Two-Order-Parameter Description of Liquids: Critical Phenomena and Phase Separation of Supercooled Liquids

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Because of the isotropic and disordered nature of liquids, the anisotropy hidden in intermolecular interactions are often neglected. Accordingly, the order parameter describing a simple liquid has so far been believed to be only density. In contrast to this common sense, we propose that two order parameters, namely, density and bond order parameters, are required to describe the phase behavior of liquids since they intrinsically tend to form local bonds. This model gives us clear physical explanations for two poorly-understood phenomena in supercooled liquids: (i) large-scale density fluctuations and (ii) phase separation of a one-component liquid into two liquid phases.

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Generally, a liquid phase is bounded by a gas phase and a solid phase, although some molecules having strong “topological” anisotropy exhibit additional phase known as a liquid crystalline phase above its solid phase \([1]\). By lowering a temperature of a gas phase, the potential energy becomes more important than the kinetic energy and intermolecular interactions come into play. At a gas-liquid phase transition point, the attractive interaction leads to the formation of a “liquid” phase. The principal physical quantity distinguishing the liquid and the gas phases is their density. Both phases have complete translational and rotational symmetry, and they are isotropic and homogeneous. Because of these features, a liquid state is usually assumed to be described by only one order parameter, density.

The physical properties of liquid are rather well understood at the temperature far from its stability limit, while very poorly understood especially near its liquid-solid phase transition \([2]\). Here we mention three of such examples: (i) glass transition phenomenon itself \([2, 3]\), (ii) large-scale density fluctuations in supercooled liquids \([4, 5]\), and (iii) an unusual phenomenon of phase separation of a simple one-component liquid into two liquid phases in a supercooled state \([6, 7]\). The key to understand these phenomena, we believe, is to realize that the above common sense that a liquid state can be described by only density order parameter is basically “wrong”. There are a number of studies that try to improve a theory of liquid by including many-body effects, or higher-order density correlations. The most important concept is the local bond orientational order (LORO) \([8, 9]\) based on the fact that even spherical molecules locally favor a tetrahedral configuration in a liquid phase: For example, Frank \([10]\) pointed out that icosahedral clusters of 13 particles have a significantly lower energy than more obvious “crystallographic” arrangements of the corresponding fcc or hcp structures. Based on this idea, he explained why a simple liquid metal can be so deeply supercooled. This concept of LORO leads to the recent development along this direction \([11, 12]\). However, we also need consider the anisotropic specific interactions that commonly exist in molecules having no spherical symmetry \([13]\). The most extreme case is the network formation due to hydrogen bondings, as in SiO\(_2\). For a general physical description of real liquids, thus, we need to introduce a new, non-trivial order parameter that can describe both topological and energetical effects inducing the locally favored configuration of liquid molecules or atoms and, then, to clarify the effects of its frustration with crystallization on the phase behavior of liquids.

The thermodynamic state of condensed matter can be described solely by the balance between the energetic interactions and the entropy of the system. Thus, we here focus our attention on an intermolecular attractive potential. The attractive interaction potential between a molecule and its neighbors is generally given by the form \(V(r, \Omega) = V(r) + \Delta V(r, \Omega)\), where \(r\) is the distance from the molecules and \(\Omega\) expresses the orientation. \(V\) represents the isotropic part of the interaction, while \(\Delta V\) its anisotropic part. This anisotropy comes from both (i) locally favored geometrical packing under attractive interactions \([14, 15]\) and (ii) specific anisotropic interactions, as explained above. We believe that these two types of anisotropic interactions, which can be commonly expressed by \(\Delta V\), play crucial roles in the physical properties of liquids.

It should be noted that the effects of the anisotropic part becomes more and more important with approaching to the liquid-solid phase transition, since the system becomes very sensitive to the strength and shape of the attractive potential; thus, even weak energetic anisotropy can lead to the dramatic effects. The dependence \(\Delta V\) on \(\Omega\) is not necessarily consistent with the symmetry favored by the isotropic part \(V\). This causes the energetic frustration, which plays key roles in the phase behavior of a supercooled liquid.
In this Letter, we propose a simple phenomenological Landau-type theory based on the coupling between two order parameters: (a) density \( \rho \) determined by the isotropic part \( \delta S \) of intermolecular attractive interactions and (b) bond order \( S \) determined by its anisotropic part \( \Delta V \). Here the bond parameter \( S \) is defined as the local number density of molecules having active bonds (i.e. molecules having a local configuration favoring \( \Delta V \)): 
\[
S(\vec{r}) = \Sigma_i \delta(\vec{r} - \vec{r}_i),
\]
where \( \Sigma_i \) is the sum over a unit volume and \( \vec{r}_i \) is the position vector of a molecule having active bonds \( i \). We are here aiming at making the simplest model that gives us a physical intuition to the phenomena. We demonstrate that the frustration between \( \rho \) and \( S \) is responsible for glassification phenomena and the related unusual phenomena such as critical-like large-scale density fluctuations and phase separation of a supercooled liquid into two liquid (glassy) phases. The two order parameters are prerequisite for describing the physical properties of liquid near its lower stability limit. On the basis of this two-order-parameter description, we here construct a phenomenological model, focusing only on large-scale fluctuations and the associating slow dynamics. We average out all the high wavenumber components of \( \rho \) and \( S \) by coarse-graining the system over the length scale much larger than the molecular spacing. In the standard theory of liquids \([6]\), the free energy of liquid is given by

\[
F_\rho = \frac{\tau}{2} \delta \rho(\vec{r})^2 - \frac{\alpha_3}{3} \delta \rho(\vec{r})^3 + \frac{\alpha_4}{4} \delta \rho(\vec{r})^4,
\]

where \( \tau = a_2(T - T^*) \) (\( T^* \): the lower stability limit of a liquid) and \( a_i \) is a positive constant. By including the gradient terms and the coupling between \( \rho \) and \( S \) into the above standard Hamiltonian of liquid, we obtain the following Hamiltonian that we believe is relevant to the description of liquid:

\[
\beta H = F_\rho + \int d^3 r \left( \frac{K_\rho}{2} \nabla \delta \rho(\vec{r})^2 - c_{1\rho} \delta \rho(\vec{r}) S(\vec{r}) - c_{1S} \rho(\vec{r}) \delta S(\vec{r}) - \frac{\kappa_2}{2} \delta S(\vec{r})^2 S(\vec{r}) - \frac{\kappa_3}{2} \rho(\vec{r}) \delta S(\vec{r})^2 \right) + \frac{\kappa}{2} \delta S(\vec{r})^2 + \frac{K_S}{2} (\nabla \delta S(\vec{r}))^2,
\]

where \( \beta = 1/k_B T \). \( S = \bar{S} + \delta S \), where \( \bar{S} \) is the average of \( S \) and given by \( \bar{S} = S_0 \exp(\beta \Delta V) \). We neglect a possible tensorial character of \( S \) and treat \( S \) as a scalar. The appearance of \( \bar{S} \) and \( \rho \) in the coupling terms instead of \( \delta S \) and \( \delta \rho \) is to take into account the fact that they are strongly dependent upon temperature, which directly affect the couplings. In Eq. (1), for \( c_1 > 0 \) bond formation increases density and helps the density ordering, which leads to an increase in the ordering temperature, while for \( c_1 < 0 \) it decreases both of density and the ordering temperature. We call the former case the “positive” coupling between the order parameters and the latter case the “negative” coupling. As explained later, we believe that this “negative” coupling between the order parameters is the physical origin of glassification phenomena.

The dynamics of \( \delta \rho \) and \( \delta S \) is, then, described by

\[
\frac{\partial \delta \rho(\vec{r},t)}{\partial t} = L_\rho \nabla^2 \frac{\delta \beta H}{\delta (\delta \rho(\vec{r},t))} + \zeta_\rho(\vec{r},t), \tag{2}
\]

\[
\frac{\partial \delta S(\vec{r},t)}{\partial t} = -L_S \frac{\delta \beta H}{\delta (\delta S(\vec{r},t))} + \zeta_S(\vec{r},t), \tag{3}
\]

where \( \zeta_\rho \) and \( \zeta_S \) are the usual Gaussian noise terms and \( L_\rho \) and \( L_S \) are the bare kinetic coefficients. The diffusive equation \([\delta S]\) likely describes the dynamics of \( \delta \rho \) for a system under the strong damping due to large viscosity. We propose that Eqs. (2)-(3) are the fundamental equations universally describing slow dynamics of supercooled liquids.

First we consider the density fluctuations in liquids. Since the average values of the order parameters are shifted by their couplings, we here redefine the fluctuations of density and bond order parameters around their thermal equilibrium values as \( \delta \rho^* = \delta \rho - < \delta \rho > > 0 \) and \( \delta S^* = \delta S - < \delta S > > 0 \), where

\[
< \delta \rho > = \frac{c_{1\rho} S_0 (\kappa - c_2 S_0) + c_{1S}(c_1 \rho + c_1 S)}{(\tau - c_2 \rho S_0)(\kappa - c_2 S_0) - (c_1 \rho + c_1 S)^2},
\]

\[
< \delta S > = \frac{c_{1S} \rho(\tau - c_2 \rho S) + c_{1\rho}(c_1 \rho + c_1 S)}{(\kappa - c_2 S_0)(\tau - c_2 \rho S) - (c_1 \rho + c_1 S)^2}.
\]

Then, the structure factor at small \( q \) can be obtained as:

\[
F(q) = < |\delta \rho_q|^2 > = \frac{K_\rho (\kappa - c_2 S_0 + K_\rho q^2)}{(\tau - c_2 \rho S_0 + K_\rho q^2)(\kappa - c_2 S_0 + K_\rho q^2) - (c_1 \rho + c_1 S)^2} \approx \frac{\xi^2}{K_\rho (1 + q^2 \xi^2)}, \tag{4}
\]

where

\[
\xi^2 = K_\rho/a_2[T - T^{**}(\bar{S})]. \tag{5}
\]

Here \( T^{**}(\bar{S}) = T^* + (c_2/a_2)\bar{S} \). In the derivation of the final relation of Eq. (4), we use the weak coupling approximation to neglect the terms proportional to \( (c_1 \rho + c_1 S)^2 \) in the denominator. Equations (4) and (5) tells us that the coupling between two order parameters leads to large-scale density fluctuations near the temperature \( T^{**}(\bar{S}) \). The smallness of the parameter \( a_3(\bar{S}) \) leads to the second-order-like transition as in isotropic-nematic transition of liquid crystals \([13]\). It is natural to expect that \( a_3 \) is a decreasing function of \( \bar{S} \) for the case of \( c_i < 0 \) simply because active bonds prevent the formation of a high density phase. The decay rate of fluctuations can also be obtained straightforwardly from Eq. (3) as

\[
\Gamma_q = \frac{L_\rho q^2}{F(q)} = \frac{L_\rho K_\rho}{\xi^2} (1 + q^2 \xi^2)^q. \tag{6}
\]
Our model indicates that the avoidance of crystallization (positional ordering) at $T^*$ [$T^{**}(S) < T^* = T^*(0)$] and the resulting stabilization of a supercooled state of liquid are due to the frustration coming from anisotropic interactions having non-crystallographic symmetry; and, thus, a “negative” coupling between $\rho$ and $S$ is a necessary condition for good glass formers. According to our picture, any liquid that has a “positive” coupling between $\rho$ and $S$ does crystallize without glassification, since crystallization is even induced by bond ordering. Thus, we conclude that the way (sign) of coupling between $\rho$ and $S$ directly determines whether molecules just crystallize without supercooling or can easily form a glass without crystallization.

Next we consider phase separation below $T^{**}(S)$. Because of the coupling between $\rho$ and $S$, phase separation can proceed on the $(\rho, S)$ plane in the unstable region even for one-component liquid. Differently from the phase separation in two component systems, the quenching path is automatically determined by the shape of the Hamiltonian and the temperature dependence of $\rho$ and $S$. By changing pressure, however, we can, of course, change the path. For our Hamiltonian, the system is more stable along the $S$ axis than along the $\rho$ axis. Thus, the phase separation takes place rather along the $\rho$ axis initially and then the bond order starts to deviate largely from $S$. Eventually, the system phase separates into two phases given by the condition of thermal equilibrium $\delta H_{eq}/\delta (\delta \rho) = \delta H_{eq}/\delta (\delta S) = 0$ ($H_{eq}$: the equilibrium part of $H$ without the gradient terms). Figure 3 schematically shows how phase separation of a one-component liquid can proceed in the $(\rho, S)$ plane. The location of the hidden crystal phase is also drawn in the figure. This unusual phase separation of a single-component liquid that are beyond the value determined by the isothermal compressibility $K_T$. In contrast to this common sense, however, Debye reported that long-range density fluctuations with a correlation length $\xi_{\text{cluster}}$ of 200 nm exist in a glassy polymer. Recently Fischer and his coworkers have found experimentally that the large-scale density fluctuations exist near the glass-transition temperature $T_g$ commonly in several fragile glasses, such as orthoterpheynyl, poly(methyl methacrylate), and polysiloxane. The results strongly suggest that large-scale density fluctuations universally exist in various fragile glasses, which cannot be understood in the framework of the conventional theory of liquids. The structure factor $F(q)$ can be described by the Ornstein-Zernike-type one with a correlation length of $\xi_{\text{cluster}}$, namely, $F(q) \sim 1/(1 + (q\xi_{\text{cluster}})^2)$. On the other hand, the decay rate of the fluctuation, $\Gamma_q$, is found to depend on the wavenumber $q$ as $q^2$, which is suggestive of simple diffusion. This unusual phenomenon observed in supercooled liquids can also be naturally explained by our model: The Ornstein-Zernike shape of the observed structure factor $F(q)$, the growth of the correlation length $\xi_{\text{cluster}}$, and the diffusive character of the fluctuating slow mode are all very much consistent with our predictions [see Eqs. (4), (5), and (6)].

Our model further predicts weaker critical effects for a stronger glass former because the distance between $T_g$
and $T_{\star\star}(\bar{S})$ increases with an increase in the strong nature of glass ($\bar{S}$) and, thus, a strong glass former likely becomes glassy before approaching to the critical point $T_{\star\star}(\bar{S})$. This is consistent with the fact that the large-scale density fluctuations have so far been observed only in rather fragile glasses.

In conclusion, we propose a simple universal picture of liquids near the liquid-solid phase transition. We demonstrate that the energetic frustration between the isotropic and anisotropic parts of intermolecular attractive interactions (the “negative” coupling between the density and bond order parameter) is a prerequisite to the physical description of supercooled liquids. Our simple Ginzburg-Landau-type theory based on the two-order-parameter description provides us with intuitive physical explanations for the unusual phenomena of supercooled liquids: (i) large-scale density fluctuations in supercooled liquids (“Fischer cluster”) \cite{6}, and (ii) phase-separation phenomena of a one-component supercooled liquid into two liquid (glassy) phases \cite{3-4}.

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\[\text{FIG. 1. Schematic figure of the phase behavior of a supercooled liquid on the } (\rho, S) \text{ plane below a spinodal line. A homogeneous one-component liquid can demix into two phases having different } \rho \text{ and } S.\]