

Icosahedral Ordering in the Lennard-Jones Liquid and Glass

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We have simulated the cooling of Lennard-Jones fluids from liquid temperatures to below the glass transition by using molecular-dynamics calculations and periodic boundary conditions. At higher temperatures the "inherent" structure is independent of temperature, but slightly above the glass transition temperature T_g the structure changes and local fivefold symmetry becomes more prominent. At T_g this process is slow and a hysteresis is observed on heating. The low-temperature two-component glass has a cluster of interpenetrating and face-sharing icosahedra percolating throughout the sample.

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The structure of glasses and the dynamics of glass formation are incompletely understood even for the simplest systems.¹ Characterization of the short-range order is important for our understanding of the properties of these materials. Experimental data such as x-ray scattering give only the radial distribution function and contain limited information about the short-range order. Structural models of simple (metallic) glasses have been generated by the assembly of hard spheres (by use of ball bearings or a computer algorithm¹) to give what is called dense random packing. It has been argued, however, that real metallic glasses and supercooled liquids are better described in terms of ordered but noncrystalline clusters. Frank² pointed out that an icosahedral arrangement of thirteen Lennard-Jones (LJ) atoms has a binding energy that is larger by 8.4% than an fcc or hcp arrangement. It is impossible to form a crystalline structure in which each atom has such an environment because of the fivefold symmetry of the icosahedron ("frustration"). Hoare³ proposed that the size of such non-crystallographic clusters increases as the liquid is cooled, until the growth is limited near the glass transition by frustration effects. The importance of icosahedral structure in bulk systems is illustrated by the Frank-Kasper crystals, which have large unit cells containing icosahedra, and by the recently discovered icosahedral phase, which exhibits diffraction patterns with sharp spots (suggesting crystallinity) but with symmetry of the icosahedral point group.^{4,5} One of the contending structural models of the icosahedral phase, the icosahedral glass model, assumes that connected icosahedra are packed randomly but with the same orientation throughout the material.⁶

Molecular-dynamics simulations^{7,8} can generate realistic structural models for amorphous materials and provide information about the dynamics of the glass formation. Previous molecular-dynamics simulations by Steinhardt, Nelson, and Ronchetti⁹ suggested the importance of fivefold symmetry in the bulk LJ system. On the basis of calculated correlation in the orientation of "bonds" joining near neighbors, they concluded that an

increase in icosahedral ordering occurs as the liquid is supercooled.

Here we report the results of extensive simulations of the cooling of LJ systems at constant pressure.¹⁰ The systems consisted of 500 and 1500 atoms subject to periodic boundary conditions. Both the one-component system and a two-component system with 20% *A* atoms and 80% *B* atoms were studied. The *A* atoms are larger ($\sigma_{AA}=1.0$, $\sigma_{AB}=0.9$, $\sigma_{BB}=0.8$), but all three interaction potentials have the same well depth ($\epsilon=1$). The cooling was carried out by use of stochastic collisions with an external heat bath¹⁰ whose temperature was a decreasing function of time.

Figure 1 shows the enthalpy of the two-component liquid during a stepwise cooling run (bath temperature was lowered by 0.05 every 50τ).¹¹ The heat capacity has a large value at high temperatures but drops over a transition region around $T=0.38$ to a smaller value near 3, appropriate for a harmonic solid. This behavior is typical of a glass transition. Another characteristic property of glasses is thermal hysteresis. After annealing at $T=0.3$ for 1300τ , the system was heated (Fig. 1). The enthalpy curve for heating overshoots and lies under the extrapolation of the equilibrium liquid curve. When the heating and cooling curves finally meet there is a maximum in the heat capacity ($T\approx 0.48$), as is often observed for real glasses.

The prevailing view of the glass transition would explain the temperature dependence in the following way^{12,13}: A change in temperature leads to a change in the average molecular configuration of the liquid, i.e., a structural relaxation, in addition to an instantaneous, solidlike response. If the temperature is raised, for example, the system explores configurations of higher potential energy and therefore the structural relaxation contributes to the heat capacity. As the temperature is lowered, the time scale of the structural relaxation increases rapidly and in the transition region becomes comparable to the time scale of the cooling. At even lower temperatures, structural relaxation cannot take place, causing the total heat capacity to be smaller than

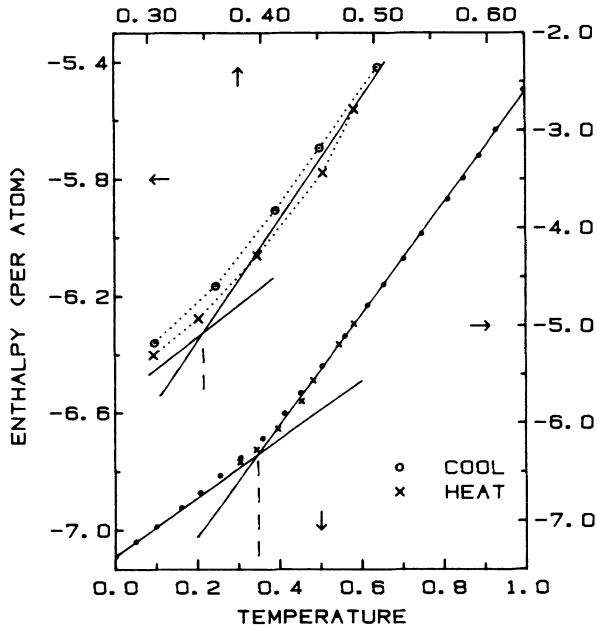


FIG. 1. Enthalpy as a function of temperature in a 500-atom simulation of the two-component LJ system: circles, cooling at a rate of $q = \Delta T / \Delta t = 0.001$; crosses, heating at a rate of 0.001 after annealing at $T = 0.3$ for 1300τ [upper and left axes go with the upper curves (expanded scale)]; straight solid lines, a harmonic system (low T) and a least-squares fit to the liquid (high T); dashed lines, T_g defined as the intersection of the two straight lines.

at higher temperature. By analyzing the structure of the simulated liquid as a function of both temperature and time, we have been able to identify clearly a structural relaxation which indeed becomes slow near $T = 0.4$, but the picture described above needs to be modified.

The structures were analyzed by our characterizing pairs of atoms with four indices.¹⁴ The first indicates whether the pair of atoms is closer than a given cutoff distance, chosen to equal the position of the first minimum in the appropriate pair correlation function ($A-A$, $A-B$, or $B-B$). Such atoms are referred to as neighbors or, equivalently, are considered to form a bond. The first index is 1 if the pair is bonded and 2 otherwise. The second index is the number of neighbors common to the two atoms, and the third is the number of bonds between the common neighbors. Sometimes there is ambiguity about the arrangement of the bonds and to resolve this a fourth index is added.

Two problems arise in the application of this technique directly to analyze structural changes in the liquid. As the volume changes (systematically as the temperature is lowered, or randomly as the result of fluctuations), the numbers of the various kinds of pairs change even though the underlying structure might not be changing. Furthermore, the thermal motion of the atoms causes noise and obscures the underlying structure. To solve both problems, we use a technique that is essentially the

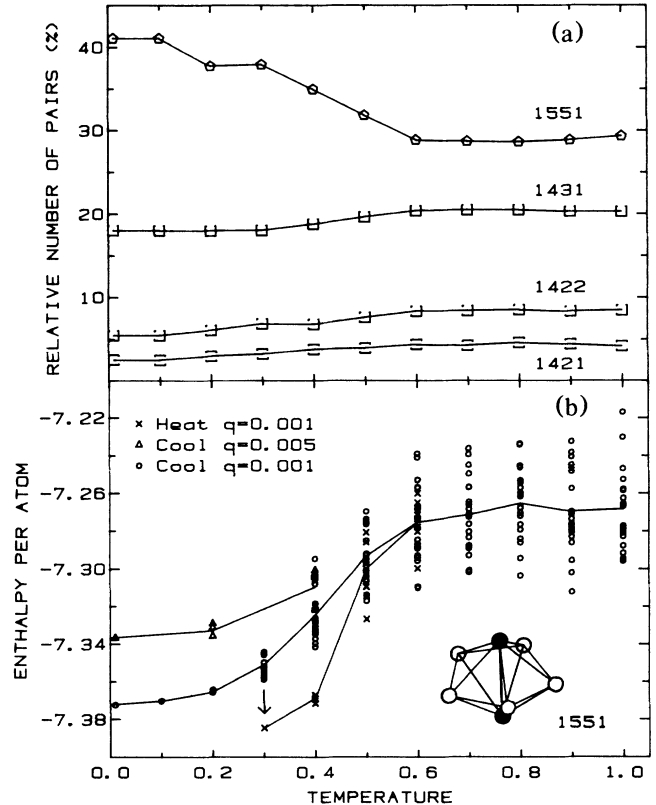


FIG. 2. (a) Relative numbers of some bonded pairs on cooling of the 500-atom system. (b) Enthalpy of configurations obtained after steepest-descent minimization at constant pressure: circles, cooling rate $q = 0.001$ (twenty configurations are sampled at each temperature value); triangles, faster cooling, $q = 0.005$; crosses, heating at a rate of 0.001 after annealing; solid lines, averages for each temperature. Inset: A 1551 pair.

same as the steepest-descent minimization used by Stillinger and LaVolette¹⁵ and Stillinger and Weber,¹⁶ except that we treat the volume as one of the coordinates and allow it to change as the atoms move toward the potential minimum. Following Stillinger and Weber, we call the structure of the system at its local minimum the "inherent structure."

Figure 2 shows the relative numbers of different kinds of bonded pairs of atoms in the inherent structures as functions of temperature on cooling. None of the types of pairs shows any significant change as the temperature is varied in the range $T > 0.6$. We therefore find that the structure does not change with temperature at the higher temperatures where the heat capacity is large.¹⁷ At low temperatures, however, there is a substantial increase in two types of pairs, the 1551 and the 2331. The 1551 pairs correspond to two neighboring atoms with five common neighbors that form a pentagon of near-neighbor contacts [Fig. 2(b)]. The 2331 pair corresponds to two atoms that are not neighbors but have three common neighbors that form a triangle of near-neighbor contacts. The two types of pairs are charac-

teristic of icosahedral ordering, being found in the 13-atom icosahedron. The numbers of 1421 and 1422 pairs, which are characteristic of fcc and hcp crystalline structures, decrease slightly at the same time. Figure 2(b) shows the enthalpy of the inherent structures, i.e., the enthalpy at the local minimum on the potential-energy surface. Just as the numbers of the various types of pairs are independent of temperature for $T > 0.6$, so is the average enthalpy. However, as the icosahedral ordering increases, the average enthalpy decreases.

The formation of the icosahedral pairs was found to be slow in the glass transition region. At a temperature of 0.4, the 1551 and 2331 pairs continue to form over the entire time interval (50τ) spent at that temperature.

Very similar results were obtained in simulations of the one-component system when crystal nucleation did not interfere. Crystal nucleation and icosahedral ordering are two competing tendencies with a similar time scale in the one-component liquid, and we find clear anticorrelation between the crystal pairs (1421+1422) and the icosahedral pairs in low-temperature configurations obtained in repeated cooling runs. The increase in icosahedral ordering that we observe is not the same as the bond-orientational-order transition reported by Steinhardt, Nelson, and Ronchetti.⁹ In fact, configurations with large numbers of 1551 pairs have small values of the orientational-order parameter, Q_6 . However, configurations with some crystal nucleation (10–20 fcc/hcp atoms, small enough that the pair correlation function does not show a crystal peak) have large values of Q_6 , similar to those reported by Steinhardt, Nelson, and Ronchetti.

The picture that emerges from these simulations is quite simple, but it is different from the one described in the introduction. In the high-temperature region ($T > 0.6$) the system sees a large distribution of local minima [see the spread in enthalpies in Fig. 2(b)], but the average enthalpy and structure of the inherent structures are independent of temperature. By calculating the rms displacement during the steepest-descent minimization, we find that the distance to the local minimum (in scaled coordinates¹⁰) is about 3 times larger than would be expected for a harmonic system. Starting in a region of rather high potential energy far from the local minimum, the system often slides over inflection points in the potential surface during the steepest-descent minimization, as is manifested by an irregular rate of potential-energy decrease (see Fig. 2 in Ref. 16). The high heat capacity of the liquid at $T > 0.6$, as compared with the low-temperature harmonic system, is not due to a structural change with temperature but rather due to thermal expansion on this highly anharmonic potential surface.

As the temperature is lowered ($T < 0.6$), the system starts to become localized in a single potential-energy minimum and the heat capacity starts to drop toward the harmonic value. Given time, however, at the lower tem-

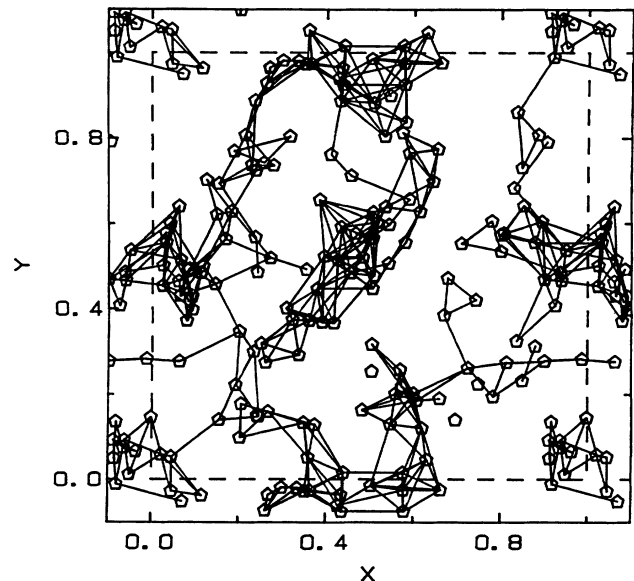


FIG. 3. Icosahedra in a 1500-atom system (same as in Figs. 1 and 2 but larger) at $T=0.2$ after steepest-descent minimization. A solid line connects centers of icosahedra (pentagons) that are interpenetrating or sharing a face. Dashed line shows the boundary of the simulation cell. Some of the periodic images outside the cell are shown. The coordinates are projected onto the X - Y plane.

peratures the system will seek out and prefer to stay in minima that represent denser packing (systems with purely repulsive potentials show similar behavior under high pressure). This is the structural-relaxation process. Even in the absence of this structural relaxation, however, the system would become localized and the heat capacity would drop.

In the computer simulation, the two distinct processes contributing to the drop in heat capacity, namely the localization of the system into a single potential-energy minimum and the arrest of structural relaxation, occur at a similar temperature. In laboratory studies on real liquids, where the cooling is much slower, the structural relaxation can presumably also occur at lower temperatures. It is plausible, therefore, that for real liquids these two processes might occur at distinctly different temperatures and that only the arrest of relaxation contributes to the drop in heat capacity at the glass transition. This is in agreement with the ideas of Goldstein,¹⁸ who argued that the necessity for transitions from one local potential-energy minimum to another dominates the flow process in "viscous" liquids even well above the glass transition but not necessarily in the higher-temperature liquid. He estimated that when the shear relaxation time is about 10^{-9} sec or longer, the potential barriers dominate the dynamics. This would correspond to a time of about 1000τ in the simulation (comparable to our longest annealing time).

As shown in Fig. 3, the structure of the two-component glass is predominantly icosahedral. We find 138 icosahedra in a sample of 1500 atoms, with 61% of the atoms in icosahedra. On average, each icosahedron interpenetrates 1.9 and shares a face with 1.7 other icosahedra. A large cluster is formed which percolates throughout the material. There is a strong system-size dependence in that smaller, 500-atom, simulations give relatively fewer icosahedra, 36, and each icosahedron interpenetrates 1.4 and shares face with 1.0 other icosahedra, on average. This suggests that the tendency to form icosahedral structures would be even greater in macroscopic systems.

The simulations may have implications for our understanding of the structure, nucleation, and growth of the icosahedral phase. Various quasicrystal and icosahedral glass models assume the existence of icosahedral units that are attached in various ways⁶ or interpenetrate.¹⁹ Our simulations show that such structural motifs, with the icosahedra being simply thirteen-atom clusters, can arise spontaneously on a rapid time scale for atomic systems with realistic interactions, even when cubic periodic boundary conditions are applied.

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