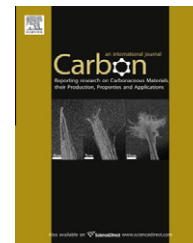


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High-pressure high-temperature equation of state of graphite from Monte Carlo simulations

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ABSTRACT

The thermoelastic behavior of graphite is experimentally accessible in a limited range of pressures and temperatures. Here we perform Monte Carlo simulations based on the accurate long range carbon bond-order potential (LCBOPII) in order to study graphite in a wider range of thermodynamic conditions. We present the volume-pressure equation of state and related thermoelastic properties up to 4000 K and 20 GPa.

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1. Introduction

Graphite is the most stable phase of carbon at ambient conditions. It is a strongly anisotropic material, composed of honeycomb carbon layers held together by weak interactions. The boundary of the thermodynamic stability with respect to diamond ranges from ~ 1.7 GPa at room temperature up to ~ 15 GPa at 4000 K. However, graphite is metastable over a large pressure range beyond the graphite-diamond boundary. In these regions there is evidence for transitions to (metastable) carbon phases other than diamond [1–4]. The graphite phase is very stable at high temperature, having a melting line being located around 4000 K [3,5,6].

The compressibility of graphite at room temperature has been extensively investigated by Raman and X-ray experiments [7–9,2]. The dependence of compressibility on temperature has been addressed only very recently by means of neutron diffraction techniques [10] in the limited pressure-temperature range of 0–6 GPa and 0–1250 K.

Here we use Monte Carlo simulations of a model for carbon based on the of the long range carbon bond order potential (LCBOPII potential) [11] to study graphite in the pressure-temperature range of 0–20 GPa and 0–4000 K. LCBOPII is an accurate, state-of-the-art, empirical potential for carbon. It

accounts for covalent bonds in the various hybridization forms, but also for weaker long-range interactions such as those between graphite layers [12]. The use of LCBOPII enable us to provide data for the compressibility over a wide range of pressures and temperatures. This information, that is relevant for modeling the carbon phase diagram, as well as for the synthesis of graphite intercalation compounds [13,14], is not easy to access by other means. Not only there is a lack of experimental data above 1500 K, but also the most common large scale ab-initio simulation methods, like density functional theory methods with the local density approximation (LDA) or the generalized gradient approximation (GGA), are not able to describe properly the weak interaction between layers in graphite [15]. The latter reference also demonstrates that more accurate methods in the framework of DFT, capable to describe weak interactions, do exist. However, presently they are computationally too expensive to perform large-scale, finite-temperature simulations.

The outline of the paper is as follows. In Section 2 we give the details of our simulation approach; in Section 3 we compare our results to available experimental data; in Section 4 we present our calculated pressure-volume equation of state up to 4000 K, we discuss the temperature dependence of the bulk-modulus and its pressure derivative, and finally we

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propose a parametrization of our results valid up to 3000 K; in Section 5 we make a summary of our results.

2. Methods and models

We performed Monte Carlo (MC) simulations of a hexagonal graphite sample of $N = 288$ particles in a periodic cell, arranged in four sheets with ABAB stacking. We model the carbon–carbon interactions with the LCBOPII potential [11]. LCBOPII includes a weak, long-range (up to 0.66 nm) interaction, yielding a graphite interplanar distance of 0.335 nm, and binding energy of 25 meV per atom. To simulate the isothermal–isobaric ensemble, we employed a standard NpT–MC scheme (see e.g. [16]). As graphite is a strongly anisotropic layered material, it is necessary to perform independent volume moves in the cartesian directions (x, y, z). For each (N, p, T) state point we performed simulations of 2×10^4 MC cycles, each MC cycle corresponding to N single particle moves. The volume moves were performed with an average frequency of one every five MC cycles. Each simulation has been performed on well-equilibrated samples (2.5×10^3 MC cycles or more). We use Kelvin, nm, and GPa as units of temperature, length and pressure respectively. To compare to experiments at ambient pressure and room temperature, we perform simulations at $p = 0$ GPa and $T = 300$ K.

At constant temperature, the volume change in solids under high pressure can be described well by the third-order Birch–Murnaghan equation of state [17,18]:

$$p(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \times \left[1 + \frac{3}{4} (B'_0 - 4) \left(\left(\frac{V_0}{V} \right)^{2/3} - 1 \right) \right] \quad (1)$$

where the free parameters are the equilibrium volume V_0 , the bulk-modulus $B_0 = -\frac{1}{V} \frac{\partial V}{\partial p} \big|_{p=0}$, and its derivative with respect to pressure $B'_0 = \frac{\partial B_0}{\partial p} \big|_{p=0}$.

In order to include the dependence of the pressure on the temperature, we fitted a series of $p(V)$ curves at different temperatures with Eq. 1, yielding the temperature dependence of the fitting parameters $V_0(T)$, $B_0(T)$ and $B'_0(T)$. This point will be discussed in detail in Section 4.

3. Comparison with experiments

In this section we compare our simulation results for the equation of state with available experimental data, mostly at low temperature. In Fig. 1 we present the volume–pressure equation of state up to 20 GPa. LCBOPII appears to reproduce well the experimental data, especially the most recent ones by Hanfland et al. [9]. In Fig. 2 we plot a/a_0 and c/c_0 as computed with LCBOPII and as reported by experimental investigations [7–9]. With a we indicate the length of the in-plane primitive vectors, and with c the length of primitive vector in direction perpendicular to the planes (i.e. twice the inter-layer distance for ABAB graphite). The subscript “0” labels the values at ambient pressure.

The LCBOPII results for a/a_0 fall on top of the experimental data. The c/c_0 curve is also close to experimental data, although it seems that the inter-planar repulsion in LCBOPII

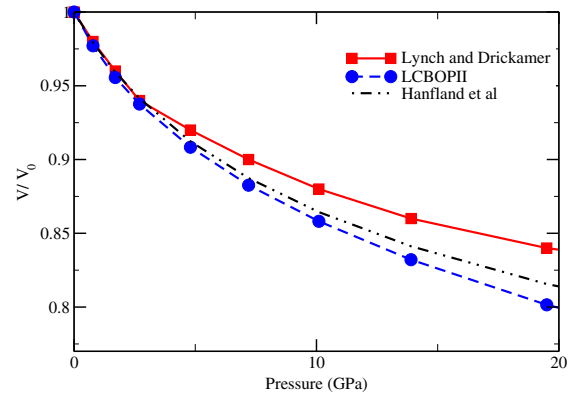


Fig. 1 – Volume-pressure equation of state of graphite up to 20 GPa at room temperature. Solid (red) and dash-dotted (black) lines are taken from references [7] and [9], respectively. The LCBOPII MC data are represented by the dashed (blue) line. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

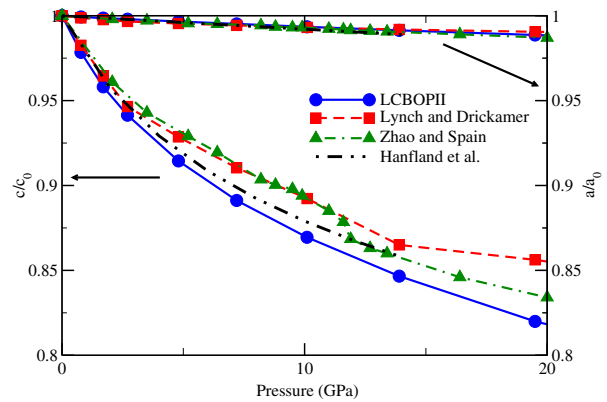


Fig. 2 – Relative variation of the in-plane lattice parameter a/a_0 (top lines) and perpendicular lattice parameter c/c_0 (bottom lines) for graphite under a pressure at ambient temperature as a function of pressure in the range 0–20 GPa. LCBOPII results (solid line, blue) are compared to the experimental data of Ref. [7] (dashed, red), [8] (dashed-dotted, green), and [9] (dash-dotted-dotted, black). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

is slightly too soft. Note that all recent experimental results either stop or have a kink between 12 and 18 GPa. This discontinuity is attributed to a phase transition to “cold-compressed graphite”. The nature of this phase is still not clear. Although Yagi et al. [2] identify the new phase as hexagonal diamond [1], it has recently been suggested that it may correspond to the “M-carbon” phase [4]. Our simulations are not expected to show evidence of a transition, as the transition requires the crossing a significant free energy barrier. This barrier has a two-fold origin: firstly, the transition has an intrinsic barrier due to the presence of a two-phase interface, and secondly the rectangular simulation box employed in our

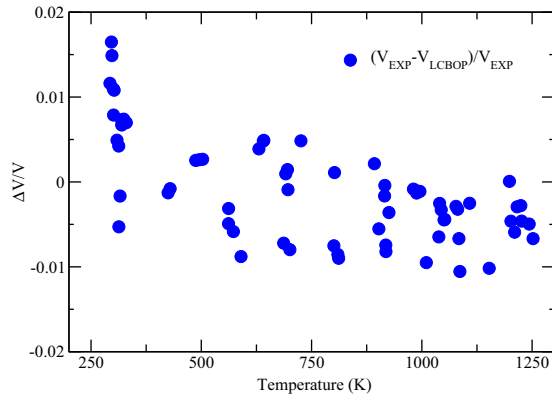


Fig. 3 – Relative errors $\Delta V(p, T)/V_{\text{EXP}}(p, T)$, where $\Delta V = V_{\text{EXP}} - V_{\text{LCBOPII}}$. V_{EXP} are experimental values of the volume taken from Ref. [10], corresponding to pressures ranging from 0 to 6 GPa.

simulation may not be commensurate with the crystal structure (triclinic, monoclinic, or other) of the “cold-compressed graphite” phase. Moreover, even if the final structure is commensurate with a rectangular box, like in the case of hexagonal diamond, it may happen that the transformation path involves the formation of monoclinic structures as intermediate step [19]. All these factors prevent the observation of a large class of phase transitions in our model for graphite.

The volume per particle ($V(p, T)$) predicted by the LCBOPII model under the simultaneous application of pressure and temperature has been compared to the experimental results of Lowitzer et al. [10]. A summary of the results is given in Fig. 3, where we show that the relative error on the volume is smaller than 1%, except for a few points where it is close to 2%. Overall, LCBOPII appears to be able to reproduce the volume per particle with good accuracy in the whole range of pressures and temperatures where experimental data are available. This indicates that the weak interactions and the inter-planar repulsion are well described by our potential.

4. High temperature equation of state

We present in Fig. 4 the calculated volume-pressure equation of state of graphite at temperatures of 100, 500, 1000, 2000, 3000, and 4000 K, namely almost up to the melting temperature of graphite, 4250 K according to LCBOPII [6]. The pressure range is 0–20 GPa up to 2500 K, and 2–20 GPa for higher temperatures. Indeed, at 3000 K the thermal energy is so high that the layers of graphite detach, if no pressure is applied. The experimental sublimation temperature for graphite in vacuum is around 3000 K [5], a value consistent with the LCBOPII interlayer instability. These equation of state can be fitted with the third-order Birch–Murnaghan equation of state (Eq. 1) to obtain the bulk modulus (B_0), its pressure derivative (B'_0), and the equilibrium volume (V_0) at different temperatures. However, above 2500 K it has been impossible to assign an accurate value to B_0 and B'_0 . Indeed, in this temperature range the $p(V)$ curves of graphite can be equally well fitted by the Birch–Murnaghan equation with different pairs of B_0 and B'_0 parameters, preventing the attribution of a meaningful

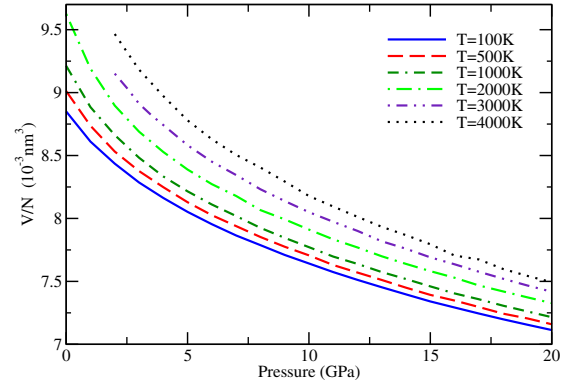


Fig. 4 – LCBOPII volume-pressure equation of state of graphite up to 4000 K. We plot the volume per particle $V/N(10^{-3} \text{ nm}^3)$ at temperatures of 100, 500, 1000, 2000, 3000, and 4000 K. The curves with higher temperature are the ones with larger volume. Note that at 3000 K and above there are no ambient pressure data.

physical value for those quantities. The resulting temperature dependence of B_0 , B'_0 , and V_0 is shown as symbols in Figs. 5–7, respectively.

In order to introduce the dependence on temperature in the Birch–Murnaghan equation of state (Eq. 1), we interpolated the $V_0(T)$, $B_0(T)$, and $B'_0(T)$ data with simple functional forms. The use of a point-wise temperature interpolation of the Birch–Murnaghan equation (Eq. 1) is not the only possibility to get a $p(V, T)$ equation of state. In high-pressure physics a large number of equations of state has been proposed. Lowitzer et al. [10] discuss other possibilities for the case of graphite.

As shown in Figs. 5 and 6, the $V(T)$ and $B_0(T)$ data are well represented by a quadratic curve. The $B'_0(T)$ data instead could not be fitted with a low-order polynomial. We define $B'_0(T) = a + b * T + c * e^{T/d}$ as a fitting curve. This form is not based on any physical ground, and it is chosen because it fits well the data-points. The resulting $p(V, T)$ parametrization of our simulation data in the range 0–20 GPa and 0–2500 K is

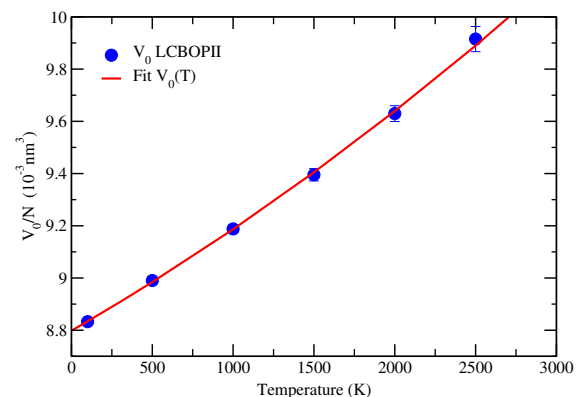


Fig. 5 – Change in the equilibrium volume $V_0(10^{-3} \text{ nm}^3)$ as a function of temperature. The data have been fitted with the quadratic curve (solid line) reported in Eq. 3.

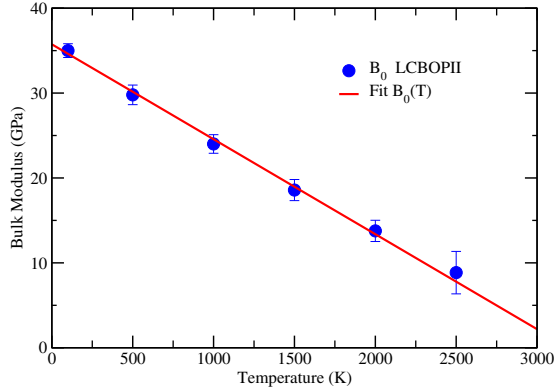


Fig. 6 – Bulk modulus B_0 as a function of temperature. The data have been fitted with the quadratic curve reported in Eq. 4. The low temperature values compare well with the experimental results reported in Table 2.

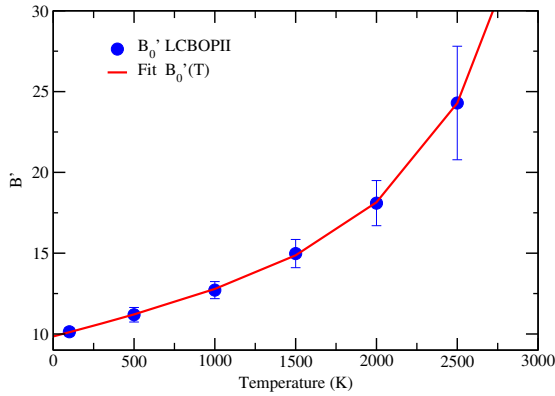


Fig. 7 – Derivative of the bulk modulus over pressure (B'_0) as a function of temperature. The solid line is the interpolating line reported in Eq. 5. The low temperature values compare well with the experimental results reported in Table 2.

$$p(V, T) = \frac{3B_0(T)}{2} \left[\left(\frac{V_0(T)}{V} \right)^{7/3} - \left(\frac{V_0(T)}{V} \right)^{5/3} \right] \times \left[1 + \frac{3}{4} (B'_0(T) - 4) \left(\left(\frac{V_0(T)}{V} \right)^{2/3} - 1 \right) \right] \quad (2)$$

Table 1 – Value of the parameters used in Eq. (3)–(5) to fit the temperature dependence of the equilibrium volume V_0 , of the bulk modulus B_0 and of its pressure derivative B'_0 , respectively.

| Parameter | Value |
|-----------|--|
| $a_1 =$ | $8.79831 \times 10^{-3} \text{ nm}^3$ |
| $a_2 =$ | $3.56 \times 10^{-7} \text{ nm}^3$ |
| $a_3 =$ | $3.23 \times 10^{-11} \text{ nm}^3$ |
| $b_1 =$ | 36.27 GPa |
| $b_2 =$ | $-1.321 \times 10^{-2} \text{ GPa K}^{-1}$ |
| $b_3 =$ | $9.45 \times 10^{-6} \text{ K}^{-2}$ |
| $c_1 =$ | 9.7356 |
| $c_2 =$ | $2.41 \times 10^{-3} \text{ K}^{-1}$ |
| $c_3 =$ | 1.12110^{-1} |
| $c_4 =$ | 577.4 K |

where the temperature-dependent parameters are given by Eqs. (3)–(5) with the fitting parameters of Table 1.

$$V_0(T) = a_1 + a_2 T + a_3 T^2 \quad (3)$$

$$B_0(T) = b_1 - b_2 T + b_3 T^2 \quad (4)$$

$$B'_0(T) = c_1 + c_2 T + c_3 e^{T/c_4} \quad (5)$$

We stress that Eqs. (2)–(5) interpolate the LCBOPII pressures up to 2500 K, and should not be used to extrapolate data above 3000 K. As shown in Fig. 8, the relative error on pressures is of the order of few percent up to 2500 K, and up to 10% at 3000 K. Reference data at higher temperature can be found in Table 3. Finally, in Table 2 we show that our LCBOPII results for $V_0(T)$, $B_0(T)$, and $B'_0(T)$ compare well to existing experimental data.

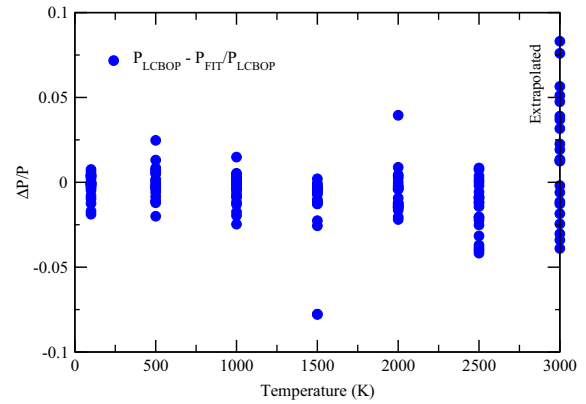


Fig. 8 – Relative error of the equation of state Eq. 2 with the temperature parametrization given in Eq. (3)–(5). For the temperature range where the data have been fitted (0–2500 K) the relative error $\Delta P(V, T)/P(V, T)$ is generally a few percent for pressures ranging from 0 to 20 GPa. The pressure should not be extrapolated above 3000 K, where the relative error is already of the order of 10%.

Table 2 – LCBOPII bulk modulus B_0 , and its derivative over pressure B'_0 , as extrapolated at 0 and 300 K, compared experimental data from Refs. [8–10]. The data of Ref. [8] has been reanalyzed in [10]. The error-bars are reported in brackets.

| | Fit T = 0 K | Fit T = 300 K | Exp [10] | Exp [9] | Exp [8] |
|-------------|-------------|---------------|----------|-----------|---------|
| B_0 (GPa) | 36.3(0.1) | 33.16(0.1) | ≈38 | 33.8(0.3) | 37(2.5) |
| B'_0 | 9.85(0.1) | 10.65(0.01) | ≈9 | 8.9(0.1) | 14(2) |

Table 3 – Volume per particle (10^{-3} nm^3) of graphite, as calculated with the LCBOPII potential.

| p/T | 1000 K | 2000 K | 3000 K | 4000 K |
|----------------------|--------------|--------------|-------------|-------------|
| $p = 2 \text{ GPa}$ | 8.66(0.01) | 8.90(0.015) | 9.15(0.02) | 9.47(0.025) |
| $p = 5 \text{ GPa}$ | 8.26(0.001) | 8.39(0.01) | 8.58(0.015) | 8.78(0.02) |
| $p = 10 \text{ GPa}$ | 7.77(0.0075) | 7.91(0.01) | 9.05(0.01) | 8.18(0.015) |
| $p = 15 \text{ GPa}$ | 7.46(0.0075) | 7.58(0.0075) | 7.69(0.01) | 7.79(0.01) |
| $p = 20 \text{ GPa}$ | 7.46(0.005) | 7.33(0.0075) | 7.42(0.01) | 7.49(0.01) |

5. Conclusions

The thermodynamic properties of graphite under extreme conditions of temperature and pressure are of fundamental interest for different fields, from geology to crystal growth, but very difficult to access experimentally. We have shown that the equation of state and thermoelastic properties of graphite in the pressure-temperature range where experimental data are available are reproduced to a high accuracy by means of Monte Carlo simulations based on the accurate empirical potential LCBOP. We have provided a parametrized equation of state and values of the bulk modulus and its derivatives in the unexplored regime, up to temperatures of 4000 K and pressures of 20 GPa. Further we find a sublimation temperature of about 3000 K at zero pressure. We believe that our results are relevant in different fields, in particular for the design and understanding of graphite-based strong materials.

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