temperatures are low. Therefore, it is customary to use the corresponding Einstein relations, which are mathematically equivalent to the Green-Kubo identity. For the TDOF D is then determined from the mean squared displacement

$$D=\lim_{t\to\infty}\frac{1}{6tN}\sum_{n=1}^{N}\langle|\vec{x}_n(t)-\vec{x}_n(0)|^2\rangle.\tag{5}$$

To obtain the analog to this equation for the ODOF we replace $\vec{x}_n(t)$ by the corresponding variable $\vec{\phi}_n(t)$, which is defined as

$$\vec{\phi}_n(t)-\vec{\phi}_n(0)=\Delta\vec{\phi}_n(t)=\int_0^t dt'\,\vec{\omega}_n(t').\tag{6}$$

In analogy to Eq. (5) we thus obtain the following Einstein relation for the ODOF,

$$D_r=\lim_{t\to\infty}\frac{1}{4tN}\sum_{n=1}^{N}\langle|\vec{\phi}_n(t)-\vec{\phi}_n(0)|^2\rangle.\tag{7}$$

Note that $\vec{\phi}_n(t)$ is not bounded, in contrast to $\vec{u}_n(t)$, which is restricted to the surface of a unit sphere. This is the reason why a replacement of $\vec{x}_n(t)$ by $\vec{u}_n(t)$ in Eq. (5) would yield $D_r=0$.

Let us now recapitulate those predictions of the idealized version of MCT that are relevant for the present work. More details can be found in Refs. [1–4]. The theory predicts that, in the vicinity of the critical temperature T_c, all time correlation functions $\phi(t)$ that couple to the density correlation function should show a two-step relaxation behavior, i.e., exhibit a plateaulike region when plotted versus the logarithm of time. The time window in which ϕ is in the vicinity of this plateau is called the β-relaxation regime. The time window in which the correlator falls below this plateau is called the α-relaxation regime.

MCT predicts that upon approaching T_c from above, the α-relaxation time $\tau(T)$ diverges with a power law, i.e.,

$$\tau(T)\propto(T-T_c)^{-\gamma},\tag{8}$$

with a critical exponent $\gamma>1.5$. Note that the values of T_c and γ are predicted to be independent of the correlator. Furthermore, the theory predicts that also the translational diffusion constant D shows in the vicinity of T_c a power-law behavior, i.e.,

$$D(T)\propto(T-T_c)^{\gamma},\tag{9}$$

with the same γ as in Eq. (8).

Finally, the theory makes the prediction that the correlators should obey the so-called time-temperature superposition principle. This means that if a correlator $\phi(t,T)$ is plotted versus the reduced time $t/\tau(T)$, the curves corresponding to the different temperatures fall, in the α-relaxation regime, on a master curve $\hat{\phi}$, i.e.,

$$\phi(t,T)=\hat{\phi}(t/\tau(T)),\tag{10}$$

the shape of which is approximated well by a Kohlrausch-Williams-Watts function, i.e., $\hat{\phi}(t/\tau)\approx A\exp[-(t/\tau)^{\beta}]$, where the amplitude A and the exponent β are *not* universal, i.e., will depend on ϕ.

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 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 $\epsilon_{BB}=0.8$ and were chosen such that the system did not show any sign of crystallization even at the lowest temperatures investigated here. In the following we will use reduced units and 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 argonlike, this time unit corresponds to approximately 0.3 ps.

The choice of the intramolecular distance d between the A and B particles requires some consideration. On the one hand, d has to be large enough to allow for a sufficiently strong coupling between the translational and rotational degrees of freedom. On the other hand, it has to be so small that first the formation of liquid-crystalline structures is unlikely [32] and that second the energy barrier involved in the intersection of two molecules is so large that at the temperatures and on the time scale of the simulation such a crossing does not occur. We found that a value of 0.5 is a good compromise.

In order to make the simulation more realistic we did it at constant external pressure $p_{\mathrm{ext}}=1.0$. For this we equilibrated the system in the NpT ensemble, using the algorithm proposed by Andersen [33] and by setting the mass of the piston to 0.05. The length of these 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. After having determined from this equilibration run the appropriate density of the system for the temperature of interest, we fixed the total density to the so-obtained density and started a production run in the microcanonical ensemble using the rattle algorithm [34]. Note that it is advisable to make the production run in the

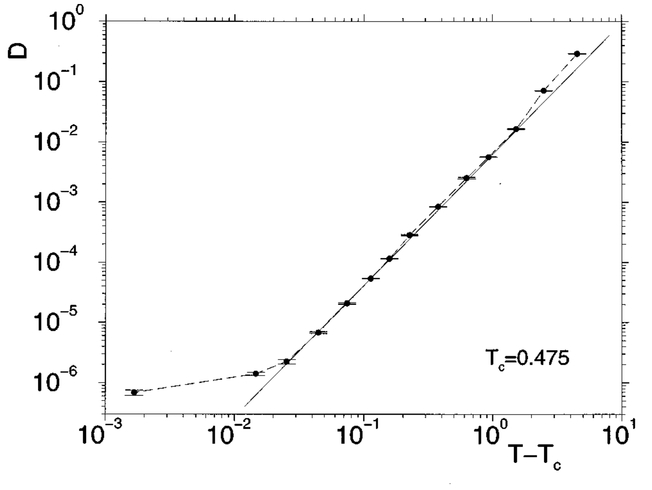

FIG. 1. Self-diffusion constant D versus $T-T_c$. The solid line is a fit with a power law with the exponent 2.20. The dashed line is a guide to the eye.

microcanonical ensemble if one wants to investigate the dynamics of the system, since the algorithms used for constant pressure simulations introduce an artificial dynamics that might lead to unphysical results. The step size we chose was 0.01 for the higher and 0.016 or 0.02 for the lower temperatures. For runs shorter or equal to 1.4×10^5 time units these step sizes are sufficiently small to allow one to neglect the drift in the total energy during the runs. This is not the case for the long runs at the two lowest temperatures, which had lengths of 3.0×10^5 and 4.0×10^5 time units, respectively ($=1.5\times10^7$ and 2.0×10^7 time steps). During these runs the value of the total energy was reseted periodically (about 30 times during the whole run) to its value at the start of the run by rescaling the velocities of all the particles appropriately. Since this interference with the dynamics is only very weak, it can be expected that the final result will essentially be independent of it.

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.

IV. RESULTS

Before we start to present the results on how the ODOF freezes, it is useful to investigate the dynamics of the TDOF, since this allows us to estimate the temperature range in which the system is supercooled. Therefore, we computed from the mean squared displacement of the center of the molecules the translational diffusion constant D. MCT predicts that, in the vicinity of the critical temperature T_c, the diffusion constant will show a power law [see Eq. (9)]. Thus we fitted our data for D with such a law, using T_c as a fit parameter. In Fig. 1 we show the diffusion constant versus $T-T_c$ in a double logarithmic plot. Also included is the fit with the power law of Eq. (9). We recognize that this fit is very good for a surprisingly large range in T and D. In particular, this range is significantly larger than the one found for the atomic Lennard-Jones system [14,15]. Since no analogous analysis was done for the molecular systems studied in Refs. [16–20] and the range in D explored in Ref. [21] was significantly smaller than the one considered here, it is at the moment not clear whether the fact that the power law can be observed over such an extended range in D is a peculiarity of the present system or whether it is a general feature of molecular systems.

From the figure we also note that at the two lowest temperatures the diffusion constant is significantly higher than it would be estimated from the power law that fits the data well at higher temperatures. The reason for this are likely the so-called hopping processes [35], the contributions to the relaxation that are not accounted for in the *idealized* version of the MCT. Thus it can be expected that for such low temperatures the predictions of this idealized version of the theory are no longer valid.

The value of the critical temperature T_c is 0.475 ± 0.005, which allows us to conclude that the TDOF of the system become very slow in the vicinity of this temperature. This is also corroborated by our investigation of the intermediate scattering function (coherent as well as incoherent) for which we found that their α-relaxation time shows also a power law with a critical temperature at 0.475 [23]. The critical exponent γ of the power law for D is 2.20, which is in the range of values found for γ in simple supercooled systems. In passing we mention that for this molecular system the dynamics of the TDOF is qualitatively similar to the one of simple liquids [23] and therefore the molecular character of the particles does not seem to affect the dynamics of the TDOF significantly.

We now focus our attention on the ODOF. The first quantity we investigate is the correlation function $C_1^{(s)}(t)$, which was defined in Eq. (2). In Fig. 2(a) we show this time correlation function for all temperatures investigated. From this figure we recognize that for high temperatures $C_1^{(s)}(t)$ decays quickly to zero. At intermediate temperatures it starts to show a weak shoulder, which on lowering the temperature further becomes more pronounced. The time range for which this shoulder is observed coincides with the one in which a plateau is observed in the intermediate scattering function [23] and thus can be identified with the β-relaxation regime.

From this figure we also recognize that for intermediate and low temperatures the shape of the curves in the α-relaxation regime seems to be almost independent of temperature, i.e., that the so-called time-temperature superposition principle (TTSP) holds [see Eq. (10)]. In order to investigate this point closer we plot in Fig. 2(b) the same curves versus the rescaled time $t/\tau_1^{(s)}(T)$, where $\tau_1^{(s)}(T)$ is the α-relaxation time. We define $\tau_1^{(s)}(T)$ to be the time it takes the correlation function to decay to e^{-1} of its initial value. From this figure we recognize that the TTSP does not hold very well, in that the slope of the curves at $t/\tau_1^{(s)}\times(T)=1.0$ changes significantly even at low temperatures. Thus we conclude that for this type of correlation function of the ODOF the TTSP does not hold very well, which is in contrast with the behavior of the TDOF of simple liquids [14,15] and of the present system [23] as well as for $C_1^{(s)}\times(t)$ for the methanol model of Sindzingre and Klein [17] or the OTP model studied by Wahnström and Lewis [19]. We also note that defining the α-relaxation time $\tau_1^{(s)}(T)$ in a different way, namely, by the time it takes the correlation

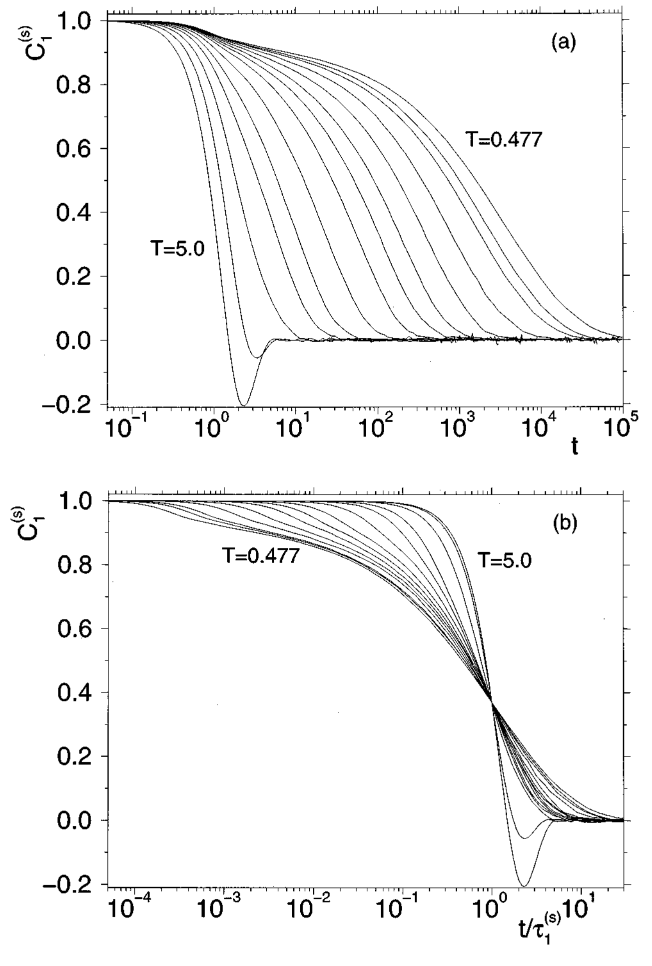

FIG. 2. Time dependence of $C_1^{(s)}$ [see Eq. (2)] for all temperatures investigated versus (a) time t and (b) rescaled time $t/\tau_1^{(s)}(T)$, where $\tau_1^{(s)}$ is the α-relaxation time.

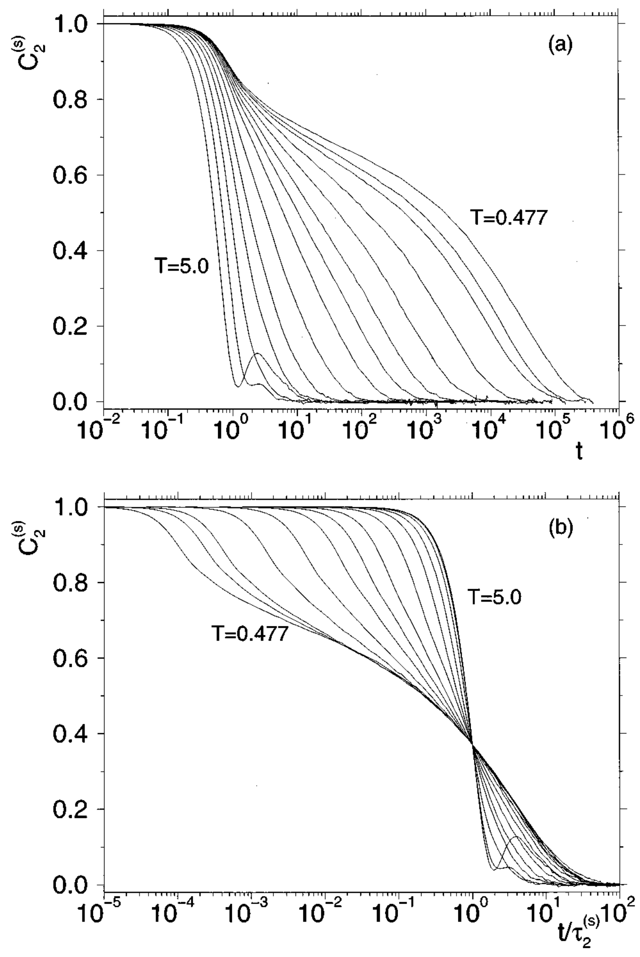

FIG. 3. Time dependence of $C_2^{(s)}$ [see Eq. (2)] for all temperatures investigated versus (a) time t and (b) rescaled time $t/\tau_2^{(s)}(T)$, where $\tau_2^{(s)}$ is the α-relaxation time.

function to decay to 10% of its initial value, or by using a fit with a Kohlrausch-Williams-Watts function (which gives a very good fit to the curves), does not change this conclusion, since the TTSP does not hold with these definitions of $\tau_1^{(s)}$ either. For example, we find that the Kohlrausch exponent β depends on temperature for $C_1^{(s)}$ (changing from values around 1.0 at high temperatures to 0.87 for $T=0.7$ and to 0.48 for $T=0.477$), whereas it is, at low temperature, constant to within the noise for $C_l^{(s)}$ with $l \geqslant 2$ [36]. The reason why, in the present system, the TTSP does not hold, whereas it seems to hold very well for the more complex molecules, is, at the moment, not clear. It *might* be that in our case the coupling between the TDOF and the ODOF is weaker than in the other cases, but further investigations on this point are needed.

Next we investigate the time and temperature dependence of $C_2^{(s)}(t)$ [see Eq. (2)], which is shown in Fig. 3. From Fig. 3(a) we see that $C_2^{(s)}(t)$ decays qualitatively similarly to $C_1^{(s)}(t)$ [Fig. 2(a)]. For the former, however, the height of the shoulder is lower than the one in $C_1^{(s)}(t)$, which is reasonable since, to a first approximation, this height is given by the value of the second Legendre polynomial evaluated at the height of the shoulder in $C_1^{(s)}$ [see Eq. (2)]. Note that this height is a measure of the corresponding nonergodicity parameter $f_l^c = \lim_{t\to\infty} C_l(t)$ at T_c.

Since the areas under the α peak and under the remaining part of the spectrum χ_l'' (i.e., the critical decay and the microscopic peak) are related to f_l^c and to $1-f_l^c$, respectively, our result suggests that the minimum between the two peaks is less pronounced for χ_1'' than for χ_2'', provided that the width of the microscopic peak is about the same for $l=1$ and $l=2$. This could be the reason why the detection of this minimum is so difficult in dielectric measurements, i.e., $l=1$, whereas it was readily found in light scattering experiments. These arguments recently were also put for the independently by Lebon *et al.* [37].

From Fig. 3(b) we recognize that for this correlation function the TTSP holds well for times larger than $\tau_2^{(s)}(T)$, the α-relaxation time for $C_2^{(s)}(t)$, but that for shorter times quite significant discrepancies are observed, as it was the case for $C_1^{(s)}$. Thus we come to the conclusion that the relaxation behaviors of $C_1^{(s)}$ and $C_2^{(s)}$ are qualitatively different.

Since the time dependence of $C_1^{(s)}$ seems to differ from the one of $C_2^{(s)}$, we have also studied the one of $C_l^{(s)}$ for $l=3,\ldots,6$, which, for the lowest temperature investigated, are show in Fig. 4. From this figure we recognize that (i) the height of the plateau decreases with increasing l, which can be rationalized by the same reasoning given above, (ii) with

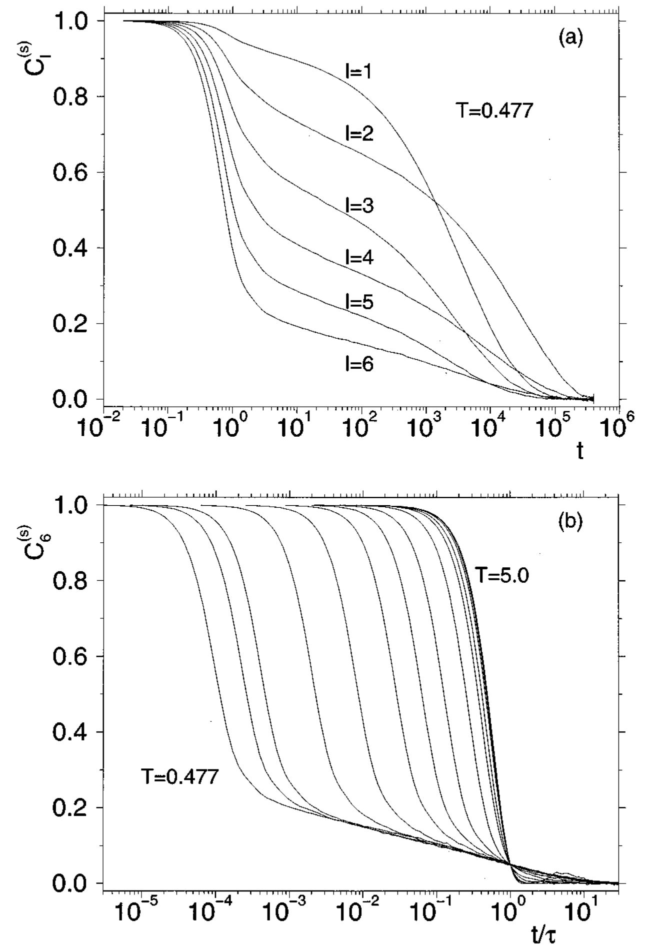

FIG. 4. (a) Time dependence of $C_l^{(s)}$ for $l=1,\ldots,6$ for $T=0.477$, the lowest temperature investigated. (b) Time dependence of $C_6^{(s)}(t)$ for all temperatures investigated.

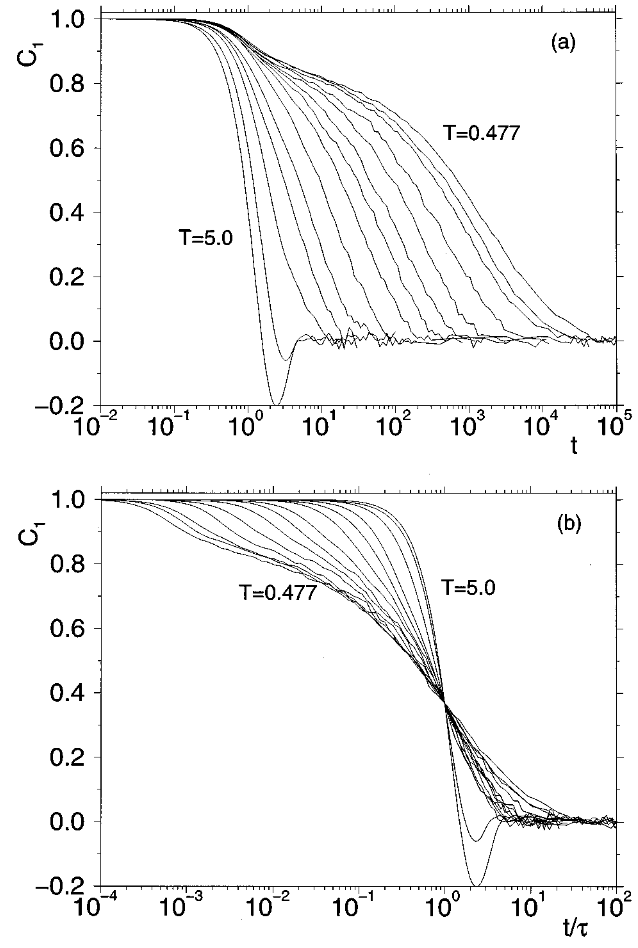

FIG. 5. Time dependence of C_1 [see Eq. (1)] for all temperatures investigated versus (a) time t and (b) rescaled time $t/\tau(T)$, where τ is the α-relaxation time.

increasing l the correlators seem to show more and more a logarithmic time dependence in the β-relaxation regime, and (iii) the correlators for odd values of l decay faster than the ones for even values of l. This effect can be understood by taking into account that at low temperatures the molecules make jumplike orientational flips of 180°, described in more detail below, which lead to a relaxation in $C_l^{(s)}$ if l is odd, but do not affect the correlators with even values of l. Furthermore, we have found that with increasing value of l the TTSP holds better and better [36], thus showing that from a qualitative point of view the correlators for the ODOF become more similar to the ones of the TDOF. For $C_6^{(s)}$, e.g., the TTSP holds very well [see Fig. 4(b)].

In addition to the self-parts $C_l^{(s)}$, we have also determined the time dependence of $C_1(t)$, one of the collective correlation functions of the ODOF [see Eq. (1)]. This correlation function is shown in Fig. 5 for all temperatures investigated. Although the noise in the data is significantly larger than the one in $C_1^{(s)}$, as it is often the case for collective quantities, we can clearly recognize that the time dependence of C_1 is qualitatively similar to the one of $C_1^{(s)}$ and that the TTSP (cf. Fig. 5) does not seem to hold. Furthermore, we note that, e.g., at the lowest temperature and for $t=10^3$ time units, $C_1^{(s)}(t)$ is about 25% larger than $C_1(t)$, which demonstrates that the cross terms in $C_1(t)$ should not be neglected, at least not in the strongly supercooled regime.

From Figs. 2(a), 3(a), and 5(a) we recognize that with decreasing temperature the relaxation of the ODOF slows down dramatically. Thus it is interesting to investigate the temperature dependence of the relaxation times. Since we have found that the diffusion constant (Fig. 1) as well as the α-relaxation times of the TDOF [23] show a power-law dependence on temperature, with the same critical temperature T_c, we checked whether also the α-relaxation times $\tau_1^{(s)}(T)$, $\tau_2^{(s)}(T)$, and $\tau_1(T)$ can be fitted with such a power law (with the same $T_c=0.475$). That this is indeed possible for about two orders of magnitude in τ is demonstrated in Fig. 6, where we show these quantities versus $T-T_c$ in a double logarithmic plot. As it was the case for the diffusion constant D, the values of τ for the two lowest temperatures deviate from the power laws since also here the relaxation is too fast, which is likely to be related to hopping processes. Thus we conclude that these processes affect the ODOF also.

From Fig. 6 we also note that the fitted power laws do not extend to such high temperatures as they did in the case of the diffusion constant. This is evidence that, similar to *simple* liquids, the presence of a large temperature range for which such a power law is observed is rather the exception than the rule. The critical exponents γ of the three power laws [see

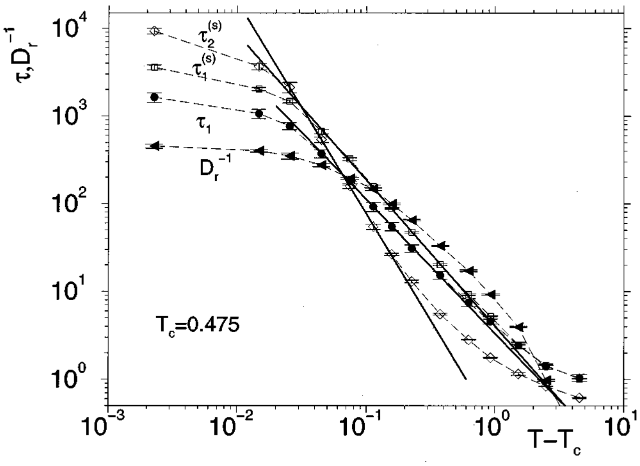

FIG. 6. α-relaxation time $\tau_1^{(s)}$ (squares), $\tau_2^{(s)}$ (diamonds), and τ_1 (circles) versus temperature. Solid lines are fits with a power law. Also included is the inverse of the rotational diffusion constant D_r (triangles). The dashed lines are guides to the eye.

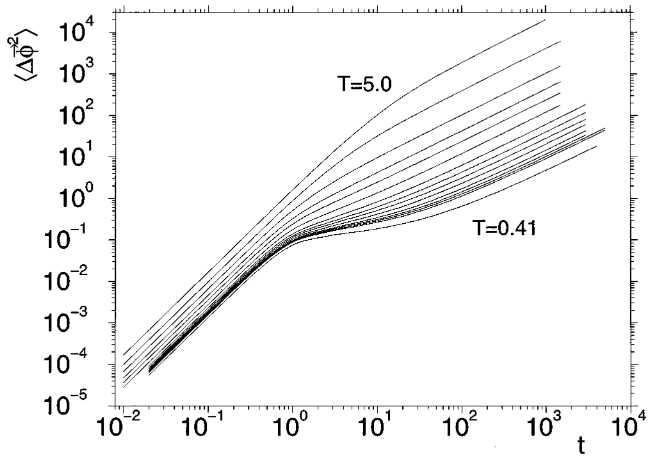

FIG. 7. Time dependence of $\langle (\Delta\vec{\phi}(t))^2 \rangle$ [see Eq. (6)] for all temperatures investigated.

Eq. (8)] are 1.66, 2.42, and 1.52 for $\tau_1^{(s)}$, $\tau_2^{(s)}$, and τ_1. Since the critical exponent for the diffusion constant is 2.20, we thus find that the four critical exponents are all different from each other, which disagrees with the prediction of MCT for simple liquids. However, if we determine the critical exponents for $C_l^{(s)}$ for $l=3,\ldots,6$, we find the values 2.25, 2.78, 2.55, and 2.80. These values have to be compared with the critical exponent for the TDOF, which is around 2.6 [23] and thus quite close to the one of $C_l^{(s)}$ for the larger values of l. Thus this is more evidence that the latter correlators behave qualitatively similarly to the ones for the TDOF.

We also mention that a power-law fit to $\tau_l^{(s)}$ and τ_1, with the critical temperature T_c as a free parameter, leads to a slightly improved fit. The optimal values of the critical temperature were to within 2% equal to 0.475, the value of T_c from the diffusion constant. Thus we find that the ODOF, measured by $C_l^{(s)}$ and C_1, would indeed freeze very close to $T_c=0.475$ if the hopping processes were absent.

Furthermore, we note that a fit of $\tau_1^{(s)}$ and $\tau_2^{(s)}$ with the popular Vogel-Fulcher law $A\exp[B/(T-T_0)]$ also works remarkably well. In particular, we find that this functional form is able to fit the data well at *all* lower temperatures, i.e., also the data points at the two lowest temperatures, for which the power law fails to fit the data. Thus we conclude that if seen as a mere fitting function, the Vogel-Fulcher law gives a better fit than the power law. However, the Vogel-Fulcher temperature T_0 was determined to be 0.328 and 0.386 for $\tau_1^{(s)}$ and $\tau_2^{(s)}$, respectively. Thus we find that the two temperatures differ by about 20%, hence indicating, that, according to the Vogel-Fulcher fits, there is no unique temperature at which the system ceases to relax. Therefore, this sort of fit is, from a physical point of view, less appealing.

The α-relaxation times $\tau_l^{(s)}(T)$ and $\tau_1(T)$ are analogous quantities to the α-relaxation time $\tau(T)$ of the intermediate scattering function. Since in supercooled liquids the temperature dependence of τ and of the diffusion constant can be different (see, e.g., Refs. [15, 21]) it is interesting to investigate also the *rotational* diffusion constant D_r and compare it with the temperature dependence of the relaxation times $\tau_1^{(s)}$ and $\tau_2^{(s)}$.

As already mentioned in Sec. II, the calculation of D_r is numerically difficult when one uses a Green-Kubo relation. Instead, it is much simpler to compute D_r from the Einstein relation given by Eq. (7). In Fig. 7 we show the time dependence of the mean squared displacement of the angles $\vec{\phi}(t)$, i.e., $\langle [\Delta\vec{\phi}(t)]^2 \rangle = \langle |\vec{\phi}_n(t)-\vec{\phi}_n(0)|^2 \rangle$, where $\vec{\phi}_n(t)-\vec{\phi}_n(0)$ is defined in Eq. (6).

From this figure we recognize that, analogous to the mean squared displacement [23], $\langle [\Delta\vec{\phi}(t)]^2 \rangle$ shows at short times a power law with exponent 2.0, which corresponds to the free rotational motion of the molecules. For high temperature this type of motion crosses over directly into a diffusional behavior, i.e., $\langle [\Delta\vec{\phi}(t)]^2 \rangle$ is given by a power law with exponent 1.0. This is not the case for the low temperatures, where the time regimes of the free rotation and the one of the diffusive behavior are separated by a time regime where the increase of $\langle [\Delta\vec{\phi}(t)]^2 \rangle$ is slower than diffusive. The time at which this subdiffusive behavior *starts* is essentially the same as the one in which also the mean squared displacement (MSD) of the particles starts to show a subdiffusive behavior [23]. In contrast to this, the time where $\langle [\Delta\vec{\phi}(t)]^2 \rangle$ starts to show the diffusive behavior is, at the lowest temperatures, significantly less (by about 1–2 decades) than the times where the MSD starts to show the diffusive behavior. Thus, despite the qualitative similarity of the time dependence of $\langle [\Delta\vec{\phi}(t)]^2 \rangle$ and the MSD, there are some distinct differences between the two quantities and thus we conclude that the plateaulike region in $\langle [\Delta\vec{\phi}(t)]^2 \rangle$ should *not* be identified with the β-relaxation regime. We will return to this point later.

From the time dependence of $\langle [\Delta\vec{\phi}(t)]^2 \rangle$ it is simple to compute D_r [see Eq. (7)]. Note that, because $\langle [\Delta\vec{\phi}(t)]^2 \rangle$ reaches its diffusive limit at shorter times than the MSD does, the rotational diffusion constant can be calculated reliably from a relatively short run, an observation of which we will make use of below.

In Fig. 8 we show the temperature dependence of D_r in an Arrhenius plot. In order to facilitate the comparison between

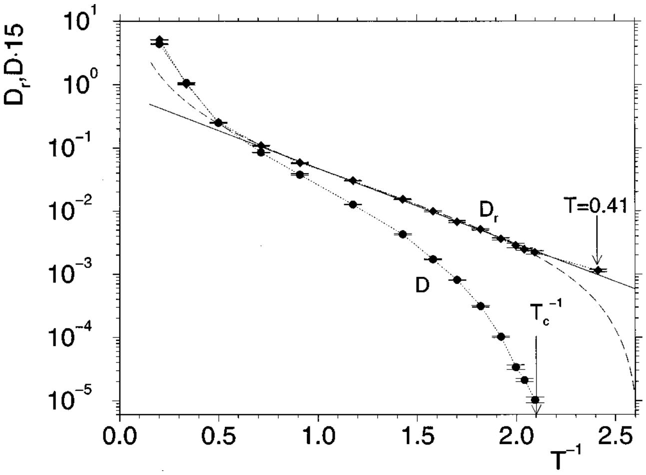

FIG. 8. Temperature dependence of the rotational diffusion constant D_r (diamonds) and of the translational diffusion constant D (circles). D is multiplied by 15 so that the two curves coincide at high temperatures. The straight solid line is an Arrhenius behavior and the dashed line is a power law with a critical temperature 0.38. The dotted lines are guides to the eye.

the rotational and translational diffusion constant, we have included the latter in the figure as well. (Note that we have multiplied D by 15 in order to make D and D_r coincide at high temperatures. Also it should be remembered that D and D_r have different units.) We see that for temperatures less than 2.0 the data (diamonds) can be fitted well with an Arrhenius law (solid straight line). Furthermore, we recognize that the temperature dependence of D_r follows the one of D for high temperatures, but that when the system starts to become supercooled, the curve for D drops significantly below the one for D_r. Thus we find that at high enough temperatures the ODOF and the TDOF couple strongly enough to show the same temperature dependence of D_r and D, which is in agreement with the well-known Stokes-Einstein and Stokes-Einstein-Debye relations. For lower temperatures D shows the power law discussed in Fig. 1, the reason for which are likely the mode-coupling effects. In contrast to this, D_r shows an Arrhenius law from which we can conclude that the rotational motion of the molecule is an activated process. We will study this process in more detail below.

We have also checked whether at low temperatures, i.e., $2.0 \geqslant T \geqslant 0.477$, the temperature dependence of D_r can be fitted well by a power law and found that this is indeed possible with a critical temperature around 0.38 (dashed line in Fig. 8). This temperature is significantly lower than the critical temperature T_c we found for the diffusion constant, the intermediate scattering function, and the relaxation times of $C_l^{(s)}$ and C_1, which was 0.475. In order to discriminate between the two functional forms (Arrhenius and power law) we made use of the observation described above that the rotational diffusion constant can be determined from a relatively short run (compared to the α-relaxation times of the TDOF); see Fig. 7. Thus we used the temperature dependence of the density (obtained from our equilibrated runs at temperatures $T \geqslant 0.477$) to estimate the volume of the system at $T=0.41$. We then set up the volume of the system such that its density corresponded to this extrapolated value and quenched the system to $T=0.41$. After allowing the system to relax for 2.0×10^5 time units we started to measure the time dependence of $\langle(\Delta\vec{\phi})^2\rangle$ for three independent runs. Note that this time is clearly not sufficient to equilibrate the system with respect to its TDOF, but it should at least allow the system to get reasonably close to its equilibrium state at this temperature. The so-obtained $\langle[\Delta\vec{\phi}(t)]^2\rangle$ is included in Fig. 7 as well (bottom curve). We see that even at this low temperature the diffusive rotational behavior can be observed on the time scale of our simulation. Thus we could extract the corresponding value of D_r and have included it in Fig. 8 as well. This data point lies reasonably close to an extrapolation for the previously fitted Arrhenius law and is completely off the curve for the power law. (The fact that this point lies slightly above this Arrhenius law can be understood by taking into account that at this temperature the TDOF are not quite relaxed. Hence it can be expected that all the relaxation times are smaller than they would be in an equilibrated sample and that therefore the measured diffusion constant is too large [38].) Thus we conclude that the rotational diffusion constant, as defined in Eq. (7), follows an Arrhenius law even at very low temperatures and that it is very unlikely that its temperature dependence is given by a power law.

In Fig. 6 we have seen that the relaxation times of the orientational correlation functions show a power-law dependence on temperature and that the critical temperature T_c is very close to the one of the translational diffusion constant or the one of the intermediate scattering function. From Fig. 8 it is recognized, however, that the rotational diffusion constant D_r does *not* show any exceptional temperature dependence in the vicinity of T_c [to see this we have included in Fig. 6 also the inverse of D_r (triangles) and it can clearly be seen that no power law is observed for this quantity]. At first view these two facts seem to contradict each other, but as we will show now this is not the case at all. In order for the time correlation functions $C_1^{(s)}$ and $C_2^{(s)}$ to decay to zero it is necessary that the orientation of the molecules changes by an angle on the order of 180° and 90° in the case of $C_1^{(s)}$ and $C_2^{(s)}$, respectively. In order to undergo such a large change of orientation, a molecule has to wait until the cage formed by the surrounding molecules breaks up. The time for this to happen is related to the relaxation time of the translational degrees of freedom and thus we find that the relaxation times of $C_1^{(s)}$ and $C_2^{(s)}$ become very large when the temperature approaches T_c.

For the rotational diffusion constant the situation is different. As can be seen from Eqs. (6) and (7), D_r remains finite as long as there is a possibility that $|\Delta\vec{\phi}(t)|^2$ increases (linearly) with time. At low temperatures a molecule will not be able to make large changes of its orientation, but a small librational (tumbling) motion is still possible (for the TDOF this corresponds to the rattling of the particles in their cage), which was nicely demonstrated by Renner *et al.* for a system of infinitely thin rods on a cubic lattice [31]. It is not hard to see that this librational motion gives rise to a diffusive movement of the z component of the vector $\vec{\phi}$ and hence to a finite value of D_r (here the z axis is defined by the molecular axis of the molecule at time zero).

In order to see this effect more clearly we have investi-

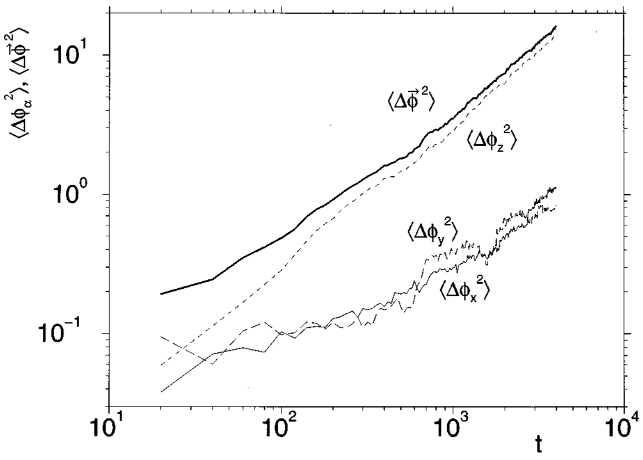

FIG. 9. Time dependence of $\langle(\Delta\phi_x)^2\rangle$, $\langle(\Delta\phi_y)^2\rangle$, and $\langle(\Delta\phi_z)^2\rangle$ and their sum $\langle(\Delta\vec{\phi})^2\rangle$ [see Eq. (6)] for $T=0.41$. See text for details.

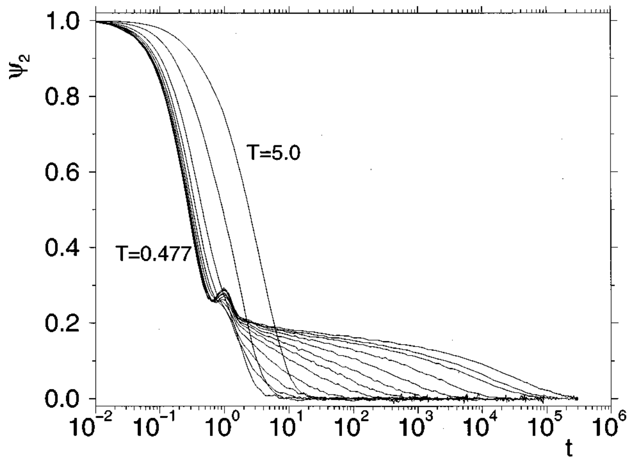

FIG. 10. Time dependence of the autocorrelation function $\Psi_2(t)$ of the angular velocities [see Eq. (4)] for all temperatures investigated.

gated the orientational dynamics of the molecules at $T=0.41$ in more detail. At this low temperature the orientation of most of the molecules stays for a long time in the vicinity of the direction it was at time $t=0$. Thus we determined the mean orientation of the z axis of each molecule by averaging its direction over a period of 4×10^3 time units. Note that such a mean direction makes only sense if the orientation of the molecule does not change significantly. Hence we will restrict the following analysis to only those molecules for which the maximum deviation from this mean axis was less than 45°. In the considered time window this is the case for 74% of the molecules. Having determined the mean z axis, we chose an x and a y axis perpendicular to the z axis and computed the time dependence of $\langle[\Delta\phi_\alpha(t)]^2\rangle=\langle|\phi_\alpha(t)-\phi_\alpha(0)|^2\rangle$, with $\alpha\in\{x,y,z\}$. The time dependence of these three functions are shown in Fig. 9. We see that $\langle[\Delta\phi_z(t)]^2\rangle$ is indeed significantly larger than $\langle[\Delta\phi_x(t)]^2\rangle$ and $\langle[\Delta\phi_y(t)]^2\rangle$. This is in accordance with the picture put forth above that the orientational diffusion of the molecules in the z direction is much larger than the one in the x and y directions. We also recognize that the latter are not *completely* suppressed, which is likely due to the fact that the cage in which the molecule sits is still slowly changing with time. It is important to notice that similar arguments do not hold for the TDOF. The rattling of the center of mass within a cage is isotropic on the average. It is the direction of the molecular axis that breaks this isotropy on a ''mesoscopic'' time scale.

The fact that at low temperatures the molecules perform for a long time a librational motion can also be demonstrated nicely by considering the autocorrelation function $\Psi_2(t)$ of the angular velocity $\vec{\omega}(t)$; see Eq. (4). As illustrated by Renner *et al.*, $\Psi_2(t)$ is expected to show a plateau with a height equal to or less than 0.25 if the motion of the molecule is of a librational type [31]. In Fig. 10 we show the time dependence of Ψ_2 for all temperatures investigated. From this figure we recognize that the *short* time relaxation time of Ψ_2 *decreases* with decreasing temperature and that at low temperatures the correlation function shows indeed a plateau.

A different way to study the orientational motion of the molecules is to investigate the time dependence of the distribution function $G(\theta,t)$, which is defined analogously to the self part of the Van Hove correlation function, i.e.,

$$G(\theta,t)=\frac{1}{N\sin\theta}\sum_{i=1}^{N}\langle\delta(\theta-\cos^{-1}[\vec{u}_i(t)\cdot\vec{u}_i(0)])\rangle, \tag{11}$$

where $\vec{u}_i(t)$ is the unit vector parallel to the axis of molecule i at time t. In Fig. 11 we show $G(\theta,t)$ for different temperatures. Note that $G(\theta,t)$ is defined such that for long times it approaches 1.0 for all values of θ. From Fig. 11(a) we recognize that for $T=2.0$ this function decays monotonically in θ for all times. This changes when the temperature is decreased to $T=0.63$ [Fig. 11(b)] since then, e.g., the curve for $t=77.7$ (bold dashed curve) shows a small additional peak at 180° that is separated from the main peak at 0° by a shallow minimum around 120°. This additional peak stems from molecules that underwent a rotation of 180°. This feature becomes much more pronounced when the temperature is decreased further to $T=0.477$ [Fig. 11(c)]. The mentioned minimum now exists for a large time range before it starts to disappear on the time scale of the α relaxation. At even lower temperature, $T=0.41$ [Fig. 11(d)], the minimum does not show any sign of filling up at all on the time scale of our simulation. However, we see that the peak at 180° is still observable, which means that a significant fraction of the molecules made a flip of 180°.

To study these 180° jumps on a more microscopic level, we have also investigated the time dependence of the angle θ of *individual* molecules. From such studies we found that at low temperatures, i.e., $T=0.41$, the z axis of the molecules stays for a long time in the vicinity of its orientation at $t=0$ and then undergoes *relatively* quickly a flip of 180° (see Fig. 12 for three representative trajectories). Qualitatively similar results have been reported in Ref. [17]. The typical time for this flip is around 50 time units, but also faster [see, e.g., Fig. 12(b)] and slower transitions can be observed. This transition time is relatively long compared to the time scale of a (translational) vibration of a molecule in its cage, which is on the order of two time units. Therefore, we conclude that such a 180° flip is not a fast process in which the molecule overcomes one barrier in a quasiballistic way, but rather the sum

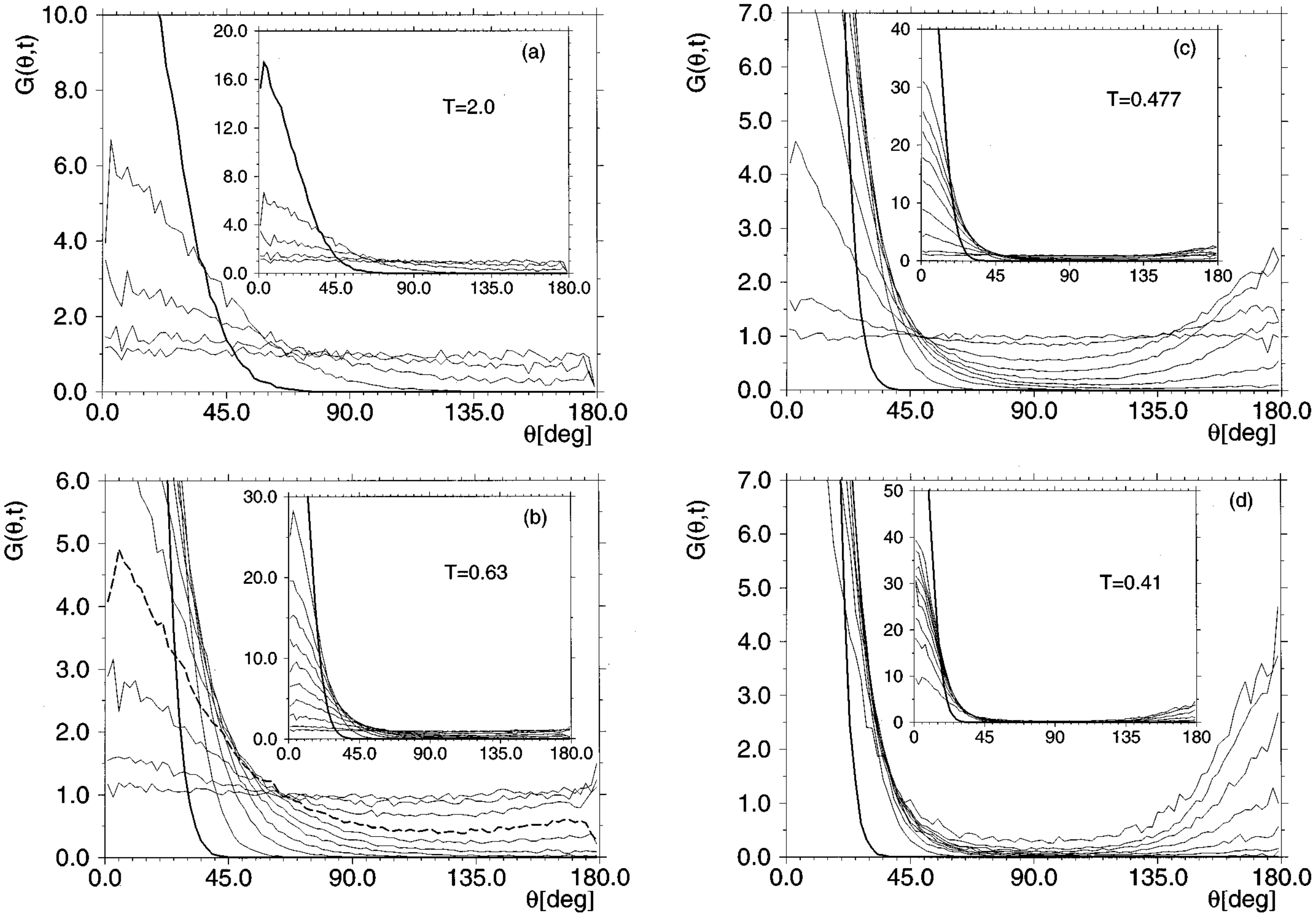

FIG. 11. Function $G(\theta,t)$ for different times and temperatures. Consecutive curves are spaced by about a factor of 2 in time. The bold curves correspond to a time of approximately 0.64. The insets show the same curves on an expanded scale. (a) $T=2.0$, (b) $T=0.63$, (c) $T=0.477$, and (d) $T=0.41$.

of a quick succession of smaller jumps. Finally, we mention that the molecules do not show this sort of little jump either before or after they undergo a 180° flip, which shows that these little jumps are associated with the flips.

Finally, we note that the observed 180° jumps resemble the ones found in mixed crystals. For instance, the CN molecule in $\mathrm{KCN}_x\mathrm{Br}_{1-x}$ undergoes a glass transition at a temperature T_g, where the *quadrupolar* degrees of freedom freeze into an orientational glass, whereas the *dipolar* order, i.e., the head-tail dynamics, remains ergodic [25]. These 180° jumps of CN below T_g also exhibit Arrhenius behavior [25] and are thus similar to the dynamics of our diatomic molecules.

V. CONCLUSION

The main motivation of this paper has been to investigate the dynamics of the orientational degrees of freedom in a supercooled molecular liquid. This was done by means of a molecular-dynamics simulation for a very simple molecular system, a liquid of diatomic, rigid molecules.

The first question we addressed was how the translational and the orientational degrees of freedom slow down if the temperature is decreased and the system becomes strongly supercooled. Since the mode-coupling theory is presently the only microscopic theory that predicts, in its idealized version, a glass transition at a temperature T_c, we have checked the consistency of our results with the predictions of this theory.

In the α-relaxation regime MCT predicts in the vicinity of T_c a power-law behavior for the temperature dependence of the corresponding relaxation times and the diffusion constants [cf. Eqs. (8) and (9)]. We find that the translational diffusion constant D as well as the relaxation times τ for the orientational correlators $C_l^{(s)}$ and C_1 can indeed be fitted by a power law and that the transition temperature T_c is 0.475 ± 0.005. This fit describes the data for D and τ very well for about four and two decades, respectively. The fact that a *single* critical temperature exists is consistent with the molecular MCT [27,28]. Different transition scenarios with more than one critical temperature can only exist for linear molecules with head-tail symmetry, which is not the case for our molecule.

The exponents of the power laws are not universal, but vary between 1.52 and 2.42. The universality of these exponents for the α relaxation of various correlators, as predicted by MCT for *simple* liquids, is based on the factorization theorem [1]. It is expected that for *molecular* liquids the same reasoning can be applied and that therefore MCT pre-

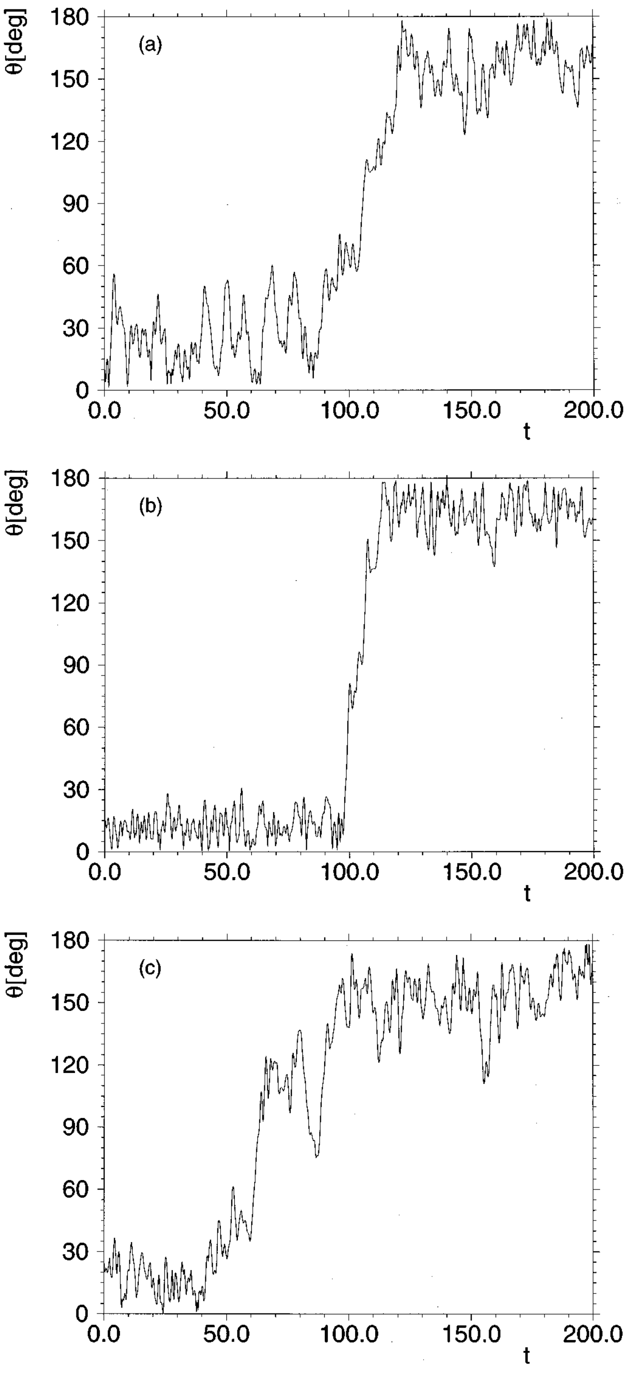

FIG. 12. Time dependence of the angle θ of an individual molecule in the time range where the molecule makes a 180° flip. Three representative curves are shown. $T=0.41$.

dicts also for such systems the universality of γ [27]. The fact that this is in contrast to our findings is, however, probably not a consequence of the molecular character of our system since it has been shown that also for *atomic* systems, e.g., the diffusion constant and the α-relaxation times do not have the same exponent [15]. Thus is seems that with regard to this, the theory is not as reliable as with regard to its other predictions. The reason why this is the case is, however, presently not understood.

The next interesting result is that the rotational diffusion constant D_r, as defined by Eq. (7), shows a significantly different temperature dependence from the quantities just discussed. For high temperatures, D_r and D are proportional to each other, in accordance with the hydrodynamic Stokes-Einstein and Stokes-Einstein-Debye relations. However, below a temperature $T^* \approx 1.4$, which is far above T_c, D is described well by the mentioned power law, whereas D_r shows an Arrhenius dependence. We find that T^* is the temperature at which the cage effect starts to become important, i.e., the system begins to be supercooled. This can be inferred from the fact that at T^*, $\langle \Delta r^2 \rangle$ and $\langle (\Delta \vec{\phi})^2 \rangle$ start to show anomalous diffusion behavior at intermediate times. Thus we conclude that the breakdown of this aspect of the hydrodynamic equations and the onset of the cage effect in supercooled liquids occur at the same temperature. We stress, however, that the different temperature dependence of D and D_r below T^* is *not* related to the similar phenomenon observed in experiments [39]. In these experiments the relaxation of the orientational vector $\vec{u}_n(t)$ of the nth molecule is studied. The measured quantity corresponds to the correlator $C_l^{(s)}(t)$ [see Eq. (2)]. In most theoretical approaches the rotational dynamics is described by a Smoluchowski equation in which it is assumed that the angular velocities can be eliminated adiabatically. This crucial assumption, as well as the subsequent linearization, leads to an *exponential* relaxation with an α-relaxation time $\tau_l^{(s)}$ that is proportional to $1/D_r l(l+1)$ [40]. Using this relationship, D_r can then be deduced. Our results at lower temperatures are not consistent with this theoretical result because (i) $D_r(T)$ is *not* proportional to $[\tau_l^{(s)}(T)]^{-1}$ and (ii) $\tau_1^{(s)}(T)/\tau_2^{(s)}(T) \neq 3$. The reason for this is the nonexponential relaxation we have found for which the proportionality of D_r and $(\tau_l^{(s)})^{-1}$ and the relation $\tau_1^{(s)}/\tau_2^{(s)}=3$ are not granted.

In the vicinity of T_c the data for D and $\tau_l^{(s)}$ deviate from the power law observed at intermediate temperatures. (The same deviations are found for the α-relaxation times of the coherent and incoherent intermediate scattering functions of the center of the molecules [23].) This is likely due to the hopping processes, which restore ergodicity even at low temperatures. If hopping of the center of mass of the molecules becomes important at lower temperatures, this should be seen in the self part of the Van Hove correlation function $G_s(r,t)$ (see, e.g., Ref. [13]). Surprisingly, even at the lowest temperature $T=0.477$, $G_s(r,t)$ does not show any sign of a second (smaller) peak at a distance $r \approx 1$, which corresponds to the mean distance between two neighboring molecules [23]. That $D(T)$ nevertheless deviates from a power law at low T may be explained by the jumplike reorientations of the ODOF, which we have identified in the distribution function $G(\theta,t)$ as 180° flips. These jumps, which were also observed in earlier molecular-dynamics simulations [16–18], may lead to a local "melting" of the neighborhood of a molecule that just jumped, thereby allowing a translational diffusion without the molecule having to jump over the walls of its cage. The rotational diffusion measured by D_r is an activated process, at least for lower temperatures. Its T dependence can be described by an Arrhenius law even for a temperature $T=0.41$ that is far below T_c. This Arrhenius dependence is somewhat reminiscent of the temperature dependence of the Johari-Goldstein β peak in the dynamic susceptibility [41]. Since we have shown that the Arrhenius dependence of D_r is related to the librational motion of the molecules, one thus might speculate as to whether the dynamics leading to the β peak are indeed related to such librations. However, in order to decide this one would have to investigate the equilibrium dynamics of the systems at significantly lower temperatures than is presently possible.

Regarding the time dependence of the various correlators at low temperatures, we have found a two-step relaxation process, with a strongly nonexponential behavior, for all of them. This is in agreement with the results in Refs. [16–19, 21] and also with MCT. However, in contrast to the prediction of MCT, the time-temperature superposition principle does not seem to work very well for the orientational correlators investigated here, although it does so for $C_l^{(s)}$ with $l \geqslant 3$ and for the correlators of the TDOF. This shows that, despite the fact that the temperature dependence of the relaxation times of the TDOF and of the ODOF are very similar, the relaxation dynamics of the two types of correlation functions is, if $l = 1$ or $l = 2$, qualitatively different. Finally, we mention that at low temperatures $C_1^{(s)}(t)$ and $C_1(t)$ differ from each other in the α-relaxation regime by about 25%, which demonstrates that the cross terms in $C_1(t)$ should not be neglected.

ACKNOWLEDGMENTS

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