Hard Numbers on Soft Matter

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Today, materials theory is a full-fledged partner in the development of new materials [1,2]. Bonds, structures, and other properties come out impressively well, a clear success of the now "standard" density-functional theory (DFT), present for hard materials, like diamond. However, soft matter is just as abundant and important to understand. Here we consider the weak physical interactions in graphite, a textbook-prototype soft layered material with large interlayer separation. First the failure of the standard DFT is documented. Then we apply our recently proposed general density functional [3] that meets the requirement to include nonlocal correlations and van der Waals interactions, physical effects not present in the standard DFT. This revised DFT gives separations, binding energies, and compressibilities in close agreement with experiment. These numbers, together with intrinsic soundness of the new density functional, open avenues for revised DFT use for broad classes of soft matter, like polymers and liquid crystals, chemistry, wet matter, nanoscience, bioscience and biotechnology.

While standard DFT has an enormous predictive power for hard and closely packed materials, it has, hitherto, provided only disinformation on soft matter. Standard DFT offers highly accurate descriptions of hard materials like metals, semiconductors, dielectric insulators, ionic crystals, ceramics, magnets, etc. Here we can determine bond lengths within about 1 per cent [4], proper stable structures with an edge of 30 meV/atom compared to competing structures [5], diffusion barriers in crystal growth with an accuracy of about 10 meV [6], and compressibilities typically within 10 per cent of measured numbers [4]. Standard DFT is equally successful for hard-material surfaces. These are strong driving forces to develop an improved DFT, as they provide meeting places for numerous accurate experimental techniques and advanced theory, thus enabling detailed comparisons on the quantum level between experiment and theory [7]. However, being based on local and semilocal electron correlations, the standard DFT omits key physical interactions and cannot provide a consistent and accurate calculations for sparsely packed soft matter—a class of materials at least as abundant and important as the hard ones.

This letter reports results for graphitic systems that open the way for broad applications of a revised DFT to soft matter, *i.e.* to the sparse systems that define most physical, chemical, and biological phenomena. Materials such as biomacromolecules, biosurfaces, polymers, liquid crystals, and membranes (not to speak of many common substances like mica, ice cream, and ski wax), and phenomena such as lubrication, physisorption, adhesion, van der Waals complexes, van der Waals bonds in crystals, liquids, liquid crystals, biomolecules, biosurfaces, and most other organic-molecule interactions are

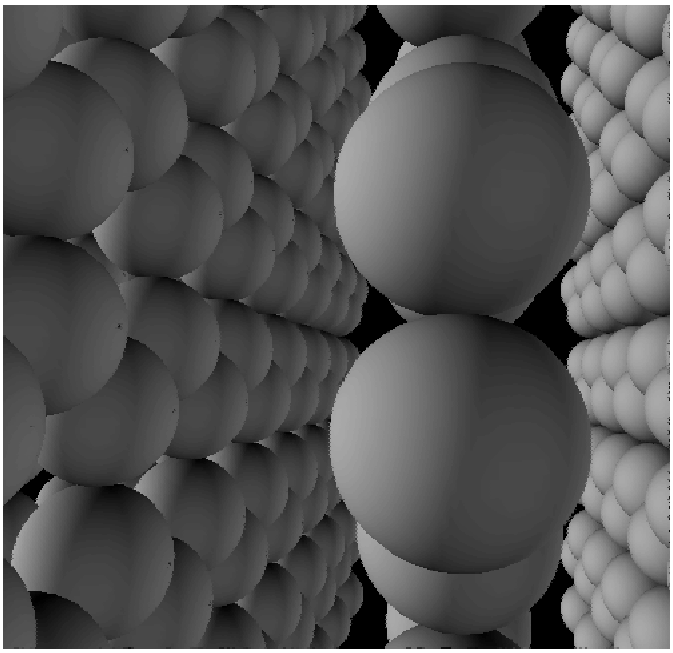

FIG. 1. The hexagonal layered structure of graphite. The intraplanar ($a/\sqrt{3}$) bond length (adjacent atoms in foreground) is shorter than in diamond, whereas the interplanar ($d = c/2$) bond length (distance between adjacent layers) is large.

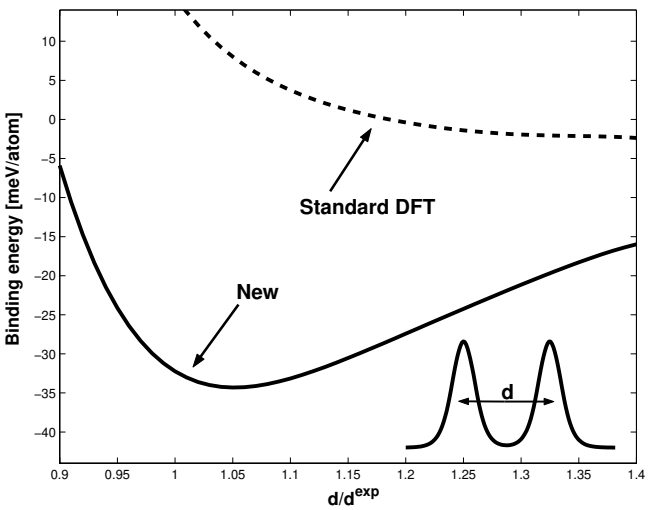

FIG. 2. The graphene-graphene binding-energy curve calculated with standard DFT and with our new nonlocal-correlation corrected functional [3]. A pseudopotential code and a semilocal approximation [8] are used to calculate the standard DFT energy. The new correlation functional [3] is simply replacing the correlation energy of the standard calculation, and the new energy is calculated as $E^{\rm new} = E^{\rm standard} - E_c^{\rm standard} + E_c^{\rm new}$, using the standard-DFT densities as input. The new correlation functional is composed of local and nonlocal parts [3], where the latter is laterally averaged. The system-specific component of the correction is fixed by a separate calculation of the induced surface charge [3].

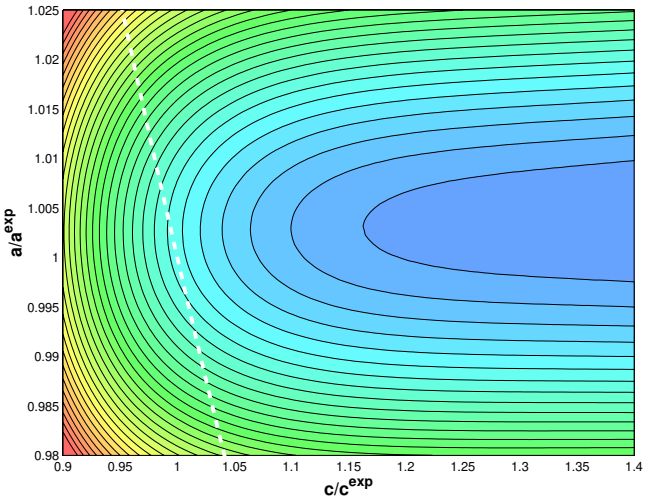

FIG. 3. Total-energy contour plot (10 meV line spacing) for graphite in the c–a plane, calculated with standard DFT. The lattice parameters are defined in Fig. 1. An all-electron projector augmented-wave method [17,16] and a semilocal approximation [8] are used. The dashed curve shows how a variation is performed with the constraint of a constant volume, equal to the experimental volume, indicating the likely procedure of Ref. [18].

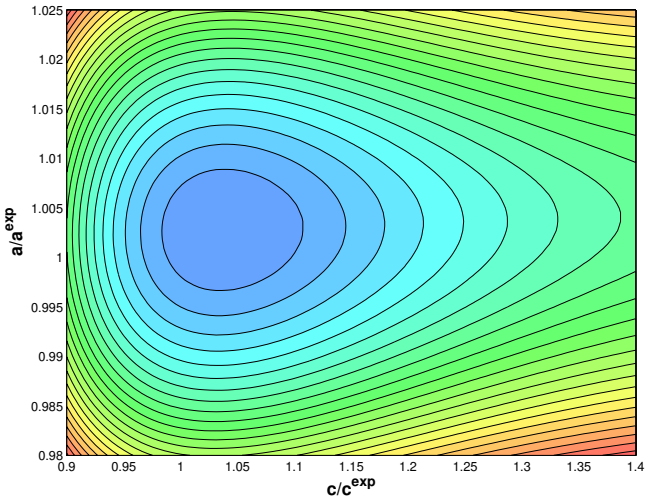

FIG. 4. Total-energy contour plot (10 meV line spacing) for graphite in the c–a plane, calculated with a nonlocal-correlation corrected DFT, as described in Fig. 2.

characterized by and, in fact, operate through the weak ubiquitous van der Waals interaction. A DFT approach that also accounts for these important van der Waals forces is in great demand. Since these forces are, indeed, present in the exact DFT, the challenge is to provide an approximate van der Waals density functional that is generally applicable, efficient, and accurate, and that has a nonlocal density dependence. We have proposed successively more versatile functionals with such properties [9–11,3], and so have others [12–14]. Here our systematic and tractable van der Waals density functional [3] is applied successfully to graphitic systems. In view of the recent implementation for arbitrary geometries [15], it achieves this goal of a revised or new-standard DFT materials theory using just the standard-DFT electron densities, for which accurate and efficient algorithms exist.

We choose graphite for our study of soft matter because of its simplicity and because of its juxtaposition with diamond, another solid composed solely of the element carbon. Whereas graphite is one of the softest minerals, diamond is the hardest; graphite is opaque and black, while pure diamond is transparent and colorless; and graphite is a conductor, while diamond is an insulator. Graphite's technological importance also provides a motivation. Applications include fuel cells, sealing materials, powdered metallurgy, friction products, shapes, steel-mill and foundry products, lubricants, and plastics, not to mention pencils. The prime reason for choosing graphitic systems, however, is the textbook-sharp distinction between regions for covalent and van der Waals bonding, respectively, in these systems.

The structure of graphite is that of a staggered stacking of flat layers of carbon atoms a distance $d \approx 3.34$ Å apart [19] (Fig. 1). Individual layers, referred to as "graphene" sheets [20], are composed of strongly bonded carbon atoms at the vertices of a network of regular hexagons of side $a/\sqrt{3}$ in a honeycomb pattern with lattice constant $a \approx 2.46$ Å [21]. Graphene, alone, is not only an ideal test system, but it is also materialized in nature, for example in collapsed carbon nanotubes [22] and on surfaces [23]. In graphite, the graphene layers are weakly bonded to each other.

It is surprising that there have been no published reports that standard (semilocal) DFT gives results for graphite in strong disagreement with experiment, with the only publication [18] being incomplete and unfortunately misleading (energy minimum likely searched with the constraint of a constant volume). All this may be due to the fact that for a long period, the early (local-density) version of DFT was repeatedly shown to give reasonable predictions at equilibrium separations [24–26,5,27,28], thus obscuring the fortuitousness of this result and providing demotivation for further work. Here the complete breakdown of the current standard DFT is documented, and a generalization that includes the applicable physical mechanism is applied.

First the binding-energy curve of two parallel graphene sheets is calculated, *i.e.* the difference in the total-energy values at separation d and at infinite separation, respectively, for varying d (Fig. 2). The standard-DFT curve is completely wrong. The indications of van der Waals effects from semilocal standard DFT [29] are thus nullified by this result. With results from our van der Waals correction added, the "revised-DFT" method, a binding-energy value of 34 (35 ± 10) meV/atom at the equilibrium interplanar distance 3.5 (3.35) Å is obtained in the ABAB stacking, where the values within parenthesis are experimental numbers, obtained from collapsed carbon nanotubes [22].

The second application is on graphite. The total-energy $E(c, a)$, calculated in standard DFT, is shown in Fig. 3 as energy contours in the c–a plane. It documents that standard DFT gives unphysical results. Its minimum, if any, appears for $c \gg 3a$. Experimentally, $2.7 \leq c/a \leq 2.73$ [19,5]. The revised-DFT binding-energy curve for varying lattice constant c differs negligibly from that for two parallel graphene

sheets (Fig. 4). It gives the potential-energy minimum at 34 meV/atom at the equilibrium interplanar distance $c = 2.85a$.

The concept of softness gets ample illustration by the following bulk-modulus values. For graphite, the early-standard DFT gives values for the bulk modulus that are too high ($\sim$ 51 GPa), the current standard gives values too low ($\sim$ 7 GPa), while the revised form gives a value (33 GPa) close to the experimental one (33 GPa) [30] On the other hand, the corresponding diamond values are much closer to each other and an order of magnitude higher (440 GPA).

In summary, with the key examples of graphene-graphene and graphite, the standard DFT is shown not to be applicable for calculating properties of soft matter. Use of our van der Waals density functional [3] seems to be one way to proceed. As the outcome is so positive, we judge that we have in our hands the first practically working version of such a functional [3]. This is a very promising development for a broad range of applications.

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