Liquid-Liquid Phase Transitions of Phosphorus via Constant-Pressure First-Principles Molecular Dynamics Simulations

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Pressure-induced phase transitions in liquid phosphorus have been studied by constant-pressure first-principles molecular dynamics simulations. By compressing a low-pressure liquid which consists of the tetrahedral P_4 molecules, a structural phase transition from the molecular to polymeric liquid (a high-pressure phase) observed in the recent experiment by Katayama *et al.* [Nature (London) **403**, 170 (2000)] was successfully realized. It is found that this transition is caused by a breakup of the tetrahedral molecules with large volume contraction. The same transition is also realized by heating. This indicates that only the polymeric liquid can stably exist at high temperature.

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Liquid-liquid phase transitions have been extensively investigated in both experimental and theoretical studies [1–4]. In a one-component liquid such as liquid carbon and sulfur [1,3,5], these transitions are characterized by two distinct densities which are closely related to different atomic configurations in liquid phases [6]. Also in supercooled water, first-order transitions between low density and high density phases are observed in molecular dynamics (MD) simulations [4].

In a recent experiment, Katayama *et al.* observed liquid-liquid structural phase transitions of phosphorus by pressure changes around 1 GPa [2]. Phosphorus has several allotropes and black P is the most stable under ambient conditions. A low-pressure liquid (phase I) which is the melt of solid black P (the orthorhombic structure) consists of tetrahedral P_4 molecules. In compression of this molecular liquid, a drastic change of the structure factor was observed around 1400 K [2]. Figure 1 shows the phase diagram of black P [7]. Dashed lines around 1 GPa denote the boundary of the two liquid phases observed in the experiment [2]. It is speculated that the high-pressure liquid (phase II) has the polymeric form in which atoms are connected by anisotropic bonds leading to a network configuration [2]. Detailed investigations of the structural changes are demanded but experiments cannot reveal the structures in the atomistic level.

In this Letter, structural phase transitions of liquid phosphorus (*l*-P) were investigated by constant-pressure first-principles molecular dynamics (FPMD) simulations [8–10]. FPMD is a powerful tool to investigate structures in the atomistic level which are sensitive to changes of electronic states. By combining constant-pressure methods [11,12] with FPMD, we can simulate pressure-induced structural phase transitions directly. In the present simulations, we successfully realized the liquid-liquid phase transitions as observed in the experiment by Katayama *et al.* [2]. These transitions are obtained not only by compression but also heating in our simulations. The process of the polymerization of the P_4 molecules by heating was studied in FPMD simulations by Hohl and Jones [13]. However, they employed a constant volume condition so that density changes which are crucial in liquid-liquid phase transitions could not be observed. In our simulations, large volume changes were clearly observed in phase transitions, and we confirmed the importance of the constant-pressure condition in phase transitions between liquid phases.

The original Car-Parrinello method [8] was employed as FPMD combining the constant-pressure method [11]. The simulation cell was a cube containing 64 P atoms, and periodic boundary conditions were imposed. The norm-conserving pseudopotential [14] with a separable form [15] was employed and the exchange-correlation

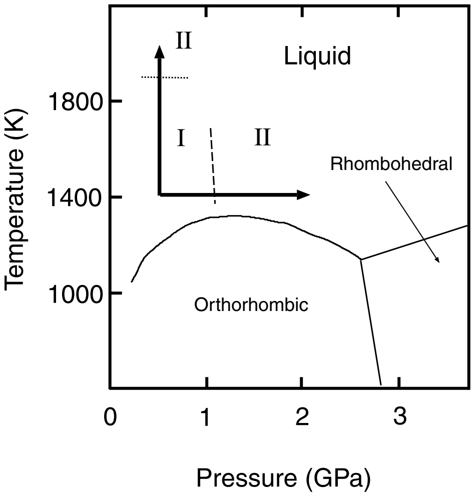

FIG. 1. The pressure-temperature phase diagram of black P [7]. Dashed lines denote the boundary between the two liquid phases (phase I and II) observed in the experiment by Katayama *et al.* [2]. Dotted lines are the predicted boundary in a heating process of the present simulation (see text). Two arrows indicate the compression and heating processes in the simulations.

energy was described in the local density approximation (LDA) [16]. Wave functions for occupied valence states were expanded in a plane wave basis with cutoff energy (E_{cut}) 30 Ry at a single point (Γ) in the Brillouin zone. It has been shown that the present condition of the electronic state calculation is adequate to obtain accurate atomic structures in liquid phases in previous studies [13,17–19]. It should be noted that relatively low E_{cut} tends to give nominally negative pressure at low density (especially with the LDA) [20–22]. This is obviated by 30 Ry E_{cut} in the present simulations. Two Nosé-Hoover thermostats [23,24] connected to ionic and electronic systems, respectively, were introduced [25] and constant-pressure–constant-temperature MD simulations were performed with a time step of 0.126 fs. Periodic resetting of total ionic momentum suppresses the ionic flow due to thermostats [26].

The molecular liquid was prepared by heating the initial arrangement of 16 P_4 tetrahedra in the bcc structure. Over ~1000 K, P_4 tetrahedra highly diffused, and the molecular liquid (the low-pressure phase) was obtained after annealing for ~4 ps at 1400 K. External pressure was set to 0.7 GPa to adjust density to ~1.6 g/cm^3 at 1400 K [27]. Two processes (compression and heating) were performed independently after equilibrating the molecular liquid, which are denoted by two arrows in Fig. 1.

In a compression process, pressure was changed from 0.7 to 2.5 GPa in stepwise, while temperature was kept to 1400 K throughout the compression. In Fig. 2 (upper panel), time evolution of volume per atom is shown in the compression process. The molecular liquid was compressed to 2.5 GPa at time step 17 000. The volume instantaneously shrank at the moment with ~40% reduction (density was increased to 2.77 g/cm^3 [27]). The radial distribution function $g(r)$ was calculated before and after the compression. The upper panel in Fig. 3 shows $g(r)$ at 0.7 GPa and the lower one shows $g(r)$ at 2.5 GPa. At 0.7 GPa, $g(r)$ exhibits characteristic features of the tetrahedral molecular liquid. The first peak reflects the distribution of the interatomic distance within the tetrahedral molecules. The coordination number N_c obtained by integrating $4\pi r^2 g(r)$ up to the first minimum r_m (2.6 Å) is 3.0, which is consistent with the tetrahedral molecule. Overall shape of the $g(r)$ agrees very well with the previous simulations and experiment of the tetrahedral molecular liquid [2,13].

At 2.5 GPa, $g(r)$ shows very different characters from that of the molecular liquid. The first peak became broader and the second peak (around 3.5 Å) appeared, which cannot be found in $g(r)$ at 0.7 GPa. These characters are consistent with the polymeric liquid: overall shape of the $g(r)$ agrees well with the previous results of the polymeric liquid [2,13,19,28] and also that of l-P obtained by melting the simple cubic crystal at high pressure in our previous study [22]. Integrations of $4\pi r^2 g(r)$ up to r_m (2.8 Å) lead to 4.1.

Snapshots of the atomic configurations before and after the compression are shown in Fig. 4. Before the compression, the tetrahedral P_4 molecules stably exist having an

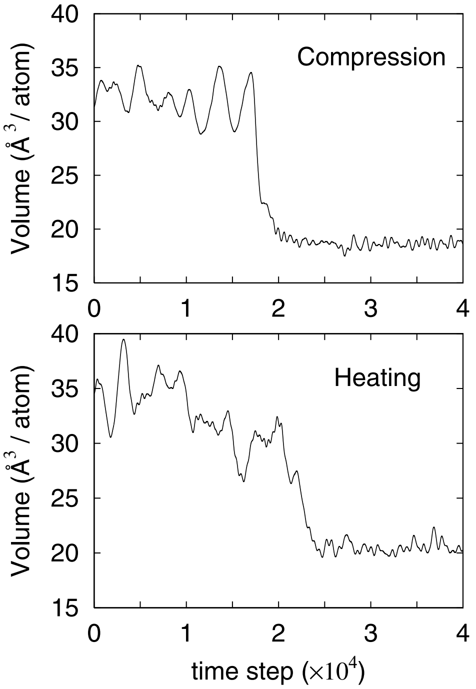

FIG. 2. Time evolution of volume per atom in the compression and heating processes. In the compression, pressure was raised up at time step 17 000, while, in the heating, temperature was at time step 0.

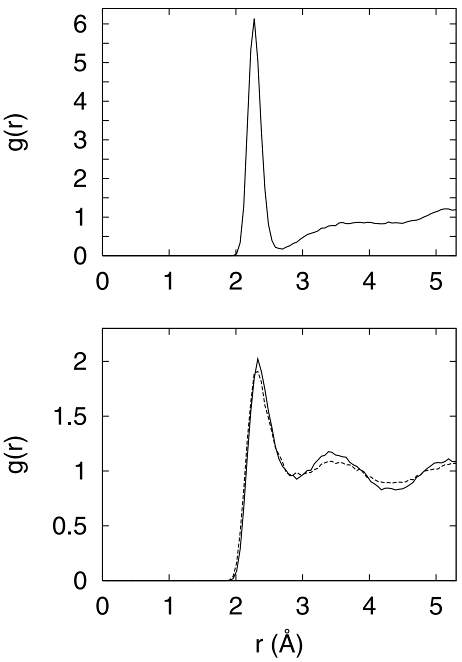

FIG. 3. The radial distribution function $g(r)$ for the molecular liquid (upper panel) and transformed liquid (lower panel). Solid and dashed lines in the lower panel show $g(r)$ after the compression and heating, respectively.

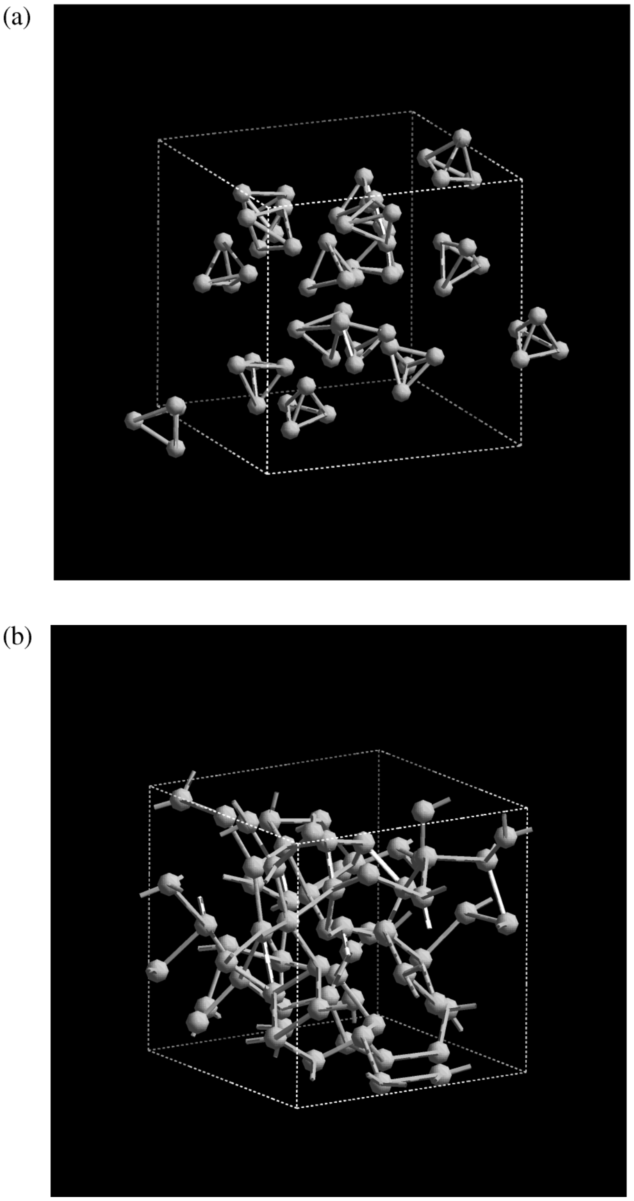

FIG. 4. Snapshots of atomic configurations before (a) and after (b) the compression. Atoms are connected when separated by r_m or less.

open atomic configuration [Fig. 4(a)]. It is clearly shown that, after the compression, all tetrahedral molecules collapse and a polymeric form is generated [Fig. 4(b)]. Atoms form a dense network configuration, which is consistent with the previous result by Hohl and Jones [13]. The dissociation of the P_4 tetrahedra is caused by the increase of collisions between the tetrahedra [13]. Thus, it is easily recognized that compression induces the dissociation.

Details of structural differences are quantitatively shown in the bond-angle distribution function $A(\cos\theta)$. It counts angles between the two vectors that join a central particle with two neighbors within the bond length r_b. In the present calculations, r_b is taken as r_m. $A(\cos\theta)$ at 0.7 and at 2.5 GPa are shown in Fig. 5. At 0.7 GPa, the only one sharp peak is found at $\cos\theta = 0.5$ (60°), indicating the existence of the tetrahedral molecules (upper part of this peak is not shown). On the other hand, $A(\cos\theta)$ at 2.5 GPa have a main peak around 0 (90°) and a subpeak around 0.5 (60°). This confirms that the P_4 tetrahedra were broken and the polymeric phase was generated. The peak around 0 (90°) indicates that the covalent p-state bonding is dominant within the first nearest neighbors. The subpeak at 0.5 (60°) is considered to be due to the reduction of the covalent bonding in the long-range order [18,22,29] and also incomplete dissociation of P_4 tetrahedra [13]. It is noted that the detailed investigation revealed that the Peierls-like distortion seems to be present in the short-range order in the polymeric phase of l-P. This analysis will be reported elsewhere.

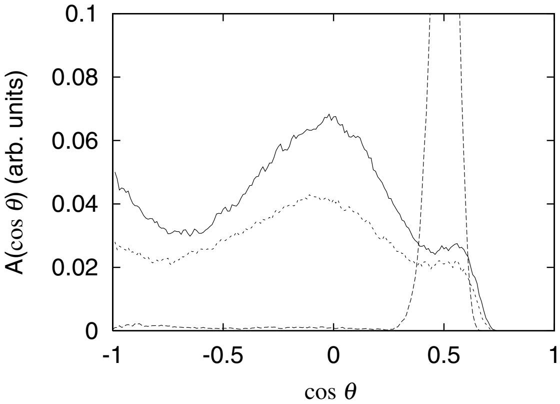

FIG. 5. The bond-angle distribution function $A(\cos\theta)$ at 2.5 GPa (solid lines) and 0.7 GPa (dashed lines) in the compression process. Dotted lines denote $A(\cos\theta)$ obtained in the heating process.

By heating the molecular liquid, the same structural phase transition is realized. Simulations in the heating process were carried out maintaining pressure at 0.7 GPa. Time evolution of volume per atom in the heating process is given in Fig. 2 (lower panel). Temperature was raised up from 1400 to 2000 K at time step 0. For ~1 ps after raising the temperature, the molecular liquid phase was still preserved, but suddenly the tetrahedral molecules began to break with large volume contraction (~35%), which resulted in a denser liquid (2.49 g/cm^3). In the lower panel of Fig. 3, $g(r)$ of this phase is shown as dashed lines. Obviously, this phase is coincident with the polymeric liquid at 2.5 GPa realized in the compression process. This is also confirmed by $A(\cos\theta)$ for this phase (dotted lines in Fig. 5).

From our simulations, it is found that there is another phase boundary between phases I and II at high temperature (dotted lines in Fig. 1) corresponding to the transition by the heating. It is noted that dotted lines in Fig. 1 are just for showing the existence of the boundary. The transition temperature does not correspond to the actual one because of large hysteresis in MD simulations.

In conclusion, we successfully realized the liquid-liquid phase transition of phosphorus via constant-pressure FPMD. The present study shows that the transition is caused by the breakup of P_4 tetrahedral molecules, and the polymeric liquid is generated with large volume contraction. This means that the collapse of the open atomic configuration plays an important role in the liquid-liquid phase transition of phosphorus. It is also found that the transition is realized not only by compression but also heating with large volume contraction. Owing to the constant pressure condition, the volume change was clearly observed and this leads to the prediction that phosphorus forms only the polymeric liquid over 2000 K even at low pressure.

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