Semiempirical approach to the energetics of interlayer binding in graphite

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The interlayer binding energy of graphite is obtained by a semiempirical method in which *ab initio* calculations based on the density functional theory (DFT) are supplemented with an empirical van der Waals (vdW) interaction. The local density approximation (LDA) and generalized gradient approximation (GGA) are used in the DFT calculations, and the damping (or interpolation) function used to combine these DFT results with an empirical vdW interaction is fitted to the observed interlayer spacing and c-axis elastic constant. The interlayer binding energies calculated in the LDA and GGA are quite different, but the combined results are nearly the same, which may be a necessary condition and provide reinforcements for validating the method. The present results are also consistent with those obtained by the empirical method based on the Lennard-Jones potential, and both are in reasonable agreement with the recent experimental data. These results indicate that, in contrast to the prevailing belief, the LDA underestimates the interlayer binding energy of graphite.

I. INTRODUCTION

Graphite is a typical solid of layered structure and characterized by relatively weak interlayer binding compared to rather strong binding within the layers. The bonding due to threefold sp^2 hybridized orbitals is responsible for the strong binding within the layers and the resulting hexagonal network of carbon atoms provides a useful starting point in the studies of graphitic systems such as fullerenes and carbon nanotubes.[1] The weak interlayer binding is supposed to arise from the dispersion or van der Waals (vdW) interaction and the decrease in kinetic energy due to delocalization of partially occupied $2p_z$ orbital perpendicular to the graphitic planes. Two types of methods have been used to describe the vdW interaction in graphitic systems: one is based on the density functional theory (DFT) and the other on empirical potentials, mostly on the Lennard-Jones (LJ) potential. The recent work based on these methods and the relation between them have been discussed in some detail by Girifalco and Hodak.[2]

The standard approximations currently in use in the DFT calculations are the local density approximation (LDA)[3] and, to less extent, the generalized gradient approximation (GGA).[4–8] The DFT-LDA calculations for graphite have repeatedly given excellent results for the in-plane and even the c-axis lattice constants of graphite.[9–16] Some of these authors have also claimed that their predictions for the interlayer binding energy are reasonably well compared to experiments.[11–13,16] However, there has been confusion in quoting the experimental data given by Girifalco and Lad[17] and some corrections such as that due to thermal effect have been ignored in comparisons between theoretical predictions and experiments.[17–19] The apparent success of the LDA for the interlayer binding in graphite has obscured its ability to describe the vdW interaction, and thereby diminished motivation for further work. On the other hand, the semilocal approximation (GGA) badly failed to predict the c-axis lattice constant and interlayer binding energy of graphite,[15,20] but no further investigation has been made to clarify the reason for that. While the LDA (and GGA also) yields by

construction correct results for a system with uniform electron distribution, these approximations can not capture long-range vdW interaction in systems with sparse electron distribution and several challenges to incorporate vdW interaction in the DFT have been made.[21–29] Rydberg *et al.* have actually devised a tractable scheme for planar geometry[30] and applied it to graphite and other materials of layered structure.[20,31] Their calculations for graphite have provided an improvement over the LDA and GGA results in that the interlayer binding energy as a function of the interlayer separation shows a desired behavior expected from the presence of vdW interaction. However, their predictions for the characteristics of interlayer binding are quantitatively still unsatisfactory and no better than those predicted by the LDA calculations.

The empirical method based on the LJ potential has been used more extensively in the studies of structural properties of graphitic systems.[2,32,33] The potential parameters in this method have usually been determined empirically using experimental data. We also repeated such calculations for the purpose of comparisons. The method used in the present work is semiempirical and a combination of the earlier empirical method and *ab initio* DFT calculations. As noted earlier the standard approximations (LDA and GGA) in the DFT calculations do not account for the long-range part of vdW interaction. In the present semiempirical method we supplement such DFT calculations with an empirical vdW interaction.

II. RESULTS OF THE DFT CALCULATIONS

We performed *ab initio* total-energy DFT calculations for the most stable phase of graphite with *ABAB* stacking using the VASP code.[34] The details of the calculations are as follows. We employed the ultrasoft pseudopotential[35] with the outermost cutoff radius of 1.81 a.u. (1.63 a.u. for s state and 1.81 a.u. for p and d state), which provides a compromise between the conflicting requirements for convergence in the plane-wave expansion and psudopotential transferability.[36] The exchange-correlation energy functionals we used were

TABLE I. Results of the DFT calculations in various approximations for the equilibrium lattice constants (a_0, c_0), total cohesive energy (E_c), interlayer binding energy (ΔE_c) and c-axis elastic constant (c_{33}) of graphite with *ABAB* stacking and their comparisons with experiments. (Experimental values of E_c and ΔE_c are listed in the row corresponding to $T \sim 300$ K, but the temperatures are not explicitly given in the literatures.)

	a_0 (Å)	c_0 (Å)	E_c (eV/atom)	ΔE_c (meV/atom)	c_{33} (GPa)
LDA (this work)	2.441	6.64	8.90	27	30.4
LDA (Ref. 9)	2.47	6.73	7.70	⋯	54
LDA (Ref. 10)	2.459	6.828	8.83	82–136	56
LDA (Ref. 39)	2.448	6.752	9.04	81	⋯
LDA (Ref. 11)	2.453	6.873	8.60	30	13
LDA (Ref. 12)	2.451	6.72	8.80	25	24.3
LDA (Ref. 13)	2.45	6.60	⋯	20	⋯
LDA (Ref. 36)	2.443	6.679	9.00	⋯	⋯
LDA (Ref. 14)	2.448	6.784	8.88	⋯	40.8
LDA (Ref. 16)	2.44	6.62	⋯	25	⋯
GGA (this work)	2.461	∼9.0	7.87	∼3	∼0.8
GGA (Ref. 20)	2.47	>7.5	⋯	∼5	∼7
vdW-DF (Ref. 31)	2.47	7.52	⋯	24	13
Exp't. (0 K)	2.46[a]	6.674[a]	⋯	⋯	40.7[b]
Exp't. (∼300 K)		6.709[a]	7.37[c]	43[e] 35^{+15}_{-10}[f] 52 ± 5[g]	36.5[d]

[a]Ref. 40.
[b]Ref. 41.
[c]L. Brewer (unpublished) (as cited in Ref. 9).
[d]Ref. 42.
[e]Ref. 17.
[f]Ref. 18.
[g]Ref. 19.

that of Ceperley and Alder[37] as parametrized by Perdew and Zunger[38] in the LDA and that of Perdew and Wang[8] (PW91) in the GGA. The **k**-point sampling was made by using 56 special **k** points in the irreducible Brillouin zone generated from uniform $12 \times 12 \times 4$ mesh. The cutoff energy limiting the plane-wave basis set was chosen to be 358.2 eV in both the LDA and GGA calculations. The calculations were carried out for five values of the in-plane lattice constant a about 2.44 Å (LDA) and 2.46 Å (GGA), with the c-axis lattice constant c fixed at an appropriate value, and the equilibrium value of a (denoted a_0) was determined for each value of c using a polynomial fit. The value of a_0 determined in the LDA was 2.4406 Å for $c = 6.0$ Å and slightly increased up to 2.4417 Å for $c = 7.5$ Å, beyond which a_0 practically remained unchanged. So we fixed a at this saturated value for $c \geq 7.5$ Å. On the other hand, the values of a_0 in the GGA remained almost unchanged at 2.461 Å in the whole range of c (6 Å $\leq c \leq$ 15 Å) we considered. We also performed calculations for monolayer (graphene) and confirmed that the total energies calculated for large c smoothly converged, within 0.1 meV, to that of graphene. The total energies obtained in this way as functions of c were used to calculate the equilibrium lattice constants, total and interlayer binding energy, and c-axis elastic constant. The present and previous results of DFT calculations for these properties are summarized and compared to experiments in Table I.

We first note that the lattice parameters predicted by the LDA calculations are all in good agreement with experiments but the GGA fails to predict c-axis lattice parameter and interlayer binding energy. The total cohesive energies, E_c, calculated in the LDA and GGA are 10.154 and 9.266 eV/atom, respectively. These values were calculated with respect to the ground state energies, -145.3437 eV (LDA) and -146.0548 eV (GGA), of the nonspin-polarized carbon atom, which are used to generate pseudopotential in the VASP code.[34] However, the ground state of the carbon atom is a spin-polarized state[43] and we found, by the spin-polarized DFT calculations, the lowering in energy of 1.251 eV (LDA) and 1.401 eV (GGA) compared to the nonspin-polarized calculations. This value in the LDA is well compared to the corresponding result of 1.25 eV obtained by all-electron calculations.[43] The results for E_c of graphite with the atomic spin-polarization correction are now 8.903 (LDA) and 7.865 (GGA) in eV/atom, which are the values given in Table I. This LDA value is slightly smaller than 9.001 and 9.036 eV/atom obtained, respectively, by similar calculations based on the ultrasoft pseudopotential[36] and all-electron calculations with the use of Gaussian-type fitting function.[39] On the other hand, the present LDA result is slightly larger than another all-electron result of 8.878 eV/atom.[14] These small differences cannot be traced at this stage but may be attributed to either different computational accuracies or treat-

ments of the atomic ground-state energy, the latter of which are not explicitly given in the previous calculations. If we take into account the zero-point vibrational energy estimated as 0.166 eV/atom,[44] the present results for E_c are further lowered to 8.737 (LDA) and 7.699 (GGA) in eV/atom. Even if corrected in this way by including the zero-point vibrational energy, all the LDA results for E_c (except that of Yin and Cohen[9]) summarized in Table I are larger than the experiment value by 1.1–1.5 eV. It was suggested that the discrepancy comes mainly from the so-called multiconfiguration correlation which is expected to lower the atomic ground-state energy,[43] and the lowering in energy estimated from Hartree-Fock calculations was found to be ~1.4 eV relative to the spin-polarized results. Inclusion of this correction lowers E_c by the same amount and the resulting LDA values for E_c are now in good agreement with experiment. This agreement, however, must be marginal without more accurate estimate of the correction. On the other hand, the present GGA result of 7.865 meV/atom is more favorably compared to experiment (Table I), but inclusion of the HF multiconfiguration correlation correction together with the zero-point vibrational energy leads to a substantial underestimation of E_c. We also note that the present GGA result for E_c is in good agreement with the LDA result of Yin and Cohen[9] but this agreement should be accidental.

The atomic ground-state energy and zero-point vibrational energy discussed earlier are irrelevant in the calculations of the interlayer binding energy, ΔE_c, and c-axis elastic constant, c_{33}. Here, ΔE_c is defined as the energy (per atom) required to separate graphite into planes an infinite distance apart. The relative accuracy of the total energy as a function of the interlayer separation, $d=c/2$, is of primary concern in these calculations. The present results for the total energy show extremely smooth variations with d (see the DFT results in Fig. 1, which are the results for fixed values of a but essentially the same), indicating that the calculations are quite accurate and free from computational noise. Our LDA result for ΔE_c is consistent with those of Trickey et al.,[11] Schabel and Martins,[12] Charlier et al.,[13] and Wang et al.[16] All these results are somewhat smaller than experimental values of 35–52 meV/atom,[17–19] implying the need for taking account of vdW interaction which certainly plays a role of increasing ΔE_c as we discuss in the next section. In contrast, the large values of ΔE_c (>80 eV/atom) predicted by all-electron calculations[10,39] are difficult to interpret from physical point of view and should be an issue of computational accuracy. We also confirmed that the GGA yielded almost perfect in-plane lattice constant but completely failed to predict all the properties related to the interlayer binding.[15,20] Finally, the vdW version of the DFT (vdW-DF) of Rydberg et al.[31] gives qualitatively right character of the interlayer binding in graphite but the predicted c_0, ΔE_c, and c_{33} are not well compared to experiments. These results suggest that their vdW-DF still has room for improvement for quantitative purposes, and study on this type of density functional is in a rapid development. It is also expected that vdW-DF applicable to wider range of soft matter will be developed. Quite recently, Rydberg et al. have made a step toward this direction by extending their vdW-DF to general geometries and applied it to rare gas and benzene dimmer with moderate success.[45]
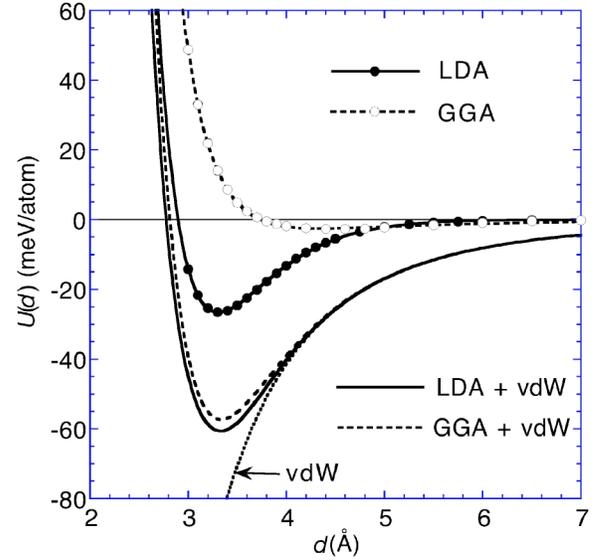
FIG. 1. Interlayer separation (d) dependence of the interlayer binding energies of graphite obtained by *ab initio* DFT calculations (LDA, GGA) and by the semiempirical method (LDA+vdW, GGA+vdW), in which the DFT results are combined with an empirical vdW interaction with $A=16.34$ eV Å^6 via Eq. (5). The solid and dashed lines drawn through the LDA and GGA data points are the fits by the Morse potentials given by Eqs. (2b) and (2a), respectively, and the dotted line (vdW) shows the asymptotic vdW contribution given by Eq. (4).

III. SEMIEMPIRICAL METHOD

In our semiempirical method we first performed DFT total-energy calculations for graphite with the in-plane lattice constant fixed at the experimental value, $a_0=2.46$ Å (C-C bond length is 1.42 Å). These results in the LDA and GGA, which we denote $U_{DFT}(d)$ together, as functions of the interlayer separation, $d=c/2$, are shown in Fig. 1. Here, $U_{DFT}(d)$ is the calculated total energy measured from that of graphene, or $U_{DFT}(d)$ in the limit of $d\rightarrow\infty$, which are -8.873 and -7.862 eV/atom in the LDA and GGA, respectively, relative to the spin-polarized ground-state energy of the carbon atom. As we have noted in the previous section, the constant energy shift arising from the different treatments of the atomic ground-state and zero-point vibrational energies is irrelevant in what follows. Highly accurate total-energy calculations are required for evaluating the interlayer binding energy which is only small fraction (typically less than 1%) of the total cohesive energy. It is convenient to express $U_{DFT}(d)$ in terms of an analytic function. For this purpose, we assumed that $U_{DFT}(d)$ can be written as

$$U_{DFT}(d) = \frac{1}{2}{\sum_{n=-\infty}^{\infty}}' V_{DFT}(nd) = \sum_{n=1}^{\infty} V_{DFT}(nd), \qquad (1)$$

where the prime on the summation implies to exclude the $n=0$ term and $V_{DFT}(R)$ is interpreted as the interaction between layers separated by R. We found that $V_{DFT}(R)$ was well represented by a Morse potential, which we write as

TABLE II. Parameters of the Morse potentials in Eqs. (2b) and (2a) fitted to the LDA and GGA rusults for the interlayer binding energy.

	M_0 (meV)	D_0 (Å)	$\tau(=\tau_1)$	$\Delta\tau(=\tau_2-\tau_1)$
LDA	26.5	3.311	8.065	0
GGA	2.3	4.407	2.523	12.47

$$V_{DFT}(R) = -\frac{M_0}{\tau_2 - \tau_1}\{\tau_2 \exp[-\tau_1(R/D_0 - 1)]$$
$$-\tau_1 \exp[-\tau_2(R/D_0 - 1)]\} \qquad (2a)$$

with $\tau_2 > \tau_1$. We have fitted the four parameters in the earlier potential to the calculated DFT data in the range between $d = 3$ Å and $d = 7.5$ Å by the least-mean-square method and found that the limiting case, $\tau_2 \to \tau_1 = \tau$, provided the best fit for the LDA results as in the case of C_{60} solid.[46] In this limit Eq. (2a) reduces to

$$V_{DFT}(R) = -M_0[1 + \tau(R/D_0 - 1)]\exp[-\tau(R/D_0 - 1)]. \qquad (2b)$$

Both potentials in Eqs. (2a) and (2b) have the minimum at $R = D_0$ with the depth of M_0. The fitted parameters are summarized in Table II. We note that $U_{DFT}(d) \approx V_{DFT}(d)$ since $U_{DFT}(d)$ saturates quite rapidly for large d and, as its consequence, $V_{DFT}(nd)$ almost vanishes beyond neighboring separation ($n \geq 2$) even for d as small as 3 Å. These results clearly indicate that the long-range part of vdW interaction between layers is not taken into account at all in both the LDA and GGA calculations.

To estimate vdW contribution not taken into account in the standard DFT calculations, we start with assuming that the vdW interaction between layers is given by the sum of those between carbon atoms, $\phi_{vdW}(r) = -A/r^6$. We further assume that carbon atoms can be treated as continuously distributing within the layer. This continuum model simplifies the calculation of the vdW interaction between layers and we have

$$V_{vdW}(R) = -\frac{\pi\rho A}{2R^4}, \qquad (3)$$

where R is the separation between layers as in Eq. (2a) and ρ is the number density of carbon atoms in the layer, i.e., $\rho = 4/(\sqrt{3}a_0^2)$. We note in passing that $V_{vdW}(R)$ given by Eq. (3) is the interaction energy per atom in the layer and calculated as the interaction between a carbon atom in one layer and all those in the other. Girifalco et al. confirmed that there was not much difference between the discrete atom and the continuum models for graphite when the LJ potential with the same parameters were used.[32] We also confirmed that, if we are concerned only with the r^{-6} term as earlier, the difference is much smaller and the two models are practically the same. Then, the interlayer vdW interaction (per atom) of graphite can be calculated as
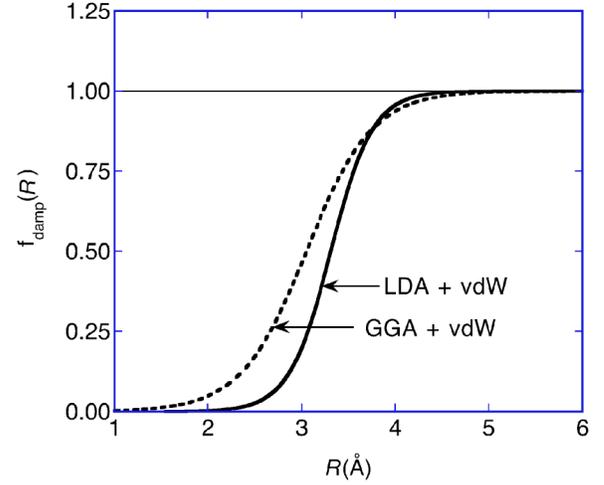
FIG. 2. Damping functions determined empirically and giving rise to the combined results (LDA+vdW, GGA+vdW) shown in Fig. 1.

$$U_{vdW}(d) = \sum_{n=1}^{\infty} V_{vdW}(nd) = V_{vdW}(d)\zeta(4), \qquad (4)$$

where $\zeta(4) = \pi^4/90 = 1.082\,32$, $\zeta(m)$ being the Riemann's zeta function defined by $\zeta(m) = 1 + 1/2^m + 1/3^m + \cdots$.

The interlayer binding energy, $U(d)$, of graphite with large d would be dominated by the vdW contribution given by Eq. (4). For smaller values of d, however, the asymptotic form given by Eq. (4) cannot be used even as the vdW contribution, if not mentioning the unphysical divergence at $d = 0$, and some modification must be made.[31] On the other hand, the DFT results for sufficiently small d would provide a good account of $U(d)$, because there would be substantial overlap of the electron density in the interlayer region of such a graphite. These observations lead us to write $U(d)$ of graphite with realistic values of d as in the following:

$$U(d) = \sum_{n=1}^{\infty} \{[1 - f_{damp}(nd)]V_{DFT}(nd) + f_{damp}(nd)V_{vdW}(nd)\}$$
$$\approx [1 - f_{damp}(d)]V_{DFT}(d) + f_{damp}(d)V_{vdW}(d)$$
$$+ V_{vdW}(d)\Delta\zeta(4), \qquad (5)$$

where $f_{damp}(R)$ is a function approaching to unity as R becomes large and to zero in the limit, $R \to 0$, and $\Delta\zeta(4) = \zeta(4) - 1$. In the second step in Eq. (5), we have assumed that $f_{damp}(R) = 1$ at $R = 2d$ and beyond that as actually it is for the relevant values of d (see Fig. 2). The function $f_{damp}(R)$ may be viewed as a damping function which modifies the asymptotic form of vdW interaction to yield realistic one at finite R. The use of such a damping function has been the common practice in the empirical method of calculating intermolecular forces, and various forms of $f_{damp}(R)$ have been proposed.[47,48] In such a method the damping function has been introduced for the atom-atom vdW interaction and usually treated as a universal function. The spirit of the present method is different from this in that the function $f_{damp}(R)$

plays another role of interpolating the interactions in both the extremes of large and small R, and thereby takes account of the contribution not included in the standard DFT calculations. Therefore, the damping function necessarily depends on the approximations used in the DFT calculations, but the resulting $U(d)$ given by Eq. (5) should be independent of the underlying DFT approximations if the interpolation scheme, including the functional form of $f_{damp}(R)$, is of physical significance as we have implicitly intended. This requirement may provide one of criterions for testing validity of the scheme, which is just the reason why we have used two approximations in the *ab initio* DFT calculations. Following Pacheco and Ramalho[49] and others we employed a complementary Fermi-Dirac type function as the damping function in Eq. (5):

$$f_{damp}(R) = 1 - \frac{1}{\exp[(R - D_W)/\delta] + 1}$$
$$= \frac{1}{1 + \exp[-(R - D_W)/\delta]}. \quad (6)$$

The two parameters of $f_{damp}(d)$ were determined by requiring that $U(d)$ given by Eq. (5) yields the observed interlayer distance d_0, i.e., $U'(d_0)=0$, and that the c-axis elastic constant calculated as $c_{33}=\rho d_0 U''(d_0)$ reproduces experimental result, where $U'(d)$ and $U''(d)$ represent the first and second derivatives of $U(d)$ with respect to d.

Similar interpolation schemes have also been used by Pacheco and Ramalho[49] and Hasegawa *et al.*[46] in their calculations of the interaction potential between C_{60} molecules, but the underlying spirits of their schemes are different from each other. In fact, the method of Pacheco and Ramalho have been based on the implicit assumption that the LDA works well in calculating the intermolecular potential of C_{60} at short range including the equilibrium separation of molecules. However, this is not the case and the LDA calculations account for only half of the intermolecular binding of C_{60},[46] and the situation is quite similar to that for graphite as we see later.

We used the value of $A=16.34$ eV $Å^6$ as the vdW constant, which has been obtained by Wu and Yang[47] as the appropriate value for carbon atoms in the sp^2 bonding state in their analyses of the intermolecular vdW interactions. The parameters of the damping function determined for this value of A and the resulting interlayer binding energies, $\Delta E_c = -U(d_0)$, are summarized in Table III. The corresponding $U(d)$ and $f_{damp}(d)$ as functions of d are illustrated in Figs. 1 and 2, respectively. We find that the LDA and GGA results for $U(d)$ are quite different (Fig. 1), but those combined by Eq. (5) with the empirical vdW contribution (LDA+vdW, GGA+vdW) are similar to each other. Such similarity is a necessary condition as we have discussed, and provides reinforcements for validating the present semiempirical approach. To see the dependence of the calculated ΔE_c on the empirical vdW interaction we also used the value of $A = 15.0$ eV $Å^6$. The results for this value are also given in Table III and we find that ΔE_c are reduced by ~4 meV/atom and more favorably compared to experiments. This value of

TABLE III. Parameters of the damping function [Eq. (6)] and the interlayer binding energies, $\Delta E_c = -U(d_0)$, obtained by the semiempirical method based on Eq. (5) (LDA+vdW, GGA+vdW). The results obtained by the empirical method based on the LJ potential are also given and the experimental value at 0 K was estimated from those at room temperature (given in Table I) as described in the text.

	D_W (Å)	δ (Å)	ΔEc (meV/atom)
LDA+vdW[a]	3.313	0.220	60.7
LDA+vdW[b]	3.312	0.209	56.8
GGA+vdW[a]	3.052	0.351	57.4
GGA+vdW[b]	3.035	0.335	53.9
LJ[c]			55.5
LJ[d]			53.9
Experiments			50–60

[a]$A = 16.34$ eV $Å^6$ is used as the vdW constant.
[b]$A = 15.0$ eV $Å^6$ is used as the vdW constant.
[c]The continuum model ($A = 17.7$ eV $Å^6$, $B = 2.64 \times 10^4$ eV $Å^{12}$).
[d]The discrete atom model ($A = 17.0$ eV $Å^6$, $B = 2.45 \times 10^4$ eV $Å^{12}$).

A falls between that appropriate for the sp^2 bonding ($A = 16.34$ eV $Å^6$) and that for sp^3 bonding[47] ($A = 13.18$ eV $Å^6$), and is close to that used by Girifalco and co-workers[17,32] ($A = 15.2$ eV $Å^6$) in their analyses for graphitic systems.

The experimental result for ΔE_c of Benedict *et al.*[18] was obtained from the analysis of collapsed multiwall carbon nanotubes and subject to large uncertainties as discussed by Zacharia *et al.*[19] We also note that the curvature effect and long-range vdW interaction could be important in comparing their results with those of graphite, but at this stage we cannot estimate the correction due to these effects without detailed knowledge of the experimental situation. The thermal effect must also be taken into account in quantitative comparisons between theoretical predictions and experiments.[17] We have estimated the increase in potential energy due to the longitudinal thermal vibration of layers along the c axis and found it to be ~13 meV/atom at room temperature. The total potential energy is increased by half of that since the vibrational potential energy comes from the interaction between layers. The cohesive energy is then lowered by ~6.5 meV/atom compared to that at 0 K. This estimate of the thermal effect is consistent with that suggested by Trickey *et al.*[11] Assuming room temperature and adding this value to the selected experimental ones,[17,19] we find that the interlayer binding energy to be compared with theoretical predictions at 0 K is roughly in the range, 50–60 meV/atom, as given in Table III. The present semiempirical results for ΔE_c somewhat depend on the underlying DFT approximations, but all of them are in that range of the corrected experimental results. We also find, as we have already noted, that the LDA results given in Table I (20–30 meV/atom) are much smaller than the experimental values in contrast to the previous belief.[11–13,16] This belief may partly be attributed to the misidentifications of the experimental data given by Girifalco and Lad.[17]

For the purpose of comparisons we also repeated empirical calculations of the interlayer binding energies by assuming the LJ potential, $\phi_{LJ}(r) = -A/r^6 + B/r^{12}$, for the interaction between carbon atoms. If we use the continuum model as we did in deriving Eq. (4), we can easily obtain the expression for $U(d)$ in this model

$$U_{LJ}(d) = -\frac{\pi\rho A\zeta(4)}{2d^4} + \frac{\pi\rho B\zeta(10)}{5d^{10}}, \qquad (7)$$

where $\zeta(10) = \pi^{10}/93555 = 1.000\,99$. The LJ parameters were fitted to the experimental values of d_0 and c_{33}. The interlayer binding energies, $\Delta E_c = -U_{LJ}(d_0)$, were also calculated by using the discrete atom model. Both results are summarized in Table III and found to be in reasonable agreement with the present semiempirical results as well as experiments. There is not much difference between the continuum and the discrete atom models in accordance with the previous finding[32] and the small difference was found to arise primarily through the evaluations of the repulsive r^{-12} term. The fitted parameters are slightly different from those of Lu *et al.*[50] ($A = 18.5$ eV Å^6, $B = 2.90 \times 10^4$ eV Å^{12}) obtained by the same method and part of the difference may be explained by the different experimental data used to fit the parameters. We note that the attractive r^{-6} term in the LJ potential does not provide a realistic dispersion interaction in the short range and the repulsive r^{-12} term is nothing but a convention not based on any physically significant motivation. Hence, the success of the empirical method based on the LJ potential should be the consequence of fortuitous compensation between the two terms in the relevant range, and the vdW constant, A, determined by the empirical method does not necessarily provide a realistic dispersion interaction. In fact, the values of A determined by the empirical method are somewhat larger than that used in the present semiempirical method.

IV. CONCLUSIONS

In conclusion, we have developed a semiempirical method of calculating the interlayer binding energy of graphite and obtained the results in reasonable agreement with experiments. The present results are also consistent with those obtained by the empirical method based on the LJ potential, although this agreement can be explained by the accidental compensation of the two terms in the LJ potential. We have confirmed from these results that, in contrast to the previous belief, LDA calculations substantially underestimate interlayer binding energy of graphite, ΔE_c, and the discrepancy can be explained by the substantial contribution due to vdW interaction not taken into account in this DFT approximation. The GGA generally provides improvements over the LDA for systems with sufficient overlap of electron distribution, but it also fails, to a greater extent, in predicting ΔE_c and c-axis lattice constant of graphite.

The present semiempirical method has already been used successfully, in a slightly different way, in the calculations of intermolecular interaction of C_{60}.[46] The method can also be applied to other systems if we have knowledge of vdW constant A as well as the basic experimental data such as the lattice constant and elastic constant. In fact, such knowledge is prerequisite for the semiempirical method to be used. A step toward wider applications is to treat vdW constant as another parameter in addition to those of the damping function, but such a treatment requires additional experimental data and ambiguity arising from multiparameter fitting procedure is unavoidable. The method is of limited use in such circumstances but, in the absence of accurate vdW-DF, provides a useful means of supplementing DFT approximations currently in use. The atom-atom LJ potential has most frequently been used in calculating the interactions among graphite, fullerenes and carbon nanotubes.[17,32,33] If we can express the interaction between layers in graphite in terms of carbon-carbon interaction, it may be used in place of the LJ potential. Such an approach is not successful at this stage but expected to be useful in the study of graphitic systems.

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[1] See, for example, M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).

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The experimental result for the interlayer binding energy, 260 erg/cm^2, given in the original paper had been misidentified by several authors as pointed out by Trickey *et al.* (Ref. 11) and it seems that the confusion still continues. The earlier result is given as 16.23 meV/Å^2 in different units and, by multiplying this by the area per atom in the layer, $1/\rho = \sqrt{3}a^2/4 = 2.62$ Å^2/atom, we have 42.5 meV/atom as given in Table I (also quoted in Ref. 19). This result has been quoted differently as 21 meV/atom (Ref. 11) and 23 meV/atom (Refs. 12 and 16). Also note, for the sake of further confidence, that the theoretical result, 330 erg/cm^2, obtained by the authors using the LJ potential ($A = 15.2$ eV Å^6, $B = 2.41 \times 10^4$ eV Å^{12}) is given as 54.0 meV/atom and consistent with the corresponding results in Table III.

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