Polymerization in liquid phosphorus: Simulation of a phase transition

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We have performed simulations of liquid phases of phosphorus using the molecular-dynamics–
density-functional method. Starting from a system of 26 P₄ tetrahedra in a simple cubic unit cell of
constant volume, we determine radial, angular, and defect distribution functions for the molecular
liquid and for polymeric high temperature liquid red P. Comparison with available experimental data
and earlier calculations shows that the structures of the amorphous and liquid polymeric phases are
very similar. The polymerization of molecular phosphorus is a complex process that may be viewed
as a defect-induced chain reaction, in which the elevated temperature and the environment of the
tetramers play decisive roles.

I. INTRODUCTION

The structural versatility of phosphorus makes it one of the
most fascinating elements in the Periodic Table, with
only boron, sulfur, and selenium showing a comparable
range of structures. In addition to four crystalline modi-
fications with well-established structures [orthorhombic
(black); monoclinic (violet, Hittorf's); rhombohedral (α-
arsenic structure); simple cubic (metallic)], phosphorus
also forms a molecular solid (white P) comprising tetra-
hedral P₄ units, and a great variety of "red" forms. The
last are usually amorphous, but the color, density, and
structure depend on the method of preparation. The rela-
tive ease with which structures can be interchanged and
the complexity of the phase diagram make it difficult to
perform definitive studies (both experimental and theo-
retical). A detailed understanding of some of the most
basic properties of phosphorus has been lacking to the
present day.

Recently we carried out extensive studies of both phos-
phorus clusters (Pₐ, up to n=11) (Ref. 5) and amorphous
phosphorus (α-P) (Ref. 6) using density functional (DF)
calculations combined with molecular dynamics (MD).
The DF approach, with a local spin density (LSD) ap-
proximation for the exchange-correlation energy, pro-
vides a reliable method for calculating energy surfaces
that is free of adjustable parameters. The combination
with MD allows us to probe large regions of the energy
hypersurface and to perform traditional MD simulations
at nonzero temperatures. The present study extends this
work to the liquid phase (β-P), which has some remark-
able properties.

If molecular white P (an insulator) is heated above its
melting point (315 K), the resulting liquid also comprises
tetrahedral P₄ molecules with bond length 2.210 Å (4.176
a.u.). In spite of the compact, almost spherical form of
P₄, neutron diffraction studies of β-P show that spatial
correlations between the molecules extend farther (~20
Å, 38 a.u.) than in any other known liquid. This in-
dicates orientational ordering of the tetrahedra, but the
precise nature is not known. Very pure β-P can be main-
tained in a stable, supercooled state more than 100 K
below its melting point for much longer than any other
liquid, and the spatial correlations are very similar at
T=323 K in the supercooled liquid at 283 K. Liquid
phosphorus turns red if heated above 473 K (the boil-
ing point is 553 K) and red amorphous phosphorus
(α-P) precipitates if the reaction is allowed to proceed.
Most industrial processes for converting the poisonous
and combustible white P to the more stable α-P oper-
ate in the vicinity of 500–600 K and require several days
for completion. Little is known about the mechanism of
this reaction, and we know of no systematic experimental
studies of it.

The various forms of red α-P are semiconducting poly-
mers with high molecular weights and predominantly
threefold coordination. The average values of the bond
lengths and angles are 2.24 Å (4.23 a.u.) and 103°,
respectively, and red P melts (under pressure) at
~875 K to form an almost colorless liquid similar in ap-
pearance to molten white P. We are not aware of any
tests of the statement that these two liquids are iden-
tical. Our simulation of α-P (Ref. 6) started from a
liquid at 2000 K, and showed no tendency to form P₄
molecules. Some forms of "white P" that result on an-
nealing the condensate from P₄-rich vapor above (solid
or liquid) red P (Ref. 3) probably contain both molecular
and polymeric components. Polymerization proceeds
even more readily in the neighboring group V element
arsenic. Condensing As₄-rich vapor on cold (30 K) surfaces
gives well-defined solid molecular yellow As₄, and sub-
sequent warming (even to only 78 K) leads irreversibly to
a fully polymerized sample. As₄ is less stable than P₄
(the binding energy per atom is 2.55 eV in As₄, 3.11 eV
in P₄), and the activation barriers for the breakup of As₄
are probably lower than for P₄. Simulations of liquid
As show a polymeric structure, and the similarities
between the structures of P and As are well known. It
is interesting that the highly symmetric tetrahedral
forms of both phosphorus and arsenic polymerize to give
low-symmetry disordered forms. This is consistent with
the observation that the polymeric allotropes of P (or-
thorhombic black, black rhombohedral, and monoclinic
violet) and As (rhombohedral) are thermodynamically
more stable than the molecular solids (white P and yellow As, respectively). Furthermore, our simulations on α-P have indicated that the structure resembles a network of P₄₄ clusters, which usually favor low-symmetry structures. An example is P₈, where the wedge-shaped "cuneane" isomer (C₂ᵥ) is over 1.7 eV more stable than the cubic (O₃) form. The structural constraints imposed by high symmetry [both the cube (O₃) and tetrahedron (T₄)] allow only a single bond length and a single bond angle) lead to a preference for lower-symmetry structures, where a range of bond lengths and bond angles can occur. This picture is consistent with all our theoretical work on the structural chemistry of phosphorus⁵,⁶ and arsenic.²⁰

In the present work, we analyze the structures of the molecular and polymeric forms of α-P, and seek to identify the crucial steps in the transition between them. The P₄₄ tetrahedra, stable in molecular α-P at room temperature, react at higher T to form a polymeric network of threefold coordinated atoms. The formation of bonds between the atoms in different P₄₄ monomers requires the breakup of the tetrahedra, and two mechanisms have been suggested: (a) the formation of a chain of P₄₄ units, each with a single broken bond (Fig. 1), and (b) possible cascades of increasingly stable aggregates involving dimers and tetramers.¹⁹ A reliable model of the chemical bond is indispensable in simulating such a phase transition involving drastic changes of bond characteristics (the bond angle changes here from 60° to ~100°). MD with empirical two- or three-body interatomic potentials is therefore inappropriate. While traditional methods of quantum chemistry lead to reliable energies, they are restricted to relatively few atoms and neglect the effects of neighboring ("solvent") molecules and of nonzero temperature.

The MD-DF method that we use has been described in detail previously in other applications to phosphorus⁵,⁶ and we restrict this discussion to essentials. The approach does not suffer from the above restrictions, but it should be noted that the dynamics observed in all MD-DF simulations may differ from those of the system being modeled: (i) The simulations are performed on a classical system; quantum effects, such as the quantization of the vibrational motion, can change the picture at low temperatures, (ii) the coupling of the system to a heat bath can change the MD trajectories of the system, and (iii) the time required to polymerize white P to the red form is far beyond the scope of any present MD simulation method. We have addressed this problem by using much higher temperatures, and different reaction pathways may be favored. Calculations at high T and constant pressure can lead to high internal pressures and possibly to structures and dynamics that differ from those observed at constant pressure.

![FIG. 1. Model of the structure of α-P proposed by Pauling and Simonetta (Ref. 18).](image)

**II. COMPUTATIONAL DETAILS**

As in our work on α-P,⁶ we use a constant-volume simple cubic unit cell with lattice constant 27.11 a.u. We therefore expect a good description of local order up to interatomic distances of about 13.5 a.u., i.e., a central tetrahedron in white P together with a complete shell of neighboring molecules. The density was adjusted to that of white P at its melting point (ρ = 1.81 g cm⁻³) (Ref. 3) by filling the available volume with 104 P atoms, initially in the form of 26 P₄ tetrahedra, randomly oriented on 3³ cubic lattice sites with one vacancy. The only subsequent external restrictions on the atomic positions are those required by constant density and periodic boundary conditions. The tetrahedra are then held together by chemical bonding, not by the imposition of symmetry or rigidity.

We have shown⁵,⁶ that an excellent description of the bonding properties of phosphorus is obtained if the occupied valence electronic states ψᵣ (260 in the present case) are expanded in a plane wave basis with cutoff energy 5.3 hartree a.u. at a single point in the Brillouin zone (k=0). The electron-ion interaction is described by a pseudopotential.²⁰ Using the approximation lₘₐₓ = 2 ("sp nonlocality") (Ref. 5) leads to bond lengths in P₄ and P₄ in excellent agreement with experiment, and to a series of predictions for the shapes and geometries of Pₙ clusters with n=5–11. The predictions for P₆ and P₈ were later confirmed by self-consistent field (SCF) calculations.¹⁹,²¹ One isomer of P₁₀ found in the SCF work¹⁹ was shown subsequently to be one of the most stable in DF calculations.¹⁷ The use of only lₘₐₓ = 1 ("s nonlocality"), as in the α-P calculations and the present work, leads to bond lengths that are about 1.5% longer than the experimental ones and those calculated with lₘₐₓ = 2. The description of the energy surfaces is otherwise very satisfactory. The local density approximation (LSA) we use²² leads to atomization energies that are overestimated by ~1 eV/atom. The inclusion of nonlocal (gradient) corrections to the exchange and correlation energy removes much of the error in the calculated atomization energies for P₂₋₄, As₂, and As₄, without affecting the excellent description of the geometries.¹⁷

With physical masses for the P atoms and a fictitious mass μ=500 a.u. for the electronic degrees of freedom ψᵣ, the coupled equations of motion could be solved accurately with a Verlet integrator and a time step Δt=9 a.u. (2.2 × 10⁻¹⁶ s). During most of the MD runs, the deviation from the ground state energy of the system of 520 electrons was less than ~0.2 eV. A larger deviation (up to 2 eV) was permitted temporarily only at the highest temperatures we used (3500 K).

**III. RESULTS AND DISCUSSION**

**A. The molecular liquid**

The simulation of liquid molecular phosphorus proceeded as follows: The initial geometry with 26 P₄ tetrahedra was heated in stages to a temperature just be-
low where a breakup of the tetrahedra became observable on the time scale of our simulations (≈3000 K, see Sec. III B). This destroyed any memory of the initial geometry of the tetrahedra, and the system was then cooled to and equilibrated at T=500 K. This "simulated annealing phase" lasted approximately 13000 steps. A subsequent MD run (5000 steps), corresponding to a microcanonical ensemble, provided the basis for the structural and dynamical analysis of the molecular liquid. Performing the simulation well above the melting point allows us to accumulate much better statistics for all quantities sought. Phosphorus is very viscous at the melting point, and the viscosity at 500 K is four times smaller than at 317 K. The density in the melt changes by only ≈10% in this temperature range, and we expect only minor effects of the pressure on the quantities calculated here.

Neutron-scattering experiments also indicate that the local order in ℓ-P is remarkably insensitive to temperature changes. To verify that the sample is in a diffusive liquid state, we have computed the diffusion coefficient D from the Einstein relations to be ≈5×10⁻⁴ cm²s⁻¹. This is within the range of typical liquids, although we know of no measurements of this quantity for ℓ-P.

Very little is known about the microscopic structures of any of the disordered forms of phosphorus, and the only experimental study of liquid molecular phosphorus that we can compare with are neutron-scattering data near the melting point. In Fig. 2 (top) we compare the radial distribution functions derived from our simulations and from the scattering data. The most likely first-neighbor distance (i.e., the interatomic separation within the tetrahedral molecules) is slightly larger in our simulations (4.26 a.u.) than in the experimental data (4.18 a.u.). We have shown previously that this is primarily a consequence of the pseudopotential approximation we use ("s nonlocality"), not of the different temperatures in simulation and experiment. The first-neighbor shell defined by the location of the first minimum in J(r) at 5.0 a.u. contains 3.0 atoms, reflecting the intact tetrahedra (with a very small number of defects with collision-induced fourfold coordinations; see Table I and Fig. 3, upper frame). The overall shape of the J(r) function with a sharp first peak of high intensity dominating over a broader, low-intensity, second-neighbor region (≈5–9 a.u., with the peak at 6.9 a.u.) is reproduced well. The third peak near 10.5 a.u. is at a shorter distance than in the experimental data. This is not surprising, since the effects of the finite size of the unit cell increase as we approach the cell boundary. Nevertheless, the overall shape of the J(r) function—a sharp first peak with a broader, low-intensity, second-neighbor region (≈5–9 a.u.)—is reproduced satisfactorily, particularly as our calculation contains no adjustable parameters. Peak intensities in the simulation data are slightly lower, and peak widths slightly larger than in the data derived from experiment because of the temperature difference and the short time span of the simulation.

In our simulation at 500 K, the closest distance of approach of atoms in different molecules is only ≈5.2 a.u., substantially less than the sum of two phosphorus van der Waals radii (7.2 a.u.). The "softness" of the tetrahedra

**FIG. 2.** Comparison of calculated radial distribution functions J(r) = 4πr²ρ(r) (full curves) with experiment (dashed curves). (a) Upper frame: molecular liquid at 500 K, compared with neutron-scattering data (Ref. 9) at 323 K; (b) lower frame: polymerized liquid, compared with data for α-P (Ref. 11, no experimental data are available for the polymeric liquid).

**FIG. 3.** Projection of structures of (a) molecular liquid P (upper frame), (b) polymerized liquid P (lower frame). Bonds are shown by a line when atoms are separated by 5.0 a.u. or less.
TABLE I. Concentration (%) of N-fold coordinated defects in molecular l-P at 500 K (1) and 1500 K (2), at the beginning of the equilibration at 3500 K (3), after 3300 Δt at 3500 K (4) and after 27000 Δt (6 ps) of equilibration at 1500 K (5). The simulation proceeded from left to right. The defect concentration in a-P (Ref. 6) is shown (6) for comparison. A sum of less than 100% reflects the presence of onefold and fivefold defects.

<table>
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<th>500 K (1)</th>
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<th>3500 K (3)</th>
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is a crucial element in the polymerization process (see below). The distribution of bond angles (Fig. 4, dashed curve) shows a pronounced peak at 60°, indicating tetrahedral structural units with little angular flexibility.

Scattering experiments provide little information about the nature of intermediate- and long-range order. In molecular liquid P we define the former as ordering phenomena involving neighboring molecules, and the latter as those extending beyond one shell of neighboring molecules. While the details of such long-range order are inaccessible in the present simulations of l-P, we now show that an analysis of the intermediate-range correlations in this liquid yields useful insights into the probable long-range order.

Plots of the pair distribution function J(r) (Fig. 2) and its integral show that the second-neighbor peak between 5.0 and 8.8 a.u. contains ten atoms, and the third peak from 8.8 to 12.7 a.u. contains ~ 32 additional atoms. Intermediate-range and orientational order has been discussed in other systems comprising tetrahedral molecules, examples being CCl₄ (Ref. 23) and CBr₄ (Ref. 24). Misawa has shown that differences in the ratio of intertetrahedral to intratetrahedral bond distances ζ = L/l suffice to explain the basic features in the measured structure factors of liquid P₄ and other tetrahedral liquids like VCl₄. P₄ has a much larger ζ (~1.6) than all XY₄ molecular liquids because the tetrahedron is “empty.” Assuming a fixed intermolecular orientation with one atom on one molecule cradled into the hollow formed by three atoms on another at a certain angle, ζ variations alone lead to large variations in the model structure factor, in agreement with experimental measurements.

The approximate 1:3 ratio of the number of second- and third-neighbor atoms we observe in our simulation is indeed compatible with Misawa’s model, but studies of structure factors and pair correlation functions alone cannot reveal directly preferred relative intermolecular orientations. The ability to study more complex distribution functions than those accessible experimentally is an obvious advantage of MD simulations. In Fig. 5 we show the distribution of distances between the center of a P₄ molecule and the atoms of its four closest neigh-
bors. On average there are about three times as many "near" atoms as there are "far" atoms, indicating that neighboring molecules turn their faces towards a central tetrahedron. There is also a strong tendency for the angles between vectors normal to the faces of neighboring molecules to be near 180°, further supporting a picture in which faces of adjacent tetrahedra tend to be parallel. The free rotation of molecules is thus significantly inhibited. This ordering becomes more pronounced as the molecular centers approach. At nonzero temperatures, of course, remaining rotational motions of the molecules relative to each other can still lead to some local departures from this alignment. Nevertheless, radically different orientations (e.g., "edge on," "apex to apex," or "apex to face") are definitely not favored.

The structural ordering shows similarities to that of vapor-deposited films of molecular arsenic, where the structural units are As₄ molecules. Daniel and Leadbetter showed that a staggered face-to-face orientation gave the best agreement with x-ray diffraction measurements on amorphous As films. A preference for either the "staggered" or "eclipsed" configurations of the face-to-face alignment was not evident in our simulations at 500 K, so that there is an upper bound on the rotational energy barrier in phosphorus. The presence of significant, directed chemical interactions between neighboring molecules in the liquid is not consistent with the picture of P₄ as a nearly spherical object.

B. The reaction and the polymeric liquid

As mentioned above, the polymerization of white P to liquid red P is a very slow process, requiring typically several days at temperatures between 500 K and 600 K. This presents an onerous problem for MD simulations, where accessible time scales are orders of magnitude shorter. The polymerization process has been accelerated in the present simulations by using temperatures that are much above the melting point. This, in turn, can change the reaction pathways accessible to the system, and the relationship between the results of the calculation and the actual mechanism of polymerization at lower temperatures must be made with caution (see Sec. I). Nevertheless, we are confident that the main features of the polymerization process will be described much more reliably than is possible in simulations using parametrized interatomic potentials.

In the course of the polymerization reaction, it is obvious that the individual P₄ structural units must break up and then recombine to form a three-dimensional network similar to that of the amorphous material. In our simulation the disintegration of the tetrahedra begins at \( T \sim 3000 \) K, and no tetrahedron remains intact after 3300 time steps at 3500 K. The calculations show that the breakup mechanism is clearly thermally induced collisions between the tetrahedra. Increasing the temperature continuously over several thousand time steps up to 3500 K increases primarily the number of fourfold coordination defects: The molecules collide with each other, but the kinetic energy is too low to cause breakup on the time scale of our observation; fourfold defects are locally stable but their formation requires the energy of the system to pass over a barrier. Once this barrier can be overcome sufficiently often (in the present calculations beyond 3000 K), chemical bonds form between different molecules. However, fourfold defects apparently destabilize the tetrahedral molecules, and we observe rapid deformations from the tetrahedral to the "roof" isomer (similar to those in Fig. 1) in those tetrahedra that contain a fourfold defect. The process of breaking a single bond is similar to that proposed by Pauling and Simonetta and generates a large proportion of twofold coordinated atoms [see Fig. 6(a)]. It is clear that the motion of the atoms surrounding an individual tetrahedron plays a central role in their dissociation. Semi-empirical calculations of the dissociation of an isolated tetrahedron into two P₂ molecules suggest that the most favorable path involves the simultaneous opening of four bonds, with the shortening of the remaining two.

We have not observed this process during the present simulations.

According to a range of tests that we have performed, the sample will polymerize rapidly and isotropically at all temperatures between 3500 K and 1500 K once there are sufficient reactive twofold coordinated defects. The dominant processes in this second phase of the simulation are (i) recombinations of twofold defects and (ii) a chain reaction of processes involving reactive twofold defects that approach and break up intact tetrahedra [see Fig. 6(b)].

After a total of 3300 time steps at 3500 K, the system was annealed to 1500 K and then followed for 27,000 time steps (6 ps) at this temperature. At this point the liquid has become almost completely polymerized (three tetrahedra reform), and the projection of a typical configuration (Fig. 3, lower frame) shows that the final disordered structure is reminiscent of that of a-P. One can easily distinguish interlinked clusters of atoms with shapes resembling closely those of stable, isolated P₄ clusters, the basic structural model we developed for a-P. An analysis of a set of distribution functions with which we characterized a-P, such as the radial distribution function \( J(r) \), confirms the close similarity between polymeric \( \ell \)-P and a-P. Although we are unaware of any scattering experiments on the polymeric liquid, the following comparison between our data for this liquid and experimental data for \( \ell \)-P is useful until experimental data for a-P become available.

It is natural that the peaks in the liquid are much broader than in the amorphous material at room temperature (Fig. 2, bottom). Apart from this, the most characteristic differences between the molecular and polymeric substances (Fig. 2, top and bottom, respectively) are the substantial increases in the intensity of the second peak relative to the first in molecular P, and the shift of its center of mass to lower \( r \). The same behavior is evident in the solid-state polymerization of arsenic films. Both features are reproduced well by our simulation and we are confident that polymeric liquid phosphorus is indeed structurally very closely related to amorphous phosphorus.
The bond angle distribution (Fig. 4) shows the same effect that we observed in α-P, a sharp reduction in the number of bond angles near 60° and an increase in the range ∼90°–110°. As in the case of the amorphous material, the structures with α=60° arise from triangles and “roof” (or “butterfly”) structures and from the three tetrahedra that have reformed.

Table I clearly shows the three stages of the process, (i) thermal generation of fourfold defects [columns (1)–(3)], (ii) breaking of intramolecular bonds and generation of twofold defects (“roof” structures, column (4)), and (iii) restructuring into a three-dimensional network and annealing of the defects [column (5)], to yield a disordered liquid very similar in nature to α-P [column (6)]. It is difficult to find an unambiguous term to describe this process, but “defect mediated chain reaction” contains the essence of the polymerization mechanism that we observe in our MD simulation.

The present simulations indicate therefore that, while the details of the polymerization process are very complex, there are underlying features that are of a simpler nature. (1) As the temperature is increased, the increased mobility of the P₄ units in the molecular liquid means that they undergo more collisions with other tetrahedra. Above a threshold thermal energy, locally stable defects with fourfold coordination link P₄ molecules, but the resulting objects decay by breaking a single bond to form “roof” structures. At the same time, individual P₄ units can show bond elongation or even a temporary transition to a “roof” structure. This is accompanied, of course, by the increase in the number of twofold coordinated atoms that we noted above and by a change in the bond angle distribution from the single 60° peak found in the tetrahedron to larger angles. (2) The increased number of — apparently very reactive — twofold coordinated atoms (−P*P*) means that reactions between P₄ units are more probable, a chain reaction [Fig. 6(b)] can take place, and recombination and bond formation between twofold coordinated atoms on adjacent units can eliminate both as recognizable tetramers (termination of the reaction chain). This reaction, which is an essential part of the polymerization process, can be initiated not only by those atoms that have twofold coordination but also by its neighboring atoms, and the species attacked include all twofold or threefold coordinated atoms. The result is a wide spectrum of branched growing species not limited to linear chains of multiples of four atoms as in Fig. 1.

Many years ago, Pauling and Simonetta proposed that α-P consists of chains of P₄ fragments resulting from breaking a single bond in each tetrahedron, as illustrated in Fig. 1. This model does not agree with more recent work on the amorphous material and have calculated that infinite chains (−P₄−∞) of this type are less stable than white P by about 10 kcal/mol P₄. An alternative scheme proposed by Häser et al. considered cascades of structural changes involving dimers and tetramers. Some features of both models are consistent with the results of the present simulations, namely, the opening of the tetrahedral units and the formation of objects that resemble stable clusters in vacuum.

IV. CONCLUSIONS

The structural variety of phosphorus and the complexity of its energy surfaces mean that it has remained a challenge to both experiment and theory for many years. In the present work, we have performed molecular-dynamics simulations on the molecular liquid (comprising P₄ molecules) and red liquid P, and studied the polymerization process that takes the former into the latter. There are clear parallels to the structures of both the amorphous form of red phosphorus and the group Va neighbor arsenic. It has been possible to identify essential features of the polymerization process. The most likely pathway involves an initial opening of the P₄ tetrahedra similar to that first proposed over 40 years ago by Pauling and Simonetta. The transformation then spreads through the sample via a (twofold) defect mediated chain reaction. We hope that the calculations of the structural parameters of the red liquid will stimulate more experimental work on this interesting material.

We have noted in Sec. I that the dynamics observed in such simulations can differ from those of the real system that we are modeling. Nevertheless, the features of the polymerization process evident in our simulations provide a plausible basis for further work. There is little doubt that two aspects of the present study, the incorporation of the effects of elevated temperatures and the influence of the environment (solvent) on the reactivity of the P₄ monomers, are necessary to describe this, one of the most interesting polymerization processes involving a single element.
ACKNOWLEDGMENTS

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