

## Glass formation in a simple monatomic liquid with icosahedral inherent local order

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In this Rapid Communication simple monatomic liquid, possessing the distinctive icosahedral inherent local order, is reported. It has been generated by a special form of pair potential employed in a molecular dynamics system of 16384 particles, and remained stable within a wide range of temperatures explored. Pronounced stability of this model with respect to crystalline nucleation has been tested in a very long run under supercooling which was found to enhance its icosahedral inherent structure. The inherent structure factor exhibits an anomalous long-wavelength maximum which is interpreted as being indicative of the tendency for icosahedral clustering.

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Understanding the structural aspects of the glass formation in simple systems remains a formidable problem for the statistical theory of liquids. The mode-coupling approach [1], which proved to be successful in interpreting the basic dynamical phenomena in the supercooled liquid domain, postulates the system to be in thermodynamical equilibrium; so, the phenomenon of structural stability of glass-forming liquids under supercooling is still beyond the scope of the kinetic theory of liquid state, in its present form. Thus, the molecular-dynamics (MD) simulation remains a unique tool for investigating the underlying mechanisms of that phenomenon, on the atomic level.

Configurational evolution of a condensed system of simple constitution may be conveniently discussed in the terms of topography of the relevant area of its potential energy hypersurface [2,3]. The latter can be probed by the steepest descent minimization which maps its points onto the nearest local energy minima representing stable packing configurations [2,4]. These configurations statistically determine the so-called inherent structure which was found to be state independent, within a single liquid-phase domain [2]. Structural relaxation in a supercooled liquid, dominated by configuration-controlled activation processes, may be decomposed in a set of transitions between the topologically connected energy minima. Therefore, topology of inherent local order controls access to the configurational space areas which correspond to crystalline nucleation.

In a simple liquid composed of identical particles, variation of the pair potential produce a discrete set of well-defined prototypes of inherent local order [4-6]. Each of those prototypes which have been found until now appeared to be a distorted version of the crystallographic pattern into which the corresponding liquid is known to freeze. Consistent with this observation, those systems exhibit pronounced structural instability, when supercooled.

Icosahedral arrangement of the first coordination shell is the only conceivable noncrystallographic pattern of local order in a stable packed configuration. Recent studies revealed that this type of local order plays a crucial role in the glass formation in the simple systems [7-10]. The inherent structure of metallic glass formers was, indeed, found to be accounted for by the icosahedral polytope

{3,3,5} [8-10]. However, those systems are multicomponent, and formation of their structures involves the chemical short-range ordering [7]. An issue of profound interest is whether or not the structure in question might be formed by a simple liquid composed of identical particles. The study reported in this paper demonstrates that a stable liquid phase possessing distinctive icosahedral inherent local order can be generated by a pair potential utilized in a one-component MD model. This pair potential is introduced by the following form:

$$\begin{aligned}
 V &= V_1 + V_2, \\
 V_1 &= A(r^{-m} - B) \exp\left\{\frac{c}{r-a}\right\}, \quad r < a, \\
 V_1 &= 0, \quad r \geq a, \\
 V_2 &= B \exp\left\{\frac{d}{r-b}\right\}, \quad r < b, \\
 V_2 &= 0, \quad r \geq b.
 \end{aligned} \tag{1}$$

The parameters listed in Table I have been chosen to construct the potential shown in Fig. 1. At short distances, up to the main minimum, the potential approximates the Lennard-Jones one. The minimum is followed by a maximum, which is located within the interval of distances bound by the first and the second shells of neighbors in the icosahedral polytope [9,10]. At the same time, the maximum covers a range of coordination distances characteristic of crystallographic local order [4-6]. Thus, the described potential is expected to encourage formation of icosahedral local order by suppressing competing crystallographic configurations.

This potential was tried in a standard constant-density MD simulation. The latter was carried out in reduced units: the units of length and energy follow from the

TABLE I. Parameters of the pair potential.

$m$	$A$	$c$	$a$	$B$	$d$	$b$
16	5.82	1.1	1.87	1.28	0.27	1.94

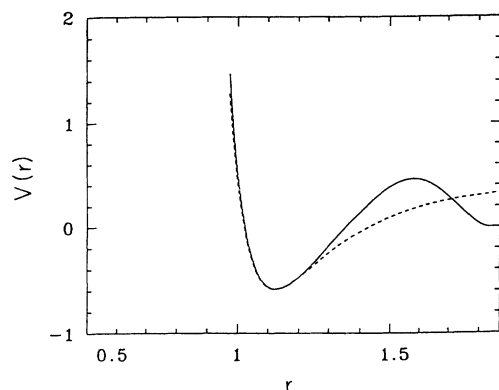


FIG. 1. Solid line, pair potential given by Eq. (1). For comparison, the Lennard-Jones potential, added with a constant, is shown by the dashed curve.

definition (1), and the unity particle mass was assumed. In these units, the integration time step was 0.01. The system was simulated at the constant density  $\rho^* = 0.88$ . Two temperatures were investigated:  $T^* = 1.6$ , where the system is a normal liquid with high diffusion rate, and  $T^* = 0.5$ , that corresponds to the supercooled liquid state (Fig. 2). These runs will be referred to as *A* and *B*, respectively. Simulation of a liquid in the supercooled state poses problems related to the system size: (i) highly collective relaxation processes, including those leading to the creation of a critical crystalline nucleus, may interfere with the boundary conditions imposed [11]; (ii) inadequate sampling of the relevant configurational space area might result in poor statistical reliability and history dependence. To avoid these problems, a system of 16384 particles was employed here. Its size also enabled us to explore structural correlations in the important long-wavelength region.

The supercooled state, simulated in run *B*, was reached by the stepwise equilibrium cooling. At every step, the temperature was reduced by momenta scaling, which was followed by an equilibration run. The latter continued until stability of the thermodynamical parameters was

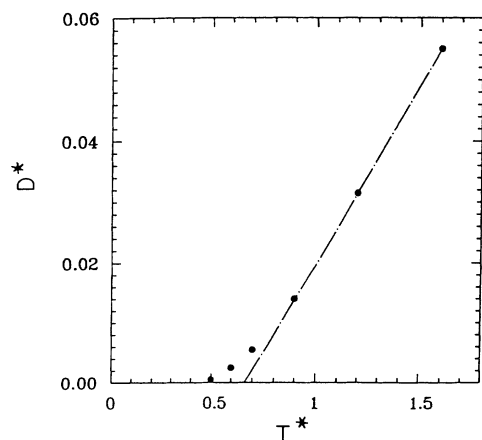


FIG. 2. Temperature variation of the diffusion coefficient during the cooling process.

achieved. Under the cooling, the diffusion coefficient dramatically decreased, and marked change in the character of its temperature variation (Fig. 2) indicates onset of the supercooled dynamics regime. After initial equilibration, the system *B* has been run for  $3 \times 10^5$  time steps. During that run, no systematic shift in the thermodynamical parameters has been observed, which indicates that the system remained stable with respect to crystalline nucleation. Besides systems *A* and *B* described, a reference model was simulated, in which the trial pair potential was truncated at its minimum; to make it continuous at the truncation point, a constant equal the minimum value was subtracted. This case corresponds to the truncated Lennard-Jones potential (TLJ) (Fig. 1). The TLJ system was simulated close to its triple point, at  $T^* = 0.7$  and  $\rho^* = 0.88$ . An interesting observation was that the potential truncation dramatically increased the diffusion rate in the system: its value obtained for the TLJ liquid was, in reduced units,  $D^* = 0.03$ , as compared with  $D^* = 0.0027$  for the system simulated at the same temperature and density using the full potential.

For each of the three liquid states simulated here, the inherent structure was derived by the steepest descent minimization [2]. In systems *A* and *B*, generated by the trial potential, the inherent pair-correlation functions (Fig. 3) are consistent with the distinctive pattern of distance distribution in the icosahedral polytope [10]. Accordingly, the two inherent structure factors (Fig. 4) exhibit characteristic splitting in the second peak and a small additional maximum following the third peak, which unambiguously identify them with the interference function obtained from the icosahedral polytope [10]; this type of inherent structure was also found in metallic glass formers [7]. These two inherent structure factors also demonstrate a remarkable similarity to that calculated within the framework of statistical mechanical theory of icosahedral short-range order in a simple liquid [9]. A particular result of that study was that if the positions of the first three peaks of  $S(Q)$  denoted as  $Q_1$ ,  $Q_2$ , and  $Q_3$ , then  $Q_2/Q_1 = 1.71$  and  $Q_3/Q_1 = 2.04$ . The liquid structure simulated here seems to be in good agreement with this

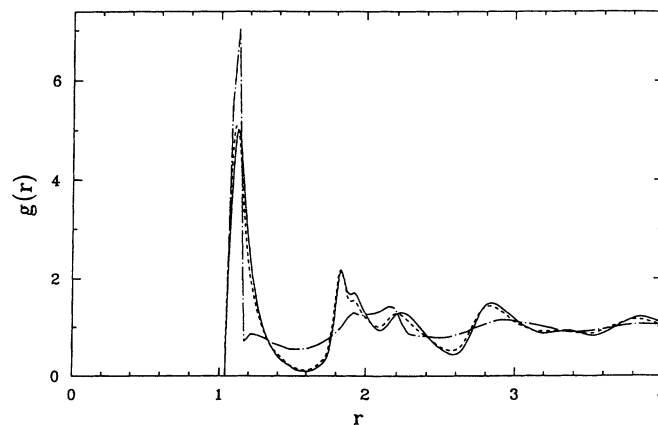


FIG. 3. Inherent pair correlation functions for the three configurations simulated (see in the text). Dashed line, system *A*; solid line, system *B*; dashed-dotted line, TLJ system.

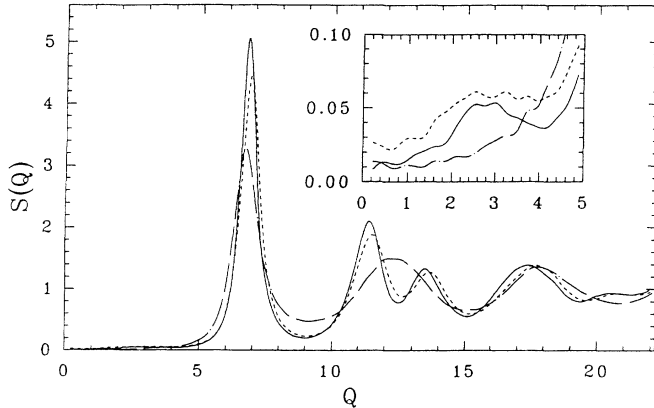


FIG. 4. Inherent structure factors for the same systems as presented in Fig. 3. Dashed line, system *A*; solid line, system *B*; dashed-dotted line, TLJ system.

relationship. In the configuration *A*  $Q_2/Q_1=1.69$  and  $Q_3/Q_1=2.01$ , while in the configuration *B*  $Q_2/Q_1=1.69$  and  $Q_3/Q_1=2$ .

A remarkable novel feature of the two inherent structure factors discussed above is an anomalous long-wavelength prepeak, which may be interpreted as an indication that the icosahedral ordering has a tendency to extend beyond the first-neighbor shell. In this interpretation, the position of the maximum might be related to two characteristic distances in the icosahedron,  $1.62\sigma$  and  $1.9\sigma$ ,  $\sigma$  being the effective diameter of a particle [8]. The fact that the prepeak survives high diffusion rate in system *A* suggests that this ordering is of dynamical nature. The prepeak has not been observed in the metallic glasses; in those systems, however, such a fine detail of topological order could be screened by the large-scale chemical short-range order effects [7]. By contrast, the distinctive features of icosahedral inherent local order displayed by the systems *A* and *B* have not been found in the TLJ inherent structure, which is known to be related to the fcc local order [5]. When supercooled, that system has, indeed, demonstrated rapid fcc nucleation.

Comparison between structures *A* and *B*, presented in Figs. 3 and 4, shows that the onset of the supercooled dynamical regime had no effect on the inherent short-range order. However, the supercooling markedly reduced the  $S(Q)$ , in the long-wavelength domain. This implies that the supercooling induces long-range ordering, which results in formation of more stable and less compressible icosahedral aggregations of particles. This picture of long-range ordering is consistent with the considerable enhancement of the anomalous prepeak of  $S(Q)$ , which is another perceptible structural effect of the supercooling observed.

In order to analyze the patterns of local order in the simulated configurations in the terms of statistical geometry, their first coordination shells were decomposed using the approach introduced by Honeycutt and Andersen [12]. Two particles were considered to be neighbors if the separating distance did not exceed the bond length; here it was chosen to be 1.5. Thus defined neighbors are

also neighbors in the sense of Voronoi tessellation. Each pair of neighbors was classified according to the patterns formed by their common neighbors. If the bonds connecting these neighbors formed a closing ring, such a pair was counted as the closed one. In the context of this study, the main point of interest is a fivefold bipyramid formed by a closed pair with five common neighbors. Statistics of these elements represent an important measure of the icosahedral local order [8]. A particle with the coordination number 12 was regarded as a center of a 13-atom icosahedron, if it formed fivefold closed bonds with all its neighbors.

The results presented in Table II give a significant insight into the pattern of local order behind the distinctive inherent structure generated in this study. In systems *A* and *B*, the local order is apparently dominated by the fivefold bipyramids. At the same time, only a minority of the constituent particles was found to have the regular icosahedral environment. This result is consistent with the models of icosahedral local order [10]. Presumably, most of the fivefold bipyramids participate in the Friauf polyhedra or Bernal polyhedra [7]. Accordingly, a marginal increase in the number of the fivefold bipyramids, induced by the supercooling, doubles the number of the icosahedra. The process of glass-forming icosahedral ordering can also be associated with the development of the long-wavelength prepeak in the structure factor.

The above results are in a great contrast with those on the TLJ system. While the latter has about the same number of neighbors in the first coordination shell as configurations *A* and *B*, those neighbors are arranged in a fundamentally different way. The number of closed fivefold bonds is much smaller, and icosahedra are practically nonexistent. Another important distinction between the two types of local order is that the TLJ system has a much larger number of nonclosed bonds, which may be associated with a more shallow first minimum in its pair correlation function. This indicates the presence of a large number of rather loose local configurations, and it is conceivable that their transformation under supercooling is responsible for the fcc nucleation in that system. By contrast, in the system generated by the trial potential, the supercooling apparently reduces the number of potentially unstable local configurations by transforming the non-closed bonds into the fivefold bipyramids.

TABLE II. Statistics of local order in the simulated configurations.

Configuration	<i>A</i>	<i>B</i>	TLJ
Number of bonded pairs	104 769	106 088	102 423
Number of closed bonds	57 580	62 982	28 436
Number of fivefold bipyramids	41 912	51 662	17 552
Number of icosahedra	707	1505	33

The finding that a glass-forming liquid with icosahedral inherent short-range order might be formed by a simple one-component system, opens a new possibility for analyzing the mechanisms of glass formation in the systems of simple constitution. The model reported here may be regarded as a one-component reference system for the multicomponent metallic glass formers. In these systems, the relaxation under supercooling involves both the topological and the chemical ordering. The one-component model reported here provides a unique opportunity for separating the contributions of these processes in the glass formation. In this respect, it is interesting to note that the potential utilized in this simulation resembles those derived for

$Mg_7Zn_3$  glass [7]. This suggests that the structural stability in that glass is mostly provided by the topological ordering induced by the pair potential. That metallic glass is known to exhibit a tendency for transformation into the Frank-Kasper phase. Whether or not such a tendency could be observed in the system reported here is a question of profound interest. However, the problem of global stability in the simulated supercooled system is a problem of macroscopic time scale which is far beyond the reach of the MD simulation technique, in its present state.

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