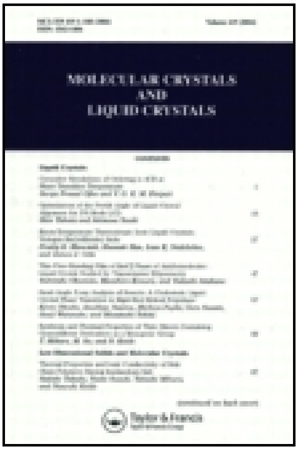

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Space Correlations of Steric Origin in Plastic Crystals

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I INTRODUCTION

In plastic crystals, space correlations between molecular orientations can be of very different kinds. The most frequent ones are associated with steric hindrance and are more especially strong as molecules are less globular. X-rays studies have often shown them, for example in cyclohexane, succinonitrile, *t*-butyl chloride and bromide, camphene etc. . . . These correlations strongly influence both the static and dynamical behaviours of molecules. Here we care for the first case alone. The purpose of this paper is the theoretical study of entropy, X-ray scattering and dielectric constants, which have not been yet examined with accuracy. We present a systematic way of studying this kind of correlations, by use of a graphical series expansion of the thermodynamical functions. This method has been used successfully in the ice and dimer problem by Nagle.[1,2] It is very convenient here because we are dealing with "all or nothing" correlations. So we can evaluate the partition function and the correlation lengths. A similar calculation, in presence of an applied electric field, gives the Kirkwood orientational correlation factor g_k.

We take first interest in succinonitrile because its structure is known[3] and because it shows steric hindrance; moreover some molecular configurations have a dipol and the dielectric experiments give a Kirkwood factor g_k higher than 1.[4] Therefore succinonitrile has a local tendency to be ferroelectric. Besides, the X-ray diffuse scattering is intense and the quite structured areas appearing on Laüe photographs can be only interpreted in a quantitative way, whenever the effect of space correlations of steric origin is taken into account.[5]

II CALCULATION OF THE CORRELATION ENTROPY

A Weak Graph Method

The entropy increment, which occurs during the LT–HT transition, is in a great part due to the variation of the configurational entropy. If correlations are not being taken into account, we have: $\Delta S_{\text{conf}} = Nk \log D$, where D is the number of the molecular orientations. The effect of correlations is to reduce this value. Particularly, the steric hindrance limits the number of orientations that a molecule can actually take on its site: for two neighbouring molecules, there is a complete steric hindrance between configurations that would bring, for both of them, on the edge joining them, atoms which overlap.

The precise calculation of the configurational entropy needs the evaluation of the following partition function:

$$Z^N = \sum_{S_1=1}^{D} \cdots \sum_{S_N=1}^{D} \prod_{\langle i,j\rangle}' A(S_i, S_j) \tag{1}$$

where the product is restricted to all nearest-neighbour pairs of sites and S_i represents the state of the i molecule.

$A(S_i, S_j)$ is a compatibility function; the definition of which is

$$\begin{aligned} A(S_i, S_j) &= 1 \quad \text{if } S_i \text{ and } S_j \text{ are compatible} \\ &= 0 \quad \text{if not} \end{aligned}$$

The computation of Eq. 1 can be led with a high precision by using the weak-graph method.[2] Then $A(S_i, S_j)$ has the following form:

$$A(S_i, S_j) = \frac{a - C_{ij}(S_i)C_{ji}(S_j)}{\Phi(S_i, S_j)}$$

where $C_{ij}(S_i) = +x$ if the i molecule brings an atom on to the edge $(i-j)$; $= -y$ if not, one individual pair (C_{ij}, C_{ji}) is placed into bijective correspondence with the edge $(i-j)$ of the lattice. The product of n of these terms corresponds with a graph of n edges and Z^N can be developed in successive powers of graphs. $\Phi(S_i, S_j)$ is a normalization factor; the incompatibility imposes $a \doteq x^2$. The definition of the $C_{ij}(S_i)$ terms has been taken in a general way in order to use a renormalization. Indeed, if we impose:

$$\sum_{s_i=1}^{D} C_{ij}(S_i) = 0 \tag{2}$$

Only graphs of a certain type are non-null terms when the summation $\sum_{(s)}$ is carried out: i.e. all the closed polygons drawn on the lattice. So the serie converges much faster; the zero order term Z_0^N (no graph) is the preponderant term and recovers the Bethe approximation.[2] The serie expansion has the following form:

$$Z^N = Z_0^N[1 + \varepsilon(n) + \cdots]^N \tag{3}$$

Where $\varepsilon(n)$ corresponds to the first closed graphs having n edges. Thus the configurational entropy is $S = Nk \log Z$.

B Succinonitrile's Case[10]

In plastic phase the crystal is b.c.c. (m3m). There is an equilibrium between trans and gauche isomers. The middle bond C—C of the molecule may direct itself along the four three-fold axis of the cubic cell.[3] Around the three-fold axis bearing its middle-bond the molecule may occupy three equilibrium positions derived from one another by a $2\pi/3$ rotation around this axis. Each isomer can take twelve equilibrium positions which determine a mean molecular configuration compatible with the symmetry of the crystal. For two second neighbours molecules, there is complete steric hindrance between configurations that would bring, for both of them, a nitrogen atom to middle of the side.

The steric interactions occur only on each of the two intermingled simple cubic sublattices which correspond to the b.c.c. structure. The isomerism brings complications; but the structure and the correlations can be described in the following schematic way:

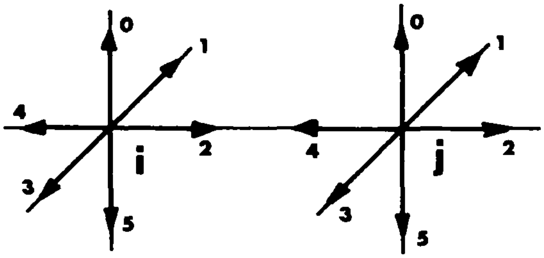

FIGURE 1

All possible states can be obtained by associating the arrows two by two. Accordingly there are fifteen states, but in this description each state has a 0.8 weight. Obviously, five states of the i molecule are incompatible with five states of the j molecule. Without steric hindrance $Z^N = 12^N$, i.e. a configurational entropy about 4.93 e.u. Steric hindrance changes Z and the weak-graph method applied to the simple cubic lattice gives:

$$Z^N = Z_0^N[1 + \varepsilon(4)]^N = \left[\frac{16}{27} \times 12\right]^N \left[1 + \frac{3}{10^4}\right]^N \tag{4}$$

Here the first occurring closed polygons are squares. Then the entropy is $\Delta S_{\mathrm{conf}} = 3.8843$ e.u.; When limiting to $Z = Z_0$, $\Delta S_{0_{\mathrm{conf}}} = 3.8840$ e.u. This shows that the predominant term accounts for most of the correlations. These ones reduce the entropy of more than one e.u.: $\Delta S_{\mathrm{corr}} = 1.056$ e.u., while the experimental increment is $\Delta S_T = 6.35$ e.u.[6] Although we have neglected the weak dipolar interactions between the two sub-lattices, we have now, by means of this precise calculation, an idea of the value of the correlation entropy in plastic crystals with strong correlations.

C Others Plastic Crystals's Case

* Steric hindrance in the plastic phase (c.f.c.) of cyclohexane[7] appears in the following way: a molecule can take 24 equilibrium positions on its site; it looks like ellipsoïde whose the longest axis lies along the two-fold axis of the cube. Two neighbouring molecules can not bring simultaneously their principal axis on the same edge without overlapping. The formula (3) gives $Z^N = Z_0^N[1 + \varepsilon(3)]^N$ ($n = 3$ for a c.f.c.) with $Z_0 = 24 \times 0.817 = 19.622$ (which represents, in a way, the effective orientations number) and $\varepsilon(3) = 5.12\ 10^{-4}$; i.e. $\Delta S_{\mathrm{conf}} = 5.917$ e.u. So the corresponding $\Delta S_{\mathrm{corr}} = 0.40$ e.u. while the experimental ΔS_T is 8.655 e.u. This shows that the correlations are, here, less restrictive than in succinonitrile.

* Nagle has shown that Z^N could be evaluated by the weak graph method in the case of a dimers assembly.[2] We know now a crystal whose plastic phase (c.f.c.) is a disordered assembly of dimers: the pivalic acid.[8] The experimental increment of entropy is $\Delta S_T = 6.07$ e.u. It is interesting to know exactly what is the part of entropy which is due to the dimers formation. Each monomer can take twelve orientations. The hydrogen bonds lie along the two-fold axis. Because the measured density of monomers is quasi null we have $Z^N = (12 \times 0.178)^N$ i.e. $\Delta S_{\mathrm{conf}} = 1.5276$ e.u. This proves that the orientational disorder of monomers and the correlations due to hydrogen bonds can not justify alone $\Delta S_T^{\mathrm{exp}}$. Over and above the vibrations of the whole molecule, the difference could arise from the character of the hydrogen bond and from the position of the $(CH_3)_3$ groups.

III THE KIRKWOOD DIELECTRIC CORRELATION FACTOR: g_k

Because the free energy of a polar crystal in presence of an electric field is expressed by:

$$F(E) = F(E = 0) - \frac{N\mu E g_k}{2} \langle \cos\theta \rangle$$

where $\theta = (\boldsymbol{\mu}, \mathbf{E})$, we can evaluate g_k from $Z(E)$, the partition function in presence of an electric field.[9] The weak graph method can be still used, if each state S_i is weighted by a Boltzmann factor: $b(S_i) = e^{\beta \mu_i \mathbf{E}}$. Then the formula (1) becomes:

$$Z(E) = \sum_{\{s\}} \prod_{\langle i, j \rangle}' A(S_i, S_j) \prod_i b(S_i)$$

and the closed weak graphs condition can be written now:

$$\sum_{S_j} C_{ij}(S_i) b(S_i) = 0.$$

This condition is very restrictive; if it cannot be used, all the graphs, including opened ones, must be taken into account, and consequently the serie converges more slowly. Here, the 0 order term represents the maximum disorder. This difficulty arises in the case of succinonitrile.[10] By limiting to the 2 order term we find: $g_k = 1 + 0.265 + 0.0415$. g_k is higher than 1; therefore steric hindrance imposes a local ordering tendency of ferroelectric type. This result is in accordance with the conclusions issued from experiment ($g_k = 1.87$).

IV CONCLUSION

The strong correlations (steric hindrance, hydrogen bonds, ...) often occur in plastic crystals. Our study shows that the weak graph method is a very suitable way to know exactly their importance: by use of it, it is easy to evaluate their contribution to the transition entropy and to the dielectric constants. We prove, by this way, that it would be wrong to neglect them. Furthermore, this method leads to an accurate value of the orientational conditional probabilities. So, as we have shown elsewhere,[5] we can explain the X-ray scattering modulations, induced by steric hindrance in reciprocal lattice.

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