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ARTICLE *in* SOLID STATE COMMUNICATIONS · OCTOBER 2000

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# LDA calculations of the Young's moduli of polyethylene and six polyfluoroethylenes

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Received 5 July 2000; accepted 19 July 2000 by D.E. Van Dyck

## Abstract

The Young's moduli of the linear chain polymers, polyethylene and six polyfluoroethylenes, constrained to the planar conformation, are calculated by means of the local density approximation (LDA) using the Perdew–Zunger (PZ) correlation potential and a linear combination of Gaussian-type orbitals (LCGTO). © 2000 Published by Elsevier Science Ltd.

**Keywords:** A. Polymers; D. Elasticity

**PACS:** 62.20.–x; 62.20.D; 71.20.Rv

## 1. Introduction

Because of the simplicity of its structure and its technical importance, the electronic structure [1–12] and the crystal-line structure [13–22] of the polyethylene and its fluorine-substituted derivatives have been intensively investigated in recent decades. The Young's modulus of polymer chains is an important parameter for their application. A lot of theoretical calculations [25–37] and experimental measurements [38–45] of the Young's modulus of the polyethylene chains have been done.

In general, the bond lengths and bond angles obtained from local-density (LDA) optimization are smaller than the experimental values or than the results of Hartree–Fock calculations [27,28]. In this work, we calculate Young's moduli of polyethylene and all six polyfluoroethylenes by LDA with Gaussian basis sets.

## 2. Methods

Two equivalent formulae of the Young's modulus  $Y$  ([23]

or [24]) are:

$$Y = \frac{F/A}{\Delta c/c_0}, \quad (1)$$

and

$$Y = \frac{c_0}{A} \left. \frac{d^2 E}{dc^2} \right|_{c=c_0} \quad (2)$$

where

$$F = \frac{dE(c)}{dc} \approx (\Delta c) \left( \left. \frac{d^2 E}{dc^2} \right|_{c=c_0} \right) = 2 \frac{E(c) - E(c_0)}{\Delta c}$$

is the force needed to produce an elongation  $\Delta c$  of a polymer chain, which has an original length  $c_0$  and  $A$  is the area of the cross-section of the polymer chain. Eq. (2) is frequently used in the practical calculations of Young's modulus by many authors [25–31].

In order to use Eqs. (1) or (2), the total energies  $E(c)$  per unit cell of a polymer in the undeformed and elongated state are required. They are computed by the local density approximation (LDA) with a Gaspar–Kohn–Sham exchange term and a Ceperley–Alder correlation term, using the Perdew–Zunger analytic fitting [46,47].

The orbital basis sets have in Huzinaga's notation the contraction scheme for oH (centered on the nuclei) (41/1\*), oC(7111/411/1\*), oN(7111/411/1\*) and oO(7111/411/

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1<sup>\*</sup>). The auxiliary Gaussian functions used to express the density, the exchange and correlation terms are aH(3,1;3,1) aC(4,4;4,4) aN(4,4;4,4) aO(4,4;4,4). These contracted Gaussians and auxiliary functions are optimized for LDA calculations by Godbout et al. [48]. The number of  $K$  points in the half Brillouin zone  $[0, \pi]$  is 9.

In the previous work, the optimized geometry of the undeformed polyethylene and six polyfluoroethylenes [11,12] was found, especially the C–C bond length  $l$  and the C–C–C bond angle  $\theta$ . These two undeformed parameters are denoted by  $(l_0, \theta_0)$ . It was also found in both cases that the minimum of the screw angle was 180°. Therefore in the

and

$$g = \left( \frac{\partial^2 E}{\partial \theta^2} \right)_{l_0}$$

can be calculated directly at  $(l_0, \theta_0)$  or by fitting the paraboloid  $E(l, \theta)$ . In order to check the validity of the method, we have done both.

When the polymer chain is elongated from  $c_0 = 2l_0 \sin(\theta_0/2)$  to  $c = 2l \sin(\theta/2)$  per unit cell, one easily finds the energy minimum  $E(c)$  and its position  $(l, \theta)$  under the elongated state by the Lagrange multiplier method in the harmonic approximation:

$$(\Delta l)_{\min} = \frac{b \left( \frac{l_0}{2} \operatorname{ctg} \frac{\theta_0}{2} \right) - g}{l_0 \cos \frac{\theta_0}{2} \left( b - a \frac{l_0}{2} \operatorname{ctg} \frac{\theta_0}{2} \right) + 2 \sin \frac{\theta_0}{2} \left( b \frac{l_0}{2} \operatorname{ctg} \frac{\theta_0}{2} - g \right)} (\Delta c),$$

$$(\Delta \theta)_{\min} = \frac{b - a \left( \frac{l_0}{2} \operatorname{ctg} \frac{\theta_0}{2} \right)}{l_0 \cos \frac{\theta_0}{2} \left( b - a \frac{l_0}{2} \operatorname{ctg} \frac{\theta_0}{2} \right) + 2 \sin \frac{\theta_0}{2} \left( b \frac{l_0}{2} \operatorname{ctg} \frac{\theta_0}{2} - g \right)} (\Delta c)$$

calculations of the Young's moduli, we will adopt this planar backbone conformation as our starting point and neglect the changes in C–H and C–F bond lengths as well as the changes in the H–C–H, F–C–F and H–C–F bond angles. The C–C bond length  $l$  and C–C–C bond angle  $\theta$  of the backbone will be the two main parameters to determine the Young's moduli. A calculation of the Young's moduli investigating the influence of the change of other parameters is reported elsewhere [50].

Because the code used in the calculation [46,47] can only do a single-point energy calculation for fixed geometry, the Lagrange multiplier method is used to find the energy minimum under a fixed strain, which greatly reduces the computation. Three second-order derivatives of energy

$$a = \left( \frac{\partial^2 E}{\partial l^2} \right) \Big|_{\theta_0}$$

$$b = \left( \frac{\partial^2 E}{\partial \theta \partial l} \right) \Big|_{l_0, \theta_0}$$

where  $(\Delta l)_{\min}$  and  $(\Delta \theta)_{\min}$  are the changes of C–C bond length and C–C–C bond angle with respect to their equilibrium values  $(l_0, \theta_0)$  under the strain  $\Delta c/c_0$ . Therefore the stress in the deformed state and the Young's modulus can be calculated. The expression for Young's modulus is

$$Y = 2 \frac{l_0}{A_2 \sin \frac{\theta_0}{2}} \frac{\frac{ag - b^2}{2}}{a \left( \frac{l_0}{2} \operatorname{ctg} \frac{\theta_0}{2} \right)^2 - 2b \left( \frac{l_0}{2} \operatorname{ctg} \frac{\theta_0}{2} \right) + g} \quad (4)$$

Eqs. (3) and (4) express the properties of a elongated chain in terms of  $(l_0, \theta_0, a, b, g)$  of the undeformed state. They are applicable for polymer chains with a backbone-like polyethylene.

We also calculate Young's modulus by making use of Eq. (2). In this procedure, we first optimize  $(l, \theta)$  for different elongations  $\Delta c$ , then calculate

$$\frac{d^2 E}{dc^2} \Big|_{c=c_0}$$

Table 1  
Unit cell and geometry of polyethylene and polyfluoroethylenes

Polymer	Abbreviation	Chemical repeat unit	X11	X12	X21	X22
Polyethylene	PE	CH <sub>2</sub> CH <sub>2</sub>	H	H	H	H
Polyvinylfluoride	PVF	CH <sub>2</sub> CHF	H	H	H	F
Poly(vinylidene fluoride)	PVF2	CH <sub>2</sub> CF <sub>2</sub>	H	H	F	F
<i>syn</i> -Poly(1,2-difluoroethylene)	sPDFE	CHFCHF	H	F	H	F
Poly(1,2-difluoroethylene)	PDFE	CHFCFH	H	F	F	H
Polytrifluoroethylene	P3FE	CHFCF <sub>2</sub>	H	F	F	F
Polytetrafluoroethylene	PTFE	CF <sub>2</sub> CF <sub>2</sub>	F	F	F	F

directly or by fitting a parabola

$$E(c) = E(c_0) + \frac{1}{2} \frac{d^2 E}{dc^2} \bigg|_{c=c_0} (c - c_0)^2$$

The method based on Eq. (4) and the method based on Eq. (2) are carefully compared in the case of polyethylene where they give very close results. Then these methods are applied to six polyfluoroethylenes.

### 3. Results and discussion

#### 3.1. Young's moduli of polyethylene and polyfluoroethylenes

The unit cell of polyethylene and polyfluoroethylenes is given in Table 1. The area of the cross-section of the polyethylene chain obtained from X-ray crystalline structure [13–22] is  $A = 18.24 (\text{\AA})^2$ . It was adopted by many authors in the calculations of the Young's modulus of the polyethylene chain [25–31]. If we take the van der Waals radii of atoms  $r_H = 1.20 \text{\AA}$  and  $r_C = 1.60 \text{\AA}$  [49], and take  $\angle HCH = 109.5^\circ$ ,  $\angle HCH = 112.984^\circ$ ,  $r_{C-C} = 1.54 \text{\AA}$ ,  $r_{C-H} = 1.09 \text{\AA}$ , then the area of the cross-section of the polyethylene chain is  $A = 17.89 (\text{\AA})^2$ . These two values should close each other since the van der Waal's radii of atoms are derived from the lattice parameters of the molecular crystals.

The methods described in the last section yield converged results of the Young's modulus of the polyethylene chain. By Eq. (2) with 1 and 2% strains we calculate

$$\frac{d^2 E}{dc^2} \bigg|_{c=c_0}$$

and get  $Y = 368 \text{ GPa}$ . If one computes

$$\frac{d^2 E}{dc^2} \bigg|_{c=c_0}$$

by fitting  $E(c)$  for strains 0.1, 0.2, 0.4, 0.79 and 1.19%, the result is  $Y = 360 \text{ GPa}$ . In these calculations, we first need find the set of values of  $(l, \theta)$ , which satisfy the constraint  $c = 2l \sin(\theta/2)$  for each  $\Delta c$ , and then scan this set to find the minimum of the deformed state with elongation  $\Delta c$ .

We also estimate the Young's modulus from Eq. (4), where the three second-order derivatives can be calculated

at the point  $(l_0, \theta)$  by taking  $\Delta l = 0.01 \text{\AA}$  and  $\Delta \theta = 1^\circ$ :

$$a = \left( \frac{\partial^2 E}{\partial l^2} \right) \bigg|_{\theta_0} = 1.068115 \left[ \frac{\text{Hartree}}{(\text{\AA})^2} \right],$$

$$b = \left( \frac{\partial^2 E}{\partial \theta \partial l} \right) = 0.2185661 \left[ \frac{\text{Hartree}}{(\text{Radian } \text{\AA})} \right],$$

$$g = \left( \frac{\partial^2 E}{\partial \theta^2} \right)_{l_0} = 0.4758707 \left[ \frac{\text{Hartree}}{(\text{Radian})^2} \right]$$

then substitute these in Eq. (4). This yields  $Y = 380 \text{ GPa}$ . If we calculate  $a$  by fitting  $E(l, \theta = \theta_0)$ ,  $g$  by fitting  $E(l = l_0, \theta)$  and  $b$  by averaging several calculated values from  $E(l_i, \theta)$  for several different  $l$  (making use of above  $a$  and  $g$  values), all the calculated values of  $Y$  dropped in the range 340–380 GPa. Finally  $a$ ,  $b$  and  $g$  are extracted from fitting  $E(l, \theta)$  by different random sampling points, the results of  $Y$  give again values of 340–380 GPa. The Young's modulus of the polyethylene chain obtained by our work and other theoretical and experimental methods is given in Table 2.

In the case of the six polyfluoroethylenes, the data of some crystal structures are not available. Therefore, we need to estimate the area of the cross section from the van der Waals radii of the atoms, by  $r_C = 1.60 \text{\AA}$ ,  $r_F = 1.35 \text{\AA}$  [49]  $r_{C-C} = 1.560 \text{\AA}$ ,  $r_{C-F} = 1.346 \text{\AA}$ ,  $\angle CCC = 131.1^\circ$ ,  $\angle FCF = 108.98^\circ$  (the parameters for PTEF). This gives  $A_{\text{van}} = 24.62 (\text{\AA})^2$ . To compare the difference for the other polyfluoroethylenes, we take the above  $A_{\text{van}}$ . If the crystal structures are known, the Young's moduli are also calculated with the values of area obtained from the lattice parameters. We will calculate the Young's moduli of six polyfluoroethylenes from Eq. (2) with strains 1 and 2%. It should be pointed out that in order to meet the requirement of screw symmetry, we force all the C–C bond lengths and the C–C–C bond angles to be the same and neglect the possible bend of the chains.

The Young's moduli and force constants are listed in Table 3. It is worthy of notice that the values of the force constant  $a$  are exactly the same for PVF2, PDFE and P3FE, the values of  $b$  are exactly the same for PVF2, sPDFE, P3FE and PTFE, the values of  $g$  are exactly the same for PVF and PVF2.

Table 2  
Young's moduli (GPa) of polyethylene

This work	X-ray	Neutron scattering	Raman	Mechanical	MD	HF/6-31G* +MP2	HF/6-31G*	Force field
360	240–255 [39,40]	329 [41]	280–358 [42–45]	288 [38]	334 [29]	336 [28]	339 [27]	286–368 [25–33]

Table 3

Young's moduli (GPa) and force constants. The sixth column is the area of the cross section of the chains obtained from the known crystalline structures, the numbers of  $Y$  in last column are obtained by the values of area in sixth column. The numbers of  $Y$  in the second column are obtained from  $A_{\text{van}} = 24.62 \text{ (\AA)}^2$  for six polyfluoroethylenes

Polymer	Young's moduli (GPa)	$a$ (Hartree/ $\text{\AA}^2$ )	$b$ (Hartree/ $(\text{\AA} \text{ rad})$ )	$g$ (Hartree/(rad) $^2$ )	Area <sup>[13–22]</sup> ( $\text{\AA}^2$ )	Young's moduli (GPa)
PE	360	1.07	0.22	0.48	18.24	
PVF	235	1.98	0.26	0.80	21.21	273
PVF2	170	1.83	0.17	0.80	21.06	199
sPDFE	299	1.07	0.17	0.55		
PDFE	255	1.83	0.25	0.20		
P3FE	253	1.83	0.17	0.70		
PTFE	249	0.92	0.17	0.75	24.84	247

### 3.2. Changes of the geometry parameters, band structure and Mulliken charge in the elongated states

The equilibrium C–C bond length increases with the increasing of the number of F atoms, about 1% per F atom. The changes of the C–C bond length and the C–C–C bond angle with strains in the elongated states are well described by Eq. (3) with an accuracy 0.1%. The order of magnitude of the changes of the conduction band and the valence band is 0.05 eV for a strain of 1% and 0.10 eV for a strain of 2%. Increasing strain will increase the absolute values of the Mulliken charges on two carbon atoms, the variations are very small and about 0.002 for a strain of 1% and 0.004 for a strain of 2%.

## 4. Conclusion

We have calculated the Young's moduli for polyethylene and polyfluoroethylenes and various properties of the elongated states. The computed Young's modulus of polyethylene is in good agreement with the experimental measurements and values obtained by other theoretical methods.

## Acknowledgements

Z.M.L. would like to express his gratitude to Drs F. Bartha and V. Popov for fruitful discussions. We are indebted to the Flemish Science Foundation (Grant No. G 2131.94) and to the Concerted Action of the University of Antwerp (Grant No. GOA-BOF-UA 23).

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