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

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Abstract

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 $C_1(t)$, $C_2(t)$ and $C_1(t)$ show at low temperatures a power-law with the same critical temperature $T_c$, and 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 that also the critical exponent $\gamma$ depends on the correlator. 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 that 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 $C_1(t)$) and $D_r$. Finally we present results which show that at low temperatures $180^\circ$ flips of the molecule are an important component of the relaxation dynamics for the orientational degrees of freedom.

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I. INTRODUCTION

In the last ten years mode coupling theory (MCT) 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 which 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. 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 formers salol, e.g., it has been shown that MCT gives a satisfactory description of the relaxation behavior of these systems. This conclusion seems to contradict the outcome of experiments in which the dielectric response of this system was probed 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 $\omega_{\text{min}}$, if one is very close to $T_c$. Light scattering experiments have shown that in salol this minimum occurs at a frequency of about 2GHz if $T = 253$ K. However, Dixon et al. showed that no such minimum is observed in the dielectric function $\varepsilon''(\omega)$ for frequencies up to 18GHz for $T = 255$ K thus seemingly contradicting the conclusions of Ref. [1] 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 $\beta$-correlator of MCT for simple liquids, 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 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. We also note that very recently evidence has been given that a minimum exists in $\varepsilon''(\omega)$ for salol also. 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 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 $[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}$ (CKN), where the NO$_3$ unit was treated as a rigid molecule [16] and Sindzingre and Klein studied methanol [17]. OTP was investigated by Lewis and Wahnström [18,19], who modelled the molecule with a rigid isoscale triangle of Lennard-Jones particles, and by Kudchadkar and Wiest [20] who used a 18-site, three-ring model. Very recently Sciortino et al. presented their results on supercooled H$_2$O (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 [23]).

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 $\alpha$-relaxation and discuss our findings regarding the $\beta$-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 dumb-bell shaped molecule and argued that the molecular character leads to a decrease of the MCT parameter $\lambda$ [24].

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. [16–18,20–22] and thus allows to make a more stringent test of the theory. Although the MCT equations for a diatomic molecule in a simple liquid [25] and for molecular liquids have recently been derived [26,27], 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 [28] for MCT equations which 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 section IV the model as well as the details of the computer simulation are presented. The results are given in Sec. IV and are discussed in the final section in which 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.

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 follows:

\[
C_l(t) = \frac{1}{N} \sum_{n,n'} \langle P_l(\vec{u}_n(t) \cdot \vec{u}_{n'}(0)) \rangle \quad l \geq 1 .
\]

and its self part

\[
C_l^{(s)}(t) = \frac{1}{N} \sum_{n=1}^{N} \langle P_l(\vec{u}_n(t) \cdot \vec{u}_n(0)) \rangle \quad l \geq 1 .
\]

Here \(P_l(x)\) is the Legendre polynomial of order \(l\) and \(\vec{u}_n\) is the normalized orientational vector of the \(n\)-th 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. [23]) 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.

Besides 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 auto-correlation functions of the velocities \(\vec{v}_n(t)\) of the particles

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

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

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

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 [30]. 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:

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

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

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

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

$$D_r = \lim_{t \to \infty} \frac{1}{4tN} \sum_{n=1}^{N} \langle |\vec{\phi}_n(t) - \vec{\phi}_n(0)|^2 \rangle .$$  (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 which are relevant for the present work. More detail can be found in Refs. [1 –4]. The theory predicts that, in the vicinity of the critical temperature $T_c$, all time correlation functions $\phi(t)$ which couple to the density correlation function should show a two-step relaxation behavior, i.e. exhibit a plateau-like region when plotted versus the logarithm of time. The time window in which $\phi$ is in the vicinity of this plateau is called the $\beta$-relaxation regime. The time window in which the correlator falls below this plateau is called the $\alpha$-relaxation regime.

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

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

with a critical exponent $\gamma > 1.5$. Note that the values of $T_c$ and $\gamma$ 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.

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

with the same $\gamma$ as in Eq. (8).

Finally the theory makes the prediction that the correlators should obey the so-called time-temperature superposition principle (TTSP). 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 $\alpha$-relaxation regime, on a master curve $\hat{\phi}$, i.e.

$$\phi(t, T) = \hat{\phi}(t/\tau(T)) ,$$  (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 $\beta$ are not universal, i.e. will depend on $\phi$. 

5
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 $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left\{ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right\}$ were $\alpha, \beta \in \{A, B\}$. 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 use $\sigma_{AA}$ as the unit of length, $\epsilon_{AA}$ 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 0.3ps.

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 firstly the formation of liquid crystalline structures is unlikely \cite{31} and that secondly 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 $p_{ext}=1.0$. For this we equilibrated the system in the $(N, p, T)$ ensemble, using the algorithm proposed by Andersen \cite{32} 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 \cite{33}. Note that it is advisable to make the production run in the microcanonical ensemble if one wants to investigate the dynamics of the system, since the algorithms used for constant pressure simulations introduce an artificial dynamics which 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 than $1.4 \cdot 10^5$ time units these step sizes are sufficiently small to allow 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 a length of $3.0 \cdot 10^5$ and $4.0 \cdot 10^5$ time units, respectively, $(= 1.5 \cdot 10^7$ and $2.0 \cdot 10^7$ 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 $T = 5.0, 3.0, 2.0, 1.4, 1.1, 0.85, 0.70, 0.632, 0.588, 0.549, 0.520, 0.500, 0.489, \text{ and } 0.477$. 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 square 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. [16–18,20], 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 which fits the data well at higher temperatures. The reason for this is likely the so-called “hopping processes” [34], 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 $0.475 \pm 0.005$ 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 $\alpha$-relaxation time shows also a power-law with a critical temperature at 0.475 [23]. The critical exponent $\gamma$ of the power-law for $D$ is 2.20, which is in the range of values found for $\gamma$ 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 that therefore the molecular character of the particles does not seem to affect the dynamics of the TDOF significantly.

We now focus our attention to the ODOF. The first quantity we investigate is the correlation function $C_1^{(s)}(t)$ which was defined in Eq. (3). In Fig. 2a 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 $\beta$-relaxation regime.

From this figure we also recognize that for intermediate and low temperatures the shape of the curves in the $\alpha$-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. 3b the same curves versus the recaled time $t/\tau_1^{(s)}(T)$, where $\tau_1^{(s)}(T)$ is the $\alpha$-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 \( t/\tau_{1c}^{(s)}(T) = 1.0 \) 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 \( C_1^{(s)}(t) \) for the OTP model studied by Wahnstöm and Lewis [19]. We also note that defining the \( \alpha \)-relaxation time \( \tau_{1c}^{(s)}(T) \) in a different way, namely by the time it takes the correlation function to decay to 10\% of its initial value, does not change this conclusion, since the TTSP does not hold with this second definition of \( \tau_{1c}^{(s)} \) either.

Next we investigate the time and temperature dependence of \( C_2^{(s)}(t) \), see Eq. (2), which is shown in Fig. 3. From the upper panel of the figure we see that \( C_2^{(s)}(t) \) decays qualitatively similar to \( C_1^{(s)}(t) \) (Fig. 2a). 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 for the corresponding nonergodicity parameter \( f_1^{(s)} = \lim_{t \to \infty} C_1(t) / T_c \). Since the area under the \( \alpha \)-peak and under the remaining part of the spectrum \( \chi''_{1c} \) (i.e. the critical decay and the microscopic peak) are related to \( f_1^{(s)} \) and to \( 1 - f_1^{(s)} \), respectively, our result suggests that the minimum between the two peaks is less pronounced for \( \chi_1'' \) than for \( \chi_2'' \), 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.

From Fig. 3b we recognize that for this correlation function the TTSP holds well for times larger than \( \tau_{2c}^{(s)}(T) \), the \( \alpha \)-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 behavior 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. 4b. 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) that with increasing \( l \) the correlators seem to show more and more a logarithmic time dependence in the \( \beta \)-relaxation regime, and iii) that 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 jump-like 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 [35] thus showing that from a qualitative point of view the correlators for the ODOF become more similar to the ones of the TDOF.

In addition to the self parts, \( C_1^{(s)}(t) \) 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. 3 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. 3, 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
appealing.
The system ceases to relax. Therefore this sort of fit is, from a physical point of view, less indicating that according to the Vogel-Fulcher fits there is no unique temperature at which and \( \tau \) lowest temperatures, for which the power-law failed to fit the data. Thus we conclude that if \( T \) the Vogel-Fulcher temperature \( T_0 \), 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 \( \gamma \), 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 similar to the ones for the TDOF.

We also mention that a power-law fit to \( \tau_1^{(s)} \) and \( \tau_1 \), 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 failed to fit the data. Thus we conclude that if seen as a mere fitting function the Vogel-Fulcher law gives the 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 \( \alpha \)-relaxation times \( \tau_1^{(s)}(T) \) and \( \tau_1(T) \) are analogous quantities to the \( \alpha \)-relaxation time \( \tau(T) \) of the intermediate scattering function. Since in supercooled liquids the temperature dependence of \( \tau \) and of the diffusion constant can be different (see, e.g., Refs. \[23,24\]) 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 square displacement of the angles \( \phi(t) \), i.e. \( \langle (\Delta \phi(t))^2 \rangle = \langle |\phi_n(t) - \phi_n(0)|^2 \rangle \), where \( \phi_n(t) - \phi_n(0) \) is defined in Eq. (6).

From this figure we recognize that, analogous to the mean square displacement [23], \( \langle (\Delta \phi(t))^2 \rangle \) 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. \( \langle (\Delta \phi(t))^2 \rangle \) 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 \( \langle (\Delta \phi(t))^2 \rangle \) 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 of the particles (MSD) starts to show a subdiffusive behavior [23]. In contrast to this the time where \( \langle (\Delta \phi(t))^2 \rangle \) 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 \( \langle (\Delta \phi(t))^2 \rangle \) and the MSD there are some distinct differences between the two quantities and thus we conclude that the plateau-like region in \( \langle (\Delta \phi(t))^2 \rangle \) should not be identified with the \( \beta \)-relaxation regime. We will come back to this point later.

From the time dependence of \( \langle (\Delta \phi(t))^2 \rangle \) it is simple to compute \( D_r \) [see Eq. (7)]. Note that, because \( \langle (\Delta \phi(t))^2 \rangle \) 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 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 \( D_r \) to 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 by 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. 4, 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. \( 2.0 \geq T \geq 0.477 \) 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 \( C_1(s) \) and \( C_1 \), which was 0.475. In order to discriminate between the two functional forms 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 $T \geq 0.477$) 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 $2.0 \cdot 10^5$ 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 [36].) 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 $T_c$. 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 [30]. 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 clearer we have investigated 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 \( 4 \cdot 10^3 \) 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 a \( x \) and \( y \) 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 forward above that the orientational diffusion of the molecules in the \( z \) direction is much larger than the one in the \( x \) and \( y \) direction. We also recognize that the latter ones are not completely suppressed which is likely to be 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 an 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 auto-correlation function \( \Psi_2(t) \) of the angular velocity \( \vec{\omega}(t) \), see Eq. (4). As was illustrated by Renner \textit{et al.}, \( \Psi_2(t) \) is expected to show a plateau with a height equal or less than 0.25 if the motion of the molecule is of a librational type [30]. In Fig. 10 we show the time dependence of \( \Psi_2 \) for all temperatures investigated. From this figure we recognize that the short time relaxation time of \( \Psi_2 \) 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 \( \theta \). From Fig. 11a we recognize that for \( T = 2.0 \) this function decays monotonically in \( \theta \) for all times. This changes when the temperature is decreased to \( T = 0.63 \), Fig. 11b, since then, e.g., the curve for \( t = 77.7 \) (bold dashed curve) shows a small additional peak at 180° which is separated from the main peak at 0° by a shallow minimum around 120°. This additional peak stems from molecules which underwent a rotation of 180°. This feature becomes much more pronounced when the temperature is decreased further to \( T = 0.477 \) (Fig. 11c). The mentioned minimum now exists for a large time range before it starts to disappear on the time scale of the \( \alpha \)-relaxation. At even lower temperature, \( T = 0.41 \) (Fig. 11d), the minimum does not show any sign to fill 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 $\theta$ 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 $180^\circ$ (see Fig. 12 for three representative trajectories). The typical time for this flip is around 50 time units, but also faster (see, e.g., Fig. 12b) as well as 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 $180^\circ$ flip is not a fast process in which the molecule overcomes one barrier in a quasi-ballistic way, but rather the sum of a quick succession of smaller jumps. Finally we mention that the molecules do not show these sort of little jumps neither before nor after they undergo a $180^\circ$ flip which shows that these little jumps are associated with the flips.

V. CONCLUSIONS

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 MD-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 (TDOF and ODOF, respectively) slow down if the temperature is decreased and the system becomes strongly supercooled. Since the mode coupling theory (MCT) is presently the only microscopic theory which 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 the theory.

In the $\alpha$-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 $\tau$ 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 $0.475 \pm 0.005$. This fit describes the data for $D$ and $\tau$ very well for about four and two decades, respectively. The corresponding exponents are not universal, but vary between 1.52 and 2.45.

The next interesting result is that the rotational diffusion constant $D_r$, as defined by Eq. (7), shows a significantly different temperature dependence than 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 $T^*$ $\langle \Delta r^2 \rangle$ as well as $\langle (\Delta \vec{\phi})^2 \rangle$ 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 [37,38]. In these experiments the relaxation of the orientational vector $\vec{u}_n(t)$ of the $n$-th 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, and the subsequent linearization, leads to an exponential relaxation with a $\alpha$-relaxation time $\tau_1^{(s)}$ which is proportional to $1/D_r l(l + 1)$ [33]. 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 $[\tau_1^{(s)}(T)]^{-1}$ 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 $(\tau_1^{(s)})^{-1}$ and the relation $\tau_1^{(s)}/\tau_2^{(s)} = 3$ is not granted.

In the vicinity of $T_c$ the data for $D$ and $\tau_1^{(s)}$ deviate from the power-law observed at intermediate temperatures. (The same deviations are found for the $\alpha$-relaxation times of the coherent and incoherent intermediate scattering function 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 jump-like reorientations of the ODOF which we have identified in the distribution function $G(\theta,t)$ as $180^\circ$-flips. These jumps, which were also observed in earlier MD-simulations [13,15], may lead to a local “melting” of the neighborhood of a molecule which just jumped, whereby 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 $T = 0.41$ which is far below $T_c$. This Arrhenius dependence is somewhat reminiscent to the temperature dependence of the Johari-Goldstein $\beta$-peak in the dynamic susceptibility [10]. Since we have shown that the Arrhenius dependence of $D_r$ is related to the librational motion of the molecules, one thus might speculate whether the dynamics leading to the $\beta$-peak is 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 it 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. [16,18,21] 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 $l \geq 3$ 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 the one 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 $\alpha$-relaxation regime by about 25%, which demonstrates that the cross-terms in $C_1(t)$ should not be neglected.

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REFERENCES

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[1] W. Götze in Liquids, freezing and the glass transition, Eds. J. P. Hansen, D. Levesque and J. Zinn-Justin (North-Holland, Amsterdam, 1991).
[2] W. Götze and L. Sjögren, Rep. Prog. Phys. 55, 241 (1992).
[3] R. Schilling in Disorder Effects on Relaxation Processes, Eds. R. Richert and A. Blumen (Springer, Berlin, 1994).
[4] W. Kob in Experimental and Theoretical Approaches to Supercooled Liquids: Advances and Novel Applications, Eds.: J. Fourkas, D. Kivelson, U. Mohanty, and K. Nelson (ACS Books, Washington, 1997).
[5] Theme Issue on Relaxation Kinetics in Supercooled Liquids-Move Coupling Theory and its Experimental Tests; Ed. S. Yip. Volume 24, No. 6-8 (1995) of Transport Theory and Statistical Physics.
[6] G. Li, M. Du, A. Sakai and H. Z. Cummins, Phys. Rev. A 46, 3343 (1992).
[7] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams and J. P. Carini, Phys. Rev. B 42, 8179 (1990); P. K. Dixon, Phys. Rev. B 42, 8179 (1990).
[8] P. Lunkenheimer, A. Pimenow, B. Schiener, R. Böhmer and A. Loidl, Europhys. Lett. 33, 611 (1996).
[9] P. Lunkenheimer, A. Pimenow, M. Dressel, Y. G. Gonchunov, R. Böhmer and A. Loidl, Phys. Rev. Lett. 77, 318 (1996).
[10] T. Franosch, M. Fuchs, W. Götze, M.R. Mayr, and A.P. Singh, Phys. Rev. E 55, xxxx, (1997).
[11] P. Lunkenheimer, A. Pimenow, M. Dressel, Y. G. Gonchunov, U. Schneider, B. Schiener R. Böhmer and A. Loidl, Proc. MRS Fall Meeting, Boston 1996.
[12] W. Kob, p.1 in Vol. III of Annual Reviews of Computational Physics, Ed.: D. Stauffer (World Scientific, Singapore, 1995).
[13] J.-N. Roux, J.-L. Barrat and J.-P. Hansen, J. Phys.: Cond. Matter 1, 7171 (1989); G. Wahnström, Phys. Rev. A 44, 3752 (1991).
[14] W. Kob and H. C. Andersen, Phys. Rev. Lett. 73, 1376 (1994).
[15] W. Kob and H. C. Andersen, Phys. Rev. E 51, 4626 (1995); ibid. 52, 4134 (1995).
[16] G. F. Signorini, J.-L. Barrat and M. L. Klein, J. Chem. Phys. 92, 1294 (1990).
[17] P. Sindzingre, M. L. Klein, J. Chem. Phys. 96, 4681 (1992).
[18] L. J. Lewis and G. Wahnström, Phys. Rev E 50, 3865 (1994).
[19] G. Wahnström and L. J. Lewis, Prog. Theor. Phys. (in press).
[20] S. R. Kudchadkar and J. M. Wiest, J. Chem. Phys. 103, 8566 (1995).
[21] P. Gallo, F. Sciortino, P. Tartaglia and S.-H. Chen, Phys. Rev. Lett. 76, 2730 (1996); F. Sciortino, P. Gallo, P. Tartaglia and S. H. Chen, Phys. Rev. E 54, 6331 (1996).
[22] F. Sciortino, P. Tartaglia and P. Gallo, Proc. MRS Fall Meeting, Boston 1996.
[23] S. Kämmerer, W. Kob and R. Schilling, (unpublished).
[24] W. J. Ma and S. K. Lai, Phys. Rev. E 55, 2026 (1997).
[25] T. Franosch, W. Götze and A. P. Singh, (unpublished).
[26] T. Scheidsteger and R. Schilling, (unpublished).
[27] R. Schmitz, (unpublished).
[28] W. Götze, Z. Physik B 60, 195 (1985).
[29] H. Z. Cummins, G. Li, W. Du, R. Pick, and C. Dreyfus, Phys. Rev. E 53, 896 (1996).
[30] C. Renner, H. Löwen and J. L. Barrat, Phys. Rev. E 52, 5091 (1995).
[31] M. P. Allen and D. Frenkel, Phys. Rev. Lett. 58, 1748 (1987).
[32] H. C. Andersen, J. Chem. Phys. 72, 2384 (1980).
[33] H.C. Andersen, J. Comp. Phys. 52, 24 (1983).
[34] W. Götze and L. Sjögren, Z. Phys. B 65, 415 (1987).
[35] S. Kämmerer, PhD Thesis, University of Mainz, 1997.
[36] See, e.g., J. Baschnagel, Phys. Rev. B 49, 135 (1994); J.-P. Bouchaud, L. Cugliandolo, J. Kurchan, and M. Mézard, Physica A 226, 243 (1996); W. Kob and J.-L. Barrat cond-mat/9704006.
[37] F. Fujara, B. Geil, H. Sillescu, and G. Fleischer, Z. Physik B 88, 195 (1992).
[38] E. Rössler, Phys. Rev. Lett. 65, 1595 (1990).
[39] B. Bagchi and A. Chandra, Adv. Chem. Phys. 80, 1 (1991).
[40] G. P. Johari and M. Goldstein, J. Chem. Phys. 53, 2372 (1971); ibid. 55, 4245 (1971).
FIGURES

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.

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

FIG. 3. Time dependence of $C_2^{(s)}$ [see Eq. (2)] for all temperatures investigated. a) versus time $t$ b) versus rescaled time $t/\tau_1^{(s)}(T)$, where $\tau_1^{(s)}$ is the $\alpha$-relaxation time.

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

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

FIG. 6. $\alpha$-relaxation time $\tau_1^{(s)}$ (squares), $\tau_2^{(s)}$ (diamonds) and $\tau_1$ (circles) versus temperature. Solid lines: fits with power-law. 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.

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.

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 auto-correlation function $\Psi_2(t)$ of the angular velocities [see Eq. (4)] for all temperatures investigated.

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

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

17
$T_c = 0.475$
$T = 0.477$

$T = 5.0$
\( C^{(s)}_2 \)

\[
\begin{align*}
T &= 5.0 \\
T &= 0.477
\end{align*}
\]

\( t \)
\[ C^{(s)}_2 \]

(b)

\[ T = 5.0 \]

\[ T = 0.477 \]
\( C_l(T = 0.477) \)
\( C^r \)

\( T = 0.477 \)

\( T = 5.0 \)
$T_c = 0.475$
\[ \langle \Delta \vec{\phi}^2 \rangle, \langle \Delta \vec{\phi} \rangle \]

\[ \langle \Delta \phi^2 \rangle \]

\[ \langle \Delta \phi_z^2 \rangle \]

\[ \langle \Delta \phi_y^2 \rangle \]

\[ \langle \Delta \phi_x^2 \rangle \]

\[ \langle \Delta \phi^2 \rangle \rightarrow \langle \Delta \phi^2 \rangle, \langle \Delta \phi \rangle \]

\[ t \rightarrow \langle \Delta \phi^2 \rangle \]

\[ t \rightarrow \langle \Delta \phi^2 \rangle \]

\[ t \rightarrow \langle \Delta \phi^2 \rangle \]

\[ t \rightarrow \langle \Delta \phi^2 \rangle \]
$G(\theta, t)$

$T = 2.0$
The graph shows the function $G(\theta, t)$ plotted against $\theta$ [°] for different values of $t$. The inset highlights the behavior of the function at $T=0.63$. The function appears to exhibit a characteristic pattern as $\theta$ increases.
$G(\theta, t)$

$\theta^\circ$

$T=0.41$
