

# Atomistic calculations of fold defects in polymers: 1. Polyethylene

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Semiempirical atomistic calculations of the conformations and energies of fold defects in polyethylene are reported. The calculations were carried out in different approximations: in a 'single' chain, in crystalline surroundings and in a crystal surface. The problem of finding an appropriate reference structure is discussed. The calculation of fold surfaces yields the surprising result that—in agreement with experimental results but in contrast to other atomistic calculations in the literature—the diagonal fold is more favoured than the *b*-axis fold.

(Keywords: atomistic calculations; semiempirical potentials; conformational analysis; fold defect; polyethylene)

## INTRODUCTION

Semiempirical atomistic calculations are a powerful tool for the investigation of ideal and defect conformations as well as the corresponding energies of chain molecules. The defect energies basically determine the properties of the material. In previous papers we presented results concerning our calculations of special point defects (e.g. kinks) in single polymer chains and in the polyethylene crystal<sup>1,2</sup>.

The semiempirical set of atomistic potentials we use has many times been proven to be valid for intramolecular as well as intermolecular interactions<sup>3–5</sup>.

In this paper we report results that we have taken from the calculation of fold defects in polyethylene (PE) using the same tested semiempirical potential set. In order to account for the parallelism of the straight-chain segments on both ends of the fold bend we used appropriate penalty functions as well as neighbouring chains fixed to lattice sites.

## METHOD OF CALCULATION

### Potential

In our semiempirical atomistic calculations the total energy of molecules and crystals is composed of several terms, which describe the contributions of intra- and intermolecular interactions:

$$E_{\text{tot}} = E_{\text{nb}}^{\text{intra,inter}} + E_{\text{val}} + E_{\text{rot}}$$

$$E_{\text{nb}}^{\text{intra,inter}} = \sum_{j < k} [-A_{jk} r_{jk}^{-6} + B_{jk} \exp(-C_{jk} r_{jk}) + q_j q_k / r_{jk}]$$

$$E_{\text{val}} = \sum_j \frac{1}{2} k_l (l_j - l_{0j})^2 + \sum_j \frac{1}{2} k_\theta (\theta_j - \theta_{0j})^2$$

$$E_{\text{rot}} = \sum_j \frac{1}{2} U_{03} (1 - \cos 3\phi_j)$$

where *A*, *B*, *C* are potential constants (Buckingham potential), *q* are partial charges, *k<sub>l</sub>*, *k<sub>θ</sub>* are force constants for bond length and bond angle deformation, *U<sub>03</sub>* is the rotational force constant, *r<sub>jk</sub>* is the distance between

non-bonded atoms *j* and *k*, *θ* is the bond angle and *φ* is the dihedral angle (*trans* = 0°).

The first two terms account for the attractive and repulsive van der Waals interaction and the Coulomb interaction of not directly bonded atoms (non-bonded interaction). The third term accounts for the valence angle deformation in harmonic approximation and the last term for the contribution of the orbital interaction between atoms separated by a rotated bond (rotational potential). The values of the potential constants are given in table 1 in Aich and Hägele<sup>6</sup>. In the case of PE no partial charges are introduced and bond lengths are fixed.

### The problem of the reference structure

The conformation (geometry) of a folded chain is obtained by minimizing the total conformational energy starting with appropriate values of the variables. This conformational energy must be referred to the energy of an appropriate reference structure so that the resulting defect energy does not depend on the length of the chain but is localized to the 'head' of the fold. While a single chain cannot act as a reference structure, this is achieved by a pair of chains.

The situation is shown schematically in Figure 1, where the different energy contributions are shown separately. The interaction energy is labelled with a *K* for the pair of chains ('Kette'), and with an *F* for the pair of folds.

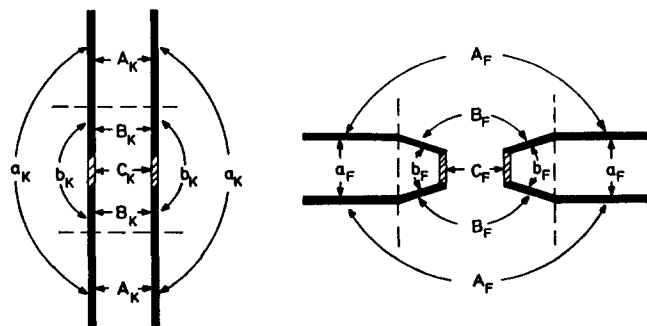


Figure 1 Interactions in a double fold and in a chain pair as reference structure (the energy contributions are explained in the text)

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Upper-case letters indicate interchain interactions, lower-case letters intrachain interactions. The total energy is subdivided into parts originating from the chain ends ( $A$ ,  $a$ ) and the region of the fold head ( $B$ ,  $b$ ,  $C$ ). This subdivision is somewhat arbitrary but nevertheless illustrates the problem of the reference structure. Note that there are two folds (a double fold) that correspond to a chain pair. The necessary condition for length independence:

$$a_F = A_K$$

holds if, in the double fold and in the chain pair, (1) there is an equal number of equivalent interactions, and (2) the conformation, the distance and the relative orientation of the parallel undisturbed chains are equal. A mathematically more rigorous treatment is given by Schmiege<sup>7</sup>.

The second requirement is achieved by the surrounding chains in a crystalline region. In a single folded chain, however, it is generally not fulfilled: the conformation of the fold is governed by the head of the fold, which often does not even allow parallelism of chains. But with the help of penalty functions it is possible to simulate the crystalline surrounding (see following section).

A special problem is folds in amorphous regions. Even if the chain ends are approximately parallel, there will be a variety of chain distances and relative orientations of the chain ends. Which reference pair is the correct one? In this case we think the concept of defect energy to be not well defined. But if there is an obvious reference pair, we can proceed as follows.

As the energy contributions:

$$A_F \approx a_K \approx 0$$

the defect energy per double fold is:

$$2\Delta E_F = \Delta E_{2F} = 2(b_F - b_K) + 2(B_F - B_K) + (C_F - C_K)$$

In this equation the magnitude of the head-head interaction energies  $B_F$  and  $C_F$  are somewhat arbitrary depending on the distance of the two folds. There are two limiting cases:

(1)  $\Delta E_{2F}^{eq}$ , where the two folds are at equilibrium distance, and  $B_F$  and  $C_F$  have maximal (absolute) values ( $B_F^{eq}, C_F^{eq} < 0$ ); and

(2)  $\Delta E_{2F}^\infty = \Delta E_{2F}^{eq} - 2B_F^{eq} - C_F^{eq} > \Delta E_{2F}^{eq}$ , where the two folds are separated by a long distance, i.e.  $B_F^\infty = C_F^\infty = 0$ . This seems to be the case of the single folds that are discussed in the literature<sup>8,9</sup>.

The more realistic case is given by  $\Delta E_{2F}^{eq}$ , because a fold defect is no typical single chain defect. In the bulk there is necessarily a second fold (or a pair of chain ends or a jog) that avoids big vacancies. In practice, we calculated  $\Delta E_F^\infty = \frac{1}{2}\Delta E_{2F}^\infty$  as the difference between the conformational energy of a single fold and half the conformational energy of a chain pair. The head-head interaction was calculated separately by minimizing the interaction energy of two enantiomorphic rigid folds with respect to their distance. From these contributions  $\Delta E_F^{eq}$  is obtained.

#### Penalty function

The simplest case of the calculation of folds is that of a fold in a single chain. But when minimizing the energy of a folded chain starting with appropriate geometrical data, the calculation yields a 'free fold' conformation

where the chain ends do not fit into lattice sites: the chain ends are not parallel and in most cases are twisted. Their distance differs from the experimental values.

In order to get the correct lattice position of chain ends in the case of the calculation of a single fold, we simulated the influence of other surrounding chains by adding the following penalty functions to the conformational energy (cf. Figure 2):

$$U_X = k_{X_0}(X_0 - X)^2 \quad (1)$$

$$U_N = k_{\beta_0}(\cos \beta_0 - N_1 \cdot N_2)^2 \quad (2)$$

$$U_T = k_{\gamma_0}(\cos \gamma_0 - T_1 \cdot T_2)^2 \quad (3)$$

Equation (1) fixes the chain distance whereas the orientation (parallelism and twisting of the fold ends) is determined by equations (2) and (3). The values  $k_{X_0}$ ,  $k_{\beta_0}$  and  $k_{\gamma_0}$  are weight factors of the penalty functions. The higher the factors chosen, the better the correct lattice positions are approximated. Too big values, however, give a badly scaled energy function, and the minimization procedure shows a slow convergence behaviour. After the minimization of the conformational energy plus the penalty functions the (normally small) amount of 'penalty energy' is subtracted.

An alternative procedure would be the use of a minimization routine that allows one to include boundary conditions (method of Lagrangian multipliers; see e.g. Fletcher<sup>10</sup>).

In the case of the third penalty function (equation (3)) the calculation of the gradient (which is essential for the minimization procedure) is difficult. For this reason we preferred to use the first penalty function (equation (1)) for two different atoms at the same fold end.

In all cases where the folded molecule is surrounded by neighbouring chains, no penalty function was used.

## RESULTS AND DISCUSSION

In PE crystals there are two different types of tight folds:

- (1) the fold in  $[200]$  direction ( $b$ -axis fold), and
- (2) the fold in  $[110]$  or  $[1\bar{1}0]$  direction (diagonal fold).

For chain folding in amorphous PE we discuss only one type of helix fold: the amorphous chains consist of a statistical mixture of *trans* and helix segments, so that there is only an average chain distance and the relative orientations of the fold ends are not well defined.

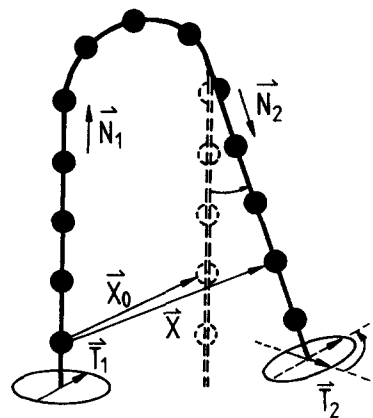


Figure 2 Variables for penalty functions

**b-axis fold (single chain)**

In order to calculate the *b*-axis fold in a single PE chain we started the energy minimization with the following dihedral angles in the head of the fold:

$$\dots \quad 0^\circ \quad 120^\circ \quad 120^\circ \quad 0^\circ \quad 120^\circ \quad 120^\circ \quad 0^\circ \quad \dots$$

$$t \quad g \quad g \quad t \quad g \quad g \quad t$$

(*t* = *trans*, *g* = *gauche*). During minimization 18 CH<sub>2</sub> (methylene) groups were kept flexible (18 × 6 variables), and the chain ends (2 × 9 methylene groups) of the fold remained rigid whereas their relative orientation was fixed to lattice sites by means of the penalty functions. The resulting data are given in Table 1. The constraints lead to a bending of the fold head so that the sequence

**Table 1** *b*-Axis fold in polyethylene ((200) face)

	'Free fold'	Fold with penalty function	
Dihedral angles (head)	-13.5°	-5.8°	
	115.1° 115.2°	113.0°	121.1°
	119.4° 119.5°	116.5°	123.0°
Angle between chain ends (ideal 180°)	166.7°	179.5°	
Rotation angle between chain ends (arccos $T_1 \cdot T_2$ in Figure 1; ideal 0°)	12.5°	0.5°	
Defect energy (incl. head-head interaction)	not defined (cf. section on reference structure)	11.3 kJ mol <sup>-1</sup>	
Head-head interaction	—	-4.2 kJ mol <sup>-1</sup>	

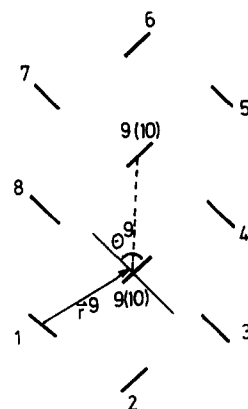
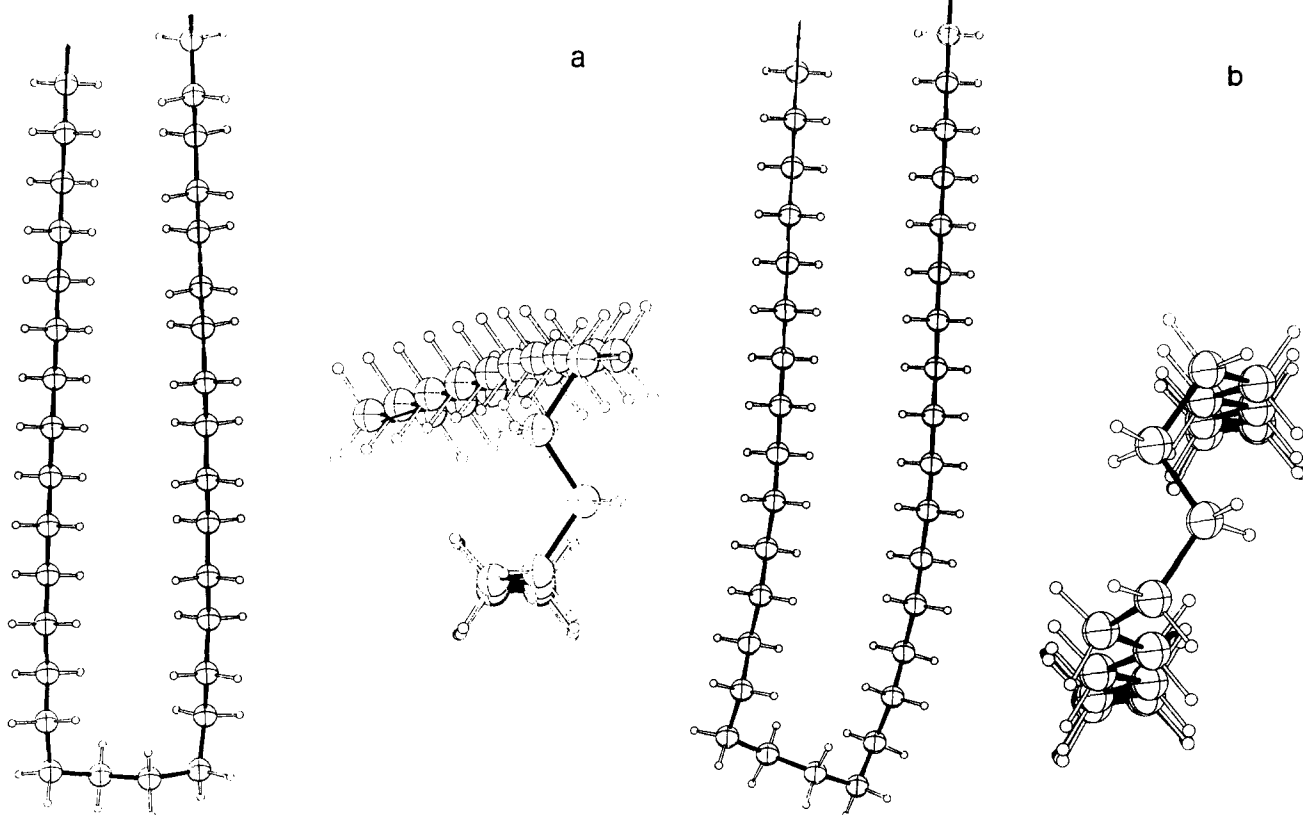
of dihedral angles becomes asymmetric (see Figure 3b).

If the penalty functions are switched off, the 'free' folded chain has no longer parallel chain ends (Table 1, Figure 3a). In this case it is not possible to calculate a defect energy as there is no corresponding reference structure.

**b-axis fold (crystalline surroundings)**

The method of penalty functions was tested by explicitly calculating a double fold with surrounding chains. This arrangement is shown schematically in Figure 4. Chains 1 to 8 are rigid and fixed to lattice sites corresponding to one of three temperatures. The corresponding lattice parameters are given in Table 2.

Chains 9 and 10 form the double fold consisting of two opposite enantiomorphic folded chains. The energy of these chains was minimized with respect to intra- as


**Figure 4** Arrangement of a double fold in the crystal (schematically)

**Figure 3** (a) *b*-axis fold ('free'); (b) *b*-axis fold (with penalty function)

**Table 2** Lattice parameters of orthorhombic PE at three temperatures

Temperature (K)	Polyethylene lattice parameters		
	<i>a</i> (nm)	<i>b</i> (nm)	
0	0.711	0.490	} Atomistic calculations <sup>14</sup> Experiment <sup>16</sup>
300	0.755	0.495	
400	0.765	0.499	

**Table 3** Conformation, total defect energy and part of the defect energy of half a double fold in the PE lattice

	Lattice parameters corresponding to		
	0 K	300 K	400 K
Angle between chain ends (ideal 180°)	179.5°	177.5°	176.2°
Rotation angle between chain ends (arccos $T_1 \cdot T_2$ ) (ideal 0°)	0.5°	1.5°	2.0°
Total defect energy of half a double fold (kJ mol <sup>-1</sup> )	204.7	123.5	95.9
Portions of the defect energy of half a double fold (kJ mol <sup>-1</sup> )			
Double fold without surrounding chains* (incl. head-head interaction)	68.2	36.8	26.8
Head-head interaction	-7.1	-7.5	-7.5
Interaction with the surrounding chains	136.5	86.7	69.1
Energy due to formation of a vacancy (estimated)	41.0	39.8	38.5

\* The portions of these energies are given in Table 4

**Table 4** Portions of defect energies of half a double fold (without the contribution of the surrounding chains)

Portion of defect energy of half a double fold (kJ mol <sup>-1</sup> )	Lattice parameters corresponding to			Single chain with penalty functions
	0 K	300 K	400 K	
$U_{val}$	33.1	18.4	14.7	6.9
$U_{rot}$	10.5	6.3	5.0	2.7
$U_{ster}$	31.7	19.6	14.6	5.9
$U_{head-head}$	-7.1	-7.5	-7.5	-4.2

well as intermolecular variables (18 flexible and  $2 \times 8$  rigid methylene groups per chain). The resulting dihedral angles in the heads of the folds are:

$$\begin{array}{cccccc} 5.2^\circ & -6.6^\circ & -16.2^\circ & -10.8^\circ & 130.9^\circ & 95.8^\circ \\ 1.2^\circ & 122.5^\circ & 128.2^\circ & 14.3^\circ & 2.7^\circ & 5.8^\circ \end{array}$$

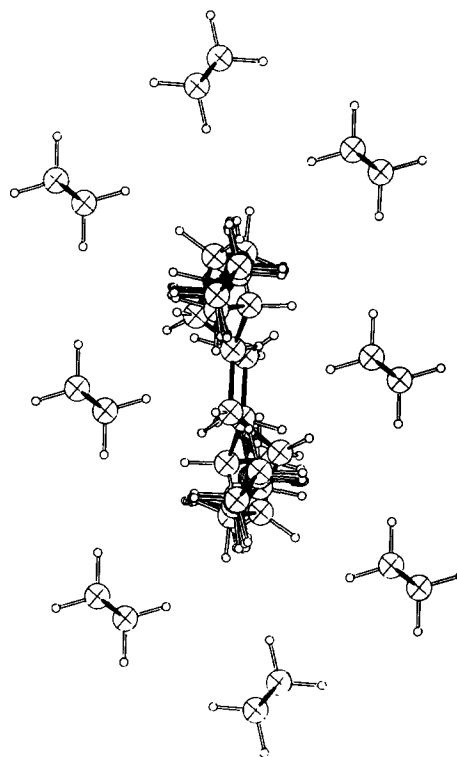
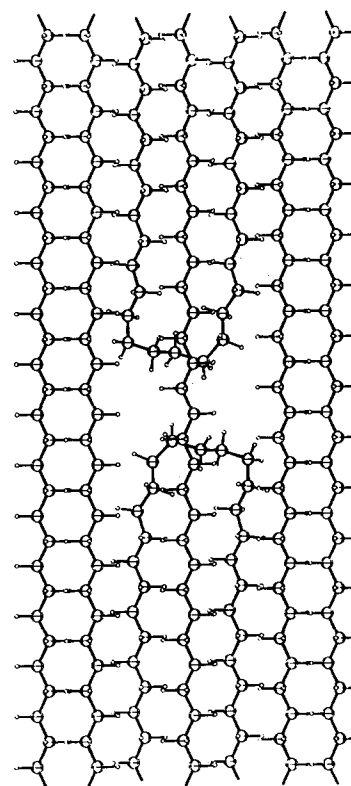
and

$$\begin{array}{cccccc} -5.4^\circ & 6.3^\circ & -16.7^\circ & 11.0^\circ & -130.5^\circ & -95.4^\circ \\ -1.5^\circ & -122.5^\circ & -128.5^\circ & -14.1^\circ & -3.0^\circ & -5.8^\circ \end{array}$$

The conformations prove to be enantiomorphic (within 0.5°) and show considerable deviations from the single chain fold data (Table 1). The other results are given in Tables 3 and 4 and Figures 5, 6 and 7 (for 0 K).

The defect energies are surprisingly high compared with that of the single chain (Table 1) and depend sensitively on the lattice distances. It follows that the

lattice is a stronger constraint than our penalty functions. Moreover, a double fold does not fit into the lattice as easily as one might think: a dumbbell-like vacancy is generated that contains a lot of energy (Table 3). It can be estimated with the help of the cohesion energy  $U_{coh}$  of the PE crystal. In order to form the vacancy about


**Figure 5** Arrangement of a double fold in the crystal ([001] view, 0 K)

**Figure 6** Arrangement of a double fold in the crystal ([100] view, 0 K)

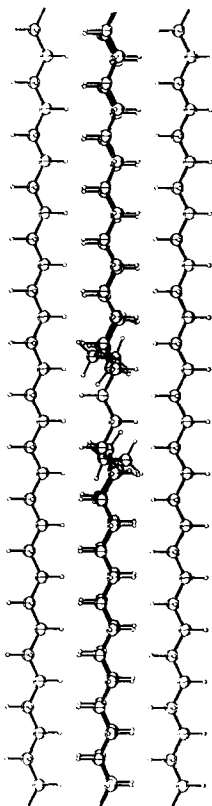


Figure 7 Arrangement of a double fold in the crystal ([0 1 0] view, 0 K)

Table 5 Diagonal fold (type 1) in PE (see Figure 8a)

	Type 1 ( $(1\bar{1}0)$ face)	
Dihedral angles (head)	76.9°	106.6°
	-118.6°	-8.6°
	-117.3°	100.5°
Angle between chain ends (ideal 180°)	179.4°	
Rotation angle between chain ends (arccos $T_1 \cdot T_2$ in Figure 1) (ideal 90°)	94.3°	
Defect energy (including head-head interaction)	39.3 kJ mol <sup>-1</sup>	
Head-head interaction	-3.3 kJ mol <sup>-1</sup>	

six methylene groups are to be removed from their neighbours, which takes about  $(1 + \frac{5}{6})U_{\text{coh}}$ .

Table 4 shows the rather high portions of the energy of valence angle deformation and steric interaction compared with the single chain calculation. This is mainly due to distortions in the fold heads, which tend to tilt out of the plane of the fold ends. The energies decrease rapidly with increasing lattice parameters.

#### Diagonal fold (single chain)

There are two types of diagonal folds in PE due to the crystal symmetry: type 1 in the  $[1\bar{1}0]$  direction and type 2 in the  $[110]$  direction. Their chain ends differ by a shift of  $c/2$  (or an equivalent rotation of 180°).

The calculations were performed in the same way as for the  $b$ -axis fold. During minimization 20 methylene groups were kept flexible ( $20 \times 6$  variables), and the rigid chain ends consisted of  $2 \times 9$  methylene groups. The results are summarized in Tables 5, 6 and 7 and are shown in Figures 8a, 8b and 8c.

Table 6 Diagonal fold (type 2) in PE (see Figure 8b)

	Type 2 ( $(110)$ face)	
Dihedral angles (head)	87.4°	108.2°
	-111.1°	-6.5°
	-113.8°	113.2°
Angle between chain ends (ideal 180°)	179.3°	
Rotation angle between chain ends (arccos $T_1 \cdot T_2$ in Figure 1) (ideal 90°)	88.0°	
Defect energy (including head-head interaction)	29.7 kJ mol <sup>-1</sup>	
Head-head interaction	-3.3 kJ mol <sup>-1</sup>	

Table 7 Diagonal fold (type 2) in PE (see Figure 8c)

	Type 2 ( $(110)$ face)	
Dihedral angles (head)	86.1°	114.1°
	-119.2°	10.3°
	-116.6°	109.8°
Angle between chain ends (ideal 180°)	179.2°	
Rotation angle between chain ends (arccos $T_1 \cdot T_2$ in Figure 1) (ideal 90°)	90.02°	
Defect energy (including head-head interaction)	30.1 kJ mol <sup>-1</sup>	
Head-head interaction	-3.3 kJ mol <sup>-1</sup>	

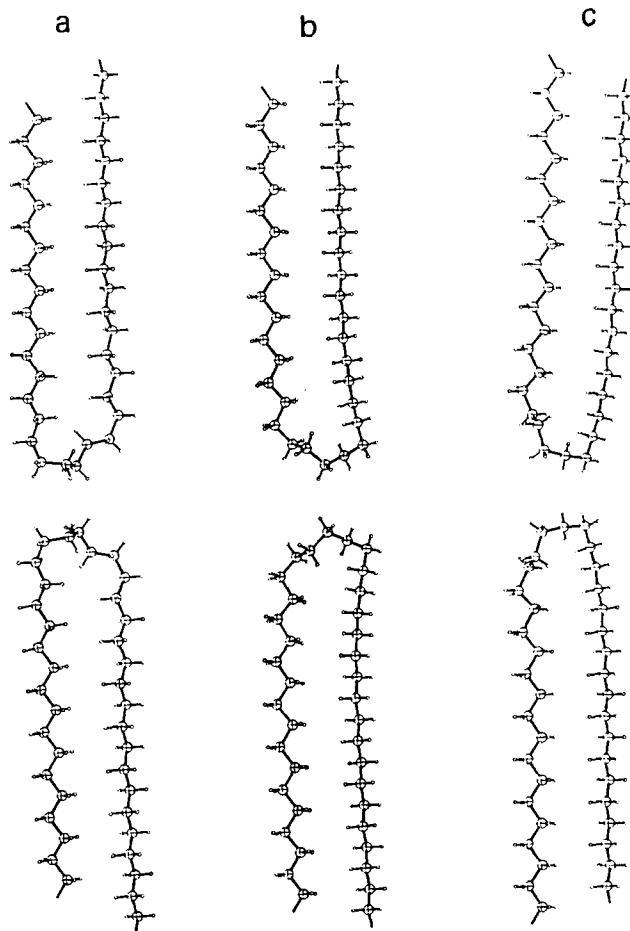


Figure 8 (a) Diagonal fold (type 1); (b) diagonal fold (type 2); (c) diagonal fold (type 2)

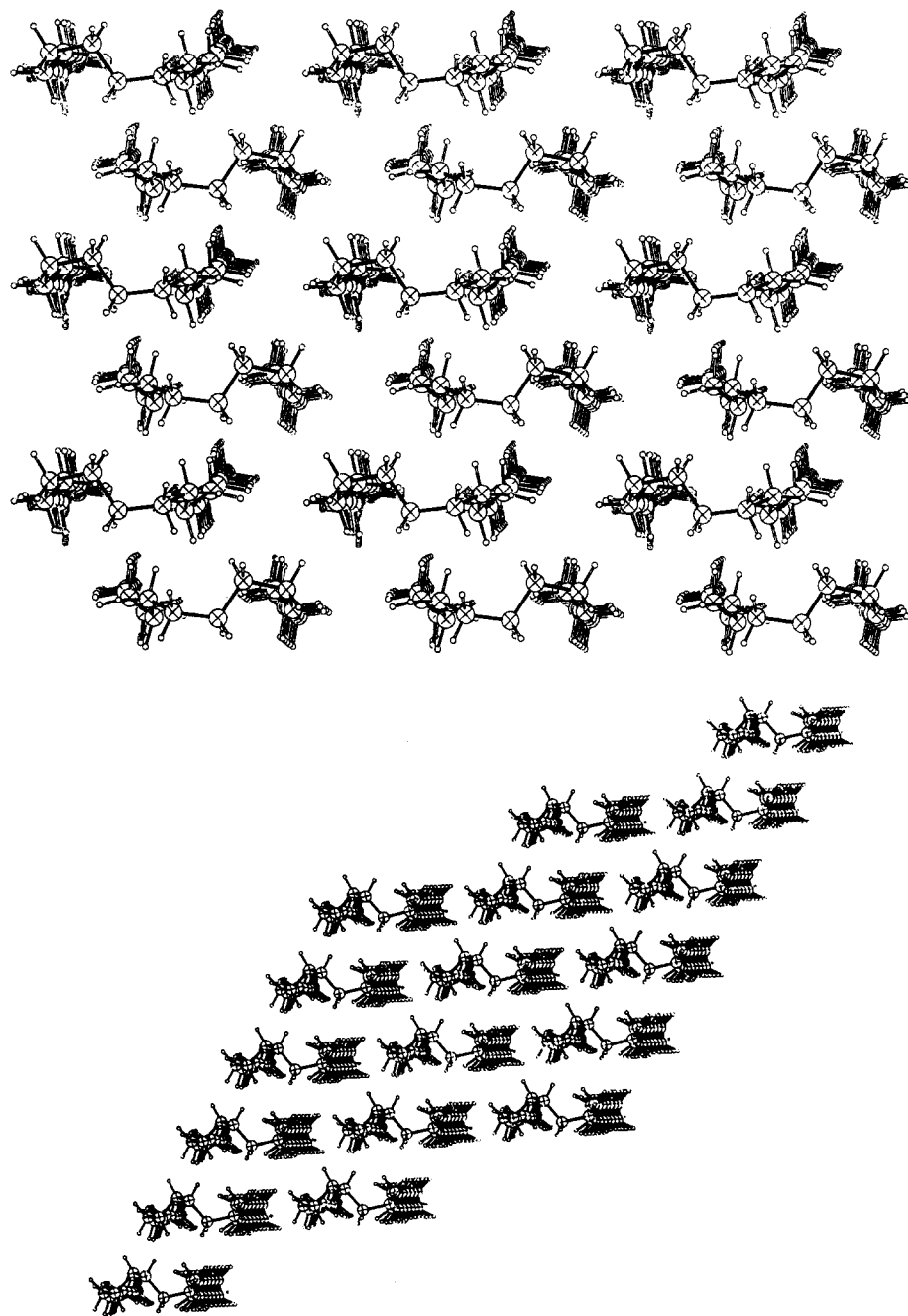


Figure 9 (a) Block of *b*-axis folds ([001] view); (b) block of diagonal folds ([001] view)

There are two conformations of type 2, which differ in their dihedral angles but have approximately the same defect energies. As in the case of the *b*-axis fold the 'free' fold is found to be a minimum energy conformation but has no parallel chain ends. Therefore no defect energy is reported.

#### Fold surfaces

It is well known that in PE single crystals grown from solution the chains are tightly folded mainly in the [110] direction<sup>11,12</sup>. Considering the results of the single chain calculations reported above, one should expect that the *b*-axis folds in PE single crystals are more probable than the diagonal folds because the *b*-axis fold has lower defect energy than the diagonal fold. The subsequent calculations showed that it was necessary to consider a block of folds (fold lamellae) in order to solve this contradiction.

For this purpose we arranged 18 folded chains—with conformations as obtained by the energy minimization of the double fold defect—in a block with a plane surface of folds perpendicular to the chain axes. Only one end of each fold was fixed to a crystal site. During the minimization of the intra- and intermolecular energy the block was treated as an 'ideal crystal' with 20 flexible methylene groups per chain. The cohesion energy per chain (consisting of 40 methylene groups) included the interaction of the central chain with the other 17 chains arranged in two shells. The results are shown in Figures 9a and 9b. We obtained the cohesion energies:

−164.7 kJ mol <sup>−1</sup>	for a block consisting of diagonal folds
−144.6 kJ mol <sup>−1</sup>	for a block consisting of <i>b</i> -axis folds

**Table 8** Comparison of defect energies with other atomistic calculations in the literature

Authors	Defect energy (kJ mol <sup>-1</sup> )	
	<i>b</i> -axis fold	Diagonal fold
McMahon <i>et al.</i> <sup>8</sup>	51.5	61.1
Petraccone <i>et al.</i> <sup>9</sup>	9.6	16.7
This work	11.3	29.7–39.3
This work (without head–head interaction)	15.5	33.0–42.6

This result shows that—in agreement with the experimental data—an arrangement of diagonal folds is energetically more favoured than an arrangement of *b*-axis folds. It follows that single chain calculations do not suffice in this case.

It is also possible to calculate defect energies. In this case, however, it would be necessary to compare two interacting blocks with a block of 36 ideal chains! Further calculations should better consider the more realistic case of fold planes with non-perpendicular chain axes.

#### Folds in the *tg*<sup>-</sup> conformation of polyethylene

So far for all reference structures the all-*trans* conformation of the PE chains was assumed. In the case of the melt, however, this is no longer realistic. In the meander model of the PE melt, for example, a chain conformation with a high density of kinks (*gtg*<sup>-</sup>) is postulated<sup>13</sup>. We therefore took chain pairs with a *tg*<sup>-</sup> conformation as idealized reference structures. These pairs occur in a quasi-hexagonal crystal structure of PE calculated by Schmiege<sup>14</sup>.

In order to approximate the amorphous surroundings only weak boundary conditions were applied. This means that only the parallelism of the chain ends was required. The flexible part of the chain contained 22 methylene groups and the chain ends eight methylene groups each. The calculations yielded eight folds with distances in the range of 0.44–0.50 nm and defect energies (including the negative head–head interaction energy) in the range 4.8–17 kJ mol<sup>-1</sup>. These energies are lower than the defect energies in the all-*trans* conformation because the reference conformation already contains *gauche* conformations.

#### Comparison with other authors

There are a few atomistic calculations of PE folds in the literature. In *Table 8* the results are compared with our work. The data of McMahon *et al.*<sup>8</sup> are considerably higher than our data. This may be due to the neglect of valence angle deformation and to the substitution of a rotational potential term by too 'hard' non-bonded interactions. Petraccone *et al.*<sup>9</sup> use potential functions similar to ours. Their potential constants are taken from Abe, Jernigan and Flory<sup>15</sup>. These constants are fitted to data of small *n*-alkanes under the assumption of constant valence angles. As the potential set of Petraccone<sup>9</sup> includes a valence angle term there arises an inconsistency that probably leads to too 'weak' potentials. This explains the fact that the data given by Petraccone<sup>9</sup> are lower than ours and stresses the necessity of consistent and well proven potentials.

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