Carbon: The Nature of the Liquid State

Giulia Galli and Richard M. Martin
Department of Physics, University of Illinois, Urbana, Illinois 61801

Roberto Car and Michele Parrinello
International School for Advanced Studies, Strada Costiera 11, 34014 Trieste, Italy
(Received 3 April 1989)

The liquid state of carbon at low pressure is investigated with a first-principles molecular-dynamics simulation. Its controversial electronic properties are elucidated in terms of density-of-states and conductivity calculations, showing that the system is a metal, in agreement with experiments reported last year. Furthermore, an accurate analysis of the atomic structure indicates that the liquid is composed of twofold, threefold, and fourfold coordinated atoms, which display different bonding properties.

PACS numbers: 61.20.Ja, 61.25.Mv, 71.25.Lf, 72.15.Cz

The carbon phase diagram has been investigated in different fields of science, such as condensed matter physics,[1] astrophysics,[2] and geology[3,4] for nearly a century. Nevertheless, outstanding questions concerning its properties at high temperature, especially the liquid state (*l*-C), remain unanswered. The phase diagram originally proposed by Bundy,[4(a)] and experiments of the 1960s and 1970s,[4(b)] indicate the occurrence of a triple point in the high-temperature, low-pressure regime, suggesting that *l*-C does not exist at atmospheric pressure. However, recent reports[5–7] of graphite surface melting by high-energy laser pulses show that there is at least a small range of T for which *l*-C may be obtained at low P and, in particular, that carbon undergoes a solid-liquid phase transition[7(a)] at $T = 4450$ K and $P \leq 4$ bars.

There have been no measurements which determine directly the atomic properties of the liquid, but only indications of structural transformations as graphite or diamond melt.[3(b),5–7] Speculations[3(c),8] based on thermodynamics data depict *l*-C in the low-P regime as a mixture of C_n chains, similar to those found in carbon vapors. According to spectroscopic investigations at high T, several authors[9] have proposed that, at $T \gtrsim 2600$ K, graphite transforms to a so-called "carbyne" solid, composed of chainlike structures containing triple bonds. If so, this would support the picture that *l*-C is low coordinated, with *sp*-bonded carbon atoms. However, the existence of the carbyne region of the phase diagram has been often questioned in the literature[10] of the last decade.

The electronic properties of *l*-C have also been the subject of many controversies. One proposal that *l*-C is a semi-insulator at low P has been supported by picosecond reflectivity studies.[6] However, more recent optical and dc conductivity measurements[7(a)] lead to the conclusion that *l*-C is metallic, with a low, nearly temperature-independent, electrical resistivity ($\rho = 30$–70 $\mu\Omega$ cm). In other experiments, pulse heating of glassy carbon under pressure (4 kbar) has been shown[11] to yield a melt with a roughly constant ρ around 1 mΩ cm, for T up to 6000 K.

In this Letter we discuss the atomic and bonding properties of *l*-C at low pressure, as well as its electronic structure, which we have investigated with a first-principles molecular-dynamics (MD) simulation.[12] In our calculation, we have used a supercell containing 54 carbon atoms and 216 valence electrons, with fcc periodic boundary conditions. The ions and electrons have been described in the local-density approximation (LDA), within the pseudopotential framework.[13] The single-particle orbitals at the Γ point of the Brillouin zone have been expanded in plane waves with a cutoff of 32 Ry, corresponding to 12000 basis functions. Time evolution has been simulated with a time step of 10^{-16} sec and a fictitious mass parameter for the electronic degrees of freedom of 200 a.u.

Melting and the equilibration of the system at high temperature have been achieved with a constant-volume–constant-temperature (CVT) MD technique, originally proposed by Nosé[14] for systems described by classical potentials. To this end, a Lagrangian appropriate for an interacting system of electrons and ions, with the ions in thermal equilibrium with an external heat reservoir of fixed temperature, has been defined and equations of motion consistently derived. This procedure is different from that used before in first-principles MD,[15,16] including our previous work on amorphous carbon (*a*-C),[15] and is necessary to overcome the problem of energy transfer to the electronic degrees of freedom, which may occur in the simulation of metallic systems with the original method of Ref. 12. Within the present scheme, a correct computation of time averages in the canonical ensemble is accomplished, if quenches of the electronic coordinates to their Born-Oppenheimer surface are periodically performed. Statistical averages for the liquid state have been computed as time averages over about 10000 steps (corresponding to 1 psec); the results obtained from averaging over a shorter interval

(6500 steps) have been found to be nearly identical, thus confirming that a reliable equilibration of the system had been achieved.

The liquid has been generated by heating up an a-C structure, previously obtained[15] with *ab initio* constant-volume MD runs, at a fixed macroscopic density (ρ_d) of 2 $\mathrm{g\,cm^{-3}}$. According to the (ρ_d, T) diagram proposed in Ref. 8, this is possibly a reliable density for the liquid at low P.[17] As the initial a-C structure is heated up in our procedure, changes in both the structure and electronic properties are first observed at $T = 2500$–3000 K. The main characteristic of this transformation concerns the appearance of twofold coordinated sites (their concentration increasing almost continuously with increasing T up to 5000 K), accompanied by the onset of metallic features, as a result of π and π^* states merging. At temperatures around 4000 K, the system begins showing a diffusive behavior, possibly to indicate that a melting transition is taking place. Above 4500 K, the continuous increase of the atomic mean-square displacement as a function of simulation time shows that a liquid state has been generated. Temporal averages to compute electronic and atomic properties have been taken at $T = 5000$ K: At this temperature the self-diffusion coefficient of the system is calculated to be $2.4\times10^{-4}\ \mathrm{cm^2 sec^{-1}}$.

The liquid state at 5000 K is composed of 32% twofold, 52% threefold, and the remaining fourfold coordinated atoms; the total coordination of the system is 2.9, compared, e.g., with that of 3.2 computed for a-C. As indicated by the peak positions of the radial distribution function $g(r)$, shown in Fig. 1(a), the average first- and second-neighbor distances in l-C are found to be 2.72 and 5.18 a.u., respectively. The analysis of the partial correlation functions $g_{ii}(r)$, and $g_{ij}(r)$, and of the angular distributions A_{ii} [$i,j = 2,3,4$], displayed in Figs. 1(b)–1(d), provides a description of the differently coordinated sites present in the system. g_{44} and A_{44} indicate that fourfold coordinated atoms have a wide range of preferred bond lengths, spread over an interval of about 1 a.u., as well as of bond angles, ranging from 90° to 115°. In particular, each of these atoms are found to have four bonds of different length, quite unlike an sp^2 diamond site. The threefold coordinated atoms may be regarded as distorted graphitic sp^2 units: The first maximum of g_{33} is indeed at a distance slightly larger (4%) than the computed[18] bond length for graphite at $T=0$, and the peak of A_{33} lies between 110° and 125°. When linked to each other, twofold sites have the shortest bond lengths, suggesting that they are mostly triple bonded. Their average bond distance of 2.55 a.u. is a few percent larger than that obtained[18] for C_2 (2.43 a.u.) and C_3 (2.50 a.u.) molecules. Their angular distribution, A_{22}, shows that angles between 180° and 110° are almost equiprobable, whereas those smaller than 100° are very unlikely. This is consistent with the small bending frequencies[19] found for C_3 and C_4 linear clusters. The ratio $\int dr\, g_{23} / \int dr\, g_{24} = 3.0$ (where the integrals are extended from zero up to the first minimum of the correlation functions) indicates that twofold sites are preferably connected to threefold rather than fourfold ones, and the peak of g_{23}, between 2.55 and 2.80 a.u., suggests a possible alternation of sp-sp^2 bonds, differing in their proportion of π character. We finally notice that the second peak of $g(r)$ arises mainly from the second-neighbor distribution of threefold coordinated atoms.

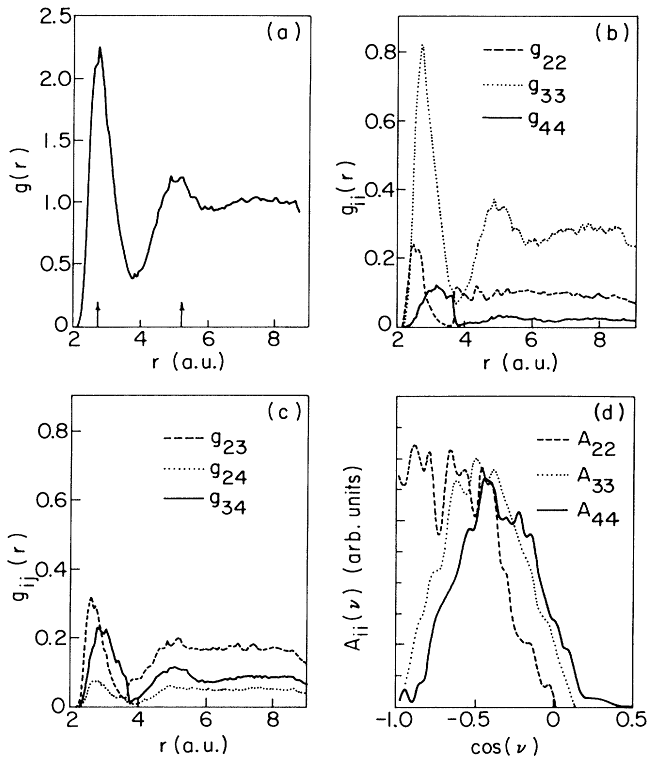

FIG. 1. Radial distribution functions (a) $g(r)$, (b) $g_{ii}(r)$, and (c) $g_{ij}(r)$, and (d) angular distribution $A_{ii}(\nu)$. $g(r) = \sum_i g_{ii} + 2\sum_{i\neq j} g_{ij}$, $i,j = 2,3,4$. (a) Arrows indicate first- and second-nearest-neighbor distances; (d) ν indicates bond angles.

From a ring statistic analysis we find that N-fold rings with N larger than 9, i.e., chainlike structures, are the great majority in the liquid, although fivefold, sixfold, and sevenfold membered units are also present; in contrast, the low-T (300 K) a-C was found to have essentially no rings with N larger than seven.[15]

The computed electronic density of states $N(E)$, displayed in Fig. 2(a), shows that l-C at low P is a metal, in agreement with reflectivity and resistivity measurements reported last year,[7(a)] and in apparent disagreement with the conclusions of earlier[6(a)] reflectivity studies.[20] The average participation ratio[21]

$$p(\epsilon) = \frac{1}{V} \frac{\sum_i p_i \delta(\epsilon - \epsilon_i)}{\sum_i \delta(\epsilon - \epsilon_i)}$$

{where $p_i = [\int dr\, |\psi_i(r)|^4]^{-1}$ and ψ_i are single-particle

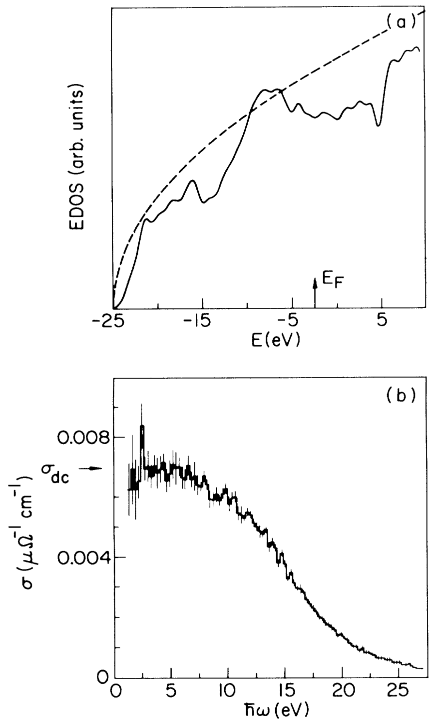

FIG. 2. (a) Electronic density of states and (b) electrical conductivity σ, computed as averages over ten atomic configurations; these have been chosen among the total number generated in our computed simulation, one about every 1000 steps. The accuracy has been checked by computing the density of occupied states using all 10000 configurations, which turns out to be nearly identical to that shown here. Note the similarity to the free-electron density of states, shown by the dashed line in (a). The extrapolated conductivity at zero $[\sigma(\omega \rightarrow 0)]$ gives a dc value (σ_{dc}) of about 0.007 $\mu\Omega^{-1}\text{cm}^{-1}$.

wave functions normalized in the volume V, with corresponding eigenvalues $\epsilon_i\}$ is found to have values between 0.06 and 0.09 for all energies ϵ, indicating that no mobility edges are revealed in our calculation. Figure 2(b) shows the electrical conductivity (σ) as a function of frequency (ω), computed from the following formula:[21]

$$\sigma = \frac{2\pi\hbar^2 e^2}{3m^2 V\omega} \sum_{i,i'} (f_{i'} - f_i) |M_{i,i'}|^2 \delta(\epsilon_{i'} - \epsilon_i - \hbar\omega) , \quad (1)$$

where $|M_{i,i'}|$ is the momentum-operator matrix element between states i' and i, whose occupation numbers are $f_{i'}$ and f_i. In the range $\hbar\omega \leq 12$–13 eV, σ can be approximated by a Drude-type function, whereas its falloff at higher frequencies is much more rapid, mainly because of the width of the conduction band considered in our calculation. From the limit of Eq. (1) for $\omega \rightarrow 0$, an estimate of the dc electrical conductivity (σ_{dc}) and of the resistivity ($\rho = 1/\sigma_{dc}$) of the system can be extracted. The main contribution to σ_{dc} comes from electrons with energies close to the Fermi level (E_F). Indeed, the results obtained from Eq. (1) and from the approximate expression[22]

$$\sigma_{dc} = \frac{2\pi\hbar^3 e^2}{m^2} a [N(E_F)]^2 ,$$

a being the average nearest-neighbor distance, agree within 10%. The computed[23] value of ρ is 140 ± 28 $\mu\Omega$ cm, larger than that measured by Heremans *et al.*:[7(a)] $\rho = 30$–70 $\mu\Omega$ cm, but much smaller than the value reported in Ref. 11 ($\rho = 1000$ $\mu\Omega$ cm). Uncertainties upon the calculated resistivity are introduced by finite-size effects and inaccuracies can possibly derive from the LDA of density-functional theory used in our calculation; but other reasons may be responsible for the discrepancy with experiment. The macroscopic density of the liquid obtained in Ref. 7(a) is not known, neither is the extent of justification of the assumption of the authors of no volume change as graphite fibers are melted. (Shaner,[11] for example, reported a 100% expansion of highly disordered graphite, upon melting). Furthermore, the comparison between the data of Refs. 7(a) and 11 suggests that the resistivity of *l*-C might be significantly dependent upon pressure.

In summary, we have presented a detailed analysis of the electronic and structural properties of liquid carbon at low pressure, showing that the system is a metal composed of differently coordinated atoms (twofold, threefold, and fourfold), which display a variety of bonds, from single to triple. Work in progress includes investigation of the dependence upon pressure and temperature of the properties of the liquid, as well as of the slope of the solid-liquid phase boundary.

This work has been supported by the NSF Grant No. DMR86-12860 and the Scuola Internazionale Superiore di Studi Avanzati–Centro Di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale collaborative project (under the sponsorship of the Italian Ministry for Public Education). Part of the computational work has been done at the National Center for Supercomputing Applications. We benefited from many useful discussions with P. Ballone.

[1]For a review, see, e.g., F. P. Bundy, Physica (Amsterdam) **156A**, 169 (1989).

[2]M. Ross, Nature (London) **292**, 435 (1981).

[3](a) J. S. Dickey, W. A. Bassett, J. M. Bird, and M. S. Weathers, Geology **11**, 219 (1983); (b) M. S. Weathers and W. A. Bassett, Phys. Chem. Miner. **15**, 105 (1987); (c) D. A. Young and R. Groover, in *Shock Waves in Condensed Matter,* edited by S. C. Schmidt and M. C. Holmes (Elsevier, New York, 1988), p. 131.

[4](a) F. P. Bundy, J. Chem. Phys. **38**, 631 (1963); (b) J. Geophys. Res. **85**, 6930 (1980).

[5]T. Venkatesan, D. C. Jacobson, J. M. Gibson, B. S. Elman, G. Braunstein, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. Lett. **53**, 360 (1984).

[6](a) A. M. Malvezzi, N. Bloembergen, and C. Y. Huang, Phys. Rev. Lett. **57**, 146 (1986); (b) E. A. Chauchard, C. E.

Lee, and C. Y. Huang, Appl. Phys. Lett. **50**, 812 (1987).

[7](a) J. Heremans, C. H. Olk, G. L. Eesley, J. Steinbeck, and G. Dresselhaus, Phys. Rev. Lett. **60**, 453 (1988), and references therein; (b) J. Steinbeck, G. Braunstein, M. S. Dresselhaus, T. Venkatesan, and D. C. Jacobson, J. Appl. Phys. **58**, 4374 (1985); **64**, 1802 (1988).

[8]H. R. Leider, O. H. Krikorian, and D. A. Young, Carbon **11**, 555 (1973).

[9]A. G. Whittaker, Nature (London) **276**, 695 (1978); Science **200**, 763 (1978); **229**, 485 (1985); R. B. Heimann, J. Kleinman, and N. M. Salansky, Nature (London) **306**, 164 (1983).

[10]P. P. K. Smith and P. R. Buseck, Science **216**, 985 (1982); **229**, 487 (1985).

[11]J. W. Shaner, Bull. Am. Phys. Soc. **32**, 607 (1987).

[12]R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[13]We have used a fully nonlocal pseudopotential of the form suggested by L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982), with *s*-only nonlocality.

[14]S. Nosé, Mol. Phys. **52**, 255 (1984); J. Chem. Phys. **81**, 511 (1984).

[15]G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. Lett. **62**, 555 (1989); in Proceedings of the Conference on Atomistic Modeling: Beyond Pair Potentials (Plenum, New York, to be published).

[16]R. Car and M. Parrinello, Phys. Rev. Lett. **60**, 204 (1988).

[17]An extrapolation from thermodynamical data and the somewhat arbitrary assumption of a volume expansion of 20% for graphite melting gives an estimate of $\rho_d = 1.6$ g cm^{-3} for *l*-C close to the melting point (Ref. 7). On the other hand, the hypothesis that carbon behavior upon melting parallels that of the other group-IV elements would indicate a density larger than that of graphite in the liquid phase. A value of $\rho = 2.7$ g cm^{-3}, for example, has been proposed in the literature [Ref. 7(b)].

[18]The bond lengths in the crystal structures and for the molecules have been obtained with the same pseudopotential and kinetic energy cutoff as those adopted for *l*-C.

[19]See, e.g., J. R. Chelikowsky and M. Y. Chou, Phys. Rev. B **37**, 6504 (1988), and references therein.

[20]Discussion of the possible differences in the experimental measurements of Refs. 6(a) and 7(a) are given in Refs. 1 and 7(a).

[21]See, e.g., D. J. Thouless, Phys. Rep. **13**, 93 (1974).

[22]See, e.g., N. F. Mott, Philos. Mag. **19**, 30 (1969).

[23]The occupation numbers (f_i) entering formula (1) have been treated as Fermi-Dirac distributions. If we consider the f_i the electrons would have at $T = 0$, the computed value for ρ turns out to be 100 ± 20 $\mu\Omega$ cm.