

Fragility control using the liquid-liquid transition in molecular liquid

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It is widely believed that there is only one unique liquid state for any material and the properties are decided only by pressure and temperature. However, recent evidence suggests that there can be more than two liquid states even for a single component liquid and their properties are different from each other[1]. The transition between the different liquid states is called a "liquid-liquid transition (LLT)". Although the existence of LLT has become more and more convincing, the nature and origin of it is still unknown. This situation mainly comes from the experimental difficulties; that is, the transition is located at high pressure and high temperature for atomic liquids or is hidden by crystallization.

Recently, we discovered LLT in molecular liquid, Triphenyl Phosphite [2]. This LLT occurs at ambient pressure and ordinary temperature. Thus, we can observe the kinetics of LLT with phase contrast microscopy. We found two patterns of transformation, nucleation-growth type (discontinuous) and spinodal-decomposition type (continuous). We also studied the kinetics of SD-type transformation. We found that the correlation length diverges as $\xi = \xi_0 [T_{SD} - T/T_{SD}]^{-\nu}$ (where $\xi_0 = 60$ nm and $\nu = 0.5$). This is an indication of a critical-like anomaly associated with LLT [3].

We propose that the order parameter controlling LLT is the number density of the locally favored structures (LFS)[4]. During the transformation from Liquid I to Liquid II, the number density of LFS increases steeply but continuously. We define the scaled number density of LFS \tilde{S} as $\tilde{S}(t) = [S(t) - S(0)] / [S(\infty) - S(0)]$. Note that $S(0) = S_I$ and $S(\infty) = S_{II}$: \tilde{S} is zero for liquid I and 1 for liquid II. We found that the physical properties of liquids and glass states such as the diffusivity and the fragility change as a function of \tilde{S} . We measured the heat capacity of TPP with calorimetric measurement and it shows steplike change at the glass transition. Figure 1 shows T_g^L as a function of the heating rate Q at $\tilde{S} = 0, 0.66$ and 0.95 where T_g^L is the low edge temperature of the steplike change. We obtained the fragility index $m = \frac{d \log \tau}{d(T_g/T_g^L)}|_{T_g=T_g^L}$. For liquid I ($\tilde{S} = 0$), the fragility parameter m is 154. This value is consistent with those reported previously for TPP [6]. However, when \tilde{S} increases from 0.66 to 0.95, m decreases from 50 to 34. We found that the fragility is changed by the number density of LFS [5].

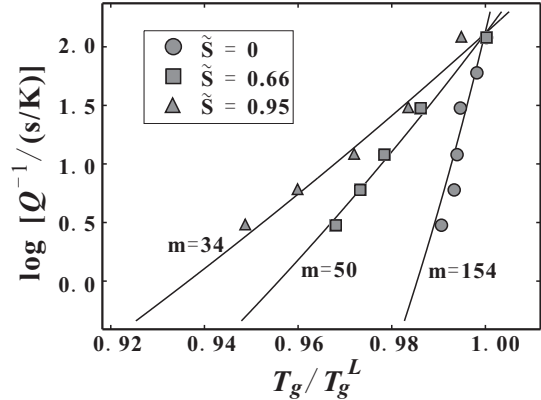


Figure 1: Heating-rate dependence of T_g for a liquid with $\tilde{S} = 0$ (circles), 0.7 (squares), and 1 (triangles). The solid curves are the fitted theoretical curves of the form $Q^{-1} = A \exp(DT_0/T - T_0)$. The fragility parameter m decreases from 154 ($\tilde{S} = 0$) to 34 ($\tilde{S} = 0.95$) with an increase in \tilde{S} .

At presentation, we report a new way to continuously control the physical properties of liquid and glass using continuous LLT.

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