JOURNAL OF MATERIALS SCIENCE 18 (1983) 853–863

Computer simulation of polyethylene crystals

Part 1 *Method, structure and elastic constants for perfect crystals*

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A suite of computer programs has been developed for the simulation of defects in polyethylene crystals. The programs assume model crystals in which intramolecular distortions are excluded and the molecular chains are straight and infinite in length. Intermolecular interactions are described by non-bonded interatomic potentials, and, for defect modelling, it is considered desirable to extend their ranges from the values used previously. In the present paper (Part 1), the simulation method is outlined and the potentials employed are described. The lattice parameters given by the potentials are presented and discussed, and the elastic contstants for these rigid-chain crystals are comcomputed. The constants for the orthorhombic phase are significantly different from those calculated previously, and it is argued that this is due to the restriction of the range of atom–atom interactions in earlier studies. Elastic constants for the monoclinic phase are given here for the first time. The developments described provide for the simulation of defects in model polymer crystals reported in Parts 2 and 3.

1. Introduction

The still-increasing use of crystalline polymers in engineering applications has set in train extensive research into their mechanical properties. Experiments on bulk crystalline and semicrystalline specimens and on single crystals have revealed that polymer crystals deform plastically in similar ways to other crystalline solids: that is, they can undergo slip, deformation twinning and stress-induced martensitic transformations, the modes which are operative being dependent on the test conditions. There are, however, important differences between the factors which control these mechanisms in polymers and, say, metals. They arise from the marked anisotropy engendered by the presence of molecular chains and the (relatively) complicated arrangement of atoms within the unit cell. Furthermore, the direct observation of defects responsible for deformation is not so straightforward in polymers and many of their properties have been inferred from indirect evidence. Thus, although there is a substantial body of knowledge about the deformation mechanisms in crystalline polymers [1–3], some aspects are only little understood and there is a scarcity of information about the atomic structure of important defects such as stacking faults, dislocations and twin boundaries, etc. Even at the simpler level of elastic loading, knowledge of the crystal response is incomplete, for most of the elastic constants related to intermolecular deformation require theoretical evaluation [4]. Calculations have been made for polyethylene, for instance, but the dependence of the constants on the form of the interatomic potentials has not been examined. Moreover, no estimates appear to have been made for the monoclinic phase.

It is clear, therefore, that scope exists for an investigation of the structure of polymer crystals at the atomic level, in the hope that the information gained can shed light on the mechanical behaviour of such systems. One way of undertaking an investigation of this sort is by simulating crystals via computer models. Although this

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0022–2461/83/030853–11$03.82/0

approach has the limitations which usually attend theoretical work – such as dependence on simplifying assumptions and validity of input data – it often has the distinct advantage of being the only means by which atomic configuration and energy can be studied.

The results of such a study are reported here. The crystals simulated have been restricted to polyethylene, partly because of their simplicity of structure and partly because of the wealth of published work on this polymer. In the present paper (Part 1), the method and assumptions used are described. The interatomic potentials employed in the simulations are discussed, and although they are the same as those used by earlier workers, it will be seen that their range has to be extended here to beyond that used hitherto. Accordingly, the crystal parameters predicted are not quite the same as those given previously. The elastic constants derivable from the intermolecular potentials have been computed for the stable orthorhombic and monoclinc phases of polyethylene. The dependence of the constants on the parameters and range of the potentials has been investigated, and, as implied from the preceding discussion, the monoclinic constants are given here for the first time.

The stable molecular configurations at the boundaries of stacking faults and twins have been investigated, again for both the orthorhombic and monoclinc phases. The results and discussion of the energy of these interfaces are presented in a subsequent paper (Part 2). Finally, the molecular structures of the dislocations believed to be responsible for slip have been simulated. Changes in the structure under the application of external stress have also been modelled, and the results of this study are reported in Part 3.

2. Methods

2.1. Crystal structure

The arrangement of carbon (C) and hydrogen (H) atoms in a polyethylene molecule are shown in Fig. 1a, and the arrangement of molecules within

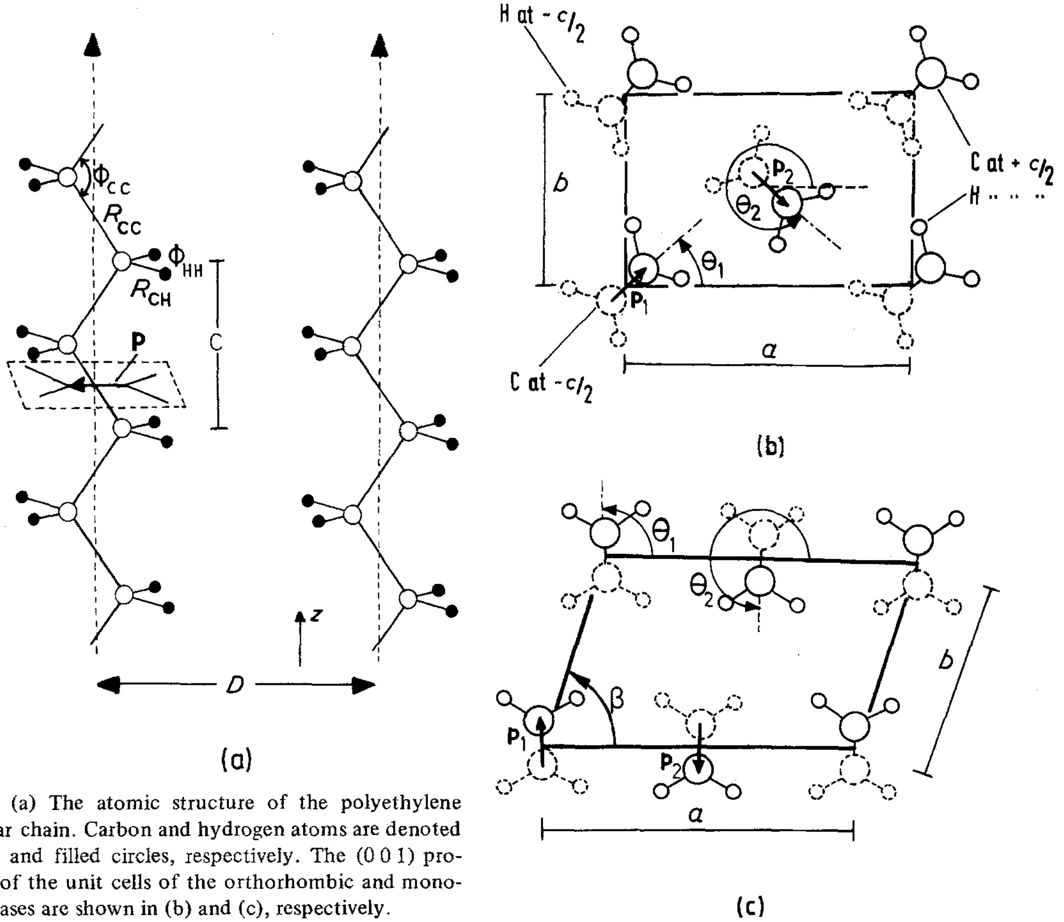

Figure 1 (a) The atomic structure of the polyethylene molecular chain. Carbon and hydrogen atoms are denoted by open and filled circles, respectively. The (0 0 1) projections of the unit cells of the orthorhombic and monoclinic phases are shown in (b) and (c), respectively.

the unit cells of the orthorhombic and monoclinic phases of polyethylene is depicted in Fig. 1b and c, respectively: in the latter figures, the molecules are viewed along the [0 0 1] crystal axis, which is the dashed chain-axis direction of Fig. 1a. (The convention adopted here for the monoclinic phase is that the [0 0 1] or *c* direction is the diad axis; [1 0 0] is chosen to be the *a* direction, see Fig. 1c.) The covalent interactions between neighbouring atoms on the same chain are orders of magnitude stronger than the intermolecular interactions, which are mainly van der Waals in origin, and this leads to the first assumption employed to make the simulations tractable. The intramolecular bond lengths and angles – R_{CC}, R_{CH}, ϕ_{CC}, ϕ_{HH} in Fig. 1a – and chain repeat distance *c* are taken as fixed in any one simulation, and rotation of bonds with respect to others on the same molecule is not permitted. In other words, the only distortions allowed are those which displace or rotate chains rigidly, and for many problems these are quite sufficient.

A second simplification is, perhaps, more restrictive: it is assumed that the molecules are infinite in length. The crystals are therefore taken to be infinitely thick in the [0 0 1] direction, and the surfaces of molecular folds which bound single-crystal lamellae and crystallites in semicrystalline material are ignored. This is undoubtedly a limitation of the model used, for surface folds do influence the deformation modes at large strain [1–3]. It was considered necessary to adopt this approach for two reasons, however. First, the atomic structure in folds is comparatively complex and open to speculation [5], and to include it in the model would introduce an extra degree of uncertainty. It was thought better first to study the effects of intermolecular interactions within a crystal. Second, a discrete lattice model which includes all the atom–atom interactions associated with folds would be cumbersome and, because of the heavy demand on computer processing and storage, would place a severe limit on maximum crystal size.

The two assumptions employed lead to the following simplifications in the computer model. First, the lattice is periodic in [0 0 1] and the computer-generated lattice points need only be two-dimensional, for the *z* coordinates of all atoms need not be stored explicitly. Second, only intermolecular interactions need be summed for lattice energy evaluation. Third, each molecule can be treated as six rows of regularly spaced atoms, thereby making the geometry of atomic positions and calculation of interatomic distances easier to handle.

Despite this apparent simplicity, a crystal of N molecules has $4N$ degrees of freedom, for the position and orientation of any molecular chain is given by four parameters $(x_i, y_i, z_i, \theta_i)$, where $1 \leqslant i \leqslant N$. Here, x_i and y_i are the rectangular Cartesian coordinates of the axis of the ith chain on a reference (0 0 1) plane, z_i is the displacement coordinate of that chain in the [0 0 1] direction measured from the reference plane, and θ_i in the setting angle defining the orientation of the chain. The reference plane is chosen to intersect a C–C bond, and a chain orientation vector $\mathbf{p}_i$ is defined by the projection of the line from the C atom immediately below the plane to the one immediately above (Fig. 1a). If the chain subsequently undergoes a displacement z_i in the [0 0 1] chain-axis direction, the vector $\mathbf{p}_i$ is taken to point from the C atom immediately below or on the plane to the one immediately above. The setting angle θ_i is then measured anticlockwise from the positive x-direction to $\mathbf{p}_i$, the x-axis usually being a low index direction such as [1 0 0], [1 1 0], etc. The parameters z_i and θ_i are periodic, z_i with period c and θ_i with period 2π, and are interdependent because of the two-fold screw axis of symmetry, i.e. $(x_i, y_i, z_i, \theta_i) = (x_i, y_i, z_i + nc/2, \theta_i + n\pi)$, where n is an integer. The conventions adopted for $\mathbf{p}_i$ and θ_i are required not only for computation but also, as will be seen, for representation of the results.

2.2. Simulation package

The lattice generation, relaxation and other computer routines used in the simulations are developments of the XLITE library written by Martin (see [6]) for simulation of defects in crystals, which in turn was based on the DEVIL (Defect Evaluation in Lattices) programs of M. J. Norgett at the A.E.R.E., Harwell. The important feature of these simulation routine libraries is that by limiting the range of interaction and using position-relative indexing of atoms, they only require one list of relative neighbours for each sub-lattice: these neighbour lists are permanent during subsequent lattice summations, and so lattice energy evaluations are undertaken efficiently with respect both to processing and storage. The polymer version of DEVIL, described in details elsewhere

[7], is a command-driven, modelling system called DEVILS (DEVIL System) which allows many and varied modelling runs (simulations) using the same object program. Consequently, DEVILS may be run interactively, allowing the user to take tactical decisions during modelling or, alternatively, the system may be run in batch mode from a sequence of modelling commands. DEVILS uses the ICL George 3 System for editing Fortran source, generating programs and communications. However, the programs themselves are written in ICL extended Fortran and are easily adaptable.

Briefly, the programs generate a perfect crystal of infinite, rigid chains, with up to ten chains per unit cell; the lattice parameters, Miller indices of the *xz*-plane, lattice basis vectors, etc., are specified by the user. The crystal block generated need not be rectangular in section and its size is also specified by the user. This "inner region" of the crystal is surrounded by a boundary mantle whose molecules are not free to move during subsequent relaxation in the independent manner characteristic of the inner ones. The "outer region" is of sufficient thickness to ensure that every chain of the inner region has a complete shell of neighbours within the range of molecular interaction. The boundary conditions in the x and y directions may be specified to be either "fixed", in which case the outer chains do not move during the relaxation steps of the inner region, or "periodic", in which case the outer regions replicate the inner crystal and the outer chains move in the same way as their "parent" chains in the inner region during relaxation. Periodic boundaries, therefore, mimic an infinite array of cells identical to the inner region, and are required, for instance, for the modelling of defects of infinite extent, e.g. stacking faults and twins. In the present work, crystals of up to 1000 chains in the inner and fixed-outer regions were allowed.

The DEVILS suite has routines to produce in the model crystal general distortions, e.g. homogeneous strain and random chain displacements, and to introduce specific defects, e.g. dislocations, stacking faults and twins. The initial, perfect crystal is usually chosen to be in equilibrium under a chosen intermolecular potential, and so the chain movements associated with these routines, which are based on simple algorithms such as rigid-body shifts for stacking faults and elastic displacement fields for dislocations, generally leave the crystal in a non-equilibrium state. The required equilibrium structure and energy of the defect crystal is therefore obtained by allowing the inner-region of (N) molecules to relax until the lattice energy is minimized with respect to the ($4N$) free coordinates. The minimization procedure of DEVILS is the method of conjugate gradients [8], but the choice exists for the user to freeze selected coordinates during minimization and also to relax one part of the crystallite rigidly with respect to the other if required. These innovations are particularly useful for the simulation of planar defects.

2.3. Interatomic potential and lattice energy

The efficiency of the minimization step depends to a large extent on the way in which the lattice energy and its ($4N$) gradients are calculated. Several methods are available, but all require information on the interaction energy of atoms on neighbouring chains. A number of semi-empirical potentials for the non-bonded interaction between hydrocarbon atoms have been discussed in the literature, the most widely used being in the form of a Buckingham potential with Born–Mayer repulsion and van der Waals attraction, namely:

$$V(r) = A \exp(-Cr) - Br^{-6}, \qquad (1)$$

where r is the atom–atom spacing and A, B and C are constants for the atom species involved. A wide variety of possible values for A, B and C has been proposed but the sets most widely adopted are those of Williams [9], who derived eight sets for the Buckingham potential by weighted least-squares fitting to empirical crystal parameters of low-molecular-weight hydrocarbons and polyethylene. Despite the limitations of these potentials [10], they were fitted using a wide data base and have proved successful. They have been validated by McCullough and Lindenmeyer [11] who used linear programming techniques to assess the range of acceptability for the constants and showed that other published sets fall outside the permitted range.

The sets labelled I, IV and VII by Williams have been used in the present work: the corresponding values of A, B and C for the three atom–atom interactions C–C, C–H and H–H are given in Table I. The variation of $V(r)$ with r for the three potentials of set I is shown in Fig. 2; potentials for the other sets are similar in shape. In the derivation of Williams, the range of interaction was taken to be 6.0, 5.5 and 5.0 Å for C–C, C–H and

TABLE I The potential parameters used for polyethylene

Property		Potential set			
Coefficient	Interaction	I	IV	VII	VII (Truncated)
A	C–C	86 910	83 630	61 900	61 900
(kcal mol^{-1})	C–H	7 880	8 766	11 000	11 000
	H–H	2 920	2 656	2 629	2 629
B	C–C	586	586	505	505
(kcal Å^6 mol^{-1})	C–H	112	125	128	128
	H–H	33.5	27.3	32.3	32.3
C	C–C	3.6	3.6	3.6	3.6
(Å^{-1})	C–H	3.67	3.67	3.67	3.67
	H–H	3.74	3.74	3.74	3.74
Range	C–C	11.0	11.0	11.0	6.0
(Å)	C–H	8.5	8.5	8.5	5.5
	H–H	7.0	7.0	7.0	5.0
Structure constants					
R_{CC} (Å)		1.54	1.522	1.522	1.522
R_{CH} (Å)		1.09	1.04	1.04	1.04
ϕ_{CC} (deg)		112	113.1	113.1	113.1
ϕ_{HH} (deg)		110	104	106	106
c (Å)		2.553	2.540	2.540	2.540

H–H atom pairs, respectively, on the grounds that interactions within these distances yield about 80% of the total lattice energy. Inspection of Fig. 2, however, reveals that at these cut-off values $V(r)$ is still a sizeable fraction of its value at the minimum. Abrupt truncation of the potentials in this way is generally unsatisfactory for defect modelling, for it can lead to difficulties with energy minimization and lattice instability. For defect simulation, it is usually considered desirable to use potentials for which $V(r)$ and its first derivative go smoothly to zero, and so in the present work the Williams potentials were used with ranges of 11, 8.5 and 7 Å for C–C, C–H and H–H pairs, respectively. These values were determined by the distances at which the set I functions decrease to 0.5% of the C–C well depth. At these cut-off values, the potentials were truncated smoothly by a cubic-spline tail of range 0.01 nm with coefficients chosen for continuity of V and $\mathrm{d}V/\mathrm{d}r$ at the cut-off distance and to ensure $V = \mathrm{d}V/\mathrm{d}r = 0$ at the end of the range. For comparative purposes, potentials with the original cut-off ranges of Williams have been used in some calculations: they are designated "Truncated" in Table I.

As explained in Section 2.1, the polyethylene molecule is treated in the present work as six atom rows – two of carbon and four of hydrogen – and so the energy and gradients of a chain-pair interaction are calculated by a summation of 36 atomic row–row interactions, as in the method of Yemni and McCullough [12]. These row–row energies and their gradients are calculated and summed to give the total chain–chain potential energy and the x, y, z components of the forces on each chain. The molecules are modelled as rigid bodies, and therefore the x and y row–row forces contribute to a net couple on every chain, which is treated as the negative of the fourth gradient, i.e. that with respect to θ_i, by the energy-minimization procedure. The presence of the fourth free coordinate requires that special precautions are taken to ensure that a true energy minimum is achieved when the lattice is relaxed: it is often possible, for example, to find different equilibrium structures by rotating a chain about its axis [13, 14].

The DEVILS package offers a choice of three methods for computing the row–row potential: they employ either exact atomic summation, stored row potentials or the "row formulation" procedure [7]. The atomic summation method simply involves explicit pair-wise evaluation of the atom–atom potentials given by Equation 1. With the regularity of the rows, it is only necessary to sum the interaction of *one* atom on one row with those of another, and even in the worst possible case of two carbon rows of small separation and a C–C potential range of 11 Å, only 9 pair interactions are summed. For the special situations in

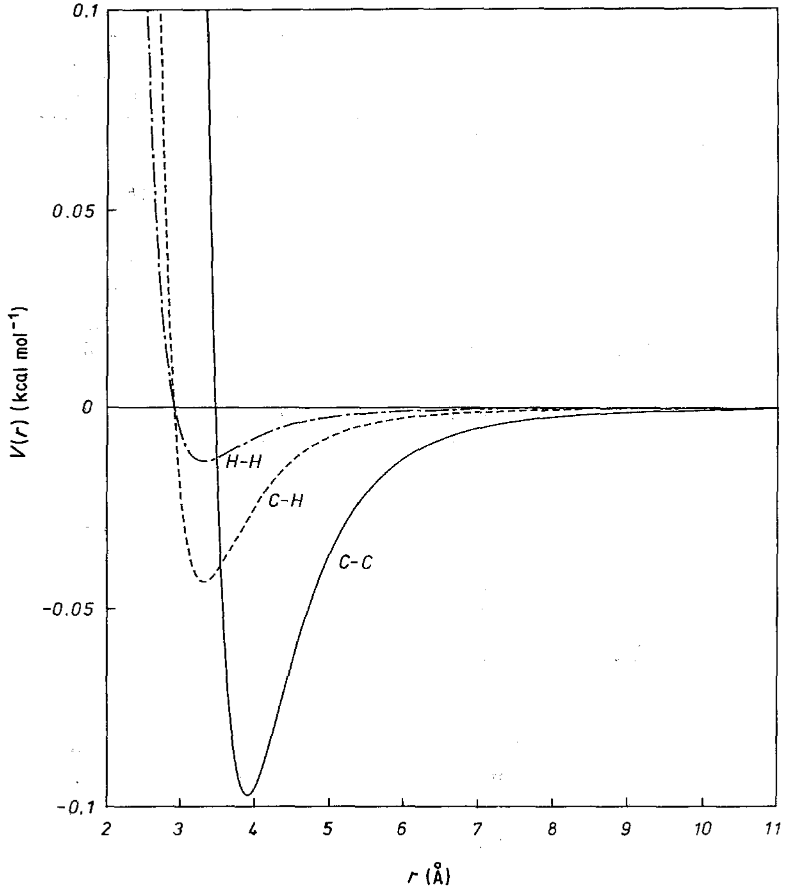

Figure 2 The non-bonded interatomic potentials of set I.

which the relative z displacement of the chains is 0 or $c/2$, symmetry is exploited, resulting in the worst case in only 5 or 4 interactions, respectively. Also, the z gradient of the row–row energy is zero under either of these conditions. (In practice, cases with $z = 0$ or $c/2$ are not particularly special, for only a few defects, e.g. the chain-axis screw dislocation, produce more general values.)

The stored-row-potential approach of the second option provides a fast alternative to the method of atom–atom summation. In a "once-and-for-all" evaluation for each atom type, the interaction of one atom with a row was computed at 41 atom–row spacings for relative z displacements of 0 or $c/2$. Each of the six functions was then represented by a series of 40 cubic splines, the coefficients of the splines being chosen so that the atom–row energy and its first derivative with respect to spacing were continuous. The row–row interactions could therefore be calculated rapidly from a stored table of 960 coefficients. This method was found to produce errors of less than 0.02% in comparison with the "exact" procedure. Rapid estimation of approximate row–row interactions for general z displacements is also provided in DEVILS by using the stored coefficients and assuming a sinusoidal variation with respect to z displacement between 0 and $c/2$.

The row formulation procedure for evaluating row–row interactions is a semi-analytical method developed by McCullough and Hermans [15]. It utilizes the periodicity of the row–row energy with respect to z by expressing the energy as a Fourier series, the coefficients of which are found by integration of infinite sums of the atom–atom potential. The coefficients involve either exponential or Bessel functions, and their evaluation therefore offsets much of the time saved by avoiding pair-wise sums. Furthermore, the achievement of high accuracy by retention of more terms in the Fourier series has a serious effect on mill-time. Thus, despite its previous use by the present authors [13, 14] and others [11, 12, 15], this method was little used in the present work in view of its lack of efficiency in comparison with the other two approaches.

TABLE II Equilibrium lattice parameters and cohesive energy for orthorhombic ("O") and monoclinic ("M") polyethylene for the potentials used. The setting angles are measured from the a-axis [1 0 0]. Temperatures and references for the experimental values are (i) 77 K [17], (ii) 297 K [18], (iii) 77 K [19] and (iv) 297 K [20]

Phase	Cell parameters (Å)		Cell angle, β	Setting angle, θ_1	Cohesive energy (kcal (mol C_2H_4)$^{-1}$)	Potential set
	a	b				
O	7.108	4.925	90°	42.7°	3.626	I
O	6.891	4.809	90°	43.3°	3.944	IV
O	6.985	4.824	90°	43.2°	3.887	VII
O	7.133	4.874	90°	43.4°	3.054	VII (Truncated)
O	7.155$^{(i)}$	4.899$^{(i)}$	90°	42.3°$^{(ii)}$	3.68$^{(iii)}$	Experimental
M	8.015	4.446	77.4°	84.6°	3.675	I
M	7.737	4.436	77.5°	83.7°	3.980	IV
M	7.784	4.423	77.4°	84.3°	3.929	VII
M	7.768	4.518	76.0°	82.5°	3.071	VII (Truncated)
M	8.09$^{(iv)}$	4.79$^{(iv)}$	72.1°$^{(iv)}$	90.0°$^{(iv)}$	–	Experimental

3. Results

3.1. Lattice cell parameters

The equilibrium lattice parameters a, b, θ_1, θ_2 ($= 2\pi - \theta_1$) for the orthorhombic phase (Fig. 1b) and a, b, β, θ_1, θ_2 ($= \pi + \theta_1$) for the monoclinic structure (Fig. 1c) were determined for the potential sets I, IV and VII of Table I. The values of the structural constants R_{CC}, R_{CH}, ϕ_{CC}, ϕ_{HH} and c ($= 2R_{CC} \sin(\phi_{CC}/2)$) are, to a limited extent, open to a choice for, once selected, they remain invariant during a simulation. For the present work, the constants used with set I potentials were those given by Yemni and McCullough [12] (and claimed to be "experimental"), whereas for sets IV and VII the values employed by Twisleton *et al.* [16] in their study of the lattice dynamics of polyethylene were adopted; they are mainly the same as those chosen by Williams [9]. The values are given in Table I: most properties are insensitive to the precise choice. The lattice energy (calculated using the exact sum procedure) for a given potential set was minimized (to an accuracy of 0.001%) using the lattice parameters as variables, and the resulting parameters are listed in Table II. The calculated lattice cohesive (sublimation) energy is also given in the table, together with some experimental data.

The effects of changes in the interatomic potential coefficients on the lattice parameters are small, and the differences between the parameters of set IV and set VII crystals, in particular, are slight. Schematic diagrams showing how the choice of ranges of the atom–atom potentials affects the chain–chain interaction are shown in Fig. 3a and b. With the "truncated" ranges of Williams, see Table I, the molecule at the origin 0 interacts with some or all of the atoms on the eight molecules denoted by bold vectors, whereas with the extended ranges employed here, the interactions encompass all the molecules shown, i.e.

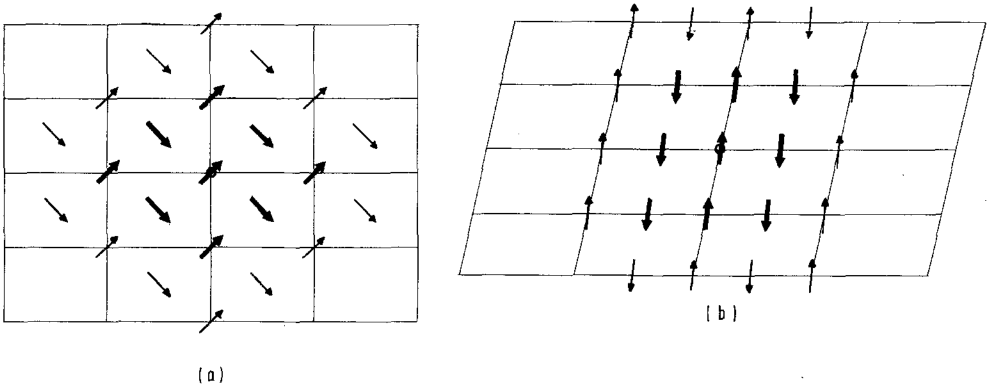

Figure 3 Neighbour chains to O indicating the interaction ranges employed. Only the chains marked bold are included for the truncated potential set.

TABLE III The non-zero elastic stiffness constants C_{ij} for (a) orthorhombic and (b) monoclinic crystals

(a) Orthorhombic						(b) Monoclinic					
C_{11}	C_{12}	(C_{13})	0	0	0	C_{11}	C_{12}	(C_{13})	0	0	C_{16}
	C_{22}	(C_{23})	0	0	0		C_{22}	(C_{23})	0	0	C_{26}
		(C_{33})	0	0	0			(C_{33})	0	0	(C_{36})
			C_{44}	0	0				C_{44}	C_{45}	0
				C_{55}	0					C_{55}	0
					C_{66}						C_{66}

Note: the Cartesian reference axes x_1, x_2, x_3 for C_{ij} are chosen in the monoclinic case such that x_3 is the diad axis, i.e. [0 0 1], and x_1 coincides with the a-axis, i.e. [1 0 0]. The constants in parentheses cannot be determined using a rigid-chain model as in the present work.

22 neighbours. From the data of Table II, it is seen that the influence of truncation on the lattice parameters is fairly small and of the same order as the effects produced by changes in the potential coefficients. The influence on the lattice cohesive energy is, however, significant, as expected.

3.2. Elastic constants

The elastic, strain energy density, W, of a body is related to the strain components e_i ($i = 1, 2, 3, \ldots, 6$) by the elastic stiffness constants C_{ij} thus [21]:

$$W = \tfrac{1}{2} \sum_{i,j=1}^{6} C_{ij} e_i e_j, \tag{2}$$

where the strains are expressed in "matrix" (or "engineering") notation. The 6 x 6 matrix of constants is symmetrical, resulting in 21 independent constants in the general case. For orthorhombic and monoclinic crystal systems, however, application of the symmetry elements reduces the number to 9 and 13, respectively. The non-zero elements of the matrix in these cases are given in Table III.

The elastic constants can be obtained theoretically by either calculation of elastic wave velocity in terms of lattice force constants or direct computation of W for a model lattice under prescribed strain. The latter approach has been adopted here. An inner region of two chains was generated by DEVILS with periodic boundary conditions in the x and y directions, and the increase in energy density was calculated for certain strains using the exact sum procedure. The strains which were applied for a given constant are listed in Table IV. It will be noted that distortion involving e_3, i.e. normal strain along the molecular axis [0 0 1], was not applied: this is a consequence of the rigid-chain model employed, and thus the constants in parentheses in Table III could not be determined. Ideally, the C_{ij} should be calculated for vanishingly small strains, but the direct method used here is prone to numerical inaccuracy in just this region. Each constant was therefore calculated for both positive and negative strains with magnitudes in the range 0.0001 to 0.08, and the value for zero strain found by graphical interpolation. Although non-linearities in the elastic behaviour were discernible by this method, they were not pursued further.

The resulting constants for orthorhombic and monoclinic polyethylene are given in Table V for the three atom–atom potential sets; the ortho-

TABLE IV The energy–strain relationships used to determine the eleastic constants, C_{ij}, of orthorhombic (O) and monoclinic (M) polyethylene

Non-zero strains	Elastic constant	Other constants required	Strain energy, W	Structure
e_1	C_{11}		$\frac{1}{2}C_{11}e_1^2$	O, M
e_2	C_{22}		$\frac{1}{2}C_{22}e_2^2$	O, M
e_3	C_{33}		$\frac{1}{2}C_{33}e_3^2$	O, M
e_4	C_{44}		$\frac{1}{2}C_{44}e_4^2$	O, M
e_5	C_{55}		$\frac{1}{2}C_{55}e_5^2$	O, M
e_6	C_{66}		$\frac{1}{2}C_{66}e_6^2$	O, M
$e_1 + e_2$	C_{12}	C_{12}, C_{22}	$\frac{1}{2}(C_{11}e_1^2 + C_{22}e_2^2 + 2C_{12}e_1e_2)$	O, M
$e_1 + e_6$	C_{16}	C_{11}, C_{66}	$\frac{1}{2}(C_{11}e_1^2 + C_{66}e_6^2 + 2C_{16}e_1e_6)$	M
$e_2 + e_6$	C_{26}	C_{22}, C_{66}	$\frac{1}{2}(C_{22}e_2^2 + C_{66}e_6^2 + 2C_{26}e_2e_6)$	M
$e_4 + e_5$	C_{45}	C_{44}, C_{55}	$\frac{1}{2}(C_{44}e_4^2 + C_{55}e_5^2 + 2C_{45}e_4e_5)$	M

TABLE V Theoretical elastic constants (units GN m^{-2}) of polyethylene derived in the present work

Potential set	Phase	C_{11}	C_{22}	C_{44}	C_{55}	C_{66}	C_{12}	C_{16}	C_{26}	C_{45}	E_a	E_b
I	O	17.8	18.0	5.5	3.0	8.8	8.2	0	0	0	14.1	14.2
IV	O	27.3	18.1	2.1	2.6	10.8	10.1	0	0	0	21.7	14.4
VII	O	21.9	29.0	6.5	1.8	10.2	8.9	0	0	0	19.2	25.4
VII (Truncated)	O	12.8	11.8	3.4	2.1	6.7	6.3	0	0	0	9.4	8.7
I	M	20.7	23.6	1.5	2.1	3.9	3.2	−2.8	1.9	1.8	–	–
IV	M	20.9	30.0	8.0	6.0	3.6	3.1	−2.3	−0.1	−0.5	–	–
VII	M	29.0	30.0	5.7	5.4	4.9	4.8	−0.6	−0.6	−1.0	–	–

rhombic constants are also given for the truncated potentials. In comparison to the lattice parameters, the elastic constants, which are related to the first and second derivatives of the potentials, are markedly dependent on the choice of potential set. They are also strongly influenced by the inclusion of more-distant neighbour–neighbour interactions.

Whilst C_{44}, C_{55} and C_{66} are the shear moduli as would be measured in, say, a mechanical test, the tensile moduli E_a and E_b in the a- and b-axis directions, respectively, for the orthorhombic system are given by $1/S_{11}$ and $1/S_{22}$, respectively, where the compliance constants S_{ij} are elements of the inverse matrix of the C_{ij}. It is found that if C_{33} is much larger than the other C_{ij}, $S_{11} \simeq C_{22}/D$ and $S_{22} \simeq C_{11}/D$, where $D = (C_{11}C_{22} - C_{12}^2)$. The moduli calculated in this way from the orthorhombic data of Table V are also given in that table.

4. Discussion

4.1. Lattice structure

The orthorhombic lattice parameters calculated here are within a per cent or so of the experimental values, irrespective of the interatomic potential used (see Table II). The experimental values selected for comparison should be low-temperature ones, for the computer model simulates a crystal at 0 K. Unfortunately, experimental values in the literature for setting angle θ_1 all refer to room temperature, and measurements range between 41° and 48°. Previous theoretical estimates show a similar variation. For example, Yemni and McCullough [12] found $\theta_1 = 42°$ for the set I potentials allowing chain–chain interactions out to 12th neighbours and Tai *et al.* [22] obtained 42.5° with Lennard–Jones potentials taken to only 8 neighbour chains; whereas Wobser and Blasenbery [23] calculated $\theta_1 = 46°$ using interatomic potentials of the Buckingham type, but with different coefficients from Williams and interactions out to only 6 neighbour chains, and Twisleton *et al.* [16] found $\theta_1 = 46.5°$ using the set VII (Truncated) potentials. (We were unable to reproduce the lattice parameter and cohesive energy values of Twisleton *et al.* with these potentials, and this may reflect the variable potential ranges which these workers effectively adopted.) Clearly, therefore, many semi-empirical potentials give satisfactory values for a and b (and even the cohesive energy if the range is long enough or the potentials are deep enough), but the experimental uncertainty over θ_1 prevents a clear preference being made from the fit to that parameter.

The situation with the monoclinic phase is similar. Again, the potentials give reasonable values for a and b, particularly when it is borne in mind that the experimental data were obtained at room temperature, but the cell angle β and setting angle θ_1 are not as satisfactory. The angles obtained here are close to those of other workers, however, for Yemni and McCullough [12] found $\beta = 77°$ and $\theta_1 = 84°$ with set I potentials and Tai *et al.* [22] observed that $\beta = 78$–$80°$ and $\theta_1 = 85$–$88°$ for their Lennard–Jones models. It may be concluded that the potential sets used here are adequate until further experimental data are to hand.

It is of interest to note that for a given potential set, the monoclinic phase has a higher cohesive energy, i.e. is more stable, than the orthorhombic structure. A similar result was found by Yemni and McCullough [12] and Tai *et al.* [22], the latter workers using quite different potentials. This apparently general feature is at variance with experience, for the stable phase in practice is orthorhombic, the monoclinic variant only occurring as a result of stress [1]. An explanation for this effect has been proposed by Kobayashi and Tadokor [24], who calculated that the vibrational contribution to the free energy is sufficiently greater for monoclinic polyethylene to offset the discrepancy in the static energy. This re-emphasizes the point that the simulations undertaken in the present study apply strictly to 0 K.

TABLE VI Theoretical and experimental elastic constants for orthorhombic polyethylene in units of GN m^{-2}

Source	C_{11}	C_{22}	C_{12}	C_{44}	C_{55}	C_{66}	E_a	E_b
Theory [25]	7.3	10.0	2.3	3.3	1.1	3.5	6.8	9.3
Theory [25]	9.3	10.9	3.7	3.5	1.3	5.0	8.0	9.4
Theory [23]	13.8	12.5	7.3	3.2	2.0	6.2	9.5	8.6
Theory [26]				5.0	2.4			
Theory [16]	12.5	10.9					8.9	7.8
Theory [16]	12.4	11.1					8.8	7.9
Theory [27]	8.0	9.9	3.3	3.2	1.6	3.6	6.9	8.5
Experiment [28]							3.2	3.9
Experiment [16]	11.5							

4.2. Elastic constants

A complete set of elastic constants for polyethylene has not been obtained experimentally, only a few selected moduli being available, and most mechanical-property and lattice-defect studies have therefore used theoretical estimates. Some of the most-commonly quoted values of the constants dealt with here are listed in Table VI. The theoretical figures are all obtained from the acoustic phonon ("long wave") velocities and therefore assume values of the harmonic lattice force constants, which have usually been derived in turn from non-bonded interatomic potentials of the sort discussed above. It is at first sight surprising, therefore, to find the theoretical values of C_{11}, C_{22}, C_{12} and C_{66} obtained here (Table V) to be, with one exception, significantly higher than the previous estimates. These differences are not believed to be due to non-linear elastic behaviour in the computer model, nor to the neglect of inner strains, for when the strained crystallites were allowed to relax by permitting chain rotation, no detectable energy changes occurred for small strains. Furthermore, the constants for the set VII (Truncated) potentials are close to the long-wave values of Twisleton *et al.* [16] – their second entry in Table VI – who used the same set VII potentials (but marginally different lattice constants, as discussed above).

The common characteristic of the calculations referred to in Table VI is that they assume short ranges for the interatomic potentials in comparison with the present simulations and include molecular interactions with only a few neighbours. Odajima and Maeda [25] and Tadokoro *et al.* [27], for example, neglected C–C interactions altogether and truncated the other interactions at 4 Å and approximately 3 Å, respectively. (In [25], furthermore, the C_{ij}s were calculated for a nonequilibrium lattice [4].) Wobser and Blasenbury [23] used the Williams cut-off distances and neglected intermolecular interactions beyond the sixth-nearest neighbours. It can be seen from Fig. 2, however, that the interatomic force contants, which are proportional to $\mathrm{d}V/\mathrm{d}r$ and $\mathrm{d}^2V/\mathrm{d}r^2$, are not negligible beyond these critical spacings. For example, even at $r = 6$ Å, minus $\mathrm{d}^2V/\mathrm{d}r^2$ for the C–C potential is more than 20% of its maximum value. Such problems do not arise for the longer ranges selected here.

It is unfortunate that the experimental data are so sparse. The small numbers of Sakurada *et al.* [28] were obtained by X-ray measurement of strain in specimens under load and the C_{11} figure of Twisleton *et al.* [16] was measured from the acoustic phonon frequencies found by neutron inelastic scattering. If this value is confirmed by subsequent experiments, it will be necessary for theoretical modelling to either find a suitable way of smoothly truncating the existing potentials at small atom–atom separations, which seems improbable, or develop new potentials which can cater for greater ranges of interaction. For the moment, it seems prudent to continue to use the existing potentials with ranges extended to avoid instability and numerical problems in defect modelling, and to consider the crystals simulated as "model" systems rather than accurate replicas of polyethylene.

It has sometimes been assumed for simplicity that polyethylene crystals are transversely isotropic, i.e. $C_{11} = C_{22}$, $C_{44} = C_{55}$ and $2C_{66} = (C_{11} - C_{12})$ for the orthorhombic constants, but inspection of Tables V and VI reveals that this is not generally an accurate approximation and may be a particularly inaccurate one when long-range interactions are important.

Finally, the elastic constants for the monoclinic phase have been obtained for the first time. They show the same sort of variation from potential set to potential set as the orthorhombic constants, and in this case there are no experimental or theoretical values for comparison. If subsequent investigations provide a firm lead, it would be possible to scale the values of Table V, or perhaps to use means of the calculated values. In the meantime, they should find use as parameters for model calculations.

Acknowledgements

The original lattice-generation programs were provided by Dr M. J. Norgett, The authors also acknowledge the valuable discussions with Dr J. W. Martin on the development of the DEVILS package, and thank Drs A. P. P. Nicholson and K. Tharmalingam for helpful discussions, and the S.R.C. for the award of a research studentship to N.A.G.

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Received 18 May
and accepted 29 July 1982