Monte Carlo simulation of molecular motion and phase transition in poly(ethylene) crystal

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Conformational properties of a chain and a phase transition in poly(ethylene) crystal are studied by extending a previous Monte Carlo calculation for a chain in a cylindrical crystalline potential. The crystalline potential is here estimated from van der Waals interactions between one CH_2 group of a chain and its six neighbouring chains. Firstly, conformational disorders of the chains of various chain length are examined, and a definite dependence of the chain conformation on its length is demonstrated. Secondly, the behaviour of the chain at atmospheric pressure is simulated, where the modes of molecular motions and the associated disorders in conformation are clarified as a function of temperature. Thirdly, the phase transition at high temperature and pressure, from orthorhombic phase to hexagonal one, is simulated by assuming a proper molecular field for the chain. All these calculations show the present Monte Carlo calculation to have a wide variety of applications in the studies of polymer crystals.

Keywords Monte Carlo method; poly(ethylene); crystal; chain length; conformational disorder; phase transition

INTRODUCTION

In a previous paper[1], a Monte Carlo (MC) method was applied to a problem of disorders in the chain conformation in crystals, where the intermolecular potential energy for each CH_2 group $\Phi(r)$, hereafter called crystalline potential for brevity, was assumed to be cylindrical, as will be the case for the high-pressure phase of poly(ethylene), for example, and furthermore the one end of the chain was treated as fixed. The value of the parameter G involved in the expression of the crystalline potential was so determined that the calculated fibre period, $\langle c \rangle$, reproduced well that observed by X-ray diffraction. The main purpose was to show the MC method to be useful when applied to the conformational problems in polymer crystals.

In this second paper of the series, the assumptions made in the previous paper[1] are removed, i.e. the assumption of cylindrical symmetry for the crystalline potential and that of the fixed chain-end. This allows simulation of the behaviour of poly(ethylene) molecules with free chain-ends in the usual orthorhombic phase. Furthermore, the crystalline potential is directly estimated, though considerable simplifications are necessary to avoid making the MC calculations intractably complicated, from van der Walls interactions of a CH_2 group with the six neighbouring chains instead of assuming a plausible function as previously.

CALCULATION METHOD

In the previous paper[1], the crystalline potential was assumed to be cylindrical. This assumption is reasonable for such highly-disordered phases with hexagonal packing of molecules as the high-pressure phase of poly(ethylene) or the high-temperature phase of poly(tetrafluoroethylene). In general, however, the

crystalline potentials have lower symmetry than that of cylindrical one. In the following discussions, it is assumed that the crystalline potential can be described by an elliptic cylinder as:

$$\Phi(X, Y, Z) = G(Y^2/S^2 + Z^2)/2$$

$$(0 < S \leqslant 1)$$

(1)

where in a special case of $S = 1$, $\Phi(X, Y, Z)$ represents a cylindrical potential (*Figure 1*). This model of crystalline potential, though simplified considerable, represents that in the orthorhombic phase of poly(ethylene).

In the previous paper[1], the value of the parameter G was so estimated at each temperature and pressure that the calculated values of the average fibre period $\langle c \rangle$ accurately reproduced the observed one. In the present paper, however, the values of G and S in equation (1) are estimated by the rigorous calculation of the crystalline potential. The detailed procedure and the assumptions made are described in Appendix 1. A rigorous crystalline potential cannot, of course, be described by an elliptic cylinder. However, it is considered here that the essential feature of the crystalline potential can be expressed by such a simplified potential.

In the previous paper[1], the first and the second atoms of each sample chain, which was composed of 30 carbon atoms, were treated as fixed at predetermined positions, with positions of remaining 28 atoms being selected at random. This assumption is plausible for a chain one end of which is rendered sluggish by some interactions with the end groups of the neighbouring chains, as will be the case for higher alcohols or bilayers of liquid membrane. This is, however, not a reasonable assumption for the poly(ethylene) molecules, where atoms at the both ends of the chain move as freely as inner ones. Here, therefore, the
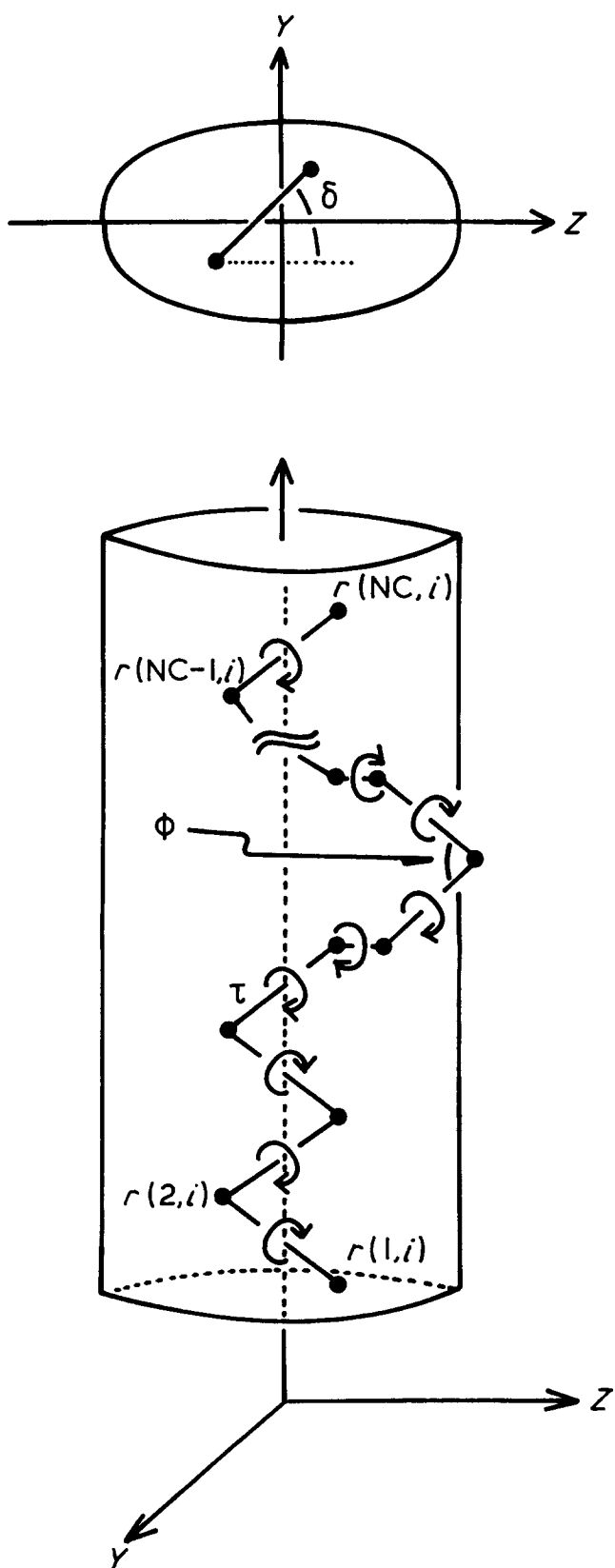
Figure 1 Polyethylene chain in an elliptic cylindrical potential $\Phi(Y,Z)$. Carbon atoms (●) are used as representatives of CH_2 groups. Following values of the structural parameters of poly(ethylene) molecules are assumed: C–C bond length, 1.54 Å; C–H bond length, 1.07 Å; C–C–C bond angle, ϕ, 109.5°; and H–C–H bond angle, 109°. Parameters $\{\delta_i\}$ represent the angles between the projections of C–C bonds on Y–Z plane and Z-axis

following cyclic boundary scheme for the chain ends is adopted.

Suppose up to the i-th chains of NC carbon atoms are generated. Then, the next $(i+1)$-th chain is generated by taking the positions of the first and the second atoms of the $(i+1)$-th chain, $r(1, i+1)$ and $r(2, i+1)$, as $r(1, i+1) = r(NC-1, i)$ and $r(2, i+1) = r(NC, i)$ (*Figure 1*). Taking such a cyclic boundary scheme, the restrictions previously imposed on the first and the second atoms can be removed and a chain with free ends can be treated.

The details of the calculation method are the same as that previously used except for the treatments of the crystalline potential and the chain end.

EFFECTS OF CHAIN LENGTH

Before considering the detailed calculation for poly(ethylene) in the crystal, the effects of chain length, more specifically the number of carbon atoms in the chain, on the conformational properties are discussed. A homologue of poly(ethylene) ranges from a low molecular weight paraffin, made of only a few carbon atoms, to a high molecular weight poly(ethylene) of several tens of thousands of carbon atoms. To clarify the properties characteristic of long-chain molecules is one of the most interesting subjects in polymer physics. Though a vast amount of experimental work has been carried out on the structure and the properties of this homologous series in the crystal[2], there has been no rigorous theoretical approach to the effects of the chain length. This is not surprising considering the mathematical difficulties involved in the analytical treatment of this problem. The MC method, however, allows calculation, with any desired accuracy, of the equilibrium conformational properties of the chain in the crystal.

Figure 2 shows an average fibre period, $\langle c \rangle$, calculated by the MC method *versus* the length of the chain NC in the cylindrical potential $(G = 3000 \text{ cal mol}^{-1} \text{ Å}^{-2}, S = 1.0)$ at 550K. The increase in the fibre period $\langle c \rangle$, in the present case of poly(ethylene), means an increase in order in the chain conformation. *Figure 2* shows, therefore, that the conformation of the chain becomes more ordered as the chain becomes longer. The details of this situation are illustrated in *Figure 3*, where the distribution $P(\tau)$ of an
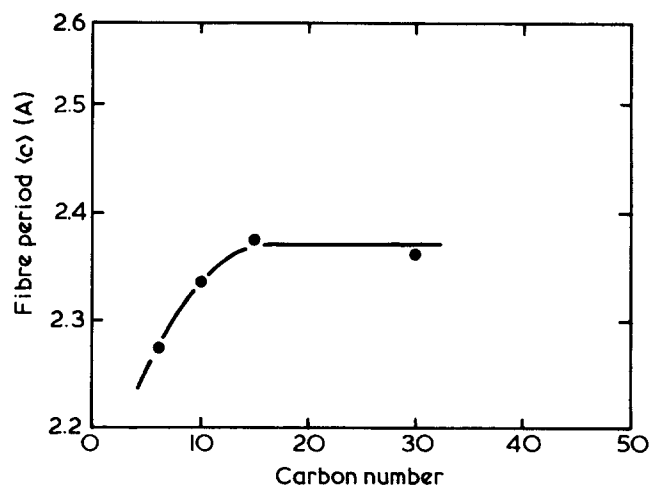

Figure 2 Average fibre period $\langle c \rangle$ of the chain in a cylindrical potential $(G = 3000 \text{ cal mol}^{-1} \text{Å}^{-2}, S = 1.0)$ at 550K as a function of chain length
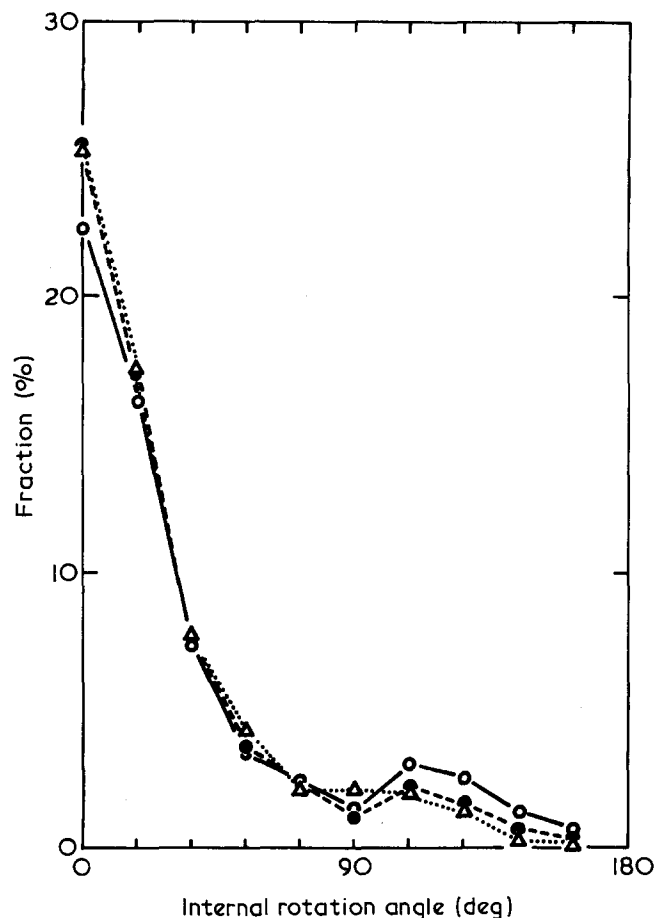
Figure 3 Distributions of internal rotation angles $\{\tau_i\}$ for chains of NC=6 (○), NC=10 (●), and NC=30 (△) at 550K in a cylindrical potential ($G=3000$ cal mol^{-1}Å^{-2}, $S=1.0$)

internal rotation angle are shown for chains of 6, 10, and 30 carbon atoms. From *Figure 3*, the increase in $P(\tau)$ around *trans* ($\tau=0°$) with the increase in the chain length is apparent, accompanied with the associated decrease in $P(\tau)$ around *gauche*($\tau=120°$). This can be understood as follows. The longer the chain becomes, the less is the probability of laying the whole chain inside the cylindrical potential, unless each τ is properly chosen. This makes the chain increasingly ordered in conformation with the increase in the chain length.

Another interesting point noted in *Figure 3* is that the distribution $P(\tau)$ has a definite maximum at the *gauche* position for shorter chain of NC=6 and NC=10, whereas for longer chains of NC=30 it has only a plateau. The increase in the chain length in the cylindrical potential tends to make the rotational isomerism increasingly unrealistic.

As the calculations for much longer chains than NC=30 require very long CPU time of computation, the obtained results must be extrapolated for longer chains to study the behaviour of real polymer chains. Though the convergence to the limiting value for an infinitely long chain depends on the temperature and the crystalline potential, as shown later, it is considered that the rapid change in conformation with the increase in chain length occurs only below a critical length NC* of ≈ 20. The chain of NC=30 can be regarded, therefore, as a proper model of a real polymer chain.

DISORDER AT ATMOSPHERIC PRESSURE

The molecular motions and the associated disorders in conformation in poly(ethylene) crystal have been discussed in many papers, for example, in the studies of dielectric relaxation in crystals[3,4] or in the studies of the axial chain-transport in a process of thickening of lamellae[5,6]. These discussions have been based on more or less arbitrary molecular models. Here, the molecular motions and the disorders can be studied by the MC method on the firm basis of statistical mechanis.

To study the behaviour of poly(ethylene) molecules in the crystal, it is necessary to evaluate first the crystalline potential $\Phi(X, Z)$: the interchain interaction energy between one methylene unit and the six neighbouring chains. The values of the parameters G and S in equation (1) at each temperature, estimated through the calculation given in Appendix 1, and the lattice constants a and b of the orthorhombic phase used in the calculation are listed in *Table 1*.

The experimental methods to detect the disorder in the chain conformation within the crystal are at present very scarce. I.r. absorption method directly shows a presence of a *gauche* bond, but suffers from the ambiguity in determining the base-line of the spectrum in the estimation of the population of the *gauche* bonds in the crystal[9]. An X-ray method, however, though it cannot clarify the local structure of the conformational defect, affords accurate information about the conformational disorders within the crystal through, for example, a decrease of a fibre period with the increase in temperature[10,11].

In *Figure 4*, the fibre period, $>c<$, calculated by the MC method and that observed by X-ray diffraction are shown *versus* temperature. As shown in *Figure 4*, the results of the present MC calculation accurately reproduce the observed decrease of the fibre period in poly(ethylene) crystal at least at relatively low temperatures. The disagreement at high temperature in *Figure 4* is mainly because of the effect of chain length, as described later.

The distribution $P(\tau)$ of the internal rotation angles for the chain (NC=30) at 303K and 373K are shown in *Figure 5*. At atmospheric pressure, the chain has an ordered planar zig-zag conformation with most of the internal rotation angles distributed around *trans*. The root-mean-square deviations of τ from *trans* $\langle \tau^2 \rangle^{1/2}$, are obtained at $\approx 8°$ and 12° at 303K and 373K, respectively.

The excitation of defects in the conformation having *gauche* bonds in the ordered orthorhombic phase has been frequently discussed for poly(ethylene) and for low molecular weight paraffins[6,12]. These defects are thought to be closely related to the mode of molecular motions of the chain in the crystal and are significant, for example, in

Table 1 Values of the parameter G and S in equation (1), and those of the lattice parameters a and b of orthorhombic lattice at each temperature

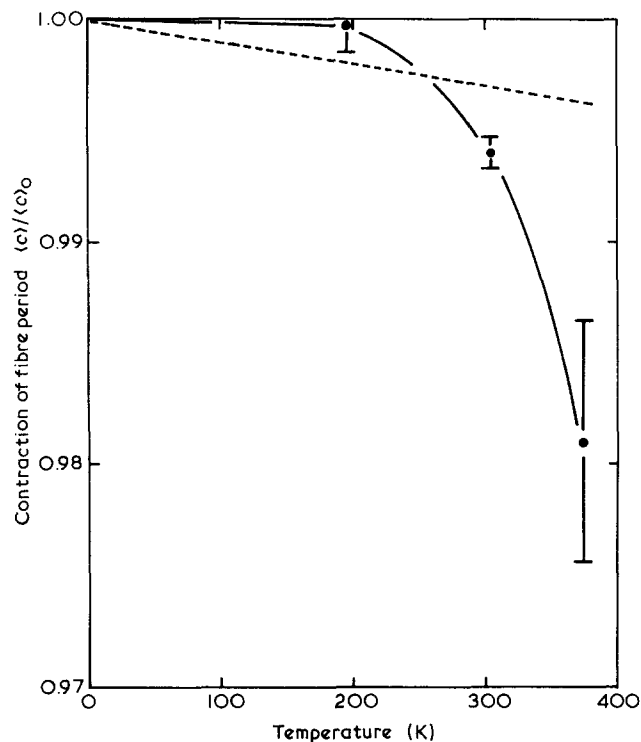| T (K)	G (cal mol^{-1} A^{-2})	S	a (A)	b (A)
195	1922	0.44	7.270[a]	4.910[a]
303	1145	0.38	7.414[b]	4.942[b]
373	647	0.31	7.567[b]	4.942[b]

[a] Data of Shen *et al.*[7]
[b] Data of Swan[8]

Figure 4 Average fibre period $\langle c \rangle$ at atmospheric pressure *versus* temperature of the chain of NC=30 calculated by the MC method (●), and that of poly(ethylene) crystal (———) observed by X-ray diffraction[10]

the dielectric relaxation or in the thickening of lamellae. However, there are some doubts about the excitation of such defects or its role in the dielectric relaxation[4]. As clearly shown in *Figure 5*, a peak, though small, is present around the *gauche* position in the distribution $P(\tau)$. This evicently shows a thermal excitation of *gauche* bonds in the chain even at room temperature. Though some of these *gauche* bonds should be ascribed to the defects at the chain ends, this strongly suggests the excitation of locallized defects, point dislocation-type, kink-type, or others, in the interior of the chain stems.

The population of the defect in the chain conformation is considered to be related to the mobility of the chain in the crystal. *Figure 6* shows a change in the population of the *gauche* bonds W_g, which is the sum of $P(\tau)$ at four internal rotation angles (τ_6–τ_9) around *gauche* , with temperature. The value of W_g at 373K in *Figure 6* will be considerably larger than that in real poly(ethylene) crystals, which is due to the effect of short chain length (NC = 30) as described later. It is, however, reasonable to think that the *gauche* defects are excited at least of an order of 0.1% near the melting point of poly(ethylene).

Figures 7 and *8* show the changes in the distribution $P(\tau)$ with chain length NC at 303K and 373K, respectively, at atmospheric pressure. With increase in NC, a sharpening of the *trans* peak occurs accompanied with a lowering of the *gauche* peak. These changes in conformation are summarized in *Figure 9*, where the calculated fibre period $\langle c \rangle$, the width of the *trans* peak $\langle \tau^2 \rangle^{1/2}$, and the fraction of *gauch* bonds W_g are shown *versus* NC. At 303K, each quantity closely approaches the limiting value for an infinitely long chain at small NC as NC = 30, whereas at 373K a little further change may be expected at NC > 30. This difference with temperature in the limiting behaviour of the conformation will be the
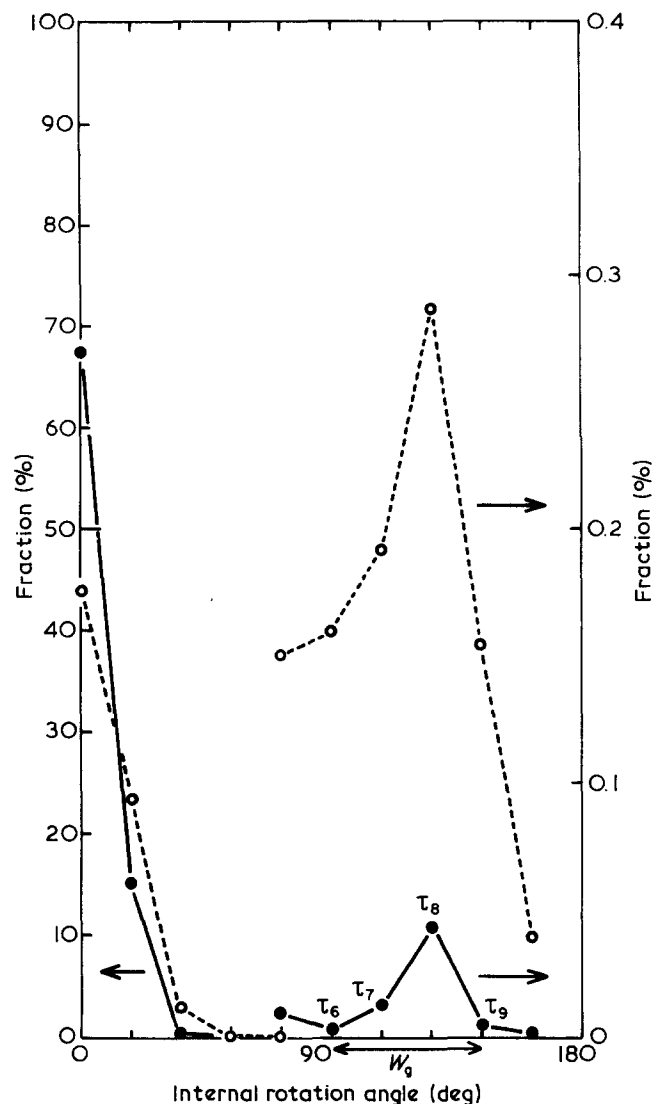

Figure 5 Distributions of internal rotation angles $\{\tau_i\}$ at atmospheric pressure at 303K (●) and at 373K (○)
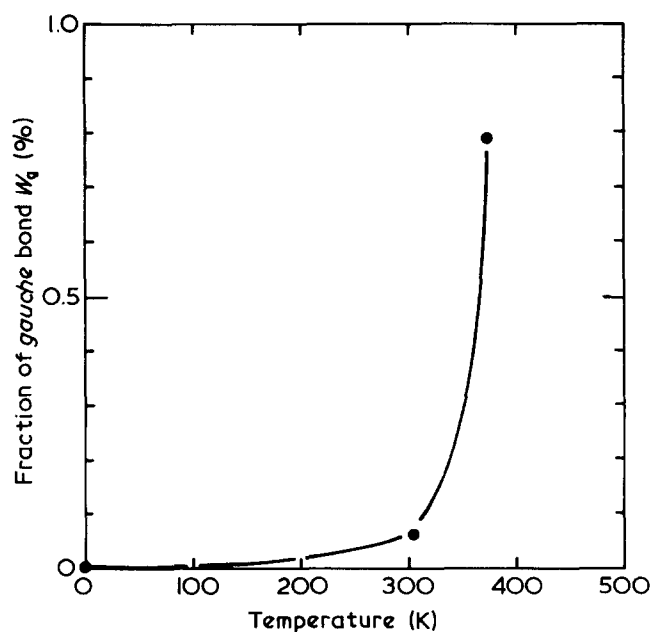

Figure 6 Fraction of *gauche* bond W_g, which is defined as a sum of $P(\tau)$ from $P(\tau_6)$ to $P(\tau_9)$ in *Figure 5*, as a function of temperature
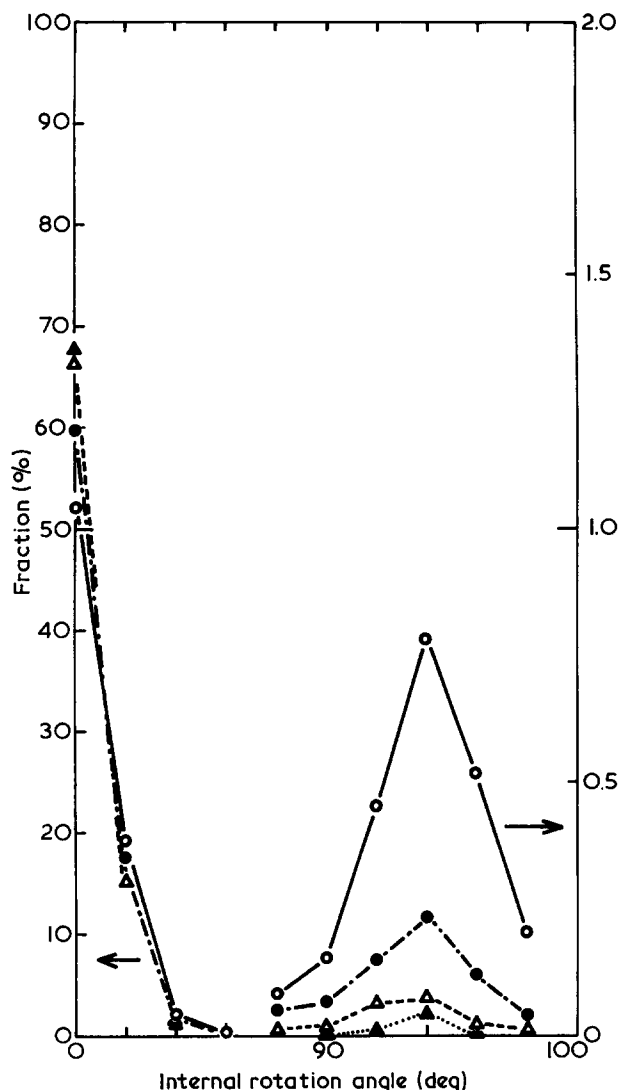
Figure 7 Distributions of internal rotation angles $\{\tau_i\}$ for chains of NC=6 (O), NC=10 (●), NC=15 (△), and NC=30 (▲) at 303K and atmospheric pressure
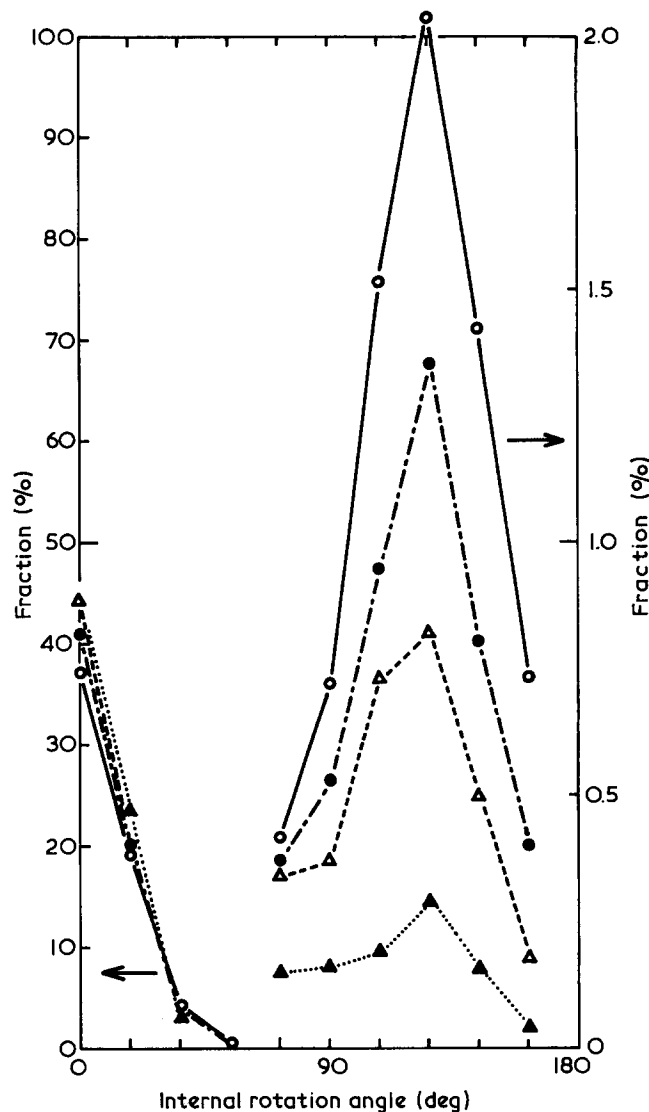

Figure 8 Distributions of internal rotation angles $\{\tau_i\}$ for chains of NC=6 (O), NC=10 (●), NC=15 (△), and NC=30 (▲) at 373K and atmospheric pressure

main origin of the discrepancy at high temperature in *Figure 4* between the fibre period calculated for the chain of NC = 30 and that observed in poly(ethylene). Such change with temperature in the limiting behaviour is itself significant. It shows that the weaker the crystalline field is and consequently the more disordered the chain is, the slower is the approach of the conformational properties of the chain to those of infinitely long chain.

The excitation of disorders in conformation at atmospheric pressure is, in this way, clarified by the MC method. The roles of such disorders are, however, not clear in the various physical phenomena such as the dielectric relaxation or the thickening of lamellae. These are, for the most part, problems of a kinetic process.

DISORDER AT HIGH PRESSURE

Poly(ethylene) shows a unique crystalline phase transition at high pressure and temperature. The usual orthorhombic phase of ordered planar zig-zag chains transforms to a hexagonal phase of highly disordered ones, for example, at 550K at 900 MPa. Here, this phase transition is considered in detail, and the behaviour of the chain at 550K and 900 MPa is examined.

The lattice parameters in the orthorhombic phase near the phase transition point have been reported by some workers[13,14], who carried out the X-ray diffraction experiments at high temperature and pressure. The parameters G and S involved in the crystalline potential Φ in the orthorhombic phase can be calculated in the same way as before using these observed lattice parameters. From the lattice parameters $a = 7.43$ Å and $b = 4.72$ Å at 550K and 880 MPa[14], the values of G and S of $G \approx 2450$ cal mol^{-1} Å^{-2} and $S = 0.44$ are obtained. The crystalline potential in the hexagonal phase, alternatively, can be represented by a cylindrical potential as described previously. The value of G is, however, difficult to evaluate by a rigorous calculation of van der Waals interactions between chains due to the large disorder in the chain conformation. However, the value of G can be estimated, as reported in the previous paper, from the requirement that the calculated value of the fibre period, $\langle c \rangle$, should reproduce accurately the observed one by X-ray diffraction. The calculated value of the fibre period at 550K for $G = 3000$ cal mol^{-1} Å^{-2} is ≈ 2.36 Å, which indicates a contraction of the fibre period of $\approx 6\%$ in reasonable agreement with experimental result[15]. Therefore, the value of G at ≈ 550K in the hexagonal
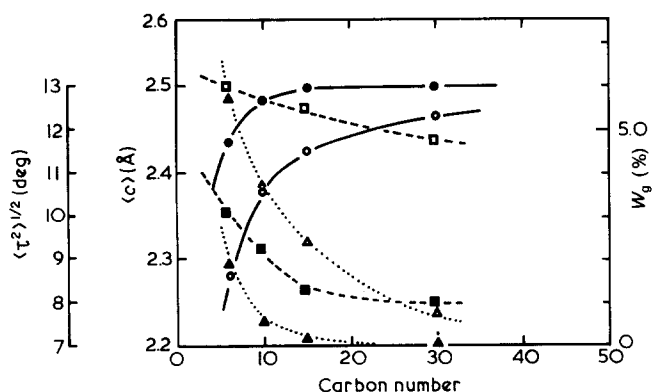
Figure 9 The average fibre period $\langle c \rangle$ (●), the width of the *trans* peak $\langle \tau^2 \rangle^{1/2}$ in $P(\tau)$ (■), and the fraction of *gauche* bond W_g (▲) *versus* chain length at 303K, and those ((○), (□), and (△)) at 373K

Figure 10 Disorder $\langle \delta^2 \rangle$ of the chain as a function of S at 450K (▲), 500K (○), and 550K (●)

phase may be ≈ 3000 cal mol^{-1} Å^{-2}. In the following discussions of the phase transition from orthorhombic to hexagonal, only the changes in the conformational properties with S are considered, where the value of G is treated as fixed at $G = 3000$ cal mol^{-1} Å^{-2}.

Here, a parameter $\langle \delta^2 \rangle$ is introduced to describe the order in conformation projected onto the $Y - Z$ plane, where δ represents an angle between the projection of a C—C bond onto the Y—Z plane and the Z-axis (*Figure 1*). In a perfectly-ordered state in the orthorhombic phase, the chains will be in an ordered planar zig-zag structure with the zig-zag plane parallel to the Z-axis: $\langle \delta^2 \rangle = 0$. In a highly-disordered state, however, each projected bond will have a random orientation:

$$\langle \delta^2 \rangle = (2/\pi) \int_0^{\pi/2} \delta^2 \, d\delta = \pi^2/12 = 2700 \text{ deg}^2.$$

In *Figure 10* is plotted the value of $\langle \delta^2 \rangle$ *versus* S calculated by the MC method at 450, 500 and 550 K. The value of $\langle \delta^2 \rangle$ evidently follows the general tendency described: it increases monotonically at any temperature from 0 deg.^{2} at small S to 2700 deg.^{2} at $S = 1.0$. Near $S = 1.0$, however, the increase in $\langle \delta^2 \rangle$ becomes less marked with the increase in temperature.

Data in *Figure 10* show the order parameter $\langle \delta^2 \rangle$ of a single chain within the crystalline potential specificied by the value of S. Similar to the usual molecular field approximation, the value of S for the chain of interest can be related to the value of $\langle \delta^2 \rangle$ of the neighbouring chains. Thus, a self-consistent equation for $\langle \delta^2 \rangle$ or S can be established from this relation together with the data of *Figure 10*. The anisotropy of the molecular field $\Phi(Y, Z)$, which is expressed by S^{-1}, is thought to be reduced by the increase in disorder $\langle \delta^2 \rangle$ of the neighbouring chains. A simple model of the molecular field obtained by extension of the treatment given by Peterlin and Fischer[16] is used (Appendix 2).

In *Figure 11* is plotted the parameter S of the molecular field obtained in Appendix 2 *versus* $\langle \delta^2 \rangle$, superposed on the results of the MC calculation in *Figure 10*. The intersection of the two curves gives a self-consistent solution for $\langle \delta^2 \rangle$ or S at each temperature. At 450K and 500 K, there are ordered, thermodyamically-stable solutions at $S \approx 0.5$. At 550 K, however, there is only a disordered solution at $S \approx 1.0$. The self-consistent
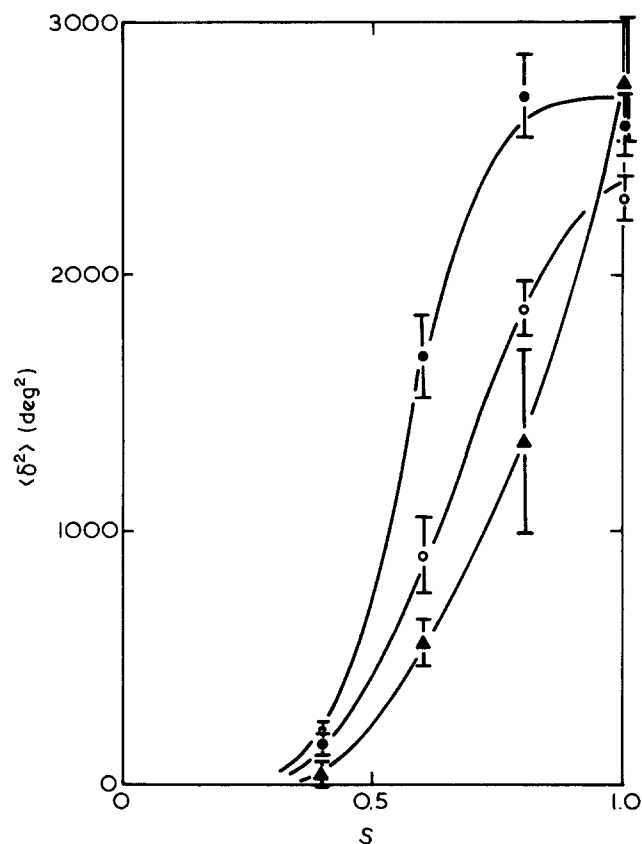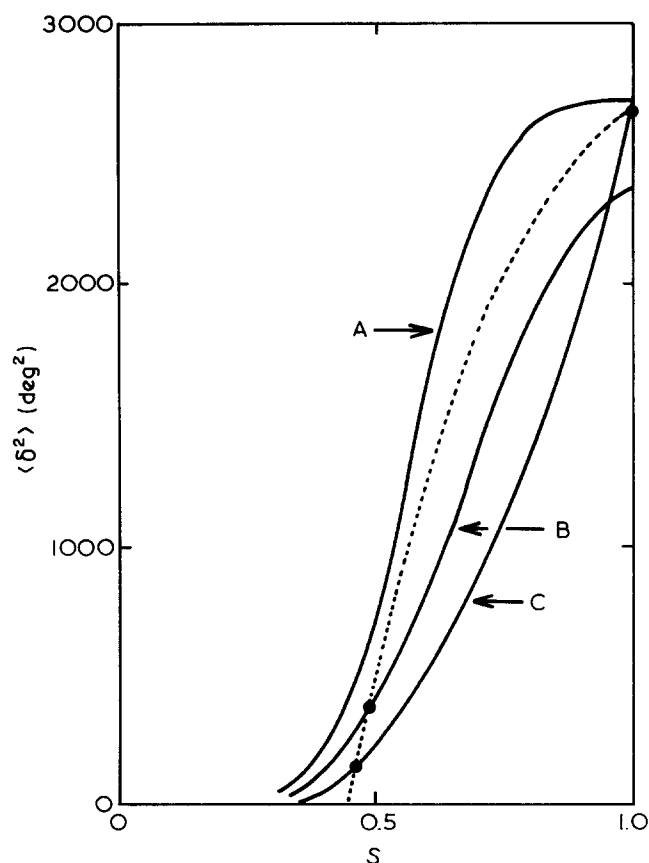

Figure 11 Mean field value of S as a function of $\langle \delta^2 \rangle$ of the neighbouring chains (— —), superposed on *Figure 10*, where S_0 is assumed to be 0.44. A, 550; B, 500; C, 450K

solutions for $\langle \delta^2 \rangle$ and S obtained in this way, and the fibre period $\langle c \rangle$ for the corresponding state are shown in *Figure 12 versus* temperature. Each quantity clearly shows a transition at ≈ 530 K, from that in the ordered state ($S = 0.48$, $\langle \delta^2 \rangle^{1/2} = 20°$, and $\langle c \rangle = 2.50$ Å) to that in the disordered state ($S = 1.0$, $\langle \delta^2 \rangle^{1/2} = 52°$, and $\langle c \rangle = 2.36$ Å). The value of 2.50 Å for $\langle c \rangle$ just below the transition point indicates a contraction of $\approx 0.6\%$, where the maximum value of $\langle c \rangle$ for the fully extended chain is in the present work 2.515 Å[1]. This contraction of the fibre period of $\approx 0.6\%$ shows good agreement with the observed contraction of $\approx 0.5\%$ by X-ray diffraction[13].

In this way the crystalline transition at high temperature and pressure was successfully simulated by assuming that during the transion only the value of S varies, while that of G is fixed at $G = 3000$ cal mol^{-1} Å^{-2}. For the rigorous treatment of the present transition phenomena with a change in volume, however, the MC calculation based on temperature–pressure (T-P) ensemble should be used instead of the present canonical (T-V) ensemble.

ACKNOWLEDGEMENT

APPENDIX 1

In this Appendix, a method is described of estimating the values of G and S in equation (1) from a direct calculation of the interaction energy between a CH_2 group of a chain and its 6 neighbouring chains. A 6-exponential potential for the van der Waals interactions is used
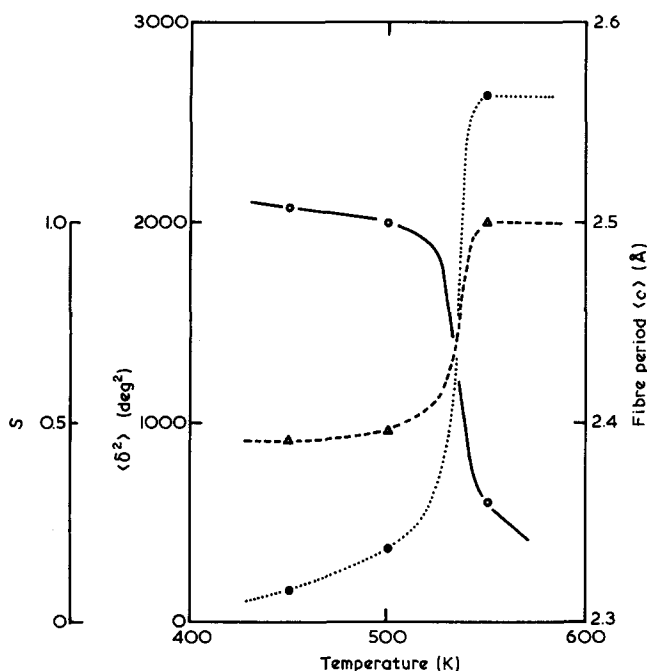
$$u(r) = -A/r^6 + B \exp(-Cr) \qquad (A-1)$$

Figure 12 Self-consistent solutions of the disorder $\langle \delta^2 \rangle$ (●), the parameter S (△), and the fibre period $\langle c \rangle$ (○) as a function of temperature

where the values of the parameters A, B, and C used for C—C, C—H, or H—H interactions are those of Kimel *et al.*[17], and are listed in *Table 2*.

According to the row potential formulation by McCullough and Peterson[18], the interaction energy between two parallel rows of atoms $U(d, t)$ can be written as follows:

$$U(d, t)/N = U_0(d) + \sum_{m=1}^{\infty} U_m(d) \cos(2\pi tm/\lambda) \qquad (A-2)$$

$$U_0(d) = -(3\pi A/8\lambda)/d^5 + (2B/\lambda)dK_1(Cd) \qquad (A-3)$$

where K_1 is a modified Bessel function of the second kind, d is a separation distance between rows, t is a relative translational displacement of the rows, λ is a spacing of atoms along the row, and N is the number of atoms on the row. As the crystalline potential Φ in equation (1) does not depend on the co-ordinate X, the dependence of $U(d, t)$ on the variable t can be ignored, therefore:

$$U(d, t)/N = U_0(d)$$
$$= -(3\pi A/8\lambda)/d^5 + (2B/\lambda)d \cdot K_1(Cd) \qquad (A-4)$$

By the use of equation (A-4), the interaction energy E between one CH_2 group of the chain and its six neighbouring poly(ethylene) chains can be calculated as a function of (r, θ) or (Y', Z'), where the orientation of the central CH_2 group is so assumed that the line OC bisects the angle HCH (*Figure 13*). Here this energy E, which is a function of the position of the central carbon atom, is regarded as the crystalline potential Φ given in equation (1).

Figure 14 shows typical graphs of E versus r and θ. For small values of r, which satisfy the inequality $|E(r,\theta) - E(0,\theta)| \leqslant kT$, $E(r,\theta)$ may be represented by a quadratic function of r. Furthermore, the dependence of $E(r,\theta)$ on θ may be described approximately by a cosine function of θ of period π. On the basis of these simplifications, the values of G and S can be estimated from the change of $E(r,\theta)$ along the two directions $\theta = 140°$ and $\theta = 65°$, which correspond to the directions of the long axis and the short axis, respectively, of the elliptic cylindrical potential Φ.

APPENDIX 2

In this appendix, a mean field value of the parameter S in equation (1) is estimated as a function of $\langle \delta^2 \rangle$ of the neighbouring chains, following the procedure adopted by Peterlin and Fischer.[16]

Let a crystalline potential $\Phi(Y, Z)$ in equation (1), when the neighbouring chains are ordered, $\langle \delta^2 \rangle = 0$, be described by G_0 and S_0 as follows:

$$\Phi(Y, Z) = \Phi_0(Y, Z) = G_0(Y^2/S_0^2 + Z^2)/2 \qquad (A-5)$$

Table 2 Values of the parameters *A*, *B*, and *C* in equation (1) for C—C, C—H, and H—H interactions

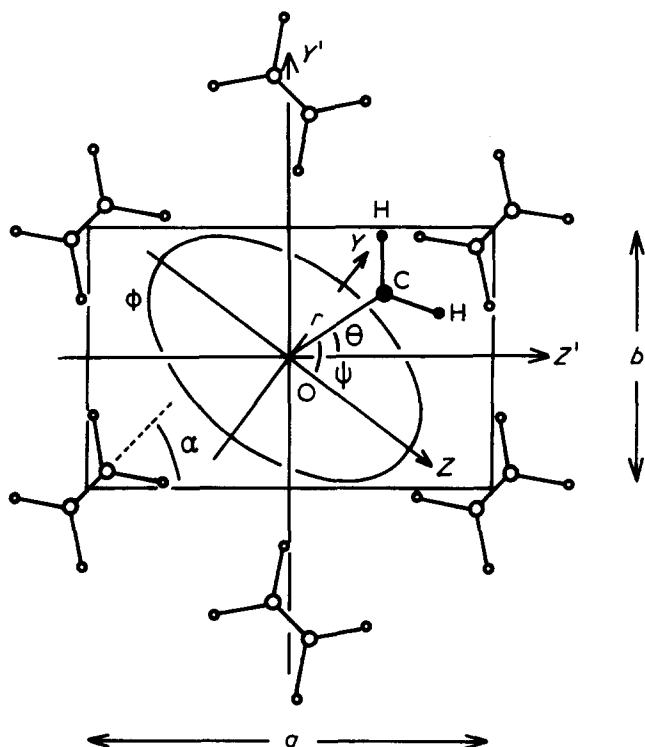| Atomic pairs	A (erg Å^6)	B (erg)	C (Å^{-1})
C—C	22.6 × 10^{-12}	25.7 × 10^{-10}	4.26
C—H	8.68 × 10^{-12}	5.55 × 10^{-10}	3.90
H—H	3.42 × 10^{-12}	1.20 × 10^{-10}	3.54

Figure 13 Crystal structure of poly(ethylene) in the ordered orthorhombic phase projected onto *Y–Z* plane. Setting angle of the zig-zag plane α is taken to be 45°. The position of the central carbon atom (X', Y') or (X, Y) denoted by the larger filled circle is expressed as $Y' = r \sin(\theta)$ and $Z' = r \cos(\theta)$, or $Y = r \sin(\psi)$ and $Z = r \cos(\psi)$
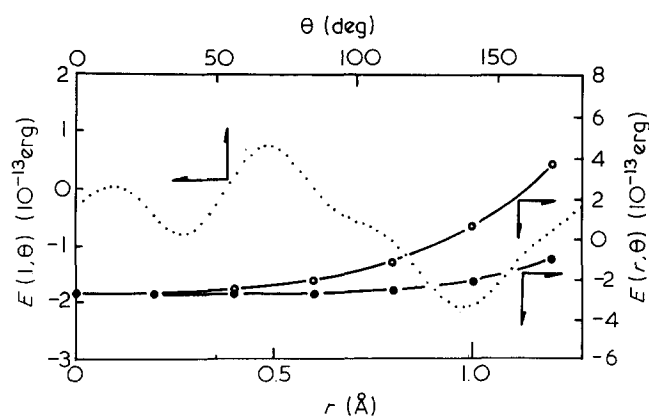

Figure 14 Interaction energy $E(r,\theta)$ between the central CH_2 group and its six neighbouring chains at 195K, as a function of θ at $r = 1.0$ Å (.....), and as a function of r at $\theta = 65°$ (O) and at $\theta = 140°$ (●)

Introducing a polar co-ordinate $(Z = r \cos(\psi))$ and $Y = r \sin(\psi))$:

$$\Phi_0(Y, Z) = \Phi_0(r, \psi)$$

$$= G_0 r^2 \{(1 + S_0^{-2}) - (S_0^{-2} - 1) \cos(2\psi)\}/4 \quad (A\text{-}6)$$

The disorder $\langle \delta^2 \rangle$ of the neighbouring chains will lead to a fluctuation of the Y and Z axis *(Figure 13)*. The following Gaussian form is assumed for the fluctuation of the axes:

$$P(\psi_0) = \exp(-\psi_0^2/(2\sigma^2)) \bigg/ \int_{-\pi/2}^{\pi/2} \exp(-\psi_0^2/(2\sigma^2)) d\psi_0$$

$$(A\text{-}7)$$

$$(-\pi/2 \leqslant \psi_0 \leqslant \pi/2)$$

where:

$$\langle \delta^2 \rangle = \int_{-\pi/2}^{\pi/2} \psi_0^2 P(\psi_0) d\psi_0 \quad (A\text{-}8)$$

From equations (A-6) and (A-7), an average of the crystalline potential $\langle \Phi_0(Y, Z) \rangle$ can be calculated as:

$$\langle \Phi_0(Y, Z) \rangle = \int_{-\pi/2}^{\pi/2} P(\psi_0) \Phi_0(r, \psi - \psi_0) d\psi_0$$

$$= G_0 r^2 \{(S_0^{-2} + 1) - \varepsilon(S_0^{-2} - 1) \cos(2\psi)\}/4 \quad (A\text{-}9)$$

where:

$$\varepsilon = \int_{-\pi/2}^{\pi/2} \exp(2i\psi) \exp(-\psi^2/(2\sigma^2)) d\psi \bigg/$$

$$\int_{-\pi/2}^{\pi/2} \exp(-\psi^2/(2\sigma^2)) d\psi \quad (A\text{-}10)$$

The coefficient of $\cos(2\psi)$ in equation (A-9), which described the anisotropy of the crystalline potential, decreases with the increase in σ^2.

As the value of G is considered to be fixed as described in the text:

$$\langle \Phi_0(Y, Z) \rangle = G r^2 \{(S^{-2} + 1) - (S^{-2} - 1)$$

$$\times \cos(2\psi) + (S_0^{-2} - 1)(1 - \varepsilon)\}/4 \quad (A\text{-}11)$$

where S, the increase of which represents a smearing of the crystalline anisotropy, is defined by ε and S_0 as follows:

$$(S^{-2} - 1) = \varepsilon(S_0^{-2} - 1) \quad (A\text{-}12)$$

As seen in equation (A-11), the average potential has an additional term, the third term in the brace, to equation (1).

Due to an increase in volume during the transition, the interchain distances increase and, therefore, the crystalline potential softens. In deriving equation (A-11), the effect of such an increment in the interchain distances was not taken into account. As described in the text, only S in equation (1) vaires during the transition with G being constant. This means that the contribution of the third term in the brace of equation (A-11) is properly subtracted due to the softening of the crystalline potential described. The crystalline potential $\Phi(Y, Z)$ can be written, therefore, as follows:

$$\Phi(Y, Z) = G(Y^2/S^2 + Z^2)/2 \quad (A\text{-}13)$$

where S is determined by S_0 and ε from equation (A-12). From equations (A-7), (A-8), (A-10), and (A-12), the value of the parameter S can be determined as a function of $\langle \delta^2 \rangle$.

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