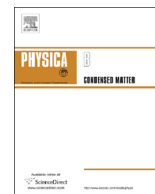




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# Refined phase coexistence line between graphite and diamond from density-functional theory and van der Waals correction



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## ABSTRACT

In the present paper, we provide the refined pressure–temperature phase coexistence line between graphite and diamond with van der Waals (vdW) energy corrected density-functional theory and quasi-harmonic approximation. A systematic comparison of the generalized gradient approximation (GGA) results for the lattice-related properties, phonon dispersion curves, and thermodynamic properties of graphite and diamond with and without vdW correction is presented. It is shown that adding the vdW interactions over the GGA exchange–correlation energy is positively necessary to obtain the reliable phase coexistence line between graphite and diamond, as compared with the experimental data. The 0 K phase transition pressure calculated with the GGA+vdW formalism is 1.6 GPa, which is sufficiently close to the value of 1.4 GPa extrapolated from the experimental values. We find the flattening of the coexistence line at low temperatures below  $\sim 300$  K with GGA+vdW as well as GGA. The slope of the coexistence line calculated by the GGA+vdW approach is  $2.5 \times 10^{-3}$  GPa K<sup>-1</sup> placed within the experimental value range.

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## 1. Introduction

The two major allotropes of the element carbon, graphite and diamond, are widely used in a variety of industrial application fields [49]. Graphite is remarkable for technically important materials such as extremely strong fibers, easily sheared lubricants, gas-tight barriers, and gas adsorbers [49]. Moreover, recent research boom on graphene (single graphite sheet), regarded as atomically thin robust components for nanoelectronic devices and as nanoscale building blocks for new materials [44,12,1], has revived the importance and interest of graphite. On the other hand, Diamond also has outstanding properties like unusually high index of refraction, extremely resistant to neutron radiation, extremely high strength and rigidity, and the highest atom-number density [49].

The major difference of material properties between graphite and diamond is in the hardness: diamond is by far the hardest-known material, while graphite is one of the softest materials. Such extreme difference in the hardness is related to the unusual chemical properties of the carbon atom. It is well known that when carbon atoms bond together to form solids or molecules, the

bonding is covalent and can take several forms: the  $sp^3$ ,  $sp^2$  and  $sp$  orbital bonds. In the case of  $sp^3$  bonding, the four  $sp^3$ -tetragonal hybrid orbitals have identical shape and form strong covalent  $\sigma$  bonds and thus  $sp^3$  orbital is a key to form diamond and aliphatic compounds. Meanwhile, in the case of  $sp^2$  bonding the three  $sp^2$ -trigonal hybrid orbitals originated from the  $s$ ,  $p_x$ , and  $p_y$  orbitals on each carbon also form covalent  $\sigma$  bonds in the same plane, resulting in a  $120^\circ$  bond angle and the well-known honeycomb plane layer. The remaining  $p_z$  orbital, a delocalized non-hybridized electron, is directed perpendicularly to the plane of the three  $sp^2$  orbitals and forms a weak  $\pi$  bond with each of its neighbors. [1,15] The delocalized electrons can move readily from one side of the plane layer to the other side but difficult to move from one layer to another. The  $sp^2$  bonding appears in highly anisotropic crystal structure such as graphite and aromatic compounds. In the graphitic structure, moreover, there is a weak van der Waals (vdW) bonding between graphite sheets, giving rise to a lubricity of graphite. It should be noted that the reasonable treatment of the weak  $\pi$  and vdW bondings in the carbon materials, especially the graphitic materials, has been challenging over the past decades.

Unlike graphite, diamond is very rare and considered the most valuable mineral, and thus many attempts were made to synthesize diamond by trying to duplicate nature, i.e., volcanic shaft at high pressure and high temperature where graphite transformed

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into diamond (see Refs. [49,15] for historical reviews.) Here the research focus was on the estimation of the graphite–diamond phase diagram. During the first half of 20th century, some preliminary conclusions on that were obtained based on the thermodynamic arguments: the temperature of the graphite–liquid–vapor triple point is around 3000 K, and the lowest pressure at which diamond would be against graphite around 1.3 GPa at 0 K, 2 GPa at 500 K, and 4 GPa at 1200 K [15]. In 1955, it was concluded by Berman and Simon [3] that the best extrapolation on the  $P$ – $T$  data of the phase coexistence between graphite and diamond would be a straight line like  $P = a + bT$ . Soon after, Bundy and the co-workers had made extensive experiments to synthesize diamond by activating the graphite–diamond transformation with the use of several solvent–catalyst metals. The experimental data by Bundy's and other groups were extrapolated to the Berman–Simon straight line, getting different  $a$  and  $b$  in different temperature ranges:  $a$  (GPa),  $b$  ( $\times 10^{-3}$  GPa K $^{-1}$ ) and the corresponding temperature range (K) founded in the literatures are 0.71, 0.027, 1500–2300 in Ref. [6], 2.05, 0.023, 1600–1900 in Ref. [58], 0.7, 0.032, 1400–1700 in Ref. [57], and 1.94, 0.025, 1400–1900 in Ref. [26].

In order to design an effective catalyst that can decrease the phase transition pressure and temperature from graphite to diamond, an accurate phase coexistence line should be predicted by theoretical and/or computational method. One of the most successful computational methods in the past was based on a family of “long range carbon bond order potential” (LCBOP) [33,13,34,14,16,15]. Through a proper incorporation of the  $\pi$  bonding effect and vdW interactions, LCBOP had given the phase coexistence line close to the Berman–Simon line as well as the experimental data. However, LCBOP and other bond order potentials did not always give a correct description of all properties of interest because of their empirical nature. Recently Khaliullin et al. [27,28] made it possible to reproduce the slope of the  $P$ – $T$  line by employing a neural-network (NN) potential mapped into the density functional theory (DFT) potential energy surface (PES) within the generalized gradient approximation (GGA). The calculated phase transition pressure at 0 K, however, was overestimated by 3.3 GPa, due to inaccuracy of the underlying DFT PES as they mentioned. Although there were *ab initio* molecular dynamics (MD) studies to predict the stable phase of carbon at extreme high pressures and temperatures [52,11,23], any DFT study on the graphite–diamond phase diagram in the experimentally available pressure and temperature ranges could not be found by our literature searching. The reason why there were not DFT works for that might be that *ab initio* MD becomes computationally too demanding for the generation of long trajectories for large systems, and furthermore vdW correction over the DFT exchange–correlation energy for graphite sheets was not easy.

Phonon dispersions of graphite and diamond, key quantities to estimate the thermodynamic properties and phase coexistence line, can be calculated based on density functional perturbation theory (DFPT) [2]. Though the phonon dispersion of diamond was calculated by the DFPT method [46,68] as close to the experimental observations [64], those of graphite previously calculated by the DFPT and supercell method [38,45,59,9,50,41] were not perfect agreed with the experimental ones [36,39,35,18] because of non-inclusion of vdW interactions in our thought. Despite the numerous DFT works on graphite and diamond, the role of vdW interactions has not been examined systematically. With recent refinements [21,61,54,53,60], it is now possible to tackle this issue and estimate the importance of vdW interactions in graphite.

In the present work, we aim to perform first-principles calculations of the phase coexistence line between graphite and diamond in the pressure range from 0 to 20 GPa and in the temperature range from 0 to 3000 K within the GGA and GGA+vdW formalism.

Through the comparison between the GGA and GGA+vdW results, the necessity of including the vdW interactions is emphasized. The rest of this paper is organized as follows. In Section 2 we describe the theoretical background and the computational method. In Section 3 the results are presented and discussed. We summarize the conclusions of this work in Section 4.

## 2. Theoretical background and computational details

Through the present work, we have employed the pseudopotential plane-wave method as implemented in the ABINIT software package [65–67] to solve the Kohn–Sham equation within DFT [24,30], using the Troullier–Martins norm-conserving pseudopotentials [63] constructed by FHI98PP code [10].

### 2.1. GGA+vdW approach

It is well established through numerous previous studies that the local density approximation (LDA) for the exchange–correlation energy gives rise to the overbinding between atoms in solids and molecules, while GGA underestimates the binding. Thus, LDA (GGA) generally underestimates (overestimates) the experimental value of the lattice constant and overestimates (underestimates) the value of the bulk modulus. This trend is also true for the phonon dispersions: LDA (GGA) overestimates (underestimates) the phonon frequencies. In the materials where the weak vdW interaction plays a crucial role such as graphite, the situation worsened with GGA: the relative error in lattice constant is more than about 10% [20]. However, since it is known that when studying the phase transition, GGA gives more reliable prediction than LDA [25] (as also proved in this work), we preferred GGA rather than LDA.

In this work, we added the semi-empirical vdW energy suggested by Grimme [21] over the GGA exchange–correlation energy. Since at long distances the vdW interaction should approach the classical dipole–dipole interaction, which decays as  $-C_6/R^6$ , the vdW energy to be added to the DFT energy could be written as follows [21,61]:

$$E_{\text{vdW}} = -\frac{1}{2} \sum_{A,B} f_{\text{damp}}(R_{AB}, R_A^0, R_B^0) \frac{C_{6AB}}{R_{AB}^6}, \quad (1)$$

where  $R_{AB}$  is the distance between atoms  $A$  and  $B$ ,  $C_{6AB}$  the corresponding coefficient, and  $R_A^0$  and  $R_B^0$  the vdW radii. The short-ranged damping function  $f_{\text{damp}}$  that eliminates the  $R_{AB}^{-6}$  singularity at small distances can be a Fermi-type as

$$f_{\text{damp}}(R_{AB}, R_{AB}^0) = \frac{1}{1 + \exp \left[ -d \left( \frac{R_{AB}}{s_R R_{AB}^0} - 1 \right) \right]}, \quad (2)$$

where  $R_{AB}^0 = R_A^0 + R_B^0$ ,  $d$  is a damping parameter ranged from 12 to 45, and  $s_R$  is a scaling factor. The damping parameter defines the damping function steepness and the scaling factor determines the onset of the vdW correction in terms of the distance.

We used the Perdew–Burke–Ernzerhof (PBE) [47] parameterization for the GGA functional and tested the Perdew–Wang (PW92) [48] formalism for the LDA functionals in case studies. The vdW coefficients  $C_6$ ,  $R^0$ ,  $d$  and  $s_R$  for the carbon atom are found to be 1.75 J nm $^6$  mol $^{-1}$ , 1.452 Å, 20 and 0.75, respectively, by fitting the experimental data and post-Hartree–Fock binding energy data in the Grimme method [21]. Note that the  $C_6$  dispersion coefficients in graphite and diamond could be different because of the long-range electrodynamic response effects [62].

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