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## LETTER TO THE EDITOR

# On the abundance and general nature of the liquid–liquid phase transition in molecular systems

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## Abstract

Even a single-component liquid may have more than two kinds of isotropic liquid states. The transition between these different states is called a liquid–liquid transition (LLT). An LLT has been considered to be a rather rare phenomenon, in particular for molecular liquids. Very recently, however, we found an LLT in triphenyl phosphite, which may be the first experimental observation of an LLT for molecular liquids. Here we report convincing evidence of the second example of LLT for another molecular liquid, n-butanol. Despite large differences in the chemical structure and the molecular shape between triphenyl phosphite and n-butanol, the basic features of the transformation kinetics are strikingly similar. This suggests that an LLT may not be a rare phenomenon restricted to specific liquids, but may exist in various molecular liquids, which have a tendency to form long-lived locally favoured structures due to anisotropic interactions (e.g., hydrogen bonding).

There are a number of experimental indications suggestive of the existence of liquid–liquid transition (LLT) for a variety of liquids covering atomic to molecular liquids [1–8]. Although there are rather clear examples of LLT for atomic liquids [2, 6], there was no direct experimental evidence for molecular liquids. LLT in water has been suggested on the basis of experimental evidence of polyamorphism [5] and numerical simulations [8], but its existence has not been confirmed experimentally yet. Recently, however, we found convincing experimental evidence for the existence of LLT in a molecular liquid, triphenyl phosphite (TPP) [9, 10]<sup>1</sup>. Both nucleation-growth-type and spinodal-decomposition-type phase transformations were directly observed with optical microscopy. In addition to the glass transition of a normal liquid, a distinct thermal signature of the glass transition of a second liquid was also detected. Namely, we confirmed the existence of two glass transitions for a single-component substance. We also

<sup>1</sup> Polyamorphism in TPP was discovered by Kivelson and his co-workers [25]. Since then, there has been active debate on the nature of the newly discovered phase. On this issue, see [9, 10] and the references therein.

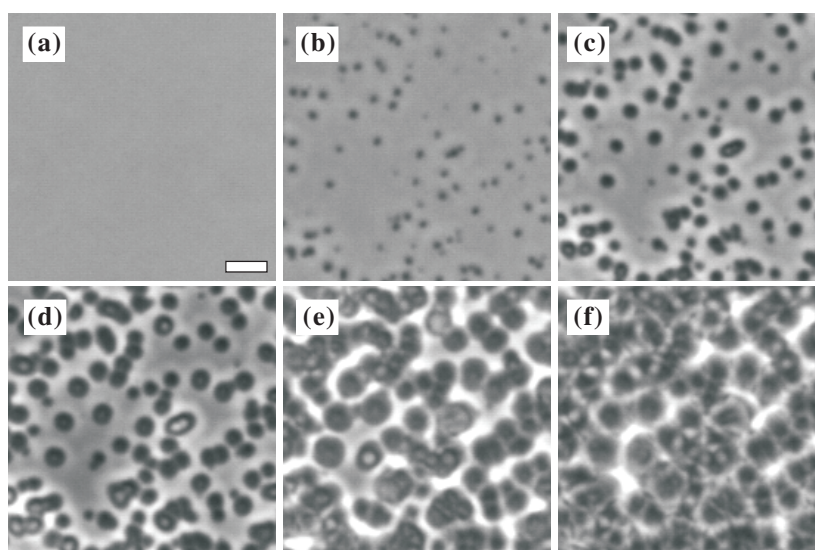
observed a critical-like anomaly associated with the mean-field spinodal behaviour of LLT. All these results suggest that TPP has an LLT in its metastable supercooled state.

We demonstrated that LLT is controlled by a non-conserved scalar order parameter and proposed that the relevant order parameter may be a number density of locally favoured structures, which we call bond order parameter and denote as  $S$  [9–12]. Here locally favoured structures are those which are stabilized by anisotropic components of the interaction (e.g., hydrogen bonding) and have lower energy than random structures usually found in liquids. Locally favoured structures may be made of several molecules. In this scenario, LLT is the cooperative ordering of the bond order parameter  $S$  whereas a gas–liquid transition is that of the density order parameter. In relation to this, Mei *et al* recently suggested that molecular conformation and nearest-neighbour interactions of liquid I may be different from those of liquid II for TPP [13]. This is consistent with our proposal that LLT is the transformation from a liquid with a low fraction of locally favoured structures (small  $S$ ) to that with a high fraction (large  $S$ ). We suggest that liquid tends to temporally form locally favoured structures and the cooperativity in the formation of locally favoured structures is the origin of LLT<sup>2</sup>. The above physical picture tells us that LLT may be observed in many liquids which tend to form locally favoured structures. Although LLT has been believed to be a rather rare phenomenon, this scenario suggests that LLT may be abundant in many liquids and not a phenomenon restricted to special substances [12]. To verify this picture, it is crucial to find other examples of LLT in molecular liquids. Here we report another example of LLT found in a molecular liquid, n-butanol.

Recently Bol'shakov and Dzhonson found an interesting phenomenon in a supercooled state of n-butanol, which is similar to that observed in TPP [14]. They reported that a supercooled state transforms to a new glassy amorphous state that is different from the crystal, when they anneal n-butanol for some hours at 120–140 K. This temperature range is below the melting point  $T_m = 183$  K, but close to the glass-transition temperature  $T_g = 118$  K. Furthermore, they stated that when they put a glass rod above the new phase and then heated it, the glass rod sank at 160 K and then stopped sinking when the new phase transformed to the crystal. From this, they conjectured that this phenomenon is an indication of a second liquid–glass transition. Motivated by this research, hereafter we study the nature of this new apparently amorphous phase. To show that n-butanol really exhibits an LLT, we need to rule out other possibilities, such as a plastic crystal, a mesophase, microcrystallites, and a new exotic phase.

We used n-butanol purchased from Merck, which is 99.9% pure. We observed the pattern evolution of the liquid–liquid transformation with phase-contrast microscopy. The sample was sandwiched between two cover glasses. The sample thickness was controlled to 10  $\mu\text{m}$  by using monodisperse glass beads as spacers. The temperature was controlled within  $\pm 0.1$  K by a computer-controlled hot stage (Linkam LK-600PH) with a cooling unit (Linkam L-600A). We calculated the intensity distribution function from images obtained by phase-contrast microscopy,  $P(I)$ , which is proportional to the density distribution function  $P(\rho)$  [15]. We also obtained the structure factor  $F(q)$  by calculating the power spectrum of the two-dimensional Fourier transformation of an image obtained with phase-contrast microscopy. The structure factor obtained by this digital image analysis (DIA) method was confirmed to be equivalent to the structure factor obtained by the static light scattering measurements [16]. Calorimetric measurements were made by a differential scanning calorimeter (Mettler Toledo, DSC-822e), which is capable of complex (AC) heat capacity measurements.

<sup>2</sup> It should be noted here that historically a two-species model with cooperativity was first applied to the problem of a liquid–liquid transition by Rappoport [26].

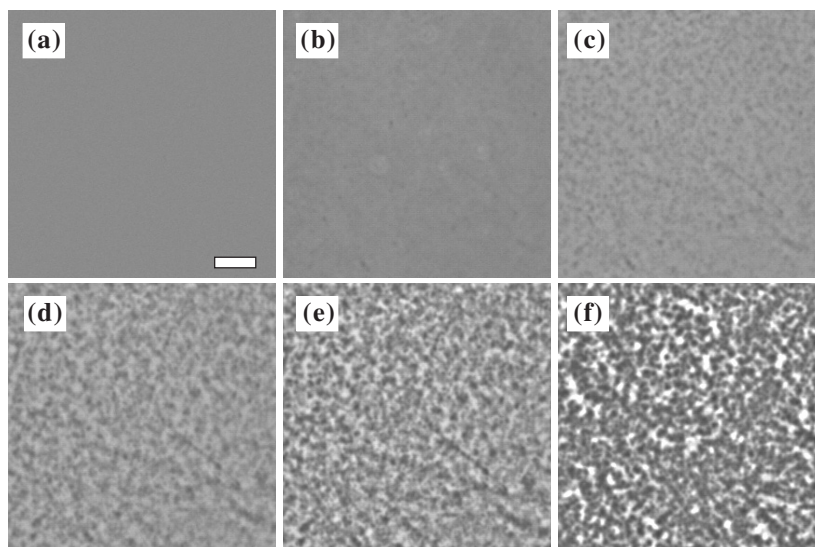


**Figure 1.** Patterns observed with phase contrast microscopy at  $T_a = 120$  K for various annealing times  $t_a$ ; (a) 30 min, (b) 45 min, (c) 60 min, (d) 90 min, (e) 120 min, and (f) 180 min. The scale bar corresponds to  $20 \mu\text{m}$ . Initially there is only liquid I (see (a)), and then droplets of liquid II with dark contrast appear and grow with time.

First we investigated the process of the transformation in n-butanol. In figure 1, we show the pattern evolution process observed when we quenched n-butanol with a rate of  $5 \text{ K min}^{-1}$  and annealed it at  $T_a = 120$  K. At this temperature, n-butanol is in a supercooled liquid state since  $T_m > T_a > T_g$  [17]. Crystallization did not occur during a cooling process with a cooling rate  $5 \text{ K min}^{-1}$ ; the transformation occurred prior to crystallization. At  $t_a = 30$  min (see figure 1(a)), a homogeneous state of the ordinary liquid (liquid I) is observed. Around  $t_a = 45$  min (see figure 1(b)), droplets with a dark contrast emerged randomly in space without any spatial correlation. As will be shown later, these droplets are nuclei of liquid II. For our microscopy, darker contrast means higher refractive index, i.e., higher density. Thus, we conclude that liquid II is denser than liquid I. Droplets grow with time. In the rather early stage, the interface between droplets of liquid II disappeared following their collisions (see figures 1(b) and (c)), as in TPP [9, 10]. In the late stage, on the other hand, the interface apparently remains. However, we confirmed that this inhomogeneity is only superficial and it is caused by the detachment of the sample from the glass cell walls, which was induced by the volume contraction upon the transformation from liquid I to liquid II (see figure 1(f)). Thus, these data suggest that liquid I eventually transforms into homogeneous liquid II.

The pattern evolution at  $T_a = 115$  K (see figure 2) was quite different from that observed at  $T_a = 120$  K. At  $t_a = 60$  min (see figure 2(a)) there was no change at all, and at  $t_a = 120$  min (see figure 2(b)) droplets with dark contrast appeared with spatial correlation. Unlike the case above, the contrast between the ordinary liquid and the droplets increases with time (see figures 2(c)–(e)). In the very late stage, the sample detached from the cover glasses due to the volume contraction as in the case of  $T_a = 120$  K.

To analyse the above pattern evolution processes more quantitatively, we employed a DIA method [15, 16]. Figure 3 shows the temporal change of the intensity distribution function  $P(I)$  calculated from the microscopy images for the case of  $T_a = 120$  K.  $P(I)$  corresponds to the density distribution  $P(\rho)$  and the lower intensity corresponds to the higher density.



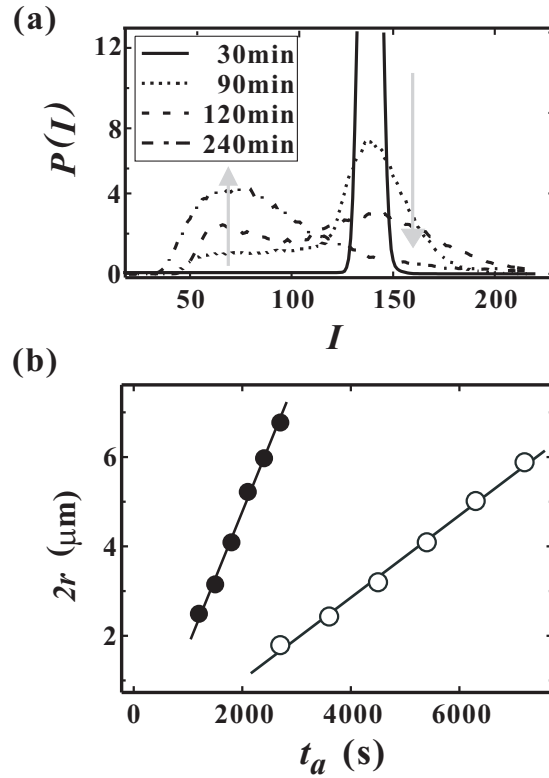
**Figure 2.** Patterns observed with phase contrast microscopy at  $T_a = 115$  K for various  $t_a$ : (a) 60 min, (b) 120 min, (c) 180 min, (d) 240 min, (e) 360 min, and (f) 480 min. The scale bar corresponds to  $20 \mu\text{m}$ . Unlike the case of  $T_a = 120$  K, droplets of liquid II appear with spatial correlation (see (b)) and, furthermore, the contrast between liquid I and liquid II increases with time (see (c) and (d)). The domain size also coarsens with time (see (e) and (f)).

$P(I)$  has only one peak (peak I) at  $I = 140$  at  $t_a = 30$  min, which corresponds to liquid I (see figure 1(a)). Reflecting the appearance of new dark droplets, the other peak (peak II) emerges around  $I = 70$ . We confirmed that the position of this new peak does not change with time. Peak II grows with time, while peak I decays, reflecting the increase of the volume (area) of the new phase. The existence of the two peaks of  $P(I)$  around  $t_a = 120$  min means that the two different phases transiently coexist.

We also measured the diameter of a droplet as a function of the annealing time  $t_a$  (see figure 3(b)). The droplet grows linearly with  $t_a$  and the growth rate is estimated to be about  $1 \text{ nm s}^{-1}$ . This linear domain growth is characteristic of the domain growth for the ordering of a system of a non-conserved parameter. Very similar behaviour is also observed for TPP, as shown in figure 3(b). For a system with a conserved order parameter, domain size is expected to scale as  $t_a^{1/3}$  in the late stage [18]. These results suggest that LLT observed at 120 K is the nucleation-growth-type (NG-type) transformation.

Next we show the temporal change of  $P(I)$  for 115 K (see figure 4(a)), which is quite different from that for 120 K. Just after quenching n-butanol to 115 K with a cooling rate  $5 \text{ K min}^{-1}$ , the peak of  $P(I)$  is located around  $I = 140$ . This peak broadens with time, consistent with the fact that the contrast between the ordinary liquid and the new phase increases (see figure 2). This time evolution of  $P(I)$  in the early stage is reminiscent of spinodal decomposition of a binary mixture [19]. The peak position eventually shifts to  $I = 80$ .

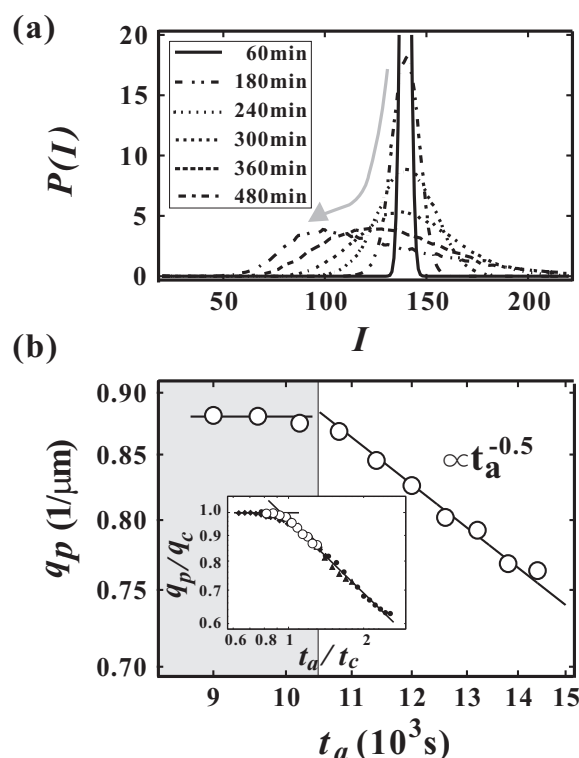
We also calculated the structure factor  $F(q)$  for the patterns observed at 115 K by using two-dimensional Fourier transformation [16]. For this case  $F(q)$  has a distinct peak at nonzero wavenumber  $q_p$ , which implies there is a spatial correlation in the density distribution, which reflects the distribution of  $S$  [11, 12]. The appearance of a peak in  $F(q)$  is also consistent with our scenario of SD-type liquid–liquid transformation where the ordering of  $S$  is coupled to the density [11, 12]. Figure 4(b) shows  $q_p$  as a function of  $t_a$  (log–log plot). In the early stage,



**Figure 3.** (a) Temporal change of the intensity distribution  $P(I)$  at  $T_a = 120$  K. Just after the quench, there is only one peak, reflecting that there is homogeneous liquid I. Upon annealing at  $T_a = 120$  K, peak I becomes smaller with time, while the other peak appears and grows with time. The two peaks are clearly seen at  $t_a = 120$  min for  $T_a = 120$  K. The pattern of the temporal change of  $P(I)$  indicates that liquid II appears and grows, keeping the density constant. This suggests that the liquid–liquid transformation at 120 K is of discontinuous NG type. (b) The temporal change in the diameter of a droplet as a function of the annealing time  $t_a$ . Open circle, n-butanol,  $T = 120$  K; filled circle, TPP,  $T = 219$  K. The droplet diameter grows as  $t^1$  and the growth rate is estimated as about  $1 \text{ nm s}^{-1}$  for n-butanol and about  $3 \text{ nm s}^{-1}$  for TPP.

$q_p$  is constant with time, but the intensity of  $F(q_p)$  grows exponentially until 10 500 s. This behaviour is known as the Cahn linear regime of spinodal decomposition [12, 18]. Then,  $q_p$ , which is proportional to the inverse of the domain size, decreases as  $t_a^{-0.5}$ . The time evolution of  $q_p$  for SD-type transformation is common to n-butanol and TPP, as shown in the inset of figure 4(b). The growth exponent (1/2) is characteristic of spinodal decomposition of a system with a non-conserved order parameter. For a system with a conserved order parameter, the exponent should be 1/3 (for a diffusion-dominated case) or 1 (for a hydrodynamically dominated case) [18]. The correlation length is estimated from the value of  $q_p$  in the linear regime as  $\xi = 1/\sqrt{2}q_p \sim 0.8 \mu\text{m}$ . This value of  $\xi$  is comparable to that for TPP [10]. Since  $T_{\text{SD}}$  is located very near  $T_g$ , its determination and the investigation of the critical divergence of  $\xi$  were quite difficult for this system.

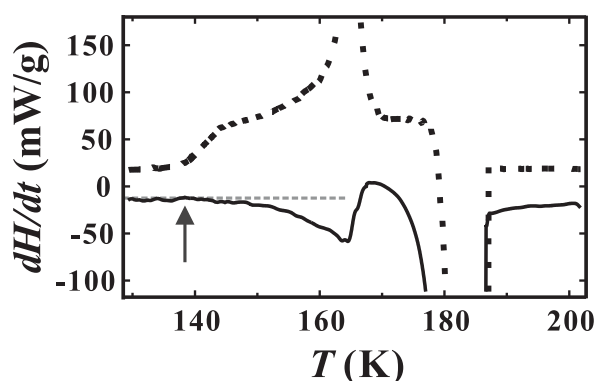
As described above, we found that there are two types of pattern transformation from liquid I to liquid II: continuous (SD-type) and discontinuous (NG-type) transformation. The existence of both types of transition is suggestive of LLT. In particular, the SD-type transformation and the disappearance of domain boundaries in a final state can be regarded as strong evidence that



**Figure 4.** (a) Temporal change of  $P(I)$  at 115 K. The peak broadens with time and the peak position shifts to the left gradually. This means that density increases continuously upon the liquid–liquid transformation. (b) Temporal change in the characteristic wavenumber  $q_p$ . We calculated the structure factor  $F(q)$  from images and obtained the peak wavenumber of  $F(q)$ ,  $q_p$ . In the early stage,  $q_p$  is constant with time. In the late stage, the domain size coarsens as  $t_a^{0.5}$ . This growth exponent is consistent with domain coarsening during spinodal decomposition for a system of a non-conserved order parameter. From these, we conclude that the liquid–liquid transformation at 115 K is of continuous SD type. In the small inset, we plot the temporal change of  $q_p/q_c$  against  $t_a/t_c$  during continuous LLT for both TPP and n-butanol. On  $q_c$  and  $t_c$ , see the text. Open circles are data for n-butanol and filled symbols are data for TPP (circles,  $T_a = 212$  K; triangles,  $T_a = 213$  K; diamonds,  $T_a = 214$  K). The fact that all the curves collapse onto a master curve indicates the universal domain coarsening for LLT.

this transformation is an LLT, and not the formation of a plastic crystal or mesophase. The behaviour observed is characteristic of the ordering of a system with a non-conserved scalar order parameter [11, 12]. Similarly to the case of TPP [9, 10], we thus conclude that the newly emerging phase in n-butanol is another isotropic liquid phase (liquid II).

To make the above conclusion more definitive, we characterize the glass-transition behaviour of liquid II, in particular the fragility, to clarify the difference between liquid I and II. If a new amorphous state is really a glassy state of liquid II, it should show its own glass-transition behaviour, which is different from that of liquid I. To check this, we measured the glass transition of liquid II,  $T_g^{\text{II}}$ . When we quenched n-butanol at 128 K and annealed it for 7 h, liquid I perfectly transformed to liquid II. Then, we made AC differential scanning calorimetry (DSC) measurements with a complex heating pattern, whose modulation amplitude and period were, respectively, 0.16 K and 20 s and whose average heating rate was  $3 \text{ K min}^{-1}$ . The reason we use AC DSC is to separate the glass transition behaviour from crystallization

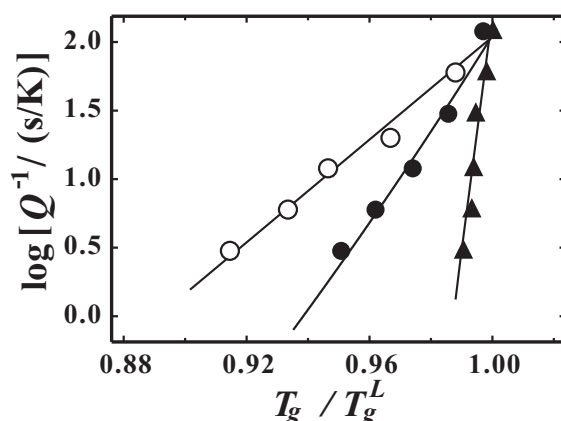


**Figure 5.** Heat flux upon heating across  $T_g$  for liquid II of n-butanol. We quenched the sample to 128 K and annealed it for 7 h to completely transform liquid I to liquid II. Then we heated it with AC DSC, where the average heating rate is  $3 \text{ K min}^{-1}$ , the modulation period is 20 s, and the modulation amplitude is 0.16 K. We measured both the reversible part (solid line) and the non-reversible part (dashed line) of the heat flux upon the heating process. The onset of the broad steplike change of the reversible part was observed around 140 K, which is typical of the glass transition. The  $T_g^L$ , which is the lower edge temperature of the steplike change of the reversible part, was determined to be 140 K. The non-reversible part starts to increase around 140 K. This means that crystallization starts to occur just after the glass transition.

induced by devitrification (see below). If we use conventional DSC, it is difficult to detect the glass transition behaviour. For AC DSC, we can divide the heat flow into two parts, namely, a reversible part,  $dH'/dt$ , and a non-reversible one,  $dH''/dt$ . The reversible and non-reversible parts correspond to the heat capacity and the relaxation part, respectively. This allows us to estimate only the heat flux of the glass transition from the reversible part without suffering from the effects of the heat flux of crystallization, which contributes to the non-reversible part. Figure 5 shows a non-reversible part (dashed line) and a reversible part (solid line) of the heat flux upon heating the glassy state of liquid II. We found a broad steplike change in the range from 140 to 165 K in the reversible part. This steplike change is characteristic of the glass transition. At the temperature of the lower side of the steplike change (the arrow in figure 5),  $T_g^L$ , the structural relaxation time  $\tau$  should be about 20 s for a heating rate of  $3 \text{ K min}^{-1}$ . In the reversible part, on the other hand, we observed the peak in the range from 140 to 165 K, which means that crystallization occurs just after the glassy state becomes a liquid state. The kinetics of crystallization around 140 K is slow since the structural relaxation time is long and viscosity is high near  $T_g$ . When the temperature reaches 20 K above  $T_g$ , the relaxation time becomes short enough for the crystallization kinetics to accelerate considerably. This gives rise to the sharp peak of the non-reversible part around 160 K.

Next we focus on the nature of the glass transition of liquid II. When a liquid approaches its glass-transition temperatures  $T_g$ ,  $\tau$  dramatically increases. This basic feature is ubiquitous, but the increase of  $\tau$  (as  $T_g$  is approached) can be classified between strong and fragile extremes using  $T_g$  as a scaling parameter. Liquids whose  $\tau$  obeys the Arrhenius law are called 'strong', while 'fragile' liquids have the super-Arrhenius behaviour [20]. Thus, the estimation of the fragility is quite important to characterize the nature of the liquid–glass transition. To characterize the fragility of liquid II, we studied the heating-rate ( $Q$ ) dependence of  $T_g^L$  [21]. We used AC DSC for  $Q < 5 \text{ K min}^{-1}$ , while DC DSC for  $Q > 10 \text{ K min}^{-1}$  for which our AC DSC cannot be applied. Figure 6 shows the  $Q$  dependence of  $T_g^L$ . The inverse of  $Q$  should be comparable to the structural relaxation time  $\tau$ . Following the convention that  $T_g$  is the





**Figure 6.** The heating-rate ( $Q$ ) dependence of  $T_g/T_g^L$ . Open circle, liquid II of n-butanol prepared by annealing n-butanol at 123 K for 10 h; filled triangle, liquid I of TPP; filled circle, liquid II of TPP prepared by annealing TPP at 213 K for 10 h. Here we define  $T_g$  as  $T_g^L$  for  $Q^{-1} = 100 \text{ s K}^{-1}$ . The  $T_g$  defined in this way is 133 K for liquid II of n-butanol, while 205 and 212 K, respectively, for liquid I and liquid II of TPP. The solid lines are fitted straight lines. We obtained the fragility parameter  $m \sim 21$  for liquid II of n-butanol,  $m \sim 154$  for liquid I of TPP, and  $m \sim 34$  for liquid II of TPP. Liquid II of n-butanol and liquid II of TPP are both very strong.

temperature where  $\tau \sim 100 \text{ s}$ , we determine  $T_g^{\text{II}}$  as 133 K. Since  $T_g$  of liquid I is 118 K [17], we found that  $T_g^{\text{II}}$  is considerably different from  $T_g^{\text{I}}$ . This supports our scenario that n-butanol has two liquid states. Strictly speaking, upon LLT liquid I transforms to the glassy state of liquid II, and not to the liquid state of liquid II, as in the case of TPP [9, 10].

From the above results, we can estimate the fragility of liquid II. We estimate the fragility parameter  $m$  from the relation

$$m = \left. \frac{d \log \tau}{d(T_g/T_g^L)} \right|_{T_g^L=T_g} = \left. \frac{d \log Q^{-1}}{d(T_g/T_g^L)} \right|_{T_g^L=T_g}.$$

$m$  is estimated as  $m \sim 21$ . Note that  $m$  is 20 for silica, which is an extremely strong liquid. This means that liquid II is quite strong and its  $\tau$  (or viscosity) almost obeys the Arrhenius law, as can be seen in figure 6. We note that it is rather rare to see such a low value of  $m$  for molecular liquids. But we have observed very similar behaviour in liquid II of TPP ( $m \sim 34$ ) [9], as indicated in figure 6. This implies that there may be a universal pattern for LLT of molecular liquids. Provided that the order parameter governing LLT is  $S$ , the above result implies that a liquid with larger  $S$  (liquid II) is stronger. This seems to be consistent with a prediction of our two-order-parameter model of a liquid–glass transition [22].

We also estimated the temperature width  $\Delta T_g$  of the glass transition from the steplike change of the reversible part near  $T_g$  (see figure 5). The  $\Delta T_g$  also has a relation to the fragility; it is larger for a stronger liquid [23]. We found that  $\Delta T_g$  of liquid II is very large ( $\sim 25 \text{ K}$ ), which is consistent with the small fragility parameter  $m$ . Since our DSC equipment cannot cool a sample below 123 K, we were not able to estimate the fragility of liquid I.

Here it is worth noting the common features of LLT between TPP and n-butanol. First, both liquids exhibit the two types of liquid–liquid transformation, discontinuous NG type and continuous SD type. The domain growth law is exactly the same between the two. For NG-type transformation, domain size grows linearly with time. For SD-type transformation, there is a linear regime in the early stage and in the late stage the domain size grows as  $t_a^{0.5}$ .

The temporal change in  $q_p$  can be collapsed on a single master curve by scaling  $q_p$  by  $q_c$  and  $t$  by  $t_c$  (see the inset of figure 4(b)). Here  $q_c$  is the characteristic wavenumber of the most unstable mode of  $S$  fluctuations and  $t_c$  is the crossover time from the linear regime where  $q_p$  is constant with time to the late coarsening regime. Both are characteristic of domain coarsening for a system of a non-conserved scalar order parameter. Lastly,  $T_g^{\text{II}}$  is different from  $T_g^{\text{I}}$  and liquid II is a very strong liquid.

We stress that the molecular structure of n-butanol is quite different from that of TPP. On the other hand, the behaviour of LLT of n-butanol is strikingly similar to that of TPP. This suggests that LLT may be abundant in molecular liquids. The fact that the behaviour of LLT is insensitive to the details of molecular or chemical structures is consistent with our physical picture that LLT is governed by the cooperative ordering of the bond order parameter  $S$  that is the number density of locally favoured structures [11, 12]. In our scenario, the only requirement for LLT is the cooperative formation of locally favoured structures. The types of locally favoured structures should depend on the details of molecular structures, but the physical scenario of the cooperative short-range bond ordering itself may be universal. For TPP and n-butanol, for example, hydrogen bonding may play a crucial role in the formation of such structures. The identification of the locally favoured structures of these liquids remains a future problem.

Our study may shed new light on the basic nature of liquid: even an ordinary molecular liquid such as n-butanol or TPP may have a hierarchical energetic structure. Thus it is neither perfectly homogeneous nor random, but possesses long-lived short-range order with cooperativity. This further implies that liquid may not be a unique state of matter, but there can often be more than two liquid states even for single-component matter. In many cases, LLT may be hidden by either crystallization or glass transition. The former may be the case of liquid water [5, 8, 12, 24].

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