First-Order Liquid-Liquid Phase Transition in Compressed Nitrogen

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We report results of first-principles molecular dynamics simulations, which predict a first-order phase transition from molecular to polymeric liquid nitrogen. The liquid-liquid phase boundary is near 88 GPa along the 2000 K isotherm and has a critical point between 4000 and 5000 K and 50 to 75 GPa. At higher temperatures, molecular nitrogen undergoes temperature-driven dissociation to an atomic liquid. The nature of the liquid-liquid transition and the structure of the new polymeric phase are characterized, and ways to experimentally confirm our findings are proposed.

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The behavior of molecular compounds under extreme conditions has been an increasingly interesting subject of research. In these materials, the breaking of molecular bonds upon compression may lead to the formation of extended structures. In nitrogen, a polymeric structure called cubic-gauche (cg-N) was predicted [1] among suggestions of possible stable monatomic solid phases [2,3]. It was eventually synthesized by Eremets *et al.* [4] at pressures (P) and temperatures (T) above 110 GPa and 2000 K, respectively. Since its discovery, cg-N has been intensively investigated with attempts to quench it to ambient conditions [5–7]. A metastable single-bonded N at normal P and T would be a high-energy-density material with an energy capacity over 5 times greater than current energetic materials [4]. A difficulty in achieving this goal is the complexity of solid nitrogen's phase diagram, where many structures are thermodynamically competitive and have a wide range of metastability [8,9].

The increased significance of short-range interactions upon compression implies that dense liquid N may also develop complex structures with local order and bonding properties similar to that found in solid N. Indeed, by drawing analogies with phosphorus [10], Ross and Rogers [11] discussed the possibility that molecular N transforms to a liquid polymer through a first-order phase transition above the stability domain of cg-N. Measurements of melting by Mukherjee and Boehler [12] seemed to support this idea in principle, although they found a peak in the N melting curve at rather low P, only 50 GPa. However, more recent experiments by Goncharov *et al.* [13] reported a different melting curve, without a sharp turnover at 50 GPa.

In this Letter, we provide evidence for the existence of a first-order liquid-liquid (L-L) phase transition and a new polymeric liquid phase of N. The coexistence of two distinct equilibrium phases of an elemental liquid is one of the most fundamental questions in the physics of liquids and has been the subject of a lot of interest. However, after phosphorus [10], this would be only the second known first-order phase transition in a simple, not undercooled, liquid. Our predicted L-L phase line differs significantly from the suggestions in Refs. [11,12] and is obtained from first-principles theory. We have characterized the structure of the new polymeric liquid, which evolves with pressure, bearing analogies to metastable and stable solid polymers.

We have performed first-principles molecular dynamics (FPMD) simulations of liquid N over the range of $0 < P < 300$ GPa and $1000 \leq T \leq 6000$ K. The calculations were carried out with VASP [14], using density functional theory (DFT) within the Perdew-Burke-Ernzerhof generalized gradient approximation [15] and Born-Oppenheimer dynamics. We employed a 5-electron projector augmented wave pseudopotential with a plane-wave cutoff of 500 eV and a Γ-point sampling of the Brillouin zone. The FPMD simulations were performed in the canonical (NVT) ensemble with 64- and 128-atom supercells and ran for 10–50 ps with a 32 a.u. ionic time step. Our calculations give vibrational frequencies in excellent agreement with liquid N measurements [16] near 2000 K and 50 GPa. Along the 1800 K isotherm, melting was found to occur below $P \sim 45$ GPa, consistent with recent experimental data [12,13]. Along the 6000 K isotherm, we observe the onset of dissociation in good agreement with shock-wave measurements at 30 GPa [17]. Our equation of state (EOS) for solid cg-N at 2000 K also agrees well with experimental data at comparable temperatures [18,19].

The structural modifications occurring upon compression along the 2000 K isotherm are illustrated in Fig. 1(a). For $P < 87$ GPa, the shape of the pair correlation function $g(r)$ remains qualitatively unchanged. Up to this pressure the liquid is molecular, and the first peak of $g(r)$ corresponds to the equilibrium triple bond length of 1.10 Å. Additional compression spawns the formation of polymeric liquid structures, which is signified by the emergence of a second equilibrium bond length at approximately 88 GPa. The persistence of the first peak demonstrates the continued presence of triple bonded N_2, while the second peak at 1.27 Å is due to clusters of N atoms networked by alternating single and double bonds. The value of 1.27 Å is comparable with bond lengths obtained

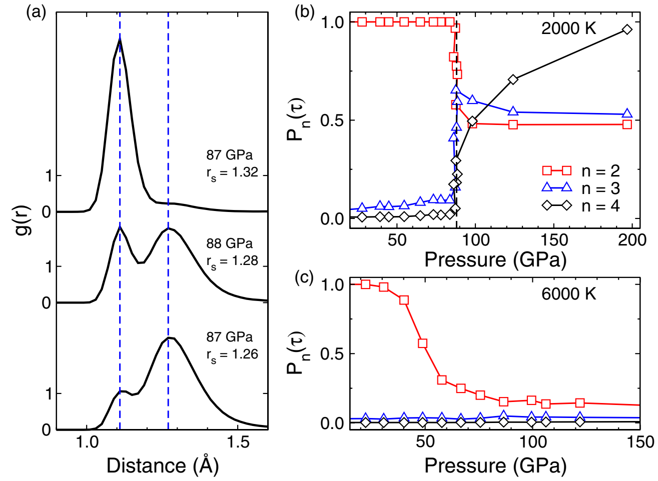

FIG. 1 (color online). (a) Pair correlation function $g(r)$ at 2000 K for selected pressures near the L-L phase boundary. Only the short-range part of $g(r)$ is shown. (b) Cluster survival probability $P_n(\tau)$ at 2000 K showing discontinuous loss of molecular stability as a function of pressure. (c) $P_n(\tau)$ at 6000 K showing gradual dissociation with P and formation of atomic liquid.

in previous theoretical studies of chainlike 0 K crystalline phases [20,21]. Further compression up to $P > 100$ GPa leads to a complete transformation to a polymeric phase with no molecules present. Note that, while the pressure range over which the modifications in $g(r)$ shown in Fig. 1 take place is less than 1 GPa, the density changes by about 14% [the density parameter defined as $r_s = \frac{1}{a_0}(\frac{3v}{4\pi})^{1/3}$ is the radius in units of Bohr (a_0) of a sphere with volume equal to the volume per valence electron v].

These observations are consistent with two-phase coexistence as found in a first-order phase transition. To verify that our 128-atom simulation cells are large enough to reproduce coexistence, we have performed simulations on initial configurations created by merging two 64-atom cells, one of molecular and the other of polymeric liquid. In the coexistence region, after initial equilibration (~5 ps), the relative fraction of the two phases stabilizes and remains constant (for simulations as long as 20 ps). It can be varied by changing the density, and above and below the pressure boundary ($P \sim 88$ GPa) the fraction of N_2 approaches zero and unity, respectively.

For further characterization of the bonding and structural changes across the L-L transition, we calculate a quantity $P_n(\tau)$, which gives the statistical probability that a cluster of n atoms (i.e., an atom and its $n - 1$ nearest neighbors) found at time $t = 0$ will exist at $t = \tau$ in the future. The choice of $\tau = 0.2$ ps allows for roughly 15 N_2 vibron oscillations to gauge molecular stability and gives well-converged probabilities with time; a different choice for τ does not lead to qualitative differences. The results [see Fig. 1(b)] show that, along the 2000 K isotherm, the survival probability of N_2 molecules is 100% below the L-L transition pressure, whereas it is near zero for all larger clusters, indicating the pure molecular character of the low-P liquid. At $P \sim 88$ GPa, the stability of N_2 decreases rapidly, alongside a significant increase in the lifetimes of larger clusters. This loss of molecular stability, which is discontinuous as a function of P, is what most clearly defines the L-L transition. Immediately above the transition, the liquid is a mixture of 1-, 2-, and 3-coordinated atoms, all with finite lifetimes. However, the persistence of single-bonded compounds [$P_4(\tau)$] continues to increase steadily with P. In contrast, the loss of molecular stability at 6000 K is gradual [Fig. 1(c)], indicating that the transition there is continuous and that there is a critical point at $T < 6000$ K. In addition, the liquid becomes atomic and not polymeric at this high T.

The new polymeric liquid phase immediately above the L-L boundary can be qualitatively described as chainlike, with the frequent formation of pentagonal compounds (isolated or branched out). Formation of similar chainlike structures was previously studied in high-pressure solid phases [20–22]; however, they have not been observed experimentally, and the calculations showed that, although energetically competitive, they are not thermodynamically stable crystalline phases. We see here that they can be equilibrated in the presence of liquid disorder. To specify their structure quantitatively, we have calculated nearest neighbor (NN) and dihedral angle distributions, as well as histograms of neighbor distances. Along the 2000 K isotherm, the NN angle distribution has a peak at 108°, the angle of a perfect pentagon, while its expectation value is skewed to 113°, reflecting the stretching behavior of the chainlike formations. The dihedral distribution is symmetric and peaked around 0.0°, reflecting the planar nature of the polymeric compounds.

Histograms of individual neighbor distance distributions are shown in Fig. 2. The peaks below 1.5 Å originate from covalent bonding. At P less than the 2000 K transition

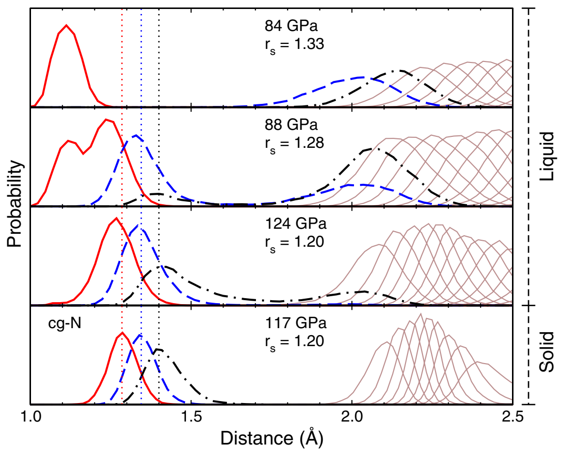

FIG. 2 (color online). Neighbor distance distributions of liquid- and cg-N along the 2000 K isotherm.

pressure $P^{2000\text{ K}} \sim 88$ GPa, the liquid is purely 1-coordinated with triple bonds. Near $P^{2000\text{ K}}$, the 2nd and 3rd NN lines develop peaks below 1.5 Å, while the 1st NN retreats to larger distances. This shows the appearance of threefold coordination, but the persistence of second peaks above 2.0 Å in the 2nd and 3rd NN indicates a mixture of all three coordinations and the presence of single, double, and triple bonds. This is similar to previous findings of 2.5-coordinated solid amorphous nitrogen observed near 150 GPa and low T [23]. By 120 GPa, the N_2 molecules have completely disappeared, and the liquid is predominantly threefold coordinated; the local order in the emerging high-P liquid is nearly identical to that of solid cg-N at 2000 K and similar P.

Computed EOS along several isotherms are shown in Fig. 3. The 64-atom unit cell simulations exhibit a van der Waals loop for $T \leq 4000$ K, confirming the first-order nature of the transition. The 2000 K EOS obtained with a 128-atom cell is flat (within the statistical standard deviation) across the transition, indicating again that this cell size is sufficient to describe the coexistence region. Outside this region, the 64- and 128-atom results agree extremely well. The 5000 K EOS does not exhibit a drop in pressure, meaning that there is a critical point at $4000 < T_c < 5000$ K, above which temperature-driven dissociation inhibits the formation of extended structures. These findings are in good agreement with shock-wave measurements that report molecular dissociation at 30 GPa and 6000 K [17]. The computed EOS of liquid N and cg-N at 2000 K [Fig. 3(b)] converge at high density, consistent with the fact that the structure (local order) of the two systems becomes similar. Our calculations of cg-N agree well with experimental data [18,19] and previous calculations performed at 0 K [1]. The inset in Fig. 3(b) shows the change in volume between molecular and nonmolecular N along the coexistence line, which can be chosen as an order parameter describing the L-L phase transition.

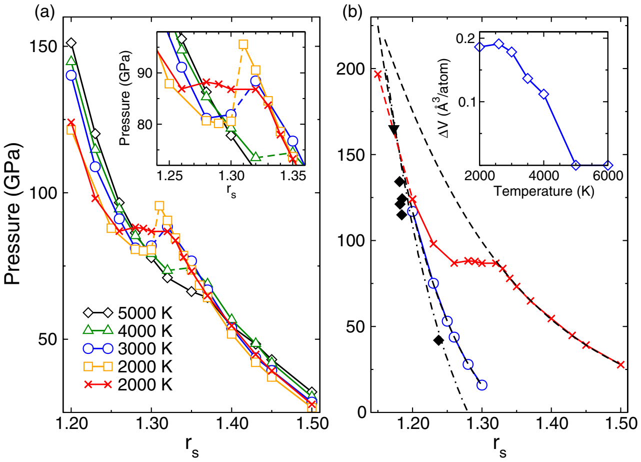

FIG. 3 (color online). (a) Computed EOS of liquid N for several isotherms. Results from 128-atom cells are given by crosses; all other data are from 64-atom cells. Inset: Enhanced view of the transition region. (b) Computed EOS data of liquid N (crosses) and solid cg-N (circles) at 2000 K. The dashed line in the liquid EOS at high density indicates possible solidification. The dashed-dotted line is a theoretical EOS for cg-N at 0 K [1]. Solid symbols are measurements of cg-N near 2000 K [18,19]. Dashed lines are 3rd-order Birch-Murnaghan EOS fits. Inset: Volume change between molecular and nonmolecular N across the coexistence region.

To account for electronic excitations, FPMD simulations with finite-T DFT [24] were performed for selected densities over the entire 2000–6000 K range. Introducing finite electronic temperature has little or no effect on the structure and EOS of the liquid before the onset and after the completion of the L-L transition. In the transition region (where the electronic band gap closes), allowing for electronic excitations slightly enhances the dissociation and accelerates the transition at densities immediately after its onset. The largest resulting change to P, a drop of 5.3 GPa, was found at $r_s = 1.35$ and 6000 K, while no changes to P larger than the statistical standard deviation were found below 4000 K. The 4000–6000 K results in Figs. 1(c) and 4 are from finite-T DFT.

The resulting phase diagram with the L-L phase boundary mapped over $2000 \leq T \leq 6000$ K is shown in Fig. 4. Transition pressures are determined by Maxwell constructions of the EOS data in conjunction with significant drops in the aforementioned molecular stability. The Maxwell

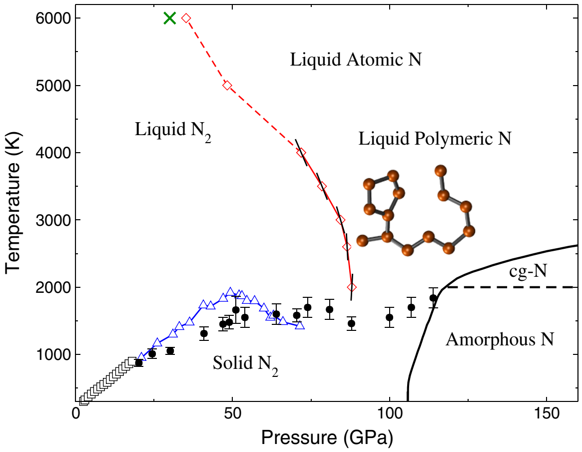

FIG. 4 (color online). Proposed phase diagram of N (region of metastable amorphous N also shown). The computed L-L transition points are indicated with diamonds. Those where the transition is first-order are connected with a solid line, while the remaining points give the P-T conditions where there is a 5% chance of dissociation after 0.2 ps. Overlaying lines are transition slopes computed independently from the Clapeyron equation. Experimental melting data are given by squares [25], triangles [12], and circles [13]. Known high-pressure polymeric solid phases are separated with solid lines (dashed where the boundaries are not precisely known) [4,23,26,27]. A visualization of the structure of the polymeric liquid is provided in the appropriate P-T region.

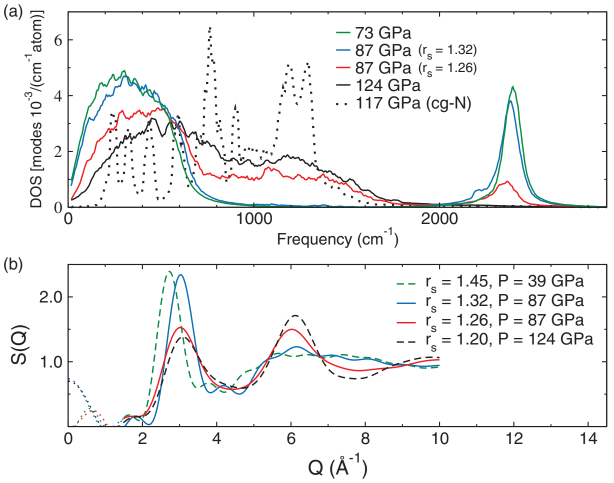

FIG. 5 (color). (a) Computed vibrational DOS of liquid- and cg-N at 2000 K. (b) Structure factor $S(Q)$ calculated from a Fourier transform of $g(r)$.

construction of the 64-atom EOS agrees with the transition P predicted using a 128-atom cell. In addition, we have calculated Clapeyron slopes, which are consistent with surrounding data points obtained from direct simulations of the phase boundary. The L-L phase boundary must form a triple point with the N melting line. The melting curve of Mukherjee and Boehler [12] has a kink, consistent with such a triple point, but it is at much lower pressure than our L-L line. The data of Goncharov *et al.* [13] have what may be a kink near 80 GPa, but the density of experimental data points does not allow us to make a definite conclusion. However, the shape of their fitted melting curve above 80 GPa is consistent with the gradual transition that we observe in the polymeric liquid above 88 GPa.

The vibrational density of states (DOS) obtained from velocity autocorrelation analysis for several pressures is given in Fig. 5. The molecular vibron at $\nu_{\mathrm{mol}} \approx 2400\ \mathrm{cm}^{-1}$ is distinct in the low P liquid. When P is increased beyond $P^{2000\ \mathrm{K}}$, the vibrational DOS near ν_{mol} diminishes, while new vibrational modes, similar to those present in cg-N, begin to appear between 1000 and 1500 cm^{-1}. This effect is enhanced upon further compression. The changes in bonding properties are also reflected in the static structure factor $S(Q)$ [Fig. 5(b)]. The shift in relative positions and weights of the 1st and 2nd $g(r)$ peaks above $P^{2000\ \mathrm{K}}$ leads to a decrease in the height of the 1st $S(Q)$ peak. The emerging periodicity of about 1 Å along the chain structures results in the appearance of a strong 2nd peak of $S(Q)$ and in the positions of the first two peaks exhibiting little density dependence.

In conclusion, we report the discovery of a new polymeric liquid phase of N and predict the transition from molecular N to this phase to be first-order up to at least 4000 K. The L-L transition is characterized by a discontinuous loss of molecular stability followed by a further gradual transformation upon compression until $P >$ 100 GPa, where the local order of the liquid becomes similar to that of cg-N. At $T \geq 5000$ K, the N_2 dissociation is gradual and leads to an atomic liquid. The P-T region where we propose the L-L transition has yet to be thoroughly investigated experimentally. One possibility for experimental detection of the new liquid phase is through spectroscopic measurements. However, we note that frequencies near ν_{mol} should still be observed even after the transition to a polymeric liquid takes place; therefore, one must also look for the appearance of the lower frequency modes that have been discussed. The reported significant changes in $S(Q)$ present another route for experimental observation.

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