

Polymerization, shock cooling, and the high-pressure phase diagram of nitrogen

Marvin Ross and Forrest Rogers

Lawrence Livermore National Laboratory, Livermore, California 94551, USA

(Received 25 July 2005; revised manuscript received 25 January 2006; published 11 July 2006)

The trajectory of states passed through by the nitrogen Hugoniot has been followed from the normal molecular liquid up to the dense plasma state near 10^6 GPa. A phase diagram is proposed that is very similar to one reported for phosphorous. The nitrogen phase diagram connects the recently observed molecular to *cg-N* polymer phase transition in the solid at 110 GPa, to a liquid-polymer phase line obtained from of shock cooling measurements. At much higher pressures, calculations of the Hugoniot predict that ionization of the tightly bound inner *L* and *K* electron shells lead to compression maxima of approximately 5–6 fold near 1000 GPa ($T \sim 3.5 \times 10^5$ K) and 40 000 GPa ($T \sim 2.3 \times 10^6$ K), respectively.

DOI: 10.1103/PhysRevB.74.024103

PACS number(s): 64.70.Ja, 62.50.+p, 61.20.-p, 31.10.+z

I. INTRODUCTION

Principles of chemical physics hold that pressure-induces electron delocalization leading to new structures, and elements in a family exhibit properties in common that lessen with increasing atomic number. In the case of molecular nitrogen the large binding energy of the triple bond makes it extremely difficult to modify. Theoretical calculations predicted that with increased pressure the solid molecular phase would be destabilized near 50–75 GPa leading to the formation of a threefold coordinated polymeric cubic-gauche (*cg-N*) structure.^{1–5} Experimental evidence for a nonmolecular semiconducting (possibly amorphous) phase of nitrogen, at a pressure above 150 GPa, was first obtained by Goncharov *et al.*⁶ and Eremets *et al.*⁷ using the diamond-anvil-cell (DAC) technique. Subsequently, synthesis of the long sort-after single-bonded cubic-gauche (*cg-N*) form was achieved by Eremets *et al.*^{8,9} near 110 GPa. In order to synthesize this phase, hysteresis barrier effects were overcome by first heating to a temperature of 2000 K.

In comparison with diamond-anvil cells, shockwave experiments have the ability to achieve simultaneously very high pressures and temperatures. Shockwave measurements of the liquid nitrogen Hugoniot have been reported by Radousky *et al.*¹⁰ and Nellis *et al.*¹¹ up to 110 GPa and 14 000 K. In addition to the single shock Hugoniot states they reported reflected, or second shock measurements, in which they observed the unusual feature of a temperature lowering, i.e., shock cooling. As such, shock methods are well suited to probe the higher energy states in the liquid nitrogen phase diagram. However, technical difficulties associated with shock experiments limit the use of diagnostics that might identify the molecular structure of the fluid. Calculations made with a semiempirical model, developed for this purpose,^{12,13} showed that shock cooling could be explained as the consequence of a molecular dissociation to polymerlike fragments characterized by the more highly coordinated polymers typically found in the heavier Group V elements, P and As.

In the present paper we propose that shock cooling results from a crossing of a liquid molecular-polymer phase line that is the high temperature liquid extension of the solid nitrogen polymer phase discovered by Eremets *et al.*^{8,9} at 110 GPa. Except for pressure scaling, the proposed nitrogen phase diagram is similar to the first order liquid-liquid phase transition

(LLPT) recently reported for phosphorous near 1 GPa.^{14,15} This is consistent with well established trends in chemical bonding.

The present paper is organized in the following manner. Section II is a review of the earlier model.^{12,13} The section includes model comparisons with the polymer total energy calculations of Mailhot *et al.*³ and with the polymer equation of state measurements made by Eremets *et al.*⁹ In Sec. III, the observation of shock cooling is explained in terms of polymer formation and a liquid-liquid phase transition. Section IV reports calculations for liquid nitrogen that extend the Hugoniot to temperatures and pressures where the covalently bonded molecular systems dissociate into atoms, and are ionized to form dense plasmas. Section V is the summary and discussion.

II. NITROGEN POLYMERS AND SHOCK COOLING

The liquid nitrogen Hugoniot and shock temperatures, shown in Fig. 1, have been measured using the LLNL two-stage light gas gun.^{10,11} The studies included a set of five

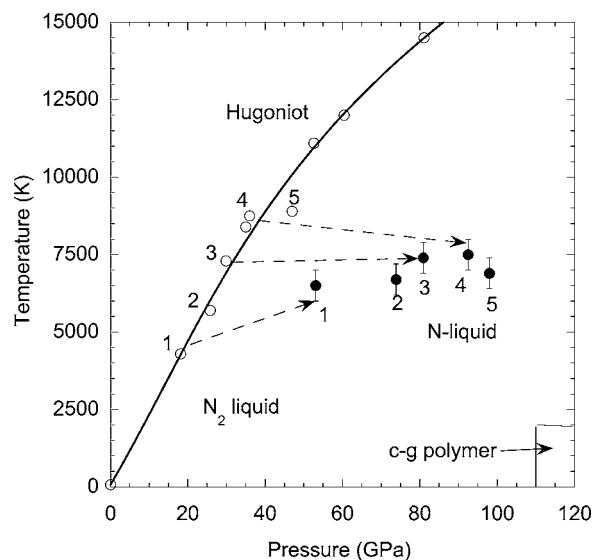


FIG. 1. Nitrogen Hugoniot (open circles) and reflected shock points (filled circles), plotted as pressure versus temperature (Refs. 10 and 11). Numerals indicate corresponding first to second shocks.

double or second shocked points starting from different initial pressures along the principal Hugoniot. In a double shock experiment the first shock is reflected back off of a stiff end plate material such as copper. Hence a double shock is also often referred to as a reflected shock. By measuring the shock velocity in the end plate, and impedance matching using the equation of state of the liquid, the pressure and density of the double shocked liquid can be determined.^{10,11} The numerals in Fig. 1 indicate double shocking from first to second shock points (i.e., 1 to 1, etc.). To avoid confusion, dashed lines are limited to only three of the reflected shock trajectories. In the lower right hand corner of the figure we have indicated the region in the phase diagram where cg- N polymeric nitrogen was stabilized.⁹

A. Free energy model of the shock compressed liquid

Some insight into the physical origin of shock cooling and its relationship to the phase diagram can be obtained from a review of the previously reported semiempirical free energy model developed for this purpose.^{12,13} The model was developed from the perspective that since dissociation into atoms by breaking a triple bond required about 9.9 eV/molecule, that this was unlikely at the ambient experimental temperatures. A model was constructed under the more realistic assumption that liquid N_2 would dissociate into fragments of the more highly coordinated covalently bonded polymers characteristic of Group V. This view has since been confirmed by the quantum molecular dynamic simulations of Mattson *et al.*⁵ They found mixtures of threefold coordinated atoms (cubic gauchelike) and twofold coordinated chainlike structures in liquid nitrogen near temperatures and densities comparable to those of the double shocked liquid.

The complexity of the theoretical problem facing an interpretation of the shock data requires reliance on a semiempirical approach where the fluid is treated as a mixture of molecules and polymer fragments, and by defining parameters easily fitted to the experimental data. The equation of state of the pure N_2 ground state liquid was modeled using soft-sphere liquid theory with an exponential-six intermolecular potential fitted to the solid isotherm.¹² The free energy of the partially dissociated fluid is described in the linear mixing approximation, written per two atoms as

$$F = (1-x)F_{N_2}^0 + x(F_{2N}^0 + D_e) + F_{\text{mix}} + F_{\text{int}} + x(E_b). \quad (1)$$

The first term is the free energy of the molecular gas. The second term is the free energy of a system of $2N$ dissociated atoms with a dissociation energy $D_e=9.91$ eV. The third term, F_{mix} , is the free energy of mixing. x is the fraction of the dissociated molecules and is obtained by minimizing the total free energy. At this point the first three terms express the free energy of a dissociated perfect gas.

If the gas is compressed then it is necessary to introduce F_{int} , the excess free energy due to intermolecular interactions between molecules, polymer fragments, etc., and a chemical binding energy, E_b . The term N polymer used below loosely defines a fragmented polymer. It was assumed that the atom-atom potentials of nonbonded atoms in molecular N_2 and in N polymers remained unchanged. This approximation

amounts to assuming that the N_2 - N potential is equal $1/2$ N_2 - N_2 potential, and N - N potential is equal N_2 - N_2 potential. As a result the total thermal free energy of the dense fluid mixture, F_{int} , determined by intermolecular forces remains unchanged upon dissociating from N_2 to an N polymer liquid. Consequently, F_{int} can be approximated using fluid variational theory with the exponential-six N_2 - N_2 potential.

The key to addressing the problem is in determining the N -polymer binding energy, E_b , because it controls predictions of the dissociation fraction and polymer stability. Practicality requires it be determined empirically, by fitting to shock data. The binding energy, E_b , is approximated as

$$E_b = -A(V_0 - V)^2, \quad V \leq V_0,$$

$$E_b = 0, \quad V > V_0. \quad (2)$$

Parameters A and V_0 were adjusted to provide a best all around fit to the shock data. At $T=0$ K, the total energy of the N -polymer phase is then

$$E_{N\text{-polymer}} = E_{N_2} + D_e + E_b. \quad (3)$$

In many respects, Eq. (3) summarizes the philosophy of the model. The first term is the energy of the N_2 solid, and is calculated as the sum over all the molecules, $E_{N_2} = \sum_{i<j} \phi(r_{ij})$. The second term, D_e , is the dissociation energy, the energy required to break the dimer bond to form atoms. The third term, E_b is the bonding energy that is returned to the polymer upon atomic recombination. $D_e + E_b$ may be thought of as an effective dissociation energy, one that breaks the dimer bond to form polymer fragments. The pressure of the polymer phase is given by the expression, $P_{N\text{-polymer}} = -\partial E_{N\text{-polymer}} / \partial V$.

B. Comparisons with total energy LDA calculations and DAC isotherm measurements

Plotted in Fig. 2 are the results of total energy calculations for several metastable structures taken from the paper of Mailhiot *et al.*,³ made using LDA electron band theory. Included in the plot is the N -polymer energy [Eq. (3)], obtained by fitting to the shock data. While the LDA calculations were made for polymers in a periodic lattice an important feature to note is the similarity in the shape of the LDA and N -polymer energy curves. Except for the chain, the cg- N , BP (black phosphorous), A7, and N polymer all have energy minima at nearly identical volumes. Since the shocked liquid consists of a mixture with polymer fragments, rather than an infinitely periodic polymer, we expect the N polymer to have the highest energy.

Figure 3, shows the isotherms of the molecular N_2 and cg- N solid phases measured by Eremets *et al.*⁹ They found a close packed N_2 to cg- N transition to occur at 110 GPa, and with a volume change from 6.7 \AA^3 to 5.2 \AA^3 . The pressure of the solid molecular phase calculated with the N_2 - N_2 potential is in agreement with the measurements. The N -polymer isotherm, determined from the fit to shock data, is in good agreement with the cg- N measurements. The reason for this is that, although their absolute energies differ consid-

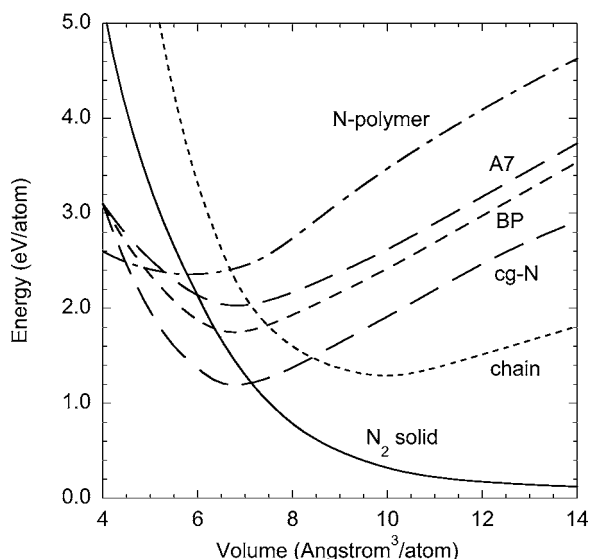


FIG. 2. Nitrogen phases. Curves labeled N_2 solid, chain, cg- N , BP, and A7 were drawn from Mailhoit *et al.* (Ref. 3). N -polymer curve was obtained from the fit to shock data (Ref. 12).

erably, the N -polymer and cg- N phases have nearly identical energy-volume curves (Fig. 2), therefore nearly identical pressures. This agreement suggests that the N -polymer fragment in the shocked fluid is threefold coordinated such as cg- N , and not twofold coordinated as in the chain.

III. SHOCK COOLING AND THE NITROGEN PHASE DIAGRAM

A. Shock cooling

From a thermodynamic or macroscopic point of view, shock-induced cooling is most readily understood by considering the Grüneisen parameter

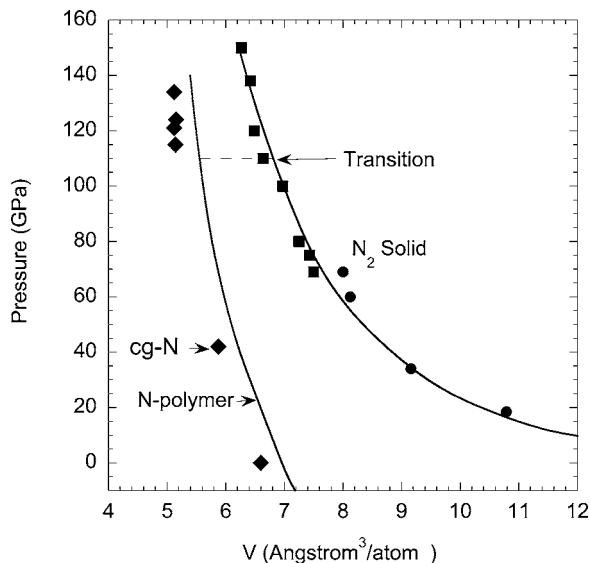


FIG. 3. Pressure-volume equation of state. Data points for the N_2 solid and cg- N phases were reported by Eremets *et al.* (Ref. 9). N_2 solid and N -polymer calculations (solid lines) are from Ross (Ref. 12).

$$\gamma = (VC_v)(\partial P/\partial T)_v = V(\partial P/\partial E)_v. \quad (4)$$

For most materials $(\partial P/\partial T)_v$, and $(\partial P/\partial E)_v$, are positive quantities. Physically, a negative γ implies that an increase in temperature or energy during a constant volume process leads to a lowering of the pressure. Negative values of γ over certain regions of the equation of state surface lead to isotherms that will cross. An inversion of the isotherm is clearly indicative of a profound change in the material properties. In the only other case of which we are aware, shock cooling also appears in experiments with liquid helium II.¹⁶ Helium II has a negative coefficient of thermal expansion due to the phonon to roton transition.¹⁷ The phonon-roton energy gap plays the same role in shock cooled helium as the molecular dissociation to polymer fragments does in nitrogen.¹³ Shock cooling may be more ubiquitous than is apparent, given the relatively few attempted reflected shock temperature measurements and the large number of low- Z molecules.

An understanding of the molecular properties leading to negative γ values may be most readily obtained using the second expression in Eq. (4), $\gamma = V(\partial P/\partial E)_v$, and examining Fig. 2. With decreasing volume the energy of the N_2 molecular solid increases continually. Hence the pressure increases with compression. In contrast the polymer energies, and pressures, decrease starting from the large volumes to an energy minimum, and then increase. As a result, converting a ground state molecule into a stable polymer increases the energy, but contributes to a decrease in the total pressure, or $(\partial P/\partial E)_v < 0$ and $\gamma < 0$. The degree to which cooling occurs depends on the number or fraction (x) of molecules thermally dissociated to polymeric fragments. This fraction will increase with decreasing volume as a consequence of the narrowing of the energy gap separating the molecular and polymer phases. In a shock experiment there is an additional contribution to a temperature lowering, the absorption of thermal kinetic energy in creating a polymer fragment.

The arguments presented above are borne out by an examination of the shock data plotted in Fig. 4. The dashed line represents the $\gamma=0$ curve predicted by the model described above.¹³ The curve divides the phase diagram into regions in which γ is greater or less than zero (shock cooling). The reflected point labeled 5, exhibits cooling and is at a volume near $6.8 \text{ \AA}^3/\text{atom}$. Examining Fig. 2, it is seen that this volume is near the energy minima of all the polymer curves, except the chainlike. In addition the energy gap has narrowed considerably, assuring a large molecular dissociation, typically of order 50%. In contrast, the reflected point labeled 1, is at a volume of $9.4 \text{ \AA}^3/\text{atom}$ well away from the polymer energy minima and the energy gap is relatively large. Point 1 does not exhibit cooling.

It appears from this analysis that shock cooling and negative values of γ occur in liquid nitrogen are associated with pressures where the doubly shocked liquid is driven into volumes near the polymer energy minimum and temperatures where dissociation is appreciable. Therefore, it is proposed that the $\gamma=0$ contour defines, at least roughly, the region of a liquid molecular-polymer phase change. The influence of the phase change on crossing the Hugoniot is apparent in Fig. 4, by a softening in the slope between 9000 K and 12 500 K, near where the $\gamma=0$ curve crosses. The stiffening of the

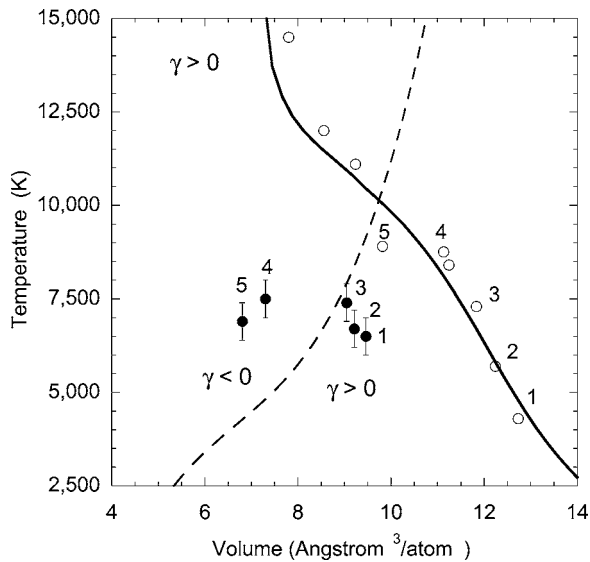


FIG. 4. Nitrogen Hugoniot (open circles) and reflected shock points (filled circles), plotted volume versus temperature (Refs. 10 and 11). Numerals indicate corresponding first and second shocks. Dashed curve is the boundary separating the regions over which the calculated Grüneisen parameter, γ , is predicted to be positive or negative (Refs. 12 and 13).

Hugoniot above 12 500 K suggests a further fragmenting of the polymer and a $\gamma > 0$.

B. Nitrogen phase diagram and phosphorous

A phase diagram for nitrogen is proposed in Fig. 5. In the solid phase, the melting curve has been measured up to

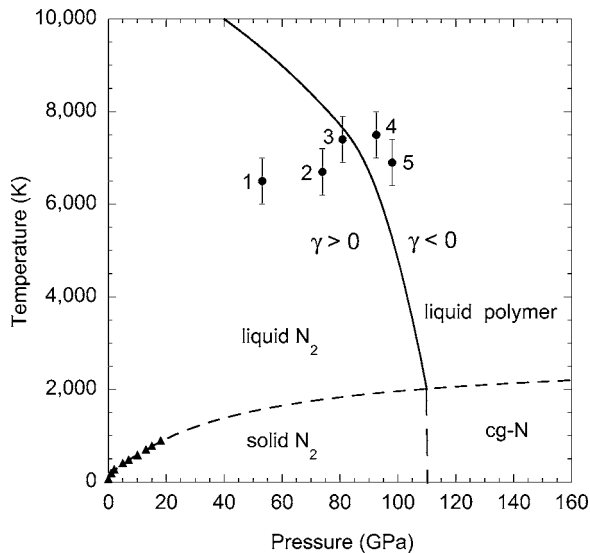


FIG. 5. Nitrogen phase diagram. The melting curve (Ref. 18) (filled triangles) has been extrapolated (small dashed curve) to higher pressure as discussed in the text. The proposed liquid molecular- N polymer liquid transition is shown by solid curve. The molecular solid to cg- N polymer transition at 110 GPa is denoted by the large vertical dashed line (Ref. 9). Included are reflected points from Figs. 1 and 4 (filled circles).

18 GPa.¹⁸ Its relative flatness was explained as due to a hindered molecular rotation in the solid. The melting curve was extrapolated to 140 GPa, and about 2000 K, on the basis of an observation by Eremets *et al.*,⁹ that in the process of their synthesis, melting of the sample “probably” occurred near this pressure and temperature. The molecular solid phase is stable to 110 GPa, where it undergoes a transition to the cg- N phase. A dark nonmolecular phase appears at 180 GPa and is semiconducting up to at least 240 GPa.⁷ In the liquid phase, the transition from a molecular to polymerlike fluid is represented by the $\gamma=0$ curve, except that below 5000 K it has been extrapolated matching the solid molecular-cg- N transition observed at 110 GPa.

The proposed phase line is predicated on an interpretation of cooling as being the result of a phase change from molecular to polymer. In other words, shock cooling is treated as the experimental diagnostic for detecting the phase change, and shock points labeled 1–5 determine a single point along the liquid-liquid phase line, near 7000 K and 90 GPa. This point represents a plausible extension of the molecular-polymer solid phase transition into the liquid. The lowered pressure of the liquid transition (compared to the solid) can be attributed to thermal enhancement of molecular dissociation. The Hugoniot and reflected shock measurements provided the data used to create the analytic model representation of $\gamma=0$ as the criteria for phase change over a broader P - T range. In subsequent work, Hamilton and Ree¹⁹ (H-R) also considered the possibility that N_2 dissociated into N atoms and recombined to form polymeric structures. H-R examined a range of N - N potential parameters and concluded they were unable to predict both shock cooling and a phase transition with the same set of parameters. A predicted phase transition, made by matching free energies of the two phases is nearly the same as proposed here. Although H-R failed to predict cooling, the agreement between two models, employing the same empirical data, adds a level of confidence.

Except for differences in the pressure scale, the proposed nitrogen phase diagram is remarkably similar to the phosphorous phase diagram where x-ray diffraction measurements have identified a first order liquid-liquid phase transition (LLPT) phosphorous,^{14,15} See for example Fig. 3 in Monaco *et al.*¹⁵ The phosphorous liquid-liquid phase line starts at the 1 GPa and 1323 K melting point and extends to near 2500 K and 0.3 GPa. The transition has been interpreted as from the P_4 low temperature phase to a higher density polymer phase of chained P_4 monomers flattened into a “butterfly” shape.^{20–22} Such as nitrogen, the phosphorous phase line has a negative slope, $(\partial P / \partial T)_v < 0$, indicating the presence of an energy gap separating the molecular and polymer phase and decreasing with increasing pressure.

IV. NITROGEN HUGONIOT, $P \gg 100$ GPa

At shock pressures well above 100 GPa polymeric nitrogen will begin to dissociate to atomic and ionic states of partial and complete ionization and finally to a dense plasma. A useful theoretical approach for treating matter under extreme conditions is the activity expansion (ACTEX) method.^{23–26} The starting point for the ACTEX program is

the Coulomb interactions between all the fundamental constituents; i.e., electrons and nuclei, in the system in bound, scattered, and free states. The standard procedure is to expand the nonideal Helmholtz free energy in terms of two-body, three-body, etc., clusters, i.e., a cluster expansion. The leading terms are

$$\frac{F - F_0}{VkT} = S_R + \sum_{i,j} S_{i,j} + \sum_{i,j,k} S_{i,j,k}, \quad (5)$$

where $S_R = \frac{1}{12\pi\lambda_D^3}$, is a Debye screening length, and, $S_{i,j} = -n_i n_j [B_{i,j}(T, \lambda_D) + 2\pi \int_0^\infty (\beta u_{i,j} - \frac{\beta u_{i,j}}{2}) r^2 dr]$. $B_{i,j}(T, \lambda_D)$ is the second virial coefficient for the static screened potential. $u_{i,j}$ are the interaction potentials. Rogers and Young²³ have provided a more detailed description of each of the free energy terms, including $S_{i,j,k}$. The free energy is transformed into an activity expansion, in terms of pressure, that accounts for the formation of ions, atoms, and molecules.

Pressure ionization results naturally from the effect of multiparticle Coulomb interactions on bound states, and without the introduction of *ad hoc* assertions. This is a definite advantage over the chemical picture (free energy minimization) methods in current use, all of which introduce *ad hoc* models to obtain these effects. Consequently, the thermodynamic properties are continuous functions of temperature and density. This method works very well for low to moderate density plasmas and for multiply ionized plasmas. However, it is not easily extended to molecular and polymeric states where higher order corrections for composite particles are required. This places a lower limit to the pressures that may be reliably predicted. Consequently, that part of the pressure range between the molecular and dense plasma regimes, in which the composite particles are dissociating, was interpolated.

Figure 6 shows the experimental nitrogen Hugoniot with an interpolation connecting to the ACTEX calculations. The molecular and polymeric liquid regions are indicated. The interpolation was based on experience derived from an earlier work using ACTEX for calculating low Z -element Hugoniots in which electron ionization led to curvatures leading to compression maxima.²⁶ The nitrogen Hugoniot exhibits a compression maxima at about $V_0/V \sim 5.3$, near 1000 GPa ($T \sim 3.5 \cdot 10^5$ K) arising from the ionization of L shell electrons. V_0 is the initial liquid volume ($28.80 \text{ \AA}^3/\text{atom}$). The ionization of L shell electrons creates a system of $Z=5$ ions bathed in a gas of electrons and a second compression maxima due to K shell electrons appears near $V_0/V \sim 5$ and $4.1 \cdot 10^4$ GPa ($T \sim 2.3 \cdot 10^6$ K). With further increases in temperature the Hugoniot approaches the ideal gas limit near 10^6 GPa. Similar features appear in the case of metals where it has been shown that the ionization of tightly held inner K and L electron shells leads to compression maxima of approximately 5–6 fold.²⁶ For extremely strong shocks the compression approaches the ideal gas limit of $V_0/V=4$, where V_0 is the initial liquid volume. The present calculations neglect relativistic effects and radiation pressure which only become significant above $2.0 \cdot 10^6$ GPa and 10^8 K and lead to an increase in the compressibility beyond fourfold.

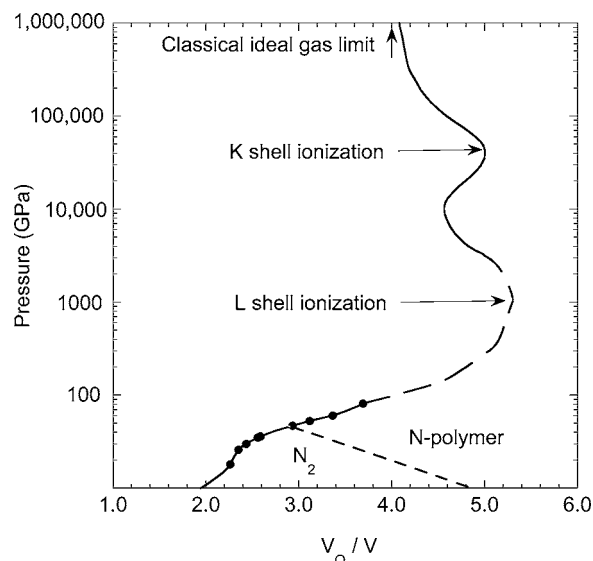


FIG. 6. Nitrogen Hugoniot calculated to extreme conditions, plotted as pressure versus compression (V_0/V). V_0 is the initial liquid volume. Experimental data (filled circles) (Ref. 11), connected to ACTEX calculations (solid curve) by a smoothed interpolation (long-dashed curve). The small dashed line locates approximately the liquid molecular-polymer transition.

V. DISCUSSION

In the process of analyzing the physics it became apparent that the five double shocked points in the liquid near 90 GPa, and 7000 K, represented a change in character from molecular to polymeric that is consistent with the discovery of a cg- N polymer in the room temperature solid at 110 GPa. A phase diagram of nitrogen could then be constructed by combining the known melting curve, with the cg- N phase transition and a proposed liquid-liquid phase line.

While similarities between the nitrogen and phosphorous phase diagrams are consistent with their s^2p^3 electron configurations, the considerably higher pressures and temperatures in the nitrogen phase diagram arise from details in their electronic structure. The absence of $1p$ electrons allows the nitrogen $2p$ valence electrons to closely approach the nucleus, while in phosphorous the $3p$ valence electrons are shielded and repelled by the inner $2p$ core yielding a much weaker chemical bonding. The comparative metallization pressures of carbon and silicon have been explained in the same terms. Si in the diamond structure metallizes near 12 GPa while carbon diamond is believed to metallize at some pressure above 500 GPa.²⁷ Although phosphorous is the only element currently known to exhibit an LLPT, the possible existence of an LLPT for carbon has been the subject of considerable speculation.^{28,29} Simulations indicate a continuous pressure induced evolution from a primarily sp -bonded liquid to sp^2 and sp^3 like.²⁸

Although the presence of an LLPT in phosphorous lends considerable credence for a similar transition in nitrogen, a stronger theoretical confirmation for the presence of polymers is desirable. Particularly, since the necessary experimental studies in the nitrogen phase diagram are difficult to carry out, and require considerable interpretation. Quantum

molecular dynamic simulations using the local density approximation at the GGA level (GGA-MD), with a plane wave basis set were made by Kress, Mazavet *et al.*³⁰⁻³² They found that while their single-shock Hugoniot points agreed well with the gas-gun experiments, the second shock temperature showed a lowered temperature with values of γ over the dissociating region “to be small and close to zero, but not as negative as found experimentally.”³¹ A cluster analysis of their MD trajectories mentions only monomers as reaction products, but makes no mention of clusters. Mattson *et al.*,⁵ however, reports MD simulations that found mixtures of threefold coordinated and chainlike polymers in the fluid up to 10 000 K. Mattson used the SIESTA code,³³ that employs a basis set of local orbitals, that is more appropriate for molecular-polymer thermochemistry, with the improved GGA Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.³⁴ Given the tenuous stability of polymer fragments at high temperature, this improvement appears to be necessary. The subject of exchange and correlation functions

and their role in providing accurate thermochemistry is beyond the scope of the present study.³⁵

Experimental validation of a nitrogen liquid-liquid phase line is likely only to be achieved by additional double shock cooling experiments and supported by a more rigorous theoretical program. Confirmation of the predicted bumps in the Hugoniot well above 100 GPa, lies in the realm of high energy density experimental shockwave methods employing large lasers³⁶ or intense magnetically pressures to drive shock waves into liquids.³⁷ The present calculations may assist in defining optimal experimental conditions.

ACKNOWLEDGMENTS

We wish to thank Mikhail Eremets for helpful comments and Gilbert Collins for his continued interest. The work presented here was partially supported under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

-
- ¹A. K. McMahan and R. LeSar, *Phys. Rev. Lett.* **54**, 1929 (1985).
²R. M. Martin and R. J. Needs, *Phys. Rev. B* **34**, 5082 (1986).
³C. Mailhot, L. H. Yang, and A. K. MacMahan, *Phys. Rev. B* **46**, 14419 (1992); T. W. Barbee III, *Phys. Rev. B* **48**, 9327 (1993).
⁴M. M. G. Alemany and J. L. Martins, *Phys. Rev. B* **68**, 024110 (2003).
⁵W. D. Mattson, D. Sanchez-Portal, S. Chiesa, and R. M. Martin, *Phys. Rev. Lett.* **93**, 125501 (2004).
⁶A. F. Goncharov, E. Gregoryanz, H.-k. Mao, Z. Liu, and R. J. Hemley, *Phys. Rev. Lett.* **85**, 1262 (2000).
⁷M. I. Eremets, A. G. Gavriliuk, R. J. Hemley, H.-k. Mao, and E. Gregoryanz, *Nature (London)* **411**, 170 (2001).
⁸M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, *Nat. Mater.* **3**, 558 (2004).
⁹M. I. Eremets, A. G. Gavriliuk, N. R. Serebryanaya, I. A. Trojan, D. A. Dzivenko, R. Boehler, H.-k. Mao, and R. J. Hemley, *J. Chem. Phys.* **121**, 11296 (2004).
¹⁰H. B. Radousky, W. J. Nellis, M. Ross, D. C. Hamilton, and A. C. Mitchell, *Phys. Rev. Lett.* **57**, 2419 (1986).
¹¹W. J. Nellis, H. B. Radousky, D. C. Hamilton, A. C. Mitchell, N. C. Holmes, K. B. Christianson, and M. van Thiel, *J. Chem. Phys.* **94**, 2244 (1991).
¹²M. Ross, *J. Chem. Phys.* **86**, 7110 (1987).
¹³M. Ross, *High Press. Res.* **10**, 649 (1992).
¹⁴Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata, and K.-I. Funakoshi, *Nature (London)* **403**, 170 (2000).
¹⁵G. Monaco, S. Falconi, W. A. Chichton, and M. Mezouar, *Phys. Rev. Lett.* **90**, 255701 (2003).
¹⁶D. M. Moody and B. Sturtevant, *Phys. Fluids* **27**, 1125 (1984).
¹⁷J. Wilks, *The Properties of Liquid and Solid Helium* (Clarendon Press, Oxford, UK, 1967).
¹⁸D. A. Young, C.-S. Zha, R. Boehler, J. Yen, M. Nicol, A. S. Zinn, D. Schiferl, S. Kinkhead, R. C. Hansen, and D. A. Pinnick, *Phys. Rev. B* **35**, 5353 (1987).
¹⁹D. C. Hamilton and F. H. Ree, *J. Chem. Phys.* **90**, 4972 (1989).
²⁰L. Pauling and M. Simonetta, *J. Chem. Phys.* **20**, 29 (1952).
²¹P. Ballone and R. O. Jones, *J. Chem. Phys.* **121**, 8147 (2004).
²²L. M. Ghiringhelli and E. J. Meijer, *J. Chem. Phys.* **122**, 184510 (2005).
²³F. J. Rogers and D. A. Young, *Phys. Rev. E* **56**, 5876 (1997).
²⁴F. J. Rogers, in *High Pressure Equations of State: Theory and Applications*, edited by S. Eliezer and R. A. Ricci (North Holland, New York, 1991).
²⁵F. J. Rogers and A. Nayfonov, *Astrophys. J.* **576**, 1064 (2001).
²⁶B. F. Rozsnyai, J. R. Albritton, D. A. Young, V. N. Sonnad, and D. A. Liberman, *Phys. Lett. A* **291**, 226 (2001).
²⁷S. J. Clark, G. J. Ackland, and J. Crain, *Phys. Rev. B* **52**, 15035 (1995).
²⁸C. J. Wu, J. N. Glosli, G. Galli, and F. H. Ree, *Phys. Rev. Lett.* **89**, 135701 (2002).
²⁹L. M. Ghiringhelli, J. H. Los, E. J. Meijer, A. Fasolino, and Daan Frenkel, *Phys. Rev. Lett.* **94**, 145701 (2005).
³⁰J. D. Kress, S. Mazevet, L. A. Collins, and W. W. Wood, *Phys. Rev. B* **63**, 024203 (2001).
³¹S. Mazevet, J. D. Johnson, J. D. Kress, L. A. Collins, and P. Blottiau, *Phys. Rev. B* **65**, 014204 (2002).
³²S. Mazevet, J. D. Kress, L. A. Collins, and P. Blottiau, *Phys. Rev. B* **67**, 054201 (2003).
³³For references and application of the SIESTA code, see Ref. 5.
³⁴J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
³⁵A. D. Boese and J. L. Martin, *J. Chem. Phys.* **121**, 3405 (2004).
³⁶L. B. Da’Silva, P. Celliers, G. W. Collins, K. S. Budhil, N. C. Holmes, T. W. Barbee, B. A. Hammel, J. D. Kilkenny, R. J. Wallace, M. Ross, and R. Cauble, *Phys. Rev. Lett.* **78**, 483 (1997).
³⁷M. D. Knudsen, D. L. Hanson, J. E. Bailey, C. A. Hall, and J. R. Asay, *Phys. Rev. Lett.* **90**, 035505 (2003).