Synchrotron X-Ray Diffraction Study of Liquid and Glassy Toluene

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Abstract

We have measured the X-ray diffraction data of toluene liquid at several temperatures between 300 K and 180 K and those of glasses prepared by liquid-quenching (LQ) and vapor-deposition (VD) at 3 K. The VD glasses annealed at 90 K and 112 K were also measured at 3 K. Throughout the measurements, we used a custom-made cryostat for VD experiments and a high energy X-ray diffractometer at BL04B2, SPring-8. The structure factor $S(Q)$ of each state was successfully fitted with potential fitting with molecular dynamics simulation and reverse Monte Carlo methods. Interestingly, in both liquid and glassy states, the most preferred intermolecular structure is not a parallel one, which is the most stable dimer in vacuo, but the T-shaped one in which two hydrogen atoms of a benzene ring are pointing toward a benzene ring of a neighboring molecule. The abundance of the T-shape and side-by-side structures increase with a decrease of temperature and annealing of the VD glass. As one possibility, we propose that the T-shape structure can be constructing elements of cooperatively rearranging region (CRR) which is conceived in Adam-Gibbs theory.

1. Introduction

The nature of glass transition is an important unsolved topic in condensed matter physics. The super-Arrhenius behavior is one of the characteristic features of the α-relaxation in super-cooled liquids. Angell has proposed a parameter "fragility" to describe this character [1]. Several theories have also been raised to explain this phenomenon [2]. An important one of them is Adam-Gibbs theory, which conceives "cooperatively rearranging region" (CRR) whose size goes to infinity at the Kauzmann temperature, explaining the divergence of relaxation time observed experimentally [3]. The formation of CRR (reflecting the heterogeneity in a supercooled liquid) has been probed by calorimetry [4][5], computer simulations [6][7] and other methods, but few direct observations by diffraction methods has been reported.

It is important for structural work on the glass transition to treat with simple molecular liquids whose intra-molecular information is easily known to analyze the inter-molecular part which is our main interest. X-ray and neutron scattering works reveled that orientational correlation exists for several molecular liquids such as halogens [8], CS_2 [9], acetone, DMSO [10], benzene and naphthalene [11]. It is expected that more definite local structure is observed in supercooled and glassy states. For amorphous metals, it was found that atoms tend to form icosahedron clusters [12]. However, compared with amorphous metals, molecular systems possess rotational degree of freedom, and little is known about the structures of simple molecule glasses due to their easy crystallization. Furthermore, there have been little experimental data on the temperature dependence of the structures of simple molecule liquids.

Toluene is an interesting molecule. Even though it is a simple rigid molecule, its glassy state can be made by liquid-quenching (LQ), thus enabling us to compare the structures between the liquid and glass. Toluene is also found to be a fragile liquid with fragility m = 122 [13] and have a large CRR size of $z^* \approx 7$ at low temperature [5]. So, it is expected that pronounced local ordering should appear in glassy state. For toluene dimer, the structure optimized at MP2 level is a parallel one [14][15][16]. The structure of liquid toluene has been studied as well [17], with the results that parallel configurations are preferred at small molecular separations, while aromatic rings are predominantly perpendicular for larger separations, which is not the same as the case of the dimer. It is unknown what structure change occurs at low temperatures and in the glassy state.

In this study, glass was produced not only by liquid quenching but also by vapor deposition (VD). This method differs from the VD techniques employed for forming films of inorganic materials or metals; it is considered a method of ultra-rapid cooling of molecular liquids. Although the deposition rate varies depending on the conditions, it can reach as high as 10^7 K/s at its fastest. This allows even low-molecular-weight compounds, which would normally crystallize upon cooling, to be vitrified. The most typical example is the creation of amorphous ice (glassy water) [18-20]. Using this technique, our group has produced glasses from low-molecular-weight compounds that traditionally crystallize under conventional rapid cooling methods, and has studied their heat capacity [5,21], structures [9,22,23], and low-energy excitations (by inelastic neutron scattering) [24,25]. Our results have revealed that VD glasses possess very high enthalpy, exhibit a more disordered structure than liquid-quenched glasses, and display a boson peak at lower energies than liquid-quenched glasses. Another major topic in VD molecular glasses is the ultra-stable glasses, pioneered by Ediger and coworkers [26-28]. Since extensive research has been conducted on this topic, we refer here a review paper by Ediger [29] and recent papers by his group [30-33]. While the formation of the low-molecular-weight glasses mentioned above is performed at the lowest possible temperatures (such as 5 K), ultra-stable glasses are prepared at temperatures 0.8–0.9 times the glass transition temperature. It is believed that this results in a structure with relatively well-ordered molecular alignment on the substrate, which is then instantaneously quenched. It should be noted that the purpose of this toluene experiment is entirely different. Since toluene, the subject of this study, can be prepared by both liquid quenching and vapor deposition, we can discuss the structural differences between these methods, as well as the differences between structural relaxation due to annealing and structural changes due to cooling.

Our objective is to study the local structures of liquid and glassy toluene from experimental data and its dependence on temperature and preparation methods. We utilized a high-energy X-ray diffractometer at SPring-8, BL04B2 combined with a custom-made cryostat to obtain the structure factors of the liquid, LQ and VD glasses of toluene. Potential fitting with molecular dynamics simulation and reverse Monte Carlo modeling were used to get the actual local structure from the experimental data.

2. Experimental

2.1 Sample preparation

2.1.1 Liquid and LQ Glass

The toluene sample was purchased from Sigma-Aldrich (purity: 99.8%). The sample was sealed in a glass capillary tube with ϕ = 2 mm and t = 0.01 mm for the measurement at room temperature (300 K). For the measurement at lower temperatures, a thicker capillary tube with ϕ = 2.7 mm, t = 0.1 mm was used to avoid breaking of a capillary tube. The sample was cooled and temperature-controlled with a cryostat with a closed-cycle refrigerator. We measured the diffraction data of liquid states at 250 K, 210 K and 180 K (just above the melting temperature T_m = 178 K). After the measurement at 180 K, the sample was cooled down to 14 K with a cooling rate of about 5 K・s^{-1} to prepare a LQ glass. No crystallization occurred during this process.

2.1.2 VD Glass

The custom-made cryostat for vapor deposition and in situ X-ray measurement is described elsewhere [9]. The sample vapor (after degassing) was deposited slowly on a substrate at 3 K using a custom-made gas line with two precision needle valves. The gas pressure during the deposition was about 60 Pa and deposition time was 12 h. The thickness of the sample is estimated to be about 100 μm; the deposition rate is about 2 nm s^{-1}. After the X-ray diffraction measurement of the as-deposited sample at 3 K (abbreviated as "As-depo" sample), the sample was heated and annealed at 90 K for 2 h which was known to be long enough for the structural relaxation in the previous measurements. Then the sample was cooled to 3 K again for the measurement of the annealed sample ("Ann-90 K" sample). Next, the sample was annealed at 112 K and cooled again to 3 K for the measurement ("Ann-112 K" sample). These annealing temperatures were selected because they were near the glass transition temperature (T_g = 117 K), where structural relaxation is observed, and still lower than the crystallization temperature. Finally, the sample was crystallized by annealing at a temperature between 120 K and 125 K for 10 min.

2.2 Synchrotron X-Ray Diffraction Measurement

All the X-ray diffraction experiments were conducted using a high-energy diffractometer at BL04B2, SPring-8. The energy of the incident beam was 61.4 keV, corresponding to a wavelength of 0.2 Å, and the scattering angle was 0.2 to 49°, covering a momentum transfer (Q) range of 0.1 to 25.7 $Å^{-1}$. The conditions for the measurements are summarized in Table 1.

Table 1 Conditions for the X-ray diffraction measurements.

Sample	Liquid/LQ Glass	VD Glass (As-depo/Ann-112 K)	VD Glass (Ann-90 K)
Angle Range (◦)	0.200 – 48.955	0.300 – 49.012	0.300 – 49.012
Sampling Step (◦)	0.05	0.1	0.1
Time (h)	4	9.7	7.8

3. Results and Discussion

3.1 Structure Factors and Inter-Molecular Reduced Pair Correlation Functions

Figures 1(A) and 1(C) show the structure factors $S(Q)$ of liquid toluene at different temperatures and glassy toluene annealed at different temperatures, respectively. They were successfully normalized by using the form factors of isolated atoms. The counting statics for the VD sample is acceptable even though its sample amount is much smaller than that for the LQ sample. The first peak position of the LQ sample shifted to the high-Q side, reflecting density increase, as temperature decreases, while that of the VD sample slightly shifted to the low-Q side, reflecting density decrease with annealing at higher temperatures. The actual density was estimated from the refs [34,35] and relative scattering intensity at high the scattering intensity at high-Q region ($Q >$ 20 $Å^{-1}$) where no intensity modulation is observed: 8.624 g cm^{-3} (L, 300 K), 9.069 g cm^{-3} (L, 250 K), 9.443 g cm^{-3} (L, 210 K), 9.733 g cm^{-3} (L, 180 K), 1.046 g cm^{-3} (LQ, 14 K), 1.042 g cm^{-3} (VD as-depo, 3 K), 1.051 g cm^{-3} (VD ann-90 K, 3 K), 1.046 g cm^{-3} (VD ann-112 K, 3 K, assumed to be the same as the LQ glass from the reduced pair correlation function at small r). The shoulder of the first peak increases as temperature decreases in liquid, and it is significantly enhanced in the LQ glass. For the VD glasses, the first peak and its shoulder are increased to reach those of the LQ glass by the annealing. The appearance of the shoulder indicates that the correlation beyond the nearest neighbor shell is developed by decreasing temperature or annealing.

The reduced pair correlation function $G(r)$ can be obtained from $S(Q)$ by Fourier transform:

$$G(r) = 4\pi\rho r(g(r) - 1) = \frac{2}{\pi}\int \mathrm{d}Q\ [S(Q) - 1] \cdot Q \sin(Qr).$$

As we are only interested in inter-molecular part, subtraction of intra-molecular part was performed. In this process, we regarded the toluene molecule as a rigid body and subtracted intra-molecular $S(Q)$ before Fourier transform. The molecular geometry was calculated at MP2 level with 6-31G* basis set by NWChem package [36], constraining that the benzene ring and the methyl carbon atom are coplanar and the methyl group has C_{3v} symmetry. The validity of the rigid-molecule approximation is confirmed by the fact that the experimental and calculated values agree in the high-Q region as shown in the inset of Fig. 1(A). Furthermore, before Fourier transform, the small angle scattering part in the VD glass data, which is due to the porous and inhomogeneous structure created by the VD process, was removed, and the $S(Q)$ curve was extrapolated to $Q = 0$ to prevent producing an artifact of long-range ordering.

Figures 1(B) and (D) show the calculated $G_{\mathrm{inter}}(r)$, where the Lorch window function is used for smoothing. The LQ glass at 14 K has definite triple peaks located at around 4, 5 and 6 Å. The first and the second peaks are enhanced in the cooling process from the liquid at 300 K to the LQ glass at 14 K. The VD glasses have clearer triple peaks, and the annealing increased mainly the second peak.

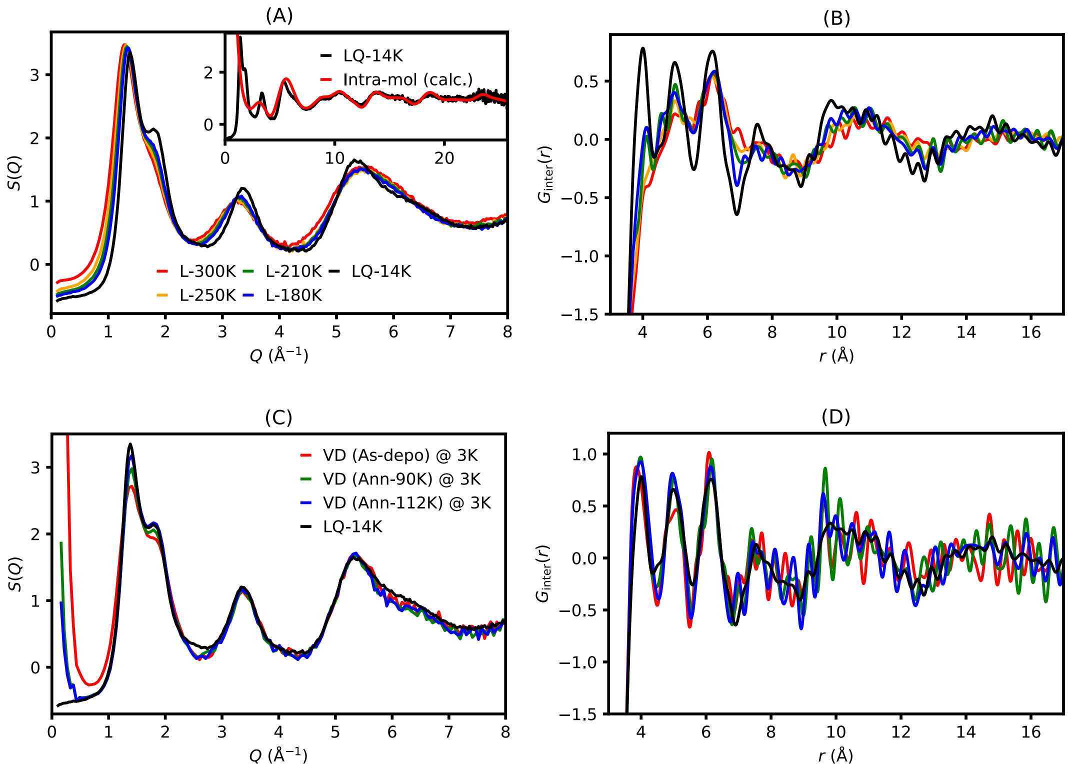

Figure 1: (A) The structure factors $S(Q)$ of the liquids and LQ glasses of toluene. The inset shows the comparison with the calculated intra-molecular contribution which dominates in the high-Q region. (B) The inter-molecular reduced pair correlation function $G_{\text{inter}}(r)$ calculated from the $S(Q)$ with the Lorch window function. (C), (D) The $S(Q)$ and $G_{\text{inter}}(r)$ of the vapor-deposited glassy toluene prepared with different annealing conditions. The larger noise in the VD glasses is due to much smaller sample amount. The data of the LQ glass is also shown for comparison.

3.2 Molecular Dynamics and Structure Refinement

To obtain the actual molecular configuration, we first performed Molecular Dynamics (MD) simulations using the LAMMPS package [37] and the Amber force field [38], which gives a fair description of the interaction energy [14]. However, the MD cannot fully reproduce experiment results, especially for low temperature states, so we performed structural refinement to fit the experimental data. Before the fitting, the $S(Q)$ data were corrected by setting $g_{\text{inter}}(r) = 0$ for $r \leq 1.4$ Å to remove the artifacts from the experimental data.

The structure may be refined by either extracting effective potential from experimental data or moving atoms directly to fit the $S(Q)$. For the liquid and LQ glass, as the only different parameters are the temperature and density, it is clearly desirable to reproduce the experimental $S(Q)$ using only one effective potential. We used a potential iteration method [39] and MD simulation with 500 molecules and NVT ensemble at experimental density to fit all the data simultaneously by a single interatomic potential U_{eff}. The contribution from hydrogen atoms to the $S(Q)$ is fully considered. For the glassy state, as the system is locally trapped, we quenched the structure equilibrated at 400 K down to 14 K in 1 ns simulation using the potential U_{eff} augmented by penalty of reverse Monte Carlo (RMC) method [40] to accelerate the relaxation process as proposed in ref [41]. After the quenching, the penalty term is turned off and the structure is finally re-equilibrated at 14 K. We averaged 5 independent simulations to reduce statistical noise, and all the $S(Q)$ data were successfully fitted as shown in Fig. 2. The simulated pressures under the effective potential U_{eff} were also reasonable (between -0.1 and 0.1 GPa).

For the VD glasses, the structural difference is due to the preparation conditions, and the sample may contain some distortion. Therefore, the experimental data cannot be reproduced by the fitted potential U_{eff}. So, these structures are refined by the RMC-like method where the procedure is almost identical to that for LQ glass explained above except that the RMC penalty is not turned off during the final equilibration. We have used a cooling time of 1 ns for both annealed samples, but for the as-depo sample, 1 ns quenching makes the shoulder of the first peak in $S(Q)$ too pronounced while 0.1 ns quenching gives better fitting. The fitting for the VD glasses are also satisfactory as shown in Fig. 2 (B).

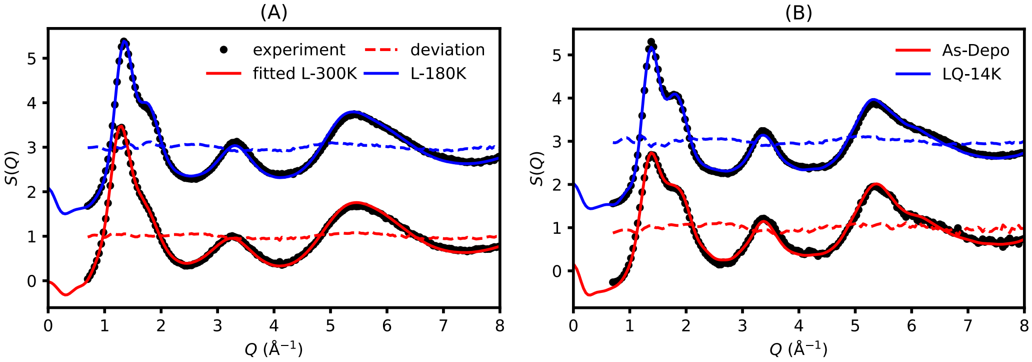

Figure 2: Fitting results under several conditions. The low-Q part of experimental data, which were not used for fitting, is not shown.

3.3 Structure of Liquid and LQ Glass

To discuss the orientational correlation between two neighboring molecules, we first treat the molecule as a disk and only consider the azimuthal angle. As shown in Fig. 3, we use the angle θ defined as the angle between the plane-normal vector and the line connecting two ring centers. The advantage of using the angle θ is that it contains the information of the relative position of the neighboring molecules as well as their relative orientation given by the dihedral angle ϕ. For each molecule pair, two angles θ_1 and θ_2 are defined, and we can draw an abundance map of nearest neighboring molecules on the ($\cos\theta_1$, $\cos\theta_2$) plane to see the preferred local structure. As shown in Fig. 4(A), the point (1,1) represents the parallel structure with benzene rings facing directly to each other, (1,0) and (0,1) are for the T-shaped structures, and (0,0) stands for the side-by-side structure (no restriction on dihedral angle ϕ). If the configuration is completely random, the abundance map will be constant and featureless.

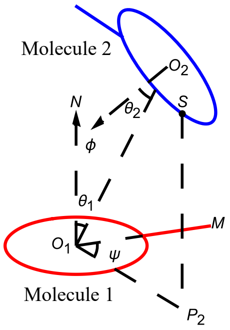

Figure 3: The definition of the angles to represent intermolecular orientational correlations. θ_1 is defined as the angle between the line connecting two ring centers O_1O_2 and plane-normal vectors O_1N; the dihedral angle ϕ is defined as the angle between the two plane-normal vectors. To define angle ψ, we first find the aromatic carbon on molecule 2 which has the shortest distance to aromatic carbons on molecule 1 (denoted by S in the figure), project it onto the plane of molecule 1 (denoted by P_2) and angle $\psi = \angle P_2O_1M$ where M denotes the methyl carbon.

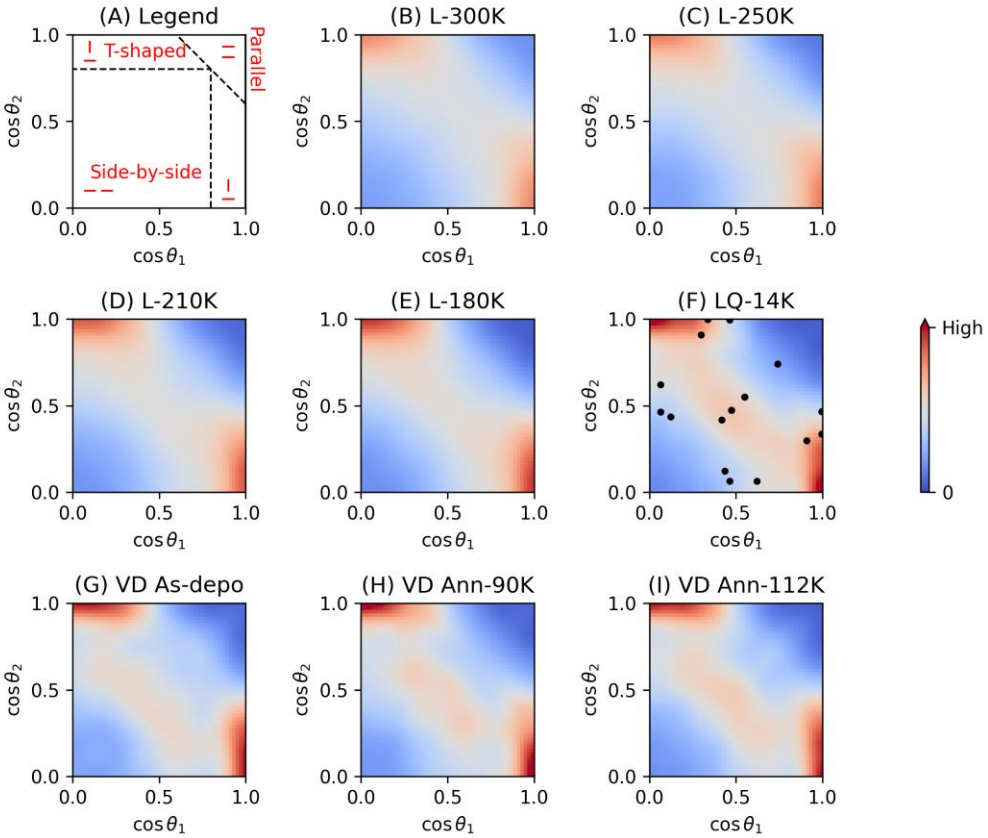

Figure 4: The abundance map of neighboring molecules on $(\cos\theta_1, \cos\theta_2)$ plane. (A) schematic configuration on the diagram and its classification. (B) – (E) abundance map of liquid at different temperatures. All maps are normalized so that the integrated value across the whole map is unity. (F) same for LQ glass. (G) – (I) same for VD glasses. The dots represent the configurations in the crystalline state.

Figure 4 (B) – (F) shows the abundance map for the orientational correlation of nearest neighbor molecules that is defined as the ones with aromatic C–C atom distance below 4.5 Å, in the liquid and glassy states. The abundance map shows that the orientational correlation is almost isotropic with a slight preference on the T-shaped structure in liquid states at high temperature. This is consistent with the previous result obtained from a neutron scattering study [17]. At low temperature, the T-shaped structure becomes more preferred and nearly side-by-side ($\theta_1 \approx \theta_2 \approx 70°$) structure appears as shown in the middle of the map. These two configurations are much more preferred in the LQ glass. It is interesting that these configurations are not stable in toluene dimer;

the most energetically stable dimer is a parallel structure with ($\theta_1 \approx \theta_2 \approx 25°$) [14]. The parallel structure is rather decreasing on cooling as shown by the upper right corner of the map. The dots in Fig. 4 represent the relative orientation of toluene molecules in the crystal [42], which is clearly similar to the one found in the present study for the liquid and glass.

To investigate shorter ranged (T-shaped) correlation more precisely (as only the azimuthal angle was considered above), we now discuss the distribution of the polar angle ψ, which is defined in the caption of Fig. 3. Here, we only take into account the neighbors with $|\cos\theta| \leq 0.5$ because the polar angle for neighbors on the top of another (θ close to 0°) does not make sense. The benzene dimer [15] is known to have a perpendicular structure with a hydrogen atom pointing to the ring center of another molecule, which corresponds to $\psi \approx n\pi/3$ with an integer n. Figure 5(A) shows the distribution of ψ for the neighboring molecules. The preferred positions clearly appear at $\psi \approx n\pi/3+\pi/6$, which means that two, not one, hydrogen atoms are pointing to the neighboring molecule as shown by the inset of Fig. 5(A). Thus, the local structure of toluene is different from that of a benzene dimer. This trait is shared with toluene crystal. And the preference is much more prominent in glassy state. It should be noted that this local structure explains the three definite peaks as well as the fourth peak in $G_{\text{inter}}(r)$ as shown in Fig. 5(B).

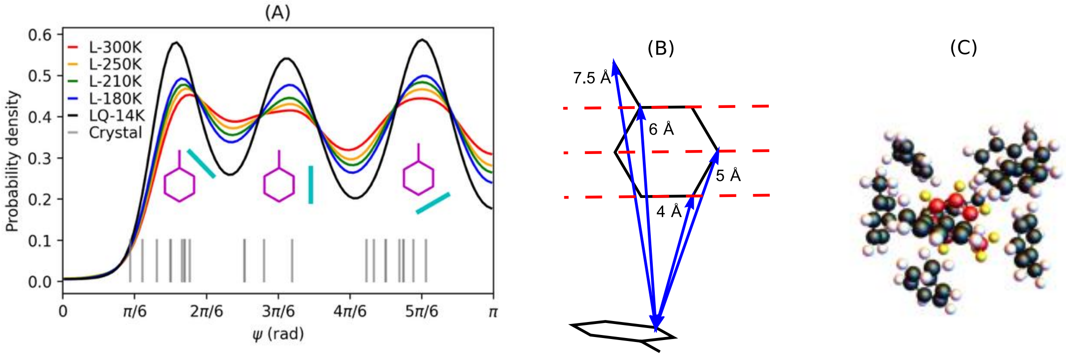

Figure 5: (A) The angle ψ dependence of the number of the contacting carbon atoms of a neighboring molecule that is placed on the side of the reference molecule. The gray vertical lines are configurations in the crystalline state, and the inset shows the corresponding structures of the three peaks. (B) The preferred local structure, which is directly related to the triplet peaks of $G_{\text{inter}}(r)$ in the glassy state. (C) An example of toluene cluster which is found in a simulation box. The center molecule is colored red and yellow for clarity.

As temperature is decreased, this preferred local structure should be grown and hinder the rotation of the molecule along the plane-normal axis. It is noteworthy that 3-dimensional T-shaped cluster can be formed easily as shown Fig. 5(C). These facts may be related to the fragile nature of the relaxation time and prominent CRR formation in the supercooled liquid of toluene which were observed in our previous thermodynamic study [4][5].

3.4 Structure of VD Glass

Figure 4 (F)–(I) gives the comparison in abundance map of ($\cos\theta_1$, $\cos\theta_2$) among the VD glasses and LQ glass. The difference between VD glasses is small compared with the one between the liquid and glass. We first discuss the annealing effects on local structures. The abundance map shows that 90 K annealing greatly increased the T-shaped structure. The side-by-side structure (around the center region of the map) is also found to increase and slightly shift to upper right corner in the map, for both 90 K and 112 K annealing. These changes are consistent with the change in $G_{\mathrm{inter}}(r)$ because the triplet peak is formed by the correlation from the side of the benzene ring in a molecule. However, the parallel configuration, from the site correlation of the parallel pairs $g_{\mathrm{inter},||}(r)$ in Fig. 6(A), we see that annealing makes the first peak decrease in intensity and shift to larger r, meaning that the parallel structure is being broken down. This resembles the change in the glass transition from liquid to LQ glass as also shown in Fig. 6(A). In this case, however, the peak position shifts to smaller r due to the thermal expansion effect of liquid.

Next, we compare the structure of the VD (Ann-112K) and LQ glass. Firstly, from Fig. 6 (A), the structure of Ann-112 K VD glass has more parallel configurations (similar to the annealing effect). Secondly, the T-shaped and side-by-side structures of VD glass seems to be more distinct in the ($\cos\theta_1$, $\cos\theta_2$) abundance map (e.g. the red part of T-shaped and side-by-side in the map is somewhat connected for the LQ glass but clearly separated for the VD glass), which in turn cause the site correlation $g_{\mathrm{inter}}(r)$ become more undulated (see Fig. 6(B)) as observed by the experimental $G_{\mathrm{inter}}(r)$ in Fig. 1(D). Interestingly, we find that the difference in $G_{\mathrm{inter}}(r)$ may be affected by the boundary condition in the MD simulation. We isolate the unit cell of the Ann-112K structure built by RMC and run the MD simulation with both free (non-periodic) and periodic boundary conditions. As shown in Fig. 6(C), the periodic boundary condition generates a structure similar to the LQ glass (less undulated), while the free boundary condition gives a structure similar to the Ann-112 K glass (more undulated). This means that it may be necessary to consider the interaction with the voids in the sample to investigate the structure of the VD glass. Indeed, as shown in Fig. 2(A), the VD glasses have intense small angle scattering showing the exitance of voids, and it decreased upon annealing.

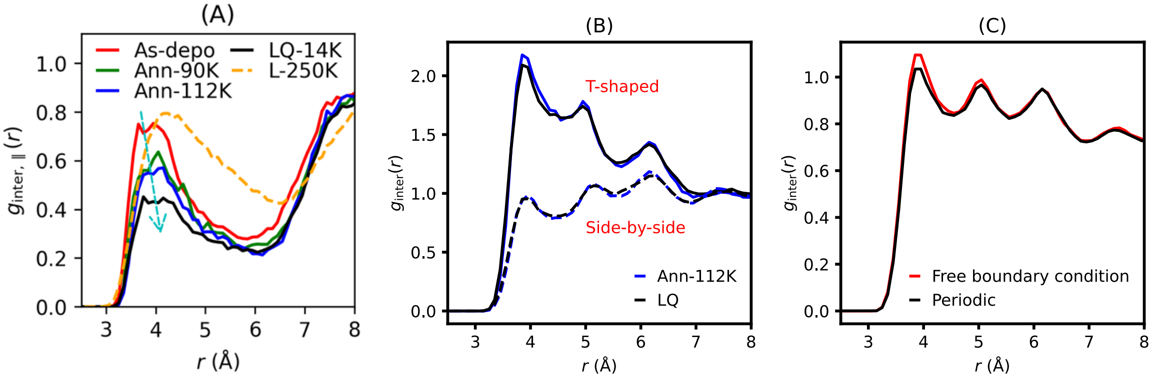

Figure 6: (A) C–C site correlation of parallel molecule pairs in glasses. The arrow indicates the changes from As-depo sample to LQ sample. (B) C–C site correlation of T-shaped and side-by-side molecule pairs in Ann-112K and LQ-14K glasses. The data of the VD glass is slightly more undulating. (C) Comparison of $g_{\mathrm{inter}}(r)$ of MD simulation with free and periodic boundary conditions. The $g(r)$ of the latter is calculated using only one MD cell without periodic images.

Finally, we discuss the relation between the preferred structures (T-shaped and side-by-side) found in this study and the cooperatively rearranging region (CRR). Because the T-shaped structure is much more preferred than side-by-side structure and energetically more stable. As one possibility, we propose a model in which the T-shaped structure constitutes the elements of the CRR, while the parallel structure functions as the boundary between CRRs. Since the annealing of VD glass involves structural changes during the vitrification of the liquid, it can also be said that annealing increases the CRR. It should be pointed out that spherical clusters can be constructed as shown in Fig. 5(C); it is difficult to construct three-dimensional clusters using parallel structure. This fact can also explain the origin of high fragility and large CRR size in other glass-forming liquids with benzene rings, such as orthoterphenyl [43], ethylbenzene [5], triphenylphosphite [44].

4. Conclusion

The structure factors *S*(*Q*) of toluene liquids at different temperatures and glasses prepared by liquid-quenching and vapor-deposition methods were measured using synchrotron X-ray diffraction technique. The diffraction pattern of each state is successfully fitted with the potential fitting and RMC methods. The structure of most stable parallel dimer is neither found in liquids nor glasses. The most preferred local structure in both liquid and glass is the T-shaped structures, in which, two hydrogen atoms in a benzene ring of a toluene molecule are pointing toward a benzene ring of a neighboring molecule. The next most preferred one is the side-by-side structure. Cooling the liquid and annealing the vapor-deposited glass increase these two structures. The T-shaped structure may serve as the fundamental structure constituting the CRR and is considered important for discussing the mechanism of the glass transition and the origin of fragility. This study is a rare example of research that has experimentally and quantitatively captured short- and medium-range ordering in both molecular liquids and glasses. Similar studies on the liquids and vapor-deposited glasses of propane and propene, which lack benzene rings, are currently underway.

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