A Computer Simulation Study of Supercooled Liquid and Amorphous-Solid Methanol

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Dedicated to Professor Jacob Bigeleisen on the Occasion of his 70th Birthday

The constant-pressure molecular dynamics technique has been used to study the structural consequences of cooling liquid methanol. We employed a periodically replicated system of 250 molecules interacting with an intermolecular potential fitted to thermodynamic properties of the liquid. Plots of the enthalpy and volume against temperature exhibit a distinct change in slope around 160 K; a feature that is identified with the onset of structural arrest, occurring on the picosecond time-scale, in the supercooled liquid. The corresponding glass transition in real methanol occurs around 103 K. The main structural feature that accompanies the structural arrest is the appearance of a splitting in the primary peak of the radial distribution function for methyl groups. This observation contrasts strongly with the behaviour of atomic systems where such splittings arise only in the second peaks of distribution functions. The calculations are discussed in the light of recent neutron scattering data on glassy methanol.

1. Introduction

In the past few years, considerable progress has been made in understanding the glass transition [1]. Much of this progress has come about through the study of idealized models – lattice systems with spin hamiltonians or atomic systems with short-ranged interaction potentials [2]. Both analytical theory [3] and computer simulation [4] have been successfully applied to this problem. A comprehensive review of the field, including many relevant references, appeared recently [5]. The focus of much of this work has been the nature of the structural arrest that occcurs as a liquid is supercooled [6, 7]. In a real glass forming system, the thermal behaviour exhibits a characteristic hysteresis as it goes through the glass transition. Also, the viscosity and self-diffusion coefficients vary over many decades as a supercooled liquid becomes glassy.

To date, the emphasis of the computer simulation work has been mainly to analyse the structural aspects of simple glass forming systems and to explore the nature of various time correlation functions in order to ascertain whether or not they follow the well known Kohlrausch (stretched exponential) law or whether the viscosity follows the empirical Vogel-Fulcher behaviour [7].

One structural characteristic of an atomic system in a glassy state is the nature of $g(r)$, the atom-atom radial distribution function. In a typical low-temperature solid, this function exhibits well defined peaks at the values of r appropriate to the various neighbour shells. These peaks are generally gaussian in appearance with widths given by the usual Debye-Waller thermal factor. In a liquid, the peaks in $g(r)$ are broadened and, as r increases, become successively damped with the function oscillating about its asymptotic value of unity. In a glass, the situation is intermediate between that of a solid and a liquid. There is a general lack of long-range order but the lower temperature, and the presence of short-range order, leads to a narrowing of the first peak in $g(r)$ compared to the liquid. Also, a splitting develops in the second peak in $g(r)$ which, in an atomic liquid, generally occurs at twice the r-value of the first peak. Although the splitting of the second peak in $g(r)$ appears to be a universal phenomenon for an atomic glass, its appearance cannot be used as a rigorous indicator of the glass transition because the split-peak is often already apparent

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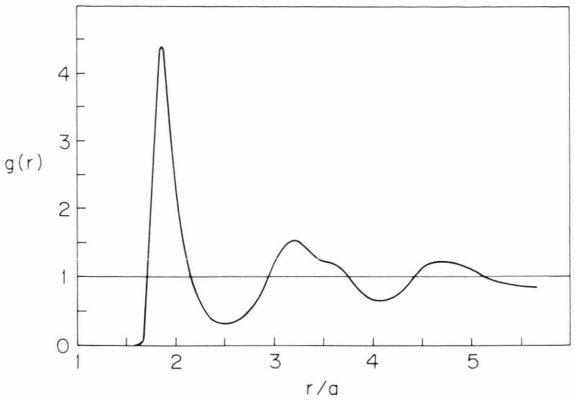

Fig. 1. An atom–atom distribution function, $g(r)$ for an atomic glass taken from [6]. The split second peak should be noted.

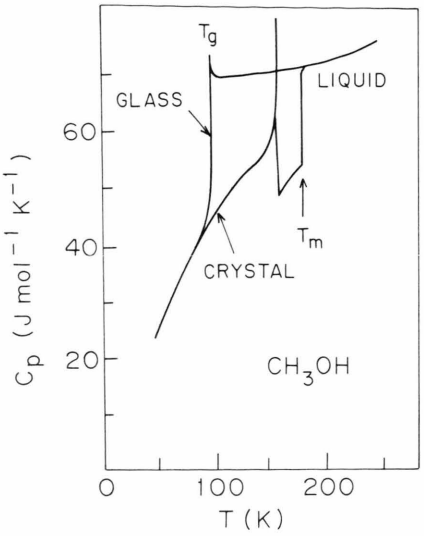

Fig. 2. Experimental temperature variation of the heat capacity of methanol taken from [14]. The solid–solid phase transition at around 160 K and the melting point, T_m should be distinguished from the glass transition, $T_g = 103$ K.

in the supercooled liquid. Nevertheless, it is a useful diagnostic tool for the onset of structural arrest and the presence of glass-like behaviour. Figure 1 illustrates the splitting of the second peak in $g(r)$ that is typical of an atomic system in a glassy state. The system in question is actually a binary (50/50) mixture of so-called soft spheres whose diameters are in the ratio 1.2:1.0. This mixture can be readily quenched into a glassy state [7]. The curve shown in Fig. 1 refers to the larger diameter spheres, but the other two $g(r)$'s look much the same.

There has been considerable excitement caused by the realization that local icosahedral ordering is the primary structural element present in many simple (model) glasses [8]. However, the recent advances generated by theory and simulation of the glass transition have yet to lead to a complete theory, even for atomic systems [3–5]. The present article is concerned with molecular glasses. Here, theory is more or less nonexistent; molecular glasses are simply viewed as having frustrated translational and orientational degrees of freedom. A considerable phenomenology exists [2], but there have been relatively few attempts to probe the structure of such systems using simultation methods [9].

Many molecular materials, which normally crystallize when the liquid is cooled, may be prepared in amorphous form either by vapour deposition, rapid quenching, intense irradiation or even compression. For example, it has been known for sometime that amorphous ice can be prepared by vapour deposition on a cold surface. Moreover, X-ray and neutron diffraction studies have yielded valuable information on the resulting structures. In a recent series of papers, Dore and coworkers [10] have investigated a variety of hydrogen bonded systems using this approach. In particular, they have contrasted the behaviour of H_2O with that of NH_3 and CH_3OH. The ordered solid phases of these molecules are characterized, respectively by hydrogen bonding with 4-fold, 6-fold and 2-fold coordination [11]. Significant structural differences between the liquids and the amorphous solids were identified. The experimental studies on methanol provided the impetus for the present calculations. We have chosen to focus on methanol because it is one of the simplest molecular systems that readily form a glass. Moreover, it is routinely used as glassy matrix for trapping reactive species. To date, there appears to have been no attempt to probe its structure using computer simulations although several analogous studies have appeared on the liquid [12, 13].

Figure 2 shows the heat capacity of solid, liquid and glassy methanol [14]. There are at least two solid phases of methanol; the spike in C_p around 160 K indicates a solid–solid phase transition. Both solid structures appear to involve infinite hydrogen bonded chains [11]. The normal melting temperature and the glass transition, that arises on supercooling the liquid, are indicated by $T_m \approx 180$ K and by $T_g \approx 103$ K, respectively. The latter is characterized by a large residual entropy [14]. The present article gives an account of

our initial attempts to unravel the structure of glassy methanol at the atomic level using constant-pressure molecular dynamics calculations [15] and realistic intermolecular interactions [13]. The outline of the article is as follows. In the next two sections we present the model and give details of the molecular dynamics calculations. Then, in Section 4, we present the detailed results. The article ends with a brief discussion.

2. The Model

The intermolecular potential we employed was taken from previous studies of liquid methanol without modification, [13]. The methanol molecule was assumed to be rigid with a C–O–H angle of 108.5° and C–O and O–H bond lengths of 1.43 Å and 0.945 Å, respectively. The methyl group (Me) was treated as a fused pseudoatom and the molecular charge distribution represented by three fractional charges (Q_α) residing on the C, O, and H atoms. The total intermolecular potential was written as the sum of atom-atom contributions plus the electrostatic interactions:

$$V_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}\,[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6] + Q_\alpha\, Q_\beta/r\,,$$

$\alpha, \beta = \mathrm{C, O, H}$. It should be noted that there is no explicit short-range interaction between H and other atoms. The potential parameters are given in Table 1. The particular choice of charges $Q_C = 0.297\,|e|$, $Q_O = -0.728\,|e|$, and $Q_H = 0.431\,|e|$, yield a molecular dipole moment, $\mu = 2.33$ Debye which is enhanced with respect to the gas phase value, $\mu_0 = 1.7$ Debye, in order to allow for many body polarization effects in some average sense. The interested reader is referred to [13] for a full discussion of the merits and deficiencies of this simple potential model. Suffice it to say that the potential gives a fair representation of structural and thermodynamic properties of liquid methanol and therefore is a reasonable starting point to investigate the supercooled liquid and the amorphous solid.

Table 1. Potential parameters for methanol*

α–β	ε (K)	σ (Å)
C–C	91.2	3.861
O–O	87.9	3.083
C–O	89.5	3.472

* Taken from [13].

3. Molecular Dynamics Calculations

The constant-pressure molecular dynamics technique was originally devised specifically to carry out simulations on the glass transition in atomic systems [14]. It is natural therefore to employ the same approach for molecular systems, also. To date, a few Monte Carlo studies have been reported for molecular glasses, [9]. The results obtained have been sufficiently encouraging that the present investigation with molecular dynamics seemed timely. The particular computational code we employed is essentially identical to that developed to study phase transitions in ionic molecular solids (MDPOLY) [16]. This program integrates the equations of motion using a predictor-corrector algorithm for both the translational and orientational degrees of freedom with a time step, $\Delta t = 2$ fs. The orientations were treated using quaternions and the long-range electrostatic interactions were handled using an Ewald summation with a real space truncation radius of 11 Å [17].

Initially, 250 molecules were arranged on a body centred cubic (bcc) lattice and then placed in a cubic box with periodic boundary conditions. The box dimensions (5a, 5a, 5a) were chosen to yield the experimental room-temperature density, which correspond to a bcc lattice constant, $a = 5.123$ Å. Next, a conventional constant-volume molecular dynamics run was carried out in order to determine the computed pressure of the liquid corresponding to the assumed intermolecular potential [13]. The resulting pressure was 1.15 kbar, without allowance for the tail correction due to truncation of the potential at 11 Å. At $V = 40.48\ \mathrm{cm^3\,mol^{-1}}$, the latter correction amounts to about -0.35 kbar, so that the net pressure is actually 0.80 kbar. This relatively small value likely indicates a minor inadequacy of the potential. The liquid structure and thermodynamic properties obtained from this run were in good accord with previous published results [12, 13].

A constant-pressure molecular dynamics calculation was then initiated starting from the well equilibrated room temperature liquid configuration generated as described above. The nominal external pressure was set to the value determined in the constant-volume calculation with an 11 Å cut-off, namely 1.15 kbar. Once the system had been re-equilibrated a series of cooling runs was carried out in order to generate an amorphous solid. Typically, at each chosen temperature, 7,000 time steps were used for

equilibration and a further 14,000–21,000 were used to generate statistics. Since this was a preliminary study, focussing only on structural aspects, we employed a mass of 16 for the H atom, 16 for O and 15 for Me.

4. Results

Table 2 gives the molecular dynamics results for the pressure, volume, enthalpy and temperature. After the cooling run was completed, several data points were extended to twice the run length. The results from these extended runs are also listed in Table 2 as independent data points and serve as a reasonable guide to the numerical uncertainties. The volumes obtained from the primary cooling run are shown graphically in Figure 3. The plotted data show clear evidence for a change in slope around $T \approx 160$ K. We interpret this change in slope as evidence for the onset of structural arrest in the supercooled liquid, at least on the time scale appropriate to the simulations. It is now widely appreciated that in computer simulations the apparent glass-transition temperature occurs at a higher temperature than in a real experiment, due to enhanced cooling rates [5]. The present case is no exception in this regard. The simulated "transition" also appears to accidentally coincide with the experimental solid–solid phase transition shown in Figure 2. The exact nature of the structural arrest observed in the present calculations has yet to be explored, but preliminary indications are that there is a simultaneous arrest of both the translations and rotations. A more definitive statement must await a careful study of the dynamical aspects of this "transition".

In an effort to unravel the structure of the simulated glassy or amorphous methanol we have calculated radial distribution functions for all atom-atom pairs. The temperature dependence of the 6 independent distribution functions is illustrated in Figs. 4 and 5. Overall, the effect of quenching the liquid at constant-pressure leads to a sharpening of the structural features and a modest contraction of interatomic separations. The O–O distribution function for liquid methanol shown in Fig. 4a, with a main peak around 2.75 Å and a second one around 4.7 Å, is reminiscent of water. At low temperatures, the coordination number obtained from the area under the first peak is exactly 2, which indicates a filamentary hydrogen-bonded structure in contrast to the tetrahedral structure found in water.

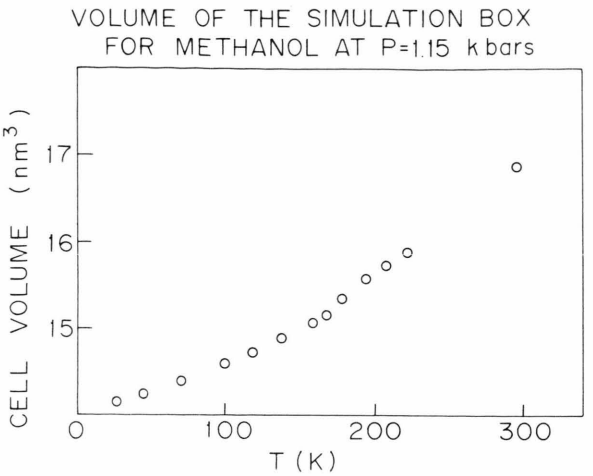

Fig. 3. Temperature variation of the volume of methanol obtained by quenching the liquid from room temperature with an externally set pressure of 1.15 kbar.

Table 2. Molecular dynamics results for quenching methanol.

T (K)	H (kJ mol^{-1})	V (cm^3 mol^{-1})	p (kbar) *
299	−23.30	40.53	0.78
297	−23.23	40.64	0.78
224	−28.95	38.27	0.73
213	−29.51	38.04	0.72
210	−29.74	37.89	0.72
202	−29.96	37.87	0.72
197	−30.84	37.51	0.71
193	−30.89	37.49	0.71
181	−31.91	36.95	0.70
176	−32.02	36.91	0.70
173	−32.54	36.52	0.69
170	−32.70	36.50	0.69
159	−33.27	36.37	0.68
143	−34.30	35.95	0.67
120	−35.64	35.50	0.66
100	−36.72	35.16	0.65
72	−38.30	34.67	0.64
46	−39.68	34.30	0.63
28	−40.61	34.08	0.62

* Quoted values include the tail correction.

The O–H distribution shown in Fig. 4b is sharply peaked at 1.80 Å with a second peak around 3.3 Å. The area under the first peak indicates exactly one hydrogen bond per O atom. The H–H distribution is also consistent with filamentary hydrogen bonding structure. The area under the main peak at 2.45 Å in Fig. 4c indicates a coordination number of about 2.

While the O–H group in methanol is striving to achieve a hydrogen bonding network the methyl groups are attempting to close-pack. The Me–Me distribution shown in Fig. 5a is much like that found

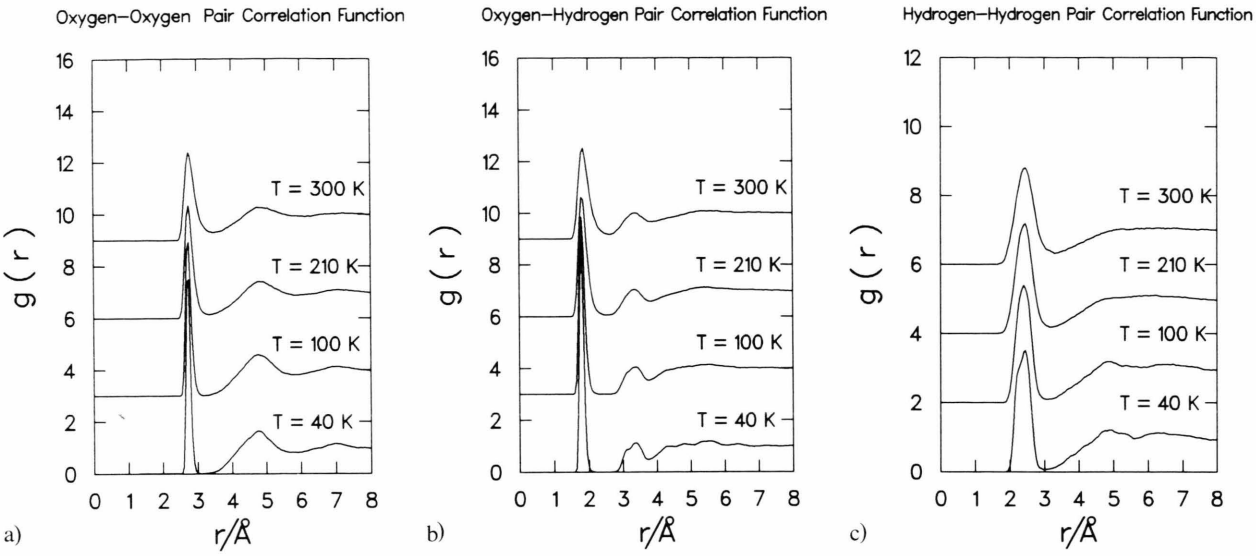

Fig. 4. Atom–atom distribution functions for methanol at 300, 210, 100 and 40 K: (a) O–O, (b) O–H and (c) H–H.

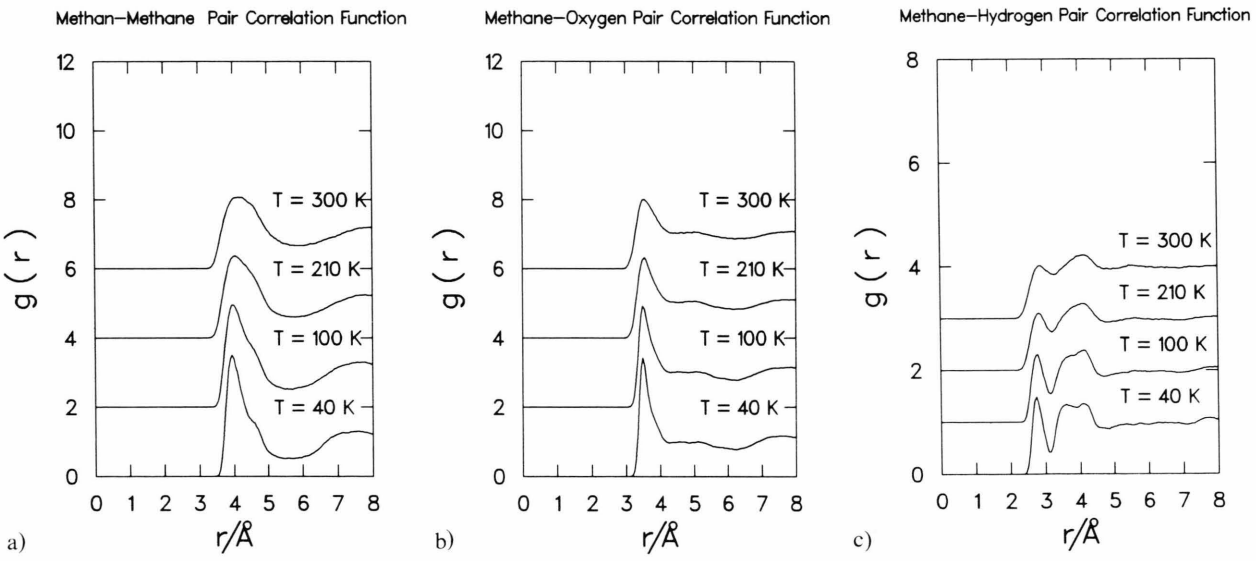

Fig. 5. Atom–atom distribution functions for methanol at 300, 210, 100 and 40 K: (a) Me–Me, (b) Me–O and (c) Me–H.

for an atomic liquid, as is the number of neighbours that are indicated by integration of $g(r)$ out to the first minimum, namely about 11. However, in contrast to an atomic fluid, Fig. 5a shows that the quenching of liquid methanol does not lead to a split second peak, such as shown in Fig. 1, but rather a split first peak. A rough partitioning of the first-peak area suggests 5 or 6 neighbours under each peak of the doublet that occurs at 4 Å and 4.5 Å, when $T = 40$ K. Because of the number of neighbours involved, the splitting cannot arise solely from Me ··· Me interactions along the hydrogen-bonded chains. The Me–O distributions shown in Fig. 5b indicate a main peak around 3.5 Å and a shoulder around 5 Å; integration out to 4 Å yields a coordination number of about 5. The Me–H distribution shown in Fig. 5c for liquid methanol is very reminiscent of the H–H function found in water and is characteristic of a hydrogen bonded system. At low temperatures, the main peak occurs at 2.75 Å. In the glassy state, the first peak simply sharpens but

the second peak splits into a doublet at about 3.6 Å and 4.1 Å. The latter two distances can arise if methyl groups are arranged in trans positions along the hydrogen bonded ··· O–H ··· O–H ··· O–H ··· chains.

5. Discussion

The constant-pressure molecular dynamics technique has been used to study structural changes that accompany the quenching of methanol from room temperature. The main structural features that emerge in the supercooled liquid or glassy solid appear to be a direct consequence of the competing interactions between the close-packing requirements demanded by the methyl groups and the more open (filamentary) structure ··· O–H ··· O–H ··· O–H ··· required by the hydrogen bonds. In the glassy state, we have identified the presence of a novel structural feature in the distribution function for the methyl groups, namely a split *first* peak. Unfortunately, this feature is too small to be extracted from existing neutron diffraction data [10] and will likely be very difficult to observe experimentally. The neutron data have so far yielded low-resolution real-space correlation functions for the liquid at 293 K and the amorphous solid at 10 K. Peaks in the amorphous structure were shifted to smaller r-values with the ratio of peak positions in the two distributions being 0.92. This value agrees exactly with the ratio of the Me–Me peak positions shown in Figure 5a. In addition to the split Me–Me peak, we also observe a splitting of the second peak in the Me–H distribution. The structure of glassy methanol, like the liquid [12, 13], appears to be somewhat akin to a tangle of clothes-lines with pegs on them; the lines are winding hydrogen-bonded ··· O–H ··· O–H ··· O–H ··· chains and the pegs are the methyl groups. Because the hydrogen bonds are so strong relative to the other interactions, the supercooled liquid is not unlike a polymer.

The preliminary results we have presented here clearly demonstrated the feasibility of studying glassy methanol using simulation methods. Indeed, we have already obtained some useful structural information. However, much still remains to be done; the nature of the structural arrest for translational and reorientational motion has yet to be explored in detail [6, 7]. Here, it is likely that some new concepts will emerge involving coupled translational and orientational degrees of freedom. Orientational glassy crystals are well known and have interesting characteristics of their own [16]. It remains to be seen whether or not any of the analysis that has been developed for these systems can be carried out over to the case of methanol.

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