

## Van der Waals Density Functional for Layered Structures

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To understand sparse systems, we must account for both strong local atom bonds and weak nonlocal van der Waals forces between atoms separated by empty space. A fully nonlocal functional form [H. Rydberg, B. I. Lundqvist, D. C. Langreth, and M. Dion, *Phys. Rev. B* **62**, 6997 (2000)] of density-functional theory (DFT) is applied here to the layered systems graphite, boron nitride, and molybdenum sulfide to compute bond lengths, binding energies, and compressibilities. These key examples show that the DFT with the generalized-gradient approximation does not apply for calculating properties of sparse matter, while use of the fully nonlocal version appears to be one way to proceed.

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Calculations of structure and other properties of sparse systems must account for both strong local atom bonds and weak nonlocal van der Waals (vdW) forces between atoms separated by empty space. Present methods are unable to describe the true interactions of sparse systems, abundant among materials and molecules. Key systems, such as graphite, BN, and MoS<sub>2</sub>, have layered structures. While today's standard tool, density-functional theory (DFT), has broad application, the common local (LDA) and semilocal density approximations (GGA) [1–4] for exchange and correlation,  $E_{xc}[n]$ , fail to describe the interactions at sparse electron densities. Here we show that the recently proposed density-functional [5] with nonlocal correlations,  $E_c^{nl}[n]$ , gives separations, binding energies, and compressibilities of these layered systems in fair agreement with experiment. This planar case bears on the development of vdW density functionals (DF) for general geometries [6,7], as do asymptotic vdW functionals [8].

Figure 1 with its “inner surfaces” defines the problem: voids of ultralow density, across which electrodynamics leads to vdW coupling. This coupling depends on the polarization properties of the layers themselves, and not on small regions of density overlap between the layers, excluding proper account in LDA or GGA. For large interplanar separation  $d$ , the vdW interaction energy between planes behaves as  $-c_4/d^4$ , while LDA or GGA necessarily predicts an exponential falloff. Layers rolled up to form two (i) nanotubes with parallel axes a distance  $l$  apart interact as  $-c_5/l^5$ , or (ii) balls (e.g., C<sub>60</sub>), a distance  $r$  apart, as  $-c_6/r^6$ . If by fluke an LDA or GGA were to give the correct equilibrium for one shape, it would necessarily fail for the others. The simple expedient of adding the standard asymptotic vdW energies as corrections to the correlation energy of LDA or GGA also fails. The true vdW interaction between two close sheets must be (i) substantially stronger (Fig. 1), (ii) seamless, and (iii) saturate as  $d$  shrinks (Fig. 2).

Like earlier work directly calculating nonlocal correlations between two jellium slabs [14], the vdW density-

functional (vdW-DF) theory [5] used here exploits assumed planar symmetry. It divides the correlation energy functional into two pieces,  $E_c[n] = E_c^0[n] + E_c^{nl}[n]$ , where  $E_c^{nl}[n]$  is defined to include the longest ranged or most nonlocal terms that give the vdW interaction and to approach zero in the limit of a slowly varying density. The term  $E_c^0[n]$  is also nonlocal, but approaches the LDA in this limit. The two terms are approximated differently. Here the LDA is used for  $E_c^0[n]$ , as the LDA should be much more accurate with the principal longest range terms separated off. Ultimately, we plan to derive a gradient or GGA expansion appropriate to  $E_c^0[n]$ , but the resulting corrections are expected to be small. Thus, we use

$$E_c[n] \approx E_c^{LDA}[n] + E_c^{nl}[n]. \quad (1)$$

Long range terms are less sensitive to details of the system's dielectric response. Thus, very simple approximations for the dielectric function are made for  $E_c^{nl}[n]$ . We care to make the polarization properties of a single layer come out reasonably.

For systems with planar symmetry, the predominant component of the nonlocal-correlation energy  $E_c^{nl}$  giving the vdW forces can be determined simply by comparing the solutions of the Poisson equation  $\nabla \cdot (\epsilon \nabla \Phi) = 0$  and the Laplace equation  $\nabla^2 \Phi = 0$  [5]. The crux of the approximation is the use of a simple plasmon-pole model for the dielectric function,

$$\epsilon_k(z, iu) = 1 + \frac{\omega_p^2(z)}{u^2 + [v_F(z)q_k]^2/3 + q_k^4/4}, \quad (2)$$

where  $\omega_p^2(z) = 4\pi n(z)e^2/m$ , and  $mv_F(z) = [3\pi^2 n(z)]^{1/3}$  are functions of the local density  $n(z)$ . The 2D wave vector perpendicular to the  $z$  direction is  $\mathbf{k}$ ,  $iu$  is the imaginary frequency, and  $q_k^2 = k^2 + q_\perp^2$  mimics the 3D wave vector, with the  $z$  direction accounted for by the  $n(z)$  dependence and  $q_\perp$  taken as a constant.

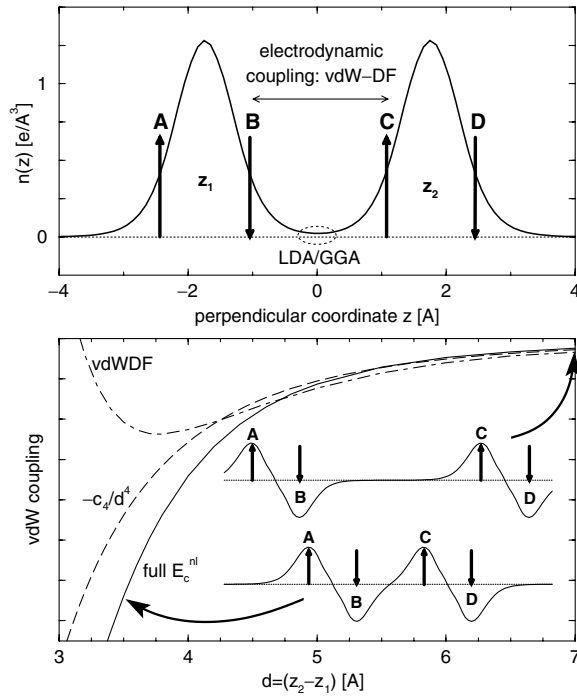


FIG. 1. Schematics of the vdW forces in sparse, layered materials. Top panel: Laterally averaged electron-density profile of two graphene layers at equilibrium separation  $d \approx 3.5$  Å. The dotted ellipse indicates the region determining the inter-layer interaction within LDA or GGA. It is unable to describe the true long range interaction (horizontal arrow) between correlated charge fluctuations (extrema illustrated by those of the finite-frequency charge response, and labeled by vertical arrows). Bottom panel: Full  $E_c^{nl}$  (solid curve) vs the asymptotic form of  $E_c^{nl} \rightarrow -c_4/d^4$  (dashed line). Also shown: Full ground-state interaction energy (dash-dotted line). Insets: Sketches of the correlated charge fluctuations for different layer separations, explaining why  $|E_c^{nl}| > c_4/d^4$ . In the asymptotic region (top inset), attractive interactions  $BC$  and  $AD$  are nearly canceled by the repulsive interactions  $AC$  and  $BD$ , leaving little more than the weak dipolar interaction. Near equilibrium separation (bottom inset), the repulsive interactions  $AC$  and  $BD$  remain specified by the layer separation  $d$ , but the relative strengthening of attractive interaction  $BC$  substantially overcompensates the relative weakening of the attractive interaction  $AD$ . At still smaller  $d$ ,  $E_c^{nl}$  becomes weaker and saturates (Fig. 2, inset).

Our scheme, applied to jellium surfaces in Ref. [5], is used here for layered systems. For simplicity we first focus on a two-layered system (e.g., two parallel graphene sheets) arranged perpendicular to the  $z$  axis at positions  $z = 0$  and  $z = d$ , respectively. The first step is to calculate the density in DFT with a suitable approximation, which we take to be an appropriate flavor of the GGA, and to average it in the lateral direction to yield  $n(z)$ . The next two steps represent the key to the success of our approximation. First, one calculates from first principles the perpendicular static polarizability  $\alpha$  of a single layer of the material (a graphene layer in this example) in the

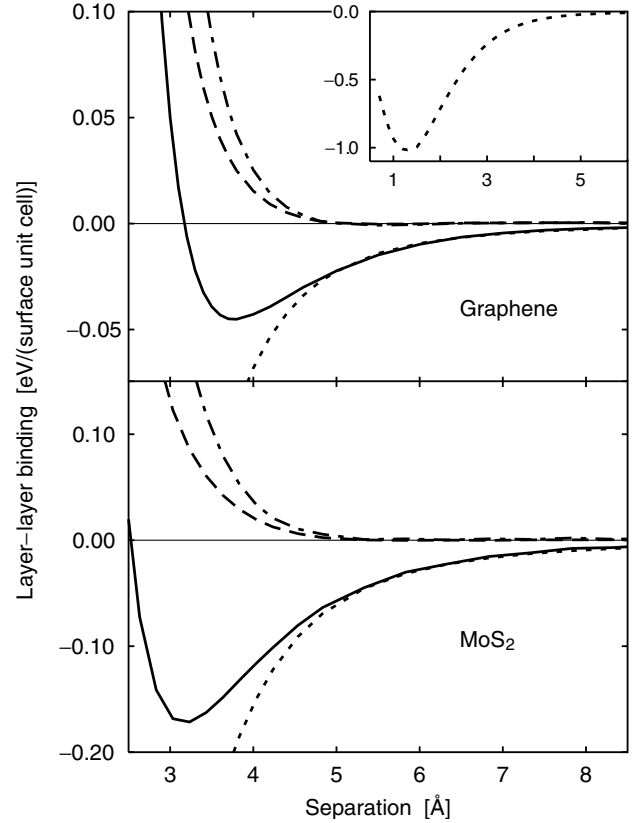


FIG. 2. Calculated vdW-DF results for the interlayer binding (adhesion) between two sheets of graphene (upper panel) and MoS<sub>2</sub> (lower panel) as functions of the interlayer separation  $d$ . In each panel it is compared (solid curves) with the underlying GGA (dashed curves), and with the adhesion in the absence of the vdW-DF term  $E_c^{nl}$  (dash-dotted curves) calculated using only the first two terms of Eq. (5) for  $E_{xc}$ . The nonlocal-correlation vdW contribution  $E_c^{nl}$  alone is shown separately (dotted curves). The figure shows that no binding results from exchange or local correlation; the vdW interactions provide adhesion in fair agreement with experiment (Table I). The inset shows that our calculated value of  $E_c^{nl}$  saturates for small  $d$  values.

ground-state DFT scheme with the above GGA flavor. Then one fixes the constant  $q_{\perp}$  so that dielectric model (2) gives precisely the same polarizability, that is,

$$\alpha = \frac{1}{4\pi} \int dz \left[ 1 - \frac{1}{\epsilon_0(z, 0)} \right]. \quad (3)$$

This step mitigates the errors introduced both by the lateral averaging and the dielectric model. The leading vdW interaction is proportional to an integral over the square of the dynamic polarizabilities. Previous work in the asymptotic limit [8] shows that simple, properly scaled dielectric functions giving the correct static polarizabilities form good approximations to the dynamic ones, hence giving accurate vdW interactions.

The correlation energy can be calculated from the charge response [15]. With planar symmetry only the

response to an arbitrarily charged sheet  $\rho \propto \exp(i\mathbf{k} \cdot \mathbf{r})\delta(z - z_-)$  placed at an offset  $z_-$  ( $z_- \ll 0$ ) from one end of the sample needs to be calculated. Integrating Poisson's equation with  $\epsilon$  as in (2), one finds the  $z$  component of the electric field  $E_z(z_+)$  at  $z = z_+ \gg d$ . Then  $E_c^{\text{nl}}$  is given by [5]

$$E_c^{\text{nl}} = -A \int_0^\infty \frac{du}{2\pi} \int \frac{d^2k}{(2\pi)^2} \ln \frac{E_z(z_+)}{E_z^0(z_+)}, \quad (4)$$

where  $A$  is the lateral area and  $E_z^0(z_+)$  is the electric field component from the charge sheet at  $z = z_-$  in the absence of the sample. In Eq. (4), the spatial dependences of the two  $E$  cancel in the ratio, leaving only the  $k$  dependence. For each of the bulk solids considered here, we apply this method to 32 and 30 layer slabs to give, by subtraction, a well converged per layer value of  $E_c^{\text{nl}}$ .

The approximation for the exchange energy functional  $E_x[n]$  should be consistent with our approximation for  $E_c^0[n]$ , that is a local or semilocal one. We use a version that best approximates exact density-functional exchange, namely, Zhang and Yang's [3] (ZY) "revPBE" [16] exchange functional  $E_x^{\text{ZY}}[n]$ , where the parameter controlling the large gradient limit in the PBE exchange functional [2] is fitted to exact density-functional exchange calculations. Unlike exchange [17] in PW91 [1], PBE [2], and RPBE [4],  $E_x^{\text{ZY}}$  shows no tendency to bind any of the vdW systems we have tried it on, unless the vdW correlation is actually included in the calculation. We thus take

$$E_{\text{xc}}[n] = E_x^{\text{ZY}}[n] + E_c^{\text{LDA}}[n] + E_c^{\text{nl}}[n]. \quad (5)$$

The first two terms form an important and recommended starting point for testing nonlocal vdW functionals. They assure a vdW attraction that actually comes from terms that in principle are capable of giving it.

The GGA is used in order to have a good account of strong valence bonds and densities of individual layers, and the above scheme is implemented by self-consistently calculating the energy  $E^{\text{GGA}}$  and density  $n^{\text{GGA}}$ , typically in the revPBE flavor of GGA. The total-energy, as a function of the lattice parameters, is then calculated as  $E \approx E^{\text{GGA}}[n^{\text{GGA}}] + \Delta[n^{\text{GGA}}]$ , where  $\Delta[n] = E_c^{\text{nl}}[n] - E_c^{\text{grad}}[n]$  and  $E_c^{\text{grad}}[n] = E_c^{\text{GGA}}[n] - E_c^{\text{LDA}}[n]$ . This approximation treats  $\Delta$  as a post-GGA perturbation. The GGA calculations are done using the plane-wave pseudo-potential [18] DFT code DACAPO [19].

The three materials considered here have layered structures with a soft direction perpendicular to the layers [20]. Strong covalent bonds occur between the atoms within the hexagonal layers (lattice constant  $a$ ), while weak vdW interactions occur between the layers. Graphite has a staggered or  $A$ - $B$ -type stacking with the intralayer C atoms in regular, planar hexagons stacked with corners on top of centers. Boron nitride, isoelectronic with graphite, has no shift in hexagon locations but

B and N atoms in alternate positions along the  $c$  direction. A similar alternation occurs between Mo and S atoms in the  $A$ - $B$ -type structure of  $\text{MoS}_2$  [21].

Calculations are also performed for bilayers of the three systems. The binding-energy curve of two parallel graphene sheets [22], i.e., the total-energy difference at separation  $d$  and at infinite separation, respectively, for varying  $d$  (Fig. 2) gives in the approximation [5] with vdW-DF, Eq. (5), a close relation to experimental findings for binding energy and equilibrium distance. The GGA curve, on the other hand, is completely wrong, which we blame on the absence of vdW effects. The inset shows that our  $E_c^{\text{nl}}$  contribution gives stronger binding than the traditional asymptotic vdW interaction. The binding-energy curve for two parallel BN sheets (Fig. 3) differs little from that of bulk BN as a function of lattice constant  $c$ . At equilibrium, the calculated  $E_c^{\text{nl}}$  difference is  $\sim 4\%$ , attributable mostly to second nearest layers in the bulk material [23].

Bulk-modulus values are computed together with other structure ( $a$ ,  $c$ ) and bonding properties [24] (Table I). It is crucial to densely sample the region of ( $a$ ,  $c$ ) values around the optimal structure ( $a_0$ ,  $c_0$ ), and we use a new method [25] for direct evaluation of both structure, binding energy, and bulk modulus  $B_0$  in the relevant range of  $a$  and  $c$  values [26]. GGA values were also computed but not shown. For all three materials, the various GGA flavors give no binding or bind very weakly at unreasonably large separation. The vdW-DF, on the other hand, gives values for lattice parameters and cohesive energy in good

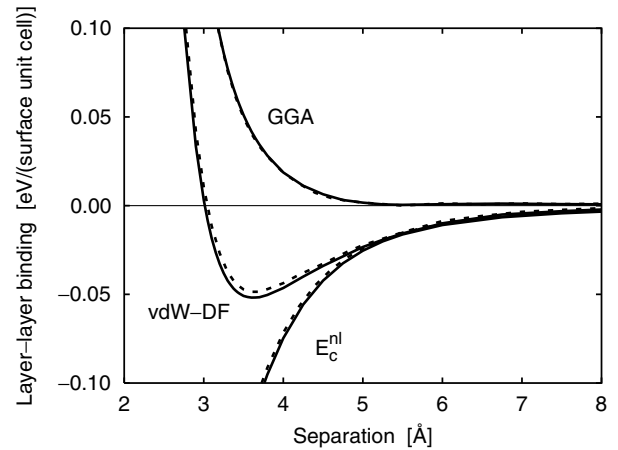


FIG. 3. Comparison of the vdW-DF layer-to-layer binding in the staggered bulk hexagonal-BN system (solid lines) and adhesion between two sheets of BN (broken lines) shown as functions of the interlayer separation  $d = c/2$ . In both descriptions, the GGA gives unphysical results for bond and equilibrium separation. The total adhesion is dominated by the contribution of the vdW interaction  $E_c^{\text{nl}}$ . The nearest-neighbor interlayer binding (broken lines) is seen to strongly dominate the bulk adhesion (solid lines) for layered materials.

TABLE I. Properties of graphite, BN, and MoS<sub>2</sub>, calculated with vdW-DF and compared to experimental data in parentheses, when available. Shown are the geometry ( $a$ ,  $c$ ), binding-energy ( $E_0$ ), bulk modulus ( $B_0$ ), and elastic constant ( $C_{33}$ ). GGA (not shown) binds very weakly at unphysically large  $c$  or not at all, depending on substance and GGA flavor.

	Graphite	BN	MoS <sub>2</sub>
$a$ [Å]	2.47 (2.46) <sup>a</sup>	2.51 (2.50) <sup>b</sup>	3.23 (3.160) <sup>c</sup>
$c$ [Å]	7.52 (6.70) <sup>d</sup>	7.26 (6.66) <sup>b</sup>	12.6 (12.29) <sup>c</sup>
$E_0$ [meV/atom]	24 (35 ± 10) <sup>e</sup>	26	60
$B_0$ [GPa]	12 (~ 33) <sup>a</sup>	11	39
$C_{33}$ [GPa]	13 (37–41) <sup>a</sup>	11	49

<sup>a</sup>Ref. [9]. <sup>b</sup>Ref. [10]. <sup>c</sup>Ref. [11]. <sup>d</sup>Ref. [12]. <sup>e</sup>Ref. [13].

agreement and for bulk modulus in fair agreement with experimental values, when available.

In conclusion, we recommend the replacement of GGA as a standard method in total-energy calculations with vdW-DF as given in Eq. (5) for descriptions of layered systems that contain sparse electron distributions. This will give the right qualitative character of soft bonds, including saturation of the vdW potential at small separations, and even quantitative ones, such as physical values of bond lengths, binding energies, and compressibilities [28].

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- [19] DACAPO code is available at <http://www.fysik.dtu.dk/CAMPOS/>.
- [20] Separation  $d = c/2$ , except for MoS<sub>2</sub>, where  $d$  is defined as the distance from the perpendicular position of the topmost sulfur atom of one layer to the position of the bottom-most sulfur atom of the next.
- [21] In the MoS<sub>2</sub> interlayer calculations, each MoS<sub>2</sub> layer is treated as a composite material (the Mo-S perpendicular separation is  $\sim 1.58$  Å). A composite  $q_{\perp}$  value ( $\sim 0.58$ ), identical in both MoS<sub>2</sub> layers, is obtained by applying an external field across a single MoS<sub>2</sub> composite and using GGA to calculate the static polarization. In the interaction study, the vdW-DF energy is then calculated as a function of the separation between the two MoS<sub>2</sub>-layer composite materials, the atom positions within each of the MoS<sub>2</sub>-layer composites being kept fixed.
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