PHYSICAL REVIEW E VOLUME 55, NUMBER 2 FEBRUARY 1997

Role of orientation in the structure and dynamics of a supercooled molecular liquid

W. J. Ma[1] and S. K. Lai[1,2]
[1]Department of Physics, National Central University, Chung-li 320, Taiwan, Republic of China
[2]Department of Applied Physics, Royal Melbourne Institute of Technology, Melbourne, Victoria 3001, Australia

(Received 21 August 1996)

We performed molecular-dynamics simulation on the pair correlation function, mean-square displacement, and self-part intermediate scattering function for supercooled liquid nitrogen dimers. Our simulation data showed that for the latter the orientational degree of freedom, if identified as a form of structural impediment, has the consequence of making more robust the structural arrest at decreasing temperature. This conclusion is consistent with the magnitude of the λ parameter determined in conjunction with the idealized mode-coupling theory for the description of the dynamics of β relaxation. [S1063-651X(97)08702-3]

PACS number(s): 61.20.Ja, 61.20.Lc, 64.70.Pf, 61.25.Em

Considerable effort has been devoted in recent years to the study of supercooled liquids. This upsurge interest can be traced to the tremendous progress in experimental techniques and, concurrently, to the rapid development of the mode-coupling theory (MCT) [1]. The present work is a study of the dynamics of supercooled molecular liquids by molecular-dynamics (MD) simulation in an attempt to contribute to a better understanding of the connection between the dynamic properties of supercooled states in a realistic system and the predictions of the MCT. The liquid nitrogen dimers were specifically chosen for this purpose since this system represents the simplest molecular liquid that possesses both the translation and orientation which are basic features of many fragile glass formers. We investigate, in particular, the role of molecular orientation in the liquid dimers by analyzing the static and dynamic data on the pair correlation function, mean-square displacement, and self-intermediate scattering function. It is demonstrated here that, at a decreasing temperature, (i) the relative importance of the orientation to translation can be differentiated at a temperature T_0 which we identify as the Wendt-Abraham-type transition point [2] and (ii) the orientational degree of freedom has the effect of enhancing the structural arrest. Our simulation data may bring to light some of the questions of relevance to the MCT. For instance, the question of the applicability of the MCT has attracted much attention in the literature. Currently this question of the usefulness of the MCT to real glass formers comes from measured dynamic data [1,3]. These experiments confirmed the existence of a dynamical transition singularity T_c above the calorimetric glass transition point. They deduced this by fitting at T_c an appropriate mode-coupling parameter λ (see below) which yields, within the MCT, the temporal evolution of the density-density correlation function. Such an empirical approach to λ is, however, questionable given that the experimental conditions and measured physical systems are generally far more complicated and often obscure the underlying physics. We have in this work utilized the MD static fluid structures for the molecular centers to calculate λ. We find that the magnitude of λ is consistent with the MD dynamic data showing the slow-down relaxation.

In our MD simulation, we consider 500 nitrogen molecules in a cubic cell. Each molecule is modeled by a rigid dumbbell [4] which consists of two sites joined by a bond of length equal to 0.329σ, σ being the core diameter for each site. The interaction potential between pairs of atoms on different molecules is assumed to be the Lennard-Jones (LJ) potential with $\sigma=3.31$ Å and $\varepsilon/k_B=37.2$ K. (From here on we use reduced units σ, ε/k_B, $\sqrt{m\sigma^2/2\varepsilon}$, and ε/σ^3 for distance, temperature, time, and pressure, respectively.) In the present simulation we have employed the extended system method for the NPH ensemble [5] (constant number of particles, pressure, and enthalpy) where the volume of the system is treated as a dynamic variable which is coupled to an external mass so as to constrain the pressure to balance at the chosen value. An advantage of this method is that the volume of the system can be allowed to fluctuate around its equilibrium value and, hence, reduce any possible artifact of nucleation induced by the periodic boundary condition. The equations of motion were integrated by Gear's algorithm for the translational variable as well as for the orientational variable which would include the angular momenta and the transformation quaternions between the space and body frames [5].

The system of fluid dimers was quenched stepwise at $P=3.7$. Between two consecutive stages the temperature difference ΔT was tested for the range $0.025<\Delta T<0.1$. It turns out that the results were insensitive to any of this range of ΔT. A typical time interval for each stage was 80 (time) units equivalent to 4×10^4 steps in our simulation. For this case, the temperature of the system was forced to a new value over the first 10^4 steps and then relaxed for another 10^4 steps. The data of static structures were collected over the last 2×10^4 steps of this stage. This information was used to locate the region of transformation.

Figures 1(a) and 1(b) display the pair correlation functions $g(r)$ for molecular centers $g_m(r)$ and atomic sites $g_a(r)$. For the $g_m(r)$ we observe a two-stage changes at the first maximum position $r_{\max}$ of $g_m(r)$, i.e., we notice in the temperature range $1.77>T>0.8$ that $g_m(r_{\max})$ increases gradually in height, signaling the slow-down translational motion of the molecules, and for $T<0.8$, $g_m(r_{\max})$ remains virtually unchanged but the left-hand side of $g_m(r_{\max})$ develops into a well-defined shoulder. For the $g_a(r)$, on the other hand, we find at the first maximum position $r'_{\max}$ of $g_a(r)$ the $g_a(r'_{\max})$ exhibits the typical enhanced T-shape arrangement,

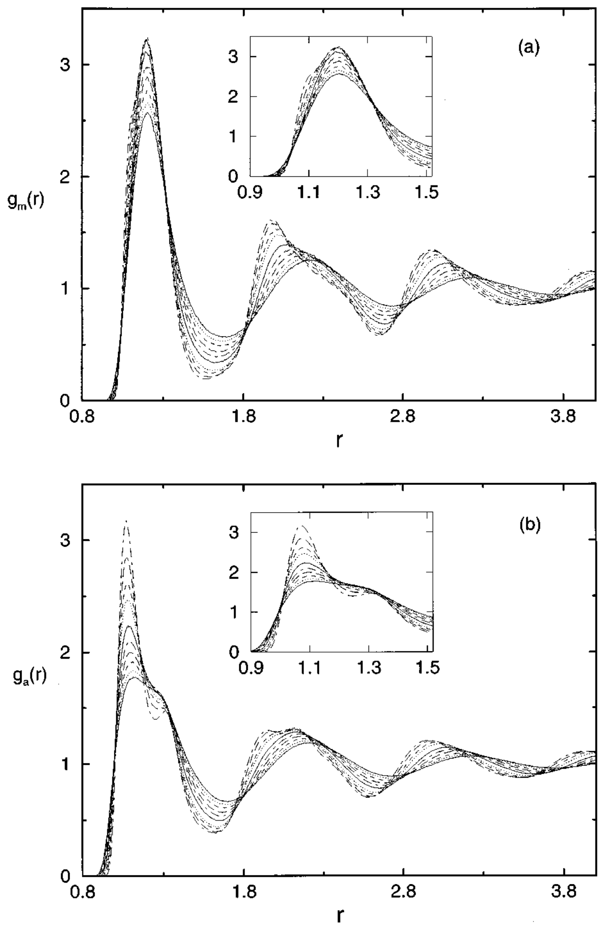

FIG. 1. The pair correlation function (a) $g_m(r)$ for molecular centers and (b) $g_a(r)$ for atomic sites at $T=0.35$ (top, short-long dashed curve), 0.48 (long-dashed curve), 0.60 (dashed curve), 0.71 (dotted curve), 0.93 (full curve), 1.11 (short-long dashed curve), 1.26 (long-dashed curve), 1.44 (dashed curve), 1.61 (dotted curve), and 1.77 (full curve, bottom). The insets show the changes of $g(r)$ around the first maxima.

as commonly seen in a dense liquid of linear molecules [6] and, beginning also at $T \approx 0.8$, changes progressively from the shoulderlike wobbling characteristics to a more solidlike structure at a lower T (<0.8). To explain the $g_m(r)$ feature we recall that our diatomic molecules possess both the translational and the orientational degree of freedom. When the temperature is high or at a lower density, the thermal agitation of molecules would result in the translational motion (like many systems with spherical symmetries) superimposed by the orientational motion due to asymmetries of molecules. In this temperature regime the molecular motion already displays some kind of an average preferred orientation which is seen as a T-shape intermolecular arrangement. Indeed such a behavior is seen more clearly in Fig. 1(b) for the temperature dependence of $g_a(r)$ where, there, we notice the atom-atom correlations thermally oriented to occupy preferred sites. This combined motion of translation and of T-shape orientation between molecules persists with decreasing temperature until at $T<0.8$, where the nearly constant magnitude and the simultaneous growth of the left-hand shoulder of $g_m(r_{\rm max})$ signify, respectively, the frozen in of the translational center-of-mass motion and the more probable overlapping between the T-shape neighboring molecules leading in this case to a ''+''-shape configuration. This picture of the $g_m(r)$ at $T<0.8$ stresses the role of molecular rotations and implies physically that the orientational degree of freedom has manifestly dominated over the entropy contribution in the distribution of molecules. To further exploit, we depict in Fig. 2 the ratio $\mathcal{I}=g_a(r'_{\rm max})/g_m(r_{\rm max})$ versus T which describes qualitatively the relative weight of the orientational to the translational motion. It is found that there exists a T_0 that differentiates the two apparently different regimes of motion discussed above. That is, when linear extrapolating the low and high temperature regimes we obtain a transition temperature $T_0 \approx 0.8$ at the interception. It is approximately the same temperature at which the $g_m(r_{\rm max})$ and $g_a(r'_{\rm max})$ signal the crossover (Fig. 2), as does the mean-square displacement of the molecular centers delineated in Fig. 3, which shows the gradual development of slow dynamics. Taking into account of all these features, we identify this T_0 as the Wendt-Abraham-type liquid-glass transition temperature [2], for the latter has been recognized to play the role of the calorimetric glass-transition temperature.

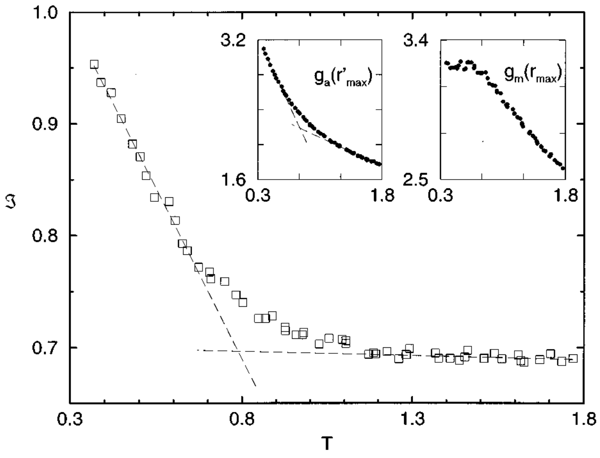

FIG. 2. The ratio of the first peaks $\mathcal{I}=g_a(r'_{\rm max})/g_m(r_{\rm max})$, giving a measure of the relative importance of the orientational degree of freedom to translation, vs quenched temperature T. A well defined kink at $T_0 \approx 0.8$ can be seen. The insets show that the crossover can also be identified for the $g_a(r'_{\rm max})$ and $g_m(r_{\rm max})$. Note that $g_m(r_{\rm max})$ starts to level off around $T \lesssim T_0$.

To proceed further, we analyze the real-time self-intermediate scattering function $F^s(r,t)=\langle \delta(\vec{r}(t)-\vec{r}(0)-\vec{r})\rangle$ of our fluid dimers in the temperature range $0.7<T<1.1$. It is, however, more convenient to present the results in the space Fourier transformed $F^s(q,t)$, as depicted in Fig. 4. There are two main points that merit emphasis. The first point is that the supercooled liquid of diatomic molecules shows a more discernible slow-down relaxation feature and probably has undergone the fast β-relaxation process. This conclusion can be inferred (a) from the extensive simulation work by Lewis and Wahnström (see Fig. 5 in [7] and their analysis on the mode coupling T_c) and (b) by our MD simulation on the monatomic LJ liquid whose $F^s(q,t)$ decays rapidly even at a lower T [8]. The second point is that, for $T \lesssim 0.98$, our detailed examination of the tagged particle distribution function [9], $P^s(r,t)=4\pi r^2 F^s(r,t)$, reveals the trace of retarded and sluggish motion of molecules within the

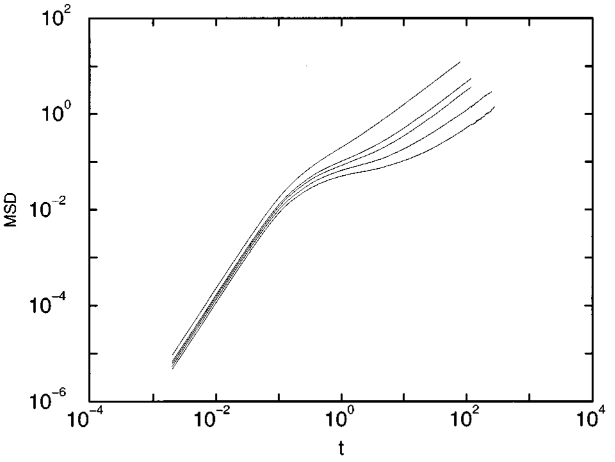

FIG. 3. The mean-square displacement (MSD) vs time plotted in log-log scale for the molecular centers of liquid dimers at $T=1.51$ (top), 1.14, 0.98, 0.90, and 0.77 (bottom).

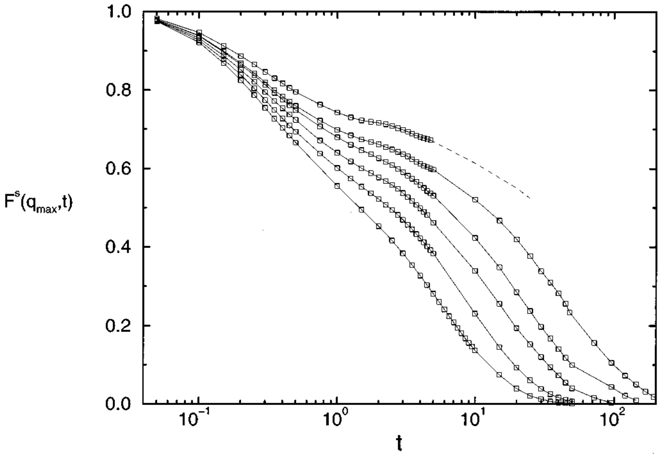

FIG. 4. The MD simulation data for the self-intermediate scattering function $F^s(q_{\max},t)$ vs the logarithm of time for molecular centers. The $q_{\max}=6.41$, 6.44, 6.45, 6.47, 6.50, and 6.52 correspond to the first maxima of $S(q)$ at $T=1.06$ (lower curve), 0.98, 0.91, 0.84, 0.80, and 0.71 (top curve), respectively. At $T=0.71$ the statistical error for $F^s(q_{\max},t)$ due to hopping mechanism becomes detectable at longer times, which we denote by the dashed line.

β-relaxation regime. In particular, we observe for $T<T_0$ that $P^s(r,t)$ displays a prolonged tail which is a signature for the rate of hopping events to become significant. In the extreme case when these collective hopping events happen the system would undergo a global change which will then lead to a catastrophic transition (dashed curve in Fig. 4).

Both the static and dynamic quantities presented above clearly exhibit the discernible role of orientation in liquid dimers. To delve further into the latter, we turn next to a discussion of its relevance to the MCT. For this purpose, a brief document of essential equations are in order. In the idealized MCT, one focuses on the nonlinear coupling of the density fluctuation $\delta\rho(\vec{q},t)$ through the normalized correlator $R(q,t)=\langle\delta\rho(\vec{q},t)\delta\rho(-\vec{q},0)\rangle/S(q)$, where $S(q)$ is the static liquid structure factor. Taking the Laplace transform of $R(q,t)$ which is defined by $\hat{R}(q,z)=i\int_0^\infty dt\,\exp(izt)R(q,t)$, $\hat{R}(q,z)$ is

$$\hat{R}(q,z)=-\frac{z+\hat{M}(q,z)}{z^2-q^2/\beta m S(q)+z\hat{M}(q,z)},\tag{1}$$

where $\hat{M}(q,z)$ is the generalized frictional term and $\beta=1/(k_BT)$ is the inverse temperature. In the long-time domain, we ignore the transient part of $M(q,t)$ and approximate $M(q,t)\approx\Lambda(q,t)$. $\Lambda(q,t)$ has been derived previously and is given explicitly in [10,2].

Given $S(q)$ the MCT predicts an ergodic-nonergodic transition. This would involve solving the nonlinear equation

$$\frac{f(q)}{1-f(q)}=\frac{\beta m S(q)}{q^2}\,\Lambda(q,t\to\infty)\equiv\mathcal{F}_q(f(k))\tag{2}$$

for the Debye-Waller factor $f(q)$, which is $f(q)=0$ for $T>T_c$ (ergodic states) and $f(q)=R(q,t\to\infty)\neq 0$ for $T\leqslant T_c$ (nonergodic states). It should be noted that, consistent with the mode-coupling approximation, the contribution from local anisotropy is averaged out for the metastable liquid states.

Now, according to MCT, near the dynamic transition point T_c and within the mesoscopic time scale in the β-relaxation regime, $R(q,t)$ deviates from $f(q)$ and can be factorized into a product of the temporal and spatial parts. It can be shown [1] that near T_c the temporal behavior is a scaled master function determined solely by a material-dependent parameter λ given by

$$\lambda=\frac{1}{2}\sum_{q,k',k''}\hat{l}_q^c[1-f(k')]^2[\partial^2\mathcal{F}_q/\partial f(k')\partial f(k'')]_T\times[1-f(k'')]^2 l_{k'}^c l_{k''}^c,\tag{3}$$

where l_q^c (or $\hat{l}_q^c$) is the right-hand (or left-hand) eigenvector of the stability matrix $C_{qk}=[1-f(k)]^2\partial\mathcal{F}_q/\partial f(k)$.

We have applied the $S(q)$ obtained by Fourier transforming the above $g_m(r)$ at different T to determine the T_c for the liquid dimers. Solving Eq. (2) iteratively, we obtain $T_c=0.977$ and at this T_c we calculate the parameter λ using Eq. (3). We find that $\lambda=0.69$ whose magnitude is (a) smaller than any of the theoretically calculated λs (hard sphere: 0.772 [2]; LJ: 0.718 [8] and liquid metal: ~0.711 [2,11]) for the simple one-component systems and (b) significantly smaller than most of the experimentally fitted λs (~0.8). The magnitude of the λ value implies that, for the liquid dimers, the orientational degree of freedom has the effect of enhancing further the structural arrest process. We draw this implication from systematic studies of various model systems. It appears that with increasing ''complexity'' of physical systems: there is a tendency for decreasing λ. The word ''complexity'' for a physical system is here a general term; it can be the different type of interparticle interactions among the monatomic systems or, for a binary mixture, the disparity in sizes, the composition of components, etc. For example, a purely repulsive one-component hard-sphere potential has a $\lambda=0.772$ which changes (i) markedly to a $\lambda=0.718$ for the one-component LJ (having an additional weak attractive tail) and to a $\lambda\sim0.711$ for a pure liquid metal (having a much softer repulsive part embellished by a relatively stronger damped oscillatory attractive tail) and (ii) noticeably [12] to a λ=0.712 for the larger hard-sphere particles in a binary mixture. The ‘‘complexity’’ in the present diatomic molecules is of somewhat different nature arising also from the orientational degree of freedom. Such ‘‘complexity’’ is certainly far more effective spatially in hindering the molecular rearrangement than the mere interparticle interactions or size disparity of particles. Considering the fact that a smaller λ would make more robust the occurrence of the β-relaxation process [2,11], it is thus not without physical ground to believe that the molecular liquid has more structural impediment than the simple monatomic liquid. Our simulated dynamic data for $F^s(q,t)$ and the tagged particle distribution are consistent with the above features, although, their signature of the slow relaxation is still somewhat weak.

To summarize, we have found from our study of the supercooled liquid nitrogen dimers that the orientational degree of freedom during supercooling process plays a discernible role in the structural arrest. This cage effect mechanism which is stressed in MCT and has its origin in the structural ‘‘complexity’’ of the physical system is just what is needed for observing the β-relaxation process. It is probable that for more sophisticated laboratory systems such a mechanism is a major cause in the β-relaxation process. The aforementioned works of Kaneko and Bosse [12], Lewis and Wahnström [7], and Signorini, Barrat, and Klein [13] give much support to the argument addressed here.

We gratefully acknowledge the financial support (NSC84-2112-M008-003) by the National Science Council of Taiwan, ROC and the support of computing facilities by the National Center for High-Performance Computing. S.K.L. would like to thank Professor W. van Megen for hospitality at the Royal Melbourne Institute of Technology, Melbourne, Australia.

---

[1] W. Götze, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991), p. 287; W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).

[2] S. K. Lai and H. C. Chen, J. Phys. Condens. Matter **5**, 4325 (1993).

[3] H. Z. Cummins, G. Li, W. M. Du, J. Hernandez, and N. J. Tao, J. Phys. Condens. Matter **6**, A51 (1994); W. Van Megen and S. M. Underwood, *ibid.*, A181 (1994).

[4] W. J. Ma, L. K. Iyer, S. Vishveswara, J. Koplik, and J. R. Banavar, Phys. Rev. E **51**, 441 (1995).

[5] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).

[6] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986), Chap. 12; L. Lue and D. Blankschtein, J. Chem. Phys. **102**, 4203 (1995).

[7] L. J. Lewis and G. Wahnström, Phys. Rev. E **50**, 3865 (1994).

[8] W. J. Ma and S. K. Lai (unpublished).

[9] W. J. Ma and S. K. Lai (unpublished).

[10] L. Sjögren, Phys. Rev. A **22**, 2883 (1980); U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17**, 5915 (1984).

[11] S. K. Lai and H. C. Chen, J. Phys. Condens. Matter **7**, 1499 (1995).

[12] Y. Kaneko and J. Bosse, J. Non-Cryst. Solids (to be published); J. Bosse and Y. Kaneko, Phys. Rev. Lett. **74**, 4023 (1995) and private communication.

[13] G. Signorini, J. L. Barrat, and M. L. Klein, J. Chem. Phys. **92**, 1294 (1990).