

Theoretical and semiempirical correction to the long-range dispersion power law of stretched graphite

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In recent years, intercalated and pillared graphitic systems have come under increasing scrutiny because of their potential for modern energy technologies. While traditional *ab initio* methods such as the local density approximation give accurate geometries for graphite, they are poorer at predicting physical properties such as cohesive energies and elastic constants perpendicular to the layers because of the strong dependence on long-range dispersion forces. “Stretching” the layers via pillars or intercalation further highlights these weaknesses. We use the ideas developed by Dobson *et al.* [Phys. Rev. Lett. **96**, 073201 (2006)] as a starting point to show that the asymptotic C_3D^{-3} dependence of the cohesive energy on layer spacing D in bigraphene is universal to all graphitic systems with evenly spaced layers. At spacings appropriate to intercalates, this differs from and begins to dominate the C_4D^{-4} power law for dispersion that has been widely used previously. The corrected power law (and a calculated C_3 coefficient) is then applied to the semiempirical approach of Hasegawa and Nishidate (HN) [Phys. Rev. B **70**, 205431 (2004)]; however, a meaningful result cannot be obtained in this approach. A modified, physically motivated semiempirical method adding some C_4D^{-4} effects allows the HN method to be employed and gives an absolute increase of about 2%–3% to the predicted cohesive energy, while still maintaining the correct C_3D^{-3} asymptotics.

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I. INTRODUCTION

The graphite form of carbon is a discretely layered material. The sp^2 hybridized orbitals keep the layers in a rigid hexagonal pattern while the π_z orbitals help bind the layers. This weak interlayer binding gives graphite a small elastic constant (c_{33}) perpendicular to the plane which allows graphite to be “stretched” by pillaring (see, e.g., Ref. 1) and intercalation (see, e.g., Ref. 2) by other substances with potentially useful applications for hydrogen storage and other new energy technology.

Standard density functional theory³ (DFT) based approaches such as the local density approximation (LDA) and generalized gradient approximation⁴ (GGA) are known (see Ref. 5 for a summary) to have problems predicting the interlayer binding energy and interlayer elastic constant of graphite at its experimental layer separation. This is presumed to be caused by the inability of these functionals to accurately include the long-range London dispersion forces (often denoted as van der Waals forces in DFT papers, a notation we adopt to maintain consistency with other work). LDA/GGA correspondingly predict an exponentially decreasing binding energy for $D \gg D_0$ (where D is the interlayer separation distance and $D_0 = 3.337 \text{ \AA}$ is the experimental interlayer separation distance) as opposed to the correct power law behavior.

Various authors^{5–10} have proposed corrections to the LDA/GGA results that yield an additional long-range attractive layer-layer potential of the form C_4D^{-4} . By contrast, Dobson, White, and Rubio¹¹ (DWR) have shown that the asymptotic power law behavior for bigraphene is C_3D^{-3} due to its unusual band structure near the K point,^{12,13} suggesting that even these *ab initio* and semiempirical corrections to LDA/GGA miss some important physics.

In this work, we first show that the C_3D^{-3} power law is universal to many-layered graphitic systems with uniform

interlayer separation, including those with an infinite number of layers such as rare gas intercalated³⁰ or pillared graphite. We then use our energy expression to calculate the correct C_3 coefficient for bulk graphite and adapt the method of Hasegawa and Nishidate⁵ (HN) to employ a corrected power law, thereby permitting empirical modeling of the nonasymptotic region when $D \approx D_0$. This investigation suggests that the different power law and coefficient could have effects on semiempirical and other methods which assume a C_4D^{-4} decay of the dispersion potential, but that such an effect may dominate only for $D > D_0$.

II. ASYMPTOTIC POWER LAW

The success of the random-phase approximation (RPA) in generating a correlation energy functional through the adiabatic connection formula and fluctuation-dissipation theorem (ACFFDT) with the correct power law for long-range dispersion forces is well studied.^{14–22} For the case of graphene compounds, DWR¹¹ used a long-wavelength approximation to the bare density-density response (χ_0) function of graphene to prove a C_3D^{-3} dispersion potential for bigraphene while also reproducing known results for other materials through the same method.

If we assume (as in DWR) that the in-plane response of a graphene plane can be approximated for low surface-parallel wave number (q) by a homogenous system of similar physics, then we can write the RPA equation for the interacting density-density response (χ) as follows:

$$\begin{aligned} \chi_\lambda(q, z, z'; u) &= \chi_0(q, z, z'; u) \\ &+ \lambda \int dx dy \chi_0(q, z, x; u) w(q, x, y) \chi_\lambda(q, y, z'; u), \end{aligned} \quad (1)$$

where λ is a coupling constant ranging from 0 to 1 to be used

in the adiabatic connection formula. In the case of a layered system where each layer is highly localized in z space and separated by a distance D so that $\chi_0(q, z, z'; u) = \sum_{i=0}^{N-1} \bar{\chi}(q; u) \delta(z-z') \delta(z-iD)$, we may rewrite Eq. (1) as a tensor equation over layer indices i and j ,

$$\chi_\lambda(q, u; D) = \bar{\chi}(q, u) \mathbf{1} + \lambda \bar{\chi}(q, u) \bar{w}(q) \mathbf{\Omega}(qD) \chi_\lambda(q, u; D), \quad (2)$$

where $\bar{w}(q) = \frac{e^2}{2\epsilon_0 q}$ and $[\mathbf{\Omega}]_{ij} = \omega_{i-j} = e^{-qD|i-j|}$ ($0 \leq i, j < N$) so that $\chi_\lambda(q, z, z'; u) = \sum_{ij} [\chi_\lambda(q, u; D)]_{ij} \delta(z-iD) \delta(z'-jD)$.

We can use the ACFDFT to write the correlation energy per layer of a two-dimensionally homogeneous system as

$$E_c = -\frac{\hbar}{4\pi^2} \int_0^1 d\lambda \int_0^\infty du \int_0^\infty q dq \int_{-\infty}^\infty dz \int_{-\infty}^\infty dz' \times [\chi_\lambda(q, z, z'; u) - \bar{\chi}(q, z, z'; u)] \bar{w}(q) e^{-q|z'-z|}. \quad (3)$$

Remember that dispersion entirely comes from interlayer correlation effects and making use of the delta functions thus lets us calculate the energy per unit area per layer of an N -layered system through

$$U_{\text{vdW}} = -\frac{\hbar}{4\pi^2} \int_0^1 d\lambda \int_0^\infty du \int_0^\infty q dq [\mathcal{F}_\lambda(q, u; D) - \mathcal{F}_\lambda(q, u; \infty)], \quad (4)$$

where

$$\mathcal{F}_\lambda(q, u; D) = \bar{w}(q) \frac{1}{N} \text{Tr}[\chi_\lambda(q, u; D) \mathbf{\Omega}(qD)]. \quad (5)$$

Due to the high level of symmetry $\mathbf{\Omega}$ takes the form of a Toeplitz matrix. This allows us to make use of Szegő's theorem (Ref. 23 contains a good review of Szegő's theorem and its applications) to calculate the trace in the limit $N \rightarrow \infty$ (these equations can also be obtained by Fourier methods). Defining

$$\tau(\xi) = \sum_{k=-\infty}^{\infty} \omega_k e^{ik\xi} = \frac{\sinh(qD)}{\cosh(qD) - \cos(\xi)} \quad (6)$$

as the Fourier transform of the tensor elements of $\mathbf{\Omega}$, we then find

$$\begin{aligned} \mathcal{F}_\lambda(q, u; D) &= \frac{1}{N} \text{Tr}[(\mathbf{1} - \lambda \mathcal{C} \mathbf{\Omega})^{-1} \mathcal{C} \mathbf{\Omega}] = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\xi \frac{\mathcal{C} \tau(\xi)}{1 - \lambda \mathcal{C} \tau(\xi)} \\ &= \frac{\sinh(qD) \mathcal{C}}{\sqrt{[\cosh(qD) - \lambda \mathcal{C} \sinh(qD)]^2 - 1}}, \end{aligned} \quad (7)$$

where $\mathcal{C} = \bar{\chi}(q, u) \bar{w}(q)$.

For stretched graphitic systems, the dominant energy contribution of χ occurs when q and u are small so that we can approximate the bare response by its small q and u expansion, $\bar{\chi}(q, u) \approx -(2\hbar)^{-1} q^2 (v_0^2 q^2 + u^2)^{-1/2}$, as calculated by DWR and Eq. (3) of Ref. 24. We can now write $\mathcal{C} = -\kappa [1 + u^2/(v_0 q)^2]^{-1/2}$, where $\kappa = \frac{e^2}{4\epsilon_0 \hbar v_0} = 12.1$ for graphene where $v_0 = 5.7 \times 10^5 \text{ ms}^{-1}$.

If we make changes in variables $\theta = qD$ and $\sinh(\eta) = \frac{u}{v_0 q}$ [so that $\mathcal{C} = -\kappa/\cosh(\eta)$], then we can eliminate D from inside the integrals. This change in variables can also be made in the energy functional of any finite number of equally spaced graphene layers making the D^{-3} power law universal for evenly spaced systems. For these cases, we can make use of the fact that the van der Waals potential energy function will be an integral functional of $\mathcal{C}(q, u/[v_0 q])$ and e^{-qD} , which can be transformed into a D -independent integral in θ and η with a D^{-3} prefactor from the change in variables.

For the infinite-layered system, we thus obtain the energy expression

$$U_{\text{vdW}} = \frac{\hbar v_0}{4\pi^2 D^3} \int_0^1 d\lambda \int_0^\infty \theta^2 d\theta \int_0^\infty \cosh(\eta) d\eta \times \{\mathcal{F}_\lambda(\theta, \eta) + \kappa [\cosh(\eta) + \lambda \kappa]^{-1}\} \quad (8a)$$

$$= C_3 D^{-3} \quad (8b)$$

with

$$\mathcal{F}_\lambda(\theta, \eta) = \frac{-\kappa \sinh(\theta)}{\sqrt{[\cosh(\theta) \cosh(\eta) + \lambda \kappa \sinh(\theta)]^2 - \cosh(\eta)^2}} \quad (9)$$

and where the second term of Eq. (8a) arises from letting $D \rightarrow \infty$ in Eq. (9).

Equation (8a) is independent of D aside from the desired D^{-3} term so that $C_3 = D^3 U_{\text{vdW}}$ depends only on κ . For the graphitic case where $\kappa = 12.1$, we find

$$C_3 = 2.12 \times 10^{-2} \frac{e^2}{4\pi\epsilon_0} = 0.80 \text{ eV } \text{\AA}^3/\text{atom}. \quad (10)$$

By contrast, the C_4 coefficient predicted by Girifalco and Hodak⁶ is $C_4 = 9.7949 \text{ eV } \text{\AA}^4/\text{atom}$ which gives a potential approximately four times (0.079 versus 0.022 eV) as large as that of the inverse cubic power law at the experimental interlayer spacing $D_0 = 3.337 \text{ \AA}$ (equivalently, this means that $C_3 D^{-3} > C_4 D^{-4}$ for $D > 4D_0$).

III. NONASYMPTOTIC BEHAVIOR

While the $C_3 D^{-3}$ power law will certainly be the dominant contributor to the dispersion potential for $D \gg D_0$, the intermediate range (when $D \approx D_0$) will include a number of other correlation effects. These include the $C_4 D^{-4}$ potential from the atomic polarizabilities in the z direction in addition to a $C_{5/2}(D) D^{-5/2}$ potential from the metallic electrons promoted from the π_z orbitals due to layer overlap and hopping. As $C_{5/2}(D)$ entirely comes from overlap of the π_z orbitals, it ought to be derivable from an analysis of the band structure. It is expected to decay as an inverse exponential in D due to localization of the π_z orbitals. The C_4 coefficient should be largely independent of D although some electrons will be promoted to metallic and graphitic response.

With such a varied collection of correlation effects, it seems unlikely that any simple *ab initio* method will adequately include the physics in the intermediate range. Full

RPA-ACFFDT calculations would be expected to provide a seamless potential through a wide range of D ; however, these are extremely difficult with current numerical approaches: for example, the van der Waals energetics of the semiconducting layered boron nitride system have been successfully described using RPA energies,²² but graphite gives convergence difficulties.²⁵

IV. SEMIEMPIRICAL METHOD

LDA calculations are expected to yield fairly accurate total energies for graphene when the interlayer spacing is compressed from its equilibrium value. Likewise, the C_3D^{-3} dispersion potential is expected to be accurate for layer spacing much greater than that of equilibrium. The intermediate range is more difficult to predict with neither method dealing sufficiently with the physics in that region.

The method proposed in HN (Ref. 5) gives a fairly simple means (with minimal empirical contribution) of connecting the two regimes through the use of a fitting function. It is a semiempirical approach as the fitting function has its parameters chosen by matching experimental values for the lattice spacing and elastic constant c_{33} . While this method predicts a reasonable value for the cohesion energy of graphite, it, as with other methods, does not exhibit the correct behavior in the tail due to the incorrect use of a C_4D^{-4} type dispersion law. In order to maintain consistency with this earlier work, we reexamine the major results of their paper utilizing the correct C_3D^{-3} dispersion law. To further maintain consistency, we use the parametrization of the LDA and GGA from the same paper.

A. Semiempirical approach with pure C_3D^{-3} dispersion

For our approach, we adapt Eq. (5) of HN to include the corrected form of the dispersion potential

$$U(D) = [1 - f_d(D)]U_{\text{DFT}}(D) + f_d(D)U_{\text{vdW}}(D), \quad (11)$$

where $U_{\text{vdW}}(D) = C_3D^{-3}$. Following HN, we use a Thomas-Fermi damping function,

$$f_d(D) = [1 + e^{-(D-D_W)/\delta}]^{-1}, \quad (12)$$

where D_W and δ are free parameters. The term involving $\Delta\zeta$ [Eq. (4)] is absent due to our C_3 coefficient being sourced from a bulk rather than a sum over pairwise potentials for multiple layers. $U^{\text{DFT}}(D)$ is the parametrized LDA or GGA potential taken from Eq. (2) of HN.

As in HN, we attempted to determine δ and D_W by ensuring that $\frac{d}{dD}U(D_0) = 0$ and $\frac{d^2}{dD^2}U(D_0) = c_{33}/(\rho D_0)$, where $c_{33} = 40.7$ GPa, $D_0 = 3.337$ Å, and $\rho = 0.382$ Å⁻² take their experimental values [from Ref. 26 for c_{33} and Ref. 27 for ρ and D_0]. Using $U_{\text{vdW}} = 0.80$ meV Å³ D^{-3} , we find that the HN fitting equations do not have a solution for the LDA or GGA. This lack of solution is not unexpected as the lack of other dispersion terms is expected to underestimate the dispersion for values of $D \approx D_0$.

B. Semiempirical approach with mixed C_3D^{-3} and \tilde{C}_4D^{-4} dispersion

While the C_3D^{-3} term will certainly dominate over C_4D^{-4} for $D \gg D_0$, we know that it insufficiently models the physics for $D \approx D_0$, which we believe to be the cause of the fitting problems with the HN method for the semiempirical method given in Sec. IV A above. The $C_4 = 9.795$ meV Å⁴ coefficient used in HN is derived from a $C_6 = 16.34$ meV Å⁶ coefficient calculated by Girifalco and Hodak⁶ and constructed to ensure good Lennard-Jones modeling for a wide variety of graphitic systems. As such, we propose to use its presumed accuracy for $D \approx D_0$ as a correction to our C_3D^{-3} van der Waals function in order to better include the intermediate range physics.

The simplest way to do this is to assume a correction to our function of the form \tilde{C}_4D^{-4} . The \tilde{C}_4 term is first introduced to cover the dispersion interaction due to the polarizability of the π_z and sp^2 electrons in the z direction perpendicular to the graphene planes and polarizability of the sp_2 electrons parallel to the plane. These contributions to the dispersion interaction do not require long-wavelength collective electronic motions and therefore¹¹ are presumably describable by conventional asymptotics. These interactions are not included in our C_3D^{-3} term, which is solely due to polarizability of the π_z electrons along the graphene planes. The \tilde{C}_4 term also has to account for the doped, metallic nature of the graphene planes near $D \approx D_0$ due to overlapping of electron bands arising from the hopping of electrons from layer to layer. The corresponding attraction depends on the doping level, which exponentially decays with D . While this is not a D^{-4} law, it does decay faster than D^{-3} and hence is reasonably represented.

Accordingly, we now choose \tilde{C}_4 so that the total van der Waals potential at the experimental lattice spacing remains the same in the two methods. This implies that

$$C_4D_0^{-4} = C_3D_0^{-3} + \tilde{C}_4D_0^{-4}, \quad (13)$$

which is true for $\tilde{C}_4 = 7.12$ meV Å⁴. This correction ensures that we maintain similar $D \approx D_0$ behavior while obtaining a correct power law for $D \gg D_0$. The van der Waals potential now takes the form

$$U_{\text{vdW}}(D) = C_3D^{-3} + \tilde{C}_4D^{-4}. \quad (14)$$

In order to ensure that Eqs. (11) and (12) correctly match the empirical data, we must set $\delta = 0.221$ and $D_W = 3.283$ for the LDA and $\delta = 0.340$ and $D_W = 3.019$ for the GGA when using the HN fitting function. Figure 1 shows the effect of this combined fit on both the LDA and GGA.

In Fig. 2, we show, for the LDA case, a more detailed comparison of three methods (the LDA, that of HN, and the second method proposed here). It is quite clear from the graph that the method proposed here with the extra \tilde{C}_4D^{-4} correction closely matches that of HN for $D \approx D_0$ but maintains different asymptotes for $D \gg D_0$. This suggests that the $C_3D^{-3} + \tilde{C}_4D^{-4}$ approximation, while a somewhat crude model of the true physics in the electron density overlap region, is able to maintain consistency with other methods.

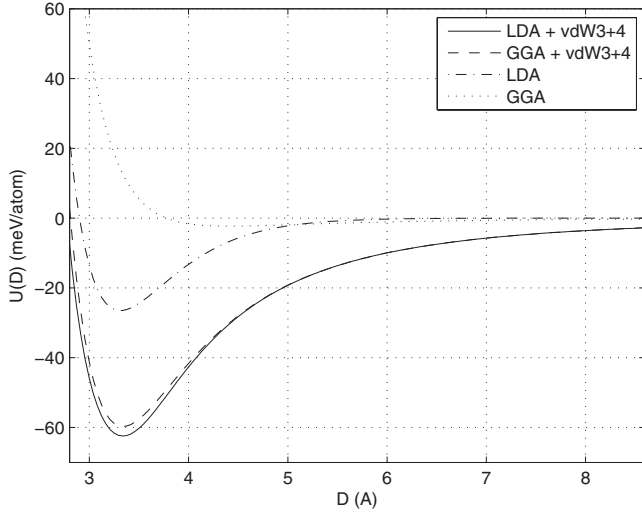


FIG. 1. Potential energy versus lattice spacing (D). The solid line is the LDA corrected by the $C_3D^{-3} + \tilde{C}_4D^{-4}$, while the dashed line is the corrected GGA. The dash-dotted and dotted lines are the pure LDA and GGA, respectively.

The most “measurable” effect of the semiempirical approach is the interlayer cohesive energy $\min[U(D)]$. Table I summarizes the results from HN with the addition of the results calculated here. The power law, used as the sole dispersion term, does not give a valid cohesive energy due to the lack of a solution to the fitting function for both the LDA and GGA. The effect of the \tilde{C}_4D^{-4} correction to the C_3D^{-3} van der Waals functional on the cohesive energy is to give a very close cohesive energy to those predicted by HN, differing by only 1.7 eV for the LDA and 2.3 eV for the GGA or about 2%–3%.

V. CONCLUSIONS AND FURTHER WORK

In this paper, we have investigated the asymptotic dispersion potential of stretched graphite and found it to obey a

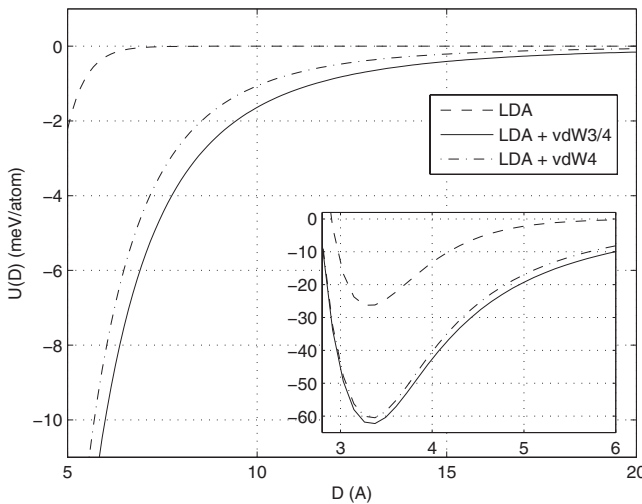


FIG. 2. Potential energy versus lattice spacing (D). The dashed line is the uncorrected LDA, the solid line is the LDA corrected by $C_3D^{-3} + \tilde{C}_4D^{-4}$, while the dashed dots are the LDA corrected by C_3D^{-3} as in HN. The inset shows the behavior near D_0 , while the main graph shows the different asymptotics.

TABLE I. Cohesive energies per atom calculated by various approximations (in –meV). The LDA/GGA in brackets refers to the DFT calculation employed as a base. GS refers to the base ground state DFT calculation while vdW4 refers to that method with a C_4D^{-4} correction (taken from HN using $C_6=16.34 \text{ eV \AA}^6$) and vdW3+4 has the combined correction $C_3D^{-3} + \tilde{C}_4D^{-4}$ proposed in this paper. The vdW3 method does not produce viable results and is left out.

Method	U_{coh}	
Expt. ^a	52.5 ± 5	
Expt. ^b	35_{-10}^{+15}	
	U_{coh} (LDA)	U_{coh} (GGA)
GS	26.5	2.3
GS+vdW4	60.7	57.4
GS+vdW3+4	62.4	59.7

^aExperimental results from Ref. 28.

^bExperimental results from Ref. 29

C_3D^{-3} type power law as opposed to the commonly employed C_4D^{-4} . This places it in the same class of power law as bigraphene but in a different class to layered insulators (D^{-4} power laws) and layered metals ($D^{-5/2}$). This result has important implications for semiempirical (and otherwise) corrections to the LDA/GGA that have employed an incorrect power law. The C_3D^{-3} behavior applies not only to graphite that is in an infinite stack of equally spaced graphene planes but also to the uniform stretching of any finite stack of graphene planes.

Furthermore, we have employed the corrected power law in the simple semiempirical method of Hasegawa and Nishidate⁵ and found that, used as the sole dispersion term, it will not allow a valid solution to the HN fitting function.

Reinclusion of a reduced \tilde{C}_4D^{-4} term to include other physics from the nonasymptotic regime allows the method to be employed and gives similar results to HN for $D \approx D_0$ while ensuring the correct asymptotic behavior is maintained. Its effect on the cohesive energy is fairly minimal with an absolute increase in the predicted cohesive energy of approximately 2%–3%.

While we believe that this power law (and the semiempirical correction to it) should be accurate and useful for large layer spacings as in nonmetallic intercalates and pillared systems, we are not convinced that it will be as accurate in predicting the behavior in the intermediate range of spacings without correction for other effects. Accurate RPA-ACFFDT calculations would provide a valuable benchmark for this and other methods. Until such a time as these are available, we hope that semiempirical techniques such as that discussed here should improve the accuracy of LDA and GGA calculations with widely spaced graphene layers.

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- ³⁰It can be shown that in the case of an insulating intercalate sitting *on* each graphene layer that the asymptotic form of the dispersion is $C_3 D^{-3}$, with C_3 unchanged from the nonintercalated but stretched bulk case. It seems highly likely that this result would be the same for a noninteracting insulating layer situated between the layers.