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FAST TRACK COMMUNICATION

Microscopic structural evolution during the liquid–liquid transition in triphenyl phosphite

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Online at stacks.iop.org/JPhysCM/19/152101**Abstract**

Recently the liquid–liquid transition (LLT) was found in a molecular liquid, triphenyl phosphite, which allows us to follow the kinetics of the transformation of one liquid to another. Here we investigate the microscopic structural change during the LLT by means of time-resolved synchrotron x-ray scattering measurements. We confirm that during spinodal-decomposition-type transformation a new peak corresponding to a particular intermolecular phosphor–phosphor distance emerges and grows with time. This indicates that short-range order develops in the liquid during LLT. We show that the short-range order does not represent the crystalline structure, but the locally favoured structure. We found that the temporal increase of the intensity of this peak, i.e., the fraction of locally favoured structures, is proportional to that of the heat released during the transformation. This means that the formation of locally favoured structures is the origin of the heat release. This is consistent with the proposal that the order parameter governing LLT is the number density of locally favoured structures. This yields a valuable insight into the nature of the ordering in the liquid–liquid transition.

(Some figures in this article are in colour only in the electronic version)

Contrary to a common sense view that any single-component substance has only one unique liquid state, it has recently been revealed that even a single-component liquid can have more than two liquid states [1–21]. The transition between these liquid states is called the ‘liquid–liquid transition (LLT)’. Many examples of LLTs have been reported for atomic liquids [1–8]. Among them, one of the most convincing examples is LLT in liquid phosphor (P) [5, 6]. Since the LLT exists at a high pressure and high temperature, however, it is not easy to study the kinetics of the LLT. For molecular liquids, on the other hand, Mishima

discovered the existence of two amorphous states for water [9]. The transition has recently been studied in details [10, 21–25]. Computer simulations also suggest the existence of LLT(s) in water [9, 10, 17–21]. Thus, it is speculated that this mechanical transition between the two amorphous states has a connection to a thermodynamic LLT. However, the LLT is hidden by crystallization in water, even if it exists. This makes an experimental study on the LLT extremely difficult especially for bulk water. Theoretically, on the other hand, generality of LLT, or possible existence of LLT in various types of liquids, was recently discussed on the basis of phenomenological [12, 13] and analytical models [15, 16].

Recently, we found firm evidence of the existence of the LLT in typical molecular liquids, triphenyl phosphite (TPP) [26–28] and *n*-butanol [29], which takes place at ambient pressure. Different from the above examples, we can investigate the kinetics of the LLT in detail since the LLT is easy to access experimentally. We found two types of the transformation pattern; one is nucleation–growth (NG) type, the other spinodal-decomposition (SD) type. Liquid II nucleates in liquid I in the form of spherical droplets and they grow with time with a constant growth speed for $T > T_{SD}$, where T_{SD} is the spinodal temperature. The system eventually becomes almost homogeneous liquid II in the final stage of LLT. This is characteristic of the ordering of a non-conserved order parameter. It should be noted that this final state contains a small fraction of microcrystallites [26]. For $T < T_{SD}$, on the other hand, SD-type transformation takes place. In the early stage, fluctuations grow exponentially and its characteristic length remains constant: Cahn’s linear regime. Then, domains coarsen in proportion to $t^{0.5}$; this is again characteristic of the SD-type ordering of a non-conserved order parameter. The system becomes homogeneous liquid II in the final stage also for SD-type LLT. In this case, the final state is a homogeneous glassy state of liquid II free from microcrystallites [26]. Both of NG-type and SD-type ordering suggest that the LLT is governed by a non-conserved order parameter. This indicates that we need a new non-conserved order parameter to describe the LLT. We proposed [12, 13] that the fraction of locally favoured structures (LFSs) should be the order parameter responsible for LLT, which we call bond order parameter S . This means that to specify a state of a liquid uniquely, the density is not enough and we need two order parameters, namely, density ρ and bond order parameter S . We note that it is widely recognized that there exist short-lived LFSs in many liquids; for example, tetrahedral structures in water, silicon, phosphor, and SiO_2 , and icosahedral structures in metallic liquids [1]. For water, the relevance of such a picture was further studied numerically [30] and also analytically [31, 32]. We consider a two state model: a liquid is composed of normal-liquid structures (NLSs) and LFSs. Then LLT can be regarded as the cooperative ordering of LFSs. We note that the order parameter S should be non-conserved (different from a simple mixture model), since LFSs can be created or annihilated independently. This two-order-parameter model captures all the essential features of the kinetics of the LLT summarized above [26–28]. However, there have been little direct evidence supporting for the existence of such LFSs for TPP and that the number density of LFSs increases upon the LLT. It is the aim of this Communication to confirm the relevance of this scenario experimentally.

There have already been intensive researches on the difference in a structure between the two liquid (or amorphous) states of TPP [33–43]. Some of them favoured the LLT scenario [33, 35, 41–43], whereas the others did not [34, 36–40]. Kivelson and his co-workers reported that a peak appears at the wavenumber $q \sim 1.1 \text{ \AA}^{-1}$ and this peak position is similar to that of a Bragg peak of the *c*-axis of the crystal [34]. Hedoux *et al* proposed on the basis of x-ray scattering measurements that liquid I transforms into a mixture of nanocrystallites and the untransformed liquid (liquid I) [36] and does not into a new liquid (liquid II). We note that their experiments were performed mostly in the temperature region above T_{SD} . We confirmed that microcrystallites (or nanocrystallites) are embedded in liquid II for the NG-type

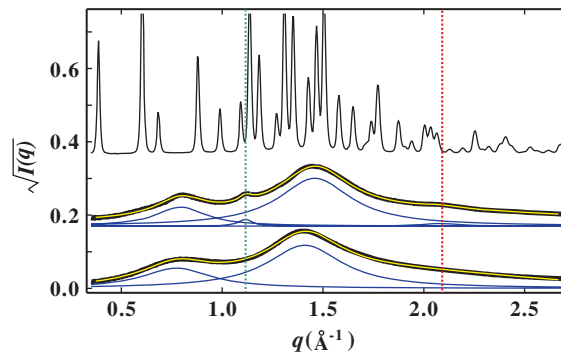


Figure 1. The scattering amplitude $\sqrt{I(q, t)}$ of liquid I at 215 K ($t = 0$ min), liquid II formed at 215 K ($t = 300$ min) and the crystal formed at 273 K (from bottom to top). Here the scattering intensity of the crystal is divided by 20. $\sqrt{I(q, t)}$ of liquid I is fitted by the summation (yellow line; white line in the printed version) of two Lorentzians (blue lines; grey line in the printed version), whereas $\sqrt{I(q, t)}$ of liquid II by the summation (yellow line; white line in the printed version) of four Lorentzians (blue lines; grey line in the printed version). We emphasize that $\sqrt{I(q, t)}$ of liquid II at 215 K has no peaks of the crystal (see the vertical dashed lines).

LLT, whereas there exist no microcrystallites (or nanocrystallites) in liquid II for the SD-type LLT [26]. Senker *et al* proposed on the basis of NMR and x-ray scattering measurements that the transformation is consistent with the LLT scenario and some of the TPP molecules in liquid II favour parallel alignment [41]. Recently, Mei *et al* performed x-ray and neutron scattering measurements over a wide q range and specified the molecular conformations and the local structures of liquid I, liquid II, and the crystal with the help of a reverse Monte Carlo method [42, 43]. They suggested that the conformation of molecules and the local liquid structure in liquid II is different from those of liquid I and the crystal. Although the structural difference between liquid I and II have been studied as briefly summarized above, there have been few studies on the temporal evolution of the microscopic structures in the liquid during LLT except for time-resolved small angle scattering [39] and NMR [41] measurements. Here we report the time evolution of the scattering amplitude $\sqrt{I(q, t)}$ during the LLT in TPP, which was measured by time-resolved synchrotron x-ray scattering.

The sample used is TPP purchased from Acros Organics and used after extracting only a crystallizable part. The temperature was controlled by a computer-controlled hot stage (Linkam LK-600PH) with a cooling unit (Linkam L-600A). We prepared a sample cell which was sandwiched between two sheets of thin mica film and its thickness was controlled to be about 1 mm by using a silicon sheet as spacers. Since the sample was rather thick, the actual temperature of the sample was different from that of the hot stage. We confirmed that the former was 2 K higher than the latter. For comparison to our previous experimental results of thin liquid films, hereafter, we use the actual temperature of the sample after the correction. The wide angle x-ray scattering was measured at BL-15A, Photon Factory (KEK, Tsukuba, Japan). The x-ray beam was focused with a bending mirror and a bending monochromator crystal. The x-ray wavelength was 1.50 Å and the beam size was about $500 \mu\text{m} \times 500 \mu\text{m}$ [44]. We used imaging plates as a x-ray detector [45]. The sample was exposed to x-ray for 30 s and measured the scattering amplitude $\sqrt{I(q, t)}$ every 10 min.

Figure 1 shows the scattering amplitude $\sqrt{I(q, t)}$ of liquid I, liquid II and the crystal of TPP. Liquid II was prepared by annealing at $T_a = 215$ K for $t = 300$ min. At this temperature, the LLT is of SD type. The crystal was prepared at $T_a = 273$ K. $\sqrt{I(q, t)}$ of liquid I has two broad peaks at $q = 0.84$ and 1.38 \AA^{-1} . $\sqrt{I(q, t)}$ of liquid I can be fitted by the summation

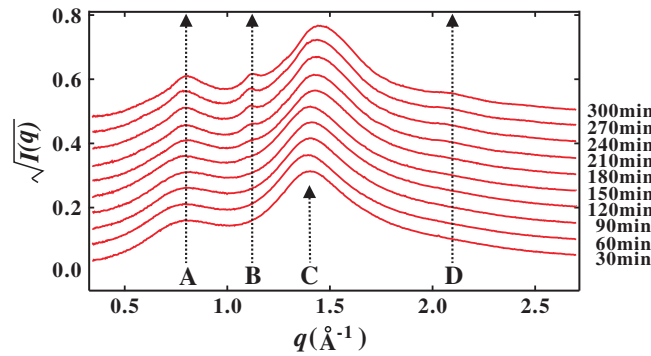


Figure 2. The temporal change of $\sqrt{I(q)}$ at 215 K (every 30 min). The peaks at $q \sim 1.12 \text{ \AA}^{-1}$ and $q \sim 2.05 \text{ \AA}^{-1}$ appear around at $t = 150$ min and then grow with time.

of two Lorentzians (yellow solid line). On the other hand, we need four Lorentzians to express $\sqrt{I(q, t)}$ of liquid II. The peaks are located at $q = 0.84, 1.12, 1.45$ and 2.05 \AA^{-1} , which are named peak A, peak B, peak C, and peak D, respectively. This shape of $\sqrt{I(q, t)}$ is consistent with that reported in previous works [33, 41]. We do not see any Bragg peak of the crystal in $\sqrt{I(q, t)}$ of liquid II. This is consistent with our suggestion that there exist no microcrystallites in liquid II if it is formed below T_{SD} [26].

Figure 2 shows the time evolution of $\sqrt{I(q, t)}$ at 215 K. Reflecting the SD-type LLT, liquid I continuously transforms into liquid II at this temperature. We found that peak B and D appear around $t = 150$ min. Their intensities continuously increase with time, whereas the intensity of peak A decreases. Furthermore, peak C starts to shift toward higher q almost at the same time when peak B and peak D emerge. After $t = 300$ min, there is no change in $\sqrt{I(q, t)}$, indicating that the transformation from liquid I to liquid II is more or less completed around $t = 300$ min.

We analysed the shape of $\sqrt{I(q, t)}$ quantitatively by fitting the sum of four Lorentzians to it. The bottom of figure 3 shows the temporal change of the summation of the intensities of peak A and B (red open circles) and the intensity of peak C (blue circles filled with yellow). They are almost constant with time. This suggests that peak A and B share the same structural origin; more specifically, these peaks stem from the spatial correlation of the intermolecular P–P distance. For liquid I, the P–P distance is estimated as 7.6 \AA from the position of peak A. This may be characteristic of a random arrangement of TPP, which characterizes the structure of liquid I (NLSs). On the other hand, the P–P distance of LFSs is estimated as 5.6 \AA from the position of peak B. The top of figure 3 shows the temporal change in the width of peak A. The width of peak A decreases with time. This seems to suggest that molecules whose intermolecular (P–P) distances are deviated from the average of NLSs tend to form LFSs. The peak wavenumber of peak C also shifts to the higher wavenumber. It is not clear at this stage whether this represents the continuous change of a structure (e.g., conformational change of the molecules [43]) or the change in the distribution of a few distinct structures. The information of a higher q range may play a crucial role in the structural determination of LFSs: wider q range time-resolved scattering experiments remain for the future investigation.

Next we show the time evolution of the intensity of peak B and D in figure 4. We can clearly see that the intensities of peak B and D both increase with time. We found that the behaviour of peak B and D coincides well with that of the heat released during the transformation $H(t)$ (see [28]). This indicates that the evolution of $H(t)$ directly reflects

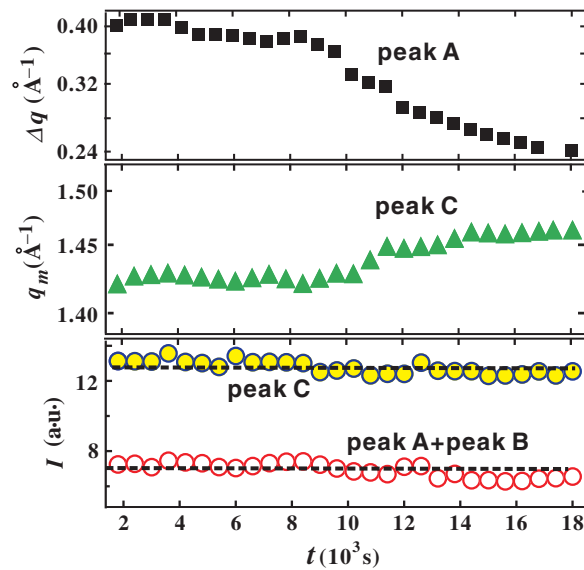


Figure 3. Top: temporal change in the width of peak A. Middle: temporal change in the peak wavenumber of peak C. Bottom: temporal change of the summation of the intensities of peak A and B (red open circles; open circles in the printed version) and the intensity of peak C (blue circles filled with yellow; grey filled circles in the printed version). Both of them are constant with time.

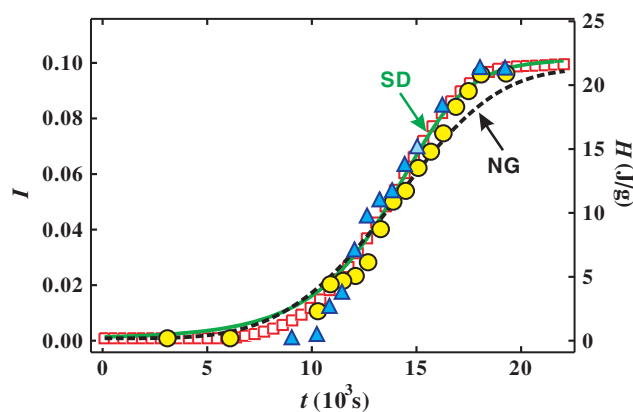


Figure 4. The temporal change of the normalized intensity of peak B (open circles filled with yellow; grey filled circles in the printed version), normalized by the summation of the intensity of peak A and peak B, the intensity of peak D (blue triangles; grey filled triangles in the printed version), and the heat released during the transformation $H(t)$ (red squares; open squares in the printed version) at $T_a = 215$ K. Here the intensity of peak D is scaled so that its final intensity equals to the final normalized intensity of peak B. The behaviour of both peak B and D coincides well with that of $H(t)$ (see [28]). This further indicates that the evolution of peak B and D is proportional to the theoretical prediction for the SD-type evolution of a non-conserved order parameter (green solid line; grey solid line in the printed version). Thus, all the data can be scaled on the theoretical green curve.

the formation of LFSs, whose intermolecular P–P distance gives rise to peak B. This further suggests that the fraction of LFSs (S) may be the order parameter governing LLT, consistent with the two-order-parameter model [12, 13]. Our two-order-parameter model of LLT predicts

that for SD-type LLT the bond order parameter S , which is the fraction of LFS, grows with time as follows:

$$S(t) = \frac{S(\infty)}{\sqrt{1 + \left[\left(\frac{S(\infty)}{S(0)}\right)^2 - 1\right] \exp(-2\gamma t)}}, \quad (1)$$

where $S(0)$ and $S(\infty)$ are the initial and final value of S , respectively, and γ is the growth rate of the S fluctuations. This equation describes the growth of a non-conserved order parameter for SD-type ordering [28, 46]. Indeed, the growth of peak B and D and the evolution of $H(t)$ can all be described by this equation for $S(t)$ (see figure 4). We obtained $\gamma = 3.3 \times 10^{-4} \text{ s}^{-1}$ from fitting. We also confirmed that the evolution of the heat released during the transformation, $H(t)$, generally obeys this relation for $T < T_{SD}$ [28]. The above value of γ at 215 K is the same as that previously obtained by our calorimetric measurements ($\gamma = 3.5 \times 10^{-4} \text{ s}^{-1}$) [28]. From the fitting, we also obtained $S(\infty) = 0.1$: the fraction of LFSs in liquid II is 10%. During LLT, thus, the fraction of LFSs changes from almost 0% to 10%. This is consistent with our previous estimate from the heat measurements that $S(\infty)/S(0) = 200$ [28]. From this, the energy difference between LFS and NLS, ΔE , is estimated to be $68.2/n$ kJ per mole of LFSs, where n is the number of molecules per LFS (n may be the order of 10). Finally, it should be worth mentioning that the fact that the growth of peak D also follows the same function $S(t)$ (see figure 4) indicates that peak D also reflects the structure of LFS, although at this moment we cannot make a specific assignment of this peak.

Next we estimate the coherence length Λ_B of a structure giving rise to peak B from its peak width, using Scherrer relation $\Lambda_B = 0.9\lambda/\beta \cos \theta$ where λ , β , θ are the wavelength of x-ray (1.5 Å), the full width at half maximum, and the scattering angle, respectively. β is 0.210 Å^{-1} for peak B of liquid II. Thus, we obtained $\Lambda_B = 30 \text{ Å}$ and this value is consistent with the previous estimation ($\sim 30 \text{ Å}$) by Hedoux *et al* [37], who interpreted this as the size of nanocrystallites, and the one ($\sim 60 \text{ Å}$) by Yarger and co-workers [39]. We note that Λ_B is almost constant with time. From the similar analysis, we also obtained the coherence length of peak D, $\Lambda_D = 34 \text{ Å}$. The fact, $\Lambda_B \cong \Lambda_D$, is consistent with our interpretation that both peaks come from the internal structure of LFS. Here we briefly discuss the assignment of peak B. First we note that there emerge no Bragg peaks characteristic of the crystal, as can be confirmed in figures 1 and 2, and that the position of peak B and D do not coincide with the peak positions of the crystal (see the dashed lines in figure 1). Furthermore, the intensity growth of peak B and D is better reproduced by the SD-type evolution of the non-conserved order parameter (green line in figure 4) than by the Avrami-Kolmogorov equation for homogeneous nucleation in three dimensions [$I = 0.103(1 - \exp(-1.83 \times 10^{-17}t^4))$] (dashed black line in figure 4), which should describe the nucleation and growth of crystals. This also supports our scenario. From these, we conclude that peak B and D do not reflect nanocrystallites but a structure of LFS. The relation between the coherence length of LFSs, Λ_B , and the bare correlation length ξ_0 of S fluctuations [27], which was determined from the critical-like divergence of S fluctuations, remains elusive. We speculate that LFSs of ~ 3 nm may form large clusters of ~ 60 nm: hierarchical ordering. Further study is necessary for clarifying this problem, which may be a key to the physical understanding of LLT.

Here we roughly estimate the density change from the peak position. Assuming that P is located at the centre of mass of a molecule, the volume per molecule is estimated as 422 Å^3 from the average intermolecular P-P distance (7.5 Å). Thus, the density of liquid I is estimated as 1.22 g cm^{-3} . For LFS, the P-P distance is 5.6 Å. Using this, the volume decrease upon the formation of an LFS is estimated as $\Delta V = 107 \text{ Å}^3$ per molecule. Using the estimation that the fraction of LFSs S is 10% in liquid II, we estimate the density of liquid II as 1.25 g cm^{-3} at 215 K. Kivelson and his co-workers directly measured the density of TPP during the phase

transition and reported that the density changes from 1.256 to 1.288 g cm⁻³ at 218 K [34]. Our estimation is fairly consistent with their results.

In summary, we succeeded in following the time evolution of the scattering amplitude $\sqrt{I(q, t)}$ during SD-type LLT at 215 K. We confirmed that liquid II formed at 215 K does not include any microcrystallites, consistent with our previous report [26]. We found that two new peaks (peak B and D) emerge during the LLT. From the quantitative analysis, we conclude that peak A and peak B both reflect the intermolecular P–P distance and peak B corresponds to the P–P distance of LFSs: liquid II may be composed of NLSs (90%) and LFSs (10%). We found that the temporal change of peak B is proportional to that of the heat released and that the fraction of LFSs continuously changes from almost 0% to 10%. From these results, we conclude that LLT is described by the temporal change of the fraction of LFSs and thus the order parameter governing LLT, which has a non-conserved nature, is the fraction of LFSs.

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References

- [1] Debenedetti P G 1997 *Metastable Liquids* (Princeton, NJ: Princeton University Press)
- [2] Aasland S and McMillan P F 1994 *Nature* **369** 633
- [3] Angell C A 1995 *Science* **267** 1924
- [4] Poole P H, Grande T, Angell C A and McMillan P F 1997 *Science* **275** 322
- [5] Katayama Y, Mizutani T, Utsumi W, Shimomura O, Yamakata M and Funakoshi K 2000 *Nature* **403** 170
- [6] Monaco G, Falconi S, Crichton W A and Mezouar M 2003 *Phys. Rev. Lett.* **90** 255701
- [7] Brazhkin V V and Lyapin A G 2003 *J. Phys.: Condens. Matter* **15** 6059
- [8] Wilding M C, Wilson M and McMillan P F 2006 *Chem. Soc. Rev.* **35** 964
- [9] Mishima O and Stanley H E 1998 *Nature* **396** 329
- [10] Debenedetti P G 2003 *J. Phys.: Condens. Matter* **15** R1669
- [11] Hemmer P C and Stell G 1970 *Phys. Rev. Lett.* **24** 1284
- [12] Tanaka H 1999 *J. Phys.: Condens. Matter* **11** L159
- [13] Tanaka H 2000 *Phys. Rev. E* **62** 6968
- [14] Jagla E 2001 *Phys. Rev. E* **63** 061501
- [15] Franzese G, Malescio G, Skibinsky A, Buldyrev S V and Stanley H E 2001 *Nature* **409** 692
- [16] Malescio G, Franzese G, Skibinsky A, Buldyrev S V and Stanley H E 2005 *Phys. Rev. E* **71** 061504
- [17] Poole P H, Sciortino F, Essmann U and Stanley H E 1992 *Nature* **360** 324
- [18] Tanaka H 1996 *Nature* **380** 328
- [19] Brovchenko I, Geiger A and Oleinikova A 2003 *J. Chem. Phys.* **118** 9473
- [20] Brovchenko I, Geiger A and Oleinikova A 2005 *J. Chem. Phys.* **123** 044515
- [21] Loerting T and Giovambattista N 2006 *J. Phys.: Condens. Matter* **18** R919
- [22] Tulk C A, Benmore C J, Urquidi J, Klug D D, Neufeind J, Tomberli B and Egelstaff P A 2002 *Science* **297** 1320
- [23] Koza M M, Schober H, Fischer H E, Hansen T and Fujara F 2003 *J. Phys.: Condens. Matter* **15** 321
- [24] Suzuki Y and Mishima O 2002 *Nature* **491** 599
- [25] Loerting T, Schustereder W, Winkel K, Salzmann C G, Kohl I and Mayer E 2006 *Phys. Rev. Lett.* **96** 025702
- [26] Tanaka H, Kurita R and Mataka H 2004 *Phys. Rev. Lett.* **92** 025701
- [27] Kurita R and Tanaka H 2004 *Science* **306** 845
- [28] Kurita R and Tanaka H 2006 *Phys. Rev. B* **73** 104202
- [29] Kurita R and Tanaka H 2005 *J. Phys.: Condens. Matter* **17** L293
- [30] Errington J R and Debenedetti P G 2001 *Nature* **409** 318
- [31] Franzese G and Stanley H E 2002 *J. Phys.: Condens. Matter* **14** 2201
- [32] Franzese G, Marqués M I and Stanley H E 2003 *Phys. Rev. E* **67** 011103
- [33] Cohen I, Ha A, Zhao X, Lee M, Fischer T, Strouse J and Kivelson D 1996 *J. Phys. Chem.* **100** 8518
- [34] Demirjian B G, Dosseh G, Chauty A, Ferrer M L, Morineau D, Lawrence C, Takeda K and Kivelson D 2001 *J. Phys. Chem. B* **105** 2107

- [35] Mizukami M, Kobashi K, Hanaya M and Oguni M 1999 *J. Phys. Chem. B* **103** 4078
- [36] Hedoux A, Hernandez O, Lefebvre J, Guinet Y and Descamps M 1999 *Phys. Rev. B* **60** 9390
- [37] Hedoux A, Guinet Y, Derollez P, Hernandez O, Ronan L and Descamps M 2004 *Phys. Chem. Chem. Phys.* **6** 3192
- [38] Alba-Simionesco C and Trajus G 2000 *Europhys. Lett.* **52** 297
- [39] Schwickert B E, Kline S R, Zimmermann H, Lantzky K M and Yarger J L 2001 *Phys. Rev. E* **64** 045410
- [40] Kivelson D and Tarjus G 2002 *J. Non-Cryst. Solids* **307–310** 630
- [41] Senker J, Sehnert J and Correll 2005 *J. Am. Chem. Soc.* **127** 337
- [42] Mei Q, Ghalsasi P, Benmore C and Yarger J L 2004 *J. Phys. Chem. B* **108** 20076
- [43] Mei Q, Siewenie J E, Benmore C, Ghalsasi P and Yarger J L 2006 *J. Phys. Chem. B* **110** 9747
- [44] Amemiya Y, Wakabayashi K, Hamanaka T, Wakabayashi T, Matsushita T and Hashizume H 1983 *Nucl. Instrum. Methods* **208** 471
- [45] Amemiya Y 2005 *J. Synchrotron Radiat.* **208** 13
- [46] Onuki A 2002 *Phase Transition Dynamics* (Cambridge: Cambridge University Press)