Structure of Liquid Arsenic: Peierls Distortion versus Friedel Modulation

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A molecular-dynamics simulation of liquid arsenic shows good agreement with recent neutron-diffraction data. The coordination number and the average bond length and bond angle are very close to their values in rhombohedral As. This shows that the short-range order in liquid As is very close to that in the crystal. The experiment has been interpreted as representing the first evidence for the existence of a Peierls distortion in a liquid. Our results suggest that the structure could also be interpreted as arising from a modulation of the random packing of atoms by the Friedel oscillations in the effective interatomic interactions.

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Very recently, Bellisent *et al.*[1] have studied the structure of liquid arsenic using elastic neutron scattering. The diffraction data show that the structure of the liquid closely resembles that of the stable rhombohedral (*A*7) crystal structure: The positions of the first two peaks in the pair correlation function $g(R)$ are very close to the nearest- and next-nearest-neighbor distances in the solid; the average number of atoms in the first coordination shell is three, and about nine in the second shell (again these numbers are identical to the crystalline coordination numbers—see Table I). These interesting results were interpreted in terms of the classical arguments for the explanation of threefold coordination in the group-V elements: The electronic configuration of a free atom is s^2p^3. As the energy of the s states lies far below the p level (by about 8.4 eV), only the p electrons contribute to the valence band in the solid. With the six lobes of the p orbitals forming right angles, this would lead to a sixfold-coordinated simple cubic structure. However, an exactly half-filled band such as the p band of the group-V elements is unstable against a doubling of the periodicity of the structure. This leads to the rhombohedral *A*7 structures of As, Sb, and Bi or the the orthorhombic structure of P and As. Both structures consist of tricoordinated layers of atoms.[2] The classical explanation of such a Peierls distortion requires periodicity. The structure of liquid arsenic would seem to offer the first evidence that such a Peierls-type distortion can exist in a liquid as well. A calculation of the structure of liquid arsenic based on this argument has not been presented as yet.

The structure of the crystalline group-V elements has also been discussed within the pseudopotential approach. It has been shown by Schiferl[3] for P and by Abe, Okoshi, and Morita[4] for As that pseudopotential calculations in the second-order approximation successfully explain the stability of the unusual crystal structures and the phase transitions that occur under pressure (orthorhombic-*A*7-simple cubic for P; and *A*7-simple cubic for As). However, it must be admitted that the pseudopotential formulation in wave-number space lacks the elegant simplicity of the Peierls-distortion argument. Hafner and Heine[5,6] have reconsidered the trends in the crystal structures of the s- and p-bonded elements in terms of real-space pair interactions. The characteristic trends in the interatomic potentials with electron density and pseudopotential can be described in terms of two simple parameters: the effective radius R_c of the ionic core and the electron-density parameter R_s (R_s is the radius of a sphere containing on the average one electron). Their interplay gives rise to two effects. (i) The "core effect": At decreasing R_s (increasing electron density) and constant R_c/R_s, the repulsive core moves over the first attractive minimum.[5,6] This explains the decreasing stability of close-packed structures with an increasing electron density and thus the trend from highly coordinated metallic structures in groups I–III to low coordination and covalency in groups IV and V (e.g., in the series Na-Mg-Al-Si-P). (ii) The "amplitude effect": A decrease in R_c/R_s leads to a strong damping of the Friedel oscillations in the pair potential. This explains the return to more symmetric structures and to more metallic behavior with increasing atomic number and under elevated pressure.[5,6] Hafner and Kahl[6,7] have extended this argument to explain the trends in the structures of the liquid elements, although with the notable exception of the group-V elements to which none of the current liquid-state theories seems to apply.

In this paper I present the first successful molecular-dynamics calculation for liquid As. The calculation is based on the same simple form of the effective pair interaction as used by Hafner and Heine. The results are in good agreement with the neutron-diffraction data: Coordination numbers, bond distances, and bond angles agree with the experimental values (Table I). It is shown that the complex noncompact structure of liquid As arises from the interplay of two characteristic distances: the effective diameter D_{rep} of the repulsive core of the pseudoatom and the Friedel wavelength $\lambda_F = 2\pi/2k_F$ of the long-range oscillatory part of the poten-

TABLE I. Interatomic distances R_i and coordination numbers Z_i for the first two coordination shells in rhombohedral and liquid As.

	R_1 (Å)	R_2 (Å)	Z_1	Z_2
Rhombohedral	2.51	3.15/3.77	3	3+6
Liquid, neutron diffraction[a]	2.50	3.75	3.0	8.9
Liquid, computer simulation	2.61	3.83	3.0	9.2

[a] After Ref. 1.

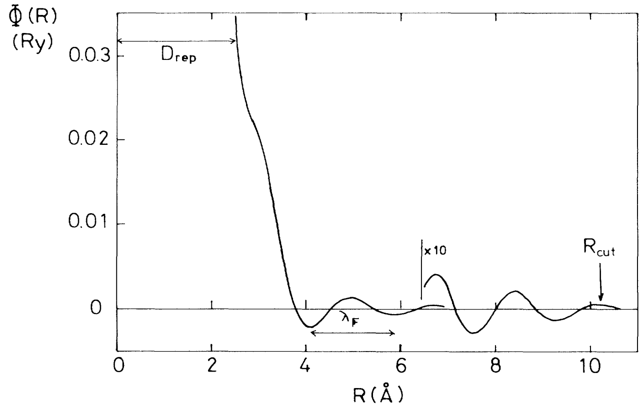

FIG. 1. The effective pair potential for liquid arsenic at $T=1103$ K. The vertical arrow shows the distance at which the potential is truncated for the small 864-atom cell.

tial. This picture of a "Friedel modulation" of the random packing of atoms applies not only to liquid As; previous calculations[7,8] have demonstrated that it explains the atomic and the electronic structure of all group-IV elements in the liquid state. It offers an explanation which seems to be radically different from the Peierls-distortion argument.

The interatomic potential $\Phi(R)$ and the volume energy $E_0(V)$ have been calculated via standard second-order perturbation theory[6] with use of the simple empty-core pseudopotential[9] and the Ichimaru-Utsumi[10] form of the dielectric screening. The choice of the Ichimaru-Utsumi local-field corrections guarantees that the screening functions satisfy all relevant sum rules. With the empty-core pseudopotential, we have the core radius R_c as the only free parameter. To a first approximation, R_c is the actual radius of the ionic core, which is then shifted slightly by nonlocal bonding effects.[5] Hafner and Heine[5] have shown, based on the analysis of empirical pseudopotential data,[11] that the ratio R_c/R_s is approximately constant within each row of the periodic table. For the third-row elements from K to As, one finds $R_c/R_s \approx 0.48$–0.50. In our calculation we find the best agreement with the experimental diffraction data for $R_c/R_s=0.51$ (corresponding to $R_c=0.53$ Å, the number density of liquid As at $T=1103$ K being $n=0.0422$ Å^{-3}, $R_s=1.043$ Å). This means that our pseudopotential is in reasonable agreement with empirical pseudopotentials adjusted to electronic properties.[11] If the ratio R_c/R_s is varied between $R_c/R_s=0.49$ and 0.53, only small changes in the liquid structure are found. The effective pair potential $\Phi(R)$ has the form characteristic for the light group-IV and group-V semiconductors and semimetals (see Fig. 1). The repulsive diameter is given by[5] $D_{\text{rep}} \approx 2R_c + 2.2\lambda_{\text{TF}}$ (λ_{TF} is the Thomas-Fermi screening length); here $D_{\text{rep}}=2.50$ Å. At the given density (which is determined by the pair forces *and* the volume energy), the nearest-neighbor distance in any close-packed (ordered or disordered) structure with a coordination number in the range between $Z=6$ (simple cubic) and $Z=12$ (close packed) would fall on the repulsive hump in the potential halfway between D_{rep} and the first minimum in the pair interaction. In such a case energy is gained by moving the atoms into the adjacent potential-energy minima (or at least into an inflection in the potential), splitting the coordination shell centered at the close-packing distance D_{cp} into two subshells centered at $R_1=D_{\text{cp}}-\lambda_F/2$ and $R_2=D_{\text{cp}}+\lambda_F/2$. If we take D_{cp} to be the nearest-neighbor distance at close packing, we have $D_{\text{cp}}=3.23$ Å and $R_1=2.38$ Å, $R_2=4.08$ Å, in reasonable agreement with the nearest-neighbor distances in As. In reality, the splitting is somewhat asymmetric because of the steep slope of the potential. A rough estimate for the number of neighbors may be obtained from the relation[5] $(R_1/D_{\text{cp}})^3 \approx (Z+1)/13$. In our case a splitting of the $Z=12$ shell into one containing three to four atoms and one with eight to nine atoms is predicted. Thus we confirm the results of Abe, Okoshi, and Morita[4] that a second-order pseudopotential calculation predicts correctly the static stability of the $A7$ structure and the pressure-induced phase transformations. However, the structure is not dynamically stable—some transverse acoustic modes have imaginary frequencies. As acoustic shear modes are overdamped in the liquid, this does not affect the usefulness of the potential for describing liquid As.

The structure of liquid As has been calculated by use of classical constant-energy molecular dynamics. The Newtonian equations of motion are integrated with a fifth-order predictor-corrector algorithm. A very effective network-cube method has been used for near-neighbor bookkeeping.[12] This allows for an efficient simulation of systems with large numbers of particles and large radii of interaction. The simulation was started with the atoms located on the points of a face-centered-cubic lattice. The system was first molten at $T \approx 1500$ K and then slowly cooled to $T \approx 1100$ K, the temperature for which diffraction data are available. To test the size dependence of the simulation results, runs with $N=864$ and up to $N=2048$ atoms in a cubic cell have been performed. The pair potential was truncated

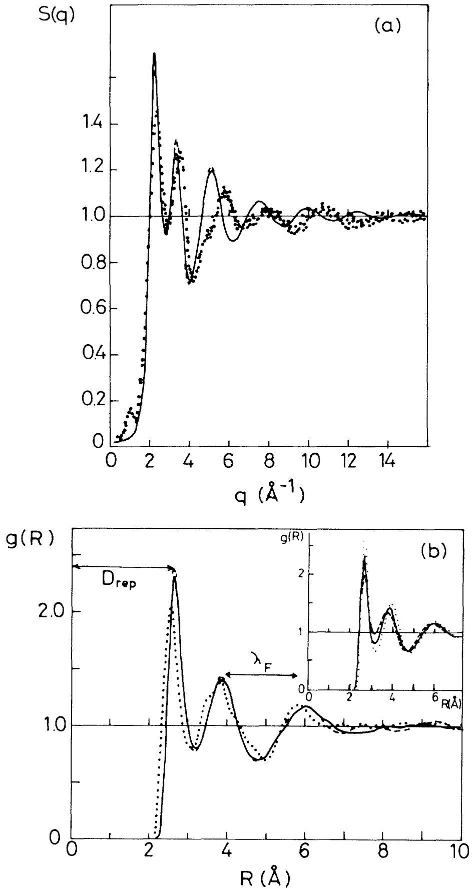

FIG. 2. (a) The static structure factor $S(q)$ and (b) the pair correlation function $g(R)$ of liquid arsenic at $T=1103$ K. The full lines show the molecular-dynamics simulations for a 864-particle ensemble, the dashed lines show the results obtained with 2048 particles in the periodically repeated cell. The dots show the neutron-diffraction data of Bellisent *et al.* (Ref. 1). The inset in (b) shows that the result is stable with respect to small changes in the potential parameter R_c (····, $R_c/R_s=0.53$; ——, $R_c/R_s=0.51$; ---, $R_c/R_s=0.49$).

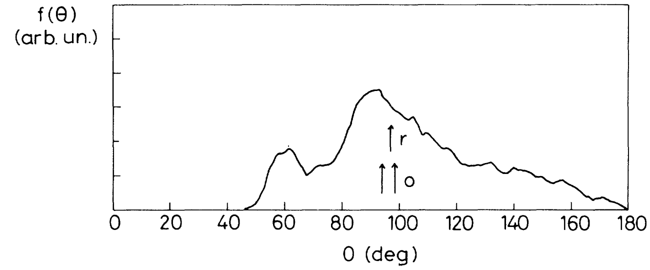

FIG. 3. The bond-angle distribution function $f(\theta)$ for liquid As. The vertical arrows mark the bond angles in the crystalline rhombohedral (r) and orthorhombic (o) phases.

at $R_{\text{cut}}=10.40$ Å for the small ensemble and at $R_{\text{cut}}=13.86$ Å for the large ensemble, i.e., at a distance corresponding roughly to 38% of the edge of the cubic cell, precisely at a point where the two-body force vanishes. With this choice of the cutoff each atom interacts with about 200 neighbors in the small cell and with 500 neighbors in the large cell. At the level of the pair and bond-angle distributions no significant size effects could be detected.

The static structure factor $S(q)$ and the pair correlation function $g(R)$ are shown in Fig. 2. Peak positions and coordination numbers [calculated by fitting Gaussians to the first two peaks in $g(R)$] are given in Table I, together with the results derived from the experimental data. The inset in Fig. 2(b) shows that the calculated correlation function is stable with respect to small variations of the potential parameter R_c. Considering the fact that only a minimal adjustment of the pseudopotential relative to the values fitted to electronic data was permitted, the agreement with experiment is certainly very good. That the calculated structure is very realistic is confirmed by the distribution of the bond angles (Fig. 3). The bond angles are distributed around $\theta\approx 94°$, with small subsidiary maxima at $\theta\approx 60°$ and 140°. From the positions of the peaks in the measured $g(R)$, the maximum in $f(\theta)$ is expected at $\theta\approx 97°$, and from the widths of the peaks at half maximum we estimate that the angles formed by nearest-neighbor bonds are distributed between $\theta\approx 65°$ and 130°. Both the experimental and the theoretical value for the bond angle are very close to the rhombohedral value $\theta=97.2°$. The appearance of the subsidiary maxima in $f(\theta)$ shows that in liquid As the dominant type of "defects" (relative to an ideal continuous network with nearly ideal rhombohedral bond angles) are tetrahedral groupings of four As atoms such as they exist in gaseous As.

We find that the structure of liquid As conforms rather well with the simple argument given above: The first peak in $g(R)$ at $R_1=2.61$ Å lies in the inflection of the repulsive part of $\Phi(R)$, very close to D_{rep}. The second and the third peaks at $R_2=3.83$ Å and $R_3=5.96$ Å fall into the minima of the Friedel oscillations; they are quite far from the positions expected for a random packing of atoms with diameter D_{rep}. At larger distances, the structure in $g(R)$ is destroyed by the interference between the geometrical packing requirements and the modulation of the interatomic distances by the Friedel oscillations. The position of the first peak in the static structure factor is determined by the diameter of the repulsive core, $Q_1=2.40\ \text{Å}^{-1}\approx 2\pi/D_{\text{rep}}=2.51\ \text{Å}^{-1}$. The second peak is determined by the Fermi momentum, $Q_2=3.50\ \text{Å}^{-1}\approx 2k_F=3.68\ \text{Å}^{-1}$. This confirms that the complex structure of liquid As arises from the interplay of two characteristic distances, the diameter D_{rep} of the repulsive core and the Friedel wavelength λ_F of the oscillatory part of the pair potential.

Preliminary results show that at very high temperatures, the modulation of the structure by the Friedel oscillation is smeared out and the structure of liquid As resembles that of liquid Sb or Bi.

Finally, I want to comment on the relation between the Peierls-distortion argument brought forward by Bellisent *et al.*[1] and my picture of a modulation of the random packing of atoms by the Friedel oscillations. First it should be noted that my argument is not based on pair interactions alone. The contribution of the volume energy to the internal pressure is essential for placing the nearest-neighbor distance in a close-packed arrangement on the repulsive hump of the pair interactions. Hence it is crucial to the argument. Second, I note that for a periodic structure the splitting of the nearest-neighbor shell caused by the form of the pair potential leads to a period doubling analogous to that caused by a Peierls distortion. The question is if we also find the gap or minimum in the electronic density of states at the Fermi level characteristic for the Peierls mechanism. My argument is not immediately concerned with the electronic density of states. However, I have been able to show[8,13] that a sharp peak in the static structure factor at Q_p induces a minimum in the electronic density of states of the liquid at $(Q_p/2)^2$ above the bottom of the band. From the positions of the peaks in the $S(q)$ of liquid As, one would expect a density-of-states minimum at about 7.4 eV below the Fermi level (this is precisely where the gap between the s band and the p band is found in crystalline and amorphous As),[14,15] and at the Fermi level itself. Preliminary calculations of the electron density of liquid As show that the expected structure does indeed exist. Thus the picture of a Friedel modulation of the structure of the liquid describes the same physical situation as the Peierls-distortion argument. The real-space argument is more general as it does not require periodicity.

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