

# VIBRATIONAL SPECTRA OF CONFORMATIONALLY IMPURE POLYMERS

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## ABSTRACT

The present status of understanding of the vibrational spectra (infra-red, Raman and neutron scattering) of organic polymers considered as structurally disordered systems is reviewed and discussed. The limitations of the results obtained from the study of polymers as translationally symmetrical systems are pointed out and one of the possible theoretical techniques for the analysis of disordered polymers is presented. It is pointed out that numerical methods are suitable for handling these rather complicated organic molecules and do not require the assumption of structural simplifications which may obscure the real physics of the phenomenon and the corresponding interpretation of the experimental results which are already available. The results obtained so far on polyethylene, polytetrafluoroethylene and hydrogen-bonded systems are discussed.

## 1. INTRODUCTION

In the past decade the main interest of vibrational spectroscopy of polymeric materials has been focused on the understanding of the finger-print region of the spectrum in terms of their molecular structure<sup>1-4</sup>. The largest source of experimental data has been the infra-red spectrum because of the high technological development of the commercial instruments and because of the relative ease in obtaining an infra-red spectrum. The recent availability of laser-Raman spectrometers has provided a sudden burst of experimental data on the Raman spectrum of polymers<sup>5</sup>. While all these data refer to the optical properties, the study of the inelastic coherent or incoherent scattering of neutrons (ICNS, IINS) from these materials has provided additional information on their lattice dynamics and bulk properties<sup>4, 6-8</sup>. The interpretation of these experimental data has been mainly carried out on the basis of an idealized molecular and crystalline model for which it has been assumed that: (i) the polymerization reaction has occurred in an ideal way, (ii) the polymer chain has taken up the most stable conformation as resulting from a balance of intra and inter-molecular forces, (iii) the consequent crystal lattice is perfectly organized. In addition to all these assumptions it has also been considered that the chain has infinite length.

The analysis of the experimental data has been carried out by a large number of authors who have followed three main approaches:

(a) Chemical analysis from group-frequency correlations. This study has proved to be very useful to the chemist in fundamental and practical applications in order chemically to characterize a polymer sample<sup>1, 9-11</sup>.

(b) Vibrational analysis using group theoretical methods. This approach

has provided valuable information on the structure (stereospecificity and conformation) of the molecular chain<sup>2, 12, 13</sup>. These types of studies have been complementary to x-ray diffraction studies even if sometimes some still unsettled disagreement has been found<sup>14</sup>.

(c) Theoretical treatment of the lattice dynamics.

No other class of organic crystals has been the subject of so thorough a treatment as have organic polymers. One of the peculiar reasons is that intra-chain forces of covalent type are at least one order of magnitude larger than inter-molecular (inter-chain) forces of Van der Waals type. In a first approximation the dynamics of one single polymer chain can then be considered neglecting the influence of the neighbouring chains<sup>4</sup>. Only in a second order approximation can inter-chain forces be taken into account from the few observed Davydov's splittings<sup>15-17</sup> or from the (so far unobserved for polymers<sup>18</sup>) static field splittings. Polymer chains can then be considered as 'one dimensional crystals'. This definition implies that we consider a translational symmetry only along the axis of the polymer chain even allowing all the degrees of freedom on three dimensions.

The lattice dynamical treatment is then restricted to the study of phonon waves propagating along the chain axis. Since at the beginning only the optical spectrum was available calculations were restricted to  $k = 0$  modes<sup>19-22</sup>. The more recent availability of phonon dispersion curves from inelastic coherent neutron scattering experiments<sup>18, 23-24</sup> and of vibrational density of states<sup>25</sup> from inelastic incoherent neutron scattering experiments has pushed various workers to predict or to verify the dispersion of phonons by a complete lattice dynamical calculation throughout the whole one-dimensional Brillouin zone<sup>4, 26-31</sup>. Theories were proposed and translated into suitable computer programmes which allowed workers to carry out several calculations on the simplest and basically most important polymers. Calculations were also extended to three-dimensional lattices in order to account for Davydov's splitting, for vibrational density of states and dispersion curves for phonons propagating along and across the chain axis<sup>8, 18, 32</sup>.

The main contribution given by the studies described in section c is to be able to give a comprehensive interpretation of a large set of experimental data and to derive dynamical properties for the understanding of thermodynamical or mechanical properties of these materials. No relevant structural information was derived from these theoretical treatments. However, the availability of theoretical methods has opened new fields in polymer dynamics which we are going to discuss in this paper.

## 2. PERFECT POLYMERS

The basic starting point of the theoretical treatment is the existence of a translational periodicity or translational symmetry of the lattice which allows us to write the dynamical matrix of the lattice in terms of the properties of the atoms of the unit cell only, thus reducing the complexity of the treatment.

Since we are going to adopt in our discussion mainly the Wilson's type

internal displacement coordinates<sup>3,3</sup>, well known to the chemist, let us write the few basic equations to which we shall refer throughout this paper.

We repeat here, for the sake of clarity, the basic theory we have developed and already presented elsewhere<sup>30</sup> for the case of three-dimensional crystals. The reduction to one-dimensional crystals is obvious.

Let us briefly introduce the internal coordinates in the case of the perfect lattice. Let  $n_1, n_2$  and  $n_3$  label each unit cell and let  $n$  indicate any given triplet. The  $n$ th unit cell contains  $N$  atoms whose vibrations can be described by  $3N$  Cartesian coordinates collected in the vector  $\mathbf{x}_n$  or by  $3N$  independent internal coordinates collected in a vector  $\mathbf{r}_n$ . Let  $\mathbf{t}_n$  be the vector which locates the  $n$ th unit cell from a suitably chosen origin. The internal phonon coordinates  $\mathbf{R}(\mathbf{k})$  can be defined as

$$\mathbf{R}(\mathbf{k}) = (1/\sqrt{2\pi}) \sum_{-\infty}^{+\infty} \mathbf{x}_n \exp(-i\mathbf{k} \cdot \mathbf{t}_n) \quad (1)$$

where  $\mathbf{k}$  is the wave vector in reciprocal space.

The potential energy of the crystal can be expressed as

$$2V = \int \tilde{\mathbf{R}}(\mathbf{k}) \mathbf{F}_R(\mathbf{k}) \mathbf{R}(\mathbf{k}) d\mathbf{k} \quad (2)$$

where the integration is extended over the entire first Brillouin zone. It can be shown that in equation 2  $\mathbf{F}_R(\mathbf{k})$  takes the form

$$\mathbf{F}_R(\mathbf{k}) = \mathbf{F}_R^0 + \sum_s \tilde{\mathbf{F}}_R^s \exp(-i\mathbf{k} \cdot \mathbf{t}_s) + \mathbf{F}_R^s \exp(i\mathbf{k} \cdot \mathbf{t}_s) \quad (3)$$

where  $\mathbf{F}_R^0$  is the matrix of the force constants relating coordinates within the same cell;  $\mathbf{F}_R^s$  is the matrix of the force constants relating the coordinates of two cells  $s$  units apart.

Even if the dynamical matrix of the perfect crystal can be written in terms of the  $\mathbf{R}(\mathbf{k})$  using equation 3 and a proper metrical tensor  $\mathbf{G}_R(\mathbf{k})$ , we prefer in this case to express it in terms of the usual Cartesian phonon coordinates

$$\mathbf{X}(\mathbf{k}) = (1/\sqrt{2\pi}) \sum_{-\infty}^{+\infty} \mathbf{x}_n \exp(-i\mathbf{k} \cdot \mathbf{t}_n) \quad (4)$$

We must then look for the transformation matrix  $\mathbf{B}(\mathbf{k})$  relating the Cartesian phonon coordinates to the internal ones. Using Wilson's technique the internal coordinate vector  $\mathbf{r}_n$  can be expressed as

$$\mathbf{r}_n = \mathbf{B}_{-l} \mathbf{x}_{n-l} + \dots + \mathbf{B}_1 \mathbf{x}_{n-1} + \mathbf{B}_0 \mathbf{x}_n + \mathbf{B}_1 \mathbf{x}_{n+1} + \dots + \mathbf{B}_l \mathbf{x}_{n+l} \quad (5)$$

$$= \mathbf{B}_0 \mathbf{x}_n + \sum_l^m (\mathbf{B}_{-l} \mathbf{x}_{n-l} + \mathbf{B}_l \mathbf{x}_{n+l}) \quad (6)$$

where  $\mathbf{x}_{n+l}$  indicates the Cartesian coordinate vector of a unit cell,  $l$  units distant from the  $n$ th cell.  $\mathbf{B}_l$  is the corresponding transformation matrix between  $\mathbf{r}_n$  and  $\mathbf{x}_{n+l}$ . Substitution of equation 6 into equation 1 and taking account of equation 4 gives

$$\mathbf{R}(\mathbf{k}) = \sum_{-m}^m \mathbf{B}_l \exp\{-i\mathbf{k} \cdot \mathbf{t}(l)\} \mathbf{X}(\mathbf{k}) \quad (7)$$

from which the desired transformation matrix  $\mathbf{B}(\mathbf{k})$  can be derived:

$$\mathbf{B}(\mathbf{k}) = \sum_{-m}^m \mathbf{B}_l \exp \{ -i\mathbf{k} \cdot \mathbf{t}(l) \} \quad (8)$$

We can now express the potential energy in Cartesian coordinates in terms of the potential energy in internal coordinates as:

$$\mathbf{F}_x(\mathbf{k}) = \tilde{\mathbf{B}}(\mathbf{k})\mathbf{F}_R(\mathbf{k})\mathbf{B}(\mathbf{k}) \quad (9)$$

from which the dynamical matrix is derived

$$\mathbf{D}(\mathbf{k}) = \mathbf{M}^{-\frac{1}{2}}\mathbf{F}_x(\mathbf{k})\mathbf{M}^{-\frac{1}{2}} \quad (10)$$

$\mathbf{M}$  being the diagonal matrix of the masses.

The  $3N$  dispersion curves for a given crystal can be obtained numerically from the solution of the eigenvalue equation

$$[\mathbf{D}(\mathbf{k}) - \omega^2(\mathbf{k})\mathbf{I}]\mathbf{L}_x(\mathbf{k}) = 0 \quad (11)$$

once the force field  $\mathbf{F}_R$  is numerically known. The eigenvectors  $\mathbf{L}_x(\mathbf{k})$  can also be obtained from the solution of equation 11. Throughout this paper it will be assumed that the force field in internal coordinates is well known†.

The previous theory has been applied by us or by other authors to several polymeric materials. The reader is referred to the corresponding literature for a detailed discussion of the results and of the problems still left unsolved for each particular polymer molecule.

With the availability of large and fast computers calculations have been extended to more and more complicated cases. While the lattice dynamics of perfect polyethylene and polyoxymethylene can at present be considered satisfactorily known<sup>4, 8</sup>, isotactic polypropylene, polyvinyl chloride and several other basic polymers still require further studies. Recently calculations have been extended to models of polypeptides in order to tackle in a more quantitative and detailed way the extremely difficult problem of biopolymers<sup>34-36</sup>. We now consider it useful to make a few general comments:

(1) Because of the large number of atoms per chemical repeating unit the number of phonon dispersion branches becomes extremely large. In practice a continuous set of phonon waves can be transmitted by the polymer throughout the whole frequency range from 0 to approximately  $1800 \text{ cm}^{-1}$  with very little or no energy gaps.

(2) Several attempts have been made to reduce the difficulty of the problem by reducing the complex polymer chain to a model of the most meaningful point masses<sup>34-35</sup>. The results of these types of studies should be treated with great caution since the reduction to a point mass model in general forcefully neglects dynamically important variables thus altering the validity of the derived conclusions. The discrepancy of the results of the studies of solid hydrogen-bonded polymers like methanol<sup>37-39</sup> and ice<sup>40-44</sup> can be taken as typical examples.

(3) Several phonon branches are calculated to be independent of  $k$  for

† For a critical discussion on force fields for polymers, see ref. 4.

the following main reasons: (i) strong covalent forces do not allow strong couplings between neighbouring oscillators, (ii) groups of atoms in side-chains are dynamically uncoupled (either through potential or kinetic energy) between each other.

(4) When forces become weaker (this generally occurs for bending and torsional motions) a large dispersion takes place and phonons belonging to the same symmetry species for a given  $k$  couple giving rise to non-crossing between phonon branches with the consequent mixing of the various oscillators. An overall description of the modes derived from potential energy distribution<sup>45</sup> becomes then impracticable. It has to be pointed out, however, that the symmetry of polymer chains is high only for very simple systems (e.g. polyethylene, tellurium, selenium, polyoxymethylene, polytetrafluoroethylene) when considered at the  $\Gamma$  point. The symmetry of phonons for  $k \neq 0$  is much lowered for most of the cases.

### 3. IMPURE AND DISORDERED POLYMERS

We wish to treat here in more detail the problem of the lattice dynamics of polymeric materials when some sort of defect or disorder is introduced into the chain.

It is now of common knowledge that the idealized model of a polymer chain is only a very rough approximation of the real polymer. Through several independent physicochemical techniques the presence of amorphous or irregular or disordered material in a solid sample of a given polymer has been proved<sup>46-49</sup>. The various types of defects which can possibly occur in a polymer have already been discussed<sup>50</sup>; they can then generally be collected into four main classes: *chemical defects* (isotopic substitution, switching of the direction of insertion of the monomer unit into the chain, chain branching, crosslinking); *conformational defects* (chain folding, kinks, jogs); *stereochemical defects* (different tacticity) and *packing defects* (amorphous phase, lack of three-dimensional order).

The vibrational spectrum (infra-red, Raman and neutron scattering) shows several non-negligible and sometimes very prominent features which should be interpreted as arising from the imperfect part of the chain. The analysis of these extra features can be carried out in two ways, namely on qualitative grounds using empirical spectral correlations<sup>51</sup> or by a quantitative approach based on lattice dynamical calculations. While the former approach has been widely adopted in industrial laboratories for a quick and qualitative characterization of a polymeric material<sup>11</sup>, we have recently carried out some studies based on a detailed quantitative approach<sup>52-56</sup>.

The dynamical quantities from experiments or calculation on the perfect lattice which we consider of basic importance for a quantitative study of the problem of real polymers are the following:

- phonon dispersion curves,  $\omega(k)$ ;
- optical phonon frequencies,  $\omega(k = 0)$ ;
- optical phonon intensities,  $I(\omega)$ ,  $\omega(k = 0)$ ;
- one phonon density of states,  $g(\omega)$ ;

amplitude weighted one-phonon density of states,  $g(\omega)^A$ ;  
 dipole or polarizability weighted density of states,  $g(\omega)^\mu$ .

As will be discussed in this paper some of the dynamical quantities just mentioned can be obtained readily from a standard lattice dynamical calculation on *perfect one-dimensional* or three-dimensional polymeric materials using equations 1 to 11. A few require more careful consideration and are now the subject of extensive studies in our laboratory. The  $I(\omega)$  determine the appearance of the optical spectrum and are influenced by the symmetry of the system. The higher the symmetry the more strict are the operative optical selection rules and thus substantially simplify the optical spectrum (e.g. polyethylene<sup>28</sup>).  $\omega(k)$ ,  $g(\omega)$ ,  $g(\omega)^A$  mainly determine the experimental results from neutron scattering experiments on single crystals, on stretch-oriented or on polycrystalline materials.

The introduction of some sort of defect into the model modifies the dynamics of the system to an extent depending on the concentration of defects and on their coupling with the host lattice or with neighbouring defects. Several efforts have been variously made by many authors for the analytical treatment of the effect of a defect on the dynamics of a defect-containing lattice. The basic concept is to treat the perturbation to the dynamics of the perfect lattice by the defects using the Green's function method<sup>57-59</sup>. The basic limitation of this method is that the lattice should be quite simple, the defect perturbation be small (e.g. isolated mass and force constant defects) and their concentration small such that the defects cannot interact. The results of these analytical treatments have been mainly applied and verified in the case of simple inorganic crystals<sup>60, 61</sup>.

One of the peculiar features of polymeric systems is that the concentration of defects is generally high and the defects entail changes of geometry and force constants throughout several atoms along the chain. One thus moves from an *impure* system to a disordered one. It then becomes impossible to apply the Green's function method to real polymeric systems and numerical methods must be developed for this purpose<sup>62, 63</sup>.

The main reason why a numerical method becomes useful is that a quantity of direct physical meaning required from such dynamical systems is the density of vibrational states  $g(\omega)$ . While the knowledge of a single eigenvalue may be of no use or only very rarely required, the knowledge of the whole vibrational spectrum is compulsory for the understanding of the physical quantities related to vibrations. On the same grounds it is not essential to derive the complete set of eigenvectors but one may need only a few which may be essential in the analysis of the experimental data such as infra-red, Raman and neutron scattering spectra.

The numerical method based on the Negative Eigenvalue Theorem (NET) we are going to discuss allows the direct calculation of  $g(\omega)$  at any desired accuracy thus reaching, if necessary, that of a single isolated eigenvalue. Approximate or exact eigenvectors can also be obtained by the so-called 'inverse iteration method'. The NET was introduced first by Dean *et al.*<sup>63</sup> who treated the vibrations of several disordered systems in this way.

Let us describe briefly the main lines of the procedure. We wish to compute the number  $n(\omega_2 - \omega_1)$  of eigenvalues of the  $3Np \times 3Np$  dynamical matrix  $D$  which lie in the interval  $(\omega_1, \omega_2)$  where  $\omega_1$  and  $\omega_2$  are positive real numbers

such that  $\omega_2 > \omega_1$ . The number  $n(\omega_2 - \omega_1)$  is given by

$$n(\omega_2 - \omega_1) = \eta(\mathbf{D} - \omega_2 \mathbf{I}) - \eta(\mathbf{D} - \omega_1 \mathbf{I}) \quad (12)$$

where  $\mathbf{I}$  is the  $3Np \times 3Np$  unit matrix and  $\eta(\mathbf{D} - \omega_i \mathbf{I})$  is the number of negative eigenvalues of the matrix

$$\mathbf{D}_i = \mathbf{D} - \omega_i \mathbf{I} \quad (13)$$

The computation of the negative eigenvalues of  $\mathbf{D}_i$  is performed by a particular partitioning of  $\mathbf{D}_i$ , which applies to any symmetrical matrix. This is particularly convenient since  $\mathbf{D}$  has a codiagonal form.

The NET states that, given a symmetrical matrix  $\mathbf{M}$  of dimensions  $r \times r$ , partitioned as follows

$$\mathbf{M} = \begin{bmatrix} \mathbf{A}_1 & \mathbf{B}_2 & & \bigcirc \\ \tilde{\mathbf{B}}_2 & \mathbf{A}_2 & \mathbf{B}_3 & \bigcirc \\ & \bigcirc & & \\ & & & \tilde{\mathbf{B}}_k & \mathbf{A}_k \end{bmatrix} \quad (14)$$

where  $\mathbf{A}_i$  has dimensions  $r_i \times r_i$

$\mathbf{B}_i$  has dimensions  $r_{i-1} \times r_i$

and  $\sum_{i=1}^k r_i = r$

then the number  $\eta(\mathbf{M} - x\mathbf{I})$  of negative eigenvalues of the matrix  $\mathbf{M} - x\mathbf{I}$  is given by

$$\eta(\mathbf{M} - x\mathbf{I}) = \sum_{i=1}^k \eta(\mathbf{U}_i) \quad (15)$$

where

$$\begin{aligned} \mathbf{U}_i &= \mathbf{A}_i - x\mathbf{I}_i - \tilde{\mathbf{B}}_i \mathbf{U}_{i-1}^{-1} \mathbf{B}_i \\ \mathbf{U}_1 &= \mathbf{A}_1 - x\mathbf{I}_1 \end{aligned} \quad (16)$$

The particular partitioning we perform on  $\mathbf{D}_i$  is the following. Let  $\mathbf{D}_i^{(1)}$  denote the matrix  $\mathbf{D}_i$  partitioned as

$$\mathbf{D}_i^{(1)} = \begin{array}{cc} \mathbf{X}_1 & \mathbf{Y}_1 \\ \tilde{\mathbf{Y}}_1 & \mathbf{Z}_1 \end{array} \quad (17)$$

where  $\mathbf{X}_1$  is a  $1 \times 1$  matrix

$\mathbf{Y}_1$  is a  $1 \times (3Np - 1)$  matrix

$\mathbf{Z}_1$  is a  $(3Np - 1) \times (3Np - 1)$  matrix

Then from equation 15, one has

$$\eta(\mathbf{D}_i) \equiv \eta(\mathbf{D}_i^{(1)}) = \eta(\mathbf{X}_1) + \eta(\mathbf{D}_i^{(2)}) \quad (18)$$

$$\mathbf{D}_i^{(2)} = \mathbf{Z}_1 - \tilde{\mathbf{Y}}_1 \mathbf{X}_1^{-1} \mathbf{Y}_1 \quad (19)$$

One can continue the process as indicated in equation 19 for  $3Np - 1$  times until one reaches the result that

$$\eta(\mathbf{D}_i) = \sum_{j=1}^{3Np} \eta(\mathbf{X}_j) \quad (20)$$

This particular partitioning avoids inversion of matrices because each  $\mathbf{X}_i$  is a  $1 \times 1$  matrix. The time for computing each  $\mathbf{D}_i^{(k)}$  is lowered by the fact that the row matrix  $\mathbf{Y}_{k-1}$  entering in its definition has only  $C - 1$  non-zero elements where  $C$  is the number of codiagonals of  $\mathbf{D}$ ; thus the elements of  $\mathbf{Z}_i$  which are modified by equation 19 are only those lying in its first  $(C - 1)$  rows and columns<sup>†</sup>.

The intervals  $(\omega_1, \omega_2)$  can be restricted to any desired accuracy. For comparison of the calculated  $g(\omega)$  with the spectra it is enough to use

$$\omega = \omega_2 - \omega_1 = 5 \text{ cm}^{-1}$$

but for the computation of eigenvectors a more precise knowledge of the approximate eigenvalues is required. For this purpose the interval  $d\omega = \omega_2 - \omega_1$  in the region of the spectrum where we wish to know the eigenvectors is restricted more and more until  $d\omega$  contains only one eigenvalue. Let us call  $\bar{\omega}_i$  the value  $\frac{1}{2}(\omega_2 - \omega_1)$  and  $\omega_i$  the (unknown) exact eigenvalue of  $\mathbf{D}$  occurring in  $d\omega$ . The procedure applied to compute  $\omega_i$  ensures that

$$\omega_i - \bar{\omega}_i < \omega_k - \bar{\omega}_i \quad (21)$$

where  $\omega_k$  is any other exact eigenvalue of  $\mathbf{D}$ . For computing the eigenvector  $\mathbf{L}_i$  associated with  $\omega_i$  we now proceed with the 'Inverse Iteration Method'<sup>64</sup>. We choose an arbitrary trial  $3Np$  vector  $\mathbf{u}_0$  and construct

$$\begin{aligned} \mathbf{v}_1 &= (\mathbf{D} - \omega_i \mathbf{I})^{-1} \mathbf{u}_0 \\ \mathbf{u}_1 &= \mathbf{v}_1 / \max(\mathbf{v}_1) \end{aligned} \quad (22)$$

where  $\max(\mathbf{v}_1)$  denotes the element of largest modulus in  $\mathbf{v}_1$  and then repeat for a certain number of times  $s$  the two steps 22 of iteration. The rapidity of convergence of  $\mathbf{u}_s$  to  $\mathbf{L}_i$  (the true eigenvector) depends on the condition 21. Let us express the arbitrary vector  $\mathbf{u}_0$  by means of the complete set of eigenvectors  $\mathbf{L}_k$  of  $\mathbf{D}$

$$\mathbf{u}_0 = \sum_{k=1}^{3Np} \alpha_k \mathbf{L}_k \quad (23)$$

Then any step in equations 22 can be re-written, apart from a normalization factor,

$$\mathbf{u}_s = \sum_k \alpha_k (\omega_k - \bar{\omega}_i)^{-s} \mathbf{L}_k$$

Equation 21 ensures that the contribution of  $\mathbf{L}_k (k \neq i)$  to  $\mathbf{u}_s$  decreases with increasing  $s$ <sup>‡</sup>.

<sup>†</sup> The time required to compute a step of the histogram for  $g(\omega)$ , as given in equation 12, for a matrix  $\mathbf{D}$  with dimensions  $1800 \times 1800$  and 30 non-zero codiagonals is about 30 seconds on a UNIVAC 1106.

<sup>‡</sup> By comparison with the Jacobi method on  $120 \times 120$  matrices three iterations are enough to ensure convergence up to the sixth decimal place, when equation 21 is satisfied.



The use on computers of equation 20 is difficult because large matrices must be inverted. This difficulty can be avoided<sup>12</sup> by using the following decomposition of  $D - \bar{\omega}_i I$

$$D - \bar{\omega}_i I = \tilde{U} \Delta U \quad (24)$$

where  $U$  is an upper triangular matrix and the elements of the diagonal matrix  $\Delta$  are chosen in such a way that the diagonal elements of  $U$  are unity. By use of equation 24 each step in the iteration can be split into three equations

$$\begin{aligned} \tilde{U} Y_s &= \mathbf{u}_s \\ \mathbf{v}_{s+1} &= (D - \omega_i I)^{-1} \mathbf{u}_s & \Delta \mathbf{z}_s &= \mathbf{v}_s \\ \tilde{U} \mathbf{v}_{s+1} &= \mathbf{z}_s \end{aligned} \quad (25)$$

each of which is very easy to solve because of the particular form of the matrices involved†.

For a better understanding of the complicated pattern of motion of defect-containing lattices we usually compute also the eigenvectors on the basis of internal or group coordinates<sup>13</sup>.

### General remarks

$g(\omega)$  calculated with the above methods is the basic dynamical quantity to be used for the interpretation of the optical (infra-red and Raman) and neutron scattering experimental data. A direct comparison of  $g(\omega)$  can be carried out only with the density of states derived from IINS experiments since for unoriented samples there is no need to take into account polarization vectors (i.e. atomic displacements) and the Debye Waller factor can be considered a second order correction to the calculated spectrum.

The comparison with the optical spectrum requires the knowledge of the transition moment for each normal mode of such a complicated atomic system. The general concepts derived from the treatment of impure lattices<sup>60, 65</sup> can be applied also to polymers and can also be extended when the concentration of the defects becomes larger or the type of defect is such that the vibrational perturbation becomes sizeable. We neglect in this discussion the problem of *out-of-band* or *gap-modes* which, with certainty, occur in simple systems containing mass defects and concentrate our attention on defects of geometry. A detailed discussion of the problem of a large concentration of mass defects has been presented in detail elsewhere for the case of isotopic mixed crystals<sup>66, 67</sup>.

For the case of organic polymers geometrical defects are more important and have been the subject of several published works.

As already pointed out in section 2 of this paper for organic polymers, even in a perfect state, the whole energy range from  $0 \text{ cm}^{-1}$  to the near infra-red region is practically covered in a continuous way by dispersion curves. Any extra mode arising from a defect introduced in the perfect host chain will be coupled to the phonons of the host lattice by an extent depending

† The time required to compute an eigenvector of a matrix  $900 \times 900$  with 30 codiagonals on UNIVAC 1106 is about seven minutes.

on the dynamical conditions (geometry and potential). We have then to consider only *resonance modes* and their dependence on concentration, on geometry and on force field.

For comparison with optical spectra we may use the following criteria:

*For a low concentration of defects: (Impure System)*

- (a)  $k = 0$  modes from the host lattice allowed by symmetry will be primarily observed.
- (b) Because of the breakdown of translational periodicity  $k \neq 0$  phonons from the host lattice will gain some spectral activity. The density of state of the host lattice will be somehow mapped in the optical spectrum.
- (c) Resonance modes of a particular defect may give rise to additional peaks which become characteristic of the defect and may be used for the diagnosis of the existence and concentration of such a defect in an unknown polymer sample.

Effects a to c can be predicted with fair certainty by the numerical calculations previously presented only if we are concerned with their frequency or shapes of modes. The knowledge of the optical transition moments which modulate the  $g(\omega)$  is still an unsolved problem which requires careful and extensive studies<sup>66,67</sup>. Most of the works so far carried out have explicitly assumed a dipole or polarizability unweighted density of states<sup>52-56</sup>. Comparison between optical intensity and height of the peaks in  $g(\omega)$  could not in principle be carried out. In a first approximation, however, it has been assumed that, since the geometry of an actual polymer sample is far from being ideal and a sizeable amount of disorder does exist, any restriction by symmetry is removed and all modes gain some activity. Hence coincidence between peaks in the spectrum and in the calculated  $g(\omega)$  can in a rough analysis be taken as positive coincidences<sup>50</sup>. Further works on model compounds and on simpler systems are required for substantiating the conclusions derived from the comparison of the optical spectrum with dipole or polarizability unweighted density of states.

When the concentration of geometrical defects increases the analysis must consider the problem of *disordered lattices*. The concept of resonance modes and phonons of the host lattice is lost and each normal mode becomes the result of a complex coupling between oscillators<sup>67</sup>. For such disordered systems the numerical method is the only one which can provide physically meaningful information from the calculated  $g(\omega)$  and the corresponding calculated amplitudes. If some sort of charge model is assumed spectral intensity can also be predicted<sup>66,67</sup>. For disordered polymers the following general criteria should be considered:

- (a) While the density of vibrational states of a disordered system cannot be compared in principle with that of the corresponding perfect lattice, some indication of residual order in the disordered network can still be derived by the experimental finding of  $g(\omega)$  peaks corresponding to the  $k = 0$  modes of the perfect lattice. The existence of quasi-phonon waves in quasi-ordered regions of a disordered lattice requires further experimental and theoretical studies. The main question which arises is the following: how large should an ordered cluster be to give rise to quasi-phonon waves? This problem is of particular importance for the understanding of the vibrational spectra of

co-polymers or block-polymers. It is well known that empirical, correlative or semiquantitative analysis of the vibrational spectrum has been the basic tool for the characterization of polymers and co-polymer structure and composition in applied and industrial research. These empirical studies require a more quantitative theoretical support.

(b) The study of lattice dynamics of disordered polymers acquires a particular importance in the field of vibrational spectroscopy of biopolymers. In fact the degree of ordering, the 'blockness' and the regularity of these substances is still a basic structural problem which needs to be clarified. Furthermore since most of these substances cannot be crystallized a large amount of disordered or irregular material is likely to exist.

(c) A relevant result from the numerical calculations based on NET is that the calculated histogram of the density of states often shows a fine structure or a large population of peaks. The identification of the origin of each peak through the calculation of the corresponding eigenvectors allows us to assign some of these peaks to islands or blocks or segments of particular dimensions<sup>67</sup>. Furthermore some of the peaks may turn out to be characteristic of a particular defect or of a cluster. If the experiments fit the calculation it is thus possible to probe with the vibrational spectrum the inside of the disordered material with regard to its structure, conformation and configuration. A clear example of 'island analysis' and its usefulness has been presented for a realistic case of isotopic mixed crystals<sup>67</sup>. The same kind of analysis has been carried out on models of three-dimensional lattices<sup>62</sup>. It has to be pointed out that no analytical treatment is able to provide such a detailed set of theoretical data to be compared with experiments.

(d) The possibility of such an 'island analysis' invites a yet unexplored theoretical treatment of co-polymers and block polymers.

#### 4. APPLICATIONS

##### **Polyethylene (PE)**

(1) The study of the infra-red spectra of copolymers of ethylene and deuteroderivatives of ethylene on the basis of the dynamics of mass disordered systems has unequivocally proved that the polymerization of ethylene with a Ziegler type catalyst occurs with the *cis* opening of the double bond<sup>52</sup>. Miyazawa had previously reached the same conclusion on somewhat weaker spectroscopic evidence<sup>68</sup>.

(2) The microstructure of solid PE, i.e. the conformation the chain takes up in the solid state, had been studied<sup>53</sup> with the methods previously discussed in this paper. While a very large amount of experimental and theoretical studies on the dynamics of a *perfect* model of PE has been carried out<sup>4, 8</sup> several non-negligible features in these spectra were left unexplained and qualitatively ascribed to the so-called 'amorphous' part of the polymer<sup>2</sup> which is known to exist even in the case of single crystals.

Since the solid state of a polymeric material is generally described as that of crystallites of various sizes non-homogeneously distributed and embedded in an amorphous substance<sup>46</sup> we have generated long planar zig-zag sequences of CH<sub>2</sub> units intermingled with regions of coiled or geometrically disordered chain segments. Such a structure has been translated into a

dynamical matrix built by appropriate mathematical devices<sup>53</sup>.  $g(\omega)$  was then derived using NET. The markovian structure of the chain has been accounted for by a proper choice of the 'allowed' geometrical defects, i.e. of the 'allowed' simplest combinations of the most common internal rotational angles. Geometrical defects of the types G, GTG, GTG', GTTG, GGTGG etc. were introduced into the polymer chain while all the other CH<sub>2</sub> units were held in T conformation. The following results were obtained:

(i) The existence of defects results in the activation in the Infra-red or Raman of several singularities in the  $g(\omega)$  of the host lattice which should be inactive for the perfect crystal. There is a general activation of all band modes.

Recently Gall *et al.*<sup>69</sup> have suggested an alternative explanation of the Raman band at  $1461\text{ cm}^{-1}$  which we have instead ascribed to the activation of a  $k = 0$  phonon only infra-red active for the perfect case. These authors suggest that the Raman line arises from two-phonon processes of the perfect lattice whose intensity is enhanced by some sort of Fermi resonance supposedly with the  $k = 0$  fundamental at  $1440\text{ cm}^{-1}$ . The interpretation suggested by Gall *et al.* does not account for the fact that the Raman line at  $1461\text{ cm}^{-1}$  depends on the content of amorphous material<sup>70</sup>.

(ii) Peaks of  $g(\omega)$  characteristic of specific defects of the disordered section of PE have been predicted and experimentally verified. Of particular interest are the two resonance modes at  $1350$  and  $1365\text{ cm}^{-1}$  assigned to GG + GTG and GTTG defects respectively. Their relative intensity changes with temperature, even before melting. It is thus possible to follow the thermal history of the sample (i.e. the structural evolution with temperature) of a solid sample of PE even before melting. It is then possible to have some indication that the melting process consists in an increase of concentrations of kinks and folds within the chain of the type GTG and GG or GTG' at the expense of all-*trans* of GTTG segments. This interpretation is also supported by additional theoretical and experimental evidence from infra-red and neutron scattering data in the lower energy region. As previously discussed in the spectrum of liquid PE it is possible to find indication of  $k = 0$  phonons of the perfect lattice thus indicating that the chains are not completely coiled in the liquid state but keep a certain degree of quasi order which generates quasi phonon waves.

(iii) It has been possible to extend the analysis to the case of single crystals grown from solution. The interpretation of the infra-red spectrum based on NET cannot disclaim the existence of some tight fold re-entry at the surface of the single crystal<sup>72</sup> (GGTGG fold) but supports the existence of additional disordered material confirming the so-called disordered or 'composite-fold' model<sup>47</sup>.

### On the far infra-red spectrum of liquid paraffins and nujol

The far infra-red spectrum of liquid octane, decane and hexadecane has been recently reported by Hall *et al.*<sup>73</sup>. The same authors report on the temperature dependence of the far infra-red spectrum of nujol from the liquid to the solid state. They observe a main band between  $250$  and  $300\text{ cm}^{-1}$  flanked by a weaker very broad band with maximum at  $\sim 150\text{ cm}^{-1}$ . Based on the fact that the spectrum of nujol decreases in intensity with

decreasing temperature these authors conclude that the observed far infra-red spectrum of liquid paraffins is mainly due to two-phonon processes. Support for their interpretation comes from calculations based on planar zig-zag chains of  $\text{CH}_2$  of various lengths with  $\text{CH}_2$  taken as a point mass. Summation processes are carried out and the intensity is calculated on the basis of two-phonon interaction theory by Lax and Burstein<sup>74</sup>.

From the results of our studies on geometrically disordered paraffins we wish to suggest an alternative explanation of the spectra of liquid paraffins and nujol and its temperature dependence. It is unlikely that paraffins in the liquid state keep the *trans* planar conformation assumed by the previous authors, but quite likely they are randomly coiled thus approaching the model of the disordered paraffins studied by us and discussed in the previous section. The density of states of the perfect long chain paraffin shows two cut-off frequencies at  $\sim 500$  and  $\sim 200 \text{ cm}^{-1}$  corresponding to the highest flat points of in-plane deformation and out-of-plane or torsional branches  $\nu_5$  and  $\nu_9$ . If a spectral activation of one-phonon transitions is accepted the very weak peak at  $\sim 150 \text{ cm}^{-1}$  is accounted for. The far infra-red spectrum of solid as well as liquid polyethylene shows two broad bands which we assign in a similar way to the two peaks of one-phonon density of states. The calculation of the density of states of all *gauche* polyethylene<sup>53</sup> in addition to two peaks at  $100$  and  $600 \text{ cm}^{-1}$  shows a broad strong peak centred at  $\sim 320 \text{ cm}^{-1}$  which is characteristic of G segments. We suggest that the absorption between  $250$  and  $300 \text{ cm}^{-1}$  observed by Hall *et al.* for liquid paraffins and nujol arises from *gauche* segments which are very likely to exist in the liquid phase. Unquestionable evidence of the introduction of other conformations in going from the solid to the liquid paraffin comes from the work by Schonhorn and Luongo<sup>75</sup> who observe that at the melting temperature a doublet at  $1350$  and  $1365 \text{ cm}^{-1}$  clearly appears in the infra-red. Just at the same frequencies we calculate resonance modes assigned to GG + GTG and GTTG segments. We then conclude that the infra-red peak of liquid paraffins and nujol between  $250$  and  $300 \text{ cm}^{-1}$  may arise from fundamental transitions coming from coiled sections of the paraffin molecules. The temperature dependence of the  $250 \text{ cm}^{-1}$  band of nujol can simply be accounted for as a continuous structural evolution of the paraffin mixture which tends to decrease the concentration of coiled chains by lowering the temperature. It should be pointed out that while solid polyethylene does not show any absorption in the  $300 \text{ cm}^{-1}$  region, molten polyethylene shows a peak at  $\sim 315 \text{ cm}^{-1}$  which we have already assigned to *gauche* or *quasi-gauche* segments<sup>53</sup>. The precise determination of the frequencies is not possible because (1) the force field is approximate, (2) the real conformation of liquid paraffin or polyethylene may not be precisely G ( $\pm 120^\circ$ ) but may take up slightly distorted values.

### **Polytetrafluoroethylene (PTFE); Spectrum and phase transitions**

From several physicochemical techniques it has been shown that solid PTFE may exist in different phases. The identification of the precise structure of these phases and the mechanism of the phase transition by x-ray n.m.r., dielectric and thermodynamical studies is somewhat confused and sometimes conflicting.

It is experimentally certain that PTFE has two main phase transitions at 19°C and 30°C. Some x-ray studies have established that below 19°C the PTFE chain coils into a translationally regular helix whose identity period of 16.8 Å contains 13 CF<sub>2</sub> groups in six turns<sup>76</sup>. Phase transitions are qualitatively ascribed to the onset of some structural disorder variously described by different authors<sup>77</sup>. Recent conformational studies<sup>78</sup> based on semi-empirical two-body interaction potentials predict that the most stable chain structure corresponds to a 13/6 helix with rotational angle of  $\tau = \pm 165.66^\circ$  in good agreement with the x-ray result. The two minima at +166° and -166° are divided by a very low potential barrier at  $\tau = 180^\circ$ . Other less stable minima are predicted at  $\sim \pm 91^\circ$  and  $\sim \pm 65^\circ$  corresponding to  $\sim 10/3$  and  $\sim 4/1$  helices respectively. Because of the very low potential barrier through  $\tau = 180^\circ$  Giglio *et al.*<sup>78</sup> tentatively suggest that above 19°C the chains might consist of a mixture of segments of left and right handed helices joined through bonds in *trans* conformation ( $\tau = 180^\circ$ ).

We have then recently treated<sup>55, 56</sup> the case of the disordered PTFE chain in the hope of contributing to the understanding of the structural features of this important polymer. Indeed the infra-red<sup>2</sup>, Raman<sup>79, 80</sup> and ICNS spectra<sup>18</sup> show several features which cannot be explained in terms of 13/6 or 15/7 helices.  $g(\omega)$  was calculated for perfect and conformationally disordered chains using NET. No dipole weighting has been performed, but consideration of intensity in the infra-red and Raman were taken into qualitative consideration in the comparison of the theoretical data with the experiments. From our studies the following conclusions were derived:

(i) At room temperature there exists a non-negligible amount of *trans*-planar segments as predicted from conformational energy calculations. The phase transition at 19°C corresponds to a sudden increase in concentration of *trans*-planar segments.

(ii) Evidence is found for the existence of another type of helix with geometry close to that of the 10/3 helix. No evidence is found for the existence of a helix with geometry close to 4/1.

(iii) Most of the spectral features which remained unexplained from a vibrational analysis based on perfect 13/6 or 15/7 models were accounted for.

(iv) The evidence of Davydov's splitting in the Raman lines claimed by Koenig *et al.*<sup>81</sup> and the consequent possibility of the existence of a unit cell containing more than one chain has been shown to be not unequivocal. Most of the temperature dependent doublets can be reasonably ascribed to a conformational equilibrium which changes with temperature.

(v) The recent additional data from coherent neutron scattering experiments<sup>18</sup> which could not be clearly explained in terms of a perfect 13/6 helix can be easily ascribed to segments of 10/3 helix which is likely to exist in most of the samples.

(vi) The disorder probed in PTFE by the vibrational spectrum is related only to that which occurs within the chain. Amorphous sections due to the lack of three-dimensional order only are not detected; contrary to what was previously assumed by many authors, no 'amorphous band' may be located in this way.

**Disordered hydrogen bonded systems**

The type of study so far discussed in this paper has been extended recently to the case of the simplest hydrogen bonded networks in the solid state namely to the cases of hydrochloric acid (HCl)<sup>67</sup>, ice<sup>43, 44</sup> and methanol<sup>39</sup>. It should be pointed out that an unequivocal understanding of the dynamics of these seemingly very simple systems is hindered by the fact that disordered phases may exist.

The combination of the analysis of the spectra based on perfect as well as disordered models has allowed a more detailed understanding of the spectrum of ice Ih<sup>43, 44</sup>. While Shawyer and Dean have already reported on the calculation by NET on a three-dimensional finite crystal of ice<sup>82</sup> we have carried out the lattice dynamical analysis on a complete perfect model which includes the hydrogen atoms and four molecules per unit cell. The works by previous authors were instead mainly based on highly simplified models<sup>40-42</sup>. On the basis of our theoretical calculations compared with the experiments the evidence claimed by other authors of the existence of long range electrostatic forces<sup>40</sup> cannot be accepted. In a similar way we cannot support the conclusions of the existence of fluctuating polar ordered domains<sup>41</sup> or of O—O bonds of different nature perpendicular and oblique to the *c*-axis of the ice crystal<sup>41-42</sup>.

In the case of solid methanol the phase transition between the  $\alpha$  phase stable below and a  $\beta$  phase above the transition temperature of 157.4 K have been studied. The combined results of CNDO, packing energy and lattice dynamical calculations<sup>39</sup> suggest that the  $\alpha$  phase is predominantly ordered and that the second order transition at 157.4 K is mainly caused by the onset of flip-flop motion of the CH<sub>3</sub> groups below and above the plane formed by the oxygen atoms. The structure of the  $\beta$  phase is disordered and accounts for several independent physicochemical measurements which were variously interpreted by several authors<sup>39</sup>.

**ACKNOWLEDGEMENTS**

I wish to express my gratitude to Dr M. Gussoni for her continuous help and for helpful discussions throughout the whole work on defects.

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