

## Observation of a Long-Lived Frozen State in the Supercooled Liquid Dimers

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We applied the molecular dynamics simulation to a system of supercooled liquid dimers and studied the effect of geometric structure on the metastable states. Within the supercooled liquid that extends down to glassy regime, we found one metastable liquid branch which transforms to glassy behavior at low temperatures and a branch of frozen amorphous states which evolve from the preceding metastable liquids and manifest by better packings. Our static and dynamic data for the frozen amorphous states illuminate the geometric frustration in fluid dimers which has led to a new type of building blocks for disordered states inaccessible for a system of monatomic spherical molecules.

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PACS. 61.25.Em – Molecular liquids.

The theoretical explanation of phenomena pertinent to the undercooled metastable states is currently an unsolved issue [2, 3] which has continued to be impacted by new experiments. One such phenomenon concerns the nature of transformation processes occurring in the supercooled liquid and extending down to the glassy region for a fast quenched system. While these transformation processes are characterized, on the one hand, by dynamic behavior at various time scales, it is conjectured, on the other hand, by some underlying thermodynamic transitions which are believed to be responsible for the many properties observed in the transformation. Thus, it has been suggested looking at the energy barrier which has its origin in the conflict between the preferred local ordering and the space-filling configuration for studying the metastability of the supercooled liquid state against decaying to the equilibrium ordered state [4]. The existence of such a geometric frustration is evidenced from computer simulations on the supercooled monatomic systems [4] and its effect, however, has been connected to the formation of domains whose kinetics of rearrangement has long been proposed for understanding the liquid-glass transition phenomenon [5, 6, 7]. Nevertheless there is still insufficient information to confirm unambiguously of its existence and the exact nature of such domains remains an open issue. Accordingly it is generally difficult to interpret various features of the laboratory molecular glass-formers beyond a qualitative description. In this respect an investigation of the role of geometric frustration exhibited by molecular systems in supercooled states is of great value.

In this work we apply the molecular-dynamics (MD) simulation to a system of supercooled liquid dimers. We examine specifically the molecular orientational degree of freedom, since such geometric asymmetry will lead to a kind of geometric frustration which is different from that in monatomic molecules and has the consequence of making robust the metastability of supercooled states [8]. The main theme of this work is, therefore, to exploit the effect of the simplest geometric asymmetry on undercooled metastable states. Beginning in the supercooled liquid and extending down into glassy region? we show, in particular, that there exist two metastable branches; one is the metastable equilibrium liquid which transforms to glassy behavior at low temperatures and the other is a long-lived frozen amorphous state which evolves from the preceding metastable liquid and manifests by a better packing.

In our MD simulation we used 500 dimers each with a bond length of  $0.329\sigma$ . Specifically we consider the nitrogen molecule and set  $\epsilon/k_B = 37.2K$  and  $\sigma = 3.31 \text{ \AA}$  which are parameters for the Lennard-Jones potential between pairs of sites on different molecules:  $V_{L-J} = 4\epsilon[(r/\sigma)^{-12} - (r/\sigma)^{-6}]$ . (Henceforth we used reduced units:  $\sigma, \epsilon/k_B, \sqrt{m\sigma^2/2\epsilon}$ , and  $\epsilon/\sigma^3$  for distance, temperature, time and pressure respectively). In this work we applied an NPH ensemble [9] and the equations of motion were integrated by the Gear's predictor-corrector algorithm. Also, the effect of finite size was examined by performing additional simulations for (i) 1372 molecules under the same simulation conditions and (ii) 500 molecules at selected temperatures but in a cell of *parallelepiped*. In both cases we found negligible effect for static quantities [10].

The quenching process was carried out stepwisely at  $P = 3.7$  by lowering the instant temperature for  $\Delta T = 0.025$  and by invoking the velocity rescaling method for a period of  $20\tau$ . Then, the system was allowed to evolve at constant pressure for the rest of the stage. To ensure that our system has passed the transient period and reached a steady state, the temperature, density  $\rho$ , enthalpy and pair correlation function were collected for the metastable states after a second period of  $20\tau$ . Two criteria were used for assessing the metastability of our system. The first criterion resorted to the stability checking by monitoring the temperature and density as functions of time and by examining the density and enthalpy as functions of temperature. Independent of the quenching rate and of the size (see Fig. 1), both the density and enthalpy vary rather smoothly with temperature beginning at the equilibrium liquid and extending down to glassy regime. All these results clearly substantiate the genuine metastability of our system.

The second criterion concerned the long time behavior following the final configuration of each stage which should be prolonged freely under the NPH constraint [10,11]. The dynamic correlation data were collected over these extended periods. For  $T \lesssim 1.1$ , our simulation for 500 dimers showed that the metastable state has undergone an activation process with the system evolving into a more stable frozen disordered state. This can be judged from Fig. 1 showing an increase in density despite the fact that there is a slight increase in the instant temperature accompanied by heat-releasing. Physically this phase-transition-like phenomenon is reminiscent of the nucleation process which would approach crystallization for a monatomic Lennard-Jones system [12], but here it leads to a better packing arrangement. Although this peculiar feature may be partly enhanced by the finite size effect [13], we, nevertheless, did not observe any further decay of the frozen state even for subsequent prolongation till approximately  $8000\tau$  [14] (the longest time in our

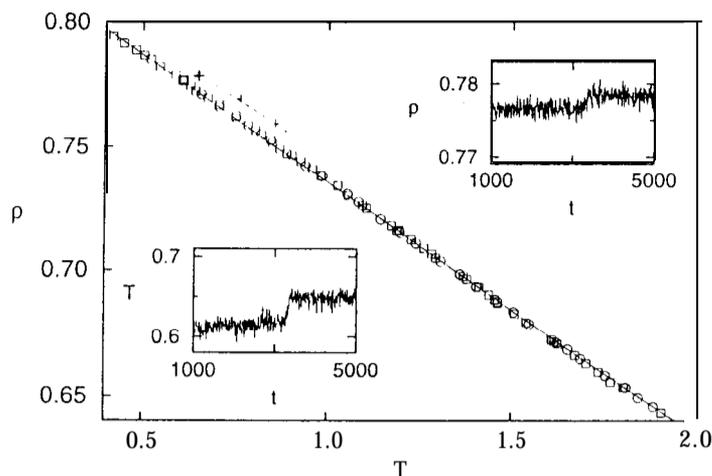


FIG.1. The density  $\rho$  versus temperature  $T$  for metastable fluid dimers at  $P = 3.7$ . The solid curve is the metastable liquid quadratically fitted to squares (500 molecules) and circles (1372 molecules). The thick square is a metastable liquid which evolves into the thick plus, one of the frozen states (dashed line); the inserts show the increase in  $\rho$  (top-right) and  $T$  (bottom-left) with time during this phase-like transition process.

simulation).

To delve deeply into the nature of the two branches of metastable states, let us examine the translational motion of molecules near a rough dividing temperature  $T_o \approx 0.8$  which differentiates the supercooled-liquid and glassy regions by use of the temperature dependence of the structure data [15,11]. Fig. 2(a) shows the diatomic molecules in the metastable liquid state at  $T = 0.84$ . One sees immediately that the motion of molecules is basically diffusive spatially described by temporary local cages and temporally characterized by regions crowded with trajectory segments. Upon lowering the temperature to  $T = 0.72$ , depicted in the same figure, the extent for each cage becomes more compact owing to the fact that each molecule spends a longer time staying within it. To gain further insight into the dynamics, we analyse the diffusion constant for the same metastable liquid branch by fitting the MD results to the power law:  $D(T) = D_1(T - T_1)^\gamma$  and to the Vogel-Fulcher law:  $D(T) = D_0 e^{A/(T_{VF} - T)}$ . We obtained  $D_0 = 3.1, A = 4.2, D_1 = 0.23, \gamma = 1.67, T_1 = 0.74 \pm 0.08$  and  $T_{VF} \approx 0.14$ . Our analysis of  $D(T)$  data indicate that (a) the power law describes very well the supercooled liquid region above the crossover temperature  $T_o$  and (b) the Vogel-Fulcher law always results in a significantly small  $T_{VF}$ . Such temperature variations agree with our common understanding of viscous properties in the transition of supercooled liquid to glassy state as observed for real glass-former.

In contrast, the dimers in frozen states, delineated in Fig. 2(b), are localized in positions and move by contiguous jumping. Such concerted jumping behavior can be visualized more closely by scrutinizing the time evolution of the tagged particle distribution function, being the probability density to find a marked dimer at time  $t$  at a distance  $r$  if it was located precedingly at the origin  $\vec{r} = 0$  at time  $t = 0$ ; the latter in the metastable branch

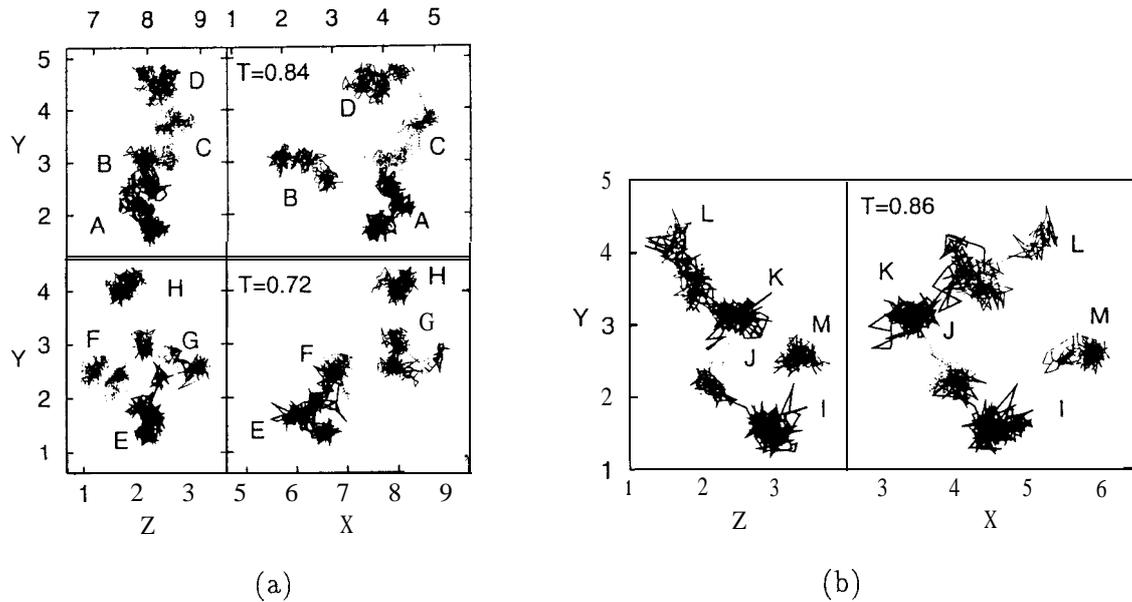


FIG. 2. Projection of trajectories on the  $y-z$  (left) and  $y-x$  (right) planes for selected molecules in (a) metastable liquid states at  $T=0.84$  and  $T=0.72$ , and (b) the frozen state at  $T=0.86$ . Note that in the frozen state (b) the molecules move by cooperative jumping. For example, in a frozen background (see molecule M), molecules  $I, J$  and  $K$  are replaced respectively by their neighbors  $J, K$  and  $L$  after hopping simultaneously.

decays and exhibits a more or less diffusive behavior for  $T$  varying across  $T_0$ , whereas in the frozen state branch it distinguishes itself by the appearance of a second packet at the falling edge of the main packet [10]. This prompts us to inquire: What is the origin for the occurrence of this long-lived frozen state? To answer this question let us recall some recent models. It was pointed out and examined by several authors [4,5,7] that the frustration between the favored short-range icosahedral ordering and the space-filling crystalline configuration was plausible cause for the metastability of glassy states prevailed among monatomic systems. At the same time there was argument advanced that stresses the formation of ordered domains whose kinetics of rearrangement was attributed to energy barriers which arise from geometric frustrations [5,6,7]. To correlate the significance of our simulated frozen states with the models, we, however, digress to advocate a more general point of view. We notice from our careful studies of these models that all simple glass-forming liquids, in reality, exist in a form of *mixtures*, such as a single species liquid contaminated by impurities, or more generally, a multicomponent system with complex geometric bondings, etc. Under different conditions, one can view the presence of any extra degree of frustration as a probable cause for affecting the real glass forming state. Thus, the very fact of an individual dimer in possession of orientation has led to a geometric frustration whose geometric origin would plausibly result in some kind of a phase-transition-like transformation between metastable states, a feature which is absent in a system of

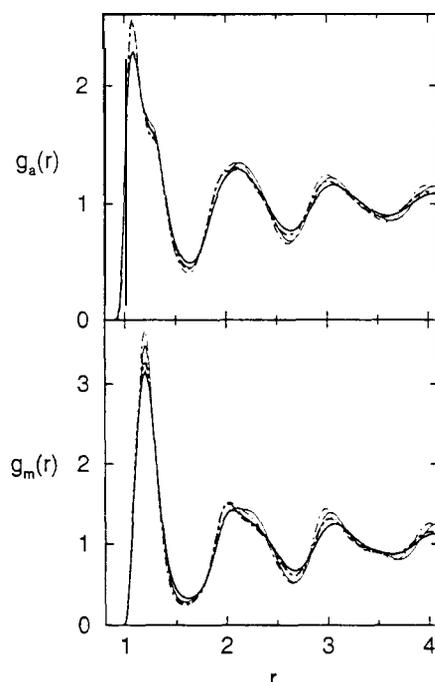


FIG. 3. The pair correlation functions for atomic sites  $g_a(r)$  (top) and molecular centers  $g_m(r)$  (bottom). The metastable liquids at  $T = 0.87$  (thick solid curve) and  $0.64$  (thick short-long dashed curve) are compared with frozen states at  $T = 0.86$  (thin solid curve) and  $0.65$  (thin short-long dashed curve).

monatomic molecules. Indeed, this presumption of frustration for any glass-forming liquid is corroborated by some of the observed phenomena [5] which necessitate the introduction of an underlying critical transition point in order to explain the transformation scenarios. In addition there are the laboratory glass-forming materials [16] that show too in the supercooled region the presence of a metastable amorphous phase, which is more stable than the liquid-like glassy state. This so-called "glacial" phase has many characteristic properties bearing close resemblance to the static and dynamic data of our dimers.

We now move on to discuss the relevance of the frozen state to the formation of domains and its kinetics of rearrangement, since currently there is still no conclusive evidence heralding of its universal existence. In Fig. 3 we give the pair correlation function  $g_a(r)$  for atomic sites at different temperatures. At a given temperature we notice the first peaks of  $g_a(r)$  virtually identical for the metastable liquid and frozen state despite their *difference in densities*, and beyond the first shell, the frozen state has an enhanced correlation. In contrast, as illustrated in the same figure, no such local correlations are observed for the molecular centers  $g_m(r)$ , although the frozen states persist to show stronger oscillations at longer ranges. The scenarios for  $g_a(r)$  and  $g_m(r)$  reveal the fact that the conflict between the preferred local ordering and the optimal space-filling configuration does play a key role

in stabilizing the supercooled states [3]. However, the lack of longer range correlation for  $g_a(r)$  suggests a different type of new building blocks [17] for disordered states which are inaccessible for a system of monatomic spherical molecules. The several features reported here for fluid dimers bring to light the possibility of probing this domains-like formation scenario in connection with liquid-glass phenomena. It would be an interesting endeavour if more complex systems (than the fluid dimers) can be studied to support or refute the conclusion made here.

In summary, a new branch of long-lived frozen states was found in our MD simulation for fluid dimers. While these frozen states have many features similar to some newly measured glass-forming liquids, we judge that the frozen states obtained are characterized by a new type of building blocks. The question of the role of new geometric frustration and its possible influences from impurities will surely deserve further attention. Such studies are useful and imperative for a thorough understanding of the kinetics of domains rearrangement in the liquid-glass transition phenomena.

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