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Relationship between structure and conductivity in liquid carbon

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We have performed extensive simulations of liquid carbon at various densities, using a highly transferable tight-binding model of carbon. In contrast to some recent theoretical suggestions, we show that the low-density liquid is primarily twofold bonded. Such a bonding arrangement leads to a low conductivity, compared to the primarily sp^2 bonded liquid that occurs at intermediate densities. This is in qualitative agreement with experiments that show that for pressures less than 100 kbar, the conductivity of liquid carbon increases with density. At high densities, the liquid is mainly tetrahedrally bonded, and the conductivity then decreases with increasing density.

I. INTRODUCTION

The phase diagram of carbon has been widely studied due to its relevance to geophysics and astrophysics, as well as diverse industrial applications.[1–3] Also, the variety of forms of carbon has led to wide speculations on new structures and applications. The possibilities are numerous, due to the fact that carbon will readily form twofold, threefold, and fourfold covalently bonded structures. Thus, at atmospheric pressures, there are numerous observed stable (or metastable) solid phases, including diamond, graphite, and solid phases of C_{60} and C_{70}. Amorphous phases with a large range of densities are also stable at atmospheric pressure, with different bonding distributions characterizing the different densities.

The strength of the covalent bonds in carbon causes graphite and diamond to dominate the equilibrium phase diagram over a wide range of temperatures and pressures.[1–3] Both structures are stable up to temperatures above $T = 4000$ K, and diamond is stable at pressures exceeding 2 Mbar. Many aspects of the phase diagram are not well understood, outside of the regions where graphite and diamond are the thermodynamically stable phases, due to the extremely high temperatures or pressures needed to form other phases.

In particular, there has been much speculation concerning the liquid phases.[1–9] Little is known about the phase diagram at the temperatures required to form liquid carbon, especially at pressures above the graphite-diamond-liquid triple point. The melting line of graphite has been explored,[10,11] and is interesting due to the fact that the slope of the melting line, dP/dT, changes sign at a pressure of about $P = 50$ kbar. This suggests some change in behavior in the liquid phase, including the possibility of a structural transition between different liquid phases.[4,9] (Such transitions have been observed in Te,[12] Bi,[13] and K.[14])

In this paper, we focus on the structure of liquid carbon, and in particular the relationship between the bonding and the conductivity. There have been a number of experiments on the conductivity of liquid carbon,[10,11,15–17] but the values obtained are quite disparate, and there is no consensus on whether or not liquid carbon (at low pressure) is metallic. (We will not review these experiments here, but refer the reader to the review articles, Refs. 1–3, as well as the discussions in Refs. 7, 9, and 17.) We are particularly interested in experiments by Bundy,[10] who demonstrated that at low pressures (< 100 kbar), the conductivity of liquid carbon increases with increasing pressure. Bundy's qualitative results for the pressure dependence of the conductivity are generally accepted, and have been supported by more recent work.[17]

It was initially believed that at low pressures, carbon would form a dense, metallic liquid phase similar to that of liquid Si.[1] This would account for the results above: as the pressure increases, the coordination increases, and the metallic conductivity rises. This would also be consistent with a negative slope of the diamond melting line. Recent work[2,6] suggests that this is not the case, but rather that the liquid phase is less dense than diamond, giving the diamond melting curve a positive slope. First-principles simulations[6] have indicated that tetrahedral bonding persists at pressures as high as 0.6 Mbar, suggesting that for $P \lesssim 1$ Mbar, the slope dP/dT is positive.

There have been various theoretical arguments relating the structure of the liquid with the conductivity. Ferraz and March[4] speculated that Bundy's results were due to a pressure-induced insulator-metal transition that occurred as the liquid transformed from an insulating twofold-bonded liquid to a metallic threefold-bonded liquid. More recently, van Thiel and Ree[9] also suggested that a structural transition occurs between liquid phases, but that the low-density, low-conductivity liquid was primarily graphitic, and that the high-density, more conducting liquid was tetrahedrally bonded.

These differing arguments strongly emphasize the importance of determining (1) the structure of liquid carbon as a function of pressure (or density) and (2) the relationship between the structure and the conductivity of liquid carbon. We examine both questions in this paper,

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through tight-binding (TB) simulations that provide information about the electronic states of the liquid. This allows us to directly examine both the structure and the conductivity of liquid carbon, and to compare with experiments on the pressure dependence of the conductivity.

First-principles simulations of liquid carbon have suggested that at low densities (2 g/cm^3), the atoms are mostly three-fold coordinated,[5,7] but with a significant fraction ($\sim$ 30%) of twofold coordinated atoms, as well as $\sim$ 20% fourfold coordinated atoms. This could support the idea of a transition between a threefold and fourfold coordinated liquid.[9] Tight-binding simulations,[8] however, have indicated that the low-density liquid is primarily twofold bonded, in accordance with the suggestion of Ferraz and March.[4] However, there is a finite electron density of states at the Fermi level, even at very low densities, indicating that the liquid is not an insulator.

Our simulations show that at a density of $\rho = 1.5$ g/cm^3 (about 2/3 that of graphite), the conductivity is $\sim$ 0.002 $(\mu\Omega\,\mathrm{cm})^{-1}$, with $\sim$ 55% of the atoms being twofold coordinated, and that the conductivity increases with increasing density, corresponding to an increase in sp^2-type bonding. Once the number of threefold bonded atoms saturate, and the number of fourfold atoms begins to become significant, the conductivity decreases with increasing density. This occurs when the density of the liquid is close to the zero-pressure diamond density. (At sufficiently high density, we will again expect the conductivity to rise, as the liquid reaches a highly coordinated metallic phase.) We observe no evidence of a transition between liquids with different coordinations over the range of densities that we examined, although we cannot rule out this possibility at low densities.

II. TIGHT-BINDING MODEL AND CALCULATION TECHNIQUES

A. Simulation techniques

Tight-binding simulations are now a well-established technique for modeling covalently bonded materials.[18] One tight-binding model for carbon has been especially successful,[19] and has been applied to carbon fullerenes,[20] amorphous carbon,[21] as well as liquid carbon.[8] This model is described by the following Hamiltonian:

$$H(\{\mathbf{r}_i\}) = \sum_i \frac{\mathbf{P}_i^2}{2m} + \sum_n 2 f_n \langle \psi_n | H_{\mathrm{TB}}(\{\mathbf{r}_i\}) | \psi_n \rangle + E_{\mathrm{rep}}(\{\mathbf{r}_i\}) + \sum_i \frac{1}{2} U (q_i - q_i^0)^2. \quad (1)$$

In this equation, the first term is the kinetic energy, the second term is that band-structure energy (with the factor of 2 due to the spin degeneracy), and the third term is the repulsive ion-ion interaction. The last term is a Hubbard-like term that helps maintain local charge neutrality, adding energy whenever the number of electrons on an ion q_i differs from $q_i^0 = 4$. Using this term will improve the accuracy of the model, but requires that the charge distribution be determined self-consistently. For our simulations, this requires about three times as much computational effort. Most of the work presented in this paper uses $U = 0$, so that the last term may be ignored. However, in Sec. III, we will examine how including this term affects our conclusions.

Note that in the band energy term, we have included a Fermi-Dirac occupation factor, defined by

$$f_n = \frac{1}{\exp\left[(\epsilon_n - \mu)/k_B T_{\mathrm{el}}\right] + 1}, \quad (2)$$

where ϵ_n is the energy of the eigenstate, T_{el} is the electronic temperature (chosen to be equal to the ionic temperature), and μ is the chemical potential, determined by the requirement that the number of electrons be conserved. Including this occupation factor is important, as the temperature involved in our simulations ($T \gtrsim 6000$ K) is not negligible compared to the Fermi temperature. With the occupation term, the contribution to the forces from the band structure is given by

$$\mathbf{F}_i^{\mathrm{band}} = -2 \sum_n f_n \langle \psi_n | \nabla H_{\mathrm{TB}} | \psi_n \rangle - 2 \sum_n \epsilon_n \frac{\partial f_n}{\partial(\epsilon_n - \mu)} \nabla(\epsilon_n - \mu). \quad (3)$$

The last term is difficult to calculate,[22] so it is convenient to introduce the Mermin free energy, given by

$$\Omega = E_{\mathrm{total}} - T_{\mathrm{el}} S_{\mathrm{el}}, \quad (4)$$

where the electronic entropy is given by

$$S_{\mathrm{el}} = -2 k_B \sum_n \left[f_n \ln f_n + (1 - f_n) \ln(1 - f_n) \right]. \quad (5)$$

It has been shown both analytically[20] and numerically[23] that if the last term of Eq. (3) is ignored, then the Mermin free energy will be conserved, and the effects of the electronic entropy are included. Therefore, we have ignored this term, and also checked that this free energy was conserved during the simulations.

For the results shown below, we used simulations of 216 atoms. We have also performed simulations of 64 atoms, both to test the conductivity calculations and to make some estimate of the effect of system size. We found no significant difference between the $N = 64$ simulations and the $N = 216$ simulations, within the scatter of our data. Both the structural trends and the trends in the conductivity were quantitatively similar. There was somewhat less scatter in the results for the larger system, as expected. As the system size is increased, we believe that there might be some small change in the quantitative results, but that this change would be difficult to detect, given the scatter in our results, and would not affect the qualitative behavior of the structural or electronic properties as a function of pressure. We note that at the highest densities, the pair-correlation function shows structure out to distances of approximately 4 Å (see Fig. 3). This indicates that the results for structural properties will be sensitive to the size of the simulation box if the box size is less than 8 Å. For a density of 4.2 g/cm^3, the box size was 10.1 Å.

If there is a transition at some pressure, a small system size (as well as short simulation times) would tend to cause large hysteresis loops as the pressure was changed. To avoid this possibility, the simulations at different densities were equilibrated independently of each other, rather than simply increasing the density from one simulation to the next. For each density, the liquid phase was formed by melting the liquid at $T = 10\,000$ K, then cooling down to the desired temperature. The system was allowed to equilibrate at this temperature for a minimum of 2000 time steps, with a time step of $\Delta t = 0.353$ fs. The high velocity of the atoms made this short time step necessary, in order to accurately predict the trajectory. The calculated properties were averaged over 1000 time steps, with the conductivity being calculated every 50 time steps, as described below. For each simulation, we verified that diffusive behavior occurred, although for the simulation times used here, we were not able to accurately calculate diffusion constants.

B. Calculation of conductivity

We are very interested in calculating the trends of the conductivity using the model discussed above. We only expect qualitative results, given that the model was primarily developed to produce accurate structural information. The electronic structure for different structures only qualitatively agrees with more exact calculations, especially for energies more than a few eV above the Fermi level. We believe, however, that the results presented in Sec. III have the correct qualitative behavior.

In general, the conductivity of a system may be calculated using the Kubo-Greenwood formula:

$$\sigma(\omega) = \frac{2\pi\hbar^2 e^2}{3m^2 V\omega} \sum_{i,j} (f_j - f_i) |\mathbf{M}_{ij}|^2 \delta(\epsilon_j - \epsilon_i - \hbar\omega), \quad (6)$$

where $\mathbf{M}_{ij}$ is the momentum matrix element between the eigenstates i and j. The problem with this approach is that for tight-binding models, the wave functions are not known, and therefore the momentum matrix elements may not be calculated directly. However, Harrison[24] has shown that the matrix element connecting the atomic state α on atom i to the atomic state β on atom j may be approximated by

$$\langle i\alpha|\mathbf{P}|j\beta\rangle = \frac{im}{\hbar}(\mathbf{r}_i - \mathbf{r}_j) E^{ij}_{\alpha\beta}, \quad (7)$$

where $E^{ij}_{\alpha\beta}$ is the tight-binding matrix element connecting the two states. This has been made more rigorous for periodic systems by making use of a reciprocal space approach, using the operator identity[25,26]

$$\mathbf{P} = \frac{m}{\hbar}\frac{\partial H(\mathbf{k})}{\partial \mathbf{k}}. \quad (8)$$

Using Eq. (7), we may directly apply the Kubo-Greenwood formula. The dc conductivity may be calculated by taking the $\omega \to 0$ limit of Eq. (6).

We may also estimate the dc conductivity using the density of states at the Fermi surface from the approximation[5,27]

$$\sigma_{\rm dc} = \frac{2\pi\hbar e^2}{m^2} a N^2(E_F), \quad (9)$$

where $N(E_F)$ is the density of states at the Fermi surface, and a is a characteristic neighbor distance. This approach may not be very accurate, as it will not have information concerning localization or other effects from the disordered nature of the systems we are considering.

By using two different approaches for calculating the dc conductivity, we have a check on the different approximations being made in Eqs. (6) and (9). In general, we find that the different calculations produce similar results, both qualitatively and quantitatively. This will be discussed further in the next section.

III. SIMULATION RESULTS

A. Structure of liquid carbon

Our primary interest is in the structure of liquid carbon at different densities. The simplest quantitative measure of the structure of liquid carbon is the distribution of the number of neighbors within a certain distance. We choose this distance to be at the first minimum of the pair-correlation function $g(r)$ (see Fig. 3). By examining the percentage of twofold, threefold, and fourfold bonded atoms, averaged over all atoms and all configurations, we obtain information concerning the types of bonding in the liquid phase.

The coordination distribution for liquid carbon at $T \approx 6000$ K is shown in the top part of Fig. 1, for densities ranging from $\rho = 1.5$ g/cm^3 to $\rho = 4.2$ g/cm^3. At the lowest densities, the system is primarily twofold bonded, with long chains of atoms running through the system. The number of twofold and threefold bonded atoms becomes equal at a density near $\rho \approx 2.2$ g/cm^3, close to the density of graphite at atmospheric pressure (2.27 g/cm^3). The atoms remain primarily threefold coordinated until a density of $\rho \approx 3.6$ g/cm^3, approximately the density of diamond (3.52 g/cm^3). Above this density, the atoms are primarily tetrahedrally bonded (for the densities examined in this work).

Most of the results shown in Fig. 1 were performed without the Hubbard term in Eq. (1). However, without this term, there is significant charge transfer that occurs, especially at low densities where the system is primarily composed of linear chains of carbon atoms, with a high density of dangling bonds. We expect that adding the Hubbard term will minimize the charge transfer associated with these bonds.[19] In "snapshot" pictures of instantaneous atomic positions, it is not uncommon (at the lowest density) to see atoms that have charge transfers of ±0.3 electron. At higher densities, the charge

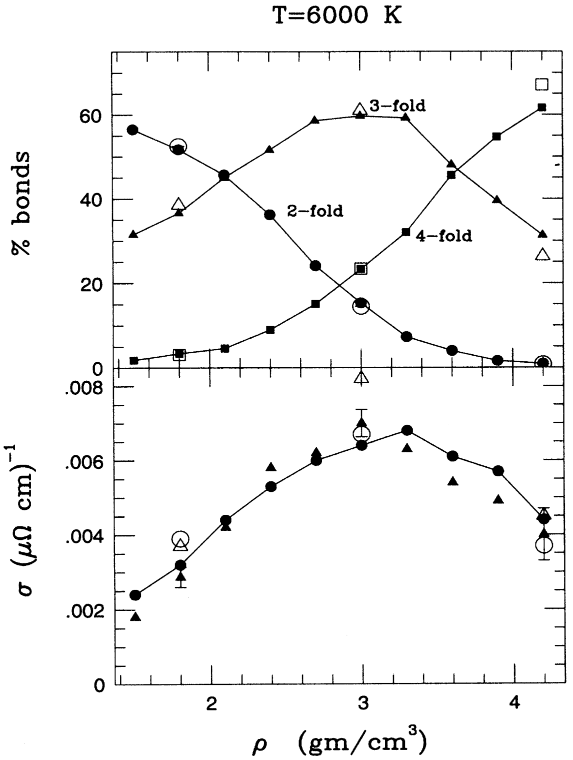

FIG. 1. The top part of the figure shows the percentage of twofold, threefold, and fourfold bonded atoms as a function of density, for temperatures near $T = 6000$ K. Results for simulations using the Hubbard term with $U = 4.0$ eV are shown with open symbols. The lower part of the figure shows the dc conductivity of liquid carbon, calculated using the Kubo-Greenwald formula (circles) and using the approximate expression of Eq. (9) (triangles). Again, the open symbols indicate results using the Hubbard term.

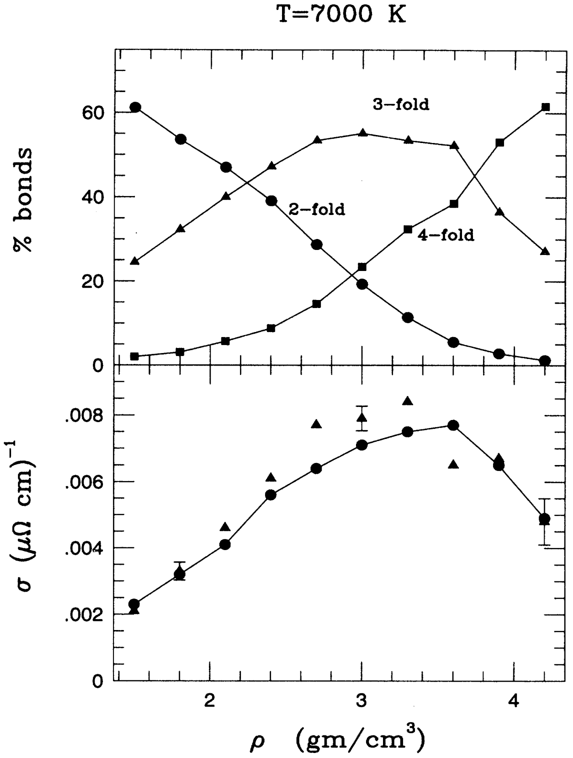

FIG. 2. As in Fig. 1, the top graph shows the coordination distribution of liquid carbon near $T = 7000$ K, and the lower part of the figure shows the dc conductivity calculated using the Kubo-Greenwald formula (circles) and using the approximate expression of Eq. (9) (triangles).

transfer is less, but still on the order of 0.1 electron.

To test the effect of the Hubbard term on the structure and on the conductivity, we performed simulations under the same conditions, but with $U = 4.0$ eV. As this calculation requires significantly more computer resources (due to the necessity of determining the charge distribution self-consistently), we only used three different densities in this calculation. The associated charge transfer was significantly decreased: only a few atoms have charge transfers greater than ±0.1 electron (again, less at the higher densities). However, the calculations of average coordination distribution and of the conductivity were not changed significantly. These results are indicated by open symbols in Fig. 1. As can be seen in the figure, these time-averaged results for both the coordination distribution and the conductivity are not significantly different than those found using $U = 0$, even at the lowest density where we expect this term to have the largest effect.

The results at higher temperatures are quite similar. The coordination distribution for $T \approx 7000$ K, shown in the top part of Fig. 2, is quite similar to that near $T = 6000$ K. A detailed comparison shows that there tends to be more twofold bonded atoms at higher temperatures, for any given density. The number of threefold bonded atoms is somewhat less at higher temperatures, for $\rho \lesssim 3.3$ g/cm^3. The density where the number of threefold coordinated atoms is at a maximum appears to be slightly higher at $T = 7000$ K, but this is a small effect.

In Fig. 3, we show the pair-correlation function $g(r)$ for a number of densities, at $T = 6000$ K. We first note that the position of the first peak r_0 is nearly independent of density, whereas for normal fluids we would expect that the position would decrease as the density was increased. This anomalous behavior is due to the balance between two competing effects. First, as in normal liquids, the increased density corresponds to higher pressure, which tends to force neighboring atoms closer together. However, for carbon, the preferred neighbor distance for sp bonding is shorter than that for sp^2 bonding, and the distance for sp^3 bonding is larger still. For the periodic structures, these distances are[19] 1.3, 1.42, and 1.55 Å, compared with a peak position of approximately $r_0 = 1.4$ Å for the liquid phases. Therefore, as the number of neighbors increases, so does the optimal near-neighbor distance. The competition between this tendency and

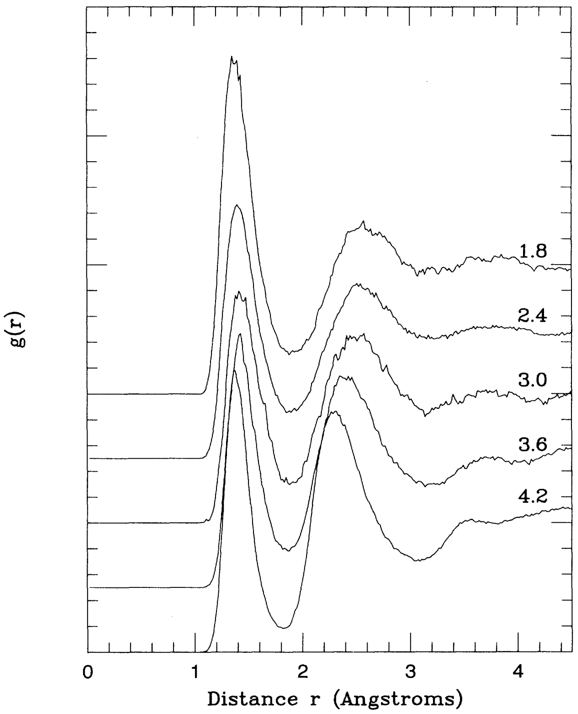

FIG. 3. The pair-correlation function $g(r)$ for a range of densities from 1.8 to 4.2 g/cm^3, at T = 6000 K. Note that the position of the first peak is nearly independent of pressure, while the second peak decreases with increasing pressure.

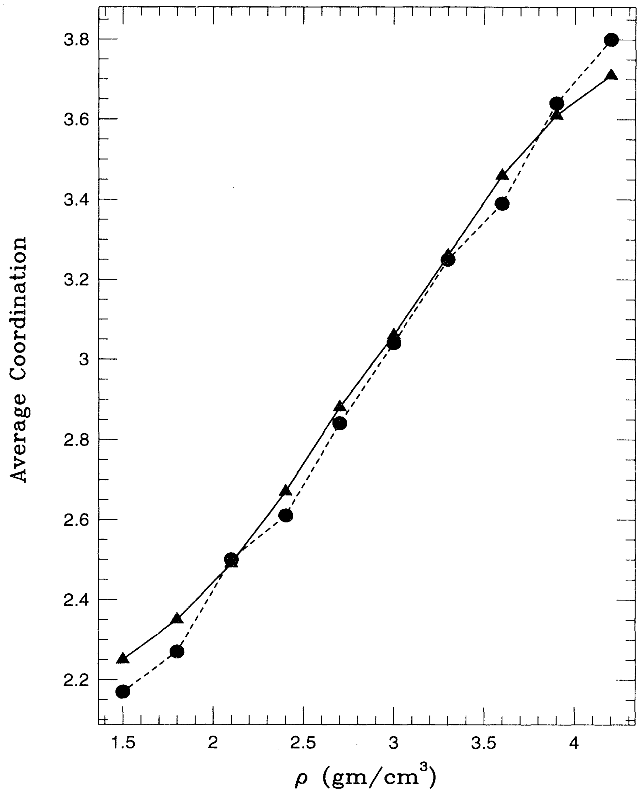

FIG. 4. The average coordination depends linearly on the density, for both T = 6000 K (solid line) and T = 7000 K. At a given density, the average coordination is nearly independent of temperature. There is no indication of any sudden changes in coordination as the density is varied.

the increasing pressure results in a peak position that is only weakly dependent on density.

The position of the second peak in Fig. 3 shows a much stronger dependence on density. This can also be understood in terms of the change in bonding. For the primarily twofold liquid, we expect that the distance between the first and second peak will be large, as the twofold bonding will prefer bond angles of nearly 180°. As the threefold bonding dominates, the second peak position shifts toward the value of $\sqrt{3}\,r_0$, which would be the position of the second nearest neighbor in graphite. Finally, at the highest densities, the second peak is close to $\sqrt{8/3}\,r_0$, corresponding to the next shell of atoms in diamond. The second peak is more pronounced at high densities, indicating that there is a reasonably well-defined bond angle.

Over this range of densities, the average coordination varies smoothly from approximately 2.2 to about 3.8, as shown in Fig. 4. The results for T = 6000 K and T = 7000 K are very close. The coordination number appears to vary linearly with density, with no indication of a sudden change in coordination or any other anomalies that could indicate a transition between differently coordinated structures. For T = 6000, there is a very slight decrease in the slope at both high and low ends of the density range. This could suggest the possibility of a transition at a lower temperature, but it is not a strong indication.

The smooth behavior does not rule out a transition, however. If there are two distinct phases present, then a change of density would correspond to altering the relative amounts of each phase while keeping the pressure fixed at the transition pressure. Therefore, if there is a transition between two different liquids, then the density (as a function of pressure) should be discontinuous at the transition pressure, for all temperatures less than the critical temperature. For higher temperatures, there will be no transition; however, near the critical temperature, we still expect that there will be a region where the density of the liquid will change rapidly with increasing pressure. This corresponds to a large compressibility, which will diverge as the critical point is approached. This is in complete analogy with the usual arguments for the liquid-vapor critical point in normal materials; indeed, we expect that it should belong to the same universality class.

With this in mind, we have examined the pressure as a function of density at both temperatures. Our results, shown in Fig. 5, indicate no region where the compressibility is large (indicated by a small slope), especially at higher densities. This suggests that there is no transi-

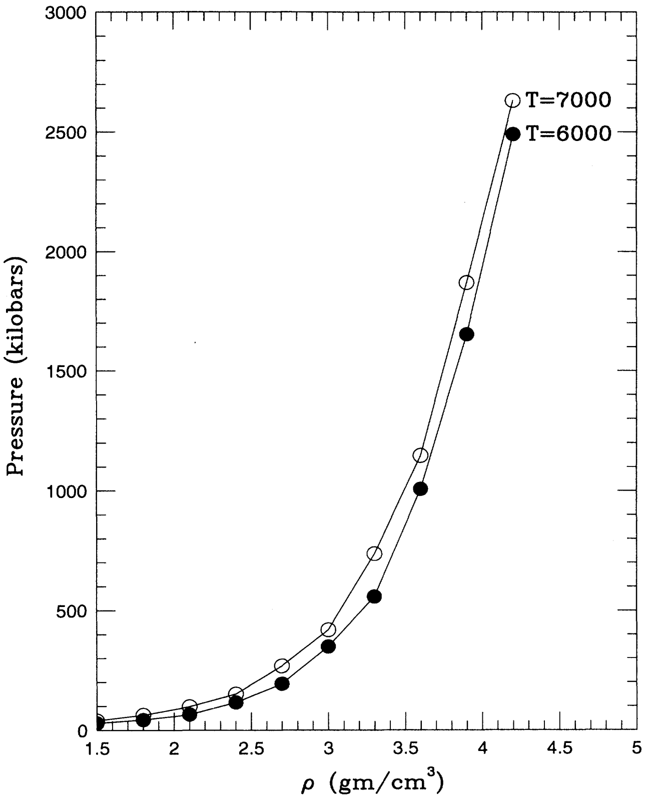

FIG. 5. This figure shows the average pressure, as a function of density. The slope is the inverse compressibility, and should be small in regions where the compressibility is large. Our results show no indication of a transition, where the pressure would be nearly independent of the density.

tion between different liquids, especially between threefold and fourfold coordinated structures. The figure is in particularly sharp contrast with the predictions of van Thiel and Ree[9] for $T = 6000\,\mathrm{K}$, as the slope of our curve continuously increases with density (see Fig. 4 of Ref. 9). The slope of the curve is smallest at very low densities, where the liquid is characterized by coupled linear chains that are easily compressed.

We note that Fig. 5 should not be taken as a quantitative prediction of the relationship between pressure and density in liquid carbon. At high densities, calculated pressures for this model are significantly higher than found using more *ab initio* techniques.[6] However, we expect that the general trends of the pressure-density relationship should be reproduced.

B. Conductivity of liquid carbon

The calculated conductivities of liquid carbon are shown in the bottom of Figs. 1 and 2. We first wish to note that the calculations based upon the Kubo-Greenwood formula, given in Eq. (6), are in good agreement with those from the density of states estimate from Eq. (9). In particular, the trend in the conductivity — peaking at intermediate densities — is clear from both calculations. The differences between the calculations are typically less than 10%. Similar agreement has been found for first-principles calculations of the conductivity of liquid carbon at low densities.[7]

We estimate the errors in the calculations of the conductivity to be on the order of $\Delta\sigma = \pm 0.0005\ (\mu\Omega\,\mathrm{cm})^{-1}$, based upon the scatter of the data shown and also upon the scatter of data for the same density and temperature. The error bars shown in Figs. 1 and 2 are larger at higher densities. We observed that at higher densities, the properties of the liquid showed some dependence upon the simulation history. We believe that there is some tendency, at the higher densities, for long-lived fluctuations to occur, resulting in long equilibration times, and possibly associated with glassy behavior. This is speculative, however, and we need to perform longer, more careful simulations to fully understand the properties at the higher densities. The error bars shown in the figure are wide enough to encompass all of the data points taken from different simulations, and are therefore reasonably conservative.

These error estimates are separate from errors that arise from the use of our tight-binding molecular dynamics model, which should only produce qualitatively correct results, due to the fact that it has been developed primarily for reproducing structural properties, not electronic properties. In order to estimate how large this systematic error may be, we compare with the first-principles simulations of Galli *et al.*[7] of liquid carbon at $T = 5000\,\mathrm{K}$ with a density of $\rho = 2.0\ \mathrm{g/cm^3}$. They find a conductivity of $0.0071\ (\mu\Omega\ \mathrm{cm})^{-1}$, significantly higher than our results for the same density. However, their bonding at that density is quite similar to the bonding we observe at $\rho = 2.4\ \mathrm{g/cm^3}$, where we calculate the conductivity to be $0.0053\ (\mu\Omega\,\mathrm{cm})^{-1}$. While the comparison is not very close, it is reasonable. As we wish to focus on qualitative results, rather than quantitative predictions, we find these calculations to be acceptable.

The most significant feature of Figs. 1 and 2 is that the trends in the conductivity closely follow the trend for the percentage of threefold bonded carbon. As the pressure increases toward $\rho \approx 3.0\ \mathrm{g/cm^3}$, the number of threefold coordinated atoms and the conductivity both rise. For higher densities, both quantities drop off rapidly. Thus, when the system is primarily twofold bonded, the system has a low conductivity, due to the low connectivity of the chains. The conductivity rises as the system becomes more threefold coordinated, analogous to the large in-plane conductivity in graphite. At high densities the conductivity drops, as the bonding becomes similar to the tetrahedral bonding in diamond.

IV. DISCUSSION

The primary purpose of this work was to examine how the structure and conductivity of liquid carbon depend upon pressure, in order to understand the experiments conducted by Bundy[10] and to further understand the melting lines of graphite and diamond. Previous simulations[5-8] and the work presented here indicate that at low densities, the liquid is primarily twofold bonded. As the density is increased, the liquid becomes primarily threefold bonded, and at sufficiently high densities, the liquid is mostly tetrahedrally bonded.

The relationship between the bonding and the conductivity is shown in Figs. 1 and 2, which demonstrate that the conductivity is highest when the number of threefold bonded atoms is highest. This is in agreement with the experiments of Bundy,[10] which show that the conductivity increases with pressure, for pressures below the equilibrium diamond-graphite-liquid triple point. This relationship may be understood by considering the periodic structures of carbon: the diamond form of carbon is insulating, while graphite has a high in-plane conductivity. We expect that the primarily twofold bonded liquid will have a low conductivity, as the primary contribution will be along the chains, which are only weakly connected. This is in partial agreement with Ferraz and March, who predicted that the twofold coordinated liquid will be insulating,[4] although we find a small but finite density of states at the Fermi level at the lower densities.[8]

Our results indicate that the conductivity will be at a maximum at some density below that of diamond. Bundy's results that the conductivity rises as a function of pressure, up to a pressure of $P \approx 100$ kbar, indicate that at this pressure the liquid will most likely be primarily threefold bonded, and will be less dense than the corresponding diamond phase. This indicates that the slope of the diamond melting curve should be positive, at least at this pressure. This is in accordance with recent descriptions of the phase diagram.[2,6] Other experimental work[28] has suggested that above this pressure, both sp^2 and sp^3 bonding is present in the liquid phase, and that the sp^3 bonding increases with increasing pressure, again in qualitative agreement with our simulations.

We note that our results are in sharp contrast to the work of van Thiel and Ree,[9] who attribute the increase of conductivity with pressure to a change from threefold bonding to a higher coordinated structure. They suggest that these are distinct liquid phases, separated by a coexistence line that is terminated by a critical point at $T_c = 5520$ K, $P_c = 70.5$ kbar, with a critical density of $\rho = 2.34$ g/cm^3. This density is approximately where we observe a crossover from twofold to threefold bonding.

The idea that there is a transition between two liquid phases is appealing, in part due to the fact that the slope of the melting line of graphite changes sign at $P \sim 50$ kbar. This indicates that at above this pressure, the liquid phase is more dense than graphite. Furthermore, the fact that carbon can form sp, sp^2, and sp^3 bonds suggests that there could be distinct phases. Our results for the pressure versus density, shown in Fig. 5, indicate that the behavior of the liquid is continuous, with no evidence for a phase transition. This could be due to the fact that our simulations were carried out at temperatures significantly higher than the melting point of graphite; however, we would expect to see some indication of a large compressibility even above the critical temperature. Thus, while we cannot rule out the possibility of a transition, we see no evidence in our simulations that would support this idea within this range of densities. If the change in slope is due to a structural change, we believe that it would be related to a transition between twofold and threefold coordinated structures, similar to that predicted by Ferraz and March.[4]

In summary, we have shown that the conductivity of the liquid phase is closely correlated with the presence of sp^2 bonding in the liquid. The low-density liquid, being characterized by the formation of connected linear chains, has a low conductivity. We believe that the experimentally observed rise of conductivity with pressure is due to the increased number of sp^2 bonded atoms. At sufficiently high densities, the conductivity should decrease, as the sp^3 bonding begins to dominate. We observe no evidence of a structural transition between different liquid phases.

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