Control of the Liquid-Liquid Transition in a Molecular Liquid by Spatial Confinement

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Generally, phase transitions are seriously affected by spatial confinement. This effect is important for its own sake, but also for applications to nanotechnology. Here we report the first systematic experimental study on confinement effects on a liquid-liquid transition of a molecular liquid. We found that one liquid can be transformed into another purely by spatial confinement. This indicates that the liquid state cannot be specified by the temperature and pressure alone, but it is also affected by its size in a discontinuous manner: the phase of a liquid in a narrow space can, in principle, be different from that in the bulk. This finding would deepen our basic understanding of the liquid state.

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The divergence of the correlation length ξ of the order parameter (e.g., density for a vapor-liquid transition and magnetization for a paraferromagnetic transition) is a key characteristic of critical phenomena [1]. It is well known that many phase transitions are dramatically affected by geometrical confinement when ξ becomes comparable to the characteristic length of confinement d. This is because critical fluctuations are suppressed at least along the direction of the confinement; even the effective spatial dimensionality may be changed. This problem of finite-size effects on phase transitions has been intensively studied both theoretically and experimentally due to its fundamental importance [2–6]. One of the main results is the d dependence of the critical temperature T_c. According to Fisher's scaling theory [2],

$$[T_c(\infty) - T_c(d)]/T_c(\infty) \propto (d/a)^{-\lambda}, \tag{1}$$

where a is the lattice (or atomic) size and $\lambda = 1/\nu$ (ν being the critical exponent for ξ). This relation was confirmed, for example, for the superfluid transition temperature of liquid He^4 [5]. Confinement effects also play an important role in a strongly first-order phase transition [4]; e.g., the freezing point of water confined in mesoporous materials is significantly lowered. This problem has recently reattracted considerable attention due to its relevance in nanotechnology.

Usually it is believed that any single-component substance has only one unique liquid state. Contrary to this common sense view, many pieces of experimental and numerical evidence have recently been accumulated for the existence of a liquid-liquid transition (LLT), namely, the existence of more than two liquid states for a single-component substance [7]. In addition to these examples, a few years ago we found firm experimental evidence for the existence of LLT in molecular liquids, triphenyl phosphite (TPP) [8,9], and n-butanol [10], at ambient pressure. We discovered two types of LLT kinetics upon the transformation of liquid I to liquid II: one is nucleation-growth (NG) type; the other is spinodal-decomposition (SD) type. For $T > T_{\mathrm{SD}}$, where T_{SD} is the spinodal temperature, liquid II is nucleated in liquid I in the form of spherical droplets and then these droplets grow linearly with time. Finally, the system becomes homogeneous liquid II. For $T < T_{\mathrm{SD}}$, on the other hand, the amplitude of the order-parameter fluctuations grows exponentially in time and its characteristic length remains constant in the early stage. This is characteristic of Cahn's linear regime [1]. Then, the characteristic domain size R grows as $R \sim t^{0.5}$. This exponent suggests that the order parameter governing the LLT is a nonconserved variable [1]. Finally, the system becomes homogeneous liquid II. We proposed that the order parameter governing LLT may be the fraction of locally favored structures, which is a nonconserved order parameter [11]. From the early stage of SD-type LLT, we estimated ξ and found that ξ exhibits the following critical divergence: $\xi = \xi_0[(T_{\mathrm{SD}} - T)/T_{\mathrm{SD}}]^{-\nu}$, where the bare correlation length ξ_0 is 60 nm, $T_{\mathrm{SD}} = 215.5$ K, and $\nu = 0.5$ [9]. This critical-like divergence near the spinodal line (far from the critical point) is rather unusual. This may be explained by the mean-field nature of LLT, which is supported by the long bare correlation length and the value of $\nu = 1/2$ (see, e.g., Ref. [1]).

Practically, this unusually large value of ξ_0 is quite useful for controlling LLT by spatial confinement, since ξ can easily reach the length scale of microns near T_{SD}. This means that in TPP a confinement of the order of microns should induce significant finite-size effects on LLT. Studying finite-size effects may also be useful for elucidating the nature of the order parameter. In particular, it is not clear why the bare correlation length ξ_0 of this system is so long compared to the molecular size (~1 nm) and what it represents. This is one of the most mysterious problems, which may be intimately related to the nature of LLT. Finite-size effects on LLT may yield valuable insight into these difficult, but important, questions.

We also mention another importance of the study of finite-size effects. Recently, confinement effects have been used to study the LLT in liquid water (see, e.g., [12]), which, even if it exists, is completely hidden by crystallization in bulk water. In these studies, a spatial confinement is used to avoid the crystallization of water.

However, there have so far been no studies on confinement effects on the LLT itself. So it is crucial to study finite-size effects on the LLT not only for elucidating the nature of the order parameter governing the LLT, but also for uncovering the LLT hidden by the other ordering phenomena such as crystallization by using a confinement.

The sample used was TPP, which was purchased from Acros Organics and used after extracting only a crystallizable part. We avoided moisture to prevent chemical decomposition. We observed the transformation process from liquid I to liquid II with phase-contrast microscopy. We prepared a wedge-shaped sample cell, whose wedge angle θ is 0.0075 rad. We also prepared a sample cell, which was made of two parallel thin glass plates. The spacing between the two cover glasses was controlled to be between 1 and 20 μm by using monodisperse glass beads as spacers. The temperature was controlled within ± 0.1 K by a computer-controlled hot stage (Linkam LK-600PH) with a cooling unit (Linkam L-600A). We confirmed that there are few surface wetting effects on LLT by using a wedge-shaped cell. We saw wetting of neither liquid I nor liquid II at the edge part of the wedge cell; in other words, there is no filling transition [13]. This enables us to study solely finite-size effects on LLT in our cells without suffering from other surface effects such as wetting and random-field effects. We also confirmed good reproducibility of the experiments. The intensity distribution function $P(I)$ and the structure factor $S(q)$ were calculated from an optical microscopy image, using digital image analysis (DIA) [14,15].

First we show a pattern observed in a wedge-shaped cell at $T = 214$ K and $t = 150$ min during the LLT [Fig. 1(a)]. Here t is the time after the temperature quench. We confirmed that for a thick enough sample (bulk) the transformation pattern is SD type at this temperature [8,9]. However, the transformation behavior clearly depends on d [Fig. 1(a)]. The transformation pattern is SD type at large d; however, droplets of liquid II nucleate and grow with time for small d, which is smaller than the critical thickness d_{SD}. We can see the increase of the droplet number density with an increase in d. To analyze this change in a more quantitative manner, we calculated the intensity distribution function $P(I, d)$ from an image [15] as a function of d. Here $P(I, d)$ represents an average of $P(I, h)$ over a region $d - \delta d < h < d + \delta d$, where h is the spacing between the upper and lower glass and we set δd to be 0.15 μm. Figure 1(b) shows the d dependence of the shape of $P(I, d)$. We can see two types of shapes of $P(I, d)$: For small d, $P(I)$ has a peak with a distinct shoulder indicative of the appearance of a small additional peak. The existence of the two peaks in $P(I, d)$ indicates that liquid I and liquid II coexist during the transformation. This is a characteristic feature of NG-type LLT [9,16]. For large d, on the other hand, $P(I, d)$ has only a broad peak, suggesting that the density distribution during the transformation is continuous, even though microscope images might give an impression that there are distinct droplets (see Refs. [9,16]). For SD, $P(I)$, which initially has a sharp peak at the intensity of liquid I, becomes broad in the intermediate stage, and finally becomes sharp again to form a peak at the intensity of liquid II [9]. The absence of a double-peak structure of $P(I)$ is characteristic of SD of a nonconserved order parameter. We use this difference in the shape of $P(I)$ as a fingerprint to distinguish NG and SD.

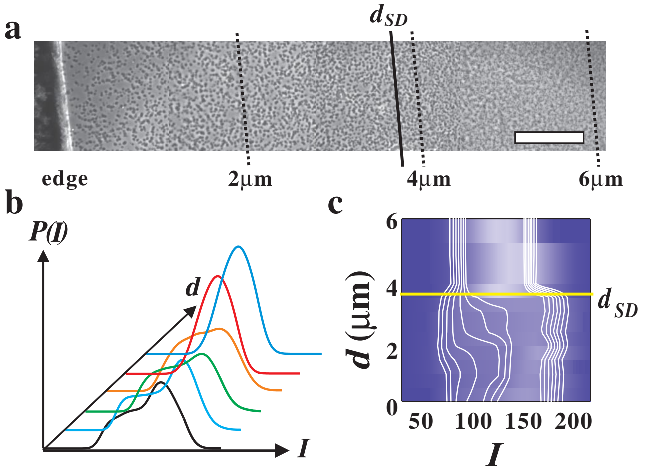

FIG. 1 (color online). (a) Phase-contrast microscopy image. A top view of a wedge-shaped sample cell filled with TPP. $T = 214$ K and $t = 150$ min. The black region on the left-hand side is the edge of the wedge-shaped cell. The sample thickness is indicated with dashed lines below the image. Scale bar corresponds to 100 μm. (b) d dependence of the intensity (I) distribution function $P(I)$ at $T = 214$ K and $t = 150$ min. (c) Contour plot of the d dependence of $P(I)$. With an increase in $P(I)$, the color becomes brighter. The white lines are the contours of $P(I)$.

Figure 1(c) indicates the intensity map of $P(I, d)$. For small d, $P(I, d)$ has a peak around $I = 150$ and has a gradual slope around $I = 100$, which corresponds to the shoulder. We can see a distinct change in the shape of $P(I, d)$ at $d = d_{\mathrm{SD}} = 3.8$ μm, reflecting the change of the shape of $P(I)$ from double peaked to single peaked [see Fig. 1(b)]. This means that $T_{\mathrm{SD}}(d) = 214$ K at $d = 3.8$ μm. This sharp change of the behavior at $d = 3.8$ μm is consistent with the mean-field nature of LLT [9], namely, a shape boundary between NG and SD behavior [16].

Next we studied the kinetics of SD-type LLT under a planar confinement at various T_a's to obtain the d dependence of the critical divergence of ξ. We calculated $S(q)$ from each image, using DIA [14,15], and extracted the peak wave number q_p. Figures 2(a) and 2(b) show the temporal change of q_p and the shape of $S(q_p)$ at 212 K, respectively, for three different d's. q_p is constant with time and the peak intensity $S(q_p)$ increases exponentially (not shown) in the initial stage of SD-type LLT: Cahn's linear regime. Then, q_p decreases as $q_p \sim t^{-0.5}$. This crossover occurs since nonlinear effects start to play an important role after this crossover time, reflecting the enhancement of the amplitude of the order-parameter fluctuations [1]. The late-stage time exponent (1/2) is consis-

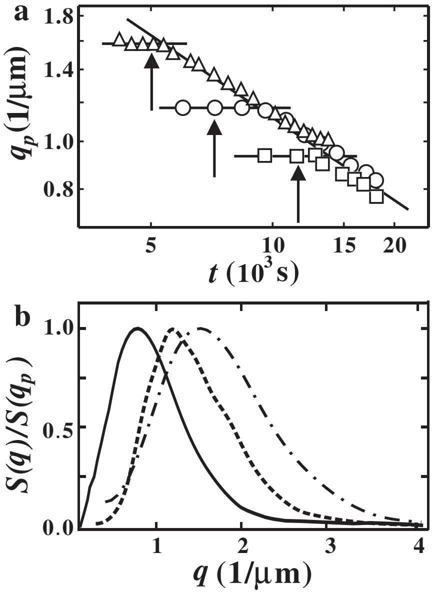

FIG. 2. (a) Temporal change of q_p at 212 K for $d = 10$ μm (△), 2.5 μm (○), and 2 μm (□). (b) Comparison of the normalized scattering function $S(q)/S(q_p)$ at the times indicated by the arrows in (a) for $d = 10$ μm (dash-dotted line), 2.5 μm (dotted line), and 2 μm (solid line).

tent with the prediction of the Allen-Cahn relation, $dR/dt \sim \sqrt{Lt}$ (L being the kinetics coefficient), which describes the domain interface motion in a system of a nonconserved order parameter [1,9]. We can see that the temporal change of q_p for various d's almost collapses on the same power law in the late stage, which indicates that L is independent of d.

On the other hand, q_p in the linear regime does depend on d. This means that ξ is a function of d since we have the relation of $\xi = 1/(\sqrt{2}q_p)$ in the linear regime [1,9]. Figure 3(a) shows $\xi(T)$ for various values of d [17]. We confirmed that $\xi(T, d)$ is well fitted by $\xi(T, d) = \xi_0(d) \times [(T_{\rm SD}(d) - T)/T_{\rm SD}(d)]^{-\nu}$. We found $\nu = 0.50 \pm 0.02$ for all the cases, which means that LLT obeys a mean-field theory under the confinement as in bulk. Thus, we fixed $\nu = 0.5$ to reduce the number of the adjustable parameters in the fitting of the above function to the data and to obtain the d dependence of $\xi_0(d)$ accurately. We independently determined $T_{\rm SD}(d)$ from optical microscopic measurements (see, e.g., Fig. 1). Figure 3(b) shows the d dependence of ξ_0, which is obtained from the fitting. We can clearly see that $\xi_0(d)$ decreases with a decrease in d. We also found the following empirical relation: $\xi_0(\infty) - \xi_0(d) = \xi_0(\infty)\exp(-d/d_c)$, where d_c is the characteristic decay length and is determined as 2.79 μm by the fitting. This decrease in the mesoscopic length ξ_0 may reflect the suppression of hierarchical ordering in a liquid induced by specific intermolecular interactions. If this is the case, it may share some common physics with the suppression of the hydrogen-bonded network in confined water under a stronger confinement [18]. This may have a significant implication on the question of the origin of the long bare correlation length. We speculate some hierarchical structural ordering takes place in this liquid and it plays a crucial role in LLT. For an extremely strong confinement, ξ_0 might become short enough to break the mean-field nature of the transition.

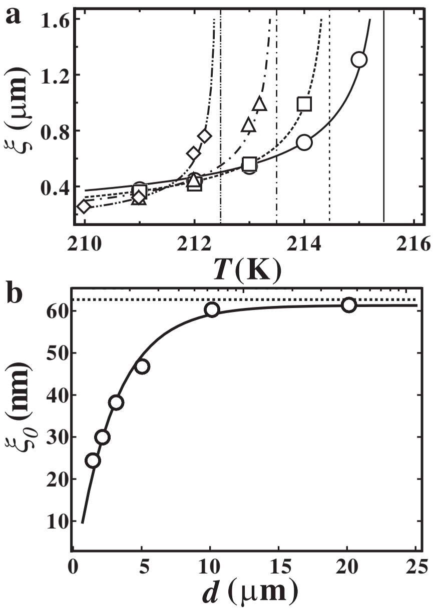

FIG. 3. (a) d dependence of the critical divergence of ξ: (○) $d = 10$ μm, (□) $d = 5$ μm, (△) $d = 3$ μm, and (◇) $d = 2$ μm. The position of the vertical lines represents $T_{\rm SD}(d)$ independently determined by optical microscopy observation of the transformation process. The fitted curves are also shown by the lines of the same types as the vertical ones. (b) d dependence of ξ_0. The dashed line is the bulk value for ξ_0.

Figure 4(a) plots $\Delta T_{\rm SD} \equiv T_{\rm SD}(\infty) - T_{\rm SD}(d)$, where $T_{\rm SD}(\infty) = 215.5$ K [8], as a function of $d/\xi_0(d)$. Usually, this shift of the critical temperature is plotted against d/a to check the prediction of Fisher's scaling [2]. Note that in ordinary systems the bare correlation length $\xi_0 = a$ is associated with the size of the elementary length scale of a system such as the size of constituent molecules or atoms. Thus, it is not expected that ξ_0, or a, depends on d. However, in our case, the bare correlation length, which is an intermediate length scale much larger than the molecular size a, does depend upon d. Using d/ξ_0 as a new key parameter instead of d/a, we recover $\Delta T_{\rm SD} \propto [d/\xi_0(d)]^{-\lambda}$ with $\lambda = 2$, which is consistent with Fisher's scaling $\lambda = 1/\nu$ (note $\nu = 0.5$ in our case). We expect that this generalized scaling relation $\Delta T_{\rm SD} \propto [d/\xi_0(d)]^{-1/\nu}$ may hold universally.

We also found that the binodal temperature $T_{\rm BN}$ is lowered by the spatial confinement. Figure 4(b) shows the temperature dependence of the growth speed of liquid II droplets, V, for strong and weak confinement. We fit to the data $V = V_0 \exp[-B/(T - T_0)]\exp[-\pi\sigma^2 l T_{\rm BN}/\Delta H(T_{\rm BN} - T)k_B T]$, where V_0, B, σ, l, ΔH, and k_B are the prefactor, the Vogel-Fulcher activation energy for vis-

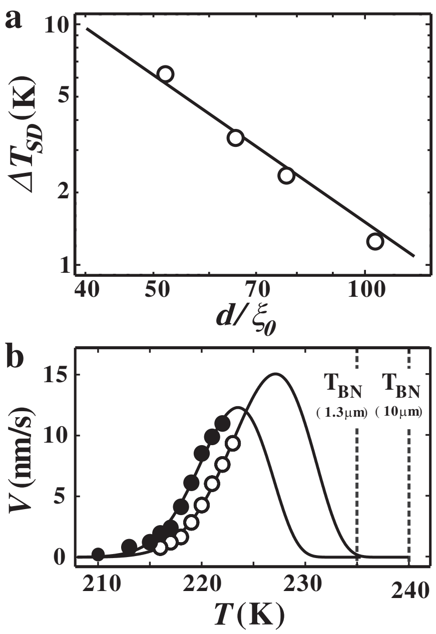

FIG. 4. (a) d dependence of ΔT_{SD}. The solid line represents the prediction of the generalized Fisher scaling: $\Delta T_{SD} \propto [d/\xi_0(d)]^{-\lambda}$, where $\lambda = 1/\nu = 2$. (b) Comparison of the growth speed V of liquid II droplets for $d = 10$ μm (open circles) and 1.3 μm (filled circles).

cous flow, the interfacial tension, the critical length of growth, the enthalpy change upon LLT, and Boltzman's constant, respectively. We determined $V_0 = 1.32$ m/s, $B = 533$ K, $\Delta H = 28 \times 10^6$ J/m^3, and $\sigma^2 l = 6.45 \times 10^{-15}$ J^2/m^3 from the fitting to the T dependence of V in bulk. Here, thus, we treat only T_{BN} as an adjustable parameter. We checked the validity of this estimation method of T_{BN} for bulk TPP [8]. T_{BN} for $d = 1.3$ μm is found to be about 5 K lower than that for $d = 10$ μm [see the dashed lines in Fig. 4(b)]. This means we can realize a transition from liquid I to liquid II solely by increasing the strength of the spatial confinement.

In summary, we succeeded in revealing the spatial confinement effects on the LLT in TPP. We found a significant decrease of both T_{SD} and T_{BN} of the LLT with increasing the confinement strength: more than several kelvin just with micronscale confinement and probably substantially more under nanoscale confinement. This means that one liquid can be transformed into another purely by spatial confinement. The strength of confinement is found to be characterized by the scaled confinement strength, d/ξ_0. The generalized Fisher's scaling relation for T_{SD} (not limited to the critical temperature) under confinement may be applicable to LLTs in any liquids. Our finding may have significant implications on the physical understanding of the LLT and the mesoscopic structure in the liquid, whose length scale is characterized by ξ_0.

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[17] Here we explain the estimation of ξ from the characteristic wavelength of SD, q_p, using $\xi = 1/(\sqrt{2}q_p)$ [1]. The shortest ξ estimated is about 0.4 μm, which is only 2 times our resolution of microscopy. However, what we actually observe in the early stage of SD is sinusoidal order-parameter fluctuations with a characteristic wavelength of $2\pi/q_p = 2\sqrt{2}\pi\xi \sim 3.6$ μm. $S(q)$ indeed has a distinct peak at q_p ($\sim$1.7 μm^{-1}). Since we get q_p from a 2D power spectrum of an image, it has a high resolution due to averaging effects [14].
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