

## Glass transition in isopentane: A Monte Carlo study

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Monte Carlo simulations with realistic interaction potentials have been carried out on isopentane to investigate the glass transition. Intermolecular pair-correlation functions of the glass show distinct differences from those of the liquid, the CH-CH pair-correlation function being uniquely different from the other pair-correlation functions. The coordination number of the glass is higher than that of the liquid, and the packing in the glass seems to be mainly governed by the geometrical constraints of the molecule. Annealing affects the properties of the glass significantly.

The phenomenon of glass transition distinguishes glasses as a unique class of amorphous materials. Most organic liquids, when cooled sufficiently rapidly, transform into glasses at the glass transition temperature  $T_g$ . At  $T_g$ , the cardinal characteristic of the liquid, namely, flow, disappears. Thermodynamic quantities such as thermal expansivity and heat capacities of the glasses and the parent liquids differ significantly. Interestingly, the radial distribution functions of glasses and parent liquids are also recognizably different in several glass forming systems.<sup>1-3</sup>

Although several models have been proposed to explain the glass transition, none of these has been able to provide details of local structural effects accompanying the transition. In principle, one can obtain such information from computer simulation studies by investigating the evolution of definite "structural entities" as a liquid is cooled towards  $T_g$ . There are, however, certain limitations in computer experiments. One of them is the rather unphysical quenching rates employed in them and the other ensues from the idealized potential functions employed to model the interactions.<sup>4-6</sup> However, there has been hitherto no Monte Carlo or molecular-dynamics study of a real system undergoing the glass transition for which reliable interaction potentials are available. We have therefore performed Monte Carlo simulations on isopentane liquid employing realistic interaction potentials of Jorgensen<sup>7</sup> which have been very successful in predicting the properties of hydrocarbons.<sup>8</sup> To our knowledge, this is the first such study of the glass transition in a real molecular liquid. Besides predicting the various features of the glass transition, the study shows that the coordination number distribution and the pair-correlation function of the glass to be considerably different from those in the liquid. The study also throws light on the nature of the glassy state and the effect of annealing on the final state of the glass obtained.

Monte Carlo calculations were carried out in the isothermal-isobaric ensemble on a system of 54 molecules contained in a cubic cell. Periodic boundary conditions were imposed. All the calculations were performed with a cutoff distance of 9.5 Å. The standard bond length of 1.53 Å for the C-C bond and the standard tetrahedral angle 109.48° were assumed; transferable intermolecular potential functions of Jorgensen<sup>7</sup> have been used in this study. The hydrogens are not explicitly considered in this potential function; instead, interaction parameters are defined for the dif-

ferent groups, CH, CH<sub>2</sub>, and CH<sub>3</sub>. In addition, the isopentane molecule is permitted to rotate around the CH-CH<sub>2</sub> bond; a potential similar to that used in the study of *n*-butane has been employed for the internal rotation after taking into account the presence of two methyl groups on the CH. The total energy is, thus,  $E(\text{total}) = E(\text{intermolecular}) + E(\text{rotational})$ . A trial molecular move involved a translation, a rotation around a randomly chosen axis and an internal rotation. A Monte Carlo move is defined as one attempted move for each of the  $N$  molecules. The volume moves were made once every five Monte Carlo moves. At first, a simulation of liquid isopentane was carried out starting with a random initial configuration at atmospheric pressure and 301.01 K, the boiling point of isopentane. The liquid was allowed to equilibrate for more than 9000 Monte Carlo moves or 500 000 configurations and an equal number of moves were used for averaging the properties. The liquid thus obtained was then quenched to 220, 120, 50, 40, and 30 K at atmospheric pressure and equilibration and averaging was carried out over 6000 or more Monte Carlo moves.

To start with we performed long runs on liquid isopentane at 301.01 K, the boiling point of isopentane. After ensuring complete equilibration, we averaged the properties. The calculated thermodynamic properties of liquid were in good agreement with the experiment. The configuration at this temperature was used as the starting configuration for runs at other temperatures. The variation of intermolecular energy of isopentane with the quench temperature is presented in Fig. 1. From the  $E(\text{intermolecular})$  vs  $T$  plot,  $T_g$  value is found to be 84.0 K, while the experimental value is 65 K.<sup>9</sup> The heat capacity for the glassy and liquid isopentane from the  $E(\text{intermolecular})$  vs  $T$  plot are 8.5 and 9.2 cal/mol K, respectively. Thus, the intermolecular contribution to the change in heat capacity on going from glass to liquid is 0.7 cal/molK. The change in the total heat capacity  $\Delta C_p$  between the glass and the liquid calculated as above by making use of linear fits to the enthalpy versus temperature plot is 5.4 cal/molK; the experimental value<sup>10</sup> is 16.3 cal/molK at  $T_g$ . In our calculations the internal vibrations in the liquid have not been considered which account partly to the low value of  $\Delta C_p$ . Another contributing factor is the high quenching rate inherent in computer experiments.

The intermolecular correlations constitute the most significant information obtained from the Monte Carlo simulations. In the present study, correlations arise from various

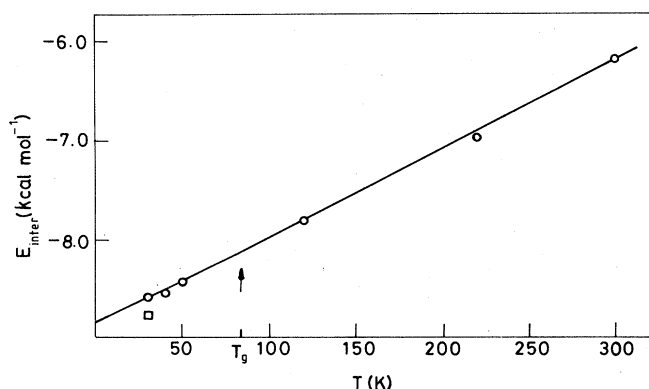
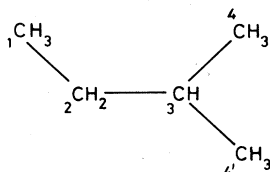


FIG. 1. A plot of intermolecular energy against temperature of isopentane obtained by quenching the liquid from the melting point ( $T_m = 301.01$  K) to 220, 120, 50, 40, and 30 K. The square denotes the point obtained by annealing the glass (see text).

carbon atoms in isopentane and they are subscripted through the numbers shown below.



In the potential scheme employed in Monte Carlo calculations, hydrogen atoms are not explicitly considered. The two methyl groups attached to the CH group are treated as equivalent in view of the free rotation on the central  $C_2-C_3$  bond. Hence, we have ten distinct carbon-carbon pair correlations of the type ( $C_m-C_n$ ) all of which have been determined in this study ( $m$  and  $n$  refer to a carbon atom on different molecules). Two typical correlation functions corresponding to  $C_1-C_4$  and  $C_3-C_3$  are shown in Fig. 2 for the liquid and for the glass.

The following important features emerge from an examination of the correlation functions. (i) The pair-correlation functions of the liquid are rather smooth and the intensities

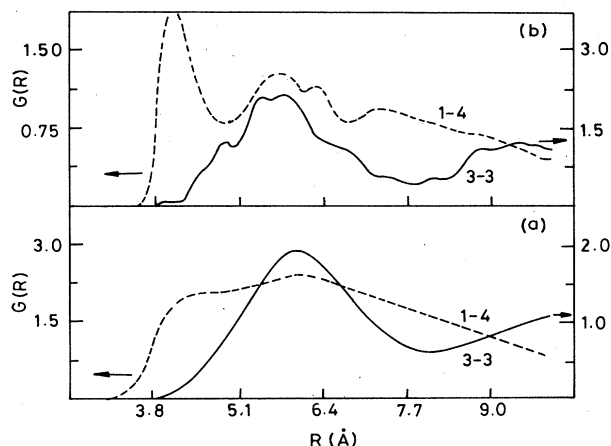


FIG. 2. Pair-correlation functions 1-4 and 3-3 (see text for abbreviation) for the (a) liquid at 301.01 K and (b) the glass at 30 K.

are contained preferentially in the higher distance peaks. (ii) The pair-correlation functions of glasses are considerably structured, intensities of the peaks are shifted to lower distances and the first peak appears to acquire intensity at the expense of the second peak of the corresponding liquid correlation function. (iii) The peak at  $\sim 3.9$  Å with roughly similar frequency (intensity) and features appears in all correlations  $C_m-C_n$  with  $m=1, 2, 4$ , or  $4'$  and  $n=1, 2, 4$ , or  $4'$ . (iv) Correlations involving  $m=3 \neq n$  always show a shoulder at 3.9 Å but with prominent peaks in pair correlations occurring at larger distances. (v) Correlation functions with  $m=n=3$  do not have a peak or a shoulder at 3.9 Å.

An examination of the pair-correlation functions reveal that the position of the first peak for  $m$  and  $n$  values 1, 2, 4, or  $4'$  indicates the absence of any preferred orientation of the molecule in either the liquid or the glass. The carbon atom  $C_3$  is attached to two methyl and one ethyl group and, therefore, the minimum approach distance to other carbon atoms is restricted to 3.9 Å, in the liquid. The glass which is more closely packed, however, shows peaks at 3.9 Å in the  $C_3-C_1$  and a shoulder in the  $C_3-(C_2 \text{ or } C_4 \text{ or } C_4')$ . The  $C_3-C_3$  correlation function (Fig. 2) indicates that the two CH groups never come closer than 4.5 Å. The packing in the glass appears to be random and influenced primarily by the geometry of the molecules, with no significant features due to the allowed internal rotation around  $C_2-C_3$ .

Since there are three methyl groups in the molecule, it would be natural to choose either CH or  $CH_2$  of these molecules in the description of the local coordination polyhedra. We have chosen CH in view of the fact that the  $C_3-C_3$  correlation in the liquid has a single well defined and fairly sharp peak. The average coordination number of molecules determined on this basis, is approximately 12 for the liquid and 14 for the glass; the corresponding histograms are shown in Fig. 3. There is about 15% increase in the coordination number upon quenching the isopentane liquid into the glass. Since the histograms indicate a rather narrow distribution of coordination numbers of the glass it may be taken to imply that the structure of the glass corresponds to an essentially random close packing of small structural units. This view is strengthened by the presence

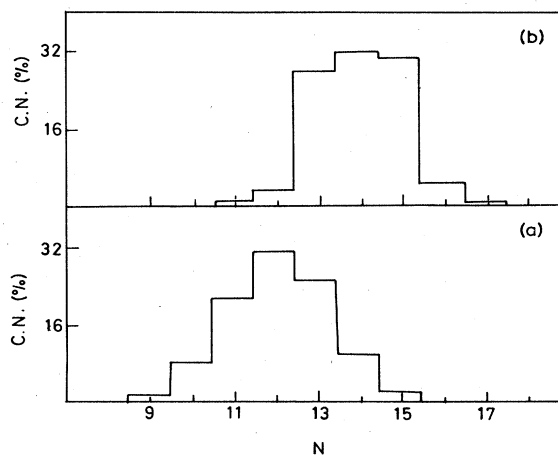


FIG. 3. Coordination number distribution function for the (a) liquid at 301.01 K and (b) the glass at 30 K. The ordinate shows the percent neighbors of a given coordination.

of voids in the snapshot picture taken along the minimum overlap direction (Fig. 4).

An important observation emerging from the present study is that the ultimate structure of a molecular glass such as hydrocarbons is determined largely by the geometrical constraints of a random assemblage. This is especially relevant in view of the molecular-dynamic calculations performed with idealized potentials (such as soft and hard Lennard-Jones) on other systems where similar coordination numbers have been observed in the resulting glasses.<sup>11,12</sup> However, the unfortunate limitations in machine calculations of this type is that it is not possible to investigate large systems in which intermediate range structures are likely to develop. That an annealing effect has been observed in these studies also points to an insufficiency of even as large a number of averaging steps as employed here, particularly if the supercooled region of liquids were to be investigated in detail.

We have investigated the effect of annealing on the isopentane glass. The annealing experiment was carried out in the following manner. The glass quenched to 30 K was heated to 60 K and allowed to anneal at this temperature for several thousand Monte Carlo moves; it was then re-quenched to 30 K. The intermolecular energy of the quenched and annealed glass are, respectively,  $-8.57$  and  $-8.72$  kcal mol<sup>-1</sup>. The difference between them is 0.15 kcal mol<sup>-1</sup>, which is beyond the expected error or  $\pm 0.03$  kcal mol<sup>-1</sup> in the determination of energy, thereby establishing the occurrence of annealing in the glass transition region. This result is significant in view of the results in the literature where the final states of the glass obtained was independent of the quenching schedule. Abraham<sup>11</sup> found that the glasses obtained by pressure and temperature quenching of a Lennard-Jones liquid were identical. Stillinger and Weber<sup>13</sup> have found in a molecular-dynamics simulation that glasses obtained from liquids at slightly above  $T_m$  and  $3.5T_m$  were also identical. However, recently Anderson and Fox<sup>14</sup> have observed dependence of properties on the history of the glass. The present study not only provides an independent confirmation of this important observation but also shows that the annealing effect is more easily exhibited by real glass-forming systems like isopentane when realistic potentials are employed.

The main findings of the present study are the following. The Monte Carlo simulation predicts general features of the glass transition satisfactorily. The pair-correlation functions of the glassy state differ significantly from those of the liquid showing considerable structure. The pair-correlation

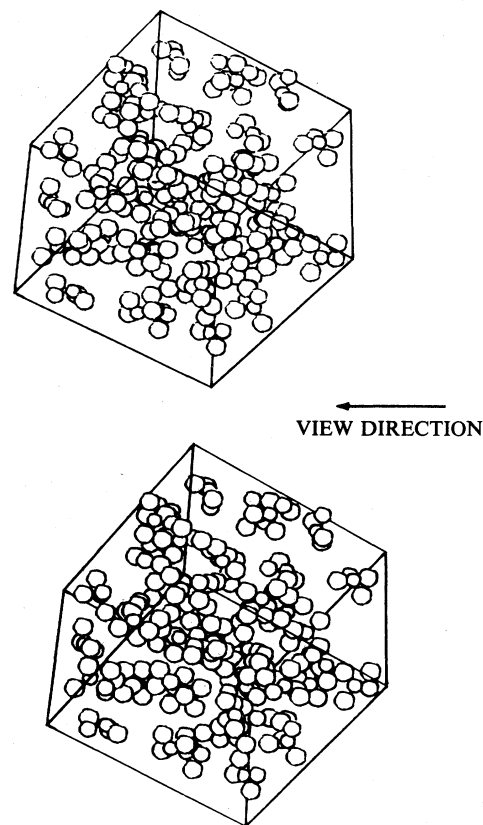


FIG. 4. A stereoscopic view of isopentane glass at 30 K along the direction of minimum overlap.

functions of the liquid are, in general, broad and diffuse, the exception being the CH-CH correlation which shows a well-defined peak. The coordination number is higher in the glass than in the liquid. The structure of the glass corresponds essentially to a random orientation of the molecules, the only constraint being that due to random close-packing geometry. Annealing seems to result in a different final state of the glass.

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