

The pressure-induced liquid–liquid crossover of GeI₄ identifiable as a percolation transition

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Fluid polyamorphism, which often shows up as pressure-induced transitions in fluids, is rather well understood on a thermodynamic basis [1]. However, microscopic identification of the transition is still lacking.

Recently, we have shown that liquid GeI₄ undergoes pressure-induced liquid–liquid crossover [2]. To identify a possible microscopic pathway of the crossover, we conducted an isothermal-isobaric molecular dynamics simulation. The model employed, which was composed of rigid tetrahedral molecules interacting via weak van der Waals forces acting at iodine sites, can semi-quantitatively predict thermodynamic properties of GeI₄ below ~1 GPa [3]. We prepared three sizes of a system consisting of 216, 1000, and 2744 molecules to allow a finite-size scaling analysis [4].

To the authors' knowledge, Stanley and Teixeira [5] were the first who tried to attribute the thermodynamic anomalies, associated with water's polyamorphic nature, to percolation of hydrogen bonds. We focus on a "bond" in the same spirit as the one in [5] and define it between electrically neutral molecules in a more specific way: We define a "physical" bond between the nearest intermolecular iodine sites satisfying the conditions of forming the metallic I₂ bond [6]. We could judge that the bonds have the characteristic lifetime of order 0.1 ps. Noting that hydrogen bonds in water also have a finite lifetime (which is about ten times longer reflecting stronger hydrogen-bond interaction than the physical one considered here), it is worth examining the aggregation of dynamic clusters consisting of physical bonds.

We then examined the formation of molecular clusters in *dynamic* networks of the bonds in the liquid state along the melting curve up to 1 GPa. Against our expectation that the vertex-to-face connection may be the key ingredient in forming a molecular network, the clusters were found to be mainly composed of nearest molecular pairs in edge-to-edge, face-to-edge, and vertex-to-edge orientations.

The clusters grow as pressure increases. We could quantify the growth of clusters in terms of the percolation probability P and the mean cluster size S . We evaluated from the variation of P against pressure p for the given system with N molecules the onset of percolation \bar{p} , which was observed below 1 GPa, and the width Δ of the transition region. We then assume the following system-size dependences for \bar{p} and Δ : $\bar{p} - p_c \sim \Delta \sim N^{-1/\nu'}$, which allows us to estimate the threshold pressure p_c in an infinite system. The scaling hypothesis worked to give $p_c = 0.85(1)$ GPa and the exponent $\nu' = 4.2$. When the

finite-size effects are taken into consideration, i.e., the correlation length $\xi \sim |p - p_c|^{-\nu'}$ is replaced by N , P and $SN^{-\nu'/\nu'}$ could be expressed by the universal functions of $z = (p - p_c)N^{1/\nu'}$. These are indeed the cases (Fig. 1).

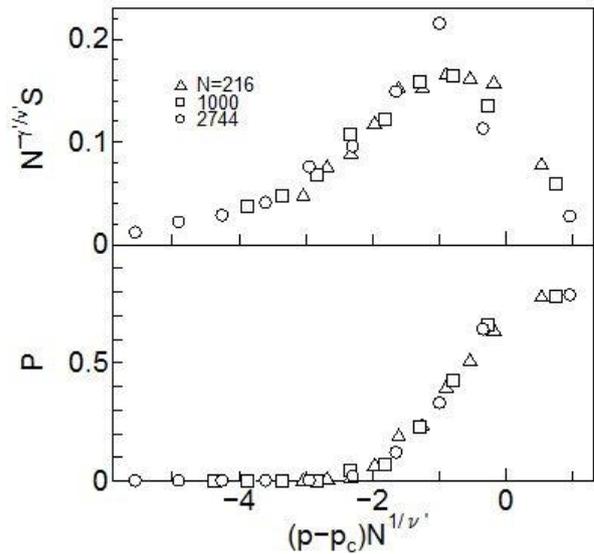


Figure 1. Scaled behaviors of the mean cluster size (upper panel) and the percolation probability (lower panel).

We do not consider that p_c is accidentally located near the extension of the phase boundary between the two liquid phases [2]. We thus speculate that the liquid–liquid crossover of GeI₄ is brought about by percolation of molecular networks.

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