Viscous flow and jump dynamics in molecular supercooled liquids. I. Translations

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The transport and relaxation properties of a molecular supercooled liquid on an isobar are studied by molecular dynamics. The molecule is a rigid heteronuclear biatomic system. The diffusivity is fitted over four orders of magnitude by the power law $D \propto (T - T_c)^{\gamma_D}$, with $\gamma_D = 1.93 \pm 0.02$ and $T_c = 0.458 \pm 0.002$. The self-part of the intermediate scattering function $F_s(k_{max}, t)$ exhibits a steplike behavior at the lowest temperatures. On cooling, the increase of the related relaxation time τ_α tracks the diffusivity, i.e., $\tau_\alpha \propto (k_{max}^2 D)^{-1}$. At the lowest temperatures, fractions of highly mobile and trapped molecules are also evidenced. Translational jumps are also evidenced. The duration of the jumps exhibits a distribution. The distribution of the waiting times before a jump takes place, $\psi(t)$, is exponential at higher temperatures. At lower temperatures a power-law divergence is evidenced at short times, $\psi(t) \propto t^{\xi-1}$ with $0 < \xi \lesssim 1$, which is ascribed to intermittency. The shear viscosity is fitted by the power law $\eta \propto (T - T_c)^{\gamma_\eta}$, with $\gamma_\eta = -2.20 \pm 0.03$ at the lowest temperatures. At higher temperatures the Stokes-Einstein relation fits the data if *stick* boundary conditions are assumed. The product $D\eta/T$ increases at lower temperatures, and the Stokes-Einstein relation breaks down at a temperature which is close to the one where the intermittency is evidenced by $\psi(t)$. A precursor effect of the breakdown is observed, which manifests itself as an apparent stick-slip transition.

I. INTRODUCTION

The relaxation phenomena and transport properties of supercooled liquids and glassy materials are topics of current interest [1,2]. It is well known that, on approaching the glass transition temperature T_g from above, diffusion coefficients and relaxation times exhibit remarkable changes of several orders of magnitude, which are under intense experimental, theoretical and numerical investigation. In the high-temperature regime the changes usually track the shear viscosity η in the sense that, if X denotes the diffusivity or the inverse of a relaxation time, the product $X\eta/T$ is nearly temperature independent. In particular, both the Stokes-Einstein law $D \approx kT/6\pi\eta a$, and the Debye-Stokes-Einstein law, $D_r \approx kT/\eta a^3$ are found to work nicely, D, D_r, and a being the translational and rotational diffusivities and the molecular radius, respectively. Conversely, in deeply supercooled regimes there is wide evidence that the product *increases on cooling*, showing the breakdown of hydrodynamic behavior at the molecular level and decoupling by the viscous flow [3–15].

Several models suggest that the decoupling between microscopic time scales and the viscous flow is a signature of heterogeneous dynamics close to the glass transition, i.e., a spatial distribution of transport and relaxation properties [16–19]. Interesting alternatives are provided by frustrated lattice gas models [20] and the ''energy landscape'' picture [2,21–24]. Most intepretations suggest the existence of crossover temperatures below which a change of relaxation mechanism must occur [3]. These temperatures are broadly found around $1.2T_g$, i.e., in the region where the critical temperature T_c predicted by the mode-coupling theory

(MCT) of the glass transition is found [25]. Recent extensions of MCT for the shear viscosity that take current fluctuations into account in addition to density fluctuations, have been reported [26].

During the last years molecular dynamics (MD) simulations proved to be a powerful tool to investigate supercooled liquids (for a recent review, see Ref. [27]). To date, MD studies investigated decoupling phenomena in atomic pure liquids [24] and atomic binary mixtures [28–33]. Most MD studies confirmed that decoupling is due to dynamic heterogeneities [28,30–34]. In fact, ''active'' [31] or ''mobile'' [34] regions which largely contribute to setting the macroscopic average value have been identified. In such regions hopping processes, enhancing the transport with respect to the hydrodynamic behavior, have been evidenced [28,31]. The occurrence of jumps in glasses has been reported several times in the recent past [29,35–37].

We are not aware of MD studies of decoupling, and, more generally, of dynamic heterogeneities in *molecular* systems. This motivated the present paper and the following paper [38], which investigate transport and relaxation in a three-dimensional, one-component, molecular system. This is an important feature, since most experimental work was carried out on that class of materials. In particular, the decoupling of microscopic relaxation from the viscous flow will be addressed in the light of the increased role played by hopping processes. The present paper is limited to the translational degrees of freedom, whereas the following paper [38] deals with rotational degrees of freedom.

The paper is organized as follows. In Sec. II the model and the details of the simulation are presented. The results concerning both single-particle and collective properties are discussed in Sec. III. The main conclusions are summarized in Sec. IV.

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II. MODEL AND DETAILS OF SIMULATION

The system under study is a biatomic molecular liquid. The model has been extensively investigated to test the MCT predictions [39–41]. Atoms A and B of each molecule have mass m and are spaced by d. Atoms on different molecules interact via the Lennard-Jones potential

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6], \quad \alpha,\beta \in \{A,B\} \tag{2.1}$$

The potential was cut off and shifted at $r_{cutoff} = 2.5\sigma_{AA}$. Henceforth, reduced units will be used. Lengths are in units of σ_{AA}, energies in units of ϵ_{AA}, and masses in units of m. The time unit is $(m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$, corresponding to about 2 ps for the argon atom. The pressure P, temperature T, and shear viscosity η are in units of $\epsilon_{AA}/\sigma_{AA}^3$, ϵ_{AA}/k_B, and $\sqrt{m\epsilon_{AA}}/\sigma_{AA}^2$, respectively.

The model parameters in reduced units are $\sigma_{AA} = \sigma_{AB} = 1.0$, $\sigma_{BB} = 0.95$, $\epsilon_{AA} = \epsilon_{AB} = 1.0$, $\epsilon_{BB} = 0.95$, $d = 0.5$, and $m_A = m_B = m = 1.0$. The sample has $N = N_{at}/2 = 1000$ molecules which are accommodated in a cubic box with periodic boundary conditions. The viscosity was evaluated by using samples of $N = 108$ molecules.

We examined the isobar at $P = 1.5$ by the following procedure. First, the sample was equilibrated in isothermal-isobaric conditions. For a time at least one order of magnitude longer the time needed by the self-part of the intermediate scattering function evaluated at the maximum of the static structure factor to become smaller than 0.1. In this step the equations of motion were integrated by using the RATTLE, algorithm with Nosè-Andersen constant temperature and pressure dynamics [42]. The data were collected in microcanonical conditions. Integration was carried out by δt steps ranging from 0.001 at higher temperatures to 0.004 at lower ones. The temperatures we investigated are $T = 6, 5, 3, 2, 1.4, 1.1, 0.85, 0.77, 0.70, 0.632, 0.588, 0.549, 0.52,$ and 0.5. The density at $T = 0.5$ was $\rho = 0.6998$, and decreased of a factor of about 3 at the highest temperatures. To check that thermal hystory is negligible, at least two independent equilibrations were performed, and the subsequent production runs compared at the lowest temperatures.

Representative plots of the radial distribution function of the center of mass $g(r)$ and the static structure factor $S(k)$ are shown in Fig. 1. The pattern is typical of a disordered system. The shoulder of $g(r)$ at $r \cong 1.1$ at $T = 0.5$ was already observed [43] and ascribed to local ''T shaped'' or cross configurations of the molecules [44].

The above results rule out possible crystallizations of the sample. No orientational order was evidenced [38].

III. RESULTS AND DISCUSSION

The section discusses the results of the study. The single-particle and collective dynamical properties of the system are characterized. A study of the Stokes-Einstein law is presented.
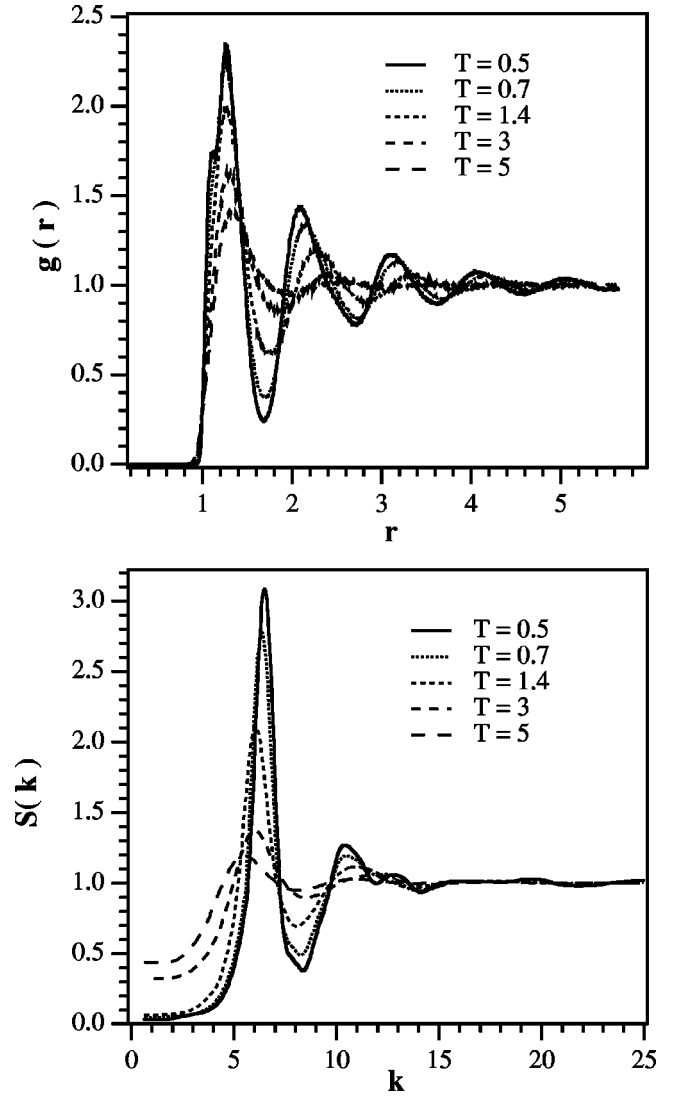

FIG. 1. Radial distribution function $g(r)$ (top) and static structure factor $S(k)$ (bottom) of the molecular center of mass for selected temperatures.

A. Single-particle dynamics

The mean squared displacement of the center of mass, $R(t)$, provides a first view of the translational motion of the molecules at intermediate and long time scales. The usual ballistic and diffusive regimes are apparent at short and long times, respectively (see Fig. 6 below, and Ref. [41]). At low temperature the molecule is effectively trapped inside the cage of the first neighbors, and $R(t)$ exhibits a plateau at intermediate times. The occurrence of oscillatory motion during trapping is shown explicitly in Fig. 2, where the mean squared displacement and the velocity correlation function are compared at $T = 0.5$. The plot evidences that velocity correlations were lost within the lifetime of the cage, and signals that on a short time scale the supercooled liquid behaves as a solid.

The translational diffusion coefficient D is evaluated by the Einstein relation [42,44]
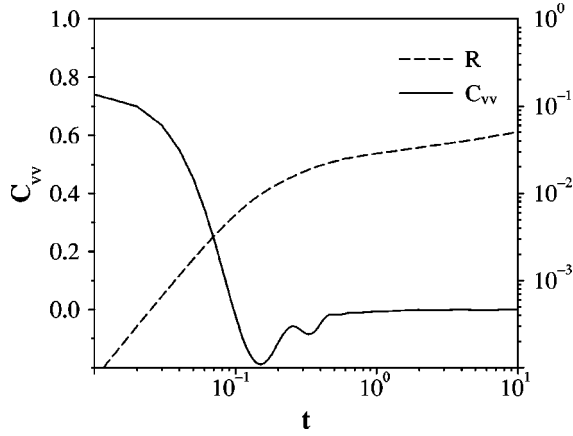
FIG. 2. Comparison of the mean squared displacement $R(t)$ and the velocity correlation function $C_{vv}(t)$ at $T=0.5$. The onset of the damped oscillations takes place at the beginning of the plateau of $R(t)$: the molecule is colliding with the cage of the first neighbors.

$$D=\lim_{t\to\infty}\frac{R(t)}{6t}. \quad (3.1)$$

In Fig. 3 the temperature dependence of D is shown. The plot emphasizes the scaling property of D, which is nicely described over four decades by the power law:

$$D=C_D(T-T_c)^{\gamma_D}. \quad (3.2)$$

Theoretical justification of Eq. (3.2) is provided by MCT [25]. In particular, the ideal MCT predicts the inequality $\gamma_D>1.5$. Our best fit values are $\gamma_D=1.93\pm0.02$, T_c
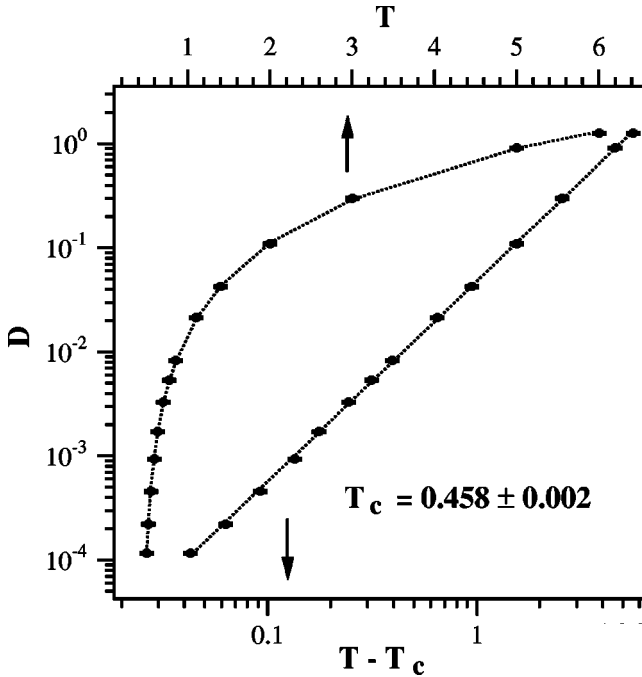

FIG. 3. Temperature dependence of the translational diffusion coefficient D. The dashed line is a fit with the power law of Eq. (3.2) with $\gamma_D=1.93\pm0.02$, $T_c=0.458\pm0.002$, and $C_D=0.0481\pm0.0004$.
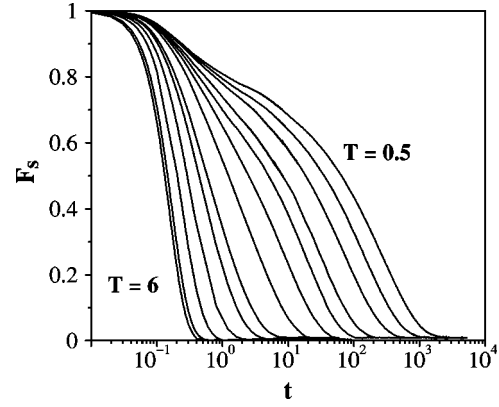

FIG. 4. Self-part of the intermediate scattering function $F_s(k_{max},t)$. The curves refer to all the temperatures under investigation but $T=0.77$.

$=0.458\pm0.002$, and $C_D=0.0481\pm0.0004$. For the same biatomic system with $N=500$ and $P=1$ it was found that $\gamma_D=2.2$ and $T_c=0.475$ [39].

It must be noted that at lower temperatures the above power law is expected to underestimate the diffusion coefficient [41]. The larger diffusivity with respect to the ideal MCT prediction close to T_c is not surprising. According to this approach, density-density correlations do not vanish at long times below T_c leading to a divergence of D at T_c. The extended MCT points out that hopping processes provide an effective mechanism to relax the density fluctuations at long time, and make the diffusivity finite close to T_c. This point will be discussed explicitly below.

To characterize the single-particle dynamics further, we evaluated the self-part of the intermediate scattering function:

$$F_s(k,t)=\langle\exp[i\mathbf{k}\cdot(\mathbf{R}_j(t)-\mathbf{R}_j(0))]\rangle. \quad (3.3)$$

In Fig. 4, $F_s(k,t)$ is plotted for all the temperatures we investigated at $k=k_{max}$. k_{max} is the position of the main peak of the static structure factor $S(k)$ at temperature T. At higher temperatures the decay is virtually exponential at long times, whereas at lower temperatures a two-step decay is observed.

The plateau which is observed at lower temperatures in $F_s(k_{max},t)$ is due to the trapping of the molecules. Predictions on the scaling features of the plateau of $F_s(k_{max},t)$ are made by MCT [25]. A thorough comparison for the present model is found in Ref. [41].

At longer times the cage where the molecule is trapped opens and the density-density correlations vanish. The long-time decay of $F_s(k_{max},t)$ is well fitted by the stretched exponential $A\exp(-t/\tau)^{\beta}$. Stretching is appreciable at lower temperatures ($\beta_{0.5}=0.677$), and becomes negligible ($\beta\approx1$) for $T>0.85$.

The knowledge of $F_s(k_{max},t)$ offers the opportunity to investigate the time scale of structural relaxation usually denoted by the α relaxation time τ_α. We have evaluated it by the condition $F_s(k_{max},\tau_\alpha)=1/e\cong0.3679$. At low temperatures a nice fit is provided by $\tau_\alpha=C_\alpha(T-T_c)^{\gamma_\alpha}$, T_c being
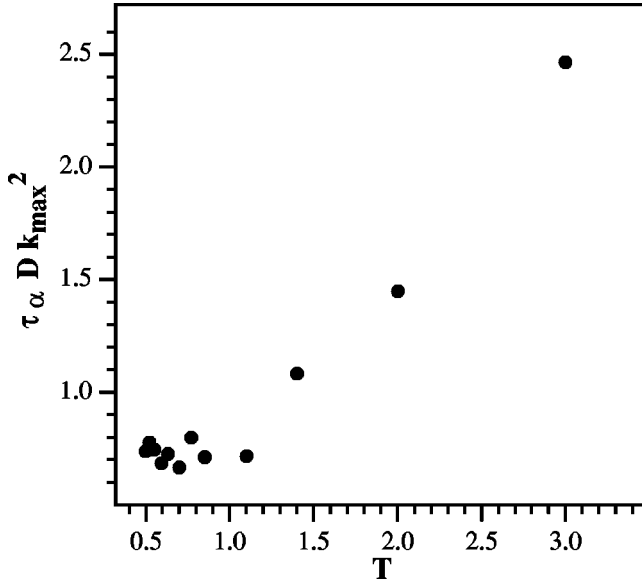
FIG. 5. Temperature dependence of the product $\tau_\alpha Dk^2_{max}$.

FIG. 6. Comparison of the non-Gaussian parameter α_2 and the mean squared displacement $R(t)$ at $T=0.5$. The maximum of the non-Gaussian parameter occurs at t^*. t^* provides an estimate of the trapping time, and is comparable with τ_α.

the same best-fit value drawn by the diffusivity. The best-fit value of the exponent is $\gamma_\alpha = -1.89 \pm 0.05$, which is quite close to $\gamma_D = 1.93$. Diffusive motion in simple liquids leads to the exponential decay of $F_s(k,t)$ with time constant $\tau = 1/Dk^2$ [44]. Even decay at long times is better described by a stretched exponential; the approximate equality $\gamma_\alpha \cong \gamma_D$ prompted us to investigate the temperature dependence of the product $\tau_\alpha Dk^2_{max}$. The results are shown in Fig. 5. For $T < 1.1$ the product approaches the constant value 0.72 ± 0.05. In this range τ_α and D change by more than two orders of magnitude. Alternative definitions of τ_α, e.g., involving the area below $F_s(k_{max},t)$, do not significantly affect the result. Removing the k^2_{max} term results in a slightly poorer fit. The k^2 scaling of the primary relaxation time τ^s_k, evaluated as the area below $F_s(k,t)$, was already noted in the hard sphere system at the critical packing fraction in the region $1.5 \leq ka \leq 30$ [45]. In particular, it was found that $\tau^s_k Dk^2 \sim 1.08$, in good agreement with our result, and that $F_s(k,t)$ exhibits stretching with $\beta(k_{max}) \sim 0.8$.

The above findings agree with some predictions of MCT: (i) T_c must be independent of the quantity under study, and (ii) γ_α must be equal to γ_D. The equality $\gamma_\alpha = \gamma_D$ must be taken with great caution. Other studies on the same model system with $N=500$ and $P=1$ found $\gamma_\alpha > \gamma_D$, even if fitting the diffusivity and τ_α provide the same T_c value [41].

Additional information on the single-particle dynamics is provided by the self part of the Van Hove function $G_s(\mathbf{r},t)$ [44]:

$$G_s(r,t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \delta(\mathbf{r} + \mathbf{R}_i(0) - \mathbf{R}_i(t)) \right\rangle. \quad (3.4)$$

The product $G_s(\mathbf{r},t)4\pi r^2$ is the probability that the molecule is at a distance between r and $r+dr$ from the initial position after a time t.
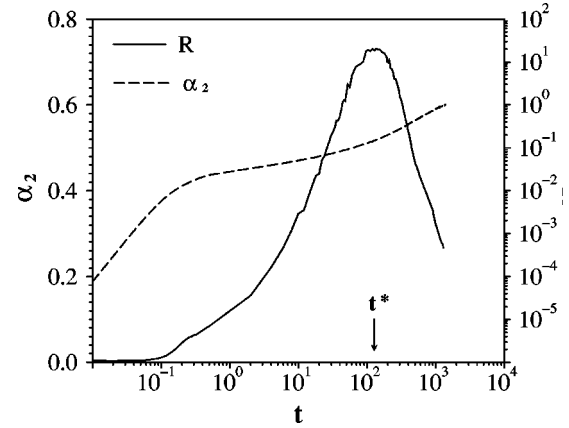
The shape of $G_s(r,t)$ in the system under study does not reveal particular features [41]. In particular, differently from other studies [29], no secondary peak at $r \approx 1$, the nearest-neighbor distance, is found to support the conclusion that hopping occurs. A deeper insight is gained by comparing $G_s(r,t)$ with the Gaussian approximation:

$$G^g_s(r,t) = [3/2\pi\langle r^2(t)\rangle]^{3/2} \exp(-3r^2/2\langle r^2(t)\rangle). \quad (3.5)$$

Equation (3.5) is the correct limit of $G_s(r,t)$ at short [ballistic regime, $\langle r^2(t)\rangle = 3kT/mt^2$] and long times [diffusion regime, $\langle r^2(t)\rangle = 6Dt$] [44]. Thirumalai and Mountain [28], and more recently Kob *et al.* [34], noted discrepancies between $G_s(r,t)$ and $G^g_s(r,t)$ in supercooled atomic mixtures. It is found that $G_s(r,t)$ exceeds $G^g_s(r,t)$ at short and long r values. The effect is particularly evident at $t \approx t^*$, where t^* is the time where the non-Gaussian parameter

$$\alpha_2(t) = 3\langle r^4(t)\rangle/5\langle r^2(t)\rangle^2 - 1, \quad (3.6)$$

reaches the maximum value [41]. At t^* the stochastic properties of $\mathbf{r}$ differ by the ones of a Gaussian variable to the maximum. A plot of $\alpha_2(t)$ is shown in Fig. 6, where it is compared to the mean squared displacement $R(t)$ at $T=0.5$. The maximum of $\alpha_2(t)$ at $t=t^*$ is located between the trapping and diffusive regimes. The decrease of $\alpha_2(t)$ for $t < t^*$ is due to the recovery of the Gaussian form of $G_s(r,t)$ in the trapping regime where molecules undergo a nearly oscillatory motion in the cages where they are accommodated (Fig. 2). t^* provides an estimate of the trapping time, and in fact is comparable to the α relaxation time. For $t \approx 0.2-0.3$, corresponding to the second maximum of the velocity correlation function, a small step is observed. The same feature of the non-Gaussian parameter was observed in dense bidimensional liquids [46].

The deviations of the Van Hove function by the Gaussian limit at short and long r values which were observed for $t \approx t^*$ shows that the sample has fractions of both trapped and highly mobile atoms [28,34]. It has been suggested that the dynamics of the latter is conveniently described by hopping
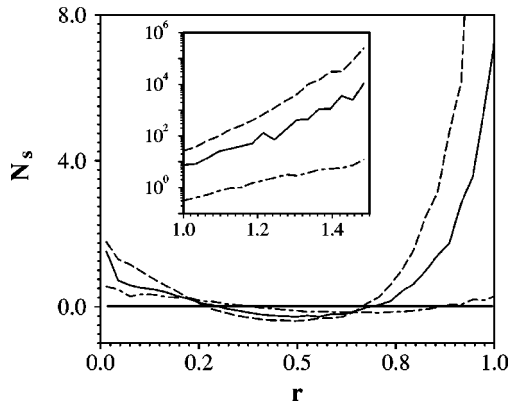
FIG. 7. The ratio $N_s(r) = (G_s(r,t^*) - G_s^g(r,t^*))/G_s^g(r,t^*)$ plotted at $T = 0.5$ (dashed line), $T = 0.588$ (solid line), and $T = 0.85$ (dot-dashed line). Inset: same quantity on a logarithmic scale.

processes [28]. To study the possible deviations of the Van Hove function in the present *molecular* system, we considered the ratio [34]

$$N_s(r) = \frac{G_s(r,t^*) - G_s^g(r,t^*)}{G_s(r,t^*)}. \qquad (3.7)$$

Figure 7 shows the ratio $N_s(r)$ for different temperatures. It exhibits increasing positive deviations at both short and large r values on cooling. This supports the conclusion that the dynamical heterogeneities evidenced in atomic two-phase systems are also present in *molecular* one-phase systems [28,34,47]. Since the positive tail of $N(r)$ at large r starts at $r \approx 1$, i.e., about the molecular size, it is tempting to ascribe it to jump motion. Indeed, by inspecting the particle trajectories, jumps are found. Examples are shown in Fig. 8. It was noted that the jump duration exhibits a distribution (roughly between 20 and 500 time units), suggesting that different degrees of cooperativity are involved [35]. The translational jumps which are detected are relatively slower than the rotational jumps (flips of about 180°) which take about 6–7 time units with little or no distribution [38,39]. Furthermore,
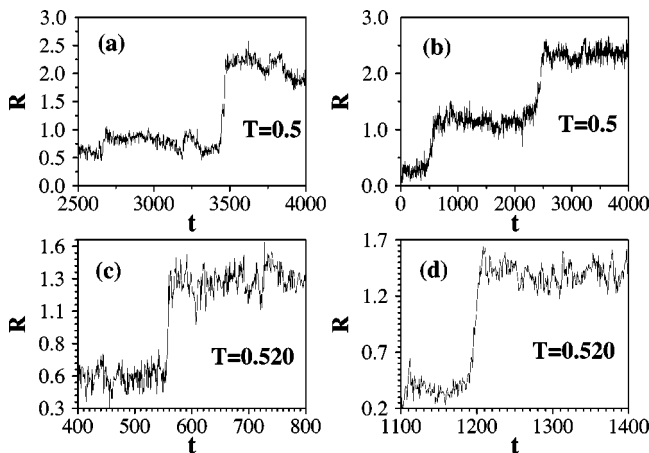

FIG. 8. Squared displacements R of selected molecules at $T = 0.5$ and 0.520. Note the distribution of the time needed to complete the jumps.

translational jumps are found to be much rarer than rotational ones [38]. In fact, differently from the translational case, the large amount of molecule flips manifests in a secondary peak of the proper Van Hove function [38,39,41].

The above remarks point to the conclusion that translational jumps are not obviously related to rotational ones. Their different character will be more clearly evidenced by studying and comparing the distributions of the waiting times, i.e., the lapse of time between successive jumps.

The waiting-time distribution $\psi(t)$ is a key quantity of models describing the trapping of glassy systems and supercooled liquids in real space [48,49], energy landscapes [50,51], and suitable fractal time subsets [52]. It is usually derived by taking proper account of the activated motion to surmount an existing distribution of energy barriers, and allows the derivation of the relevant relaxation functions and transport coefficients [53].

The explicit evaluation of the waiting-time distribution $\psi(t)$ relies on the definition of a jump event. In the present study a molecule jumps at time t if the displacement between t and $t + \Delta t^*$ ($\Delta t^* = 24$) exceeds $\sqrt{\Delta R^*} = \sigma_{AA}/2 = 0.5$ [54].

Figure 9 shows the waiting-time distribution $\psi(t)$ at different temperatures. At high temperature, $\psi(t)$ is exponential. On cooling, the exponential decay is replaced at short times by a slowly decaying regime. We fitted the overall decay by the function

$$\psi(t) = [\Gamma(\xi)\tau^{\xi}]^{-1} t^{\xi-1} e^{-t/\tau}, \quad 0 < \xi \le 1. \qquad (3.8)$$

The choice is motivated by the remark that in glassy systems rearrangements are rare events due to the constraints hampering the structural relaxation. It is believed that intermittent behavior in particle motion develops on cooling [33,49,50,52,55]. Signatures are the transitions in the energy landscapes of supercooled liquids [56], the power-law decay of $\psi(t)$ (for two-dimensional liquids, see Ref. [37]) and related quantities such as the first-passage time distribution [33]. Remarkably, the above power-law decay of $\psi(t)$ at *short times* is predicted by models of trapping in energy landscapes developed by Bouchaud and co-workers under fairly general assumptions [50]. In particular, they noted that the quantity of interest is not the *a priori* distribution of the waiting times but the effective one accounting for the fact that longer trappings have higher probability to be observed. The exponent ξ of Eq. (3.8) may be read as the fractal dimension of the set of dots marking each relaxation event (a jump) [52,57]. This interpretation helps to model the long-time decay of $\psi(t)$. If the distribution of events becomes nearly uniform ($\xi = 1$) beyond a time scale τ and homogeneous across the sample, $\psi(t)$ recovers an exponential form.

The best fits at $T = 0.5$, 0.549, and 0.632 are shown in Fig. 9. The increase of temperature results in a weak increase of the exponent ξ and a more marked decrease of τ. It was found that Eq. (3.8) also fits $\psi(t)$ by setting $\sqrt{\Delta R^*}$ and Δt^* in the ranges 0.4–0.7 and 24–48, respectively. This suggests that the character of the decay of $\psi(t)$ is not strongly dependent on how a jump is defined. Nonetheless, the best fit values of the parameters ξ and τ depend differently on $\sqrt{\Delta R^*}$ and Δt^*. For example, at $T = 0.5$, if $\sqrt{\Delta R^*}$ changes

FIG. 10. Comparison between the probability that the waiting time between consecutive jumps is larger than t, $P(t)$, and $F_s(k_{max},t)$ at $T=0.5$ and 0.549.

interplay between density fluctuations and the occurrence of jumps. This is of interest since, according to the extended version of MCT the dynamic transition occurring at T_c from an ergodic to a nonergodic state is actually smeared by hopping processes [25]. Figure 10 compares, at low temperatures, the long-time tail of $F_s(k_{max},t)$ and the probability that no jumps occurred before t, $P(t)=\int_t^\infty \psi(x)dx$. It is seen that the density self-correlations vanish at times when $P(t)$ is still meaningful [when $F_s(k_{max},t)\sim 0.1 P(t)\sim 0.5$ at $T=0.5$]. There is also some evidence that the fraction of waiting times longer than the time needed to make $F_s(k_{max},t)$ vanish [e.g., $F_s(k_{max},t)<0.1$] increases on cooling. Strong analogies with the above findings are found in a recent MD work on the viscous silica melt [58]. It was reported that the probability that a bond between a silicon atom and an oxygen atom, which was present at time zero, and is still present at time t, vanishes much later than F_s even at high temperature.

Then, at lower temperatures, two restructuring regimes are identified depending on the length of the waiting time with respect to τ_α. This is shown in Fig. 11. For waiting times shorter than τ_α, molecules jump in a nearly frozen environment. Escape from the cage becomes more difficult by lowering T and, expectedly, with a distribution of rates leading to the nonexponential decay of $\psi(t)$. For waiting times longer than τ_α a larger restructuring of the surrounding environment takes place. This averages the dynamical heterogeneities and leads to the long-time decay of $\psi(t)$.

It is tempting to note that in the time window where $\psi(t)$ exhibits the power-law decay, MCT predicts that $F_s(k,t)$ itself decays as the von Schweidler power law [25]:

$$F_s(k,t)=f_s^c(k)-h^s(k)\left(\frac{t}{\tau}\right)^b+\cdots, \qquad (3.9)$$

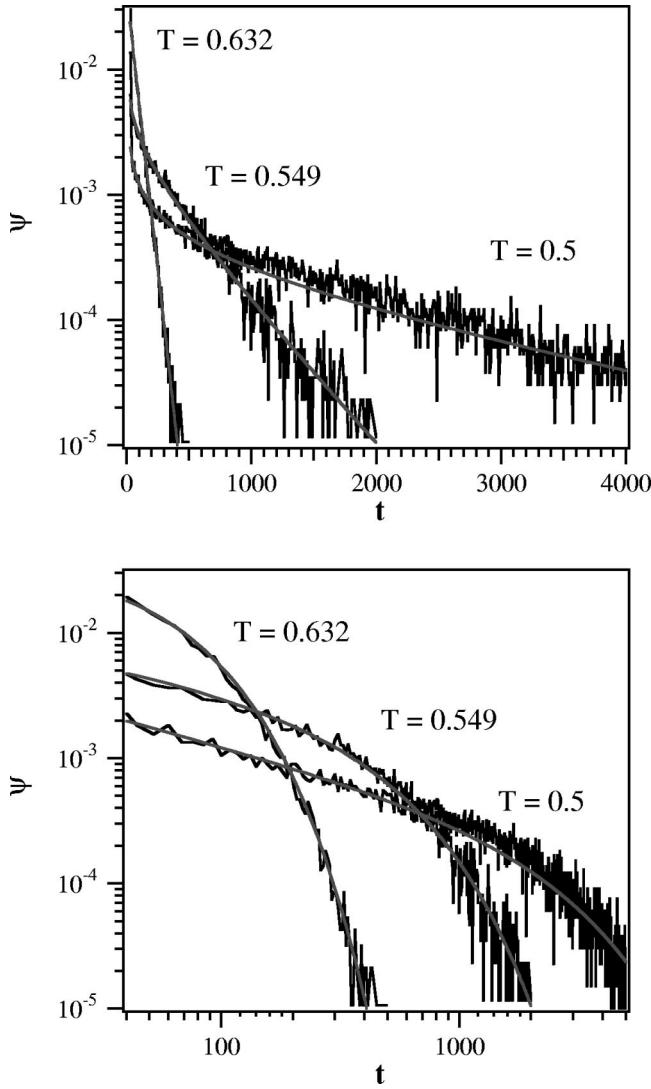where $f_s^c(k), h^s(k)$, and b are constants. $F_s(k_{max},t)$ must be

FIG. 9. Long-time (top) and short-time (bottom) behaviors of the waiting-time distribution $\psi(t)$ at different temperatures. The solid lines superimposed to the curves is Eq. (3.8) with $\xi=0.49$, $\tau=2550$ ($T=0.5$), $\xi=0.63$, $\tau=420$ ($T=0.549$), $\xi=1$, and $\tau=49$ ($T=0.632$).

from 0.5 to 0.6 with $\Delta t^*=24$, ξ does not change within the errors, whereas τ increases of a factor of about 2.4. τ also increases by decreasing the time Δt^* allowed to perform the displacement $\sqrt{\Delta R^*}$. The increase of τ is understood by noting that increasing the threshold $\sqrt{\Delta R^*}$ or, alternatively, decreasing Δt^*, reduces the number of sudden displacements which comply with the definition of ''jump'' and then increases the waiting time before a new jump occurs. Interestingly, at $T=0.5$, $\psi(t)$ exhibits small but reproducible deviations from Eq. (3.8). Bouchard and co-workers suggested that the long-time decay is *faster* than the exponential one. If the exponential decay is replaced by a Gaussian one, the fit improves quite a lot, and the ξ exponent changes from 0.49 to 0.45. Even if this refinement is rather suggestive, we prefer to consider it as *ad hoc* at the present level of understanding.

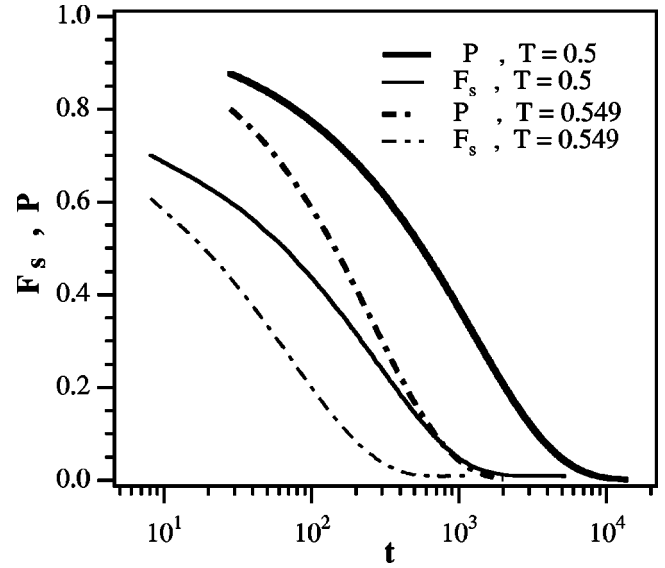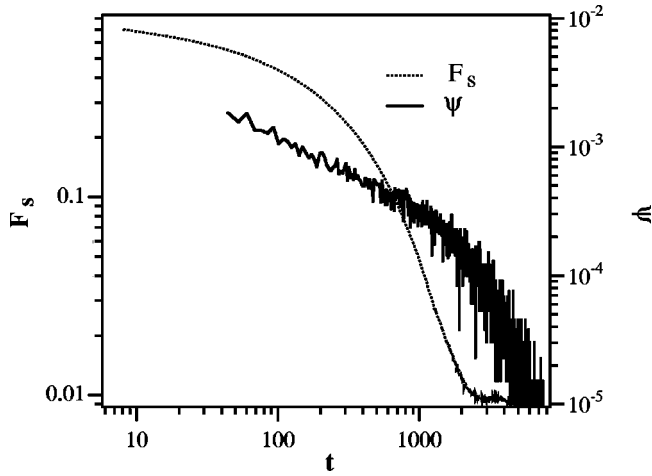Further insight into $\psi(t)$ is offered by the study of the

FIG. 11. Comparison between $\psi(t)$ and $F_s(k_{max},t)$ at $T=0.5$.

compared to $P(t)\approx A-Bt^{\xi}+\cdots$ in the region of interest. A and B are constants. If one estimates b via the β parameter of the stretched exponential fit of the long-time decay of $F_s(k_{max},t)$, it is found that $b\cong\beta=0.68$ at $T=0.5$. This must be compared to $\xi=0.45$. To make clearer to what extent the two power laws are related to each other, the analysis should be refined [41]. This is beyond the purposes of the present paper. However, we note that for times shorter than about $\Delta t^*=24\psi(t)$, $P(t)$ cannot be defined, since most jumps are not completed.

B. Collective dynamics: the shear viscosity

The shear viscosity η was evaluated by using the Einstein relation [59]

$$\eta=\frac{1}{2VkT}\lim_{t\to+\infty}\frac{1}{t}\langle\Delta A(t)^2\rangle, \qquad (3.10)$$

where

$$\Delta A(t)=V\int_0^t\mathcal{P}_{\alpha\beta}(t')dt'. \qquad (3.11)$$

$\mathcal{P}_{\alpha\beta}$ is one off-diagonal component of the pressure tensor [44,59,60] [in practice, $\Delta A(t)$ is the average over the three possible choices $\alpha\beta=xy,xz,yz$].

If the quantity $\mathcal{P}_{\alpha\beta}V$ is evaluated based on the motion of individual atoms comprising the molecules in the system, we have [61]

$$\mathcal{P}_{\alpha\beta}^{at}(t)V=\sum_{i=1}^{N_{at}}m_i v_{i\alpha}v_{i\beta}+\sum_{i=1}^{N_{at}}\sum_{j>i}^{N_{at}}f_{\alpha ij}(r_{i\beta}-r_{j\beta}). \qquad (3.12)$$

The sums involve components (denoted by Greek letters) of $\mathbf{v}_i$, $\mathbf{r}_i$, and $\mathbf{f}_{ij}$, which are the velocity and position of the ith atom having mass m_i, and the force between the atoms i and j (assumed pairwise additive), respectively. Equation (3.12) is not affected by the periodic boundary conditions employed in MD simulations [62].
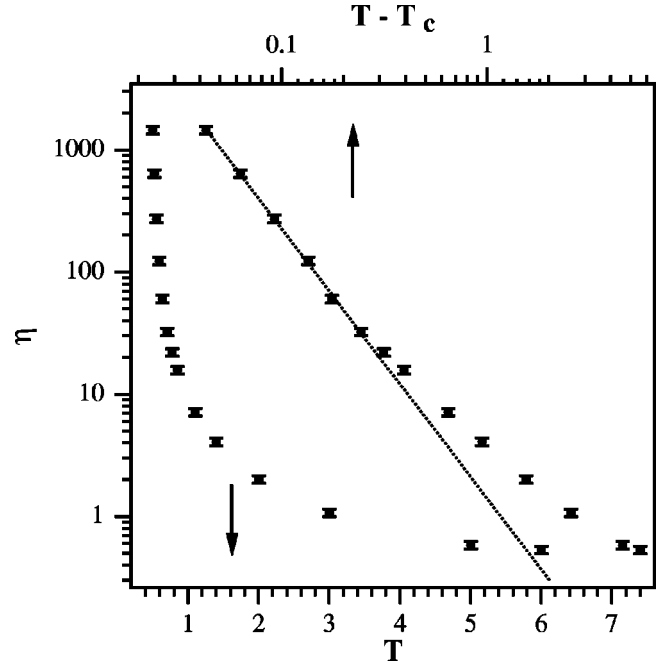
FIG. 12. Temperature dependence of the shear viscosity. The superimposed line has a slope $\gamma_{\eta}=-2.20\pm0.03$.

The evaluation of the shear viscosity is particularly time consuming, being a collective property which involves many-particle correlations. We chose samples accommodating $N=108$ molecules, and carried out runs as long as $40t°$ at least, $t°$ being the time when $F_s(k_{max},t)$ vanishes (i.e., when it drops below 0.02) [63]. $t°$ provides an estimate of the time scale to reach the limit in Eq. (3.10). At the lowest temperature, $T=0.5$, the relative error is estimated to be about 7%. This figure was confirmed by collecting several runs at each temperature. We also explicitly tested that the viscosity of small ($N=108$) and large samples ($N=1000$) at $T=0.7$ exhibit no significant difference. Small samples to evaluate η in supercooled sustems were also used by Thirumalai and Mountain [28].

In Fig. 12 the shear viscosity is shown as a function of the temperature. It covers a range of more than three orders of magnitude. The data are also plotted as function of $\log(T-T_c)$, showing that the viscosity, differently from the diffusivity, may not be described by a power law analogous to Eq. (3.2) in the overall temperature range investigated. If the fit with a power law analogous to Eq. (3.2) is limited to $T<0.85$, it is found that $\gamma_{\eta}=-2.20\pm0.03$.

C. Stokes-Einstein law

Several experimental [3,4,7–9,11,13] and numerical [20,24,28–30,33] works showed a decoupling of the translational diffusion and viscosity on approaching the glass transition. Typically, the decoupling occurs around T_c [3]. To date, MD was used to investigate the issue in one- and two-component *atomic* systems. It is therefore of interest to examine the present molecular system from that respect.

The decoupling manifests as an enhancement of the translational diffusion D with respect to the prediction of the Stokes-Einstein (SE) relation, which reads [64]
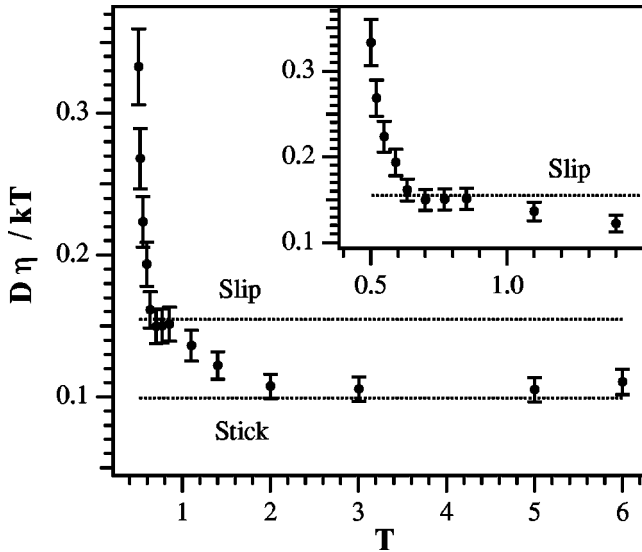
FIG. 13. The temperature dependence of the ratio $D\eta/kT$. The SE relation predicts a constant value. Dashed lines are the SE predictions for prolate ellipsoids with semiaxes $b=0.46$ and $c=0.69$, and stick or slip boundary conditions. A magnification of the low-T region is shown by the inset.

$$D = \frac{kT}{\eta\mu}. \qquad (3.13)$$

μ is a constant that depends on both the molecule geometry and the boundary conditions. For a sphere of radius a, μ is equal to $6\pi a$ or $4\pi a$ if stick or slip boundary conditions occur, respectively. The problem of uniaxial ellipsoids in the presence of stick boundary conditions may be worked out analytically [64]. Tables of μ for prolate ellipsoids with slip boundary conditions were also reported [65]. The case of a biaxial ellipsoid with a stick boundary condition was recently discussed by noting an interesting electrostatic analogy [66].

In Fig. 13 we plot the ratio $D\eta/kT$ as a function of temperature. According to the SE relation the ratio must be constant. At higher temperatures the ratio levels off at about 0.105 ± 0.007. On cooling, there is first a mild change followed by a steep increase below $T=0.632=1.38T_c$.

It is believed that the SE failure is a signature of the heterogeneous dynamics of supercooled liquids [16–19]. Alternative views are provided by frustrated lattice gas models [20] and the "energy landscape" picture [2,21–24]. Most interpretations suggest the existence of crossover temperatures broadly located around T_c [3]. From this respect it is tempting to note that the SE law breaks down at $T\sim0.632$, below which intermittent behavior is seen (see Fig. 9). Intermittence disappears for times longer than τ_α (see Fig. 11), which is consistent with a growing dynamic heterogeneity of the liquid.

Around $T=0.77$ a plateau at 0.151 ± 0.01 is reached. We have compared the results to the prediction of the SE law for prolate ellipsoids. The diatomic molecule under study may be roughly sketched as a prolate ellipsoid with semiaxes $b=3/4$ and $c=1/2$. The corresponding ratio $D\eta/kT$ for stick and slip boundary conditions is equal to 0.091 and 0.1415,

respectively. The values compare well to the high- and low-T plateaus which are observed in Fig. 13. By setting $b=0.69$ and $c=2/3b$, the agreement is improved with $D\eta/kT=0.098$ and 0.154 for stick and slip boundary conditions, respectively. The above analysis provides reasonable evidence of a precursor effect of the SE breakdown which manifests itself as an apparent stick-slip transition. A quite similar crossover from stick to slip boundary conditions is shown on approaching the glassy freezing of colloidal suspensions [67] and investigating the rotational dynamics of tracers in supercooled fragile liquids [68]. The apparent change from stick to slip boundary conditions is also observed in the rotational dynamics of the present model system [38]. However, it is quite smooth, and can hardly be described as a steep transition. The detailed molecular interpretation of the stick-slip transition is presently under study by us. One anticipates that at high viscosity, dragging the surrounding cage by the diffusing particle will require several local rearrangements, and will be considerably slower than, e.g., jumping out of the cage after some favorable rearrangement releasing the structural constraints. This may be restated in terms of relative contributions to the diffusion and the viscosity of the transverse current and density modes, and some analysis along this line has been reported [69]. The studies make it clearer the role of interacting potential to define the apparent hydrodynamic boundary conditions. However, the temperature dependence and the role of jump motion, which is expected, has not yet been addressed. Furthermore, since we are studying a one-component system, the effect seems to be conceptually different due to the apparent change of the boundary conditions of a diffusing guest tracer in a liquid host [69].

It is worthwhile to mention that the SE law shows fine modifications of the supercooled liquid behavior which are hardly found by inspecting the diffusivity. The latter exhibits a single power-law regime over all the temperature range we studied.

IV. CONCLUSIONS

The transport and the relaxation properties of a molecular supercooled liquid on the isobar $P=1.5$ has been studied by molecular dynamics. The molecule is a rigid A-B system. On cooling, the diffusivity decrease is fitted over four orders of magnitude by the power law $D\propto(T-T_c)^{\gamma_D}$, with $\gamma_D=1.93\pm0.02$ and $T_c=0.458\pm0.002$. The divergence of the primary relaxation time τ_α, drawn by the intermediate scattering function $F_s(k_{max},t)$, tracks the diffusivity at the lowest temperatures according to $\tau_\alpha\propto(k_{max}^2D)^{-1}$. The result confirms findings on hard sphere systems [45]. It disagrees with other studies on the same model system under study here, which noted that a power-law fit of D and τ_α yields the same T_c value, but that $\gamma_\alpha>\gamma_D$ with $N=500$ and $P=1$ [41].

At the lowest temperatures fractions of highly mobile and trapped molecules are evidenced, thus extending previous results on supercooled atomic mixtures to one-component molecular liquids [28,34]. Translational jumps are also shown. The duration of the jumps exhibits a distribution. The distribution of the waiting times before a new jump takes place, $\psi(t)$, is exponential at higher temperatures. At lower temperatures two regimes are evidenced: at short times $\psi(t)\propto t^{\xi-1}$ with $0<\xi\leq1$, and at long times the decay is

faster than exponential. The crossover between the two regimes occurs around τ_α. Noticeably in this time window, MCT predicts that $F_s(k_{max},t)$ also decays as a power law. The interplay between the two decays is anticipated, and a preliminary analysis has been presented. The distribution of the waiting times at short times is ascribed to the intermittent behavior which is expected to develop in glassy systems [33,49,50,52,55,56]. This was predicted by models of trapping in energy landscapes developed by Bouchaud and co-workers under fairly general assumptions [50]. If the waiting time before a new jump exceeds τ_α, the environment surrounding each molecule largely restructures. The subsequent average process results in a faster decay of $\psi(t)$. The probability that no jump occurs before time t is found to vanish more slowly than $F_s(k_{max},t)$, in close analogy with the case of viscous silica melts [58].

The shear viscosity has been studied over more than three orders of magnitude. The data are fitted by the power law $\eta \propto (T-T_c)^{\gamma_\eta}$, with $\gamma_\eta = -2.20 \pm 0.03$ at the lowest temperatures. The validity of the Stokes-Einstein relation has been examined. Previous MD studies were limited to atomic one- and two- component systems. At higher temperatures the SE relation fits the data well if *stick* boundary conditions are assumed. At lower temperatures the product $D\eta/T$ increases, and the Stokes-Einstein relation is not obeyed. The breakdown occurs near to the temperature where the intermittency is shown by $\psi(t)$. Interestingly, a precursor effect of the breakdown is observed which manifests itself as an apparent stick-slip transition. A crossover from stick to slip boundary conditions has been observed on approaching the glassy freezing of colloidal suspensions [67], and when investigating the rotational dynamics of tracers in supercooled fragile liquids [68]. The molecular origin of this effect is currently under intense study.

ACKNOWLEDGMENTS

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$$F_s(k,t) = \int_0^{+\infty} G_s(r,t) \, 4\pi r^2 \frac{\sin kr}{kr} \, dr.$$

The main contributions to $F_s(k_{max},t)$ come roughly from $r < r^*$, with $r^* \approx 2\pi/k_{max} \approx 1$. If the discrepancies between $G_s(r,t^*)$ and $G_s^g(r,t^*)$ for $r < 1$ were small, $F_s(k_{max},t) \approx \exp(-Dk_{max}^2 t)$ for $t \approx t^*$. Instead, $F_s(k_{max},t)$ is found to decay as a stretched exponential.

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$$\eta = \frac{kT}{60\pi^2} \int dt \int dk V^2(k) \left[\frac{F(k,t)}{S(k)}\right]^2,$$

where $V(k) = k^2 d \ln S(k)/dk$. The vertex $V(k)$ greatly reduces the weight of hydrodynamic wave vectors. The main contributions to the above integral are due to modes located around k_{max}, with a spread $|k_{max} - k|/\Delta \sim 1.4$. Δ is the half-width of the main peak of $S(k)$, whose inverse is a measure of the extent of correlations in direct space. Then, for a sample of volume V, one finds $r = 2(v\tau_c/Vt)^{1/2}$, with $v = \Delta^{-3}$ (see the above paper by Frenkel). In order to have runs longer than the relaxation time of $F(k_{max},t)$ and retain reasonable execution times, V must be small (but larger than v). Small samples also limit the onset of modes with very slow relaxation times, which may affect the asymptotic behavior of Eq. (3.11).

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