Energetics of chain folding in polyethylene crystals*

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Semi-empirical energy calculations have been used to investigate several aspects of chain folding in polyethylene single crystals. Calculations of isolated (1 1 0) and (2 0 0) folds indicate that the fold energy, relative to the planar zig-zag form of the molecule, is lower in the (2 0 0) fold than in the (1 1 0) fold. The minimum surface energies for isolated (1 1 0) and (2 0 0) folds were calculated to be 102.5 and 95.6 erg cm^{-2}, respectively. The energetics of packing the minimum-energy folds into an array representing a portion of a single-crystal fold surface were also investigated. For fully optimized (1 1 0) fold packing, the habit corresponding to the Reneker–Geil model I (RG I) was found to be lower in energy than model RG II. However, the packing of (1 1 0) folds at experimentally observed unit-cell dimensions in RG I and RG II packing habits gave almost equal packing energies. It was also found that the setting angle was a function of the packing habit. Results of packing (2 0 0) folds into a fold surface indicate that a crystallographically reasonable '(2 0 0)'-type fold surface would appear to be impossible. The interaction energy of a straight-chain segment in the vicinity of a fold surface was also calculated. Not surprisingly, it was found that the lowest-energy situation finds the straight chain somewhat nestled into a groove between the {1 1 0} fold planes.

(Keywords: chain folding; polyethylene crystals; energetics)

INTRODUCTION

When linear-chain polymers crystallize from dilute solution, they usually do so in the form of individual microscopic crystals that exhibit varying degrees of morphological complexity depending on the temperature of crystallization[1–3], the solvent used[4–8], the molecular weight[1,5,6,9,10] and concentration[1,11]. The simplest entity obtained when linear polymers like polyethylene are crystallized is the monolayer crystal.

The existence of polymer single crystals was first discovered by Jaccodine[4], but their basic molecular nature remained unexplained until Keller's work[6] in 1957. Based on his studies of the properties of single crystals, Keller concluded that the polymer molecules in the crystals were folded back upon themselves. His conclusions are strongly supported by subsequent morphology and fold structure studies on polyethylene crystals[1–3,5–20].

By means of dark-field electron and dark-field optical microscopy[2,7,11,13,14], it has been shown that some crystals of polyethylene are not flat lamellae but actually consist of hollow pyramids with four or more sectors. The surfaces of these crystals are either smooth or corrugated depending on the method and conditions used for crystal preparation. Also, the slope of the pyramid along a line normal to the edge was found to vary among different crystals and to depend on the habit of the crystal. Bassett, Frank and Keller[2] found by X-ray diffraction that the fold surfaces of polyethylene crystals formed at high and low supercooling were {(3 1 4)(1 1 0)} and {(3 1 2)(1 1 0)}, respectively. Reneker and Geil[7] and Niegisch and Swan[14] calculated the slope of the pyramid along a line normal to the edge to be about 32° from crystals that had folded along a domain boundary, and predicted that the fold surface was {(1 1 1)(1 1 0)}. To understand the habit features of the crystal, Reneker and Geil[7] developed models for fold packing in the (1 1 0) plane. These models are the basis of the packing arrangements considered in this study and are described in detail in a later section.

In this paper, the convention adopted in describing the packing habit follows that of Bassett, Frank and Keller[11]. A 'fold surface' is defined as being the surface of the crystal tangent to the folds and labelled with the indices of both the fold surface and growth face. Thus, a {(1 1 1)(1 1 0)} crystal is a flat-based, pyramidal, diamond-shaped crystal having {1 1 1} fold surfaces and {1 1 0} growth faces, the four individual fold domains being (1 1 1)(1 1 0), $(\bar{1}\,1\,1)(\bar{1}\,1\,0)$, $(1\,\bar{1}\,1)(1\,\bar{1}\,0)$ and $(\bar{1}\,\bar{1}\,1)(\bar{1}\,\bar{1}\,0)$. Two other terms that need to be defined are chain-folded molecule and fold. A 'chain-folded molecule' is any long-chain molecule that folds and loops back on itself, whereas a 'fold' specifically refers to the folded portion of the chain-folded molecule. *Figure 1* shows two chain-folded molecules, each of 20 methylene units. The fold shown in *Figure 1a*, consisting of C–C bonds labelled 1–7, is a (1 1 0) fold, whereas the fold shown in *Figure 1b*, consisting of C–C atoms labelled 1–8, is a (2 0 0) fold. The setting angle, defined as the angle that the plane of the C–C backbone of the stem makes with the *b* axis, is shown as θ in *Figure 1*. Another distinction that we would like to make is between an isolated fold and a fold packed into a fold surface. An 'isolated fold' is a single fold all by itself, as shown in *Figures 1a* and *1b*, whereas a 'fold packed into

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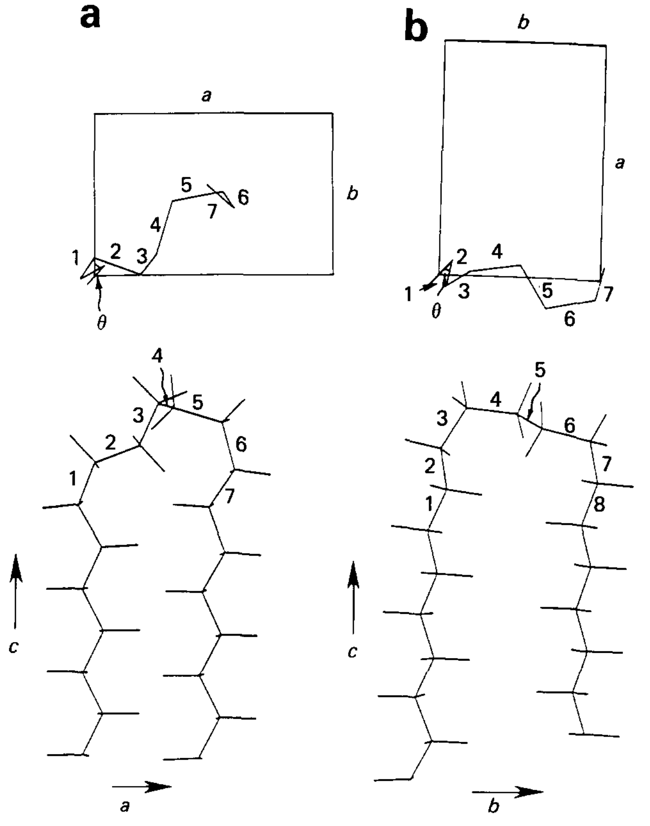

Figure 1 (a) Upper diagram: top view of the (1 1 0) fold in the unit cell with the setting angle, θ, defined with respect to the *b* axis. (Hydrogen atoms have been omitted for clarity.) Lower diagram: projection of the (1 1 0) fold onto a (0 1 0) plane. (b) Upper diagram: top view of the (2 0 0) fold in the unit cell with the setting angle, θ, defined with respect to the *b* axis. (Hydrogen atoms have been omitted for clarity.) Lower diagram: projection of the (2 0 0) fold onto a (1 0 0) plane

a fold surface' is surrounded by identical neighbouring folds (see fold labelled 1 in later *Figures 3*, *5* and *7*).

Even though experimental evidence of the habit features of a single crystal of polyethylene was established in the early 1960s, there was no direct experimental proof of tight chain folds in crystals of long linear molecules until recent years[15,17]. Jing and Krimm[15] found from i.r. spectra of mixed single crystals of hydrogenated and deuterated polyethylene grown from dilute solution that adjacent-stem cluster size, $\langle \nu_c \rangle$, is 4 to 8 in both the {1 1 0} and {2 0 0} sectors, leading to a probability of adjacent re-entry $P_{ar} = 1 - 1/\langle \nu_c \rangle$ of 0.75 or more. This evidence implies tight folds. Strong evidence of tight folding was also found by Ungar and Organ[17]. They have made the first direct observation of i.r. bands due to adjacent (1 1 0) chain folds in polymethylene. Based on their spectral data, they assigned *gauche* or *trans* bond rotation angles to the fold conformation of a (1 1 0) fold. (We shall later see that our predicted results are consistent with those of Ungar and Organ[17].)

In the absence of direct experimental proof on the configuration of a tight chain fold, several groups[18-21] tried to simulate tight chain folds by energetics calculations. Essentially, the technique of energetics calculations is computerized model building and evaluation. The molecular basis of energetics of chain folding can be further clarified with the aid of *Figure 2*, which is reproduced from ref. 22. *Figure 2a* shows a fold with work of formation q formed by bending a chain back on itself to re-enter the lattice, creating a fold surface with area $2A_0$, where $a_0 b_0 = A_0$ is the cross-sectional area of the chain with a_0 and b_0 as stem width and thickness. *Figure 2b* shows the potential energy of a segment as it rotates through angle ϕ about the bond between the ith and the $(i+1)$th chain backbone atom. The angle ϕ is measured from the plane determined by the $i-1$, i and $i+1$ atoms as shown. The barriers between the *trans* and *gauche* positions, and the potential energy of the *gauche* positions, arise from the substituent groups on the $(i+1)$th atom interacting with the ith atom. In polyethylene, a sequence of *trans* rotations represents the straight chain found in the interior of the crystal. The fold contains at least several *gauche* rotations that are the principal source of the work of chain folding q.

Having seen the significance of energetics analysis in the determination of q for polyethylene, we must now ask how this value is to be interpreted in terms of the fold surface interfacial free energy, σ_e. Hoffman *et al.*[22] have shown that σ_e is related to q as follows:

$$\sigma_e = (q/2A_0) + \sigma_{e0} \qquad (1)$$

where q is the work required to form the fold by bending the polymer chain back on itself in the appropriate conformation. The term σ_{e0} is the value the surface free energy would assume if no work were required to form the fold and can be approximated to be equal to zero[22].

Energetics analysis has previously been applied by Boyd[23], Reneker[24] and Farmer and coworkers[25] to study the defects and molecular motions occurring in crystalline or semicrystalline polymers. Polyethylene is an ideal material for energetics analysis because of its relative structural simplicity and its atomic composition, which is satisfactorily analysed using the available potential energy functions[26]. The major drawbacks of most energetics analysis are: (a) neglecting the entropic contribution to the Gibb's free energy; and (b) neglecting the effects of concentration, molecular weight, nature of the solvent and temperature (unless potential energy functions for different temperatures are available). These

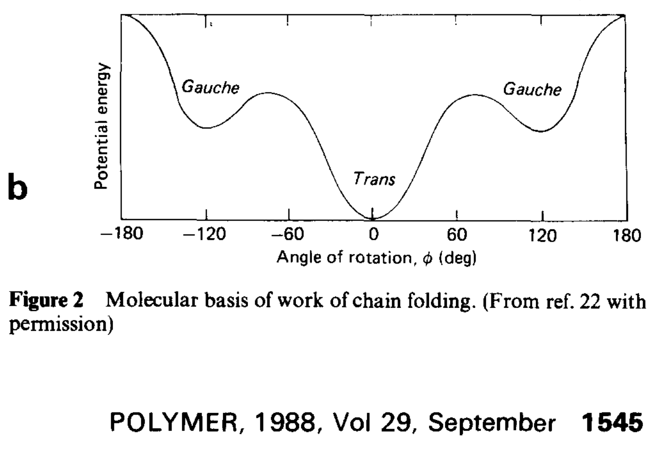

Figure 2 Molecular basis of work of chain folding. (From ref. 22 with permission)

factors must always be considered when comparing calculated and experimental results.

Based on evidence gathered from studies on truncated diamond-shaped single crystals of polyethylene with six sectors, four {1 1 0} sectors and two '{2 0 0}'-type sectors, it is commonly believed that the long chains of polyethylene are folded by distinctly different folds that lie parallel to the growth faces on which they were deposited, so that the folds in the {1 1 0} and {2 0 0} sectors lie in the {1 1 0} and {2 0 0} planes, respectively[27]. The '{2 0 0}'-type sectors and the '(2 0 0)' fold are often written within quotes in this paper because we shall see later that the situation on the {2 0 0} planes is complicated by packing problems.

The (1 1 0) fold, which connects two adjacent segments in a {1 1 0} plane, is parallel to the diagonal of the unit cell and creates planes of closest packing in polyethylene crystals. The stem separation distance of a '(2 0 0)' fold is equal to the *b* cell dimension and creates the second most closely packed planes in polyethylene crystals. It is important to note that even 30 years after the discovery of polyethylene single crystals, there is no direct evidence, either by i.r. spectroscopy[17] or X-ray diffraction[11], of the existence of a '(2 0 0)' fold array, unlike that of the (1 1 0) folds. Our work will prove to be consistent with this statement.

BACKGROUND

In the past, several groups[18–21] proposed the conformations of tight chain folds in crystals of long-chain polyethylene. The main approach to predicting the conformation of a fold was to assign different torsion (internal rotation) and bond angles within the folded segment of the long chain and then to minimize the energy of the fold. The conformation giving the lowest energy for the fold was considered the most plausible.

The results of the previous studies[18–20] are contradictory, and the differences in their results mainly arise because of the following factors:

(1) Differences in the potential energy functions used.

(2) All possible modes of deformation, i.e. internal rotation and bending (which cause changes in the torsion and bond angles, respectively) and bond stretching or compression, were not considered.

(3) Several possible conformations were ignored outright by fixing the stem separation distance at the experimentally observed cell dimensions.

In the study by McMahon *et al.*[18], the only mode of deformation allowed in the folded segments of the polyethylene molecule was that of the torsion angles. Petraccone *et al.*[19] allowed all three deformation modes but still held the stems of the fold at the experimentally observed separation distance. Also, they used different reference points for the (1 1 0) and (2 0 0) folds. They defined their reference state as follows: the zero-energy state for a fold involving *m* methylene units consisted of two facing segments of *m*/2 units in the planar zig-zag conformation, with the same relative orientation and separation as the two straight segments that are joined together by the fold. By defining the reference states in this way, the zero-energy state for the (1 1 0) fold is the interaction of two straight segments at about 4.4 Å separation, while the zero-energy state for the (2 0 0) fold is the interaction of two straight segments at about 5.0 Å separation. Thus comparison of their (1 1 0) and (2 0 0) fold energies is questionable, since they do not have a common reference state.

In contrast to the above two studies on chain folding in polyethylene crystals[18,19], Oyama *et al.*[20] considered packing of the folds into a fold surface and determined the conformation of a fold as the minimum of surface energy, not of conformation energy. However, they restricted the folds at the observed cell dimensions, limited the torsion angles to *trans* or *gauche* only, and considered only one packing habit for the (1 1 0) folds, i.e. the RG I packing with the fold surface parallel to the (0 0 1) plane.

To overcome the shortcomings of the previous studies, this work examines the following aspects of chain folding in polyethylene crystals using energetics analysis.

(1) Creation of minimum-energy (1 1 0) and (2 0 0) folds in isolation, and in the presence of six identical neighbouring folds. The (1 1 0) fold packing habits considered are: (a) RG I {(1 1 1)(1 1 0)}; (b) RG I {(3 1 1)(1 1 0)}; (c) RG II {(1 1 2)(1 1 0)}; and (d) RG II {(3 1 2)(1 1 0)}.

(2) Minimization of the energy with respect to the unit-cell dimensions and the setting angle for every packing habit considered.

(3) Investigation of the interactions between a straight segment and the fold surface.

FOLD PACKING MODELS

(1 1 0) fold packing

Reneker and Geil[7] suggested models for the (1 1 0) fold packing that are now commonly referred to as the RG I and RG II packing habits. In the RG I packing habit, the folds in successive fold planes are aligned along the [1 0 0] and [0 1 0] directions (*Figure 3*). The packing of the molecular zig-zags (straight segments) in the interior of the lamella requires that the adjacent folds in successive (1 1 0) fold planes be displaced by an integral number of repeat distances (2.54 Å). For $n=0$, a flat lamellar crystal develops. For $n=1$, the folds in adjacent $(1\bar{1}0)$ planes in *Figure 3* are displaced by one repeat distance and a hollow pyramidal crystal is formed. The pyramid is either flat-based or non-flat-based depending on whether the adjacent folds within the *same* {1 1 0} planes are displaced or not. When $n=1$, and the adjacent folds within the same {1 1 0} planes are *not* staggered, then a {(1 1 1)(1 1 0)} flat-based pyramidal crystal with a slope of 31.6° is formed, whereas a {(3 1 1)(1 1 0)} non-flat-based pyramidal crystal with a slope of 49° is formed when the adjacent folds within the same {1 1 0} fold plane are staggered by two repeat distances (*Figure 4*).

In the RG II packing habit, the folds in the successive {1 1 0} fold planes are aligned in the [1 1 0] and $[\bar{1}30]$ directions as shown in *Figure 5*. RG II differs from RG I in that every other fold plane is rotated by 180° about the chain axis through the stem of a chain-folded molecule. The packing of the molecular zig-zags in this case requires that successive fold planes be displaced by $(n+\frac{1}{2})$ repeat distances in the [0 0 1] direction. As in the case of RG I packing, the pyramid is either flat-based or non-flat-based depending on whether the adjacent folds within the same {1 1 0} plane are displaced or not. For $n=0$, a {(1 1 2)(1 1 0)} flat-based pyramid is formed when there is *no* staggering of the folds within the same {1 1 0} planes, whereas a {(3 1 2)(1 1 0)} non-flat-based pyramid is

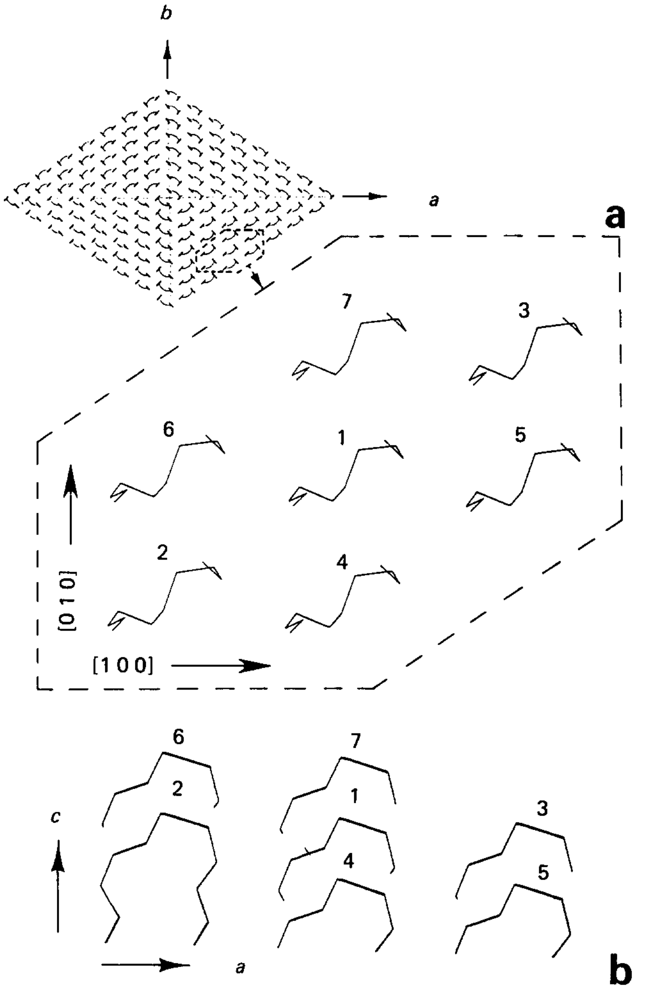

Figure 3 Schematic of RG I fold packing. (a) Projection of a section of the crystal onto a (0 0 1) plane. (b) Projection of a section of the crystal onto a (0 1 0) plane. (Hydrogen atoms have been omitted for clarity)

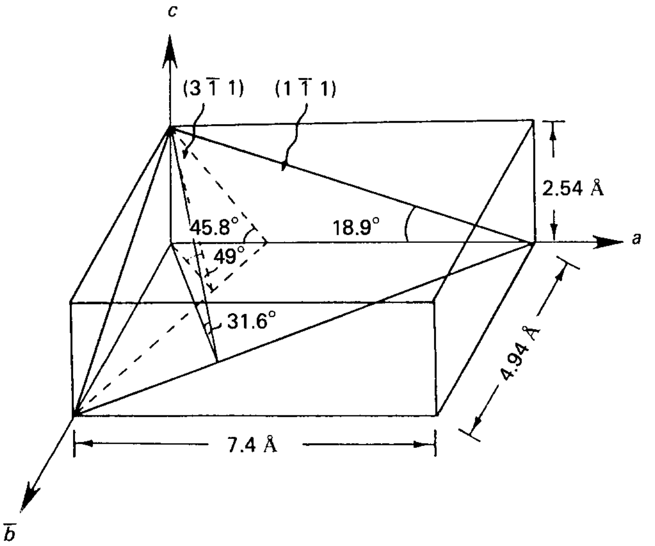

Figure 4 Illustrations of the relationship of the oblique terminal planes, (1 $\bar{1}$ 1) and (3 $\bar{1}$ 1) in this case, to the polyethylene unit cell for RG I {(1 1 1)(1 1 0)} and RG I {(3 1 1)(1 1 0)} packing habits

formed when the adjacent folds within the same {1 1 0} plane are staggered by one repeat distance. The slope of the pyramids for these two cases are about 17° and 30°, respectively (*Figure 6*).

Experimentally, the observed angles of inclination of the (1 1 0) fold surface along the *a* axis are 18–19° (refs. 3 and 14) and 29° (ref. 3). These angles of inclination along the *a* axis would result from RG I {(1 1 1)(1 1 0)} and RG II {(3 1 2)(1 1 0)} fold packing habits (*Figures 4* and *6*). These packing habits form pyramidal crystals with slopes of about 32° and 30°, respectively.

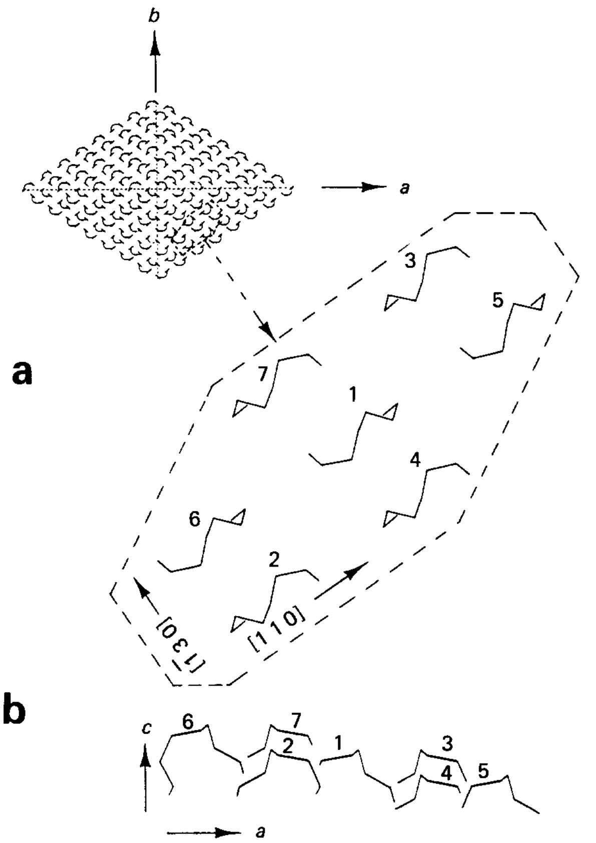

Figure 5 Schematic of RG II fold packing. (a) Projection of a section of the crystal onto a (0 0 1) plane. (b) Projection of a section of the crystal onto a (0 1 0) plane. (Hydrogen atoms have been omitted for clarity)

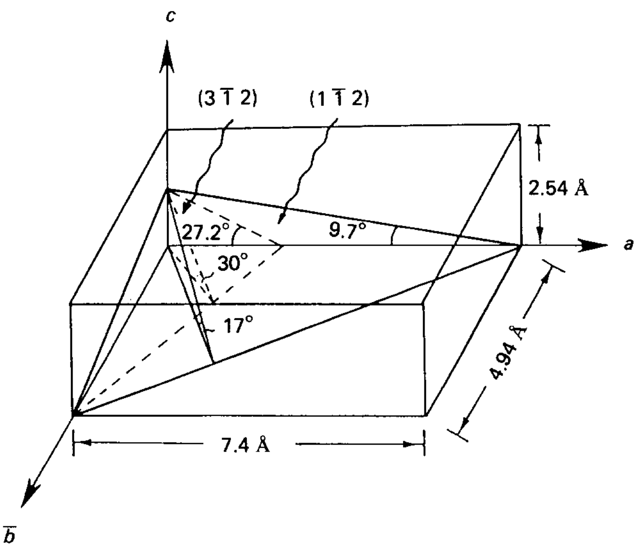

Figure 6 Illustrations of the relationship of the oblique terminal planes, (1 $\bar{1}$ 2) and 3 $\bar{1}$ 2) in this case, to the polyethylene unit cell for RG II {(1 1 2)(1 1 0)} and RG II {(3 1 2)(1 1 0)} packing habits

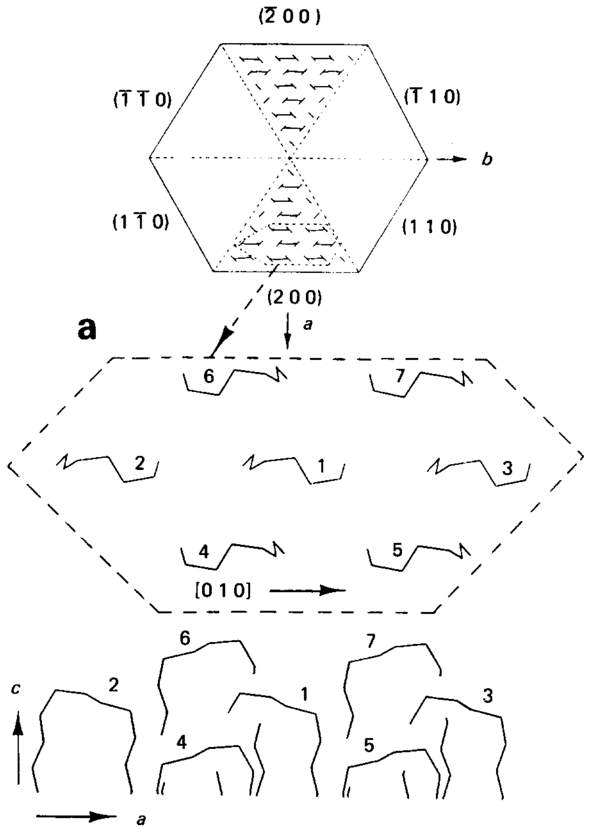

Figure 7 Schematic of (200) fold packing. (a) Projection of a section of the crystal onto a (001) plane. (b) Projection of a section of the crystal onto a (100) plane. (Hydrogen atoms have been omitted for clarity)

(200) fold packing

Figure 7 shows one possible packing habit of the (200) folds with the folds in the adjacent fold planes displaced by one repeat distance. In this case, the fold surface would lie along the {101} planes. Other possible low-index planes parallel to the (200) fold surface are {201}, {301} and {302}, depending on the staggering sequence of the (200) folds.

COMPUTATIONAL METHOD

The method used is a combination of the array-energy minimization scheme used in the previous calculations[25] and the molecular-energy minimization technique employed in the computer program MOLBD3[28].

The computer programs used were SCEAM, CREAM and MOLBD3, described previously[28,29]. SCEAM generates a molecule by specifying the bond lengths, bond angles and torsion angles. CREAM minimizes the packing energy of the molecules relative to their positions in the packed structure. MOLBD3 minimizes the energy of a molecule with respect to its bond lengths, bond angles and torsion angles. This can optionally be carried out in the presence of static neighbouring molecules to take into account the intermolecular interactions.

The steric potentials used were those in set I of ref. 26. These potential functions have been extensively used in calculations on hydrocarbons and give quite reasonable results[25] at 200 K, a temperature representative of those for the data from which the potential energy parameters were derived. The unstrained values of the molecular parameters used in the calculations were as follows: C–C–C bond angle, 112.0°; H–C–H bond angle, 109.4°; C–C bond length, 1.534 Å; and C–H bond lengths, 1.090 Å. The central chain-folded molecule was 20 methylene units (60 atoms) in length (see *Figures 3*, *5* and *7*). In any packing habit, the length of the neighbouring chain-folded molecules (marked as 2 to 7 in *Figures 3*, *5* and *7*) was adjusted such that the basal plane of the packing was parallel to the (001) plane and the total number of methylene units in the packing was 140. The fold portion of the chain-folded molecules consisted of about 7–8 methylene units (see *Figure 1*).

The calculation procedure for both {110} and {200} fold domains was as follows:

(1) Creation of an isolated fold using the torsion and bond angles from earlier calculations for an isolated fold[19], with the straight segments (stems) having the unstrained parameters given above.

(2) Minimization of the energy of an isolated fold at fixed stem separation distance, using the MOLBD3 program.

(3) Minimization of the energy of an isolated fold with respect to the stem separation distance.

(4) Minimization of the packing energy of the seven neighbouring folds packed in an array as shown in *Figures 3b* and *5b* with respect to the unit-cell dimensions and the setting angle.

(5) Minimization, using the MOLBD3 program, of the fold energy of the central fold in the presence of six neighbouring folds, which were constrained at the minimum-energy cell dimensions and setting angle.

(6) Sequentially repeating steps (4) and (5) until the minimum packing energy (i.e. surface energy) was determined.

RESULTS AND DISCUSSION

Creation of the isolated fold

The starting point of this study was the creation of a (110) and a (200) chain-folded molecule using the SCEAM program. The values of the torsion angles and the bond angles determined by Petraccone *et al.*[19] were used for creating the folds in the 60-atom chain-folded molecules, which served as the starting folded segments for this study.

Minimization on Petraccone's (110) and (200) folds was done using the MOLBD3 program by keeping different combinations of the atomic coordinates fixed for some of the carbon atoms in the chain-folded molecules. In a real crystal, the stems of any chain-folded molecule are constrained by the surrounding stems. Therefore, to make a realistic model of a chain-folded molecule, it was necessary initially to constrain the stems and then to carry out repeated minimization using the MOLBD3 program by sequentially releasing the constraints near the folded portion of the chain-folded molecule.

The stem ends of the (110) and (200) folds were constrained at separation distances of 4.42 and 4.92 Å, respectively, close to the experimental values at 200 K[30]. After repeated minimization, it was found that the energies of the isolated (110) and (200) folds were 5.67 kcal mol^{-1} of folds and 5.20 kcal mol^{-1} of folds, respectively, relative to the planar zig-zag conformation of the molecule.

Next, the energy of each isolated fold as a function of the stem separation distance was calculated. It was found

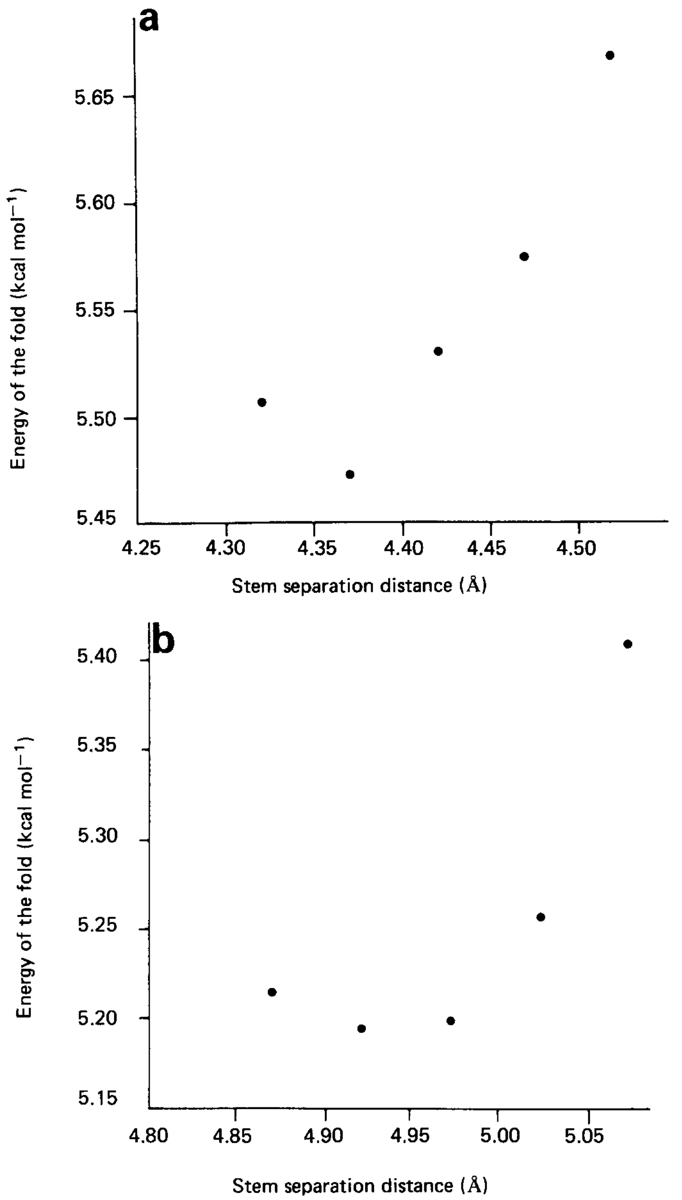

Figure 8 Energy of the fold, relative to the planar zig-zag form of the molecule, as a function of stem separation distance: (a) (1 1 0) fold; (b) (2 0 0) fold

that the *minimum* energies of the isolated (1 1 0) and (2 0 0) folds were 5.61 kcal mol^{-1} of folds and 5.20 kcal mol^{-1} of folds, respectively, relative to the planar zig-zag form of the molecule, at stem separation distances of approximately 4.37 and 4.92 Å, respectively. *Figure 8* shows the energies of (1 1 0) and (2 0 0) folds as a function of stem separation distance.

Table 1 presents the contributions from the bond deformation energy and intramolecular non-bonded interaction energy of the isolated fold to the overall deformation energy of the bonding topology of the minimum-energy (1 1 0) and (2 0 0) isolated folds. It is important to note that the values of both the bond deformation energy and the non-bonded interaction energy of the isolated folds in *Table 1* are independent of the stem length. As shown in *Table 2*, the non-bonded interaction energy of the fold was calculated by subtracting the sum of the intermolecular interaction energy between stems and the energy of the unstrained planar zig-zag form of a 20-methylene-unit all-*trans* (straight-chain) molecule from the non-bonded interaction energy of the 20-methylene-unit chain-folded molecule. Note that the non-bonded interaction energy of a 20-methylene-unit chain-folded molecule is the sum of the intramolecular non-bonded interaction energy of the isolated fold, the energy of the unstrained planar zig-zag form of a 20-methylene-unit all-*trans* molecule and the intermolecular interaction energy between the stems of the 20-methylene-unit chain-folded molecule.

Based on our calculated values of the minimum fold energies, the minimum *surface* energies for the (1 1 0) and (2 0 0) fold surfaces are 102.5 and 95.6 erg cm^{-2}, respectively. These values are in general agreement with the fold surface energy value of 93 ± 8 erg cm^{-2} obtained by Hoffman *et al.*[22] by thermodynamic means.

Table 3 compares the energies of the (1 1 0) and (2 0 0) folds, relative to the planar zig-zag form of the molecule,

Table 1 Calculated minimum energies of isolated (1 1 0) and (2 0 0) folds, relative to the planar zig-zag form of the molecule (kcal mol^{-1} of folds). The values in parentheses are the minimum surface energies

	Fold type	
	(1 1 0)	(2 0 0)
Stem separation distance	4.37 Å	4.92 Å
Energy of:		
(1) Bond deformation (bond angles, rotation angles and bond length) in the fold	4.78	3.30
(2) Non-bonded interaction in the fold[a]	0.83	1.90
(3) The fold, relative to the planar zig-zag form of the molecule, i.e. (1)+(2)	5.61 (102.5 erg cm^{-2})	5.20 (95.6 erg cm^{-2})

[a] See *Table 2*

Table 2 Calculation of the non-bonded interaction energy of the minimum energy isolated fold (kcal mol^{-1} of folds)

	Fold type	
	(1 1 0)	(2 0 0)
Stem separation distance	4.37 Å	4.92 Å
Energy of:		
(1) Non-bonded interaction of the 20-methylene-unit chain-folded molecule	3.47	5.34
(2) Intermolecular interaction between the stems of the 20-methylene-unit chain-folded molecule	−4.20	−3.40
(3) Planar zig-zag form of the 20-methylene-unit straight-chain molecule	6.84	6.84
(4) Non-bonded interaction in the fold, i.e. (1)−[(2)+(3)]	0.83	1.90

Table 3 Minimum energies of isolated (1 1 0) and (2 0 0) folds, relative to the planar zig-zag form of the molecule (kcal mol^{-1} of folds) for our folds and the folds proposed by McMahon *et al.*[18], Petraccone *et al.*[19] and Oyama *et al.*[20], recalculated using our potential energy parameters and computational method

	Fold type	
	(1 1 0)	(2 0 0)
This work	5.61	5.20
McMahon *et al.*[18]	15.26	12.86
Petraccone *et al.*[19]	8.51	8.28
Oyama *et al.*[20]	17.56	10.86

Table 4 Unit-cell dimensions, setting angle and packing energy for packing of polyethylene folds and stems at 200 K

		a (Å)	b (Å)	Setting angle (deg)	Packing energy (kcal mol^{-1})	Ref.
Stems only[a]	Exp.	7.27	4.91	–	–	30
	Calc.	7.26	4.94	48	–	23
	Calc.	7.19	4.86	47	–	26
	Calc.	7.11	4.92	48	–	37
Folds only[b] in packing mode						
RG I {(1 1 1)(1 1 0)}	Calc.	7.2	5.2	46	−44.6	This work
RG I {(3 1 1)(1 1 0)}	Calc.	7.4	5.3	48	−35.6	This work
RG II {(1 1 2)(1 1 0)}	Calc.	7.5	5.5	42	−37.8	This work
RG II {(3 1 2)(1 1 0)}	Calc.	7.4	5.5	42	−37.1	This work
Folds + stems[c] in packing mode						
RG I {(1 1 1)(1 1 0)}	Calc.	7.2	5.0	46	–	This work

[a] Stems only indicates the packing of seven planar zig-zag molecules
[b] Folds only indicates the packing of seven folded molecules, each of 20 methylene units
[c] Folds + stems indicates the packing of seven folded molecules, each of 100 methylene units

of our folds with those proposed by McMahon *et al.*[18], Petraccone *et al.*[19] and Oyama *et al.*[20], the latter energies recalculated using our potential energy parameters and method. Use of our potential energy parameters and method allows us to compare the energies of the folds proposed by past workers[18–20] with our folds on an identical basis. Interestingly, even though the trend in all four studies is identical and shows that the energy of an isolated (2 0 0) fold is less than that of an isolated (1 1 0) fold, only Petraccone and coworker's[19] and our work show that the minimum energy for isolated (1 1 0) and (2 0 0) folds are nearly equal. However, among the four studies, our study predicts the lowest-energy fold surface.

(1 1 0) fold packing

The (1 1 0) fold packing habits considered were: (a) RG I {(1 1 1)(1 1 0)}; (b) RG I {(3 1 1)(1 1 0)}; (c) RGII {(1 1 2)(1 1 0)}; and (d) RG II {(3 1 2)(1 1 0)}. In each habit, the fold packing energy was minimized with respect to the unit-cell dimensions and the setting angle. *Table 4* shows the unit-cell dimensions and the setting angles for the minimum-energy packing of seven (1 1 0) folds in RG I and RG II. Also shown in *Table 4* are the unit-cell dimensions and the setting angles for (a) the packing of seven straight segments within the core of the crystal and (b) the packing of seven long chain-folded molecules of 100 methylene units each to form a crystal with RG I {(1 1 1)(1 1 0)} habit.

On analysing the results on the unit-cell dimensions and the setting angles from *Table 4*, it is seen that some of these results are quite unique and unexpected. The unit-cell dimensions of the (1 1 0) fold packings were calculated to be slightly larger than the experimental values at 200 K, the temperature at which the potential energy parameters are most valid. The major difference between the calculated lattice dimensions of the fold surface and the experimental values was the increase in the *b* cell dimension. This increase in the *b* cell dimension resulted from an increase in the stem separation distance during the cyclic minimization of the packing energy of seven folds using CREAM, and that of the central fold, in the presence of the surrounding six folds, using MOLBD3. The stem separation distance increased from 4.37 to 4.44 and 4.65 Å in RG I and RG II packings, respectively. A similar trend of decreasing fold energy for isolated folds upon expansion of the fold structures was also reported by McMahon *et al.*[18]

Another interesting aspect of our results is the dependence of the setting angle on the packing habit. We found the setting angles in RG I and RG II to be close to 48° and 42°, respectively. In the past, several groups[31–37] have experimentally measured the setting angle in different forms of polyethylene, crystallized at different temperatures. Even though previous results[31–37] show no specific trend, the range in which the setting angles were obtained is 41–49°. One study[37] concluded that the setting angle was a function of temperature. Our results indicate that packing habit also influences the setting angle. Packing habit, in turn, may be affected by temperature.

To assess the effect of the crystalline core on the cell dimensions in the presence of the folds (and vice versa), the sum of the packing energy of a 20-methylene-unit chain-folded molecule surrounded by its six neighbouring chain-folded molecules and the interaction energy of two all-*trans* segments (of 40 methylene units each) surrounded by their neighbouring all-*trans* segments, for different cell dimensions, was also calculated. Note that this simulates one-half of the typical thickness of lamellar single crystals. The minimum energy for the RG I {(1 1 1)(1 1 0)} packing was found at $a = 7.2$ Å and $b = 5.0$ Å. (Cell dimensions were examined in increments of 0.1 Å.) The decrease in the minimum-energy *b* cell dimension from 5.2 Å (for the most favourable RG I fold packing) to 5.0 Å indicates that the influence of the straight segments in the crystalline core on the folds is to bring their ends closer to each other. Using the same energy parameters as have been used in this study, the packing energy of straight segments deep in the crystalline core was earlier calculated[25], to a greater accuracy, to be a minimum for $a = 7.26$ Å and $b = 4.94$ Å at a setting angle of 48°. The experimentally obtained unit-cell dimensions of polyethylene crystals at 200 K are $a = 7.27$ Å and $b = 4.91$ Å[30]. Our results, taken in context of the earlier calculations[25] and the experimental data[30], indicate that the influence of the fold in changing the unit-cell dimensions of the straight segments in the crystalline core is negligible, if any. The core influences the fold more than the folds influence the core.

Table 5 shows the packing energy of (1 1 0) folds in RG I and RG II habits at experimentally observed unit-cell dimensions at room temperature ($a = 7.4$ Å and $b = 4.96$ Å). The setting angles chosen for RG I and RG II packing were 48° and 42°, respectively. Interestingly, at these dimensions and setting angles, the energies of RG I and RG II packings are almost identical. This has some important ramifications. Voight-Martin and Mandelkern[3] have observed that a slight change in the crystallization temperature can lead to drastic changes in the slope of the pyramidal crystals of polyethylene. They found that the slope that the (1 1 0) fold surface makes with the *a* axis (i.e. $\tan^{-1}(c/a)$) was 18° and 27° for crystallization at temperatures of 127°C and 131.5°C, respectively. These slopes correspond to the slopes that the fold surface makes with the *a* axis by packing the (1 1 0) folds in the RG I {(1 1 1)(1 1 0)} and the RG II {(3 1 2)(1 1 0)} packing, respectively, as shown in *Figures 4* and *6*. The experimental data of Voight-Martin and Mandelkern[3], taken in context of our energetics calculations, indicate that minor changes in crystallization conditions may lead to significant changes in the crystal habit.

In *Table 6* we present the topology of the isolated (1 1 0) fold proposed by McMahon *et al.*[18] and Petraccone *et al.*[19], and compare them with our (1 1 0) folds packed in different packing habits. Petraccone's (1 1 0) fold and our (1 1 0) folds packed in different packing habits are in excellent agreement with the recent experimental data on (1 1 0) folds[17], which indicates that the torsion angles in the (1 1 0) folds are ...$gtggg^{-}g^{-}t$.... By comparing the topology of the four (1 1 0) folds in different packing habits, we found that even though the overall topology of any of the four folds is ...$gtggg^{-}g^{-}t$..., the actual values of the torsion and bond angles are different in each fold, depending on the packing habit. This indicates that topology of the fold is substantially influenced by the packing habit. There does not appear to be a single strongly dominant fold topology that dictates the packing habit.

Table 5 Packing of (1 1 0) folds in RG I and RG II packing habits at experimentally observed unit-cell dimensions at room temperature[30] ($a = 7.4$ Å and $b = 4.96$ Å)

Fold packing habit	Setting angle chosen (deg)	Fold packing energy (kcal mol^{-1} of folds)
RG I {(1 1 1)(1 1 0)}	48	−20.5
RG II {(3 1 2)(1 1 0)}	42	−21.0

(2 0 0) fold packing

(2 0 0) fold packing was performed using the minimum-energy (2 0 0) fold created earlier. The folds in adjacent {2 0 0} fold planes were displaced by one repeat distance, thereby forming a low-index plane, namely (1 0 1), which is commonly observed in truncated single crystals of polyethylene[3]. The folds were initially packed at experimentally observed room-temperature cell dimensions of $a = 7.40$ Å and $b = 4.94$ Å[30]. Interestingly, packing the (2 0 0) folds at the experimentally observed cell dimension gave very high packing energy values of about 40 kcal mol^{-1} of folds. The minimum energy of packing (2 0 0) folds into a fold surface was −41.6 kcal mol^{-1} of folds at cell dimensions of $a = 8.4$ Å and $b = 4.6$ Å, with a setting angle of 41°. While the energy is comparable to the (1 1 0) fold packing, the cell dimensions are radically different from the experimentally observed orthorhombic unit-cell dimensions of polyethylene single crystals.

The results on the (2 0 0) fold packing could possibly arise from two limitations of the analysis.

(1) Owing to limitations on computer time and storage requirements, it was only possible to simulate the top fold surface. By neglecting the influence of the lower fold surface, distorted unit-cell dimensions may result because the stems of the chain-folded molecules shown in *Figure 1* have a natural tendency to spread apart in order to minimize the energy of the fold. However, the reduced *b* cell dimension indicates that this is easily overcome by intermolecular influences. The too large *a* dimension is primarily dictated by intermolecular packing rather than fold conformation. In addition, similar packing of the (1 1 0) folds, to simulate the top fold surface, did not create excessive distortions in the cell dimensions of the minimum-energy packing of the (1 1 0) folds from the experimentally observed cell dimensions (see *Table 4*).

Table 6 Values of torsion angles (ϕ) and bond angles (θ) (deg) for the isolated (1 1 0) fold proposed by McMahon *et al.*[18] and Petraccone *et al.*[19], and our (1 1 0) fold packed in different packing habits. Also shown are the experimentally determined torsion angles in the fold[17]. For location of the angles, refer to *Figure 1*. *Trans* (t) and *gauche* ($g^{\pm}$) bonds with internal rotation significantly displaced from the minima of the rotational potential are indicated with a prime (i.e. t' or $g^{\pm\prime}$)

	Other work		This work				
			RG I		RG II		
Fold packing habit	Isolated fold[18]	Isolated fold[19]	{(1 1 1)(1 1 0)}	{(3 1 1)(1 1 0)}	{(1 1 2)(1 1 0)}	{(3 1 2)(1 1 0)}	Experimental[17]
ϕ_1	200	74.8 (g^+)	77.2 (g^+)	81.8 (g^+)	85.2 (g^+)	86.9 (g^+)	g^+
ϕ_2	248	174.8 (t)	182.0 (t)	180.0 (t)	183.2 (t)	183.0 (t)	t
ϕ_3	77	68.4 (g^+)	66.7 (g^+)	63.8 (g^+)	67.6 (g^+)	67.4 (g^+)	g^+
ϕ_4	86	91.6 ($g^{+\prime}$)	87.9 ($g^{+\prime}$)	89.2 ($g^{+\prime}$)	88.0 ($g^{+\prime}$)	86.1 ($g^{+\prime}$)	g^+
ϕ_5	206	−58.4 (g^-)	−65.5 (g^-)	−66.5 (g^-)	−70.5 (g^-)	−70.9 (g^-)	g^-
ϕ_6	82	−64.4 (g^-)	−62.1 (g^-)	−63.5 (g^-)	−63.1 (g^-)	−62.9 (g^-)	g^-
ϕ_7	235	174.4 (t)	182.9 (t)	181.1 (t)	180.2 (t)	182.0 (t)	t
$\theta_{1,2}$	112	113.6	113.96	114.44	112.58	112.57	
$\theta_{2,3}$	112	112.7	113.27	113.74	115.59	115.58	
$\theta_{3,4}$	112	114.8	115.50	115.29	114.05	114.24	
$\theta_{4,5}$	112	114.8	116.74	116.63	116.80	116.90	
$\theta_{5,6}$	112	116.2	117.06	116.45	116.10	116.13	
$\theta_{6,7}$	112	114.0	117.07	117.12	116.89	116.92	

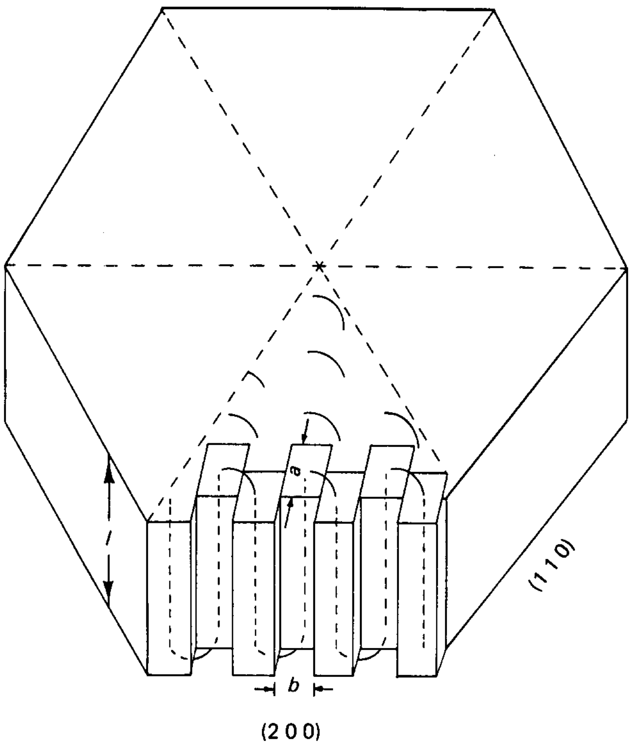

Figure 9 Proposed fold packing along the {2 0 0} planes in the '{2 0 0}'-type sectors of truncated single crystals of polyethylene according to the personal communication from Professor Keller, University of Bristol

(2) The choice of fold packing habit, specifically the {(1 0 1)(2 0 0)}, may not be the only possibility, and other arrangements could give similar energies and more reasonable cell dimensions. However, the model selected is consistent with experimental observation[3]. Further, the folds are already staggered such that further staggering (i.e. other likely packing habits) would probably have only slight influence on the minimum-energy cell dimensions.

Presuming the validity of our results—namely that (2 0 0) fold packing is energetically reasonable, but only at highly unusual cell dimensions—there are two possible conclusions. One possibility is that in the (2 0 0) sectors of polyethylene single crystals, the unit-cell dimensions are significantly different from those in the (1 1 0) sectors. We are unaware of any experimental evidence in support of this. An alternative explanation is that the (2 0 0) sectors are *not* in fact formed by '{2 0 0}' folds at all.

This viewpoint, however, evokes the following question. If the (2 0 0) fold packing does not exist, then how are the truncated diamond-shaped single crystals with {2 0 0} planes formed? One possible explanation[38] can be that the long-chain molecules are arranged in a fashion along the {2 0 0} planes as shown in *Figure 9*. If this is the situation, then the folds along the {2 0 0} planes would be nearly identical to the folds in the {1 1 0} planes with a stem separation distance of about 4.4 Å, and yet the fold planes in the '{2 0 0}'-type sectors would be parallel to the {2 0 0} planes. This is in accordance with the experimental observation of Basset, Frank and Keller[11] that the '{2 0 0}'-type sectors of collapsed truncated single crystals of polyethylene have pleats parallel to the {2 0 0} planes. On examining our results, Professor Keller[38] indicated that the jagged {2 0 0} growth faces that he has often observed in truncated single crystals could be the direct consequence of the chain folding pattern shown in *Figure 9*.

Interaction of a straight segment with the fold surface

The molecule used to examine the interaction between a straight segment and the fold surface was an eight-methylene-unit all-*trans* segment. Interaction of an eight-methylene-unit all-*trans* segment with the minimum-energy fold surface (i.e. the fold surface of RG I {(1 1 1)(1 1 0)} packing) was examined by translating and rotating the straight segment on planes *parallel* to the fold surface. Rotation about the centre and around the axis of the straight segment was allowed. Finally, after determining the minimum-energy position, the all-*trans* segment was placed at the minimum-energy position and translated *normal* to the minimum-energy fold surface. The interaction energy of the eight-methylene-unit all *trans* segment with the fold surface of RG I {(1 1 1)(1 1 0)} as a function of the distance between the segment and the fold surface is shown in *Figure 10*. The minimum interaction energy was -6.33 kcal mol^{-1} (see *Figure 10*).

The minimum-energy position of the straight segment is shown in *Figure 11*. It lies parallel to the {1 1 0} plane above the groove between two adjacent {1 1 0} fold planes at a distance of 3.75 Å from the fold surface (see *Figure 11*). The angle that the plane of the C–C–C backbone of the straight segment makes with the fold surface is 20°. Interestingly, our results are in accordance with the recent studies[16,17] on polyethylene single crystals using a polymer decoration technique, which indicated that the preferred direction of short-chain molecules on the fold surface is parallel to the {1 1 0} planes.

Patel and Farmer[25], using the same energy parameters as those used in this study, found that the interaction energy of an eight-methylene unit on the lateral {1 1 0} growth face was -7.5 kcal mol^{-1}. Compared to the minimum interaction energy on the fold surface, the minimum interaction energy on the lateral {1 1 0} surface

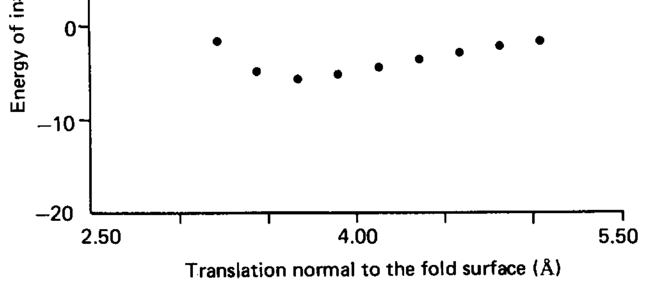

Figure 10 Interaction energy of an eight-methylene-unit straight segment for translation *normal* to the RG I fold surface. The axis of the eight-methylene-unit segment was parallel to the (1 1 0) fold planes, and the C–C–C backbone was inclined at 20° to the fold surface as shown in *Figure 11*

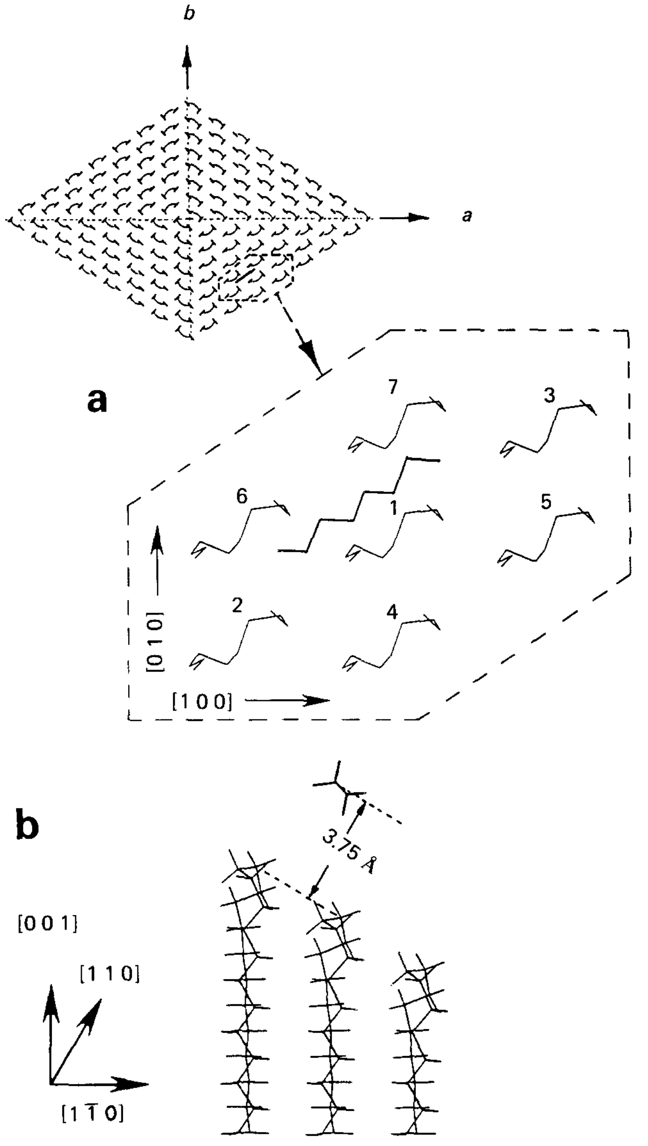

Figure 11 RG I {(1 1 1)(1 1 0)} fold surface with an eight-methylene-unit straight segment located at the position of minimum interaction energy, i.e. 3.75 Å, above the fold surface: (a) top view; (b) side view along the [1 1 0] direction

is less by about 1.2 kcal mol^{-1}. Accordingly, an adsorbed segmental molecule on the fold surface would tend to migrate from the fold surface to the lateral surface where it could make a crystallographically coherent attachment to the substrate. This is in agreement with the theory proposed by Hoffman *et al.*[22,39], that surface adsorption (i.e. physical adsorption) of the polymer molecules takes place prior to their actual crystallographically coherent attachment to the substrate.

CONCLUSIONS

Energetics analysis has been used to investigate aspects of chain folding in polyethylene single crystals. This investigation has focused on creation of isolated (1 1 0) and (2 0 0) folds, packing of folds, and interactions of a molecular segment with the fold surface. The results provide interesting insights into the nature of the packing involved, and the influence of the folds on the cell dimensions of the crystal. In particular, the important information gleaned from this study is as follows.

An isolated (1 1 0) fold has higher strain energy of deformation of the bonding topology, relative to the planar zig-zag form of the molecule, compared to the isolated (2 0 0) fold. However, the packing of the (2 0 0) folds into a fold surface indicates that a crystallographically reasonable '(2 0 0)'-type fold surface would appear to be impossible.

The bonding topology of an isolated minimum-energy (1 1 0) fold is similar to that of a (1 1 0) fold packed into a minimum-energy fold surface. The stem separation distance in both cases is about 4.4 Å.

The energetics of packing the folds into a fold surface representing a portion of a single crystal indicate that the influence of the straight segments in the crystalline core on the folds is to bring the ends of the folds closer to each other, whereas the influence of the folds in changing the cell dimensions of the crystalline core is negligible.

Packing the (1 1 0) folds in RG I and RG II habits at experimentally observed cell dimensions indicates that there is almost equal preference for either RG I or RG II fold packing habit.

The setting angle is a function of the fold packing habit.

The energetically most favourable position of a straight segment above the fold surface is at a distance of about 3.75 Å with the straight segment somewhat nestled into a groove between the {1 1 0} fold planes.

A straight segment's interaction energy with a {1 1 0} fold surface is higher than that with the lateral faces. Accordingly, an adsorbed segmental molecule on the fold surface would tend to migrate from the fold surface to the lateral surface, where it could make a crystallographically coherent attachment to the substrate.

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