Towards a working density-functional theory for polymers: First-principles determination of the polyethylene crystal structure

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Equilibrium polyethylene crystal structure, cohesive energy, and elastic constants are calculated by density-functional theory applied with a recently proposed van der Waals (vdW) density functional (DF) for general geometries [Phys. Rev. Lett. **92**, 246401 (2004)] and with a pseudopotential-plane-wave scheme. The vdW-DF with its account for the long-ranged van der Waals interactions gives not only a stabilized crystal structure but also values of the calculated lattice parameters and elastic constants in quite good agreement with experimental data, giving promise for successful application to a wider range of polymers.

Understanding of crystalline solids is greatly enhanced by the periodicity of the atomic structure, which allows very detailed comparisons between theory and experiment. Macromolecular materials, such as polymers and other complex fluids, are less well understood, due to the challenging complex natures of their structures. Features of the polymer on the atomic and mesoscopic length scales are interdependent. For instance, atomic bonds are on the Å scale, while diffusion processes involve whole chains extending some 100 Å. In order to cover the full set of length scales by theory we need atomic-scale input for mesoscopic-scale force-scheme simulations. Input forces may be determined routinely from first-principles density-functional theory (DFT) calculations, the more accurate a functional the better, for a reasonably sized unit cell. Among polymer crystals, with their typically very complex structure, the polyethylene (PE) crystal has a relatively simple structure.[1] A first-principles implementation of DFT,[2] van der Waals (vdW) DF, with a general account for vdW forces, is here shown to give results for crystal structure, cohesive energy, and elastic constants of the PE crystal in a very promising agreement with previous low-temperature measurements.

Earlier attempts to study the equilibrium properties of polymer systems have relied on semiempirical interatomic potentials, including force-field methods[3,4] and modified DFT calculations.[5] The fitting of internuclear potentials in order to reproduce experimental equilibrium properties gives serious restrictions on the predictive power of these methods for nonequilibrium situations and for molecules, for which experimental data are scarce or lacking. Further, these semiempirical methods lack information to make a systematic improvement of the interatomic potentials possible. A physically motivated first-principle description of sparse polymer crystals is highly desirable. When applied at perfect conditions, it might even render the possibility of developing consistent and transferable interatomic potentials for both force schemes and hybrid methods.

The ongoing DFT success story for ground-state electron structure calculations of dense materials systems is driven by the relatively low computational cost together with the ability to describe very diverse systems. However, the widely used local and semilocal implementations do not include long-range nonlocal correlations that are essential for a proper description of the intermolecular vdW interactions. These interactions are crucial for the stability of systems with regions of low electron density, often encountered in biological and nanotechnological applications. The recently developed vdW-DF functional[2] accounts for the vdW interaction in a seamless way both at the equilibrium binding separation and at asymptotically large separations. It applies to general geometries and accounts for the nonlocal correlation via a functional that takes only the electron density as input. It has proved very promising in describing equilibrium separations and binding energies for a range of systems, including dimers of benzene rings,[2,6] graphene sheets,[7] polycyclic aromatic hydrocarbons (PAH's),[8] monosubstituted benzene molecules,[9] and combinations thereof, such as PAH's and phenol adsorbed on graphite.[7,10]

Simple polymer crystals constructed from long parallel polymer chains,[1] such as linear PE or polypropylene, represent an important class of sparse materials that are stabilized by the vdW interaction. At low temperatures, the PE crystal stabilizes in a simple base-centered orthorhombic crystal structure ($Pna2_1$), Fig. 1, as established by x-ray and neutron scattering experiments.[11–14] Standard theory, first-principles calculations with the semilocal generalized gradient approximation (GGA) of DFT, predicts this structure to be unstable[5,15] or unrealistically weakly bound,[16,17] calling for incorporation of nonlocal interactions. Recent vdW-DF calculations on parallel, well separated PE molecules[18,19] show the vdW interaction in these systems to be nonnegligible. To account for the nonlocal correlations at all separations, in particular those relevant in the PE crystal, we here apply the general-geometry vdW-DF.[2]

The structure of the isolated polymer has earlier been calculated in the GGA,[19] and this structure is used as input for the crystal calculations.[20] The internal geometrical structure of the isolated polymer chain thus fixes the repetition length $c=2.57$ Å of the PE crystal unit cell.

Our vdW-DF calculations give binding-energy values at varying crystal-parameter and setting angle values, which are presented as contour maps, and from which equilibrium values for lattice parameters, setting angle, the cohesive energy, and elastic coefficients are extracted and compared with ex-
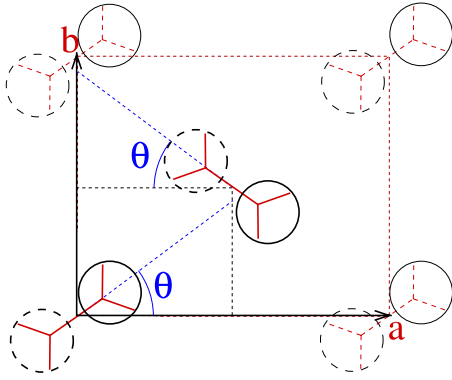
FIG. 1. (Color online) Schematics of the PE crystal structure in its base-centered orthorhombic unit cell. Lattice parameters a and b are indicated, while the parameter c, which is the polymer repetition length, is perpendicular to the plane shown. Solid (broken) circles represent CH_2 units in the plane (a distance $c/2$ out of the plane). The angular orientation of the polymers is determined by the setting angle θ, defined as the angle between the a axis ($a > b$) and the intrapolymer carbon plane.

perimental low-temperature data. Polymers might have several conformations with similar energies. Likewise, in a polymer crystal structure several local energy minima might exist. In particular, whereas the structure shown in Fig. 1 with $a > b$ is experimentally observed, the structure that approximately corresponds to pulling one of the polymers half a unit length ($c/2$) out of the plane of the paper leads to essentially the same polymer chain packing and in turn to a similar configurational energy. In fact, the structure with a polymer pulled outward can also be described by the schematics in Fig. 1, when the requirement $a > b$ is relaxed. Our first-principles method enables us to directly assess the cohesive-energy contours in both (a, b, θ) regions.

The vdW-DF functional is derived and described in Ref. 2. It divides the correlation-energy functional into local and nonlocal parts $E_c \approx E_c^{\text{LDA}} + E_c^{\text{nl}}$, where the first term is approximated by the local-density approximation (LDA) and the second term vanishes for a uniform system. The dispersive interactions give the second term a substantial nonlocality, which allows a simpler account of the polarization properties from which it originates. It is determined from the inverse dielectric function ϵ^{-1}, which is assumed to be dominated by a single pole, with a strength fixed by the f-sum rule. The functional form obtained approximately is

$$E_c^{\text{nl}}[n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r}) \phi(\mathbf{r},\mathbf{r}') n(\mathbf{r}'). \tag{1}$$

The nonlocal kernel ϕ can be tabulated[2] in terms of a dimensionless distance $D = (q_0 + q_0')|\mathbf{r} - \mathbf{r}'|/2$ and an asymmetry parameter $\delta = (q_0 - q_0')/(q_0 + q_0')$, where q_0 is a local parameter that depends on the electron density and its gradient at position $\mathbf{r}$. The quantity q_0 is related to the pole position in ϵ^{-1}, which is determined by the requirement that this ϵ should give the same appropriate semilocal exchange-correlation energy density component as that of an electron gas in a much better approximation.
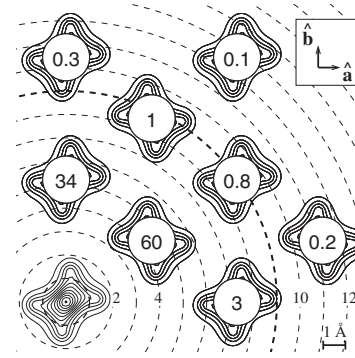

FIG. 2. The nonlocal correlation energy E_c^{nl} for pairs of PE. For the practical evaluation of E_c^{nl} in the crystal the range of integration in Eq. (1) is important. Simple pair interaction calculations give a fast estimate of the range needed, although the full calculation includes all density within the integration range. Shown here are the relative sizes (meV per polymer segment) of the polymers' contributions to E_c^{nl} (as pairs with the polymer at the circle centers), evaluated at the separations (Å) and relative angles shown. The contours show length-averaged electron densities. Polymers that are closer than 9 Å (thick dashed circle) to the center polymer contribute with an energy of 321 meV. This is 99.4% of the total nonlocal correlation energy E_c^{nl} of all the polymers shown (323 meV).

The nonlocal-energy integral (1) has the electronic density $n(\mathbf{r})$ as input. We use a self-consistently determined GGA density with the revPBE exchange flavor,[2,21,22] calculated for the full crystal unit cell using a plane-wave code[23] with ultrasoft pseudopotentials.[24] The plane-wave basis set is truncated at 400 eV, and a $(4 \times 4 \times 10)$ k-point Monkhorst-Pack sampling of the Brillouin zone is used for the periodically repeated unit cell. A spatial sampling separation of 0.13 Å between fast-Fourier-transform grid points is used.

In Ref. 2 the vdW-DF is described for and applied to finite molecules. The generalization to extended systems is straightforward. For an adsorbate system (a finite molecule plus an extended surface) this is described in Ref. 7. For a bulk system, such as the PE crystal, $E_c^{\text{nl}}[n]$ of the crystal unit cell must include the interactions from the surrounding cells. This is taken care of by letting the spatial integrals in Eq. (1) (as energy per unit cell) extend over the unit cell for $\mathbf{r}$ and "everywhere" for $\mathbf{r}'$. In practice, the $\mathbf{r}'$ integral is carried out over a region in space that is sufficiently large, i.e., by adding more space we do not change E_c^{nl} at the desired level of accuracy. We find it sufficient to include a total of five unit cells in each of the a and b directions (Fig. 1) and nine unit cells in the c direction in the $\mathbf{r}'$ integral, by which E_c^{nl} is found to deviate less than one part per thousand from the results obtained by integrating over a substantially larger region of space. Figure 2 illustrates this by showing the pairwise contributions to the polymer interaction E_c^{nl}. The figure shows that the most important contributions come from the nearest and next-nearest neighbor polymers.

The total energy of the crystal is thus

$$E_{\text{vdW-DF}} = E_{\text{GGA}} - E_{\text{GGA},c} + E_{\text{LDA},c} + E_c^{\text{nl}}, \tag{2}$$

with the revPBE flavor of GGA. The cohesive energy is obtained as the difference between the calculated total-energy
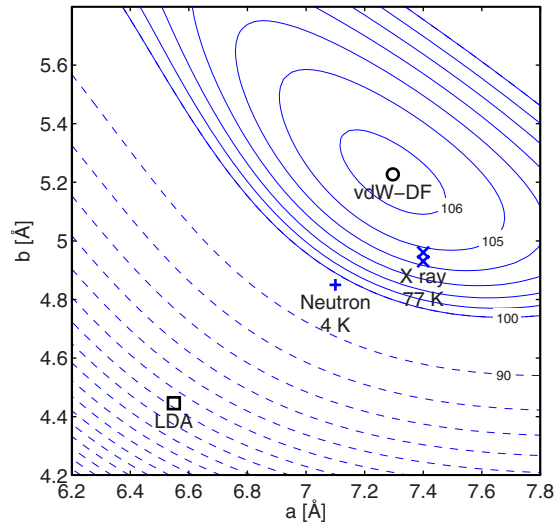
FIG. 3. (Color online) The cohesive-energy contour map calculated with vdW-DF, expressed as energy per CH_2 group as a function of the lattice parameters a and b. The plot (but not the calculation) is restricted to show the energetics at setting angle $\theta = 44°$, the optimal angle found with vdW-DF (Table I). The full (dashed) contour curves are separated by 1 (10) meV/CH_2, with values given in meV/CH_2. The equilibrium parameters (summarized in Table I) obtained from experiments and from a LDA-DFT study are shown for comparison.

values for the actual structure and for a reference structure with widely separated PE polymers. The electron-density-grid spacing as well as the polymer position relative to the grid are kept fixed for the vdW-DF reference calculation to ensure that any polymer self-interaction of the crystal calculation and most grid-related numerical errors are canceled by the reference calculation. The scheme applies also to other sparse-matter systems.

The cohesive-energy contours of the PE crystal, that is the loci of equal binding-energy values for configurations with varying values of the lattice parameters a, b, and the setting angle θ (Fig. 3), are calculated with vdW-DF, and two nearly equally deep minima are found at two different setting-angle values (Table I). The configuration approximately sketched in Fig. 1 is the most stable of the two. However, the two configurations are very close in energy, differing by only 1 meV/CH_2 (1%), and an accuracy sufficiently high to resolve such a stability issue cannot be claimed for the vdW-DF method.

Our calculated vdW-DF values of the equilibrium lattice parameters for the Fig. 1 structure $(a_0, b_0) = (7.30, 5.22 \text{ Å})$, are in good agreement with the experimental ones (Table I), with a_0 in the range of experimentally observed values and b_0 differing by at most 8% from the experiments. We judge this difference to be due to a less satisfactory representation of exchange in the tails of the electron distributions.[6] The calculated values of the cohesive energy (not including zero-point fluctuations) and the elastic coefficients (Table I) are also in good accord with experiments.

The vdW-DF results are in great contrast to the clear overbinding of LDA (Ref. 17) and to GGA results,[5,15–17,28] all of which show the PE crystal to be unstable or nearly unstable (binding energies less than 15% of experiment). In fact, the GGA values of a and b obtained spread widely over the a-b plane, as expected for calculations bordering on instability where tiny aspects, normally irrelevant, come into

TABLE I. Values of equilibrium lattice parameters a_0 and b_0, setting angle θ_0, elastic constants C_{11}, C_{12}, and C_{22}, and cohesive energy E_{coh} per CH_2 group, calculated by the vdW-DF method and compared with other theoretical and experimental data.

Method	C_{11} (GPa)	C_{12} (GPa)	C_{22} (GPa)	E_{coh} (eV/CH_2)	a_0 (Å)	b_0 (Å)	θ_0 (deg.)
vdW-DF	11.1	6.3	8.9	0.106[k]	7.30	5.22	44
vdW-DF	8.8	6.7	12.8	0.105[k]	5.29	7.28	51
LDA[a]	41.2	11.3	47.1	0.11[k]	6.55	4.45	44.4
LDA+BLYP+6−LJ[b]	14.1	7.2	11.8	0.11[k]	7.40	4.90	45
GGA[a]	39.2	2.5	32.9	$\sim 0^k$	7.30	5.02	44.1
GGA[c]				$\sim 0.01^k$	8.28	5.64	47.4
Force field (4 K)[d]	14.0	7.9	13.5	0.081	7.20	4.80	41.9
Neutrons (77 K)[e]	11.5						
Experiment[f]				0.080			
X rays (77 K)[g]					7.42	4.96	47.7
X rays (77 K)[h]					7.39	4.93	45
Neutrons (4 K)[i]					7.12	4.85	41
Experiment (213 K)[j]	8.4	4.2					

[a]Reference 17.
[b]Reference 5.
[c]Reference 16.
[d]Reference 3.
[e]Reference 25.
[f]Reference 26.
[g]Reference 12.
[h]Reference 13.
[i]Reference 14.
[j]Reference 27.
[k]Value not corrected for zero-point motion, estimated to account for approximately 0.01 eV/CH_2.

play. Calculations with *ad hoc* corrections for the dispersive interactions[29] with the BLYP functional[5] and with the force-field method[3] give results in a fair agreement with experimental data. However, the former uses an empirically damped $-R^{-6}$ internuclear potential,[5] and the latter has parameters fitted to experimental data at 4 K, such as lattice parameters,[3] providing agreement with experiment at this temperature by construction. In contrast, the vdW-DF calculations do not take any empirical input.

The vdW-DF functional used here combines the correlation-energy functional E_c^{nl} [Eq. (1)] with an exchange functional taken from the revPBE flavor of GGA. Although the latter closely represents the Hartree-Fock exchange at separations relevant for this work, it gives a slight misrepresentation of the true exchange repulsion.[2,6,9] An analysis of the PE-molecule density profile implies that this effect should be stronger in the *b* than in the *a* direction, which is indeed the case for our calculated results. Thus an improved exchange description should give an even better agreement with the experimental geometry.

In summary, the vdW-DF method successfully predicts structural, cohesive, and elasticity data for the important test case of the PE crystal. It is gratifying that the inclusion of the fully nonlocal vdW-DF correlation functional [Eq. (1)], which has no empirical input or fitted parameters, leads to a good agreement with experimental data. As similar conclusions are drawn for a variety of different carbon-based systems, such as graphene, dimers of benzene, polyaromatic hydrocarbons, monosubstituted benzene molecules, and combinations thereof,[6–10] the vdW-DF functional is certainly very promising for general kinds of geometries and molecules, like those in macromolecular materials.

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