Liquid-Liquid Phase Transition in Elemental Carbon: A First-Principles Investigation

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(Received 18 January 2002; published 6 September 2002)

It has been recently suggested that elemental carbon may be a promising candidate to exhibit a liquid-liquid phase transition (LLPT). We report the results of first-principles molecular dynamics simulations showing no evidence of LLPT in carbon, in the same temperature and pressure range where such a transition was found using empirical calculations. Our simulations indicate a continuous evolution from a primarily sp-bonded liquid to an sp^2-like and an sp^3-like fluid, as a function of pressure, above the graphite melting line. The discrepancy between quantum and classical simulations is attributed to the inability of empirical potentials to describe complex electronic effects in condensed carbon phases.

DOI: 10.1103/PhysRevLett.89.135701 PACS numbers: 64.70.Ja, 34.20.Cf, 71.15.Mb

The coexistence of two distinct thermodynamically stable liquids of a pure substance has long been a subject of scientific interest. First-order LLPTs have now been suggested for a dozen systems, including P, H_2O, SiO_2, GeO_2, C, Si, Ge, Bi, Se, Te, and I [1–3]. However, decisive experimental proofs are difficult to obtain, and in most cases LLPTs have been suggested on the basis of indirect evidence, such as that derived from the dependence of melting lines [4–6] on pressure. The only direct observation of LLPT in an elemental substance has been recently reported in phosphorus, where Katayama *et al.* used an *in situ* x-ray diffraction technique [1] to monitor the existence of two distinct liquid phases.

Similar to phosphorus, carbon is a promising candidate to show a LLPT since it is capable of forming various local bonding coordinations (sp, sp^2, and sp^3), which in turn could be responsible for different, coexisting phases in the liquid state. The P-T region of the carbon phase diagram where a LLPT is expected to occur is at a temperature maximum ($T_m^{\max}$) along the melting line of graphite [4–6]. Unfortunately, the high melting temperature ($T_m >$ 4500 K) of graphite makes it nearly impossible to obtain direct spectroscopy evidence for a LLPT. A cusp in the melting line of graphite at $T_m^{\max}$ would be evidence for a LLPT. However, experimental investigations to detect such a change in the slope of the graphite melting line have been inconclusive.

Early experiments by Bundy [4] as well as Fateeva and Vereshchagin [5] had too large uncertainties to resolve the issue of a LLPT in liquid carbon. More recently, Togaya [6] reported extensive flash-heating experiments aimed at determining the melting line of graphite. Based on his conductivity data, he concluded that the melting line may exhibit a cusp at $T_m^{\max}$, based on a fit of the melting line with two straight lines. However, his data can be fitted easily by one smooth line as well. An additional complication in interpreting Togaya's data is that all the values of T_m's derived from his experiments are referenced to T_m of graphite at ambient pressure (T_m^{zero}). The value of T_m^{zero} itself is not known with great accuracy, and it has been modified to higher values several times over the last ten years.

Theoretically, Glosli and Ree [7] have suggested the existence of a LLPT in carbon, using classical molecular dynamics (MD) calculations with the Brenner's bond-order potential [8]. They showed that in the temperature range 6000 to 8800 K, P-V isotherms exhibit a van der Waals loop, indicating the occurrence of a LLPT in the liquid. They also showed that the high-density liquid (HDL) has mostly sp^3-bonded sites, and the low-density liquid is composed mostly of sp-bonded structures, with a small presence of sp^2 sites in both phases. The existence of the LLPT is sensitive to the parameter controlling the torsional energy of sp^2 bonding in the empirically based Brenner potential. If the torsional barrier vanishes, the van der Waals loop mentioned above nearly disappears [7]. Glosli and Ree concluded that the existence of a LLPT is due to the lack of sp^2-bonded sites in the liquid, as the formation of sp^2 sites is inhibited by a large torsional barrier and a low entropy associated with the π bond. This lack of sp^2 sites is in disagreement with the results of first-principles MD of liquid carbon [9], showing a significant amount of sp^2-like sites in the liquid at a density of 2 g/cm^3 and 5000 K. Furthermore, three independent tight binding (TB) MD simulations [10–12] gave no evidence of LLPT in carbon.

In order to shed light on the current controversy about a LLPT in carbon, we have performed a series of first-principles MD simulations of the fluid as a function of density, above the graphite melting line. This is the first *ab initio* study of a LLPT in carbon. In the absence of direct experimental observations, the use of predictive, *ab initio* techniques is crucial to address the existing controversy. Our first-principles results differ substantially from those of classical MD simulations. Our calculations showed no evidence of a LLPT, and we found a substantial amount of sp^2 sites in the liquid at all densities considered here. The difference between classical and first-principles simulations is analyzed in terms of torsional barriers between various coordinated carbon sites in condensed carbon.

0031-9007/02/89(13)/135701(4)$20.00

In our study, we have performed constant volume first-principles density functional theory (DFT) simulations [13] at seven densities at 6000 K, using 128 carbon atoms, with periodic boundary conditions. We used the Perdew-Burke-Ernzerhof (PBE) exchange and correlation potential [14], plane wave basis set with 50 Ry cutoff, and only the gamma point to sample the supercell Brillouin zone. At each volume we equilibrated the system for 4 ps. Since the cell sizes and time scales used in the first-principles and classical MD simulations are different, we first repeated the classical simulations (originally carried out for 1 ns with 512 C cells) with 128 C and for 4 ps. When using the smaller 128 atom cell, we found that the van der Waals loop is slightly more pronounced than with 512 C cells. In addition, the P-V isotherms obtained with the Brenner potential at 128 C cells, averaging over 4 ps and 1 ns, were nearly identical.

Figure 1 shows a comparison between the first-principles PBE P-V isotherm (solid and open circles) and the corresponding classical simulations using the Brenner potential with (solid line) and without (dashed line) the full torsional barrier between sp^2 sites. The absence of this barrier implies that the sp^2 torsional energy vanishes. The solid circles represent PBE data obtained along an expansion path with starting density of 3.02 g/cm^3, while the open circles correspond to data obtained along a compression path starting at 1.27 g/cm^3. The initial configurations for the first-principles simulations were taken from snapshots obtained from classical simulations with the Brenner potential. Although such initial configurations might have biased the first-principles calculations and favored the occurrence of a LLPT, the final results showed no indication of a LLPT. The first-principles results were in qualitative agreement with previous TB P-V isotherm at 6000 K [10]. We also note that the first-principles P-V isotherm lies on the right hand side of the classical P-V isotherm, since the sp^2-bonded liquid occupies more volume than the sp^3-bonded liquid.

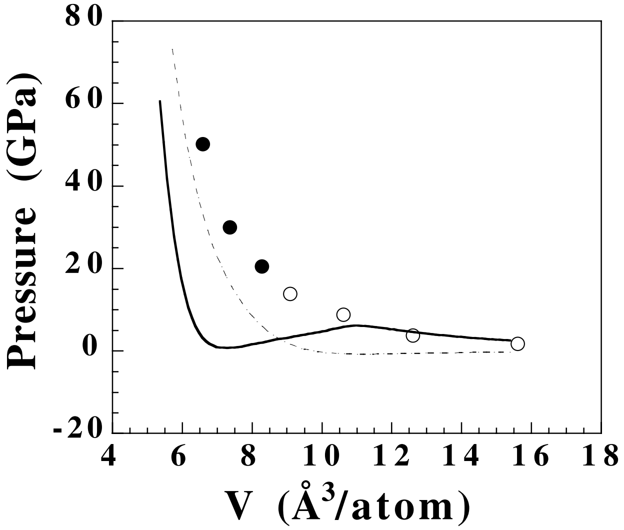

FIG. 1. PBE P-V isotherm (filled and open circles) of liquid carbon at $T = 6000$ K. Numerical errors associated with each PBE point lie within the circles. The solid and dashed lines are classical P-V isotherms of the Brenner potential with and without torsional sp^2 barriers, respectively.

A detailed analysis of the ionic trajectories and of the atomic coordination numbers as a function of the simulations' time confirmed that the liquid goes continuously from a mixture of sp- and sp^2-bonded configurations to a mixture of sp^2- and sp^3-bonded configurations as the density is increased from 1.27 to 3.02 g/cm^3. The average coordination at a density of 1.27 g/cm^3 is 2.6. Coordination analysis indicates that the liquid state is indeed a mixture of sp- and sp^2-bonded carbon atoms. The average coordination at 2.76 g/cm^3 is 3.1 close to that of graphite. The average coordination at 3.02 g/cm^3 is 3.4, pointing at a mixture of sp^2- and sp^3-bonded carbon atoms in the liquid. The positions of the first peak of the pair correlation functions [$g(r)$] are at 1.31, 1.40, and 1.42 Å, at densities of 1.27, 2.76, and 3.02 g/cm^3, respectively. In comparison, MD results obtained with the Brenner potential show larger bond lengths and higher coordination numbers in the HDL than first-principles MD results. In particular, classical simulations exhibit the presence of fivefold coordinated atoms, which are much rarer in first-principles simulations.

In order to understand the discrepancies between the classical MD simulation and our first-principles MD, we carried out a detailed investigation of the parameter controlling the existence of a LLPT in the Brenner potential, e.g., the sp^2-torsional term. Understanding where the differences between the *ab initio* and the empirical formulations originates from is important not only to understand liquid carbon, but also to assess the general validity of the Brenner potential which has been widely used in the simulation of carbon systems in the last decade. In the construction of the Brenner potential, the sp^2-torsional term is chosen to be proportional to $\sin^2\theta$, where θ is the torsional angle, and it is a function of the coordination of the nearest neighbors of a given atom. For instance, the value of the sp^2 torsional term depends on whether a sp^2 bonded site is connected to sp^3 or non-sp^3 neighbors (sp^2 and sp neighbors are treated in the same way). The atomic coordination number is calculated using a soft cutoff radius slowly varying between 1.7 and 2.0 Å.

We have studied the coordination dependence of the sp^2 torsional term for several molecules whose bonding configurations mimic those found in the fluid. In particular, we have studied two model molecules: $(CH_3)_2CC(CH_3)_2$ (see Fig. 2) and $(CH_2)_2CC(CH_2)_2$ (see Fig. 3), which mimic an sp^2 site connected to sp^3 and sp^2 neighbors, respectively, according to the coordination number defined in the Brenner potential. Hydrogen atoms are used to terminate dangling bonds. Since hydrogens lie outside the first neighbor shell, we expect them to have little effect on the

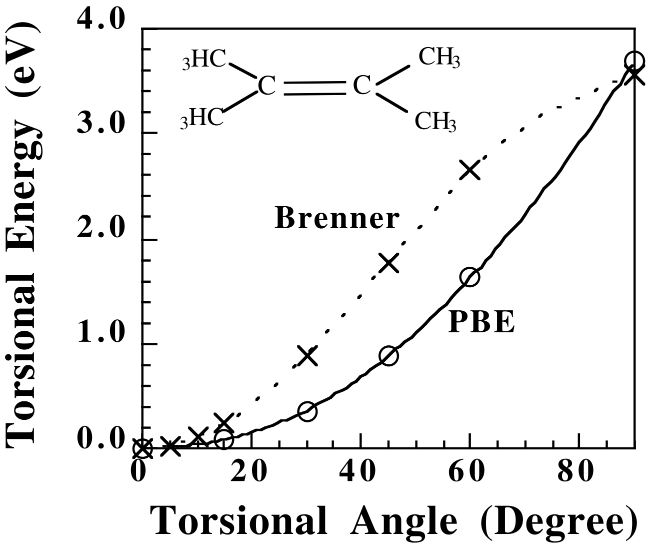

FIG. 2. Torsional energy as a function of torsional angle for $(CH_3)_2CC(CH_3)_2$. The circles are the PBE results, while the crosses are from the Brenner potential.

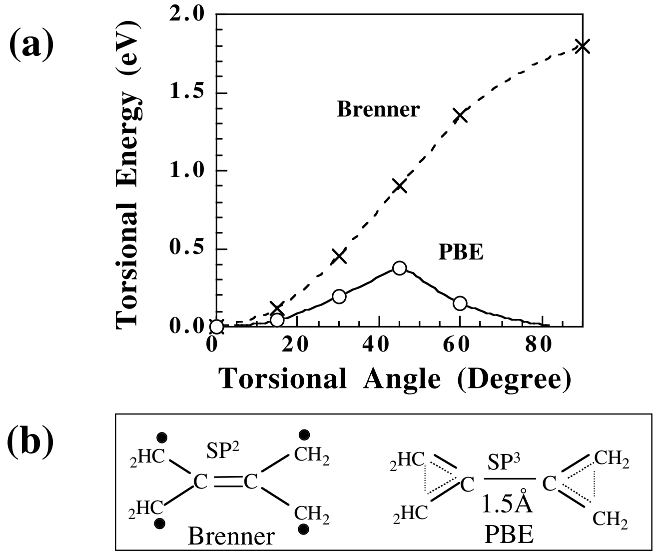

FIG. 3. (a) The torsional energy as a function of torsional angle for $(CH_2)_2CC(CH_2)_2$. The circles are the PBE results, while the crosses are from the Brenner potential. (b) Two resonant structures of $(CH_2)_2CC(CH_2)_2$.

torsional energy. First, we optimized the geometries of model molecules in their planar configuration using both the Brenner potential and PBE calculations. Then, we twisted the center carbon-carbon bond without relaxation of the other degrees of freedom. In first-principles calculations, we found that relaxation brings only a small change to the torsional energy.

Figure 2 displays the torsional energy (relative to the planar configuration) as a function of the torsional angle for the central carbon-carbon bond of $(CH_3)_2CC(CH_3)_2$, as obtained with PBE calculations and using the Brenner potential. We used this model molecule to mimic the torsional motion of a sp^2 bond connected to sp^3 atoms, a likely bonding environment in a liquid containing a mixture of sp^3 and sp^2 sites. Since the neighboring sp^3 carbons are electronically saturated, we expect them to have a limited interaction with the π bonds which will break when the sp^2 bond is twisted. With both classical and first-principles simulations, the highest energy barrier is found at 90°, when two p orbitals in the π bond are perpendicular to each other, as expected. The barrier height is similar in the two cases (~ 3.5 eV). However, the way E varies with θ as obtained with PBE calculations is substantially different from the $\sin^2\theta$ dependence in the Brenner potential. As a result, the Brenner potential significantly overestimates the barrier (0.4–1.0 eV) over a large range of angles (20°–80°).

Figure 3 shows a similar comparison between the torsional energies as a function of the torsional angle obtained classically and with first principles, for the central carbon-carbon bond of the $(CH_2)_2CC(CH_2)_2$ molecule. According to the coordination as defined by Brenner, this molecule corresponds to a sp^2 bond connected to sp^2 carbons, which is the most likely environment in a sp^2-rich liquid. In $(CH_2)_2CC(CH_2)_2$, the side CH_2 groups are electronically unsaturated. Therefore, we expect the torsional barrier to be lower than that of $(CH_3)_2CC(CH_3)_2$, since the unsaturated electron of the neighboring sp^2 atoms is likely to participate in reforming bonds, as the π bonds are broken during twisting. Indeed, the Brenner potential gives a barrier that is only half of that found in $(CH_3)_2CC(CH_3)_2$. However, PBE calculations show a completely different torsional profile than that obtained with the Brenner potential. This can be understood by looking at an alternative resonance structure of $(CH_2)_2CC(CH_2)_2$ shown in Fig. 3(b). The bonding between two central carbon atoms is well represented by a single bond. Indeed, the C-C bond length (1.50 Å) between two central carbon atoms is closer to that of diamond (1.54 Å) than that of graphite (1.42 Å). Therefore, this bond has a much lower torsional barrier than the double bond between central atoms found in $(CH_3)_2CC(CH_3)_2$. As for most single C-C bonds, side groups are preferred to be orthogonal (90° torsion) to each other, in order to minimize the static repulsion. On the other hand, there is a three-center conjugated bond on each side of the molecule, which would favor a planar conformation. The maximum torsional barrier occurs at 45° as the result of these two competing effects. The overestimation of the torsional barrier by the Brenner potential results from its inability to capture various complex electronic effects, such as the behavior of lone pair electrons. The Brenner potential defines the bonding type of an atom solely by its ionic coordination. This introduces a severe error in describing the entropy of a three-center-coordinated carbon liquid, in which lone pair electrons are expected to be present.

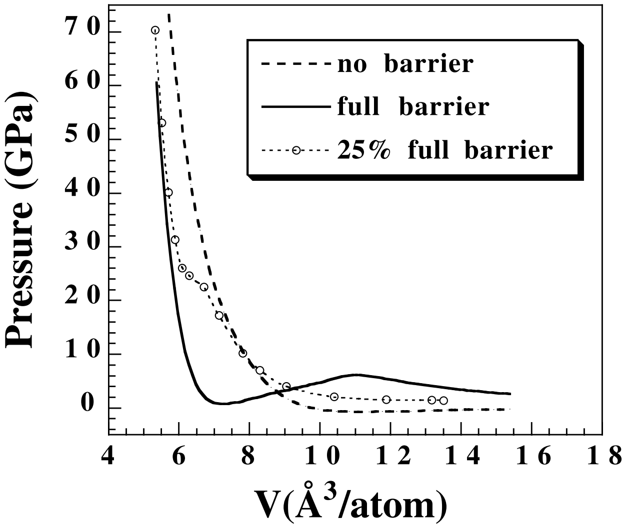

FIG. 4. P-V isotherms of liquid carbon at $T = 6000$ K obtained using the Brenner potential with different barrier heights for the sp^2 sites' torsion.

If we scale the barrier height of the Brenner potential by 25%, to bring the torsional barrier height of $(CH_2)_2CC(CH_2)_2$ in near agreement with that of PBE calculations, the van der Waals loop associated with LLPT shrinks to a small plateau in the P-V isotherm at 6000 K (see Fig. 4). Thus, there is a remote possibility that the van der Waals loops may appear at a temperature below 6000 K. However, a mere scaling of the barrier height would not account for all the differences between the first-principles and the Brenner descriptions; in particular, the functional form of the torsional energy as a function of the torsional angle would not be the same.

In summary, we have presented the first *ab initio* study of a LLPT in carbon. Our calculated P-V isotherm in the liquid shows no LLPT at 6000 K, consistent with previous TB simulations [10–12] and in disagreement with the recent classical MD simulation [7]. Although we cannot rule out a LLPT below 6000 K and above the graphite melting line ($\simeq$ 5000 K), we have shown that the physical reason proposed by Glosli and Ree to explain the existence of a LLPT in carbon is not valid. The results of our simulations clearly point at a continuous transition from a low-density sp/sp^2-like fluid to a high-density sp^2/sp^3 liquid, with sp^2 sites being present at all densities. In addition, we have examined in detail the origin of the different results obtained using first-principles and classical simulations. We found that the Brenner potential significantly overestimates the torsional barrier of a chemical bonding between two three-center-coordinated carbon atoms due to the inability of the potential to describe lone pair electrons. The definition of a sp^2 site based only on ionic coordination adopted in the Brenner potential's construction is too simplistic to account for complex bonding and electronic configurations. Our findings are consistent with a recent comparative study of DFT, TB, and the Brenner's potential in amorphous carbon by Cooper *et al.* [15]. These authors found that the Brenner potential gives excellent agreement with DFT for properties of amorphous carbon at low density (2.0 g/cm^3), but yields significant departure from DFT results at higher density. We therefore conclude that Brenner potential parameters derived from isolated hydrocarbon molecules and used in the literature to simulate various carbon systems may not be adequate to use for condensed phases, especially so in the presence of lone pair electrons.

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. We thank R. Haerle and F. Gygi for many useful discussions.

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