Carbon Phase Diagram from *Ab Initio* Molecular Dynamics

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We compute the free energy of solid and liquid diamond from first-principles electronic structure theory using efficient thermodynamic integration techniques. Our calculated melting curve is in excellent agreement with the experimental estimate of the graphite-diamond-liquid triple point and is consistent with shock wave experiments. We predict the phase diagram of diamond at pressures and temperatures that are difficult to access experimentally. We confirm early speculations on the presence of a reentrant point in the diamond melting line but find no evidence for a first order liquid-liquid phase transition near the reentrant point.

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Carbon is one of the most abundant elements in the Universe. It has exceptional chemical flexibility, which is crucial for organic molecules and is at the basis of its existence in many different forms. Yet, in spite of its fundamental importance, the phase diagram of carbon, especially the diamond-liquid phase boundary, is still incompletely known after decades of research. This is a direct consequence of the difficulty of performing experiments at the extreme temperatures and pressures that are required to melt diamond [1]. This difficulty underlines the importance of computer simulations in this area, particularly of *ab initio* simulations which associate structures to chemical bonding features. So far only the graphite/diamond and the graphite/liquid phase boundaries, which occur at lower temperatures and pressures, have been located experimentally with reasonable accuracy [1–4]. In particular, experiments indicate that the triple point where diamond, graphite, and liquid phases coexist has temperature in the range 4500–5000 K and pressure close to 12 GPa [1,4].

Prior to 1980, the melting curve of diamond was thought to have a negative slope on the *P*-*T* plane [2,5], based on a simple analogy with silicon and germanium, which both have a negative melting slope due to the higher density of the liquid compared to the solid. This conjecture was later abandoned when evidence of a positive melting slope for carbon emerged from experiments [6,7] and *ab initio* molecular dynamics simulations [8]. Further *ab initio* calculations by Grumbach and Martin [9] provided data for carbon in the BC8, simple cubic, and liquid phases over a wide range of pressures (400–4000 GPa) and temperatures (2000–36 000 K). They observed a change from fourfold to sixfold coordination in the liquid when the pressure varied from 400 GPa to 1000 GPa. Assuming that fourfold coordinated diamond is the stable crystalline phase in this pressure regime, they concluded that the melting slope should change sign at sufficiently high pressure, when the liquid becomes denser than the solid. Consequently the melting temperature should exhibit a maximum. Grumbach and Martin [9] speculated that the large structural changes caused by pressure in molten diamond may be compatible with a liquid-liquid phase transition (LLPT), which would manifest itself with a discontinuity (cusp) in the melting slope. However, they were unable to substantiate this hypothesis lacking a quantitative determination of the liquid-solid phase boundary.

Few attempts to locate quantitatively the melting curve of diamond by computer simulations have been reported to date. Glosli *et al.* [10] modeled the interatomic interactions with the empirical Brenner potential [11] and found a melting curve, which, albeit having a positive slope, is at variance with the shock wave experiment of Shaner *et al.* [6]. This experiment indicates that diamond has not melted yet at $T \sim 5600$ K and $P \sim 140$ GPa. Very recently, Ghiringhelli *et al.* [12] reported calculations with a more refined long-range carbon bond-order potential (LCBOP), partly based on *ab initio* data. These calculations predict a melting line that is consistent with the shock wave experiment but places the triple point at a temperature lower than experiment and does not exhibit a reentrant high pressure behavior.

In this Letter we calculate the diamond melting line from *ab initio* density functional theory. In our approach the changes in the chemical bonds induced by pressure and temperature derive from the changes in the quantum mechanical ground state of the electrons. By combining *ab initio* molecular dynamics with modern thermodynamic integration techniques we compute the free energy of solid and liquid carbon in an extended range of pressures and temperatures. Our calculated melting line agrees well with the known experimental data and shows a reentrant behavior at high pressure. In particular, the line extrapolates to the experimental triple-point location. Within our numerical accuracy the melting slope changes sign continuously, excluding the occurrence of a LLPT in molten diamond. This conclusion is further supported by independent calculations of the change of volume with pressure in liquid carbon near the maximum of the melting temperature.

The predictive power of *ab initio* molecular dynamics simulations for carbon phases at high pressure and temperature has been amply demonstrated by Galli *et al.* [8], Grumbach and Martin [9], and Wu *et al.* [13]. However, locating a melting line by thermodynamic integration is significantly more demanding than predicting equilibrium atomic structures, because a small error in the free energy difference between the competing phases may translate in a relatively large error in the melting temperature T_m. This places a severe requirement on the accuracy of the approximate functionals used to describe the electronic ground state. Calculations for silicon have shown that the predicted melting temperature improves systematically with the accuracy of the density functional approximation, going from $T_m = 1350$ K with the local density approximation [14], to $T_m = 1492$ K with the Perdew-Burke-Ernzerhof (PBE) [15] generalized gradient approximation (GGA) [16], and to a value very close to the experimental one ($T_m = 1680$ K), with the Tao-Perdew-Staroverov-Scuseria (TPSS) [17,18] metaGGA approximation [19]. We expect that density functional calculations of thermodynamic phase diagrams of substances with chemical bonds ranging from covalent to metallic should have a similar accuracy to that shown in the silicon case.

Here we report calculations on a periodically repeated simple cubic supercell containing 64 carbon atoms and adopt a plane-wave norm-conserving pseudopotential [20] scheme. We use the PBE-GGA exchange correlation functional. We checked on a few selected configurations that replacing the PBE-GGA functional with the computationally more expensive TPSS-metaGGA functional has only a minor effect (a reduction by ~150 K) on the calculated melting temperature. We use a kinetic energy cutoff of 76 Ryd in the plane-wave expansion, which ensures excellent basis set convergence of the electronic total energy in the pressure range of interest. We follow the *ab initio* Car-Parrinello (CP) molecular dynamics scheme [21]. Nuclear trajectories are generated from a potential energy surface U calculated by sampling the Brillouin zone (BZ) of the 64-atom supercell at the Γ point only. We correct for sampling errors by evaluating the free energy G_k in terms of G_Γ to first order in perturbation theory, i.e., $G_k = G_\Gamma + \langle U_k - U_\Gamma \rangle$. We use a $2 \times 2 \times 2$ k-point mesh and compute the average $\langle U_k - U_\Gamma \rangle$ from ten uncorrelated configurations along an equilibrated molecular dynamics trajectory. The k-point correction to T_m is small on the scale of diamond melting temperatures, ranging from a minimum of ~10 K to a maximum of ~200 K in the pressure range of interest [22].

We control the temperature of the nuclei in the simulation with a Nosé-Hoover thermostat [24,25], and apply an additional thermostat on the fictitious dynamics of the electrons to enforce adiabaticity [26]. We set the fictitious electron mass μ in the CP dynamics equal to 150 a.u. and choose a time step $\delta t = 1.6$ a.u. for numerical integration. We compute the free energy difference between the system of interest and a reference system of known free energy by thermodynamic integration using the two-stage approach suggested by Sugino and Car [14]. First we convert by adiabatic switching [27] the *ab initio* system into an intermediate reference system. Then we convert the intermediate system into a system of known free energy by a second adiabatic switch. We gain in computational efficiency by adopting the reversible scaling approach of Ref. [28], which allows us to compute a free energy difference in a finite interval of temperatures from a single molecular dynamics trajectory. Details of the reversible scaling procedure in the context of CP molecular dynamics are given in Ref. [19]. As intermediate reference we take a system in which the atoms interact via a Stillinger-Weber (SW) potential [29]. The SW parameters are optimized to mimic *ab initio* molecular dynamics configurations under similar thermodynamic conditions. A negligible error is associated to the switching and scaling protocols when 42 000 and 9000 molecular dynamics steps are used for switching and scaling simulations, respectively, to convert an *ab initio* system into an SW system. Finally, the SW solid is converted into an Einstein crystal and the SW liquid is converted into an ideal gas. We base our work on constant volume isothermal (NVT) simulations giving access to the Hemholtz free energy F. The corresponding Gibbs free energy is evaluated from $G = F + PV$, where P is the average pressure of the simulation. In order to simulate a solid and a liquid at the same pressure, we systematically adjust the volume of the simulation.

We calculate the melting temperature T_m at a given pressure from the intersection of the Gibbs free energy curves of the solid and of the liquid. The melting line obtained by interpolating the calculated melting points is reported in Fig. 1. We cover a pressure range that extends from beyond the experimental location of the triple point [1,30] up to pressures of about 1300 GPa. A relevant issue

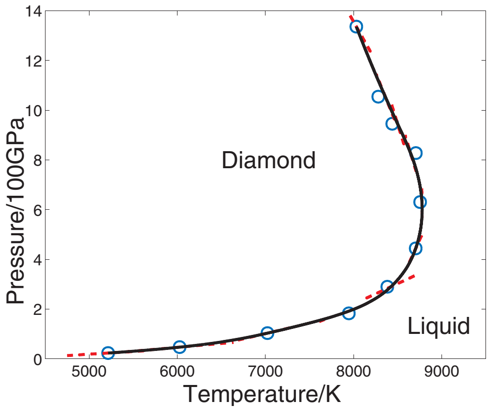

FIG. 1 (color online). Diamond melting line. The open circles are calculated melting temperatures. The dashed lines at each circle give the corresponding Clausius-Clapeyron slopes. The solid line is obtained by interpolation.

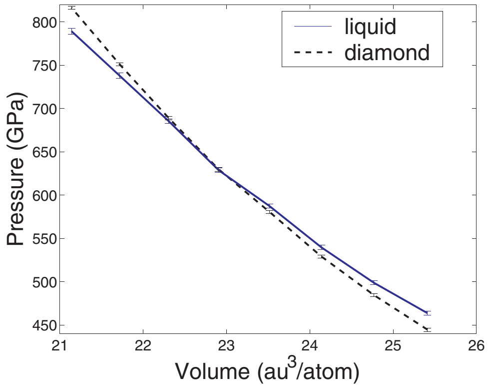

FIG. 2 (color online). P-V isotherms of diamond and liquid carbon at 8700 K. The two curves intersect at 630 GPa.

is whether diamond is stable in this pressure range. Using a kinetic energy cutoff of 76 Ry and a $6 \times 6 \times 6$ k-point mesh we place the zero temperature transition pressure of diamond to BC8 at 1060 GPa, which is somewhat lower than the value predicted in early local-density approximation calculations [31,32], but still significantly above our predicted reentrant point in the melting curve [33].

From the slope of the free energy curves of the coexisting phases at T_m we extract the entropy S_s of the solid and the entropy S_l of the liquid. Their difference, $\Delta S_m = S_l - S_s$, is the entropy of melting. We use the calculated ΔS_m and $\Delta V_m = V_l - V_s$ to estimate the slope of the melting line at (T_m, P_m) from the Clausius-Clapeyron equation. This provides an independent consistency check for the calculations. The computed Clausius-Clapeyron slopes reported in Fig. 1 agree well with the interpolated melting line. From the fluctuation of the cumulative averages we estimate a small numerical error of ±70 K in the melting temperature.

The melting curve reported in Fig. 1 shows a reentrant point at $T_m = 8755$ K and $P_m = 630$ GPa. As a further check of this result, we carried out NVT simulations at $T = 8700$ K and varying density for both liquid and solid phases. The resulting isotherms are reported in Fig. 2. The two curves intersect at 630 GPa, in good agreement with the melting curve. The calculated radial distribution and bond angle distribution functions of the liquid (not shown) exhibit substantial changes with pressure up to the reentrant point. The coordination number (CN), calculated by integrating the radial distribution function up to its first minimum, is reported in Table I. In the pressure range up to the reentrant point the liquid converts continuously from a liquid with CN slightly larger than 3 and angular correlations broadly peaked around an angle slightly below 120 degrees [35] into a liquid with CN larger than 5 and angular correlations with a broad peak around 90 degrees, resembling the correlations of liquid silicon at ambient pressure [36]. For pressures above the reentrant point the changes are more modest as reflected in the CN. The calculated melting curve does not show a discontinuous change of slope around the reentrant point. This conclusion is further supported by our analysis of the equation of state of liquid carbon, which at $T = 8700$ K and pressure between 790 GPa and 460 GPa, does not show any sign of hysteresis. This rules out the occurrence of a first order LLPT in molten diamond. The thermodynamic properties of carbon along the melting curve are summarized in Table I. Notice the change of sign of the melting slope and of the volume discontinuity at melting with pressure. Also notice the steady decrease of entropy S_s with pressure above $P_m =$ 48 GPa, reflecting the reduction of volume with pressure. By contrast the entropy of melting S_m shows only small fluctuations.

Finally, in Fig. 3 we propose a new phase diagram for carbon, including graphite, diamond, and liquid phases. The calculated diamond melting curve is in good agreement with the available experimental data and previous *ab initio* simulations. Using the Clausius-Clapeyron slope at 23 GPa to linearly extrapolate the melting curve to lower temperature, we find that the diamond melting curve intersects the experimental graphite melting line at $T =$ 4700 K and $P = 12$ GPa, i.e., right in the middle of the experimental range for the triple point. In their pioneering *ab initio* molecular dynamics investigation of liquid carbon

TABLE I. Thermodynamic properties of carbon at melting.

P_m	T_m	V_s	ΔV_m	S_s	ΔS_m	dT_m/dP_m	CN
GPa	K	a.u.^{3}/atom		J · mol/K		K/GPa	
24	5216	40.25	12.90	64.49	24.75	46.51	3.3(3)
48	6028	39.02	7.15	71.36	19.83	32.18	3.5(3)
104	7023	35.32	2.94	71.08	22.02	11.92	3.8(3)
183	7947	31.40	1.70	71.31	21.35	7.11	3.8(3)
290	8383	28.40	1.41	69.80	20.68	6.08	4.3(3)
445	8705	25.43	0.33	67.06	22.97	1.28	4.7(3)
631	8755	22.85	−0.01	65.82	19.11	−0.03	5.4(3)
828	8706	20.92	−0.19	64.08	19.75	−0.86	5.4(4)
946	8439	20.10	−0.21	62.33	21.11	−0.88	5.5(4)
1055	8280	19.33	−0.26	62.46	20.12	−1.14	5.4(4)
1337	8031	17.78	−0.34	60.68	19.04	−1.59	5.8(4)

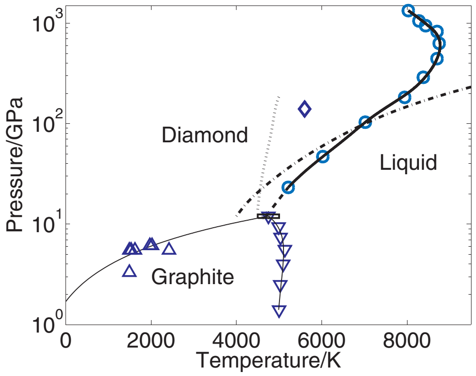

FIG. 3 (color online). Proposed phase diagram of carbon. The graphite-diamond boundary (solid line and up triangles) is from Refs. [1,39]; the graphite-liquid boundary (solid line and down triangles) is from Ref. [4]. The rectangle gives the uncertainty on the experimental triple point [1]. The solid line with open circles is the diamond melting line from our calculation, and the dashed line is the extrapolation to the triple point. The open diamond is the thermodynamic condition of the shockwave experiment [6]. The dotted line is the empirical melting curve from Ref. [10], and the dash-dotted line is the empirical melting curve from Ref. [12].

at high pressure, Galli *et al.* estimated the melting temperature of diamond at 100 GPa to be in the range 6500 K–8000 K [8]. According to our melting line, at 100 GPa diamond should melt at $T = 7000$ K.

In conclusion, we have performed an extensive *ab initio* molecular dynamics study of the melting properties of diamond. In combination with the available experimental data, our calculated melting line leads to the complete phase diagram for graphite, diamond, and liquid carbon reported in Fig. 3. The calculated melting curve of diamond has important consequences in materials science for its role in diamond nucleation. It has also important implications for the interiors of Uranus and Neptune, where pressures and temperatures are estimated to reach values of about 600 GPa/7000 K [1] and where elemental carbon is believed to precipitate after the pressure-induced dissociation of CH_4 [37,38]. Our predicted melting line implies that carbon remains in the diamond solid form all the way down to the planets' center.

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[1] F. P. Bundy, W. A. Bassett, M. S. Weathers, R. J. Hemley, H. U. Mao, and A. F. Goncharov, Carbon **34**, 141 (1996).
[2] F. P. Bundy, J. Chem. Phys. **38**, 631 (1963).
[3] F. P. Bundy, J. Chem. Phys. **38**, 618 (1963).
[4] M. Togaya, Phys. Rev. Lett. **79**, 2474 (1997).
[5] B. J. Alder and R. H. Christian, Phys. Rev. Lett. **7**, 367 (1961).
[6] J. W. Shaner, J. M. Brown, C. A. Swenson, and R. G. McQueen, J. Phys. (Paris), Colloq. **45**, 235 (1984).
[7] M. Togaya, High Press. Res. **4**, 342 (1990).
[8] G. Galli, R. M. Martin, R. Car, and M. Parrinello, Science **250**, 1547 (1990).
[9] M. P. Grumbach and R. M. Martin, Phys. Rev. B **54**, 15 730 (1996).
[10] J. N. Glosli and F. H. Ree, J. Chem. Phys. **110**, 441 (1999).
[11] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).
[12] L. M. Ghiringhelli, J. H. Los, E. J. Meijer, A. Fasolino, and D. Frenkel, Phys. Rev. Lett. **94**, 145701 (2005).
[13] C. J. Wu, J. N. Glosli, G. Galli, and F. H. Ree, Phys. Rev. Lett. **89**, 135701 (2002).
[14] O. Sugino and R. Car, Phys. Rev. Lett. **74**, 1823 (1995).
[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[16] D. Alfè and M. J. Gillan, Phys. Rev. B **68**, 205212 (2003).
[17] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
[18] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, Phys. Rev. B **69**, 075102 (2004).
[19] X. Wang, S. Scandolo, and R. Car (to be published).
[20] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[21] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[22] Second order corrections as given by Alfè and Gillan [23] are negligible.
[23] D. Alfè, M. J. Gillan, and G. D. Price, J. Chem. Phys. **116**, 6170 (2002).
[24] S. Nosé, J. Chem. Phys. **81**, 511 (1984).
[25] W. Hoover, Phys. Rev. A **31**, 1695 (1985).
[26] P. Blochl and M. Parrinello, Phys. Rev. B **45**, 9413 (1992).
[27] M. Watanabe and W. Reinhardt, Phys. Rev. Lett. **65**, 3301 (1990).
[28] M. de Koning, A. Antonelli, and S. Yip, Phys. Rev. Lett. **83**, 3973 (1999).
[29] F. Stillinger and T. Weber, Phys. Rev. B **31**, 5262 (1985).
[30] D. A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).
[31] M. T. Yin and M. L. Cohen, Phys. Rev. Lett. **50**, 2006 (1983).
[32] R. Biswas, R. M. Martin, R. J. Needs, and O. H. Nielsen, Phys. Rev. B **35**, 9559 (1987).
[33] The possibility of a different transition, from diamond to R8, should also be considered. For this transition we find a pressure of 1260 GPa, significantly higher than the value of ~500 GPa obtained with a 30 Ry kinetic energy cutoff and a coarse *k*-point mesh in Ref. [34].
[34] S. J. Clark, G. J. Ackland, and J. Crain, Phys. Rev. B **52**, 15 035 (1995).
[35] G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. B **42**, 7470 (1990).
[36] I. Stich, R. Car, and M. Parrinello, Phys. Rev. B **44**, 4262 (1991).
[37] L. R. Benedetti, J. H. Nguyen, W. A. Caldwell, H. Liu, M. Kruger, and R. Jeanloz, Science **286**, 100 (1999).
[38] F. Ancilotto, G. L. Chiarotti, S. Scandolo, and E. Tosatti, Science **275**, 1288 (1997).
[39] F. P. Bundy, H. P. Bovenkerk, H. M. Strong, and J. R. H. Wentorf, J. Chem. Phys. **35**, 383 (1961).