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# Evidence of Liquid-Liquid Transition in Triphenyl Phosphite from Time-Resolved Light Scattering Experiments

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Here, we study the phase transition kinetics in a supercooled liquid state of triphenyl phosphite by means of time-resolved polarized and depolarized light scattering to address a long-standing controversy on its mechanism, i.e., whether the phenomenon is primarily induced by liquid-liquid transition (LLT) or by nanocrystal formation. We find that the polarized scattering intensity exhibits a peak as a function of time, and its low wave number limit is nonzero for any annealing temperatures, both of which strongly indicate the nonconserved nature of an order parameter governing the transition. We also observe evolution of depolarized scattering. Above the spinodal temperature $T_{\mathrm{SD}}$, the depolarized scattering intensity monotonically increases with time since it is dominated by scattering from nanocrystallites, which are continuously formed during the process. Below $T_{\mathrm{SD}}$, on the other hand, it exhibits a distinct peak as a function of time as the polarized scattering intensity does. This appearance of the peak suggests that dielectric tensor fluctuations responsible for the depolarized scattering mainly come from isotropic density fluctuations and not from nanocrystallites, supporting the occurrence of LLT.

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Even a single component liquid may have more than two distinct liquid states, which is known as liquid polymorphism [1–3]. The transition between different liquid states is called liquid-liquid transition (LLT). The occurrence of two liquid states in a single-component liquid has attracted considerable attention not only for its counter-intuitive nature, but also for the fundamental understanding of the liquid state.

For molecular liquids, the presence of LLT has so far been reported for triphenyl phosphite (TPP), *n*-butanol, water, and aqueous solutions; however, there has been no consensus for any of them [4]. This is mainly because the transition takes place in a supercooled state and always accompanies crystallization. Thus, it is not so clear whether the transition is induced by LLT or merely by nanocrystal formation. For example, some time ago we reported experimental evidence supporting the existence of LLT in two molecular liquids, TPP [5–9] and *n*-butanol [10] at ambient pressure, following the discovery of the so-called glacial state in these materials [11–13]. We found nucleation-growth (NG)-type and spinodal-decomposition (SD)-type LLT, which suggests that LLT is a gas-liquid-type phase ordering [14]. However, this phenomenon observed in TPP was also claimed by Hedoux *et al.* [15–22] to be induced solely by formation of nanocrystallites and not by LLT. The size of crystallites was reported to be less than 10 nm for the glacial state of TPP prepared at 210–216 K on the basis of x-ray and neutron diffraction measurements (see, e.g., [22]). Similar claims were also made recently for *n*-butanol [23–26]. There is no doubt that, for both TPP and *n*-butanol, the newly formed state is not perfectly homogeneous and contains nanocrystallites. Thus, the question is whether the glassy state in which nanocrystallites are embedded is a normal liquid (liquid I) or a different liquid (liquid II). After the discovery of the glacial state by Kivelson and co-workers, some researchers, including us, thought the glacial phase to be a new amorphous phase [12,27–30] or a highly correlated liquid [31], which is basically consistent with our LLT scenario. However, most research has shown that the glacial phase has some crystallinity or anisotropy. Hence, the newly formed glacial phase appears to be neither a standard glass nor a liquid, which led some researchers to infer that the glacial phase is actually some type of defect-ordered crystals (orientationally disordered or modulated crystal) [12,32,33], liquid crystal [34], plastic crystal [29,34], aborted crystallization [15,16,18,20–22,35], or nanoclustering [36]. However, we may say that the remaining major scenarios are now LLT and nanocrystal formation. We note that a similar situation also exists for LLT in aqueous solutions: the LLT scenario [37,38] and the nanoscale cubic ice formation scenario [39–41] (see also [4] on this controversy).

In this Letter, we aim to provide clear experimental evidence useful for judging whether the transition is a LLT or merely a nanocrystal formation. To do so, we study the kinetic process of LLT in TPP by means of time-resolved polarized ($VV$) and depolarized ($VH$) light scattering, which is one of the most powerful experimental means of accessing the nature of the order parameter and the kinetics of ordering. Here $V$ and $H$, respectively, mean vertical and horizontal in an image plane, which is perpendicular to the axis of incident light.

A sample (TPP) was sandwiched between two cover glasses, and we observed the transformation process from

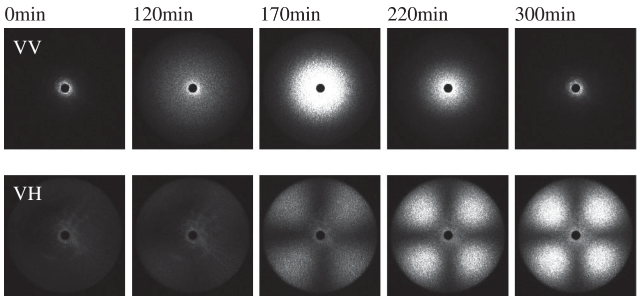

FIG. 1. Temporal change in the light scattering pattern observed during NG-type LLT at 215 K. The black dot in the center of each scattering pattern is due to the beam stopper. We show $VV$ and $VH$ scattering patterns at the same annealing time in the top and bottom raw, respectively.

liquid I to liquid II after a temperature quench from 303 K to an annealing temperature $T_a$ with a rate of 100 K/ min. The details of the experiments are described in [42].

First, we show a typical temporal change of $VV$ and $VH$ scattering patterns observed at $T_a = 215$ K in Fig. 1. We can see almost isotropic circular patterns for $VV$ scattering, whereas we see four leaf patterns for $VH$ scattering. The intensity of the former shows a clear maximum, whereas that of the latter monotonically increases with the annealing time $t$ at this temperature. For $VV$ scattering patterns, we can also notice that the scattering intensity does not decrease toward the wave number $q \to 0$, and has a finite value (see below on details).

The $VH$ scattering signal has a typical four leaf pattern, which is often observed for crystalline spherulites. This indicates that there are anisotropic scatterers which have a radial symmetry in liquid II droplets. This we confirmed by polarizing microscopy observation: droplets of liquid II show weak Maltese cross patterns under the crossed Nicols condition.

Second, we show the temporal change in the averaged intensity of a 2D scattering image for both $VV$ and $VH$ scattering signals in Fig. 2. We can immediately notice that the $VH$ scattering is much weaker than the $VV$ scattering. The $VV$ scattering intensity has a distinct maximum, whereas the $VH$ one monotonically increases with the annealing time $t$ above the spinodal temperature $T_{\mathrm{SD}}$, which we estimated as $T_{\mathrm{SD}} = 213.5 \pm 0.5$ K. This feature is common to all NG-type LLT. The temporal change in the $VV$ scattering intensity is consistent with the first observation of the turbidity change during formation of the glacial phase by Kivelson and his co-workers [12]. In addition to the fact that droplets of liquid II formed above $T_{\mathrm{SD}}$ are optically birefringent and exhibit Maltese cross patterns under the crossed Nicols condition, we can conclude that the $VH$ scattering mainly reflects the formation of microcrystallites in liquid II droplets at rather high annealing temperatures, where it monotonically increases with $t$ [see Fig. 2(a)].

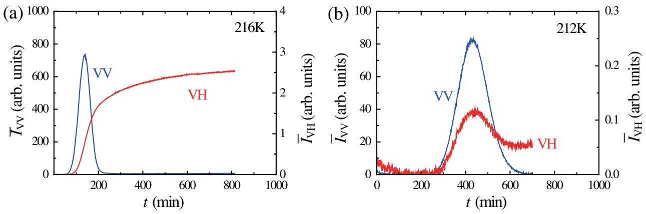

FIG. 2 (color online). Comparison of the $VV$ and $VH$ intensity averaged over $0.35\ \mu\mathrm{m}^{-1} < |q| < 4.5\ \mu\mathrm{m}^{-1}$, $\bar{I}_{VV}$ and $\bar{I}_{VH}$, at $T_a = 216$ K (a) and 212 K (b). The $VH$ intensity is much smaller than the $VV$ intensity. At temperatures above 213 K, the increase of $VH$ intensity delays from that of $VV$ intensity. At temperatures below 212 K, the $VH$ intensity has a clear maximum as the $VV$ intensity does.

For crystalline spherulites, even a $VV$ scattering pattern is known to become strongly anisotropic [44]. For droplets of liquid II, however, we see distinct anisotropy only in $VH$ scattering patterns and not as clearly in $VV$ ones. This means that the level of optical anisotropy in droplets of liquid II containing nanocrystallites is considerably lower than that of crystalline spherulites. Together with the difference in the temperature dependence of the nucleation frequency and the growth rate between the two [5], we suggest that droplets of liquid II (or the glacial phase) are distinct from crystalline spherulites formed at higher temperatures.

Third, we focus on the behavior of $VH$ scattering intensity. For $T_a \geq 213$ K, the $VH$ scattering intensity monotonically increases with an increase in $t$ [Fig. 2(a)], whereas for $T_a \leq 212$ K it exhibits a distinct peak as $VV$ scattering does, at a time when the $VV$ scattering one has a peak [Fig. 2(b)]. The $VH$ scattering intensity also becomes very weak at these low annealing temperatures. Here it is important to note that the $VH$ scattering can also arise from isotropic density fluctuations. We can see this from the following expressions for $VH$ and $VV$ scattering from an optically isotropic system [45]:

$$I^{VH}(q,\psi) = \frac{1}{4k_0^4} I_0^{VH} q^4 \sin^2\psi \cos^2\psi S(q), \tag{1}$$

$$I^{VV}(q,\psi) = \frac{1}{4k_0^4} I_0^{VV} (2k_0^2 - q^2\cos^2\psi)^2 S(q), \tag{2}$$

where $\psi$ is the azimuthal angle from the $H$ direction, $S(q) = \langle \hat{\rho}(q)\hat{\rho}^*(q)\rangle$ is a structure factor, $\hat{\rho}(q)$ is the Fourier component of density fluctuations $\rho(\vec{r})$, $I_0^{VH} = \langle |E_0^V|^2\rangle$, and $I_0^{VV} = \langle |E_0^H|^2\rangle$, and $E_0^{VH}$ and $E_0^{VV}$ are the two scattering electric fields after passing through the analyzer. Then, the angular averaged scattering function of $VH$ and $VV$ scattering, $I_{VH}(q)$ and $I_{VV}(q)$, are obtained, by integrating $I^{VH}(q,\psi)$ and $I^{VV}(q,\psi)$ in terms of $\psi$ from 0 to $2\pi$, as

$$I_{VH}(q) = \frac{\pi}{16k_0^4} I_0^{VH} q^4 S(q), \tag{3}$$

$$I_{VV}(q) = \frac{\pi}{16k_0^4} I_0^{VV}(32k_0^4 - 16k_0^2 q^2 + 3q^4) S(q). \tag{4}$$

This means that both $I_{VV}$ and $I_{VH}$ are proportional to $S(q)$ for isotropic density fluctuations. Thus, the similar temporal behavior of $I_{VV}$ and $I_{VH}$ in Fig. 2(b) strongly suggests that both of them primarily originate from isotropic density fluctuations and not from fluctuations of optical anisotropy (see below).

Fourth, we focus on the $q$ dependence of the $VV$ light scattering intensity $I_{VV}(q)$ in the course of LLT. For NG-type LLT at 218 K, we observe a clear Porod law regime where $I_{VV}(q) \propto q^{-4}$, indicating the presence of a sharp interface between the two phases [42]. This is consistent with our microscopy observation of NG-type LLT. Droplets of liquid II are formed in the matrix of liquid I with a sharp interface between them. Another important point is that $I_{VV}(q)$ approaches a nonzero constant in the limit of $q \to 0$ [42], which clearly indicates that the order parameter $S$ governing this transformation is of a nonconserved nature. This is consistent with our basic picture, but not with our previous structure factor calculated from a phase-contrast microscopy image [6], which turned out to be caused by imperfectness of an optical transfer function of the objective lens used and with our previous assumption for the conserved diffusive dynamics of density [14]. These points will be described elsewhere.

For SD-type LLT, on the other hand, we cannot see the Porod regime in our $q$ range [42], although we cannot exclude a possibility that there is a Porod regime outside our $q$ range. This is consistent with SD-type ordering, which is characterized by the absence of a sharp spatial change in the order parameter, i.e., by continuous growth and decay of the order parameter fluctuations.

Now, we focus on the temporal change in the $VH$ scattering intensity $I_{VH}(q)$ and its dependence on the annealing temperature, which is shown in Fig. 3. First, we can see a large difference in the $q$ dependence of the intensity between above and below $T_{\mathrm{SD}}$. At 218 K, after some time, a peak appears at a finite wave number $q_p$ and its position gradually shifts toward a lower wave number with time. We confirmed that $q_p^{-1} \propto t$, which is consistent with the linear growth of droplet size in NG-type LLT [5]. In the late stage, we see a well-developed Porod law regime where the intensity is proportional to $q^{-4}$. The low $q$ region has almost a constant intensity in the early stage [Fig. 3(a)], which is markedly different from ordinary $VH$ scattering from crystal spherulites, whose intensity goes to zero with decreasing $q$ due to the presence of spherical symmetry [44]. This scattering signal which is finite at $q \to 0$ is independent of $\psi$, as we can see in the $VH$ scattering pattern at $t = 300$ min of Fig. 1. This $VH$ scattering which is insensitive to $\psi$ indicates the presence of a significant contribution from random orientation fluctuations. Note that random orientation fluctuations cause an isotropic scattering contribution independent of $\psi$ for not only $VV$, but also $VH$ scattering [46]. This suggests that although there is a tendency for nanocrystallites to align along the radial direction of liquid II droplets on average, there are also nanocrystallites whose orientational correlation depends solely on the distance between them and is rather short range.

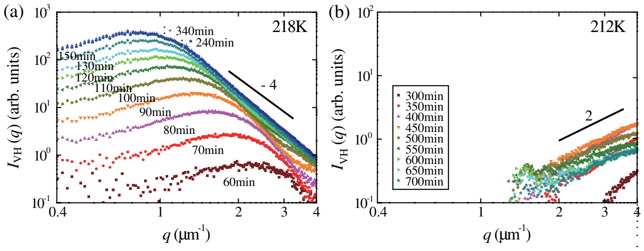

FIG. 3 (color online). Temporal change in the $q$-dependent $VH$ light scattering intensity $I_{VH}(q)$ during the transition process at 218 K (a) and 212 K (b). The intensity profile at 218 K clearly shows the $q$ dependence of exponent $-4$ known as the Porod law. At 212 K, on the other hand, we see the $q^2$ dependence at a high $q$ region.

Here, we consider the nature of structural evolution in NG-type LLT [4], focusing on the following two problems, (1) why there is the radial symmetry of nanocrystal orientation in droplets of liquid II formed in NG-type LLT, which is the primary cause of four-leaf $VH$ scattering patterns (Fig. 1), and (2) why nanocrystallites do not keep growing in size after their formation. First, we focus on problem (1). In our previous study [9], we found that liquid II is more wettable to crystals than liquid I, implying a lower nucleation barrier $\Delta G$ for crystal nucleation in liquid II than in liquid I. On the other hand, the molecular mobility $\mu$ is much higher in liquid I than in liquid II. Note that $T_a$ is in the glass transition region of liquid II but above that of liquid I [5,47], implying that liquid II, formed in NG-type LLT, is in a glassy state. Thus, the nucleation probability, which is proportional to $\mu \exp[-\Delta G/(k_B T)]$ ($k_B$ being Boltzmann's constant), should be maximum at the liquid I/liquid II interface. Furthermore, the growth should be easier in a direction perpendicular to the interface toward the liquid I side because of much larger $\mu$ there. We speculate that this coupling between the liquid I/liquid II interface and the crystal growth direction is the origin of the radial symmetry. However, imperfection of the coupling leads to randomness in crystal orientation, which may be responsible for $VH$ scattering components that remain finite for $q \to 0$ (see above). The imperfection should gradually increase when $T_a$ approaches the glass-transition temperature ($T_g$) of liquid I since the mobility gradient at the interface becomes smaller. Now, we consider problem (2). The growth of nanocrystallites is suppressed by slow dynamics associated with the glass transition of liquid II immediately after the transformation from liquid I to glassy liquid II. NG-type ordering leads to a discontinuous change from liquid I to liquid II, which results in a discontinuous drop of $\mu$. The faster growth of glassy liquid II than the crystal [5] leads to immediate inclusion of the latter in the former, preventing further growth of the crystals. This scenario also indicates that the amount of nanocrystallites should steeply decrease below $T_{\mathrm{SD}}$ since (i) there is no mechanism to rapidly lower $\Delta G$ for SD-type LLT, where the order parameter changes only continuously, and (ii) the mobility is very low even for liquid I since $T_a$ becomes closer to $T_g$ of liquid I. This is consistent with our observation [see Fig. 4(b)] and our previous estimation of the amount of nanocrystallites [5]. Since the discussion here is speculative, the above scenario is to be confirmed carefully in the future.

Next, we focus on structural evolution in SD-type LLT. The behavior of the $VH$ scattering below $T_{\mathrm{SD}}$ is very different from that above $T_{\mathrm{SD}}$. As can be seen in Fig. 3, $I_{VH}(q)$ has the $q^2$ dependence in the high wave number region for $T_a = 212$ K. As shown in Fig. 4(a), the scattering intensity along $\psi = 0°$ and $90°$ is very weak for SD-type LLT, indicating that random orientation fluctuations which produce the $\psi$-independent scattering signal for $VH$scattering (see above) are not a major cause of the $VH$ scattering. Furthermore, we cannot expect spherical symmetric optical anisotropy for SD-type LLT. Thus, it is natural to consider that the $VH$ scattering component, which exhibits a peak as a function of time [see Fig. 2(b)], primarily originates from isotropic density fluctuations. Then, we can apply Eq. (3) to this case, which implies that the $VV$ scattering may have the Ornstein-Zernike-like $q$ dependence since the $q^2$ dependence in $VH$ scattering means $q^{-2}$ dependence in $VV$ scattering. We note that this $q^2$ dependence of the intensity is difficult to explain by orientational fluctuations of optical anisotropy. A weak remaining signal at $t = \infty$ [see Fig. 2(b) and Fig. 4(b)] may still come from a small amount of nanocrystallites, whose formation is induced by the reduction of the liquid-crystal interfacial tension by LLT [4,9]. This nanocrystal formation process may be retarded from growth of density fluctuations since, for SD-type LLT, the order parameter only continuously grows with time unlike NG-type LLT.

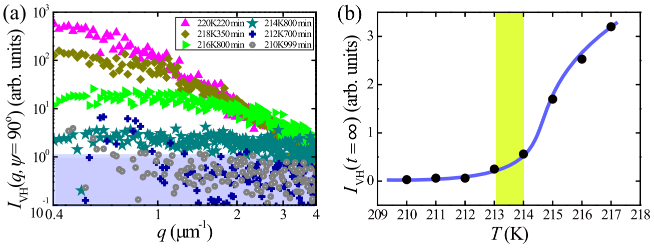

FIG. 4 (color online). (a) $VH$ scattering intensity along the line of $\psi = 90°$. We can see that the intensity steeply decreases with decreasing $T_a$ and becomes almost zero (or, below the noise level indicated by a region of tint blue color) below $T_a = 214$ K. (b) The dependence of the average $VH$ intensity at the end of the transition $I_{VH}(t = \infty)$ on $T_a$. The fact that the $VH$ intensity remains after the transformation at high $T_a$ indicates that the final phase contains nanocrystallites. On the other hand, the intensity significantly decreases with a decrease in $T_a$, suggesting that the final state formed at lower $T_a$ contains a much less amount of nanocrystallites. The vertical yellow belt indicates the location of $T_{\mathrm{SD}}$.

The most important question on the unusual transformation process of TPP is whether it is LLT or merely the formation of nanocrystallites. Our $VH$ scattering result at a low annealing temperature provides crucial information on this question. As shown above, we found that the $VH$ scattering intensity exhibits a peak as a function of the annealing time $t$. This feature cannot be explained by the scenario based on nanocrystal formation alone. This is because, within this scenario, there is no mechanism that leads to the decrease in the depolarized scattering intensity. Once crystals are formed, they do not disappear unless the temperature is increased, that is, crystallization is a one way transformation from a metastable to a stable state. On noting the similar temporal change in the $VV$ scattering intensity, the most natural interpretation is that both $VV$ and $VH$ scattering are largely due to isotropic density fluctuations at temperatures below $T_{\mathrm{SD}}$. This is consistent with our scenario that LLT is a consequence of cooperative ordering of a scalar order parameter, more specifically, the number density of locally favored structures, under a coupling to density [14].

This dominance of density fluctuations over fluctuations of optical anisotropy below $T_{\mathrm{SD}}$ is further supported by the following facts. (1) There is a steep decrease of the $VH$ scattering intensity below $T_{\mathrm{SD}}$ [see Fig. 4(b)]. (2) The $VH$ scattering intensity at $\psi = 0°$ and $90°$ is negligibly small for SD-type LLT [see Fig. 4(a)], indicating that the contribution of randomly oriented optical anisotropy is very weak there and the $VH$ scattering mainly comes from isotropic density fluctuations. (3) The strength of optical birefringence and the amount of crystals formed during LLT both become very small (see [5]).

Our study suggests that two phenomena, LLT and nanocrystal formation, are different phenomena although they proceed simultaneously in a strongly coupled manner. We argue that the key phenomenon is LLT and nanocrystal formation is induced by LLT, since the interfacial energy between crystals and liquid II is much lower than that between crystals and liquid I [4,9]. We note that this conclusion is also supported by the fact that, at high pressure, crystallization is suppressed and only LLT is observed [30]. The coupling between LLT and nanocrystal formation will be discussed in more detail elsewhere.

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