Dynamical and structural correlation in supercooled liquids: A molecular dynamics investigation of m-toluidine

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Structural and dynamical properties of liquid and supercooled liquid m-toluidine are studied by molecular dynamics simulations. Approaching the liquid–glass transition, dynamical heterogeneities, a characteristic common to all supercooled glass formers, are observed. We prove the occurrence of strict correlation between these heterogeneities and the potential energy landscape of the system, expressed in terms of molecule–molecule interactions. A slowing down of the self-diffusive motion of the molecular centers of mass is observed for particular arrangements of pairs of H-bonded molecules. Previous studies on model systems provided evidence of the correlation between dynamical heterogeneities and potential energy landscape, described in terms of the inherent structure of the system. While in this last case the structure is viewed as a collective property of the system, in m-toluidine short-range interactions are sufficient to explain the dynamical behavior in a satisfactory way. This result agrees with the view, supported also by experimental observations, that m-toluidine can be considered as an ensemble of H-bonded subsystems weakly interacting among them. © 2003 American Institute of Physics.

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I. INTRODUCTION

The nature of supercooled liquids and their tendency to form glassy states represent still unsolved problems of condensed phase physics. For these liquids self-diffusion persists well below the melting temperature, up to the so-called glass transition temperature \( T_g \), where transport properties change by many orders of magnitude. Several theories, aimed to explain the liquid–glass transition, have been proposed to incorporate the dynamical aspect of the liquid. In the last decade the mode coupling theory (MCT) became very popular for the description of the dynamical aspects of the liquid–glass transition. In its simplest version, MCT is devised for a fluid of shapeless particles, for which the only dynamical variables are the positions of the centers of mass. The earliest version, the idealized MCT, predicts a dynamical transition between two regimes at a critical temperature \( T_c \): in the first regime \( (T>T_c) \), the time correlation function of any density function decays to zero in a finite time, while in the second one \( (T<T_c) \), all these functions remain finite at infinite time, this limit being called their nonergodicity parameter. In particular, when \( T_c \) is approached by cooling, transport properties are characterized by a non-Arrhenius temperature dependence, and the structural relaxation (\( \alpha \)-relaxation) has a marked nonexponential behavior, characterized by a stretched exponential evolution of the related correlation functions. On the basis of a number of experiments and simulations, \( T_c \) is now generally accepted that the nonexponential relaxation is due to the presence of dynamic heterogeneity, i.e., to a broad distribution of particle mobilities throughout the liquid. This behavior is well accounted for by MCT above \( T_c \), where the stretched exponential behavior of the correlation functions is predicted to be scaled in a master curve. However, when the MCT predictions are compared with experimental data, approximate agreements can be obtained only if \( T_c \) is larger than \( T_g \) (see Ref. 4). Many authors argue that the breakdown of the MCT predictions might arise from the increasing importance of hopping events (not accounted for in the simplest version of MCT) in the vicinity of the glass transition. The presence of hopping events and their importance in determining the time relaxation of dynamical quantities has been studied for various glass-forming model systems. In these studies the analysis of the dynamics of model systems was performed using the concept of potential energy landscape and the correlated idea of inherent structure. Although the PEL treatment includes all details of the interaction potential of the system, its application to complex molecular liquids to obtain local structure information is actually difficult due to the large computational cost of the method. In principle, interaction potential details (molecular shape, for example) could be also included in the MCT formalism. On the other hand, the reverse way, namely the extraction of the local structure data from the MCT predictions, cannot be followed. In this framework, molecular dynamics (MD) simulation can be considered as one of the most useful tools to study the local structure of the liquids.

Previous investigations that aimed to understand the dynamical heterogeneity in supercooled liquids were mainly devoted to study model systems, and application to simple molecular liquids has started to appear only very recently.

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recently. Studies on model systems (in many cases Lennard-Jones fluids) are very attractive because their simplicity allows long simulation runs and makes the analysis easier. On the other hand, the high simplicity of the model is an obstacle to the understanding of the microscopic structural mechanisms leading to the dynamical behavior of the real systems.

For a more realistic approach, we presented in a recent paper a MD simulation of a truly molecular liquid, m-toluidine, one of the most studied glass-forming molecular systems. We suggested that the appearance of dynamical heterogeneity in liquid m-toluidine is strictly related to the occurrence of extensive structural rearrangements, involving pairs of H-bonded molecules. From an analysis of the free energy surface of these dimers, we concluded that their most probable molecular arrangement goes from T-shaped (with perpendicular displaced molecular planes) at high temperature, to stacked (with parallel displaced molecular planes) below 260 K. In the present paper we investigate the nature of both the structural and the dynamical heterogeneity in terms of the radial-angular pair distribution functions and of the time-dependent mean-square displacement of the molecular centers of mass. In addition we include in the discussion a new MD simulation at 210 K, very close to the glass transition temperature of 190 K obtained in Ref. 25. From the analysis of the atomic trajectories, we show that it is possible to interpret the observed dynamical heterogeneity in terms of well-defined subsystems, consisting of strongly interacting molecules. This treatment is consistent with the view, proposed by other authors, that a system with a large number of particles can be decomposed into weakly interacting subsystems with little correlation among each other. In the specific case of m-toluidine, the minimal subsystems, on which the dynamical properties of the system strongly depend, have a dominant contribution from pairs of H-bonded molecules.

The paper is organized as follows: in Sec. II we briefly describe the potential model used for the simulations and the essential technical details. In Sec. III the results are reported and discussed. Conclusions are given in Sec. IV.

II. POTENTIAL MODEL AND TECHNICAL DETAILS

The MD simulations were performed using an all-atom model. The molecules were assumed completely flexible by means of a CHARMM-like potential. The intermolecular potential is modeled by point charges on the atoms and by Lennard-Jones interactions. A complete description of the intra- and intermolecular potential is given in Ref. 25. The simulated sample consists of 256 molecules in a cubic box. Details of the equilibration procedure were also given previously. For the additional 210 K simulation run, the same equilibration and coordinate-storage protocols used for the 220 K simulation were adopted. Most of the results we present to discuss the different behavior of m-toluidine far from and close to the liquid–glass transition refer to the 300 and 210 K MD simulations, respectively.

III. RESULTS AND DISCUSSION

Although m-toluidine could not be properly considered as one of the strongest H-bond forming compounds like water or glycerol, several of their chemical physics properties can be explained only considering its attitude to form H-bonds. For example, there are experimental and theoretical investigations that indicate the H-bond induced clustering as the origin of the appearance of an unusual prepeak in the static structure factor of m-toluidine. In this respect, we found evidence of a relevant structural change, close to the glass transition temperature of 190 K obtained in Ref. 25. From an analysis of the atomic trajectories, we show that it is possible to interpret the observed dynamical heterogeneity in terms of the radial-angular pair distribution functions and of the time-dependent mean-square displacement of the molecular centers of mass. In addition we include in the discussion a new MD simulation at 210 K, very close to the glass transition temperature of 190 K obtained in Ref. 25. From the analysis of the atomic trajectories, we show that it is possible to interpret the observed dynamical heterogeneity in terms of well-defined subsystems, consisting of strongly interacting molecules. This treatment is consistent with the view, proposed by other authors, that a system with a large number of particles can be decomposed into weakly interacting subsystems with little correlation among each other. In the specific case of m-toluidine, the minimal subsystems, on which the dynamical properties of the system strongly depend, have a dominant contribution from pairs of H-bonded molecules.

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structures in which the axes of the aromatic rings are perpendicular to each other. As the temperature is lowered the peak becomes sharper and sharper, due to the increased H-bond association and to the localization of preferred structures. At 210 K, new peaks, labeled B, C, and D in Fig. 1, appear. Their intensity is even larger than that of A. Structures corresponding to the peaks C and D have instead a nearly parallel orientation of the two rings. Representative structures of molecular pairs belonging to the A, B, C, and D regions of Fig. 1 are shown in Fig. 2. From the figure it is easily seen that structures corresponding to peak B, C, and D derive from A by tilting in part or completely one ring with respect to the other. For the structures corresponding to the A, B, and D peaks the molecule–molecule interactions are almost exclusively limited to H-bonding. In the C structure the ring–ring and ring–methyl interactions give instead an important contribution. We notice that the strong peak C at 210 K is not present at 220 K, as can be seen from the free energy landscape at 220 K reported in Ref. 25. In addition, the peak corresponding to the D region becomes at 210 K much sharper than at 220 K. The increase with decreasing temperature of the probability of parallel displaced configurations was also observed in Ref. 25, where it was attributed to a structural transition. While the A, B, and D dimers are characterized by large exposed surfaces, the C structure is more compact, and similar to that observed for the minimum energy dimer.25 This confirms the hypothesis that, by lowering the temperature, the H-bonded dimeric structures go from entropy-favored to energy-favored configurations. We shall show below that the presence of H-bonded pair structures, like B, C, and D, is decisive for the appearance of dynamical heterogeneity in supercooled liquid m-toluidine.

As previously discussed, the dynamical properties of the system have been analyzed by calculating the mean-square displacement of the molecular centers of mass as a function of time

$$D(t) = \frac{1}{N} \sum_{i=1}^{N} \langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle. \quad (2)$$

In Eq. (2), $\mathbf{R}_i(t)$ is the vector position of the center of mass of the $i$th molecule, $N$ is the number of molecules in the sample, and the angular brackets indicate an average on the time origins. The $D(t)$ function for the MD simulations at 340, 300, 260, 220, and 210 K is shown in Fig. 3. The slope of $D(t)$ is related to the translational self-diffusion coefficient of the center of mass. Our MD model yields at 210, 220, 260, 300, and 340 K the values 0.009, 0.027, 0.851, 3.873, and 9.941 units of $10^{-6}$ cm$^2$ s$^{-1}$, respectively. From 340 to 210 K the self-diffusion coefficients vary by more than two orders of magnitude.

Since it is not possible to characterize all kinds of dynamical heterogeneity on the basis of collective properties, such as $D(t)$, some space partitioning is needed. In the lit-
erature there is not a general consensus on what kind of particle aggregates are involved in the cooperative motions at the origin of the dynamical heterogeneity. While several authors individuate the origin in compact regions of the space, other found it in string-like structures whose length increases with decreasing temperature. In principle, one should first use some computational method to characterize the dynamical heterogeneities and then individuate the regions of space (subsystems) involved in different dynamical processes. We proceed instead in the reverse way. We chose a priori and somehow arbitrarily, the putative regions (subsystems) of space and then we show that different subsystems have different dynamical behavior. For this purpose, the simulation box was divided into 27 equal cubic boxes (subsystems) and all molecules found in each subsystem at the first step of the simulation run were considered to form that subsystem during the full simulation time. The individual subsystems contain from 9 to 11 molecules each. It is then possible to associate a time-dependent mean-square displacement to each subsystem by using Eq. (2), where \( N \) represents now the number of molecules of the considered subsystem. In Figs. 4(a) and (b), the time-dependent mean-square displacements (same as Fig. 3), normalized by the \( D(0.6) \) value at 0.6 ns, are reported for the 300 and 210 K MD simulations, respectively. In the same figures, the vertical bars indicate the spread of the time-dependent mean-square displacements obtained for the various subsystems. The curves are spread on very wide ranges. Not surprisingly, the relative spread increases with decreasing temperature. At the lowest temperature (210 K) one can identify three subsystems where the translational diffusion is almost frozen, while the mobility is still relatively large in many other subsystems at the same temperature. For the subsystems characterized by slow motion, the mean-square displacements of the centers of mass as a function of time are shown in Fig. 4(c) along with those relative to the three subsystems with the highest mean-square displacement (fast motion subsystems).

In the Introduction we posed the question whether the observed heterogeneity in the dynamical behavior of different subsystems reflects also a different H-bond connectivity of the members of the subsystems themselves. The answer to this question is given in Fig. 5, where the \( g_{hb}(R, \theta) \) pair distribution function for the molecules belonging to the three slow and to the three fast motion subsystems is reported. The three slow motion subsystems, i.e., subsystems 4, 5, and 6 of Fig. 4(c), show sharp and intense peaks corresponding to the regions D, B, and C of \( g_{hb}(R, \theta) \) (see Fig. 1), respectively. In particular, the peaks observed for subsystems 4 and 6 correspond to the most intense D and C peaks. No similar correspondence is observed for the fast motion subsystems [sub-

FIG. 3. Mean-square displacements \( D(t) \) of the molecular centers of mass as a function of time, at 210, 220, 260, 300, and 340 K. For the sake of clarity, the \( D(t) \) functions at 210 and 220 K are reported in the inset.

FIG. 4. (a) Mean-square displacement \( D(t) \) as a function of time (same as Fig. 3) normalized by the \( D(0.6) \) value for the 300 K MD simulation. The vertical bars indicate the spread of the time-dependent mean-square displacement curves for the 27 subsystems of the sample. (b) Same as (a) but related to the 210 K MD simulation. (c) Time-dependent mean-square displacements for the six (fast and slow motion) subsystems at 210 K. Curves 1, 2, and 3 correspond to the subsystems with the largest self-diffusion coefficient, while curves 4, 5, and 6 correspond to the subsystems with the lowest self-diffusion.
systems 1, 2, and 3 in Fig. 4(c)], which show only broad and disperse peaks on the \((R, \theta)\) plane.

To generalize the observations made for the slow and fast motion subsystems, i.e., to extract a quantity that includes all the molecules of the sample in the statistics, we calculated a function describing the microscopic mobility of the system in the form

\[
P(R, \theta) = \frac{\langle \sum_{i=1}^{N} \sum_{j=1}^{N} (d_i + d_j) \delta(R - R_{ij}) \delta(\theta - \theta_{ij}) \rangle}{2 \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(R - R_{ij}) \delta(\theta - \theta_{ij})}.
\]  

(3)

The symbols in Eq. (3) have the usual meaning, and \(d_i\) is an approximation to the translational self-diffusion coefficient of the \(i\)th molecule, calculated according to the Einstein formula\(^\text{17}\)

\[
d_i = \frac{1}{6t_{\text{max}}} \sum_{j=1}^{N} \langle |R_i(t_{\text{max}}) - R_i(0)|^2 \rangle,
\]  

(4)

where \(t_{\text{max}}\) is the total simulation time. The \(P(R, \theta)\) function is shown in Fig. 6 for the 210 and 300 K MD simulations.

Large values of the \(P(R, \theta)\) function, for one given \((R, \theta)\) point, mean fast translational motion for the molecules which contribute to that point. At 300 K a noisy unstructured shape of \(P(R, \theta)\) is observed, indicating that no preferential structural–dynamical correlation is present at that temperature. On the contrary, clear evidence of dynamical heterogeneities is found in the low temperature plot. The freezing of the translational motions corresponding to the C and D regions of Fig. 1 is well evident in this case.

In the past, interesting studies based on MD simulations and on the inherent structure approach were carried out by Sciortino et al.\(^\text{41,42}\) to elucidate the relation existing between mobility and structure in water. The authors found that, by lowering the density, water exhibits an increase of the four-coordinated molecules at the expenses of the more-coordinated ones. In addition, they observed a lower mobility for the four-coordinated than for the five-coordinated molecules. This behavior, not usual for liquids, was in general attributed to the lower binding energy of the five-
coordinated molecules, but interestingly the authors found that five-coordinated molecules have a faster diffusion even when binding energy is strong. Apparently, this result does not agree with our findings, as we find that strong pair binding energy between r-toluidine molecules can be related to slow diffusion of them. In our opinion, such a disagreement could be attributed to the fact that Sciortino and co-workers did not include the contribution to the (de)stabilization energy between r-toluidine molecules can be related to the fast diffusion of them. In our opinion, such a disagreement could be attributed to the fact that Sciortino and co-workers did not include the contribution to the (de)stabilization energy between m-toluidine molecules can be related to five-coordinated H-bonded molecules. However, to validate this hypothesis, additional computational investigations would be necessary.

IV. CONCLUSIONS

The idea that at low enough temperature the dynamics of a (supercooled) liquid is essentially determined by the structure of the potential energy landscape (the inherent structures) goes back more than 30 years to the work of Goldstein. This approach has been recently confirmed by a MD computer simulation of a model glass-former, along the same line, the explanation of the dynamical heterogeneities in supercooled liquids in terms of the properties of the potential energy landscape has been demonstrated for a model system consisting of Lennard-Jones particles. We believe that our MD simulation provides clear evidence of such a strong correlation between dynamical and structural properties in a real system like supercooled r-toluidine. The main structural features of the deep valleys appearing in the free energy landscape of this molecular liquid in the supercooled regime have been identified from the calculation, and shown to be determined by the formation H-bonded molecular pairs with a well-defined conformation. The formation of energetically stable H-bonded molecular pairs causes a sharp decrease of the molecular mobility in those deep minima, where the concerted motion of the H-bonded pairs become more and more hindered. This is the source of the dynamical heterogeneities that are responsible for the strongly nonexponential structural relaxation observed in m-toluidine over a broad temperature range.

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38 In Ref. 25, the self-diffusion coefficient at 300 K, namely $2.3 \times 10^{-5}$ cm$^2$ s$^{-1}$, was wrongly reported.