

Liquid-Liquid Transition in the Molecular Liquid Triphenyl Phosphite

Hajime Tanaka, Rei Kurita, and Hiroshi Mataki

Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan

(Received 8 April 2003; published 15 January 2004)

We found both nucleation-growth-type and spinodal-decomposition-type transformation from one liquid state to another in a “molecular liquid,” triphenyl phosphite (TPP). Binodal and spinodal temperatures of this transition at ambient pressure were determined by the characteristics of morphological evolution, domain-growth kinetics, and rheological evolution. Furthermore, a distinct thermal signature of the glass transition of a second liquid was also detected in addition to that of an ordinary liquid. These findings strongly suggest the existence of a liquid-liquid transition; more precisely, a transformation of one supercooled liquid to a glassy state of another liquid, in TPP.

DOI: 10.1103/PhysRevLett.92.025701

PACS numbers: 64.70.Ja, 62.10.+s, 64.60.My, 64.70.Pf

Even a single-component liquid may have more than one kind of isotropic liquid state. The transition between the different liquid states is called a “liquid-liquid phase transition (LLP)” [1–5]. There are a number of experimental indications suggestive of its existence [4]. However, such a transition seems not to have been widely accepted as a convincing fact, and its existence itself is still a matter of debate. This situation partly comes from the experimental difficulties; namely, in most cases the transition is located at high temperatures and high pressures (e.g., C, Se, S, ...) [4] or hidden by crystallization, which might be the case of water [5]. However, a recent finding of first-order LLP in P makes its existence convincing [6]. In principle, there is a possibility that a single-component “molecular liquid” may have LLP [7].

Recently, quite unusual phenomena were found by Kivelson and co-workers in their study of a supercooled state of triphenyl phosphite (TPP) [8]. If TPP is cooled rapidly enough, it first enters into a supercooled liquid state below the melting point T_m (~ 295 K) as usual liquids, and then into a glassy state at the glass-transition temperature T_g^I (~ 205 K), which we call glass I. This supercooled liquid (liquid I) behaves as a typical fragile glass former. On the other hand, if TPP is quenched to a certain temperature between 210 and 223 K (above T_g^I) and then annealed at that temperature, a new phase (the so-called glacial phase) [9] emerges in a supercooled liquid and grows with time. Eventually, the entire system transforms into the glacial phase. Surprisingly, the glacial phase is at least apparently an optically transparent homogeneous amorphous phase, but it is obviously different from ordinary liquid (liquid I) and ordinary glass (glass I). This finding stimulates intensive experimental research on this unusual phenomenon. However, the nature and origin of the glacial phase is still a matter of active debate and many different, and controversial, explanations are proposed for it. They are summarized as follows: (i) Kivelson and co-workers [8,11] and Alba-Simionesco and Tarjus [12] proposed that this phase is an exotic defect-ordered phase, which is expected

from their theory of frustration-limited domains [11]. (ii) Johari and Ferrari [13] proposed that it may be in a liquid-crystal or a plastic-crystal state. (iii) Senker, Rössler, and co-workers [14] ascribed it to a new amorphous phase and pointed out that it is suggestive of the existence of LLP. They also mentioned a possibility that the glacial phase might be a plastic crystal. (iv) Similarly, Oguni and co-workers [15] interpreted the glacial phase as being a highly correlated second liquid. (v) Hedoux *et al.* [10] proposed that the glacial phase is composed of nanocrystallites or microcrystallites possibly mixed with a fraction of untransformed supercooled liquid, depending upon the annealing temperature T_a . Thus, there is no consensus even on the nature and origin of the glacial phase. In this Letter, we provide experimental evidence strongly indicating that TPP has LLP and that the glacial phase should be a glassy state of the second liquid (liquid II).

TPP was purchased from Aldrich Chemical Co. Inc. and used after purification. Pattern evolution was observed with normal, polarizing, and phase-contrast microscopy equipped with a temperature-controlled stage (Linkam TH-600PH, ± 0.1 K). Rheological measurements were made by a rheometer (Rheologica, Dynalyser VAR-CF) using a parallel plate geometry (gap = 0.5 mm). Optical birefringence was estimated by measuring the transmitted intensity I_{VH} at wave number $q = 0$, $I_{VH}(0)$, of the linearly polarized laser light that passes through a sample and an analyzer, whose polarization direction is set to be perpendicular to that of the incident light. Calorimetric measurements were made by a differential scanning calorimeter (Mettler Toledo, DSC-822e), which is capable of complex (AC) heat capacity measurements.

Figures 1(a1), 1(a2), and 1(a3) show the pattern evolution process observed after quenching an equilibrium liquid above T_m rapidly to $T_a = 220$ K. Spherical droplets of the glacial phase are nucleated in liquid I and then grow with time with a constant growth speed V (~ 3.5 nm/s). This is typical behavior of nucleation-growth(NG)-type phase transformation. This behavior

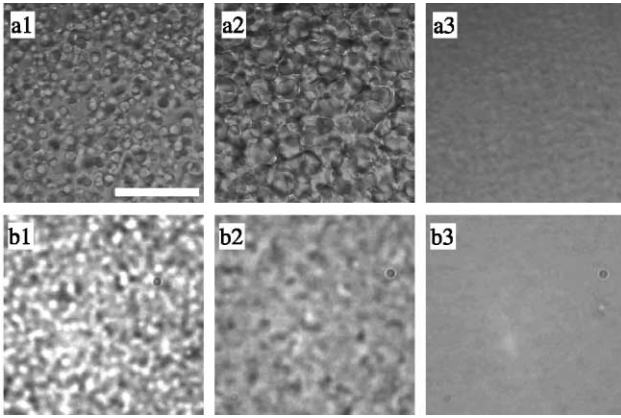


FIG. 1. Pattern evolution observed during the annealing of a supercooled liquid at T_a . (a1)–(a3) are observed with normal microscopy at $T_a = 220$ K at the annealing time $t_a = 60, 120,$ and 240 min, respectively. (b1)–(b3) are observed with phase-contrast microscopy for $T_a = 213$ K at $t_a = 120, 240,$ and 360 min, respectively. The white bar in (a1) corresponds to $100 \mu\text{m}$ for (a1)–(a3), while to $20 \mu\text{m}$ for (b1)–(b3). The sample thickness was $100 \mu\text{m}$ for (a), while $20 \mu\text{m}$ for (b).

resembles that observed in first-order LLP of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ [2]. Eventually, these domains cover an entire sample and, surprisingly, the domain boundary disappears [see Fig. 1(a3)]. Thus, the system apparently becomes homogeneous again [16]. From polarizing microscopy observation, we confirm that the nucleated domains have optical anisotropy. This seems to imply that the new phase itself has orientational order. As will be explained later, however, this is not the case, and the final state is a mixture of a new amorphous phase of the second liquid and microcrystallites embedded in it.

Figures 1(b1), 1(b2), and 1(b3), on the other hand, show the pattern evolution process observed at the lower temperature $T_a = 213$ K. Although the liquid is homogeneous just after the quench, density fluctuations very slowly, but continuously, grow. The amplitude of density fluctuations initially increases *exponentially*, but later decreases, and eventually the system becomes a homogeneous glacial phase. In the initial stage, the characteristic wavelength of fluctuations λ_p is constant with time, but in the late stage it increases as $\lambda_p \sim t^{1/2}$. These features are very characteristic of spinodal-decomposition(SD)-type ordering of a system of nonconserved order parameter [7]. We found that the change of pattern evolution from NG-like to SD-like takes place rather sharply around $T_{SD} = 215.5$ K, which may be the location of the mean-field spinodal line of LLP at atmospheric pressure that should underlie any weak LLP line. Accordingly, the nucleation frequency Γ of the glacial phase tends to diverge at T_{SD} [see Fig. 2(b)]. Interestingly, we confirm that below T_{SD} a system has no birefringence during the entire process of this SD-type transformation, contrary to the case of NG-type one observed at $T_a = 220$ K, which suggests the absence of microcrystallites below T_{SD} [see Fig. 5 (below)]. We stress here that the existence of SD-like pattern

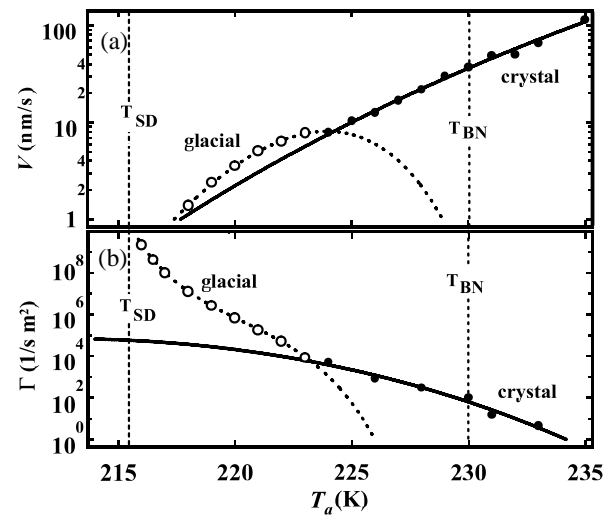


FIG. 2. Dependence of V (a) and Γ (b) on T_a for the crystal-dominated (filled circle) and the glacial-dominated (open circle) phase.

evolution is a feature unique to liquid-liquid phase transformation and is not compatible with any first-order transformations between liquid and ordered solids including crystals and plastic crystals. This strongly suggests that this phase transformation from the supercooled liquid to the glacial phase is LLP.

From optical microscopy observations, we also estimate the growth speed V and the nucleation frequency Γ of the domains as a function of T_a , for both the crystal and the glacial phase (see Fig. 2). Both V and Γ change their temperature dependencies at 223 K. The temperature below which the glacial phase appears is assigned to the binodal temperature of LLP, T_{BN} , which is located around 230 K. Furthermore, Γ drastically increases with decreasing T_a and diverges toward 215.5 K, which we assign to the spinodal temperature of the underlying LLP, T_{SD} . Such a steep increase of Γ with decreasing T_a and the change of T_a dependence of V and Γ at 223 K cannot be explained by the classical nucleation theory, and these strongly suggest the existence of LLP.

The processes of SD and NG shown in Fig. 1 were also studied by rheological measurements. Figure 3 shows the temporal change in the real part of complex shear modulus, $G'(f)$ (f : frequency) during the transformation from the supercooled liquid to the glacial phase as a function of the annealing time t_a for both NG and SD cases. It is found that rheological evolution also changes its pattern around T_{SD} : (i) Above T_{SD} , G' rather sharply increases at a certain t_a . This existence of the incubation time (~ 500 s at $T_a = 220$ K) is characteristic of the NG process. This result clearly demonstrates that the supercooled liquid is in a viscous fluid state without static elasticity, while the glacial domain is in a glassy state with it. We call this glassy state of liquid II “glass II.” (ii) Below T_{SD} , on the other hand, G' continuously increases with t_a even in the early stage, reflecting the continuous growth of density fluctuations that is characteristic of SD [see

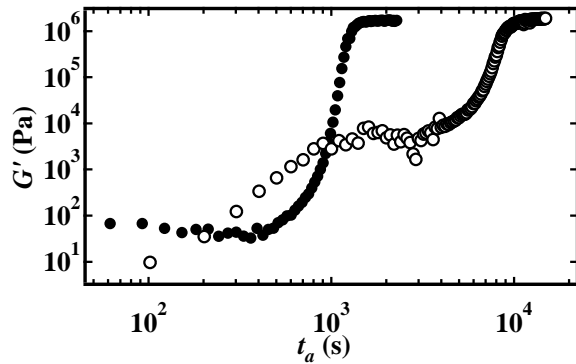


FIG. 3. Temporal change in $G'(f)$ ($f = 1.0$ Hz) at $T_a = 220$ K (closed circles) and $T_a = 213$ K (open circles). The measurements were made with a stress-controlled mode, where stress was kept at 1.0×10^3 Pa.

Figs. 1(b1), 1(b2), and 1(b3)]. The second rise of G' is due to vitrification [see Fig. 6 (below)]. These results are consistent with those of our morphological observation. They also suggest that the glacial phase is a glassy state of liquid II with static elasticity (glass II); there should exist a glass transition (T_g^{II}) for liquid II.

To check this, we performed AC calorimetry measurements (see Fig. 4). As shown in the upper figure, the glass transition for liquid I was observed at $T_g^{\text{I}} = 205$ K, consistently with the previous reports [8,15]. Furthermore, we found the steplike heat capacity (C_p) change at $T_g^{\text{II}} = 225$ K in the reversible component for glass II formed at $T_a = 220$ K (see the lower panel) (see also [15]). This steplike change of C_p is characteristic of a glass transition and cannot be explained by other types of transitions. The existence of two T_g for a single-component liquid suggests that LLP exists for TPP and that the glacial phase is the glassy state (glass II) of liquid II. The width of the glass-transition range of glass II (~ 23 K) is much broader than that of glass I (~ 4 K). This suggests that liquid II is stronger than liquid I, according to the Angell classification of glass-forming liquids [1,3]. This conclusion is consistent with the finding by Dvinskikh *et al.* [14] that the temperature dependence of the structural relaxation time τ_α is super-Arrhenius (typical for fragile liquids) for liquid I, while it is almost Arrhenius (typical for strong liquids) for liquid II. Finally, we note that the heat released upon transformation from liquid I to glass II is about 20 J/g and the heat of fusion (crystal \rightarrow liquid I) is about 70 J/g.

Next, we show the results of calorimetric and optical birefringence measurements. Figure 5 shows the heat released upon the transformation of the glacial phase to the crystal, $Q_{G \rightarrow C}$ (see the lower panel of Fig. 4) as a function of T_a at which the glacial phase is formed from a supercooled liquid. There we also plot the square root of the intensity of the birefringence of the glacial phase [$\sqrt{I_{VH}(0)}$], which should be proportional to its optical anisotropy δn . The decrease of $Q_{G \rightarrow C}$ with an increase in T_a for $T_a \geq T_{SD}$ indicates that more crystals already

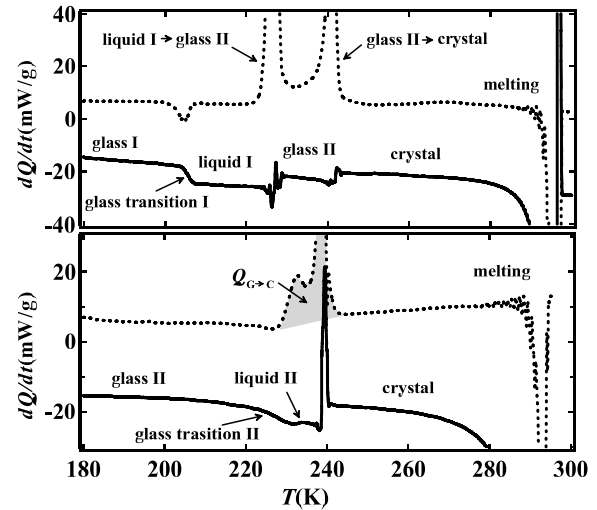


FIG. 4. Results of AC calorimetry measurements of the glass transitions for liquid I (upper panel) and liquid II (lower panel). The amplitude and period of the temperature modulation are 0.16 K and 60 s, respectively. The heating rate was 1 K/min. For the former, the sample was rapidly (20 K/min) cooled to 150 K. For the latter, on the other hand, the sample was annealed at $T_a = 220$ K for 8 h before the measurements so that a system completely transforms into the glacial phase. The solid and dashed curves represent reversible and nonreversible components of heat flux ($\frac{dQ}{dt}$), respectively.

exist in the glacial phase for higher T_a . We confirm that $Q_{G \rightarrow C}$ becomes zero above $T_a = 228$ K, which means that only crystallization occurs above this temperature instead of the glacial phase being formed. This is consistent with the fact that T_{BN} is located around 230 K, which is deduced from the domain-growth kinetics. Note that above T_{BN} the glacial phase should not be formed and only crystallization should take place. The crystallinity ϕ_X can be estimated by $\phi_X = [Q_{G \rightarrow C}(T < T_{SD}) - Q_{G \rightarrow C}]/[Q_{G \rightarrow C}(T < T_{SD}) - Q_{G \rightarrow C}(T_a = 228 \text{ K})]$. It is confirmed (see Fig. 5) that ϕ_X decreases when $T_a \rightarrow T_{SD}$, and becomes zero below T_{SD} (e.g., $\phi_X \sim 1.0$ at $T_a = 228$ K and $\phi_X \sim 0.5$ at $T_a = 223$ K). We stress

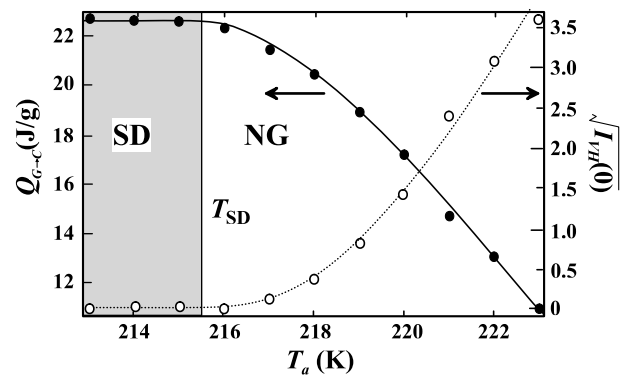


FIG. 5. Thermal and optical characterization of the glacial phase. Dependencies of $Q_{G \rightarrow C}$ and $\sqrt{I_{VH}(0)}$ measured after the completion of the transformation into the glacial phase are plotted against T_a .

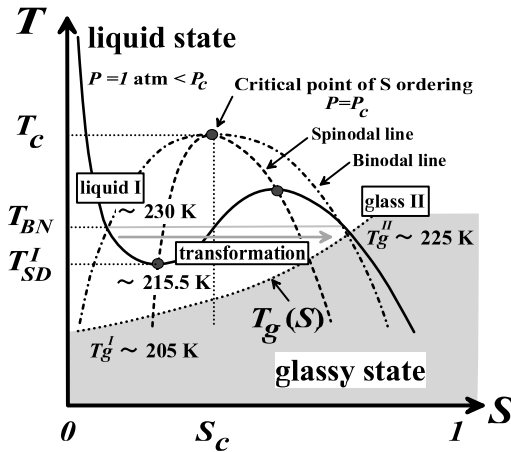


FIG. 6. Schematic LLP phase diagram of TPP in a T - S plane. Here S is a nonconserved order parameter governing LLP (see Ref. [7] for its definition). Note that LLP inevitably accompanies vitrification since a system crosses the $T_g(S)$ line during the transformation.

that the two characteristic temperatures of $\phi_X = 0$ and $\phi_X = 1$, respectively, correspond to T_{SD} and T_{BN} , which are determined by morphological observation and domain-growth kinetics. The behavior of optical birefringence is also quite consistent with the dependence of ϕ_X on T_a , strongly suggesting that the birefringence stems from microcrystallites embedded in glass II and not from glass II itself. Our results indicate that the glacial phase formed below T_{SD} is a homogeneous glassy state of liquid II (pure glass II), while that formed above T_{SD} is a mixture of glass II and microcrystallites [17]. We note that misinterpreting this mixed state formed at $T_a > T_{SD}$ as a homogeneous state seems to be the origin of all the confusion concerning the nature of the glacial phase.

Here we note that our scenario naturally explains why the boundary between the glacial droplets disappears when they meet [see Figs. 1(a1), 1(a2), and 1(a3)]: The glacial droplets are primarily made of glass II and the supercooled liquid (liquid I) between two colliding droplets should also finally transform into glass II. Thus, we do not expect any change in the refractive index across the previous boundary between the droplets. Thus, the entire system becomes a homogeneous isotropic glass II.

In summary, we demonstrate several pieces of experimental evidence strongly suggestive of the existence of LLP (strictly speaking, liquid I-glass II transition) in TPP, whose schematic phase diagram is shown in Fig. 6. (i) Both NG-type and SD-type phase transformations have been clearly observed for LLP, probably for the first time. (ii) The location of T_{BN} and T_{SD} has been determined by morphological observations (see Fig. 1), nucleation and growth kinetics (see Fig. 2), rheological measurements (see Fig. 3), and optical birefringence and calorimetric measurements (see Fig. 5). It is worth stressing that T_{SD} and T_{BN} determined by these different methods are fully consistent with each other. (iii) Two

distinct glass transitions are detected for a single-component substance. This fact can also be explained by a plastic-crystal scenario. As mentioned before, however, it is not compatible with the SD-type transformation. Furthermore, we confirm that impurities (4.8% aniline) that are miscible with liquid I of TPP are expelled from spherulites of crystals, but not from glacial droplets. This suggests that the glacial phase (glass II) can include impurities in it as liquid I can. All these facts together with the x-ray evidence of the existence of two amorphous structures [8,9] are strongly suggestive of LLP in TPP. Finally, we point out that TPP may be an ideal system to experimentally study thermodynamic and kinetic anomalies associated with LLP [1–7,18].

- [1] P.G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, 1997).
- [2] S. Aasland and P.F. McMillan, *Nature (London)* **369**, 633 (1994).
- [3] C. A. Angell, *Science* **267**, 1924 (1995).
- [4] P.H. Poole *et al.*, *Science* **275**, 322 (1997).
- [5] O. Mishima and H. E. Stanley, *Nature (London)* **396**, 329 (1998).
- [6] Y. Katayama *et al.*, *Nature (London)* **403**, 170 (2000).
- [7] H. Tanaka, *Phys. Rev. E* **62**, 6968 (2000).
- [8] I. Cohen *et al.*, *J. Phys. Chem.* **100**, 8518 (1996).
- [9] X-ray diffraction results indicate the amorphous nature of the glacial phase [8,10].
- [10] A. Hedóux *et al.*, *J. Non-Cryst. Solids* **307–310**, 637 (2002).
- [11] B. G. Demirjian *et al.*, *J. Phys. Chem. B* **105**, 2107 (2001).
- [12] C. Alba-Simionesco and G. Tarjus, *Europhys. Lett.* **52**, 297 (2000).
- [13] G. P. Johari and C. Ferrari, *J. Phys. Chem. B* **101**, 10191 (1997).
- [14] S. Dvinskikh *et al.*, *J. Phys. Chem. B* **103**, 1727 (1999).
- [15] M. Mizukami *et al.*, *J. Phys. Chem. B* **103**, 4078 (1999).
- [16] This is consistent with the finding of Kivelson *et al.* [8] that, during the transformation of a supercooled liquid to the glacial phase, a macroscopic sample first becomes turbid but finally becomes transparent again.
- [17] For example, the signatures indicative of nanocrystals or defect-ordered crystals may arise from the microcrystallites embedded in glass II. Recently, Hedóux *et al.* [10] reported that the Raman spectra can be decomposed into those of supercooled liquid and crystals, and concluded that the glacial phase is composed of nanocrystallites or microcrystallites possibly mixed with a fraction of untransformed supercooled liquid (liquid I in our terminology), depending upon T_a . This conclusion is partly consistent with our picture, but we believe that it should be decomposed into those of glass II and crystals and not into those of liquid I and crystals.
- [18] Our preliminary C_p measurement does not exhibit any critical anomaly δC_p , which may be due to the long bare correlation length ξ_0 . Note that $\delta C_p \propto \xi_0^{-3}$ [19].
- [19] A. Onuki, *Phase Transition Dynamics* (Cambridge University Press, Cambridge, England, 2002).