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

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We performed molecular-dynamics simulations 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 $\lambda$ parameter determined in conjunction with the idealized mode-coupling theory for the description of the dynamics of $\beta$ relaxation. [S1063-651X(97)08702-3]

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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 has attracted much attention in the literature. Currently this question of the applicability of the MCT...
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 and, beginning also 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.

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FIG. 2. The ratio of the first peaks \( \mathcal{I} = \frac{g_a(r'_{\text{max}})}{g_m(r_{\text{max}})} \), 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 \( g_a(r'_{\text{max}}) \) and \( g_m(r_{\text{max}}) \). Note that \( g_m(r_{\text{max}}) \) starts to level off around \( T = T_0 \).

able 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 \( \mathcal{I} = \frac{g_a(r'_{\text{max}})}{g_m(r_{\text{max}})} \) 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 \( g_m(r_{\text{max}}) \) and \( g_a(r'_{\text{max}}) \) 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.

To proceed further, we analyze the real-time self-intermediate scattering function \( F^t(q,t) = \langle \delta(\vec{r}(t) - \vec{r}(0)) \rangle \) 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 \( F^t(q,t) \), 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 \( \beta \)-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 \( F^t(q,t) \) decays rapidly even at a lower \( T \) [8]. The second point is that, for \( T \leq 0.98 \), our detailed examination of the tagged particle distribution function \( F^t(r,t) = 4\pi r^2 F^t(r,t) \), reveals the trace of retarded and sluggish motion of molecules within the
\[ R_{\text{static liquid structure factor}}. \]

\[ \text{Taking the Laplace transform of} \]

\[ R_{\hat{catastrophic transition}} \]

\[ \text{case when these collective hopping events happen the system} \]

\[ \text{would undergo a global change which will then lead to a} \]

\[ \text{catastrophic transition (dashed curve in Fig. 4).} \]

\[ \text{Both the static and dynamic quantities presented above} \]

\[ \text{clearly exhibit the discernible role of orientation in liquid} \]

\[ \text{dimers. To delve further into the latter, we turn next to a} \]

\[ \text{discussion of its relevance to the MCT. For this purpose, a} \]

\[ \text{brief document of essential equations are in order. In the} \]

\[ \text{idealized MCT, one focuses on the nonlinear coupling of the} \]

\[ \text{density fluctuation } \delta \rho(q,t) \text{ through the normalized correlator} \]

\[ R(q,t) = \langle \delta \rho(q,t) \delta \rho(-q,0) \rangle / S(q), \text{where } S(q) \text{ is the} \]

\[ \text{static liquid structure factor. Taking the Laplace transform of} \]

\[ R(q,t) \text{ which is defined by} \]

\[ R(q,z) = i \int_0^\infty dt \exp(izt)R(q,t), \]

\[ \tilde{R}(q,z) \text{ is} \]

\[ \tilde{R}(q,z) = \frac{z + \hat{M}(q,z)}{z^2 - q^2/\beta mS(q) + \hat{z}^2M(q,z)}, \]  

\[ \text{where } \hat{M}(q,z) \text{ is the generalized frictional term and} \]

\[ \beta = 1/(k_B T) \text{ is the inverse temperature. In the long-time} \]

\[ \text{domain, we ignore the transient part of } M(q,t) \text{ and approximate} \]

\[ M(q,t) = \Lambda(q,t). \]

\[ \Lambda(q,t) \text{ has been derived previously and is given explicitly in} \]

\[ \text{[10,2].} \]

\[ \text{Given } S(q) \text{ the MCT predicts an ergodic-nonergodic transition. This would involve solving the nonlinear equation} \]

\[ \frac{f(q)}{1 - f(q)} = \frac{\beta mS(q)}{q^2} \Lambda(q, t \to \infty) = F_q(f(k)) \]  

\[ \text{for the Debye-Waller factor } f(q), \text{ which is } f(q) = 0 \text{ for} \]

\[ T > T_c \text{ (ergodic states) and } f(q) = R(q, t \to \infty) \neq 0 \text{ for } T \leq T_c \]

\[ \text{ (nonergodic states). It should be noted that, consistent with} \]

\[ \text{the mode-coupling approximation, the contribution from local} \]

\[ \text{anisotropy is averaged out for the metastable liquid states.} \]

\[ \text{Now, according to MCT, near the dynamic transition point} \]

\[ \text{T}_c \text{ and within the mesoscopic time scale in the} \]

\[ \text{\beta-relaxation regime, } R(q,t) \text{ deviates from } f(q) \text{ and can be} \]

\[ \text{factorized into a product of the temporal and spatial parts. It can} \]

\[ \text{be shown [1] that near } T_c \text{ the temporal behavior is a} \]

\[ \text{scaled master function determined solely by a material-} \]

\[ \text{dependent parameter } \lambda \text{ given by} \]

\[ \lambda = \frac{1}{2} \sum_{q,k} l^+ [1 - f(k')] [\partial^2 F_q / \partial f(k') \partial f(k'')] T \]

\[ \times [1 - f(k'')]^2 l^+ l^-. \]  

\[ \text{where } l^+ (\text{or } l^-) \text{ is the right-hand (or left-hand) eigenvector of the} \]

\[ \text{stability matrix } C \rho - [1 - f(k)]^2 \partial F_q / \partial f(k). \]

\[ \text{We have applied the } S(q) \text{ obtained by Fourier transforming the} \]

\[ \text{above } g_m(r) \text{ at different } T \text{ to determine the } T_c \text{ for the} \]

\[ \text{liquid dimers. Solving Eq. (2) iteratively, we obtain} \]

\[ T_c = 0.977 \text{ and at this } T_c \text{ we calculate the parameter } \lambda \text{ using} \]

\[ \text{Eq. (3). We find that } \lambda = 0.69 \text{ whose magnitude is} \]

\[ \text{(a) smaller than any of the theoretically calculated } \lambda_s \text{ (hard sphere: 0.772 [2]; LJ: 0.718 [8] and liquid metal: ~0.711 [2,11])} \]

\[ \text{for the simple one-component systems and (b) significantly} \]

\[ \text{smaller than most of the experimentally fitted } \lambda_s \text{ (~0.8).} \]

\[ \text{The magnitude of the } \lambda \text{ value implies that, for the liquid} \]

\[ \text{dimers, the orientational degree of freedom has the effect of} \]

\[ \text{enhancing further the structural arrest process. We draw this} \]

\[ \text{implication from systematic studies of various model systems. It appears that with increasing} \]

\[ \text{ complexity } \text{of physical} \]

\[ \text{systems: there is a tendency for decreasing } \lambda. \text{ The word} \]

\[ \text{complexity } \text{for a physical system is here a general term; it can} \]

\[ \text{be the different type of interparticle interactions among} \]

\[ \text{the monatomic systems or, for a binary mixture, the disparity} \]

\[ \text{in sizes, the composition of components, etc. For example, a} \]

\[ \text{purely repulsive one-component hard-sphere potential has a} \]

\[ \lambda = 0.772 \text{ which changes (i) markedly to a } \lambda = 0.718 \text{ for the} \]

\[ \text{one-component LJ (having an additional weak attractive tail) and} \]

\[ \text{to a } \lambda - 0.711 \text{ for a pure liquid metal (having a much} \]

\[ \text{softer repulsive part embellished by a relatively stronger} \]

\[ \text{damped oscillatory attractive tail) and (ii) noticeably [12] to} \]

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a $\lambda = 0.712$ 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 $\lambda$ would make more robust the occurrence of the $\beta$-relaxation process \cite{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 $F^{\gamma}(q,t)$ 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 $\beta$-relaxation process. It is probable that for more sophisticated laboratory systems such a mechanism is a major cause in the $\beta$-relaxation process. The aforementioned works of Kaneko and Bosse \cite{12}, Lewis and Wahnström \cite{7}, and Signorini, Barrat, and Klein \cite{13} give much support to the argument addressed here.

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