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Young Modulus of Crystalline Polyethylene from *ab Initio* Molecular Dynamics

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ABSTRACT: The Young modulus for crystalline polyethylene is calculated using *ab initio* molecular dynamics based on density functional theory in the local density approximation (DFT-LDA). This modulus, which can be seen as the ultimate value for the Young modulus of polyethylene fibers, is found to be 334 GPa. For the first time the modulus is evaluated *ab initio* (no bias from experimental data) with demonstrated basis set convergence.

1. Introduction

Ultrahigh molecular weight polyethylene can be ultradrawn into high-performance fibers, exhibiting a high Young modulus and a high tensile strength. The high performance can be attributed to the length of individual molecules and their unidirectional ultraorientation.[1] For such high-performance materials, it is of interest to evaluate the difference between experimentally obtained values of the mechanical properties and the ultimate values that might be obtained for the hypothetical ideal material. Needless to say, these ultimate values are upper bounds for the performances of the actual polymer fibers. For polyethylene, the ideal material would correspond to a 100% single orthorhombic crystal composed of infinitely long polyethylene chains.

Obviously, it is not possible to measure the modulus of a hypothetical material. For this reason it is necessary to *calculate* the ultimate modulus of polyethylene. Previous studies using force field, semiempirical, and *ab initio* methods have been reported, resulting in a wide variety of values for the ultimate Young modulus (276−420 GPa), which is not satisfactory. A short overview can be found in ref 2.

Although force fields can produce reasonable values for the Young modulus, they are generally biased by experimental data. It is likewise difficult to prove that semiempirical calculations lead to the correct ultimate modulus. Only *ab initio* type simulations may provide an independent, unbiased value for the ultimate Young modulus for crystalline polymers. Thus far this type of calculation has been mostly applied to the single isolated chain and in neither of the reported studies has convergence of the value of the modulus as a function of the basis set size been demonstrated. The relatively strong dependence of the calculated modulus as a function of the basis set size[2,3] illustrates the absolute need for such a test. Since the published Hartree−Fock-based values for the modulus do not fulfill these requirements, Crist and Hereña[2] have argued that, currently, the calibrated semiempirical values[4,5] may be considered the most reliable data.

In the present study we have calculated the Young modulus for crystalline polyethylene using *ab initio* molecular dynamics. The reason for this choice is, besides the considerations mentioned above, that an extension of this work is planned toward the mechanism of chain scission, the influence of the unpaired electron in the scission process, and more general physical properties of polymers. The calculations are based on density functional theory in the local density approximation, which is very successful for crystals.[6] The plane wave basis set is systematically increased to achieve convergence of the computed Young modulus.

2. Computational Details

2.1. Young Modulus. The Young modulus is defined as follows. When a stress (σ), that is, force per area (F/A), is applied to a material, it will deform and elongate. A measure for this elongation is the strain ($\epsilon = (L - L_0)/L_0$)). The relation between stress and strain can be written as

$$\sigma = Y\epsilon \qquad (1)$$

The Young modulus is by definition the value of Y for zero strain. The force at zero temperature applied to the material is

$$F = \frac{\mathrm{d}E_\mathrm{T}}{\mathrm{d}L} \qquad (2)$$

where E_T is the total energy. This results in an equivalent definition of the Young modulus

$$Y_0 = \frac{L_0}{A}\frac{\mathrm{d}^2E_\mathrm{T}}{\mathrm{d}L^2}\bigg|_{L=L_0} \qquad (3)$$

For larger strains Y will not be equal to the Young modulus. It is a better approximation to assume that Y varies linearly with the stress; $Y = Y_0 + Y_1\sigma$. Integrating eq 3 in two steps under the condition that $L = L_0$ for $F = 0$ results in a more complicated formula for the equation of state:

$$E_\mathrm{T}(L) = \frac{AY_0L}{Y_1(Y_1 - 1)}\left[Y_1\left(1 - \frac{L_0}{L}\right) + \left(\frac{L_0}{L}\right)^{Y_1} - 1\right] + E_\mathrm{T}(L_0) \qquad (4)$$

This is a variant of the Murnaghan equation of state,[7] which describes the deformation of crystals under hydrostatic pressure.

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2.2. Car–Parrinello Method. To calculate the Young modulus with formula 4, the total energy has to be calculated for unit cells with different lengths in the chain direction. Such a deformation of the unit cell leads to the deformation of the chain. For this reason the geometry should be optimized for each unit cell.

An optimization of the geometry and a quantum mechanical treatment of the electrons in a crystalline material can be accomplished at the same time with the Car–Parrinello technique,[8] also known as *ab initio* molecular dynamics. In the present study the fhi93cp code[9] was used.

The Car–Parrinello technique is based on density functional theory[10] and solves the Kohn–Sham equations[11] to describe the electronic structure. The atoms move simultaneously under forces that are calculated from the electronic structure with the Hellmann–Feynman theorem. In order to reach the equilibrium configuration the dynamics is damped, which means that kinetic energy is extracted from the system during the simulation until the forces have vanished.

To describe the exchange-correlation energy, the local density approximation (LDA)[12] is used. It is also possible to combine this with gradient corrections, but from results reported by Corso et al.[13] it seems that no improvement for bulk moduli results. For this reason no gradient corrections were applied in this study.

The method used here has a plane wave basis set to describe the electronic wave functions. The ions and their core electrons are described with norm-conserving pseudopotentials[14] of the Kleinman–Bylander form,[15] as described in ref 16.

The size of the plane wave basis set is controlled by a cutoff energy; only those plane waves with wave vectors that hold the following condition are included in the basis set:

$$|\mathbf{k} + \mathbf{K}|^2 \le E_{\text{cut}} \tag{5}$$

The larger the basis set size, the better the description of the electronic wave functions. For this reason the basis set will be increased until the physical quantities under consideration do not change anymore.

Due to the plane wave basis set it is most convenient to use the momentum space formalism described by Ihm et al.[17] The Brillouin zone integrals are described by a summation over special *k*-points, as described by Chadi and Cohen.[18] No symmetry is imposed because full relaxation under stress is important for mechanical deformations. There is an inversion symmetry in *k*-space; due to the scalar relativistic approach and Kramers' theorem, the *k*-points *k* and −*k* are equivalent.

2.3. Finite Basis Correction. To compare the total energy of two unit cells of different size when convergence (with respect to the total energy) is not yet reached, the resolution of the wave functions has to be the same. For a finite number of *k*-points this is not the case, and this leads to an error that can be removed with the finite basis correction of Francis and Payne[19] given by

$$E_{\text{cor}} = -\frac{2}{3}E_{\text{cut}}\left(\frac{\partial E_{\text{tot}}(c,E_{\text{cut}})}{\partial E_{\text{cut}}}\right)_c \ln(R_{\text{PW}}) \tag{6}$$

where *c* is the length of the unit cell and

$$R_{\text{PW}} = \frac{N_{\text{PW}}}{n_{\text{PW}}} \tag{7}$$

is the ratio between the actually used (weighted) number of plane waves (N_{PW}) and the number of plane waves (n_{PW}) required to achieve the same resolution for the wave functions as for the different cells. The appropriate number of plane waves is based on the average density of states in the reciprocal space:

$$n_{\text{PW}} = \frac{a \times b \times c}{6\pi^2}E_{\text{cut}}^{3/2} \tag{8}$$

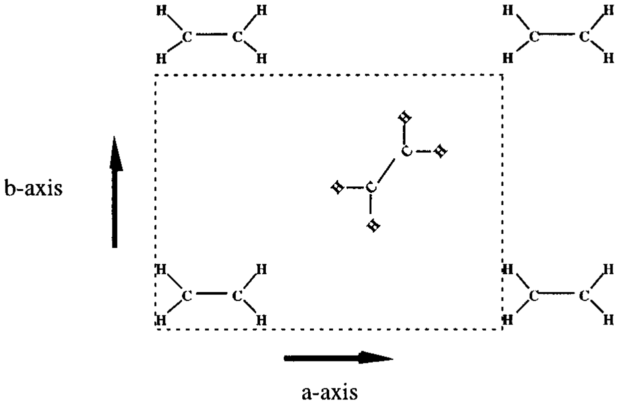

Figure 1. Projection on the *ab* plane of the unit cell that is used to calculate the basis set convergence. The chain direction is perpendicular to the paper.

The most important feature of eq 6 is the following: If there are more plane waves than the appropriate number n_{PW}, the total energy will be lower due to the increased variational freedom. In that case $R_{\text{PW}} > 1$ and the logarithm will be positive. The derivative of the total energy to the cutoff energy is always negative, because a higher cutoff results in more variational freedom and hence in a lower energy. Thus, E_{cor} is positive when $R_{\text{PW}} > 1$ and increases the energy as expected.

For eq 6 the energy derivative is needed, which can be approximated as follows: For a given E_{cut} the geometry is optimized. For this geometry the total energy is calculated for a slightly lower cutoff ($\Delta E_{\text{cut}} = 0.5$ Ry). Then the derivative is calculated by

$$\left(\frac{\partial E_{\text{tot}}}{\partial E_{\text{cut}}}\right)_c = \left.\frac{\Delta E_{\text{tot}}}{\Delta E_{\text{cut}}}\right|_c \tag{9}$$

3. Results

3.1. Basis Set Convergence. For small basis sets, the calculated Young modulus is basis set dependent, as can be seen in ref 2. For this reason the plane wave basis set is increased until the Young modulus is converged. The unit cell which is used contained two monomers. Due to the periodic boundary conditions the monomers form two parallel chains in the *c*-direction. One chain lies parallel to the *ac* plane and the other makes an angle of 43° with this plane (see Figure 1).

The area *A* perpendicular to the chains is chosen to be close to the experimental $A = 36.48$ Å^2 at room temperature[21] by taking $a \times b = 7.46 \times 4.89$ Å^2. A *k*-point set of 14 points is used and E_{cut} was 30 Ry for start.

The unit cell length in the chain direction (*L*) is varied. For each cell the total energy is calculated, and this results in a total energy curve, as can be seen in Figure 3. With the least squares method formula 4 is fitted, which led to a Young modulus of 333 GPa and an equilibrium unit cell length of 4.786 bohr. From

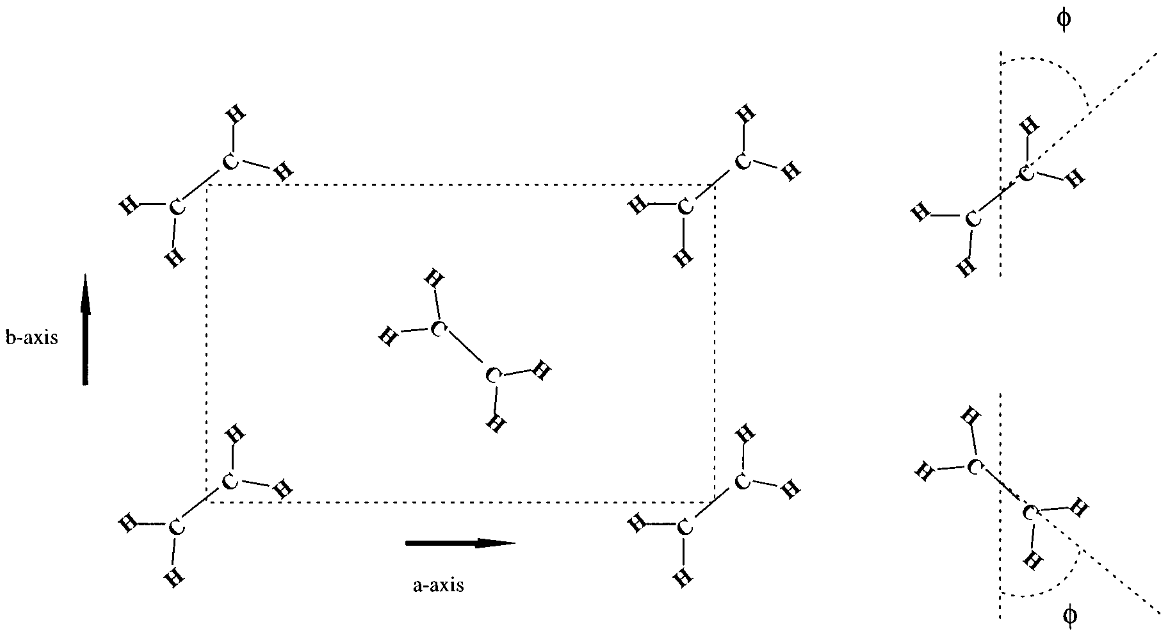

Figure 2. Projection of the orthorhombic unit cell on the *ab* plane. The right-hand side of the picture defines the setting angle ϕ.

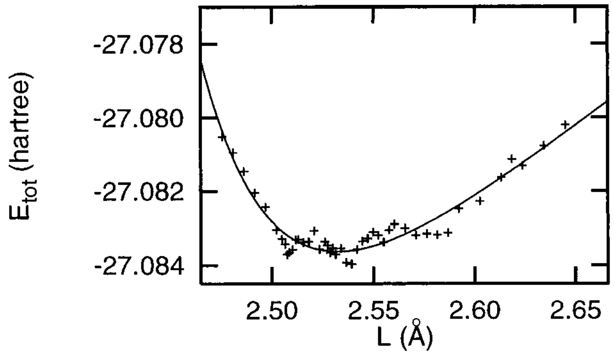

Figure 3. Total energy curve without the finite basis correction for a cutoff energy of 30 Ry. The equation of state (4) (solid line) is fitted to these data, resulting in a Young modulus of 333 GPa.

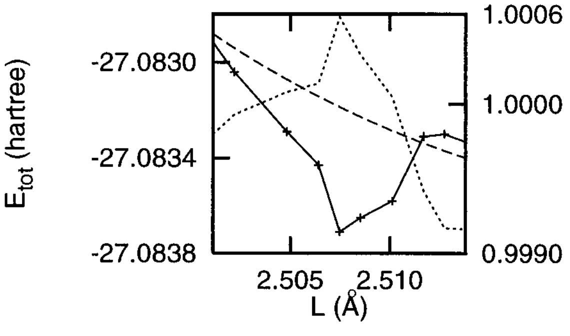

Figure 4. Total energy in more detail. The solid line connects the calculated points. The dashed line is the equation of state (4) as in Figure 2. The dotted line is the ratio between the actually used number of plane waves and the appropriate number of plane waves (7). There is clearly a correlation between the ratio and the deviation of the data from the fitted curve.

Figure 4 it can be seen that the error as described above indeed results in deviations from the fit.

The error is removed by application of the finite basis correction, which results in a smoother curve (see Figure 5). The Young modulus now becomes 407 GPa, and the equilibrium unit cell length, 4.785 bohr. The correction has a large effect on the calculated modulus, which is

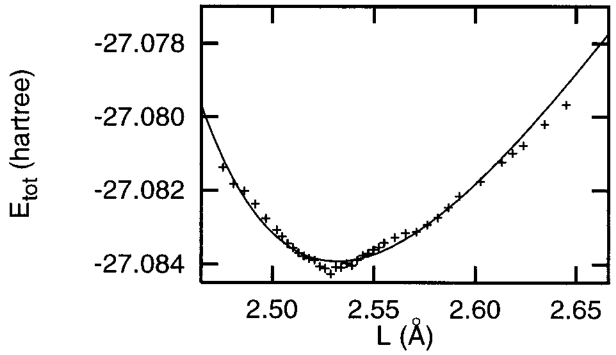

Figure 5. Total energy curve with finite basis correction. The solid line is the fitted equation of state (4). This curve is a lot smoother than the curve in Figure 2. The Young modulus is 407 GPa.

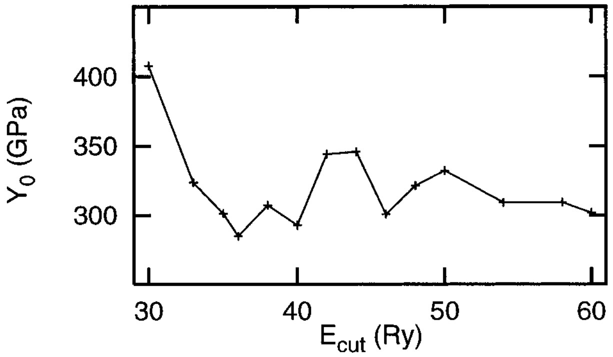

Figure 6. Young modulus as a function of the cutoff energy. Convergence is reached for a cutoff of 54 Ry.

an indication that the number of plane waves is substantially too low. (One should note that for larger basis sets the correction will be smaller, because $\Delta E_{\rm tot}$ will decrease with increasing $E_{\rm cut}$.)

To test when the modulus is converged, the cutoff energy is increased. Each different $E_{\rm cut}$ results in a different total energy curve with a different Young modulus (Y_0). The various Y_0 are plotted as a function of $E_{\rm cut}$ in Figure 6. Inspection of this curve leads to the conclusion that for $E_{\rm cut} > 54$ Ry the Young modulus is

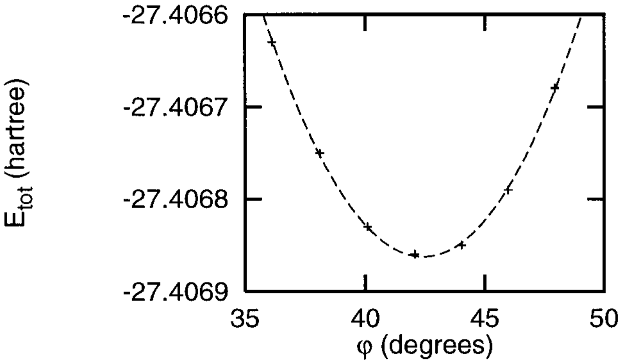

Figure 7. Total energy as a function of the setting angle ϕ. Minimal energy is reached for ϕ= 42.4°.

practically converged. The value of the Young modulus is then 309 GPa, while for $E_{cut} = 60$ Ry the value is 302 GPa. The optimized geometry changes when E_{cut} changes, but for 54 Ry the distances and angles are all converged within 1%.

The structure of Figure 1 does not equal one of the known crystal structures of polyethylene, although the density is very close. We have chosen this structure for the purpose of determining the basis set size (cutoff energy) required to achieve convergence with respect to the calculated modulus. Since we intend to perform simulations on the various crystalline structures of polyethylene in the future, we did not want the size of the basis set to be biased by a specific crystal structure. Therefore we have selected a nonexisting structure with almost the same density as the orthorhombic crystalline structure. We will comment on the validity of this choice later on in this paper.

3.2. Crystalline Polyethylene. The unit cell for orthorhombic polyethylene contains two monomers as in the previous case, but now both the chains make an angle with the *ac* plane (see Figure 2), one the setting angle ϕ, the other an angle $\pi - \phi$. The unit cell parameters at a temperature of 4 K are $a \times b \times c = 7.12 \times 4.85 \times 2.55$ Å^3.[20] The setting angle ϕ is 42°.[21]

The Young modulus of the crystalline orthorhombic polyethylene is calculated for $E_{cut} = 54$ Ry. Only 8 *k*-points of the set of 14 *k*-points are nonequivalent due to the extra symmetry in the orthorhombic crystal. The unit cell length in the *c*-direction is varied. This resulted in an equilibrium unit cell length of 2.51 Å and a Young modulus of 341 GPa.

To test whether the chosen *k*-point set was large enough to calculate the Young modulus, the calculations for the orthorhombic case were repeated with a *k*-point set of 12 nonequivalent *k*-points. The Young modulus for experimental density was 334 GPa, and the equilibrium unit cell length was 2.53 Å. This is 2% and 1% deviation, respectively, from our previous calculation. The former *k*-point set is used in further calculations.

The rotation forces for the chains are 1 order of magnitude smaller than the forces that determine the structure within the chain. So, during the calculation the angle is not optimized, but we can do it manually. The variation of the total energy with the setting angle is shown in Figure 7. The angle that gives minimal energy is 42.4°, which agrees very well with the available experimental value of 42°, measured at room temperature.[21]

Also, we have optimized the area A for a unit cell length c of 2.51 Å. First the parameters a and b are changed and they gave minimal energy for values 6.77 and 4.69 Å. Then the setting angle was optimized again, resulting in 45°. Again the parameters a and b were optimized, but this gave the same result. This means that the latter case was converged. For these parameters the Young modulus was calculated, resulting in $Y_0 = 366$ GPa.

Table 1. Comparison of the Experimental and Calculated Data[a]

	exp		calc	
	RT[21]	4 K[20]	optimized density	experimental density
a (Å)	7.40	7.12	6.77	7.12
b (Å)	4.93	4.85	4.69	4.85
c (Å)	2.53	2.55	2.51	2.53
ϕ (°)	42		45	42.4
Y_0 (GPa)		≥288[23]	366	334

[a] The first column contains the experimental data measured at room temperature, the second column contains data from measurements at 4 K (except the Young modulus, which is actually measured at 77 K). The third and the last column contain the parameters as calculated here. The third column gives the data for the case in which the chain density is optimized. For the last column the chain density from experiment at 4 K is used to optimize c and ϕ and to calculate the Young modulus.

The density of chains from calculation is 9% larger than the experimental density at 4 K. Also, the Young modulus was 7% larger at optimized area than at experimental density. This may lead to the conclusion that the interchain interaction is only of importance for the density but has a minor effect on the elasticity of the chain.

3.3. Single Chain Approximation. As we have seen that the interchain interaction is not very important, it is interesting to evaluate the Young modulus correctly for a single isolated chain. This can be done by using one monomer per unit cell and taking the area perpendicular to the chain axis so large that there is no effective interchain interaction.

The area was taken to be $A = 7.94 \times 7.94$ Å^2. Similar calculations as in the orthorhombic case were performed for an $E_{cut} = 54$ Ry. The equilibrium unit cell length as well as the second derivative of the total energy were calculated. $L_0 = 2.51$ Å. We wish to compare the result for the Young modulus from the single chain approximation with our previous results for the orthorhombic case. For this reason we use in formula 3 the experimental area A at 4 K. This results in a Young modulus of 337 GPa, which is very close to the result previously found for the orthorhombic cell.

To test whether the two chains really have no interaction, a second calculation is done with a different area, namely $A = 6.88 \times 6.88$ Å^2. The same evaluation of the results as above give a Young modulus of 337 GPa, which is exactly the same result. From this we may conclude that we have really calculated the Young modulus from the single chain approximation.

4. Discussion

The ultimate Young modulus for polyethylene is calculated from *ab initio* molecular dynamics. For a chain density that is known from experiment at 4 K[20] a Young modulus of 334 GPa was obtained. The equilibrium unit cell length is in good agreement with the experimental value at 4 K (see Table 1).

Also the chain density is optimized within LDA. This results in a density which is about 9% too large and a corresponding Young modulus of 366 GPa. That LDA also overestimates interchain forces is in agreement with calculations on interactions of benzene molecules.[22]

The increased value of the Young modulus is mainly due to the increase of the chain density. The latter conclusion is confirmed by calculations on the single chain level, which resulted in 337 GPa. Hence, the interchain interaction primarily has influence on the Young modulus due to the $1/A$ term in eq 3.

All these values were calculated with a basis set that was large enough to converge the modulus. Because of the small difference between the calculated moduli for orthorhombic polyethylene and a single isolated polyethylene chain, the choice of the nonphysical structure (Figure 1) to determine the basis set size is fully justified.

A direct comparison with experiment is difficult, as there are no temperature effects included. Hence, we should compare it with stress−strain experiments at as low a temperature as possible. The best realized performance was found in an experiment at 77 K,[23] resulting in a Young modulus of 288 GPa. This is 86% of 334 GPa, the proposed ultimate value in this paper. As it is known that a decrease of temperature will lead to an increase of the modulus, one can state that the best realized performance for the Young modulus is better than 86% of the ultimate performance.

A comparison with other theoretical data is only possible at a single chain level. It is common in literature to take the chain density at room temperature (A = 36.48 Å^2). The Young modulus from the most recently reported *ab initio* calculation is 300 GPa.[2] The value from our single chain approach at room temperature density is 320 GPa, this is about 7% larger. The calibrated semiempirical data (349 GPa[4] and 343 GPa[5]) are about 9% larger than our result.

5. Conclusions

We have calculated the ultimate value for the Young modulus of polymer fibers by calculating the Young modulus of orthorhombic polyethylene. Our proposed ultimate value at zero Kelvin temperature is 334 GPa. For the first time the modulus is evaluated *ab initio* (no bias from experimental data) with demonstrated basis set convergence. Therefore the present value may be considered the first true value for the Young modulus of perfect orthorhombic polyethylene.

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