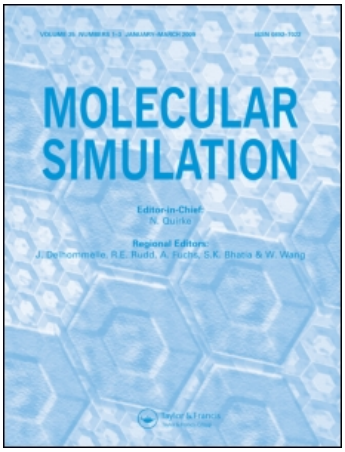

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THERMAL EXPANSION OF IDEAL POLYMER CRYSTALS: APPLICATION TO POLYETHYLENE

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There are three central force mechanisms underlying thermal expansion: bond stretching due to the asymmetry of pair potentials and two others due to tensions caused by vibrations with components away from the bond direction. Quasi-harmonic methods previously used for skeletal chain models are here applied to a central force model for orthorhombic polyethylene, giving qualitative agreement with experiment. Tension effects neglected in some earlier studies make appreciable negative contributions to α_a and α_b; conversely, bond-stretching effects make appreciable positive contributions to the negative α_c. The temperature dependence of the setting angle of the skeletal planes has little effect on the macroscopic expansion.

KEY WORDS: Thermal expansion, central force, quasi-harmonic, lattice dynamics, polyethyene

1. INTRODUCTION

At Bristol we are undertaking a systematic theoretical study of the thermal expansion of polymers. By first investigating thoroughly the behaviour of simple models and then proceeding to more complex ones, we hope to build up a detailed understanding of the important mechanisms operative in real polymeric systems. We have begun with pair potential models, in which bond angles are stiffened by central force "struts" (figure 5). Results for several models of parallel skeletal chains interacting with weak intermolecular forces have been presented elsewhere [1]; these include flexible straight chains, flexible zig-zag chains, and stiffened zig-zag chains. In the present paper we further clarify the fundamental mechanisms underlying the expansion and examine their effects in a preliminary model for ideal orthorhombic polyethylene.

We employ the quasi-harmonic approximation, in which frequencies are calculated by harmonic lattice dynamics but allowed to be strain-dependent (see, e.g., [2]). In contrast to most earlier work on polyethylene, all the crystal parameters are allowed to vary with temperature. The computation keeps strictly to the lowest order in the anharmonicity, and thus evaluates the expansion coefficients as functions of temperature *at constant strain*. This is a fair approximation at reasonably low temperatures, but neglects the softening of crystal elasticity which is important at high temperatures. We intend to carry out the more extensive computations required at high temperatures after we have developed models giving a satisfactory fit to experiment at low and intermediate temperatures.

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2. METHOD OF COMPUTATION

The thermal expansion of a solid is the elastic response to thermally induced stress. Thermal expansion coefficients $\mathscr{A}_A$ are given by [3]

$$\mathscr{A}_A \equiv \left(\frac{\partial \mathscr{E}_A}{\partial T}\right)_{\mathscr{T}} = -\sum_B \mathscr{S}^T_{AB}\left(\frac{\partial \mathscr{T}_B}{\partial T}\right)_{\mathscr{E}}, \tag{1}$$

where $\mathscr{E}_A$ and $\mathscr{T}_B$ are respectively generalised strain and stress coordinates, and the $\mathscr{S}^T_{AB}$ are isothermal compliances defined by

$$\mathscr{S}^T_{AB} = (\partial \mathscr{E}_A/\partial \mathscr{T}_B)_{\mathscr{T}',T}. \tag{2}$$

In thermal expansion the number of independent strains is restricted by symmetry. For example, we consider only one independent macroscopic strain for a cubic crystal, but three for an orthorhombic crystal. In addition, unless the relative positions of all atomic sites within a unit cell are determined by symmetry, we must also consider internal expansion, i.e., the variation with temperature of the unit cell configuration. The generalised coordinates $\mathscr{E}_A$ and $\mathscr{T}_A$ above include not only the relevant macroscopic coordinates η_i and t_i, but also the relevant internal coordinates; and similarly for the expansion coefficients.

The application of quasi-harmonic theory is then straightforward (e.g. Gibbons [4]). The $\mathscr{S}^T_{AB}$ are calculated from the potential energy function Φ of the static lattice in its equilibrium configuration by inverting the stiffness matrix

$$\mathscr{C}_{AB} = (\partial^2\Phi/\partial \mathscr{E}_A \partial \mathscr{E}_B)_{\mathscr{E}'}/V, \tag{3}$$

where V is the volume. The thermal stress coefficients

$$\left(\frac{\partial \mathscr{T}_B}{\partial T}\right)_{\mathscr{E}} = \left(\frac{\partial^2 F}{\partial T \partial \mathscr{E}_B}\right)_{\mathscr{E}'}/V \tag{4}$$

are derived from the harmonic approximation for the Helmholtz energy function F, in terms of the phonon frequencies and their strain derivatives. We use the standard computational techniques of harmonic lattice dynamics (see appendix), the strain derivatives being obtained by first order perturbation theory.

3. MECHANISMS FOR THERMAL STRESS IN CENTRAL FORCE MODELS

Crystal vibrations cause the central force between a pair of atoms to fluctuate. Thermal stress arises when the mean fluctuation is not zero. There are three ways in which this can happen.

3.1 Interatomic Repulsion due to Asymmetry in the Pair Potential (Bond Stretching)

This mechanism is the dominant effect in most simple crystals. It operates for vibrations with components of relative displacement along the bond direction (figure 1). In the harmonic approximation, the fluctuations of relative position are symmetric about the static lattice configuration, and for vibrations along the bond direction the

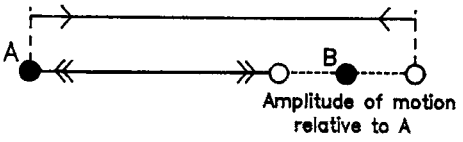

Figure 1 Mean repulsive force produced by vibrational displacements along the bond direction.

mean interatomic distance is unaltered. However, the fluctuations of force are asymmetric, giving a net repulsion.

The elastic response of the crystal is to increase the mean distance between the two atoms, giving positive thermal expansion of the distance between the mean atomic positions.

3.2 Interatomic Attraction due to Tension produced by Motion Transverse to the Bond

This mechanism operates for vibrations with components of relative displacement perpendicular to the bond direction (figure 2). For these vibrations, the mean interatomic distance is greater than the distance between the mean atomic positions, causing a net attractive force. For close-packed crystals this attraction is smaller than the repulsion due to asymmetry of the pair potential; but it can become dominant in crystals of an open structure, where there are many modes of large amplitudes with only small components along bond directions.

The elastic response of the crystal is to attempt to restore the mean atomic distance to its static lattice value, giving negative expansion.

3.3 Bond Rotations due to Tension produced by Vibrations

This mechanism operates for vibrations with relative displacments which are neither parallel nor perpendicular to the bond direction (figure 3), *in addition to* mechanisms

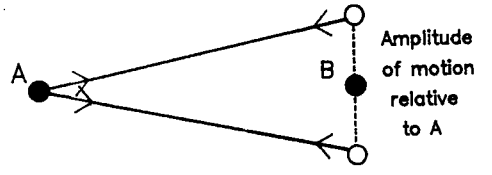

Figure 2 Mean attractive force produced by vibrational displacements normal to the bond direction.

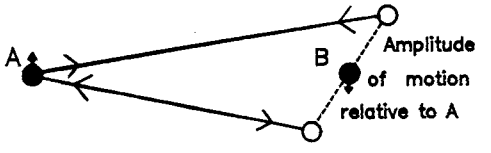

Figure 3 Mean torque (thick arrows) on bond direction produced by vibrational displacements.

Table 1 Heat capacities ($J\,K^{-1}\,mol^{-1}$) and thermal expansion coefficients ($10^{-6} \times K^{-1}$) for o-PE

T/K	*Calorimetry*	*X-ray Diffraction*			*Dilatometry*		*Present Theoretical Model*				
	C_P	α_a	α_b	α_c	α_c	$\alpha_\perp$	C_η	α_a	α_b	a_c	$\alpha_\perp$
10	0.10	–	–	–	−0.3	2.0	0.10	0.88	1.0	−0.1	0.9
20	0.73	–	–	–	−1.3	11.2	0.73	6.8	7.0	−0.6	6.9
40	3.19	50	30	−3	−4.3	40	3.50	33	29	−3.5	31
100	9.45	90	60	−6	−8.1	93	9.93	84	66	−6.4	75
150	12.9	125	60	−7	−8.2	110	12.9	96	75	−5.3	86
200	15.6	150	65	−8	−8.9	118	15.8	102	80	−4.1	91
250	18.5	170	65	−10	−10.9	126	19.1	105	82	−3.4	93

1 and 2. Over a vibrational cycle there is a net torque twisting the bond direction away from the direction of the vibrational displacements. However, different vibrations twist the bond in different directions and so tend to cancel each other. For cubic crystals the net torque is zero by symmetry, but preliminary calculations indicate that in polymers and other highly anisotropic crystals the effect is appreciable though small.

3.4 Thermal Expansion

The net thermal expansion is the elastic response of the crystal to all the thermal stresses set up by each of these mechanisms for each pair of atoms. For anisotropic crystals of complex structure this can give rise to intricate patterns of behaviour. Separate contributions from each mechanism for each different type of pair interaction can be identified with terms appearing in the quasi-harmonic theory, and if desired can be separately computed. The present computations distinguish only between the bond-stretching contributions (3.1) and the combined tension contributions (3.2 and 3.3).

4. ORTHORHOMBIC POLYETHYLENE (O-PE)

4.1 Experimental Data and Previous Theory

Expansion coefficients (table 1) are obtained either by x-ray diffraction from crystallites in the bulk [5, 6] or by dilatometry on the drawn polymer [7]. Neither method gives accurate results for the ideal crystal. X-ray diffraction is insufficiently precise at low temperatures, and measurements on the drawn polymer have to be extrapolated to 100% crystallinity [8], and then give only α_c and $\alpha_\perp = (\alpha_a + \alpha_b)/2$.

Theory is also uncertain, despite much previous work. The negative expansion in the c-direction is believed to be primarily a tension effect caused by torsional librations of the C–C bonds [9, 10]. The positive expansion along the other two crystalline axes is due primarily to the bond-stretching mechanism, and qualitative agreement with experiment has been obtained for a model with intermolecular interactions solely between hydrogen atoms [11]; but a model which included additional C · · · H interactions [12] reversed the anisotropy between α_a and α_b. Neither treatment allowed all the crystal parameters to vary freely with temperature.

4.2 The Present Model

The crystal structure (figure 4) and parameters are taken from [13]. Intramolecular pair potentials are taken for the C–C and C–H bonds, and for C -- C, C -- H and H -- H "struts" stiffening the tetrahedral angles at each carbon (figure 5). Intermolecular potentials are taken for each intermolecular pair of hydrogen atoms H · · · H less than 3 Å apart. There are no torsional force constants, and no intermolecular C · · · H interactions; restoring forces for torsional oscillations of the carbon skeletons are thus due solely to the intermolecular H · · · H interactions.

The second order force-constants ϕ'' were given rounded values of magnitudes indicated by published valence force fields [14]: 400 N m^{-1} for C–C and C–H bonds, 100 N m^{-1} for C — C, C -- H and H -- H struts, and 1 N m^{-1} for H · · · H intermolecular interactions. Comparing with experiment [15] the heat capacity computed

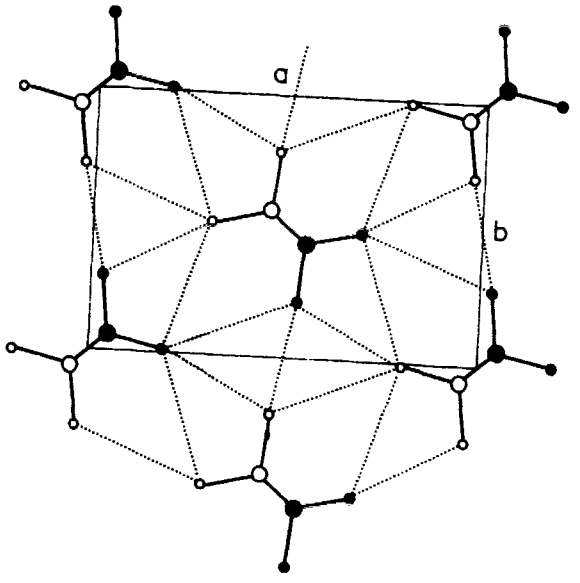

Figure 4 Primitive cell of ideal o-PE. a = 7.48 Å, b = 4.97 Å, c = 2.51 Å. At height $\frac{1}{4}$c: ●, C; •, H. At height $\frac{3}{4}$c: ○, C; o, H. • • •, model intermolecular interactions.

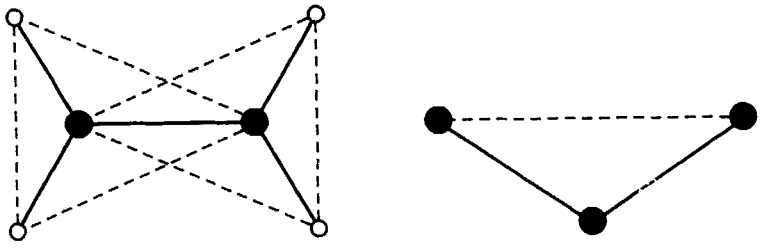

Figure 5 Struts stiffening intramolecular bond angles. ●, C; o, H.

with these force-constants (Table 1) confirms that their orders of magnitude are correct. For all pair potentials ϕ'/r was taken to be zero, and $r\phi'''/\phi''$ to be -21, the value given by a 6–12 potential when $\phi' = 0$.

The computed macroscopic expansion coefficients are shown in figure 6, together with results from two earlier models. Comparison with experiment at selected temperatures is made in Table 1.

Computations were also made with the same harmonic force-constants but with $r\phi'''/\phi'' = 0$. The thermal expansion was then negative in all directions and roughly isotropic. Comparison with results for the original model with $r\phi'''/\phi'' = -21$ indicated that negative tension contributions to α_a and α_b are of magnitude 10–20% of the total, and positive bond-stretching contributions to α_c are of magnitude 30–300% of the total.

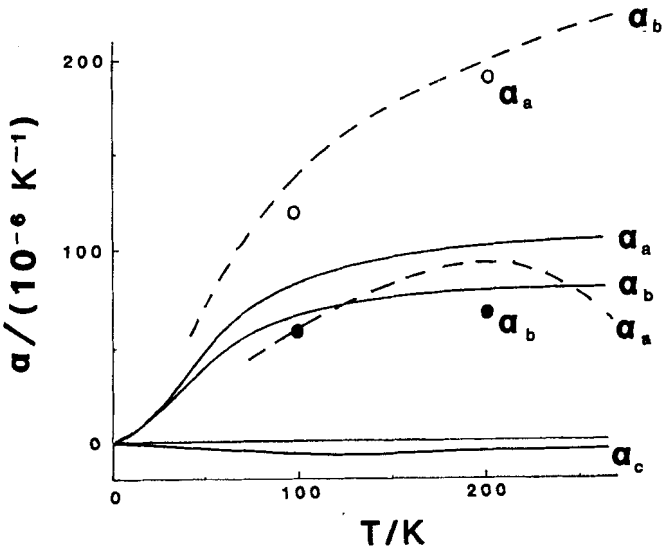

Figure 6 Thermal expansion of theoretical models for o-PE. ——, present model. – – –, Kobayashi [12], with equilibrium setting angle of 42°. O, α_a; ●, α_b; Odajima *et al.* [11].

4.3 Discussion

There is good qualitative agreement with experiment, including the correct sign of the anisotropy in the ab plane. There is also fair quantitative agreement around 100 K, at temperatures high enough for x-ray measurements to be sufficiently precise for comparison but low enough for the lowest order quasi-harmonic approximation to be reasonable. However, the expansion predicted at lower temperatures for α_c and $\alpha_\perp$ is less than that observed in the dilatometric measurements. At higher temperatures, too, the model is inadequate: it predicts that α_c should decrease in magnitude, owing to the excitation of concertina modes which contribute positively to α_c because of the asymmetric C — C strut. The absence of this effect in the real crystal suggests that the 6–12 C — C strut does not represent the correct anharmonicity of the valence bond angle. On the other hand, the failure to reproduce the observed large rise in α_a above 100 K may be largely due not to deficiencies in the model itself but to the use of the lowest order quasi-harmonic approximation, which does not take account of the softening of the crystal lattice as it expands.

The computations revealed explicitly the separate contributions from the tension mechanisms (3.2 and 3.3), which were neglected in [12]. For α_a and α_b, negative tension effects are of magnitude 10 to 20% of the net value, and should not be neglected in any quantitative study. Conversely, there are large positive bond-stretching contributions to α_c, varying in magnitude from 30 to well over 100% of the net (negative) value.

Explicit calculations were also made of the effect on the macroscopic expansion of the rotation of the skeletal planes with temperature. This was neglected in [12], although Odajima *et al.* [11] had stated that it led to the anisotropy of the expansion in the ab plane. For the present model the rotation was found to have negligible effect on the macroscopic expansion coefficients. This should not be confused with the effect of the initial choice of the setting angle, which we have not yet studied.

At low temperatures the most serious inadequacies of the model are the absence of intramolecular torsional restoring forces, the absence of C · · · H interactions, and the ascription of a single force-constant to all H · · · H interactions. Apart from further examination of the present model, the next step must therefore be to investigate whether torsional forces and differing intermolecular pair potentials will make it possible to maintain the correct magnitude of the heat capacity while softening the crystal and increasing the expansion at low temperatures. In addition, a critical study is needed of the anharmonic terms in valence bonding.

APPENDIX

Methods of lattice dynamics are described in many texts (e.g. Gilat [16]). Frequencies and atomic displacements of normal vibrations of wave vector **q** are obtained from the eigenvalues and eigenvectors of the dynamical matrix **D(q)**, which is obtained from the harmonic equations of motion as a sum over all pairs of interacting atoms. For thermal expansion we need also the first derivatives of **D(q)** with respect to each symmetry-preserving strain. First order perturbation theory then gives the strain-derivatives of the frequencies. The thermal stress coefficients are given by sums over all normal vibrations of expressions involving the frequencies and their strain derivatives, and for a bulk crystal these sums become integrals over the first Brillouin zone in q-space.

In the present calculations an integration mesh of 4096 points was taken in the Brillouin zone, each point given equal weight. Physically, the mesh is equivalent to using a cyclic boundary condition on a crystallite of 16 × 16 × 16 unit cells; it gives precision to within a few per cent (or better) at high temperatures, but is inadequate at low temperatures because then only long wave-length vibrations contribute to the bulk thermodynamic properties – i.e., those with **q** vectors near to the centre of the zone. We therefore refine the integration mesh progressively as the zone-centre is approached, using an iterative method. The first correction is obtained by recalculating the integral over an inner region of half the linear dimensions of the full zone, using a mesh twice as fine. The second correction is obtained by similarly recalculating the integral over an inner region of the first inner region; and so on until convergence is reached.

Symmetry reduces the number of independent **q** points in each iteration to 728 (the centre point is omitted because of singularities in the strain derivatives of acoustic frequencies); each iteration then takes about 3000 s of cpu time on a single processor Gould NP1, and five or six iterations are sufficient for convergence. Precision in thermal expansion coefficients is estimated to be a few per cent or better at all temperatures above 1 K.

Extension to more general short-range force-constant models for o-PE should not significantly increase the computational load. Extension to polymer crystals with more atoms per unit cell will increase the size of the dynamical matrix and so increase the time required both to calculate the matrix and (particularly) to diagonalise it. Extension to polymer crystals with long-range Coulomb forces will require Ewald summation, again increasing computational load.

The FORTRAN programmes used were developed from earlier programmes used at Bristol for other crystals. Equivalent programmes for deriving and diagonalising the dynamical matrix are widely available (e.g. CASCADE in the "CCP5 program

library," Daresbury Laboratory). The algorithms for deriving Grüneisen parameters and thermal expansion coefficients are outlined by Barron and Pasternak [17].

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