Molecular Dynamics Studies of biatomic supercooled liquids: intermittency, stick-slip transition and the breakdown of the Stokes-Einstein laws.

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The transport and the relaxation properties of a biatomic supercooled liquid are studied by molecular-dynamics methods. Both translational and rotational jumps are evidenced. At lower temperatures their waiting-time distributions diverge as a power law at short times. The Stokes-Einstein relation (SE) breaks down at a temperature which is close to the onset of the intermittency. A precursor effect of the SE breakdown is observed as an apparent stick-slip transition. The breakdown of Debye-Stokes-Einstein law for rotational motion is also observed. The divergences of the rotational correlation time τ_1 and the translational diffusion coefficient at low temperatures are fitted by power laws over more than three and four orders of magnitude, respectively. A less impressive agreement is found for τ_l with $l = 2 - 4$ and the rotational diffusion coefficient.

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1 INTRODUCTION

The relaxation and the transport properties of molecular liquids depend on both their translational and rotational motion. 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, $D \approx kT/6\pi\eta a$, and the Debye-Stokes-Einstein laws, $D_r \approx kT/\eta a^3$ are found to work nicely, D, D_r and a being the translational and the rotational diffusivity and the molecular radius, respectively. Differently, in deeply supercooled regimes there is wide evidence that the product *increases on cooling* evidencing the breakdown of the hydrodinamic behavior at molecular level and the decoupling by the viscous flow [?, ?, ?, ?] [?, ?, ?, ?, ?].

The decoupling between microscopic time scales and the viscous flow is a signature of the heterogeneous dynamics which develops close to the glass transition, i.e. a spatial distribution of transport and relaxation properties [?, ?, ?, ?]. Crossover temperatures to that regime are broadly located around $1.2T_g$, i.e. in the region where the critical temperature T_c predicted by the mode-coupling theory of the glass transition (MCT) is found [?, ?].

During the last years molecular dynamics simulations (MD) proved to be a powerful tool to investigate supercooled liquids (for a recent review see ref.[?]). Most MD studies confirmed that the decoupling is due to dynamic heterogeneities[?, ?, ?, ?, ?, ?]. In fact, "active" [?] or "mobile" [?] regions which largely contribute to set the macroscopic average value have been identified. In such regions hopping processes, enhancing the transport with respect to the hydrodynamic behavior, have been evidenced [?, ?]. The occurrence of jumps in glasses has been reported several times in the recent past [?, ?, ?, ?].

The paper discusses the decoupling phenomena in viscous liquids by presenting the main results of recent MD studies on molecular supercooled liquids [?, ?]. In Sec. 2 the model and the details of the simulation are presented. The results are discussed in Sec. 3. The conclusions are summarized in Sec. 4.

2 MODEL AND DETAIL OF SIMULATION

The system under study is a model molecular liquid of rigid dumbbells [?, ?, ?]. The 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:

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}\right], \quad \alpha, \beta \in \{A, B\} \tag{1}$$

The model parameters in reduced units are: $\sigma_{AA} = \sigma_{AB} = 1.0$, $\sigma_{BB} = 0.95$, $\epsilon_{AA} = \epsilon_{AB} = 1.0$, $\epsilon_{BB} = 0.95$, $d = 0.5$, $m_A = m_B = m = 1.0$. The sample has $N = N_{at}/2 = 1000$ molecules which are accommodated in a cubic box with periodic boundary conditions. Further details on the simulations may be found elsewhere [?]. We examined the isobar at $P = 1.5$ by equilibrating the sample under isothermal-isobaric conditions and then col-

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Figure 1: (a) Temperature dependence of the translational diffusion coefficient D. The dashed line is a fit with the power law Eq. (**??**) with $\gamma_D = 1.93 \pm 0.02$, $T_c = 0.458 \pm 0.002$ and $C_D = 0.0481 \pm 0.0004$. (b) MCT scaling analysis of τ_1. $T_c = 0.458$. (c) Arrhenius plot and (d) MCT scaling analysis of the rotational correlation times τ_l, $l = 1 - 4$ and the rotational diffusion coefficient D_r. $T_c = 0.458$. The dashed lines are guides for the eyes. The translational diffusion constant D and the best fit are also shown for comparison (open diamonds).

lecting the data by a production run in microcanonical conditions. The temperatures we investigated are $T = 6, 5, 3, 2, 1.4, 1.1, 0.85, 0.70, 0.632, 0.588, 0.549, 0.52, 0.5$.

3 RESULTS AND DISCUSSION

3.1 Diffusion

3.1.1 Translational diffusion coefficient

The translational diffusion coefficient D is evaluated by the Einstein relation [**?**]:

$$D = \lim_{t\to\infty} \frac{R(t)}{6t} \tag{2}$$

where $R(t)$ is the mean squared displacement of center of mass at time t. In Fig. **??**(a) the temperature dependence of D is shown and fitted by the power-law

$$D = C_D\,(T - T_c)^{\gamma_D} \tag{3}$$

Theoretical justification of Eq (**??**) is provided by MCT [**?**]. In particular, the ideal MCT predicts the inequality $\gamma_D > 1.5$. The best fit values are $\gamma_D = 1.93 \pm 0.02$ and $T_c = 0.458 \pm 0.002$, $C_D = 0.0481 \pm 0.0004$.

3.1.2 Rotational correlation times and diffusion coefficient

The rotational diffusion coefficient may be defined as [**?**, **?**]:

$$D_r = \lim_{t\to\infty} \frac{R_r}{4t} \tag{4}$$

where R_r is the mean square value of the angular displacement :

$$\phi_i(t) - \phi_i(0) = \Delta\phi_i(t) = \int_0^t \omega_i(t')\,dt' \tag{5}$$

The rotational correlation times τ_l are defined as the area below the rotational correlation functions [**?**]. l is the rank of the involved Legendre polynomial. Fig. **??**(c) and Fig. **??**(d) present the temperature dependence of τ_l, $l = 1 - 4$ and D_r. It is seen that a wide region exists where the above quantities exhibit approximately the same Arrhenius behavior (about $0.7 < T < 2$). At lower temperatures the apparent activation energy of the rotational correlation times increase. In particular, τ_1 becomes shorter than τ_2 and a similar crossover is anticipated between τ_3 and τ_4 at temperatures just below 0.5. Differently, the rotational diffusion coefficient D_r exhibits the same activation energy for $T < 0.9$. This behavior extends below the critical temperature T_c [**?**].

Fig. **??**(b) and fig. **??**(d) show the MCT analysis of the rotational diffusion and the correlation times. According to MCT, $\tau_l, D_r^{-1} \propto (T - T_c)^{-\gamma}$ [**?**, **?**]. Fig. **??**(b) proves that τ_l complies with MCT scaling over more than three orders of magnitude. Deviations are seen for $l > 1$.

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Figure 2: Long-time (a) and short-time (b) behavior of the waiting-time distribution $\psi(t)$ at different temperatures. The superimposed lines are best fits with Eq. (**??**) and $\xi = 0.49$, $\tau = 2550$ ($T = 0.5$), $\xi = 0.63$, $\tau = 420$ ($T = 0.549$) and $\xi = 1$, $\tau = 49$ ($T = 0.632$). (c) The rotational waiting-time distribution ψ_{rot} at different temperatures. (d) Top: best fits of ψ_{rot} at $T = 0.5$ with the exponential ($\tau = 102 \pm 3$), the stretched exponential ($\beta = 0.78 \pm 0.02$ and $\tau = 63 \pm 4$) and the truncated power law Eq. (**??**) ($\xi = 0.34 \pm 0.04$ and $\tau = 125 \pm 3$). The insert is a magnification of the short-time region. Notice that the fit with the power law is virtually superimposed to ψ_{rot}. Bottom: residuals of the fits by the truncated power-law and the stretched exponential.

3.2 Waiting-time distributions

At low temperatures a fraction of the overall biatomic molecules moves by jumps of finite size [**?**, **?**]. The waiting time between two jumps is a random quantity. The related distributions for both the translational and rotational jumps are presented here. They are denoted as $\psi(t)$ and $\psi_{rot}(t)$, respectively.

3.2.1 Translational jumps

In the present study a molecule jumps at time t if the displacement between t and $t + \Delta t^*$ ($\Delta t^* = 24$) exceeds $\sqrt{\Delta R^*} = \sigma_{AA}/2 = 0.5$. Further details on the procedure to detect jump events are provided elsewhere [**?**].

Fig.**??**(a) and Fig. **??**(b) show 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 decay by the function:

$$\psi(t) = \left[\Gamma(\xi)\tau^{\xi}\right]^{-1} t^{\xi-1} e^{-t/\tau} \qquad 0 < \xi \leq 1 \tag{6}$$

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 behaviour in particle motion develops on cooling [?, ?, ?, ?]. A signature of intermittence is the power law decay of $\psi(t)$ (for 2D liquids see [?]) and related quantities such as the first-passage time distribution [?]. The exponent ξ of Eq. (??) has a simple interpretation. If a dot on the time axis marks each relaxation event (a jump), the fractal dimension of the set of dots is ξ. For $\xi < 1$, it is found $\psi(t) \propto t^{\xi-1}$ at short times [?, ?].

The best fits at $T = 0.5, 0.549$ and 0.632 are shown in fig.??(a) and fig. ??(b). The increase of temperature results in a weak increase of the exponent ξ and a more marked decrease of τ. Interestingly, $\psi(t)$ exhibits small but reproducible deviations from Eq. (??) at $T = 0.5$. They suggest 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.

3.2.2 Rotational jumps

The distribution $\psi_{rot}(t)$ of the waiting-time, namely the residence time in one angular site of the unit vector $\mathbf{u}_i$ being parallel to the axis of the i-th molecule, offers a simple way to characterize rotational jumps. A jump of the i-th molecule is detected at t_0 if the angle between $\mathbf{u}_i(t_0)$ and $\mathbf{u}_i(t_0 + \Delta t^*)$ is larger than 100° with $\Delta t^* = 24$. Other details are identical to the translational case.

Fig.??(c) shows $\psi_{rot}(t)$ at different temperatures. At $T = 0.632$ is virtually exponential whereas at lower temperatures the short-time behavior is different. In fig. ??(d) $\psi_{rot}(t)$ at $T = 0.5$ is compared to the truncated power law eq. (??), the stretched ($exp[-(t/\tau)^{\beta}]$) and the usual exponential functions. The better agreement of Eq. (??) at short times is appreciated by the residuals.

It is worth noting that it was found that the time needed to complete the translational jumps exhibits a distribution [?, ?]. The absence of a similar distribution for the rotational jumps points to a larger freedom of the latter.

It is an important conclusion of the present study that intermittency has been evidenced at short times in both the translational and the rotational jump motion.

3.3 Breakdown of Stokes-Einstein and Debye-Stokes-Einstein laws

This section is devoted to discuss the decoupling of the single-particle dynamics from the viscosity which occurs at low temperatures.

3.3.1 The shear viscosity

The system under study exhibits a dramatic increase of the viscosity on cooling [?, ?]. Fig.??(a) shows that the divergence of the viscosity is conveniently described by the power law in eq. (??) in a smaller range than the one of the translational diffusion coefficient (see fig. ?? (a)).

3.3.2 Breakdown of the Stokes-Einstein law

Several experimental [?, ?, ?, ?] and numerical [?, ?, ?, ?, ?, ?] works evidenced a decoupling of the translational diffusion and the viscosity on approaching the glass transition. Typically, the decoupling occurs around T_c [?]. MD investigated the issue in one- and two-components *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 relation (SE) which reads [?]

$$D = \frac{kT}{\eta\mu} \tag{7}$$

μ is a constant that depends on both the molecule geometry and the boundary conditions (BC). For a sphere of radius a, μ equals $6\pi a$ or $4\pi a$ if stick or slip BC occur, respectively. The cases of uniaxial ellipsoids with both stick and slip BC were worked out [?, ?].

In Fig. **??**(b) we plot the ratio $D\eta/kT$ as a function of temperature. 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 $T = 0.632 = 1.38T_c$. We remind that SE predicts a temperature-independent ratio. It is worth noting that the SE law breaks down at $T \sim 0.632$ where intermittency is apparent at short times (see fig.**??**(b)).

It is believed that the SE failure is a signature of the heterogeneous dynamics of supercooled liquids [?, ?, ?, ?]. Alternative views are provided by frustrated lattice gas models [?] and the "energy landscape" picture [?, ?, ?, ?, ?].

Around $T = 0.77$ a plateau at 0.151 ± 0.01 is reached. The diatomic molecule under study may be sketched as a prolate ellipsoid with semiaxis $b = 3/4$ and $c = 1/2$. SE predicts that the corresponding ratio $D\eta/kT$ for stick and slip BC is equal to 0.091 and 0.1415, respectively. The values compare well to the high- and low-T plateau in fig.**??**(b). 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 BC, respectively. The above analysis provides reasonable evidence of a precursors effect of the SE breakdown which manifests itself as an apparent stick-slip transition. A similar crossover has been observed in colloidal suspensions [?].

3.3.3 Breakdown of the Debye-Stokes-Einstein Law

For large Brownian particles the reorientation in a liquid occurs via a series of small angular steps, i.e. it is diffusive. Hydrodynamics predicts that the diffusion manifests a strong coupling to the viscosity η which is accounted for by the Debye-Stokes-Einstein law (DSE). For biaxial ellipsoids it takes the form [?]

$$D_i = \frac{kT}{\mu_i \eta}, \qquad i = x, y, z \tag{8}$$

$D_{x,y,z}$ are the principal values of the diffusion tensor, k is the Boltzmann constant. The coefficients μ_i depend on the geometry and BC. For a sphere with stick BC $\mu_{x,y,z} = 6v$, v being the volume of the sphere. The cases of uniaxial ellipsoids with stick and slip BC were worked out [?, ?, ?].

If the viscosity is not high ($\eta < 1 Poise$) DSE works nicely even at a molecular level . At higher viscosities DSE is found to overestimate the rotational correlation times of tracers in supercooled liquids by time-resolved fluorescence and Electron Spin Resonance (ESR)

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Figure 3: Viscosity. (a) Temperature dependence of the shear viscosity. The slope of the superimposed line is $\gamma_\eta = -2.20 \pm 0.03$. (b) Temperature dependence of the ratio $D\eta/kT$. Dashed lines are the SE predictions for prolate ellipsoids with semiaxis $b = 0.46$ and $c = 0.69$ and stick or slip BC. Magnification of the supercooled region is shown by the inset. (c) Plots of the quantity η/XkT with $X = D_r^{-1}, l(l+1)\tau_l$. (d) Magnification of the the supercooled regime. The dashed lines in (c) and (d) are the DSE predictions for stick and slip BC. In the region $1 < T < 2$ the ratio η/XkT depends little on X due to diffusional behavior.

studies [**?**, **?**, **?**]. In this decoupling region ESR evidenced that the tracer rotates by jump motion [**?**]. On the other hand, photobleaching [**?**] and NMR [**?**], studies found only small deviations from DSE even close to T_g.

We have studied the coupling between the rotational relaxation and the viscosity. From this respect we also considered the popular alternative form of eq. (**??**) which is written in terms of rotational correlation times by assuming that the reorientation is diffusive, i.e. it occurs by small angular steps. It is well suited for comparison with the experiments which do not usually provide direct access to the rotational diffusion coefficients. In the present case the alternative form is obtained by replacing D_r^{-1} with the product $l(l+1)\tau_l$ in eq. **??**.

In fig. **??**(c) we plot the ratio η/XkT with $X = D_r^{-1}, l(l+1)\tau_l$ with $l = 1-4$ together with DSE predictions for both stick and slip BC.

At high temperatures if $X = l(l+1)\tau_l$ with $l > 1$ the ratio roughly approaches the value expected for stick BC. For $X = D_r^{-1}$ DSE with slip BC fits better. The τ_l case is intemediate. On cooling η/XkT increases. For intermediate temperatures the rotational diffusion takes place since $l(l+1)\tau_l$ and D_r are all close to the DSE expectation with slip BC. Notably, $D_r\eta/kT$ remains close to this value in the wide interval $2 < T < 6$.

At lower temperatures η/XkT diverges. The stronger deviations are exhibited by D_r and $\tau_{1,3}$. The results are readily intepreted. At low temperature molecules undergo 180° flips [**?**]. These affect the pair $\tau_{1,3}$ much more than the pair $\tau_{2,4}$. The large decoupling of D_r is also understood since the latter is mainly affected by fast dynamics.

4 CONCLUSIONS

The transport and the relaxation properties of a biatomic supercooled liquid on the isobar $P = 1.5$ has been studied. The results point out that at low temperature a fraction of the overall molecules performs jump motion with intermittent behavior. The resulting changes in the dynamics weaken the coupling with the viscosity. Interesting precursor effects to be described as apparent slip-stick transitions are observed.

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