Two-Order-Parameter Model of Liquid: A Unified Description of Water-Like Thermodynamic Anomaly, Liquid-Liquid Transition, and Liquid-Glass Transition

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A liquid generally has a tendency to form short-range bond order (or, locally favored structures with specific spatial symmetry) and thus the structure of a liquid becomes locally more ordered with decreasing temperature. This short-range order is due to specific interactions between liquid atoms or molecules that have the symmetry-selective nature. They may stem from the shape of molecules (van der Waals interactions), hydrogen bonding, covalent bonding, or electrostatic interactions. Most typical examples of short-range bond order is a tetrahedral structure for water, silicon, silica, and germania and an icosahedral structure for metallic glass formers [1]. To represent such local ordering in liquid on a phenomenological level, we recently introduced the bond order parameter in addition to the density order parameter and proposed the two-order-parameter model of liquid. We applied this model to (i) waterlike thermodynamic and kinetic anomalies of liquid [2,3], (ii) liquid-liquid phase transition in a single-component liquid [4], and (iii) liquid-glass transition [5,6]. Here we present a general framework of the two-order-parameter model of liquid to describe all these phenomena in a unified manner and discuss how these phenomena, which are apparently independent of each other, can be closely related. We view a liquid as follows: Locally favored structures, whose symmetry may not be consistent with the symmetry of the equilibrium crystal, are created in a sea of normal-liquid structures. This short-range bond ordering, is intrinsic to a liquid state. Thus, a liquid state can be expressed by a simple two-state model with cooperativity.

On the basis of this a picture, we propose that (i) water-like thermodynamic anomalies of liquids is a result of the local ordering of bond order parameter, (ii) liquid-liquid transition is a result of the gas-liquid-like cooperative ordering of the bond order parameter (while the gas-liquid transition is that of the density order parameter), and (iii) vitrification is a result of the competition between the two order parameters, namely, between long-range density ordering (crystallization) and short-range bond ordering. Our model suggests that a liquid having a stronger tendency of short-range bond ordering should be a better glass former and a stronger (or, less fragile) liquid [5]. However, if (a) locally favored structure has a structure whose symmetry is consistent with the crystalloglaphic symmtery or (b) the tendency of short-range bond ordering is too strong, a liquid may even achieve long-range bond ordering. Examples of case (a) can be seen in water and water-like tetrahedral liquids [3], while thoes of case (b) in metallic liquids [6]. For case (a), a crystal having a larger specific volume than a liquid is formed, while for case (b) quasicrystal is formed. Both ordered states can be viewed as the ordered state of the bond order parameter with translational order.

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