Commensurate and incommensurate conformations in a simple model of crystalline helical polymers

O. Heinonen
Department of Physics, University of Central Florida, Orlando, FL 32816, USA

and P. L. Taylor
Department of Physics, Case Western Reserve University, Cleveland, OH 44106, USA

(Received 27 July 1989; revised 25 July 1990; accepted 5 September 1990)

We investigate a simple model of crystalline helical polymers which includes interchain interactions and the effects of non-zero temperatures. The object is to determine the conditions under which incommensurate phases are possible at high temperatures. We find a fundamental difference between lattices of two-fold symmetry and those of the higher symmetry typified by a hexagonal lattice. For helices of a preferred handedness, only two-fold symmetry prevents the formation of incommensurate structures. In higher symmetries incommensurate helices are almost always formed at sufficiently high temperatures.

(Keywords: conformation; modelling; helical polymer)

INTRODUCTION

In this paper we study the effect of interchain interactions on the crystal structure of helical polymers at non-zero temperatures. The question that we attempt to answer concerns the relative effectiveness of intrachain and interchain interactions in determining the way in which a helical chain molecule responds to the symmetry of its crystalline environment.

The central concept in this study is the commensurability of the chain in its crystal lattice. The helix is said to be commensurate if the orientation of the nth monomer in the chain is identical with that of the $(n+m)$th monomer, with m a comparatively small integer in the context of the number of monomers contained in the length of a single chain spanning the lamellar width. This is illustrated schematically in *Figure 1*, in which the orientation of a monomer is represented by the stick and ball projecting from the chain axis. The existence of a crystal lattice defines a set of energetically preferred directions. In *Figure 1a* these interactions are dominant and the energy of the system is minimized in a commensurate structure. The necessity for the chain to form such a structure has been referred to[1] as the 'equivalence principle'.

In the absence of interchain interactions, however, there is in general no reason why a helical chain should be commensurate. The angle α between two orientations θ_n and θ_{n+1} of successive monomers in a direction normal to the chain axis will be determined by a complicated sum of various interatomic forces. There is no necessity for α to be a simple rational fraction of 2π unless the molecule itself has some particular symmetry. Examination of the intramolecular forces in isotactic polypropylene, for example, shows that a minimum in conformational energy is found[2] at an angle α which is a few degrees larger than the value $2\pi/3$ characteristic of a 3_1 helix. An isolated chain of isotactic polypropylene thus forms an incommensurate helix of the type shown in *Figure 1b*.

When the interchain potential is added to the Hamiltonian of an array of independent incommensurate helices at zero temperature there is a natural tendency for the pitch of the helix to change to a commensurate value. The cost in energy to change α by an amount $\Delta\alpha$ will be of the order $(\Delta\alpha)^2$, and for a very long chain it will require only a small $\Delta\alpha$ to reach some commensurate structure, with a corresponding non-vanishing lowering of the interchain energy. In terms of our practical definition of commensurability, in which to be observable the period of the commensurate structure must be much less than the lamellar thickness and hence have $m \leqslant 10$, it is still probable that a lowering of the energy can be achieved.

While these considerations based on energy alone are persuasive that commensurate helices are the most stable

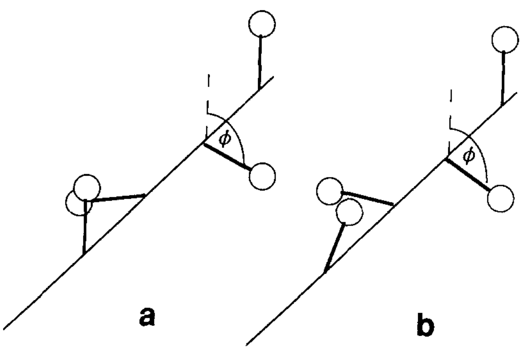

Figure 1 In the commensurate helix (a) the orientation of every third monomer is identical, while in the incommensurate structure (b), each orientation is unique

0032-3861/91/122155-06

structures at low temperatures[3], they do not necessarily indicate that such structures will always be experimentally observed. At elevated temperatures, the entropic contribution to the free energy may dominate, and in consequence the resulting helical structure may have a large degree of disorder. The time constant for transition from an incommensurate high-temperature phase may also be very long, rendering the commensurate phase inaccessible. It is consequently of interest to examine the first onset of cooperative behaviour as a helical crystalline polymer is cooled.

Because no non-trivial statistical mechanics problem in three dimensions has yet been exactly solved, it is difficult to make precise statements regarding phase transitions in assemblies of helical polymers. We can, however, solve many one-dimensional problems with arbitrarily high precision. The approach we take in this paper is to examine the tendency to ordering exhibited by an isolated helical chain. That is to say, we study the effect, on a chain whose natural structure is incommensurate, of a crystalline environment whose natural tendency is to produce a commensurate helix. The response of the chain is calculated in terms of a susceptibility to ordering induced by a helically varying effective field. We then examine under what conditions this ordering transition on cooling gives rise to a commensurate helix. This approach is limited in its application to the onset of helical order in an essentially disordered system. The system may, in addition to this initial ordering, exhibit transitions between different ordered phases as the temperature is reduced further. Although we cannot in general make quantitative predictions about the existence or nature of such transitions, there are certain cases in which we may predict general features of the phase diagram.

The statistical mechanics formalism necessary to treat polymeric chains at non-zero temperatures is rather complex, and imposes some limitations on models that can be conveniently studied. Many helical polymers are synthesized from monomers of sufficient symmetry that both left-handed and right-handed helices are possible, with defects likely at which the handedness of the chain is reversed. The construction of useful models of such systems requires the incorporation not only of nearest neighbour intrachain potentials but also of next-nearest neighbour interactions. This greatly complicates the computational task of evaluating the thermodynamic properties. In order to avoid this difficulty we consider a model with a specific preferred handedness, which can consequently be chosen to contain forces only between nearest neighbouring monomers. This model is then most directly a description of molecules like the poly(α-amino acids), in which a preferred handedness exists. We do, however, expect the conclusions to apply qualitatively also to such molecules as poly(tetrafluoroethylene) (PTFE), in which there is no preferred handedness. Preliminary calculations using a formalism which includes next-nearest neighbour interactions support this conjecture.

The approach we take begins with a simple model for the intrachain potential in a helical molecule having a preferred direction of handedness. We then use a transfer integral formalism to evaluate the temperature-dependent response of such a chain to the mean-field potential due to neighbouring chains. We identify the wavenumber at which a divergence occurs in the response of the molecule to the interchain potentials of neighbouring chains as the wavenumber characterizing the highest temperature cooperatively ordered crystal structure.

We stress that although our working definition of a commensurate structure in a helical polymer may seem imprecise, the few cases where careful measurements have been made conform to the idea that a distinction can be made. Measurements of electron diffraction in PTFE at temperatures below 19°C, for example, have been interpreted[4] as incompatible with a 15_7 helix, which would be commensurate within our terminology, and describable either as incommensurate or a 948_{439} helix, which are equivalent descriptions within our definition. Examples in materials other than polymers include magnetic systems such as CeSb[5,6] and systems with structural transitions[7–11], such as tetrathiofulvalene tetracyanoquinodimethane, K_2SeO_4 and $BaMnF_4$. In these latter materials it has also been shown that the complex phase diagrams can be understood in terms of very simple mean-field models[12–14]. Thus, we believe that the effects addressed in the present paper are observable and can be investigated in terms of the simple models described here.

THE MODEL

We represent an isolated chain by a set of directed monomers pointing in the xy-plane and equidistantly spaced along the z-axis, which we take to be the direction of the chain axis. For example, in the case of PTFE these can be thought of as pointing in the direction of the bisectors of the fluorine–carbon bonds on each monomer. The angle that the ith directed monomer on the jth chain makes with a fixed direction (taken to be the x-axis) is denoted θ_{ij} and is located at position $\mathbf{r}_{ij}$. For brevity, we will sometimes use the notation of a classical XY-spin system, in which $S_x(\mathbf{r}_{ij}) = \cos\theta_{ij}$ and $S_y(\mathbf{r}_{ij}) = \sin\theta_{ij}$.

The part of the Hamiltonian that represents the intrachain interactions of the single chain is then taken as:

$$H_0 = -J_{\parallel} \sum_{i,j} \cos(\theta_{i,j} - \theta_{i-1,j} - \alpha) \qquad J_{\parallel} > 0 \qquad (1)$$

The ground state of the Hamiltonian H_0 is then a (right-handed) helix with pitch α. For the case of PTFE, for example, we take $\alpha \approx 164°$.

We now turn to the interchain interactions. The formalism which we will use is one in which the interchain interactions are treated in the mean-field approximation, but the intrachain interactions (and hence the intrachain correlations) are treated more precisely. The justification for this lies in the strength of the intrachain covalent forces in comparison with the weaker van der Waals interchain interactions. We write the interchain potential energy in such a way as to display the two most important components, H_1 and H_2. The first of these represents the interaction of a monomer with the average of its crystalline environment. This term has the symmetry of the lattice, and can be treated as an external field in an effective single-chain Hamiltonian. The second component includes the effect of the detailed orientations of surrounding monomers, and is thus the term responsible for interchain correlations.

We identify these two components by first writing the potential energy V_T as a sum of pair potentials within a

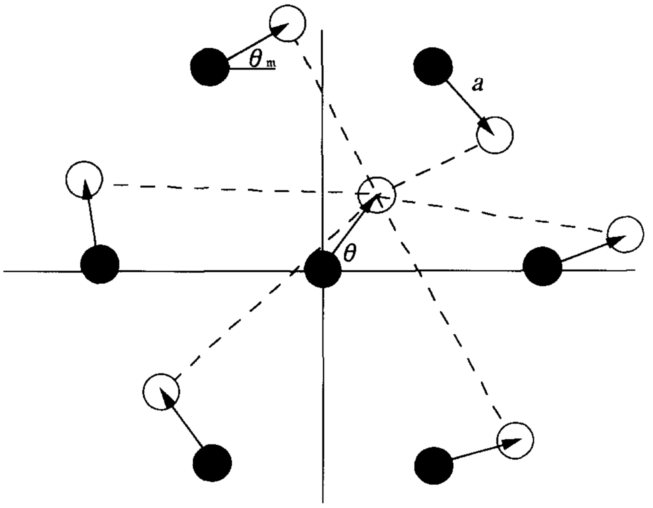

Figure 2 The directed monomer on the centre chain at an angle θ from the x-axis and a distance a from the chain axis interacts with the n monomers on adjacent chains. The lattice spacing is l, and the crystal has hexagonal symmetry in the xy-plane

plane perpendicular to the chain axis, so that:

$$V_{\mathrm{T}} = \sum_{m=1}^{n} V(r_m) \tag{2}$$

In the geometry illustrated in *Figure 2*, an atom is displaced a distance a at an angle θ from a lattice site, and its n nearest neighbours are similarly displaced at angles θ_m. The interatomic distances are given by the expression:

$$r_m^2 = l^2 + 2a^2 - 2a^2\cos(\theta - \theta_m) + 2al[\cos(\theta_m - 2m\pi/n) - \cos(\theta - 2m\pi/n)] \tag{3}$$

An expansion of V_{T} in powers of a yields a term proportional to $\cos(\theta - \theta_m)$ in first order, and this we identify as H_2. Averaging over θ_m and summing over m removes the θ-dependence of V_{T} in all terms up to the term of nth order, where we find a term proportional to $\cos n\theta$. This is the term H_1, which has the symmetry of the lattice. We now write the potential energy as $V_{\mathrm{T}} = H_1 + H_2$, with

$$H_1 = \gamma \sum_{ij} \cos(n\theta_{ij}) \tag{4}$$

and

$$H_2 = -J_\perp \sum_{\substack{i \\ <jj'>}} \cos(\theta_{ij} - \theta_{ij'}) \tag{5}$$

Here $\langle jj' \rangle$ means that the summation extends over nearest-neighbour chains j and j'.

Finally, we also allow for the application of an external field $\mathbf{F}(\mathbf{r}_{ij})$ which couples linearly to the monomers. This field need not be a physically realizable field, but is a mathematical device for calculating correlation functions. The total Hamiltonian is thus:

$$H = -J_\parallel \sum_{ij} \cos(\theta_{i,j} - \theta_{i-1,j} - \alpha) - J_\perp \sum_{\substack{i \\ <jj'>}} [\cos\theta_{ij}\cos\theta_{ij'} + \sin\theta_{ij}\sin\theta_{ij'}] + \gamma \sum_{ij} \cos(n\theta_{ij}) - \sum_{ij} \mathbf{F}(\mathbf{r}_{ij}) \cdot \mathbf{S}(\mathbf{r}_{ij}) \tag{6}$$

In the absence of external fields, this Hamiltonian then contains three energy scales, the interchain coupling $J_\perp$, the intrachain coupling $J_\parallel$ and the crystal field coupling γ. We will assume that $\gamma \gg J_\parallel \gg J_\perp$. This is not unreasonable for the case of polymers in which the crystal field arises from steric hindrance, for which the energy barrier becomes extremely high. On the other hand, the intrachain coupling represents the energy of torsional rotations around the bonds of the chain backbone. The scale of this energy can be much lower than that of steric hindrance, and is typically of the order of a few kilojoules per mole. The interchain coupling H_2, finally, can arise from weaker, long-range interactions such as van der Waals interactions or dipole interactions. This separation of the energy scales validates the use of the mean-field approximation in this paper.

FORMALISM

We will calculate the intrachain angular correlation functions of the Hamiltonian (6) and argue that, as the temperature is lowered, these correlation functions will diverge for particular helical conformations of the chains. This then means that at these lower temperatures the chains have the conformation of these helices.

The correlation function $\langle S_\mu(\mathbf{r}_{ij}) S_\nu(\mathbf{r}_{i'j'}) \rangle$ ($\mu, \nu = x, y$) is related to the susceptibility $\chi^{\mu\nu}(\mathbf{r}_{ij}, \mathbf{r}_{i'j'})$ by:

$$\chi^{\mu\nu}(\mathbf{r}_{ij}, \mathbf{r}_{i'j'}) = \beta\langle S_\mu(\mathbf{r}_{ij}) S_\nu(\mathbf{r}_{i'j'}) \rangle - \beta\langle S_\mu(\mathbf{r}_{ij}) \rangle \langle S_\nu(\mathbf{r}_{i'j'}) \rangle \tag{7}$$

where angular brackets denote a thermal average. The susceptibility can, by the fluctuation–dissipation theorem, be related to the linear response of $\langle S_\mu(\mathbf{r}_{ij}) \rangle$ to an applied field $\mathbf{F}(\mathbf{r}_{ij})$. Under the assumption that the interchain coupling $J_\perp$ is much smaller than the intrachain coupling $J_\parallel$, we can treat the chains as pseudo-one dimensional and calculate the susceptibility $\chi^{\mu\nu}(\mathbf{q})$ in a scheme where the interchain couplings are treated in the mean-field approximation[15]. In this approximation, the Hamiltonian is then written:

$$H = -J_\parallel \sum_{ij} \cos(\theta_{i,j} - \theta_{i-1,j} - \alpha) - J_\perp \sum_{\substack{i \\ \langle jj' \rangle}} [\cos\theta_{ij}\langle\cos\theta_{ij'}\rangle + \sin\theta_{ij}\langle\sin\theta_{ij'}\rangle] + \gamma \sum_{ij} \cos(n\theta_{ij}) - \sum_{ij} \mathbf{F}(\mathbf{r}_{ij}) \cdot \mathbf{S}(\mathbf{r}_{ij}) \tag{8}$$

Upon introducing the Fourier transform of the mean fields:

$$S_x(\mathbf{q}) = \frac{1}{N} \sum_{ij'} \langle\cos\theta_{ij'}\rangle\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}_{ij'}} \tag{9}$$

$$S_y(\mathbf{q}) = \frac{1}{N} \sum_{ij'} \langle\sin\theta_{ij'}\rangle\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}_{ij'}} \tag{10}$$

and of the applied field:

$$\mathbf{F}(\mathbf{q}) = \frac{1}{N} \sum_{ij} \mathbf{F}(\mathbf{r}_{ij})\, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} \tag{11}$$

where N is the number of monomers, the mean-field Hamiltonian becomes:

$$H = -J_\parallel \sum_{ij} \cos(\theta_{ij} - \theta_{i-1,j} - \alpha) + \gamma \sum_{ij} \cos(n\theta_{ij}) - \sum_{\mathbf{q},ij} J_\perp(q_\perp)\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \mathbf{S}(\mathbf{r}_{ij}) \cdot \mathbf{S}(\mathbf{q}) - \sum_{\mathbf{q},ij} \mathbf{F}(\mathbf{q}) \cdot \mathbf{S}(\mathbf{r}_{ij})\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \tag{12}$$

with

$$J_\perp(q_\perp) = J_\perp(q_x, q_y) = J_\perp \sum_{j'} \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{r}_{ij'} - \mathbf{r}_{ij})} \tag{13}$$

with j' nearest neighbours to j. This shows that $\mathbf{S}(\mathbf{r}_{ij})$ is subjected to an effective external field $\mathbf{h}(\mathbf{r}_{ij})$ given by:

$$\mathbf{h}(\mathbf{r}_{ij}) = \sum_{\mathbf{q}} \mathbf{h}(\mathbf{q})\,\mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}_{ij}} = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_{ij}}[\mathbf{F}(\mathbf{q}) - J_\perp(q_\perp)\mathbf{S}(\mathbf{q})] \tag{14}$$

For a single chain, $S_x(q_z)$ and $S_y(q_z)$ are related to the external field by the single-chain susceptibility $\chi_0^{\mu\nu}(q_z)$, so that

$$S_\mu(q_z) = \sum_\nu \chi_0^{\mu\nu}(q_z) h_\nu(q_z) \tag{15}$$

Thus, by combining equations (14) and (15) we obtain for the array of chains:

$$\sum_\nu S_\nu(\mathbf{q})[\delta_{\mu\nu} - J_\perp(q_\perp)\chi_0^{\mu\nu}(q_z)] = \sum_\nu F_\nu(\mathbf{q})\chi_0^{\mu\nu}(q_z) \tag{16}$$

The susceptibilities $\chi^{\mu\nu}(\mathbf{q})$ are then related to those of a single chain, $\chi_0^{\mu\nu}(q_z)$, by:

$$\chi^{\mu\nu}(\mathbf{q}) = \sum_{\mu'} \{[1 - J_\perp(q_\perp)\chi_0(q_z)]^{-1}\}_{\mu\mu'}\chi_0^{\mu'\nu}(q_z) \tag{17}$$

At certain temperatures and wave vectors, we will find that the matrix $[1 - J_\perp(q_\perp)\chi_0(q_z)]$ becomes non-invertible, which we will interpret as a spontaneous ordering of the chains into the structures given by these wave vectors. This leads to the determinant equation:

$$\begin{vmatrix} J_\perp(q_\perp)\chi_0^{xx}(q_z) - 1 & J_\perp(q_\perp)\chi_0^{xy}(q_z) \\ J_\perp(q_\perp)\chi_0^{yx}(q_z) & J_\perp(q_\perp)\chi_0^{yy}(q_z) - 1 \end{vmatrix} = 0 \tag{18}$$

The largest temperature at which solutions to this equation exist is then the physically relevant transition temperature.

We are then left with the task of calculating the single-chain susceptibility. This is most easily done in a transfer-integral formalism[16]. The transfer-integral equation for a single chain is:

$$\int_{-\pi}^{\pi} \mathrm{d}\theta_i\, e^{\beta J_\parallel \cos(\theta_i - \theta_{i-1} - \alpha) - \beta\gamma\cos(n\theta_{i-1})}\Psi_k(\theta_i) = \lambda_k \Psi_k(\theta_{i-1}) \tag{19}$$

Here $\Psi_k(\theta)$ and λ_k are the right eigenfunctions and the corresponding eigenvalues of the transfer-integral operator. It is easy to show that the left eigenfunctions $\Phi_k(\theta)$ are related to $\Psi_k(\theta)$ by:

$$\Phi_k(\theta) = \Psi_k(-\theta)\,\mathrm{e}^{\beta\gamma\cos(n\theta)} \tag{20}$$

With the shorthand notation $S_\mu(l) = S_\mu(\theta_l)$ and with the appropriate normalization of the eigenfunctions Φ_k and Ψ_k the correlation function can be expressed in terms of these eigenfunctions as:

$$\langle S_\mu(l)S_\nu(l')\rangle = \sum_k \langle\Phi_0|S_\mu(l)|\Psi_k\rangle\langle\Phi_k|S_\nu(l')|\Psi_0\rangle(\lambda_k/\lambda_0)^{|l-l'|} \tag{21}$$

where

$$\langle\Phi_k|f|\Psi_{k'}\rangle = \int_{-\pi}^{\pi} \mathrm{d}\theta\,\Phi_k(\theta)\Psi_{k'}(\theta)f(\theta) \tag{22}$$

and λ_0 is the eigenvalue of largest magnitude.

The n-fold symmetry of the crystal-field term causes the solutions of equation (19) to be in the form of Bloch functions, namely:

$$\Psi_k(\theta) = \exp(ip\theta)u_k(\theta) \tag{23}$$

with p an integer and $u_k(\theta)$ a periodic function of period $2\pi/n$. The eigenvalues λ_k, which are in general complex, then occur in bands, and can be written as $\lambda_{m,p}$ with m a non-negative integer representing the band index and p an integer with $-n/2 < p \leq n/2$. The matrix elements appearing in equation (21) are then of the form:

$$\int_{-\pi}^{\pi} \mathrm{d}\theta\,\Phi_{m,p}(\theta)\Psi_{m',p'}(\theta)f(\theta) \tag{24}$$

with $f(\theta) = \cos\theta$ or $\sin\theta$, and these will vanish unless $p' = p \pm 1$. Equation (21) then reduces to:

$$\langle S_\mu(l)S_\nu(l')\rangle = \sum_m \langle\Phi_{0,0}|S_\mu(l)|\Psi_{m,\pm 1}\rangle\langle\Phi_{m,\pm 1}|S_\nu(l')|\Psi_{0,0}\rangle \times [\lambda_{m,\pm 1}/\lambda_{0,0}]^{|l-l'|} \tag{25}$$

Provided the temperature is not so high that $k_\mathrm{B}T$ is comparable to $J_\parallel$ it will be true that only the closest excited states coupled by $S_\mu(l)$ to the ground state $\Psi_{0,0}$ need be included in the sum. In the region of parameters considered here, where $\gamma \gg J_\parallel$, each band m with its n eigenvalues $\lambda_{m,p}$ will be separated from the other bands by a gap of order $\mathrm{e}^{\beta\gamma}/(2\beta\gamma n^2)^{1/2}$. In this region, we then need to retain only the term with $m = 0$ in equation (25). With this simplification we have:

$$\chi_0^{xx}(l, l') = \chi_0^{yy}(l, l') = \frac{\beta}{4}\left[\left(\frac{\lambda_{0,1}}{\lambda_{0,0}}\right)^{|l-l'|} + \left(\frac{\lambda_{0,-1}}{\lambda_{0,0}}\right)^{|l-l'|}\right] \tag{26}$$

$$\chi_0^{xy}(l, l') = -\chi_0^{yx}(l, l') = \frac{\beta}{4i}\left[\left(\frac{\lambda_{0,1}}{\lambda_{0,0}}\right)^{|l-l'|} - \left(\frac{\lambda_{0,-1}}{\lambda_{0,0}}\right)^{|l-l'|}\right] \tag{27}$$

Putting

$$\Gamma \equiv \lambda_{0,1}/\lambda_{0,0} \tag{28}$$

we find

$$\chi_0^{xx}(q_z) = \frac{\beta}{2}\mathscr{R}\left[\frac{1 - \Gamma^2}{1 + \Gamma^2 - 2\Gamma\cos q_z a}\right] \tag{29}$$

$$\chi_0^{xy}(q_z) = \frac{i\beta}{2}\mathscr{I}\left[\frac{2\Gamma\sin q_z a}{1 + \Gamma^2 - 2\Gamma\cos q_z a}\right] \tag{30}$$

where $\mathscr{R}$ and $\mathscr{I}$ indicate real and imaginary parts, respectively, and Γ is assumed to be complex. Substitution in equation (18) yields the result that the susceptibility diverges when:

$$\mathscr{R}\left(\frac{1 - \Gamma^2}{1 + \Gamma^2 - 2\Gamma\cos q_z a}\right) \pm \mathscr{I}\left(\frac{2\Gamma\sin q_z a}{1 + \Gamma^2 - 2\Gamma\cos q_z a}\right) = \frac{2}{\beta J_\perp(q_\perp)} \tag{31}$$

This expression is the central result of the analysis.

APPLICATION TO HELICAL POLYMERS

In order to determine whether an assembly of helical chains will order into a commensurate or incommensurate structure we look for the wavenumber at which equation (31) first has a solution as the temperature is lowered. This is equivalent to seeking the value of q_z at which the left-hand side of equation (31) has a maximum value of $2/\beta J_\perp(q_\perp)$. In those cases where Γ is real, it is clear by inspection that the second term on the left-hand side of equation (31) vanishes, and that the maximum can only occur when $q_z a = 0$ or $q_z a = \pi$. The existence of incommensurate phases thus requires that Γ be complex.

The simplest case to be studied is that in which the chain is in an environment having only two-fold symmetry. In an orthorhombic crystal, for example, we must put $n = 2$ in the Hamiltonian (8). There are then only two eigenvalues in the principal band of solutions to equation (19), and Γ will be real. When α is closer to π than to 0, as is the case in PTFE, the eigenvalue $\lambda_{0,1}$ will be negative. This causes Γ to be negative, and the maximum of χ_0^{xx} to occur at $q_z = \pi/a$.

If, on the other hand, the chain is in an environment of higher symmetry, then the situation is considerably more complicated. In an interchain field of six-fold symmetry, as is characteristic of the low-pressure phases of PTFE, we put $n = 6$ in equation (8). The eigenvalues $\lambda_{0,1}$ and $\lambda_{0,-1}$ of equation (19) are then complex and distinct. We simplify the expression for the susceptibility by writing:

$$\Gamma = |\Gamma|\, e^{i\phi} \tag{32}$$

and find equation (31) to reduce to:

$$\frac{1 - |\Gamma|^2}{1 + |\Gamma|^2 - 2|\Gamma| \cos(q_z a - \phi)} = \frac{2}{\beta J_\perp(q_\perp)} \tag{33}$$

As the temperature is lowered, this equation will first be satisfied at the wavenumber at which $q_z a = \phi$. The question of commensurability of the highest-temperature cooperative phase is thus decided by the phase ϕ of the eigenvalue $\lambda_{0,1}$. From the structure of equation (19) we can determine that when $\alpha = 2\pi m/n$, with m an integer, then the phase of the eigenvalue will be such that $\phi = \alpha$; that is, we have the not unexpected result that a commensurate phase is formed whose pitch is equal to the pitch of an isolated helix. For values of α differing from $2\pi m/n$, however, there is no reason to have ϕ equal to α, and numerical studies show the type of behaviour illustrated schematically in *Figure 3*. The general result, then, is that an incommensurate phase will first be formed on cooling for almost all values of α.

This is analogous to the behaviour of the anisotropic next-nearest neighbour Ising (ANNNI) model, which has been used successfully[12] to explain the phase diagrams of magnetic materials such as CeSb. This model has spin chains with competing nearest neighbour and next-nearest neighbour interactions along the chain axis and with a ferromagnetic coupling in the plane perpendicular to the chain axis. The transfer-integral equation for the individual chains can be solved exactly[17] with the result that the largest eigenvalue λ_0 is real and the two eigenvalues closest to λ_0 are in general complex conjugates with arguments that vary continuously with temperature. The single-chain correlation function thus oscillates in space with a period which varies continuously with temperature. When the interactions in the plane perpendicular to the chain axes are included, it is found even in the simplest mean-field approximation[12] that the system undergoes a series of phase transitions as the temperature is lowered. The high temperature phase is disordered, and upon lowering the temperature, the system undergoes a transition to an initial ordered incommensurate phase. However, as the temperature is reduced further, the intrachain correlations do not change continuously with temperature, in contrast to the case for the single chain. The effect of the interchain interactions is to make commensurate phases energetically favourable, and the system undergoes first a transition to an incommensurate phase and then a series of transitions between different commensurate phases as the temperature is reduced. The smooth variation with temperature of the single-chain magnetic structure is thus replaced by a step-like variation, which has been given the name 'Devil's staircase'.

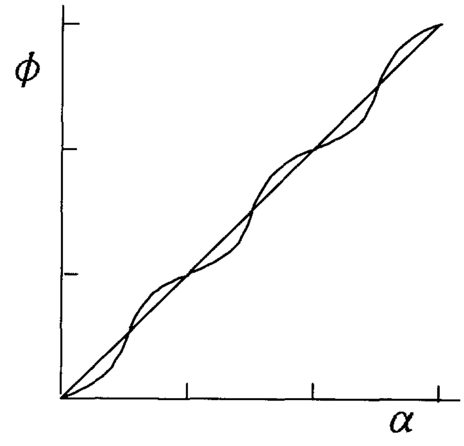

Figure 3 The value of the phase ϕ is periodic with period $2\pi/n$. Only at values $\alpha = \pi m/n$ are ϕ and α equal

On the basis of this analogy, we can then speculate that chiral helical polymers and liquid crystals may exhibit similar phase diagrams with an initial incommensurate ordered phase followed by several commensurate phases. This opens up the possibility of interesting applications. Chiral helical molecules have been shown to be optically active as a consequence of their helical asymmetry, with optical properties depending on the helical pitch[18]. These properties may thus be changed with temperature if the conformation of the helices undergoes a series of transitions. Furthermore, it may be possible in some cases to change the effective symmetry of the environment of a single chain to a two-fold symmetry by the application of a uniaxial stress or external fields. In this case, the molecules may undergo a transition to planar conformations over a range of temperatures, which implies a drastic change in the optical properties of the system.

Finally, we remark that the model we have studied has involved a helical chain in an environment of a given symmetry. In the example of PTFE, we discussed two-fold and six-fold symmetries corresponding to orthorhombic and hexagonal packing. Because a hexagonal lattice subject to uniaxial stress becomes orthorhombic, we need to ask how the transition from six-fold to two-fold symmetry will affect the pitch of the helices.

The answer to this question lies in the applicability of the single-band approximation made in moving from equation (25) to equation (26). As a hexagonal lattice is uniaxially distorted towards an orthorhombic structure, the phase ϕ of the complex eigenvalue $\lambda_{0,1}$ is reduced, until at some finite distortion $\lambda_{0,1}$ becomes real. At this point the two real eigenvalues $\lambda_{0,0}$ and $\lambda_{0,1}$ can be thought of as forming the two-component band of the orthorhombic structure. A gradual increase in the uniaxial strain thus causes a continuous change of pitch of the helix. However, a gradual increase in uniaxial stress will not necessarily cause continuous change, since the stability of the distorted hexagonal system is dependent on the free energy being a minimum in that state. A complete argument for a particular symmetry to be preferred must include such considerations. In the present paper we have merely shown the connection between higher symmetry in the interchain potential and possible incommensurate phases at elevated temperatures.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation and by the Petroleum Research Fund of the American Chemical Society. The authors are grateful to Dr A. Lovinger for a very helpful suggestion.

REFERENCES

1 Natta, G. and Corradini, P. *J. Polym. Sci.* 1959, **39**, 29
2 Wright, N. F. and Taylor, P. L. *Polymer* 1987, **28**, 2005
3 Saruyama, Y. *J. Chem. Phys.* 1983, **78**, 2077
4 Clark, E. S., Weeks, J. J. and Eby, R. K. *Am. Chem. Soc. Symp. Ser.* 1980, **141**, 183
5 Fisher, P., Lebesh, B., Meier, G., Rainford, B. D. and Voigt, O. *J. Phys. C* 1978, **11**, 345
6 Roussat-Mignod, J., Burbet, P., Villain, J., Bartholin, H., Wang, T. S., Florence, D. and Voigt, O. *Phys. Rev. B* 1977, **16**, 440
7 Denoyer, F., Comes, R., Garito, A. F. and Heeger, A. J. *Phys. Rev. Lett.* 1975, **35**, 445
8 Kagoshima, S., Anzai, H., Kajimura, K. and Tshiguo, T. *J. Phys. Soc. Jpn.* 1975, **39**, 1143
9 Comes, R., Shapiro, S. M., Shirane, G., Garito, A. F. and Heeger, A. J. *Phys. Rev. Lett.* 1975, **35**, 1518
10 Izumi, M., Axe, J. D., Shirane, G. and Shimaoda, K. *Phys. Rev. B* 1977, **15**, 4392
11 Shapiro, S. H., Cowley, R. A., Cox, D. E. and Eibschults, M. Oak Ridge Laboratory Report CONF-760601-P1, 1976, p. 399
12 Bak, P. and von Boehm, J. *Phys. Rev. B* 1980, **21**, 5297
13 Bak, P. and Emery, V. J. *Phys. Rev. Lett.* 1976, **36**, 978
14 Cowley, R. A. and Bruce, A. D. *J. Phys. C* 1978, **11**, 3577
15 Scalapino, D. J., Imry, Y. and Pincus, P. *Phys. Rev. B* 1975, **11**, 2042
16 Scalapino, J., Sears, M. and Ferrell, R. A. *Phys. Rev. B* 1972, **6**, 3409
17 Stephenson, J. *Can. J. Phys.* 1970, **48**, 1725
18 Vogl, O. and Jaycox, G. G. *Polymer* 1987, **28**, 2179