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## The role of conformational defects in solid-solid phase transitions

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**Résumé.** — Le rôle du désordre de conformation dans les transitions de phase solide-solide de couches de chaînes linéaires de molécules (*n*-alcane) est étudié à l'aide d'un modèle hamiltonien. Nous définissons un nouveau type de coordonnées de chaîne approprié aux régimes à faible taux de désordre conformationnel. En effectuant une sommation exacte sur ces coordonnées, nous obtenons un hamiltonien effectif décrivant l'interaction interchaîne dans la couche. En supposant, d'une manière phénoménologique, l'existence de deux structures cristallographiques (orthorhombique ou monoclinique-triclinique) à température nulle, nous montrons que seul le cas orthorhombique conduit à une phase rotatoire par un couplage entre degrés de liberté conformationnel et de réseau. Nous étudions les valeurs moyennes des défauts conformationnels dans les différentes phases du système.

**Abstract.** — The role of conformational disorder in solid-solid phase transitions of linear chain molecules (*n*-alkanes) arranged in a layer is studied in terms of a hamiltonian model. We define a new kind of chain coordinates appropriate to regimes with low conformational disorder. By performing an exact summation over such coordinates, we obtain the effective Hamiltonian describing the interchain interaction within the layer. Assuming, on a phenomenological basis, the existence of two zero temperature crystal structures (orthorhombic or monoclinic-triclinic), we show that only for the orthorhombic one, the coupling between conformational and lattice degrees of freedom results in a rotary phase. We study the mean values of the conformational defects in the different phases of the system.

### Introduction.

In recent years many attempts have been made to clarify some intriguing aspects of the solid-solid phase transitions in systems of linear chain molecules [1].

At very low temperature such systems have an high degree of order ; the single molecule is a sequence (chain) of identical chemical groups linked together without branchings and keeping a *trans*-planar conformation [2] ; the chains are arranged in a « perfect » lattice [3].

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At intermediate temperatures one or more distinct solid phases are observed which drive the system towards liquid state through a progressive loss of order [4]. In many cases there is experimental evidence of an interplay between intramolecular disordering processes and structural transitions [4-8].

The aim of our work is to give a detailed representation of the system in order to reach a description of intramolecular quantities, such as the mean number of conformational « defects » [2], in the various phases.

From this point of view, the most economical way is to consider a system with a simple molecular structure, so that one can obtain a model in terms of a reasonably small number of degrees of freedom. Moreover, one needs to support his modelling with experimental data from well studied systems ; this is indeed the case with some molecules of the so-called polymethylene chain class, in particular *n*-alkanes (linear hydrocarbons) [5-12].

In these systems, the linear flexible part of the molecule plays the main role in determining the equilibrium architecture of the solid phases.

With *n*-alkanes one finds, at low temperature, two possible structures (« *lamellae* ») depending on the parity of the molecule (the number of groups in the chain) : odd *n*-alkanes crystallize in the orthorhombic system [13], even *n*-alkanes are monoclinic or triclinic. At intermediate temperatures the observed transitional pattern depends on both chain length and parity [4] ; in fact all the odd *n*-alkanes, up to 41 length at normal conditions [9], show a special solid phase, just before melting, known as «  $\alpha$  » or « rotational » phase. So far it has been proved, mainly by IR and Raman Spectroscopy [5-8], that in the  $\alpha$  phase the conformational order decreases with increasing temperature, reaching the collapse at the melting point.

The interpretation of the phenomenological landscape and its comprehensive description within a coherent scheme has been the object of research for years. Efforts have been made to explain the origin of the  $\alpha$  phase in terms of two main mechanisms. On one hand (intermolecular disorder), the overall rigid roto-translations of the molecules were invoked as the dominant mechanism in driving the system to the  $\alpha$  phase [10]. On the other hand (intramolecular disorder), conformational defects localized in the flexible chains [11-13] were considered the origin of the  $\alpha$  phase.

In our previous work we examined the synergism of the above mechanisms [14, 15]. In paper [14] we introduced a Hamiltonian model where the conformational disorder was coupled with lattice elasticity.

In letter (15), we extended the model including the orientational disorder (rigid rotations of the chains around their longitudinal axes). We studied the existence of a solid-solid phase transition marked by the rotational order parameter. We showed that such transition may occur when the structure, at low temperature, is orthorhombic, while it does not occur with monoclinic-triclinic systems.

In this paper we report in detail some analytical aspects of the model and extend its applications.

We first define a set of spin variables suitable to describe the single chain conformational degrees of freedom : the choice of such variables amounts to explicitly solving the constraints arising from the fact that the chains are extended objects.

We then perform an exact summation over such spin variables, as well as over the elastic interchain couplings, obtaining an effective Hamiltonian in the orientational degrees of freedom. Such a Hamiltonian corresponds to a decorated Ising model with bilinear and trilinear terms involving nearest as well as next-nearest neighbours. The temperature dependent coupling constants are explicitly obtained in terms of single chain and lattice parameters.

The mean values of the conformational and orientational defects are then determined by a mean field treatment.

In our model the translations of the chains in the direction orthogonal to the « lamella » [5, 16] are not explicitly included : we will show that these degrees of freedom have no effect on the solid-solid transition, but only on the distribution of disorder over the different conformational defects.

In section 1 we define the set of independent « internal » spin variables for the conformational degrees of freedom of the single chain, consistently with a « low disorder » hypothesis.

In section 2 we consider the system of chains organized in the two-dimensional lattice. We give the Hamiltonian in terms of all the (internal and external) variables and obtain the effective interaction in the rotational degrees of freedom.

In section 3 we apply the mean field treatment in order to calculate the mean values of the interesting observables.

In section 4 we draw the conclusions and point out some open problems.

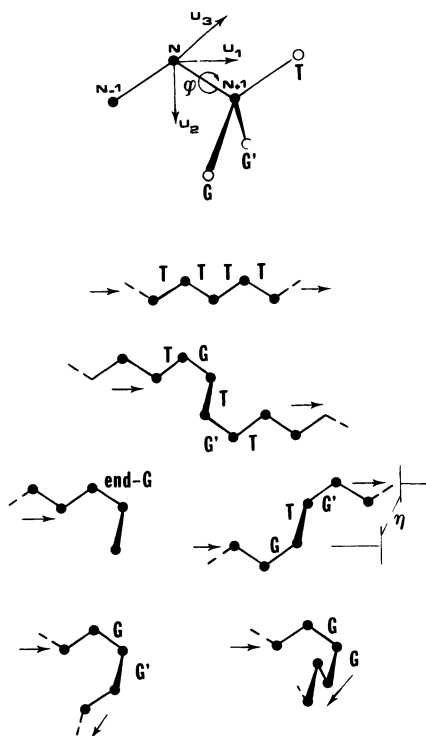


Fig. 1. — The backbone of  $n$ -alkanes. The site of the  $N + 2$ -th carbon is determined by the bond vectors  $v_{N-1} \equiv C_N - C_{N-1}$  and  $v_N \equiv C_{N+1} - C_N$  and by the variable  $s_N$  representing the Flory angle  $\varphi$ . With  $s_N = 0$  one has the *trans* (T) conformation ( $\varphi = \pi$ ), with  $s_N = +1$  one has *Gauche* (G) and *Gauche'* (G') conformations ( $\varphi = \pm \frac{2\pi}{3}$ ). The site vectors  $u_{N-1,i}$ ,  $i = 1, 2, 3$  are also reported. The drawings represent sections of chains containing the all-trans sequence ...TTTT..., the « dressed » kink ...TG TG' T..., the kink ...GTG... and the U-like defects ...GG... and ...GG'... The distance  $\eta$  between two parallel sections of the chain is the width of the kink.

### 1. Single chain coordinates.

The space coordinates of the carbon atoms of an alkane chain can be determined, for a given sequence of Flory angles [2], by means of an iteration formula which relates each C-C bond to the two preceding ones.

More precisely, we represent the  $n$ -th C-C bond by a vector  $\mathbf{v}_n$  going from the  $n$ -th carbon atom to the  $(n+1)$ -th carbon, and the Flory angles related to *trans*, *gauche* and *gauche prime* conformations (see Fig. 1) by a spin variable  $s$  with values 0, +1, -1 respectively.

We have then :

$$\mathbf{v}_{n+1} = \left(1 - \frac{3}{2}s^2\right) \mathbf{v}_{n-1} + \frac{1}{2}s^2 \mathbf{v}_n + \frac{\sqrt{3}}{2}s(\mathbf{v}_{n-1} \wedge \mathbf{v}_n). \quad (1)$$

It is convenient to associate with the ordered couple of adjacent C-C bonds  $(\mathbf{v}_{n-1}, \mathbf{v}_n)$  the set of orthogonal vectors

$$\mathbf{u}_{n-1,1} = \frac{1}{2}(\mathbf{v}_{n-1} + \mathbf{v}_n); \quad \mathbf{u}_{n-1,2} = \frac{1}{2}(\mathbf{v}_n - \mathbf{v}_{n-1}); \quad \mathbf{u}_{n-1,3} = \frac{1}{2}(\mathbf{v}_{n-1} \wedge \mathbf{v}_n). \quad (2)$$

Starting with a couple of bonds  $(\mathbf{v}_0, \mathbf{v}_1)$ , each sequence of variables  $s_1, s_2, \dots, s_k$ , through equation (1), determines the displacement  $\mathbf{d}$  from the 0-th carbon to the  $(k+2)$ -th carbon together with a new set of orthogonal vectors  $\mathbf{u}_{k,1}, \mathbf{u}_{k,2}, \mathbf{u}_{k,3}$ . We consistently associate with the sequence  $s_1, s_2, \dots, s_k$  the vector  $\mathbf{d}$  and the application from  $\{\mathbf{u}_{0,i}\}$  to  $\{\mathbf{u}_{k,i}\}$  ( $i = 1, 2, 3$ ).

From now on we will be mainly concerned with defects connecting parallel planar sections of the chains. In our terms this implies the constraint  $\mathbf{u}_{0,3} \parallel \mathbf{u}_{k,3}$ . Furthermore, due to the geometry on which the chain lies, from  $\mathbf{u}_{0,3} \parallel \mathbf{u}_{k,3}$  it follows that  $\mathbf{u}_{0,1} \parallel \mathbf{u}_{k,1}$ : hence  $\mathbf{u}_{0,1}$  identifies the overall longitudinal direction of the chain.

Let us call « allowed sequences » the particular  $\{s_1, s_2, \dots, s_k\}$  satisfying the former constraint ; we have for them :

$$\mathbf{u}_{k,2} = \sigma \mathbf{u}_{0,2}, \quad \mathbf{u}_{k,3} = \varepsilon \mathbf{u}_{0,3}, \quad \sigma, \varepsilon = \pm 1. \quad (3)$$

(note that  $\sigma \varepsilon = -1$  implies chain reversal).

We define the action  $\mathcal{T}(s_1, s_2, \dots, s_k)$  associated with an allowed sequence  $\{s_1, s_2, \dots, s_k\}$  as :

$$\mathcal{T}(s_1, s_2, \dots, s_k) \equiv (\sigma, \varepsilon, d_1, d_2, d_3) \quad (4)$$

where  $d_i$  ( $i = 1, 2, 3$ ) is the component of the vector  $\mathbf{d}$  with respect to  $\mathbf{u}_{0,i}$ . We will in general disregard the longitudinal component  $d_1$ , thus having simply :

$$\mathcal{T}(s_1, s_2, \dots, s_k) \equiv (\sigma, \varepsilon, d_2, d_3).$$

Let us consider two allowed sequences  $\{s_1, s_2, \dots, s_k\}$  and  $\{s'_1, s'_2, \dots, s'_k\}$  characterized by  $\mathcal{T}(s_1, s_2, \dots, s_k) = (\sigma, \varepsilon, d_2, d_3)$  and  $\mathcal{T}(s'_1, s'_2, \dots, s'_k) = (\sigma', \varepsilon', d'_2, d'_3)$ ; one can easily verify that for the sequence  $\{s_1, s_2, \dots, s_k, s'_1, s'_2, \dots, s'_k\}$  holds the following composition law :

$$\begin{aligned} \mathcal{T}\{s_1, s_2, \dots, s_k, s'_1, s'_2, \dots, s'_k\} &\equiv \mathcal{T}(s_1, s_2, \dots, s_k) \odot \mathcal{T}(s'_1, s'_2, \dots, s'_k) \\ &= (\sigma \sigma', \varepsilon \varepsilon', d_2 + \varepsilon d'_2, d_3 + \sigma d'_3). \end{aligned} \quad (5)$$

We now introduce a system of independent spin variables associated with chain configurations.

Let us first observe that each  $\mathfrak{C}(s_1, s_2, \dots, s_k)$  can be written as a product of various  $\mathfrak{C}$ 's, according to the composition law (5). One can think of writing  $\mathfrak{C}(s_1, s_2, \dots, s_k)$  as a product such that each factor cannot be further decomposed ; clearly  $\mathfrak{C}(s_1, s_2, \dots, s_k) = \prod_{\ell=1, k} \mathfrak{C}(s_\ell)$  is true only if  $s_\ell = 0 (\ell = 1, \dots, k)$ . In other words there is a set of minimal (not further decomposable)  $\mathfrak{C}$ 's in terms of which all conformations preserving a given chain axis can be obtained.

The first of these applications, in increasing order of complexity, are :  $\mathfrak{C}(0)$ ,  $\mathfrak{C}(1, 0, -1)$ ,  $\mathfrak{C}(1, -1, 1)$ ,  $\mathfrak{C}(1, 1, 1, 1)$ ,  $\mathfrak{C}(1, 1, -1, -1)$ , together with the corresponding ones obtained by exchanging 1 with -1.

It is easily shown that only a finite number of minimal  $\mathfrak{C}$ 's is required, if a maximal transversal width is fixed for the chain conformations.

We define such a width as the largest distance between all-*trans* portions of the distorted chain ; it turns out that this quantity is a multiple  $\Delta (\Delta = 1, 2, \dots)$  of the width  $\eta$  of the single kink (a sequence *Gauche-Trans-Gauche prime*, see Fig. 1). The variable  $\Delta$  is then an intrinsically nonlocal function of Flory angles.

If, in particular,  $\Delta = 1$ , one needs  $\{\mathfrak{C}_T \equiv \mathfrak{C}(0) ; \mathfrak{C}_K \equiv \mathfrak{C}(1, 0, -1) ; \mathfrak{C}_{K'} \equiv (-1, 0, 1)\}$ . The requirement  $\Delta = 1$  gives, furthermore, two constraints on the ordering of  $\mathfrak{C}_T$ ,  $\mathfrak{C}_K$  and  $\mathfrak{C}_{K'}$  along each chain :

- a)  $\mathfrak{C}_K$  and  $\mathfrak{C}_{K'}$  can never occur together along the same chain ;
- b) different  $\mathfrak{C}_K$  (or  $\mathfrak{C}_{K'}$ ) groups can never be separated by an odd number of  $\mathfrak{C}_T$ 's.

Hence, disregarding for the time being the problems related with the finite size of the chain, we have that an arbitrary combination of  $\mathfrak{C}_K$  (or  $\mathfrak{C}_{K'}$ ) and  $(\mathfrak{C}_T)^2$  generates each allowed conformation with  $\Delta = 1$ . (We exclude, for entropic reasons, *U*-like defects.)

It is now clear that a natural choice of independent spin variables  $\{\xi_i\}$  is simply given by :  $\xi_i = 1$  for each  $\mathfrak{C}_K$  or  $\mathfrak{C}_{K'}$  and  $\xi_i = 0$  for each  $(\mathfrak{C}_T)^2$  group.

With this definition the sum  $\chi = \sum_{i=1, L} \xi_i$  is the number of kinks in the chain.

Let us now examine how one can parametrize the chain ends. We will refer to the case with  $\mathfrak{C}_K$  defects in the bulk, the complementary case  $\mathfrak{C}_{K'}$  follows in a straightforward way.

One can think of cutting an indefinite length chain generated by  $\mathfrak{C}_K$ 's and  $(\mathfrak{C}_T)^2$ 's. As a result, modulo the bulk (generated by  $\mathfrak{C}_K$  and  $(\mathfrak{C}_T)^2$ ), one can further have a  $\mathfrak{C}_T$ , a  $\mathfrak{C}(-1)$  or a  $\mathfrak{C}(0, -1)$  on the left end, and a  $\mathfrak{C}_T$ , a  $\mathfrak{C}(1)$  or a  $\mathfrak{C}(1, 0)$  on the right end.

At each end we are left with four cases, including the « empty » case (no bond added). We label the left end with the spin variables  $(\nu_0, \mu_0)$  and the right end with  $(\mu_1, \nu_1)$  ( $\nu_i, \mu_i = 0, 1$ ), with the correspondence table I.

This choice is a convenient one, in that the sum  $\mu = \mu_0 + \mu_1$  counts the end-*Gauche* defects (Fig. 1) present both in the left terminal ( $\mu_0$ ) and in the right terminal

Table I.

left terminal	$(\nu_0, \mu_0)$	right terminal	$(\mu_1, \nu_1)$
—	—	—	—
empty	(0, 0)	empty	(0, 0)
T	(1, 0)	T	(0, 1)
G'	(0, 1)	G	(1, 0)
TG'	(1, 1)	GT	(1, 1)

( $\mu_1$ ). Furthermore the sums  $\nu_i + \mu_i$  ( $i = 0, 1$ ) and  $\nu = \nu_0 + \nu_1$  equal the number of bonds attached to each terminal and, respectively, the total number of *trans* bonds in the terminals.

Any chain conformation is then represented by the independent spins or « internal » coordinates ( $\nu_0, \mu_0, \{\xi_i\}, \mu_1, \nu_1$ ).

The number  $L$  of variables  $\xi_i$  becomes in so doing a dynamical variable, related to the number  $\ell$  of C-C bonds by :

$$\ell = 2L + \sum_{i=1,L} \xi_i + \mu + \nu + 2. \quad (6)$$

Whenever the case of low disorder is considered, namely if the occurrence of adjacent defects is excluded for energy reasons, it is convenient to associate the value  $\xi = 1$  with « dressed kinks » corresponding to  $\mathfrak{T}_T \mathfrak{G}_K \mathfrak{T}_T$  sequences (involving five bonds, see Fig. 1) instead of  $\mathfrak{G}_K$ . In this special case equation (6) becomes :

$$\ell = 2L + 3 \sum_{i=1,L} \xi_i + \mu + \nu + 2. \quad (6')$$

Within this framework of coordinates, there is a degeneracy of the all-*trans* conformation coming from the complementary class of conformers generated by the application  $\mathfrak{G}_K$ . We shall account for such degeneracy in our calculations.

## 2. Partition functions for the single chain and for the system.

In the previous section we gave the prescriptions to label all the conformations of a flexible chain forming defects with maximum transversal size equal to one. Under such conditions, the Flory conformational energy [2] in terms of our coordinates assumes the form :

$$H_C(\boldsymbol{\mu}, \boldsymbol{\xi}; L) = a\mu + b\chi + 2c(\mu_0 \xi_1 + \mu_1 \xi_L) + \frac{5}{2}c \sum_{i=1,L-1} \xi_i \xi_{i+1} \\ b = c = 2a = J. \quad (7)$$

In this expression  $J$  is the energy of the single kink ( $\sim 1$  Kcal/mole [2]). The first term in equation (7) accounts for the presence of distortions at chain ends, the second term counts the defects in the bulk of the chain and the last two terms contribute only if adjacent defects occur.

The partition function for the conformational statistics of a single chain of fixed length  $\ell$  is :

$$Z = A_0 + A_1 \\ A_0 = 1 \\ A_1 = 4 \exp(-\beta a) + 2 \exp(-2\beta a) + \\ + 2 \sum_L \sum_{\{\boldsymbol{\mu}, \boldsymbol{\nu}, \boldsymbol{\xi} | \chi > 0\}} \delta(\ell - 2L - \chi - \mu - \nu - 2) \exp(-\beta H_C). \quad (8)$$

In these equations  $A_0$  is the contribution of the all-*trans* conformation ; the first and the second terms in  $A_1$  represent the contributions from conformations with one, respectively two, end- $G$  in an otherwise transplanar chain ; the summation in  $A_1$  collects the contributions from all the kinked conformations. We account for the  $\mathfrak{G}_K \mathfrak{G}_K$  degeneracy by doubling such a sum.

In the special case excluding adjacent defects, the evaluation of  $Z$  reduces to a simple combinatory calculation. In fact the last two terms in equation (7) vanish and the weight of

states with given energy in  $Z$  is a sum of binomial coefficients. With  $\ell = 2(m + 3)$ , setting  $A = \exp(-\beta a)$ , one obtains :

$$Z = 1 + 4A + 2A^2 + 2 \sum_{k=0, k_{\max}} c_{2k+1} A^{2k+1} + c_{2k+2} A^{2k+2} \tag{9}$$

where :

$$c_{2k+1} = 2 \left\{ \binom{m-3k}{2k+1} + \left[ \binom{m-3k}{2k+1} + \binom{m-3k-1}{2k+1} \right] A + \binom{m-3k-1}{2k+1} A^2 \right\}$$

$$c_{2k+2} = \left[ \binom{m-3k}{2k+2} + \binom{m-3k-2}{2k+2} \right] + 4 \binom{m-3k-2}{2k+2} A + \left[ \binom{m-3k-2}{2k+2} + \binom{m-3k-3}{2k+2} \right] A^2.$$

With even chains one has analogous expressions.

From equations (8) or (9) one easily obtains the mean number of end-G defects and kinks for a single chain upon deriving with respect to the parameter  $a$  or  $b$  respectively.

Let us now consider the system of equivalent chains in low disorder regime.

We give a Hamiltonian model for such a system in a two-dimensional lattice of sites  $\mathbf{I} \equiv (i, j)$ .

The Hamiltonian is defined in terms of internal variables  $\{L; \mu, \nu, \xi\}$  (Sect. 1) and of two kinds of external variables : the rotations  $\tau$  and the translations  $\mathbf{x}$  (see Fig. 2). The variable  $\tau(\mathbf{I})$  represents the angle between the plane of the chain at site  $\mathbf{I}$  and a fixed direction in the lattice ; according to intermolecular potential calculations [17] we assume discrete values for such rotations :  $\tau = \pm 1$  for alignment of the chain plane along the  $x(+)$  and  $y(-)$  axis.

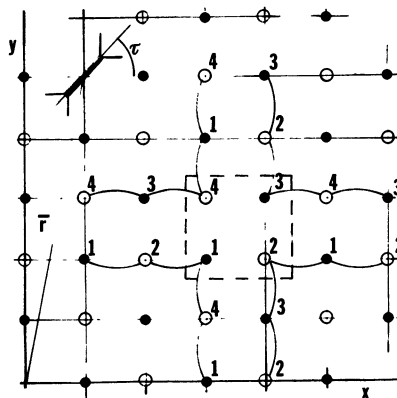


Fig. 2. — Two-dimensional lattice and lattice variables used in this work. The drawing represents the section of a layer of linear chains ( $n$ -alkanes) orthogonal to the  $(x, y)$  plane ; the variable  $x$  represents the chain axis position and the rotational (spin) variable  $\tau$  gives the orientation of the plane of the chain with respect to  $x$  axis :  $\tau = \pm 1$  for alignements along  $x(+)$  and  $y(-)$  axis. Notice the two sublattices A (full circles) and B (open circles) and the  $2 \times 2$  cell  $\mathcal{G}$  used in mean field treatment : the site numbers correspond to the labels of variational parameters referred in the text.



The mean value  $\langle \tau \rangle$  is associated with the occurrence of either the orthorhombic, or the monoclinic-triclinic or the rotatory phase. The variables  $\mathbf{x}(\mathbf{I})$  represent the chain axis position in the two-dimensional lattice ; the mean values  $\langle |\mathbf{x}_{\mathbf{I}} - \mathbf{x}_{\mathbf{I}+\mathbf{q}}| \rangle$  ( $\mathbf{I} + \mathbf{q}$  labelling the nearest neighbours of  $\mathbf{I}$  with  $\mathbf{q} \equiv (q_x, q_y)$ ,  $q_x, q_y = -1, 0, +1$ ) are associated with lattice spacings.

The total energy is :

$$H = \sum_{\mathbf{I}, \mathbf{q}} H_C(\mathbf{I}) + \frac{\mathcal{R}\mathcal{L}}{4} \tau(\mathbf{I}) \tau(\mathbf{I} + \mathbf{q}) + \frac{K\mathcal{L}}{2} [\mathbf{x}(\mathbf{I}) - \mathbf{x}(\mathbf{I} + \mathbf{q}) - \mathfrak{D}(\mathbf{I}, \mathbf{q})]^2 + \Delta(\mathbf{I}) v(\mathbf{I}, \mathbf{q}). \quad (10)$$

In this expression the first term is the Flory conformational energy of the single chain (Eq. (7)), the second and the third terms represent the rotational and the elastic interaction respectively. The last term accounts for the interaction between the defect width and the nearest neighbours orientations modelled by the potential  $v(\mathbf{I}, \mathbf{q})$ .

The conformational defects are coupled both with lattice elasticity and with nearest neighbour rotations ; the couplings are performed through the collective variables  $\Delta(\mathbf{I})$ . Such variables, in fact, determine the local value of the equilibrium lattice spacing  $\mathfrak{D}(\mathbf{I}, \mathbf{q}) = \delta \mathbf{q} + \Delta(\mathbf{I}) \eta \mathbf{q}$ ,  $\delta$  being the zero temperature interchain spacing.

We define [15] the potential  $v$  in terms of two coupling constants  $M_R$  and  $M_D$  representing the intermolecular energies of a distorted chain inserted in a locally orthorhombic or, respectively, monoclinic-triclinic environment.

$$\begin{aligned} v(\mathbf{I}, \mathbf{q}) &= |q_x| P^+(\mathbf{I}) [M_R P^-(\mathbf{I} + \mathbf{q}) + M_D P^+(\mathbf{I} + \mathbf{q})] + \\ &\quad + |q_y| P^-(\mathbf{I}) [M_R P^+(\mathbf{I} + \mathbf{q}) + M_D P^-(\mathbf{I} + \mathbf{q})] \\ P^\pm(\mathbf{I}) &\equiv \frac{1}{2} (1 + \tau(\mathbf{I})). \end{aligned} \quad (11)$$

Since in the orthorhombic configuration there is a closer packing [3], we assume  $M_R > M_D$  [18]. In particular, when  $M_R \rightarrow \infty$  the potential  $v$  acts as a constraint against defect formation on the  $\mathbf{I}$ -th chain. More precisely, for  $q_x = 0$  no defect can be formed if the neighbouring up and down chains are orthogonal to the  $\mathbf{I}$ -th chain ; similarly, for  $q_y = 0$  no defect can be formed if the neighbouring left and right chains are orthogonal to the  $\mathbf{I}$ -th chain. Hence, this constraint is active in the orthorhombic local ordering. We assume that  $M_D$  is proportional to chain length and independent of the number of defects ; in fact, any distortion, if  $\Delta = 1$ , produces a displacement of the backbone groups which is independent of such number. Hence, the energy contribution corresponding to  $M_D$  (to be added to the pure conformational term) will be indicated with  $w\mathcal{L}$ .

We shall now consider the partition function  $Z_S$  of the system. In order to obtain  $Z_S$  we have to sum over the internal variables at each site  $\mathbf{I}$  and over the external variables  $\mathbf{x}$  and  $\tau$ .

Since the internal degrees of freedom are not directly coupled, but only through the collective variable  $\Delta$ , for fixed values of  $\tau(\mathbf{I})$  and  $\Delta(\mathbf{I})$ , we sum over the internal variables. Moreover, since for a given distribution  $\Delta(\mathbf{I})$  the calculation reduces to a Gaussian integral, we can exactly integrate over the  $\mathbf{x}$  variables.

We obtain :

$$\begin{aligned} Z_S &= \sum_{\{\Delta(\cdot)\}} \sum_{\{\tau(\cdot)\}} \prod_{\mathbf{I}} \left\{ \exp \left[ -\beta \frac{\mathcal{R}\mathcal{L}}{4} \sum_{\mathbf{q}} \tau(\mathbf{I}) \tau(\mathbf{I} + \mathbf{q}) \right] \right\} \times \\ &\quad \times \left\{ [1 - \Delta(\mathbf{I})] \frac{\Lambda_0}{K\mathcal{L}} + \Delta(\mathbf{I}) \frac{\Lambda_1}{K\mathcal{L}} \exp[-\beta v(\mathbf{I}, \mathbf{q})] \right\}. \end{aligned} \quad (12)$$

We note that the contribution to  $Z_S$  from the site  $\mathbf{I}$  has a weight proportional to the term  $\Lambda_{\Delta(\mathbf{I})}$  of the single chain partition function (see Eq. (8)). The interchain potential  $v(\mathbf{I}, \mathbf{q})$  does not contain a direct interaction between the widths of adjacent chains : this allows us to sum over  $\Delta$  variables. As a result we get the effective Hamiltonian as a power series in terms of the orientational variables  $\tau$  : one readily verified that, due to the discreteness of such variables, the Hamiltonian simply reduces to a third order polynomial in the form :

$$H_{\text{eff}} = \sum_{\mathbf{I}, \mathbf{q}} [J_1 \tau(\mathbf{I}) \tau(\mathbf{I} + \mathbf{q}) + J_2 \tau(\mathbf{I} - \mathbf{q}) \tau(\mathbf{I} + \mathbf{q}) + J_3 (|q_x| - |q_y|) \tau(\mathbf{I}) \tau(\mathbf{I} + \mathbf{q}) \tau(\mathbf{I} - \mathbf{q}) + J_0]. \quad (13)$$

The coupling constants  $J_i$  directly depend on  $\Lambda_0$  and  $\Lambda_1$  ; in the limit case  $M_R = \infty$  one has :

$$\begin{aligned} J_1 &= \frac{\mathcal{R}\mathcal{L}}{4} - \frac{1}{8\beta} \log \left[ 1 + \frac{\Lambda_1}{\Lambda_0} W \right] \\ J_2 &= J_3 = -\frac{1}{16\beta} \log \left[ 1 + \frac{\Lambda_1}{\Lambda_0} W \right] \\ J_0 &= -\frac{1}{\beta} \log \Lambda_0 - \frac{1}{4\beta} \log \left[ 1 + \frac{\Lambda_1}{\Lambda_0} W \right] \\ W &= \exp(-\beta \omega \mathcal{L}). \end{aligned} \quad (14)$$

We note that the nearest neighbour coupling constant  $J_1$  at low temperature has the sign of  $\mathcal{R}$ , while at high temperatures it is always ferromagnetic ; the next nearest neighbour coupling constant  $J_2$  is ferromagnetic at all temperatures.

The trilinear term introduces an anisotropy in the coupling between the next nearest neighbours  $\mathbf{I} + \mathbf{q}$  and  $\mathbf{I} - \mathbf{q}$ . In fact, in the  $x$  direction one gets a n.n.n. coupling  $J_2 + \tau(\mathbf{I})J_3$ , while in the  $y$  direction one has  $J_2 - \tau(\mathbf{I})J_3$ . Hence if, e.g.,  $\tau(\mathbf{I}) = 1$ , only the next nearest spins aligned along the  $x$  direction are coupled ( $J_2 = J_3$ ) and *vice versa*.

This anisotropy is related to the anisotropic response of the environment to the defect formation at the site  $\mathbf{I}$ , as described by the potential  $v(\mathbf{I}, \mathbf{q})$ . One immediately verifies that such contribution disappears if  $M_R = M_D$ . The variable  $\tau(\mathbf{I})$  describes the orientation of the plane of the chain with respect to a fixed direction : e.g.  $\tau(\mathbf{I}) = 1$  means that such plane is oriented along the  $x$  direction. Hence the transformation  $\tau(\mathbf{I}) \rightarrow -\tau(\mathbf{I})$  for all  $\mathbf{I}$  is equivalent to exchanging the  $x$  and the  $y$  axes. The Hamiltonian is in fact invariant under the transformation  $\{\tau(\mathbf{I}) \rightarrow -\tau(\mathbf{I}) ; (x, y) \rightarrow (y, x)\}$ .

It is easy to see that the partition function can be written in the form :

$$Z_S = \prod_{\mathbf{I}} \sum_{\{\tau\}} R(\mathbf{I}) \Lambda_0 \left[ 1 + \frac{\Lambda_1}{\Lambda_0} W \right]^{P(\mathbf{I})} \quad (15)$$

where  $R(\mathbf{I}) = \exp \left[ -\beta \frac{\mathcal{R}\mathcal{L}}{4} \sum_{\mathbf{q}} \tau(\mathbf{I}) \tau(\mathbf{I} + \mathbf{q}) \right]$  and

$$\begin{aligned} P(\mathbf{I}) &= \frac{1}{4} + \frac{1}{8} \sum_{\mathbf{q}} \tau(\mathbf{I}) \tau(\mathbf{I} + \mathbf{q}) + \frac{1}{16} \sum_{\mathbf{q}} \tau(\mathbf{I} - \mathbf{q}) \tau(\mathbf{I} + \mathbf{q}) + \\ &+ \frac{1}{16} \sum_{\mathbf{q}} (|q_x| - |q_y|) \tau(\mathbf{I} - \mathbf{q}) \tau(\mathbf{I}) \tau(\mathbf{I} + \mathbf{q}). \end{aligned} \quad (16)$$

One can now calculate the mean values of any conformational observable  $\mathcal{O}$  by deriving the

$Z_S$  function with respect to the corresponding source  $\omega$  occurring in the single chain Hamiltonian  $H_C$  :

$$\begin{aligned} \langle \mathcal{O} \rangle_S &= \langle P \rangle_S \frac{W\Lambda_1^*}{Z_C} + \left[ 1 + \frac{W\Lambda_1}{\Lambda_0} (1 - \langle P \rangle_S) \right] \frac{\Lambda_0^*}{Z_C} \\ \Lambda_i^* &= -\frac{1}{\beta} \frac{\partial}{\partial \omega} \Lambda_i \end{aligned} \quad (17)$$

where  $\langle P \rangle_S$  is the mean value of the polynomial (16) and  $Z_C = \Lambda_0 + W\Lambda_1$  is the partition function of a chain in the external field  $\omega\mathcal{L}$ . The terms  $\frac{\Lambda_i^*}{Z_C}$  are the contributions to the mean value of the observable  $\mathcal{O}$ , coming from the conformations with  $\Delta = i$  and being evaluated for the single chain in the external field.

### 3. Calculation of order parameters.

In reference (15) we performed a mean field analysis in terms of the rotational order parameters by distinguishing two sublattices A and B (Fig. 2) in order to describe both the monoclinic-triclinic and the orthorhombic phases. In such a way we determined the range of existence of the rotational phase, which is to be identified with the paramagnetic phase of the spin Hamiltonian  $H_{\text{eff}}$ .

In this paper we are interested in the calculation of the conformational parameters  $\langle \text{eng} - G \rangle_S$  and  $\langle K \rangle_S$ ; as previously shown, these quantities involve through the polynomial  $P(\mathbf{I})$  (see Eqs. (16) and (17)), second and third order orientational correlation functions.

It is then natural to generalize the mean field by introducing new variational parameters to be associated with higher order correlations, e.g. along the lines presented in reference [19].

We fix the size of the cell to the maximal order of the correlations to be included in the generalized m.f. treatment; once the cell size is fixed, the construction is totally general and uniquely determined by assuming that the configuration outside the cell is completely described by the variational parameters.

In the present case we truncate to 2-nd order so that we consider a  $2 \times 2$  cell  $\mathcal{G}$  (Fig. 2), the order parameters involved being  $\bar{\tau}_i, \Gamma_{i,j}, i, j = 1, \dots, 4$ . We perform the exact sum of the cell partition function: evidently, only linear and quadratic terms occur in the cell Hamiltonian. We have :

$$\begin{aligned} Z_{\mathcal{G}} &= \sum_{\tau_i \in \mathcal{G}} \exp -\beta H_{\mathcal{G}} \\ H_{\mathcal{G}} &= \sum_i H_i \tau_i + \sum_{i,j} H_{i,j} \tau_i \tau_j \end{aligned} \quad (18)$$

The coupling constants  $H_i$  and  $H_{i,j}$  are determined by rearranging the different contributions from the original hamiltonian  $H_{\text{eff}}$ ; e.g., see figure 2, the cubic terms in  $H_{\text{eff}}$  contribute to the cell Hamiltonian through

$$\begin{aligned} J_3 [(\bar{\tau}_1 + \bar{\tau}_2) \tau_1 \tau_2 + (\bar{\tau}_3 + \bar{\tau}_4) \tau_3 \tau_4 + (\tau_1 + \tau_2) \Gamma_{12} + (\tau_3 + \tau_4) \Gamma_{34}] - \\ - J_3 [(\bar{\tau}_1 + \bar{\tau}_4) \tau_1 \tau_4 + (\bar{\tau}_2 + \bar{\tau}_3) \tau_2 \tau_3 + (\tau_1 + \tau_4) \Gamma_{14} + (\tau_3 + \tau_2) \Gamma_{23}] \end{aligned}$$

In particular :

$$\begin{aligned}
 H_1 &= J_3(\Gamma_{12} - \Gamma_{14} + 4 \bar{\tau}_1) + J_1(\bar{\tau}_2 + \bar{\tau}_4) \\
 H_2 &= J_3(\Gamma_{12} - \Gamma_{23} - 4 \bar{\tau}_2) + J_1(\bar{\tau}_1 + \bar{\tau}_3) \\
 H_{12} &= J_3(\bar{\tau}_1 + \bar{\tau}_2) + J_1 \\
 H_{14} &= -J_3(\bar{\tau}_1 + \bar{\tau}_4) + J_1
 \end{aligned} \tag{19}$$

and analogous expressions by cycling the indices.

From (18) we have the self consistency equations

$$\begin{aligned}
 \langle \tau_i \rangle_{\mathfrak{g}} &= \bar{\tau}_i \\
 \langle \tau_i \tau_j \rangle_{\mathfrak{g}} &= \Gamma_{i,j}
 \end{aligned} \tag{20}$$

by identifying the variational parameters with the correlations functions.

We now want to recover these equations from a variational principle, i.e. to determine the free energy  $\mathcal{F}$  of the system.

In order to do that, we add a counterterm to  $H_{\mathfrak{g}} : H_{\mathfrak{g}} \rightarrow H_{\mathfrak{g}} + \frac{1}{\beta} A$ , where  $A$  is an *a priori* arbitrary function of the variational parameters.

The variational equations for  $\mathcal{F}$  are then :

$$\frac{\partial \mathcal{F}}{\partial \bar{\tau}_k} \equiv \frac{1}{\beta} \frac{\partial A}{\partial \bar{\tau}_k} + \sum_i \langle \tau_i \rangle \frac{\partial H_i}{\partial \bar{\tau}_k} + \sum_{i,j} \langle \tau_i \tau_j \rangle \frac{\partial H_{ij}}{\partial \bar{\tau}_k} = 0 \tag{21}$$

and analogous with respect to  $\Gamma_{ij}$ .

From these equations  $A$  can be determined as a differentiable function if and only if the couplings  $H_i$  and  $H_{ij}$  are the components of an irrotational vector field.

In such a case there exists a potential  $\Phi$  such that  $H_i = \frac{\partial \Phi}{\partial \bar{\tau}_i}$ ,  $H_{ij} = \frac{\partial \Phi}{\partial \Gamma_{ij}}$  and

$$-\frac{1}{\beta} A = \sum_i \bar{\tau}_i \frac{\partial \Phi}{\partial \bar{\tau}_i} + \sum_{i,j} \Gamma_{ij} \frac{\partial \Phi}{\partial \Gamma_{ij}} - \Phi .$$

For our purposes it is sufficient to look for solutions such that  $\bar{\tau}_1 = \bar{\tau}_3 = \bar{\tau}$ ,  $\bar{\tau}_2 = \bar{\tau}_4 = \bar{\tau}'$ ,  $\Gamma_{12} = \Gamma_{34} = \Gamma$ ,  $\Gamma_{13} = \Gamma_{23} = \Gamma'$ . Such solutions include both the ferromagnetic and antiferromagnetic configurations. We are then led to the self-consistency equations :

$$\begin{aligned}
 Z_S \bar{\tau} &= K \operatorname{Sh}(A + A') + K^{-1} \operatorname{Sh}(A - A') + 2 \operatorname{Sh} A' \\
 Z_S \Gamma &= K \operatorname{Ch}(A + A') - K^{-1} \operatorname{Ch}(A - A') + \operatorname{Ch}(B + B')
 \end{aligned} \tag{22}$$

where

$$\begin{aligned}
 K &= \exp(8J_1) \\
 A &= 8J_3 \bar{\tau}' + 4J_1 \bar{\tau} + 4J_3(\Gamma - \Gamma') \\
 B &= 8J_3 \bar{\tau} .
 \end{aligned}$$

The expressions for  $A'$  and  $B'$  are obtained interchanging  $\bar{\tau}$  and  $\bar{\tau}'$  in  $A$  and  $B$ . We have the analogous s.c. equations for  $\bar{\tau}'$  and  $\Gamma'$  by changing, in equations (22), the quantities  $\bar{\tau}$ ,  $A$ ,  $B$  into  $\bar{\tau}'$ ,  $\Gamma'$ ,  $A'$ ,  $B'$  and *vice versa*. The expression for  $Z_S$  is :

$$Z_S = K \operatorname{Ch}(A + A') + K^{-1} \operatorname{Ch}(A - A') + 2 \operatorname{Ch}(B + B') + 2 \operatorname{Ch} A + 2 \operatorname{Ch} A' . \tag{23}$$

As previously said, we identify the rotational phase with the paramagnetic solution for  $\bar{\tau}$ ; furthermore we identify the orthorhombic and the monoclinic-triclinic structures with antiferromagnetic ( $\bar{\tau} = -\bar{\tau}'$ ) and ferromagnetic ordering ( $\bar{\tau} = \bar{\tau}'$ ) respectively.

The sign of the constant  $\mathcal{R}$  determines the  $T = 0$  solution:  $\mathcal{R} > 0$  implies the orthorhombic ground state (odd chains);  $\mathcal{R} < 0$  implies the monoclinic-triclinic ground state (even chains) [15].

Let us consider the case with  $\mathcal{R} > 0$ .

With the orthorhombic ansatz, equations (22) have non trivial ( $\bar{\tau} \neq 0$ ) solution for temperatures below a critical value  $T_0$ . More precisely,  $\bar{\tau} = -\bar{\tau}'$  implies  $\Gamma = \Gamma'$  so that the s.c. equation for  $\bar{\tau}$  does not contain  $\Gamma$ . The range of existence of the non trivial solution can then be evaluated by the tangent method as in the classical problem of the s.c. Ising equation. We obtain:

$$2\beta\mathcal{R}\ell > \frac{1 + 6Z_C \exp(-2\beta\mathcal{R}\ell) + Z_C^2 \exp(-4\beta\mathcal{R}\ell)}{1 + Z_C \exp(-2\beta\mathcal{R}\ell)}. \quad (24)$$

The function on the right hand increases monotonocally with  $T$  and tends to the number of states of the single chain for  $T \rightarrow \infty$ . The relation (24) is then satisfied for  $T < T_0$  ( $T_0 \equiv T_0(\ell)$ ): from (24) one estimates that the ratio  $\frac{T_0}{\ell}$  is a constant.

The free energy calculated with the orthorhombic solution is:

$$\mathcal{F}_0 = (8J_3 - 4J_1)\bar{\tau}^2 + 9J_1\Gamma. \quad (25)$$

With the monoclinic-triclinic ansatz we have in (22) two coupled equations in  $\bar{\tau}$  and  $\Delta\Gamma \equiv \Gamma - \Gamma'$ . One can argue that the non trivial solution exists above a critical temperature  $T_{M-T}$ . In fact, it is easy to see that for very low temperature the unique solution is  $\bar{\tau} = 0$ ,  $\Delta\Gamma = 0$ , while in the limit of high temperature the solution  $\bar{\tau} \simeq 1$ ,  $\Delta\Gamma \simeq 0$  occurs. A numerical estimate shows that  $T_{M-T}$  saturates for  $\ell \geq 20$ .

The free energy in the case of the monoclinic-triclinic solution is:

$$\mathcal{F}_{M-T} = (8J_3 + 4J_1)\bar{\tau}^2 + 8J_1\Gamma + (8J_3\bar{\tau} + 4J_1)\Delta\Gamma. \quad (26)$$

It is now clear that the paramagnetic (rotational) phase is accessible to the system if  $T_0 < T_{M-T}$ ; in such a case, the difference  $T_{M-T} - T_0$  measures the range of existence of the phase.

With  $\mathcal{R} < 0$ , the relation (24) is never satisfied and the accessible states have ferromagnetic ordering.

Equations (22) have been solved numerically for different values of the chain length ( $\ell$ ); we report in figure 3  $\bar{\tau}$ ,  $\Gamma$  and  $\Delta\Gamma$  as functions of temperature. The phase diagram obtained in reference (15) is confirmed by the present treatment. In particular, an intermediate rotational phase is found for short, odd  $n$ -alkanes; approximately at  $N \simeq 40$  this phase disappears. We predict a 1-st order transition for longer chains, while for shorter ones the rotational phase is reached through second order transition (see Figs. 3a, 3b). In figure 3b the two branches of  $\bar{\tau}$  refer to antiferromagnetic ordering and ferromagnetic ordering respectively, so that a discontinuity occurs in  $\bar{\tau}'$ . About the order of the transitions, one could argue, from the occurrence of the trilinear term in  $H_{\text{eff}}$  (13), that a cubic term appears in the corresponding free energy. As a consequence, by the standard Landau argument, one should exclude a 2-nd order transition.

In our model, due to the non scalar nature of the coefficient of the trilinear term in  $H_{\text{eff}}$ , the free energy  $\mathcal{F} = \log Z_S$  (see formula (23)) is an even function of the order parameter

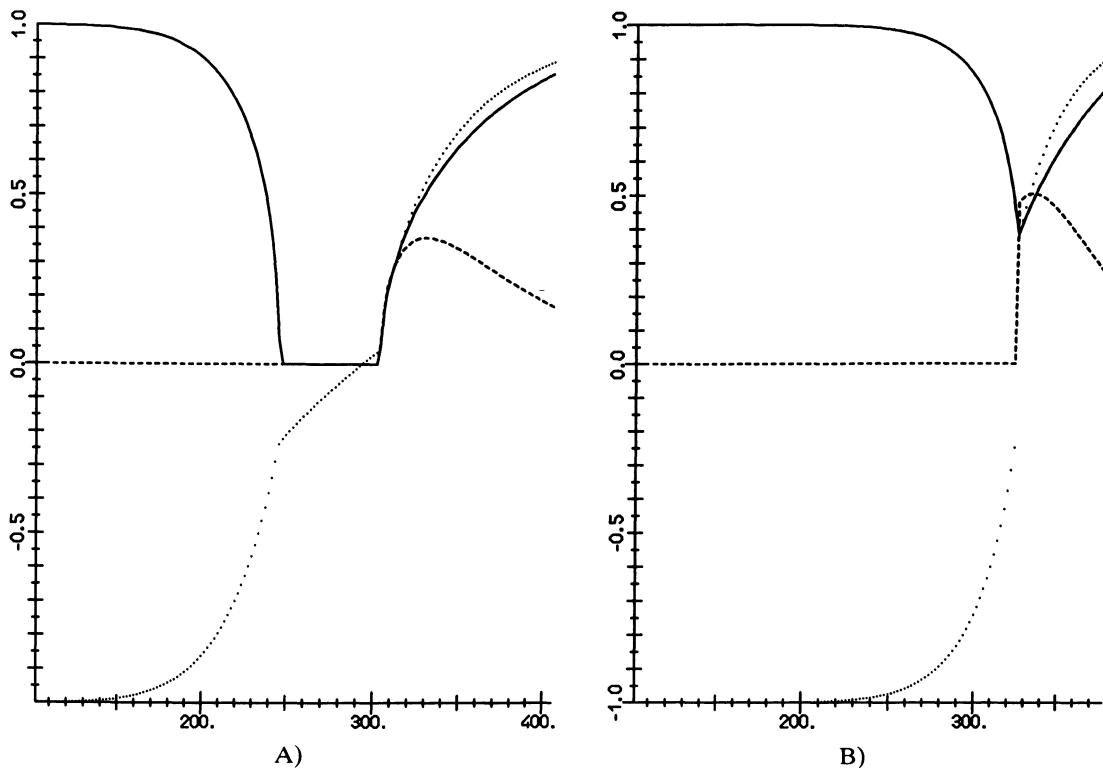


Fig. 3. — Orientational order parameter  $\bar{\tau}$  (full line), two point correlation  $\Gamma$  (dotted line) and correlation anisotropy  $\Delta\Gamma$  (dashed line) vs. temperature (K). Mean field solutions have been calculated with  $\mathcal{R} = 0.3$  Kcal/mole bond and  $\omega = 0.2$  Kcal/mole bond. A) odd chain with backbone of 21 carbons ; B) 41 carbons.

$\tau$ , both when  $\bar{\tau} = \bar{\tau}'$  and when  $\bar{\tau} = -\bar{\tau}'$ , so that the Landau argument does not apply. On the other hand it is a known fact that trilinear terms in the Hamiltonian do not necessarily imply 1-st order transitions : e.g. Baxter's exact solution of the 3-state Potts model exhibits a 2-nd order transition [20].

In our case one realizes that both the 1-st order and the 2-nd order transitions are associated with the competition between different bilinear terms ; only second and higher order correlations are sensitive to the trilinear terms.

In the present treatment we concentrate on 2-nd order correlations  $\Gamma, \Gamma'$  : we obtain that  $\Gamma$  appreciably differs from the product  $\bar{\tau} \cdot \bar{\tau}'$  in the rotational phase and at the onset of the higher temperature phase.

In the rotational phase, the result  $\Gamma \neq 0, \Delta\Gamma = 0$ , together with the very low density of distorted chains (see after), shows that the defects are trapped in the crystal structure : the predominant part of the free energy comes from the rotational interaction.

At higher temperatures, independently of chain length, the number of conformational defects abruptly increases at the same time as  $\Delta\Gamma \neq 0$  ; such a behavior stresses the occurrence of a regime where the conformational disorder « propagates », driving the thermodynamics of the system. In this regime the mean chain width  $\langle \Delta \rangle_S$  undergoes fast saturation and the frozen degrees of freedom of our model should be « switched on » in order to get a realistic description of the phase.

With mean field solutions, we evaluate  $\langle P \rangle_s$  and calculate the conformational order parameters as in equation (17) ; we have :

$$\begin{aligned} \langle \text{end} - G \rangle_s &= \langle \text{end} - G \rangle_c \cdot \langle P \rangle_s \\ \langle K \rangle_s &= \langle K \rangle_c \cdot \langle P \rangle_s \end{aligned} \quad (27)$$

where  $\langle \cdot \rangle_c$  means single chain statistics from  $Z_c$ .

The probability of the all-*trans* conformation is a further measure of disorder ; we can evaluate it as :

$$P_s(t) = P_c(t)[1 + \langle \Delta \rangle_s(1 - \langle P \rangle_s)]. \quad (28)$$

It is interesting to note that, with this calculation, we estimate that the onset of end-*G* defects always occurs at lower temperatures than kink formation. One has, in fact :

$$\frac{\langle \text{end} - G \rangle_s}{\langle K \rangle_s} = \frac{\langle \text{end} - G \rangle_c}{\langle K \rangle_c} = \frac{4 \exp(-\beta a) + 4 \exp(-2\beta a) + \dots}{\zeta \exp(-2\beta a)}. \quad (29)$$

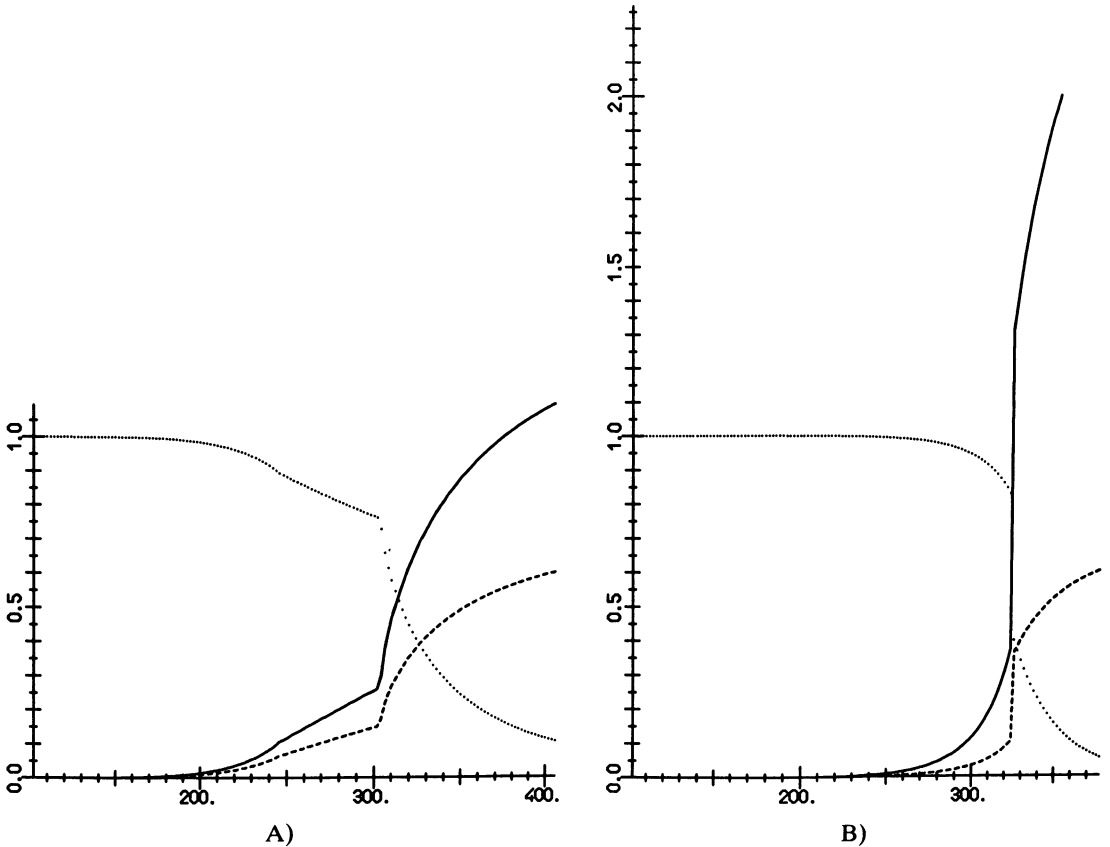


Fig. 4. — Mean number of end-*G* defects (dashed line), mean number of kinks (full line) and probability of the all-*trans* conformation (dotted line) vs. temperature as resulting from the solutions shown in Fig. 1 : A) 21 carbons ; B) 41 carbons.

The ratio (29) becomes smaller than 1 at a temperature  $T_r$  which depends on chain length. With medium-length and long chains  $T_r$  results lower than the temperature of the transition to the rotational phase  $T_0$ ; for short chains, instead, provided that, as  $T \rightarrow \infty$ , the asymptotic value of  $\langle K \rangle_C$  is larger than the asymptotic value of  $\langle \text{end} - G \rangle_C$ , one has  $T_r > T_0$ .

We show in figure 4  $\langle \text{end} - G \rangle_s$ ,  $\langle K \rangle_s$  and  $P_s(t)$  as functions of temperature for medium-length and long chains. Note that the conformational collapse occurs at the end of the rotational phase (if any), at the transition to the higher temperature phase.

The behavior of the fluctuations (reported in Fig. 5), as estimated in our treatment, stresses that both phase transitions are marked by conformational disorder. Noting that the plots of figure 5 are to be identified with the differential intensities of defect markers [8, 21], a comparison with experimental results allows us to associate the well-known observed discontinuities with the structural transitions predicted on the basis of our model.

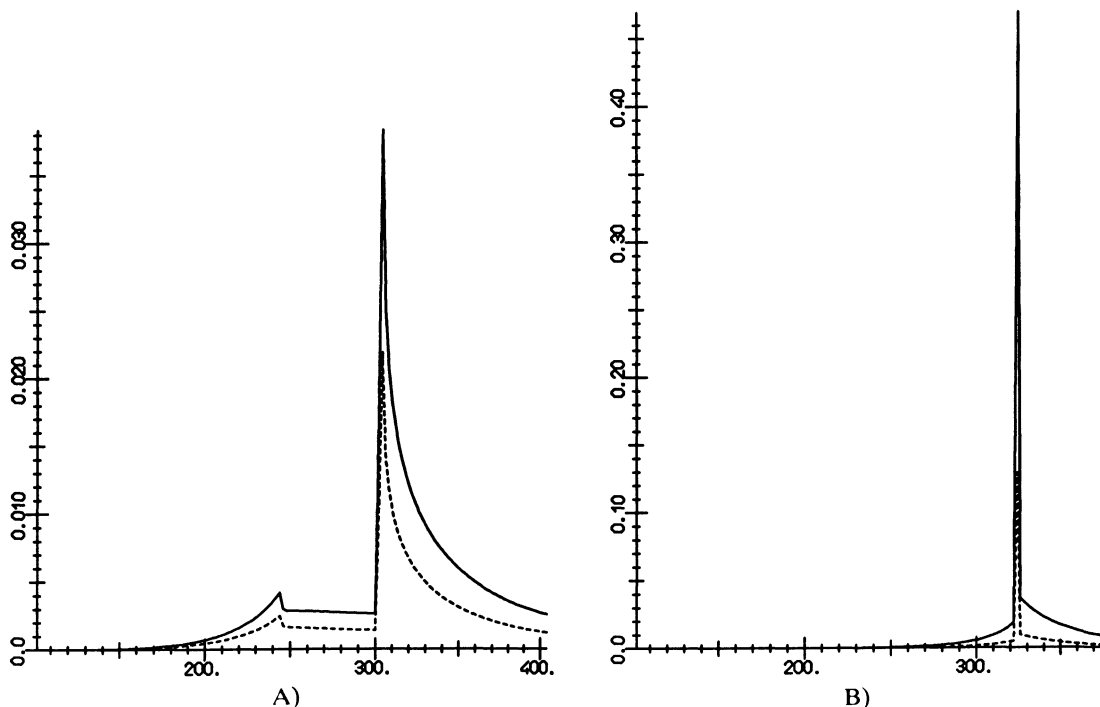


Fig. 5. — Fluctuations  $\frac{\partial \langle \text{end} - G \rangle_s}{\partial T}$  and  $\frac{\delta \langle K \rangle_s}{\partial T}$  as calculated in the model. The drawing are to be identified with the differential intensities of spectroscopic markers of conformational defects. A) 21 carbons ; B) 41 carbons.

### Conclusions.

Assuming as a phenomenological datum the existence of « lamellae » of linear chain molecules with two possible crystal structures at very low temperature, we show that only one of these structures can go over to a rotational phase through coupling of the internal degrees of freedom with the external ones. According to experiments we show that :

i) the rotational phase occurs only in systems with orthorhombic structure at low temperature (odd chains) ;



- ii) the range of existence of the rotational phase decreases with increasing chain length ;
- iii) for long odd chains and for even chains (monoclinic-triclinic cell at low temperature) the rotational phase does not exist ;
- iv) the conformational defects appear at the onset and during the rotational phase ;
- v) the conformational collapse occurs at the transition from the rotational phase to the high temperature regime.

These results have been obtained by freezing the degrees of freedom associated with translations orthogonal to the planes of the lamella, thus describing the system as a two-dimensional lattice of rotators.

We think that such degrees of freedom do not affect the overall behavior of the system as far as the existence and the stability of the rotational phase are concerned. It is instead clear that orthogonal translations strongly affect the behavior of  $\langle \text{end} - G \rangle_s / \langle K \rangle_s$  vs.  $T$ .

In the present work we assumed that end-Gauche defects, as well as kinks, can form only inside the bulk. One can try to include within the model a rough description of the formation of end-G defects also on the surface of the lamella [5, 16]. In order to do that we tried to modify the  $\Delta = 0$  sector in the partition function by adding the contribution from the states with one end-G in an otherwise trans-planar chain. We obtained that the qualitative behavior of the rotational phase does not change with respect to the previous results ; the ratio  $\langle \text{end} - G \rangle_s / \langle K \rangle_s$ , instead, changes dramatically, as shown in figure 6.

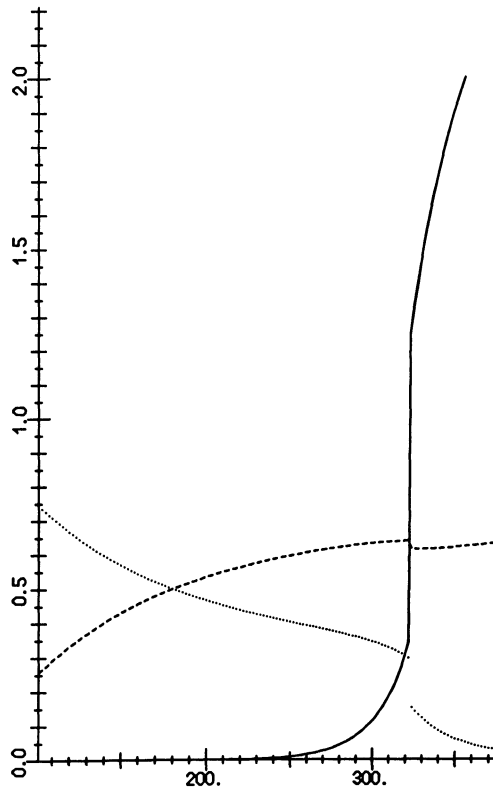


Fig. 6. — Calculation of mean numbers of defects (end-G dashed line, kinks full line) and all-trans probability (dotted line) vs. temperature when end-G defects occur both on the surface and inside the lamella (compare with Fig. 2B). Same conditions as in figure 2B.

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