Critical phenomena associated with liquid-liquid transition

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我々は分子性液体 Triphenyl Phosphite において液体・液体相転移を発見した。そのキネティクスを顕微鏡で観察した結果、核形成・成長型相転移とスピノーダル分解型相転移の 2 種類の相転移過程があることがわかった。スピノーダル分解型相転移を詳細に調べた結果、相関長 ξ がスピノーダル温度 T_{SD} に向かって $\xi = \xi_0[(T_{SD} - T)/T]^{-\nu}$($\xi_0$ = 60 nm, ν=0.5) で発散することがわかった。

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 (LLT)". There are a number of experimental indications suggestive of the existence of LLT[1]. Although the existence of LLT has become more and more convincing, the nature of the transition is still largely unknown. For example, critical phenomena associated with LLT and the kinetics of LLT have not been studied in detail so far. This situation mainly comes from the experimental difficulties. The transition is located at high temperature and high pressure for atomic liquids or is hidden by crystallization. The latter might be the case of water. For molecular liquids, the characteristic energy scale is on the order of the thermal energy at around room temperature.

Recently, we found convincing experimental evidence for the existence of LLT in a molecular liquid, triphenyl phosphite and n-butanol[2, 3, 4]. Both nucleation-growth-type (NG-type) and spinodal-decomposition-type (SD-type) phase transformations were directly observed with optical microscopy. From the image obtained with phase-contrast microscopy, we can calculate the structure factor $F(q)$. Figure 1 shows the temporal change in the peak intensity $F(q_p)$ and the peak wave number q_p during the phase transformation. In the early stage, $F(q_p) \propto \exp(\Gamma t)$ (Γ is a constant), whereas q_p is constant with time. This is the linear growth regime of phase transformation, which is known as the Cahn's linear regime for SD-type phase separation[5]. In the intermediate stage, the temporal decrease of q_p is well described by the power law $q_p \sim t^{-0.5}$. This exponent is characteristic of the late-stage coarsening of SD-type ordering of a nonconserved order parameter.

According to the linear theory of SD[5], we can estimate the correlation length, ξ, of the relevant order parameter from the value of q_p of the initial linear regime: $\xi = (\sqrt{2}q_p)^{-1}$. Figure 2 shows the temperature dependence of ξ. ξ diverges as $\xi = \xi_0[(T_{SD} - T)/T]^{-\nu}$ (where ξ_0 = 60

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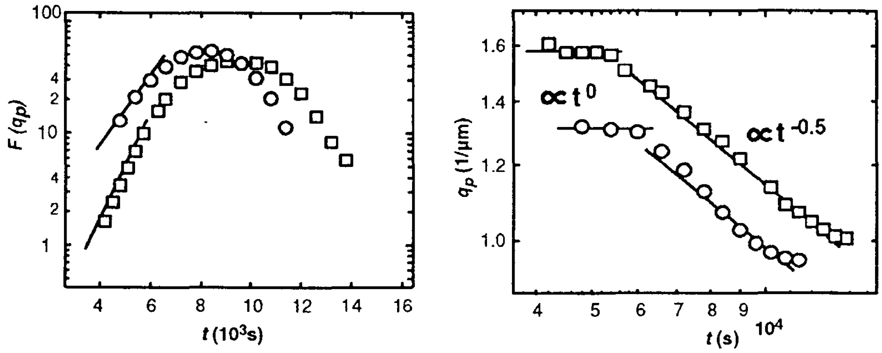

Figure 1: (Left) Temporal change of the peak intensity of the structure factor at 212K(square) and 213K(circle).(Right) Temporal change in the peak wave number of the structure factor.

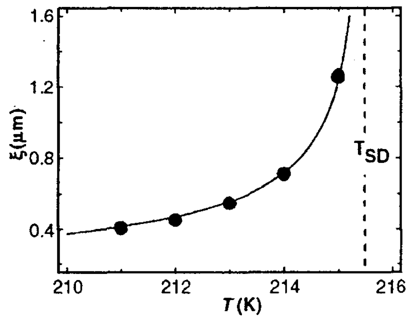

Figure 2: Temperature dependence of the correlation length ξ.

nm, ν=0.5) while approaching the spinodal temperature, T_{SD}[3]. This value for ν suggests the mean-field nature of LLT. This is consistent with the long bare correlation length.

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