

Journal of Applied Physics

Volume 37, Number 11

October 1966

Selected Papers in High-Polymer Physics

The following eighteen papers were presented as part of the program of the Division of High-Polymer Physics at the meeting of The American Physical Society 28-31 March 1966, Durham, North Carolina

Effect of Chain Conformations on the Frequency Distribution of an Idealized Chain*

G. JANNINK AND G. C. SUMMERFIELD

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan

The frequency distribution of a simplified carbon skeleton chain is calculated for several conformations, given by successions of trans- and gauche structures in various orders. It is found that the phonon frequency distribution is sensitive to these orders. Validity of the model and use of the results are discussed.

I. INTRODUCTION

AN important characteristic of a large system of atoms is the phonon frequency distribution, that is, the number of vibrational normal modes per unit frequency interval. This function will reflect both the interatomic forces and the configuration of the atomic system.

This function is directly related to a number of measurable properties of an atomic system, for example, the specific heat¹ and the cross section for inelastic neutron scattering.²

When the atomic system is arranged in a regular lattice with a few defects, the frequency distribution can be determined fairly easily by using the method of Green's functions.³ The frequency distribution can also be computed by other methods⁴ when certain types of defects occur at many locations in the lattice, as for example, in a binary alloy.

Here we determine the dependence of the frequency

distribution on the conformation for a chain of atoms. The variation of infrared and Raman active modes as a function of conformation has been given for a number of models.⁵ The model of the chain which is considered here looks like the carbon skeleton of polyethylene with the following simplifying assumptions (Fig. 1): The "in-plane" motion is approximated by the superposition of three independent motions—two longitudinal motions of the even and odd rows, respectively, and one zigzag motion along C-C bonds. The "out-of-plane" motion is approximated by the superposition of two independent transverse motions of even and odd rows, respectively.

The angle of internal rotation ϕ_j is defined with respect to the plane of vertices, j , $j-1$, $j-2$. From the geometry of the figure we have

$$\cos\beta_j = 1 - \sin^2\alpha(1 - \cos\phi_j),$$

where 2α is the valence angle.

To each vertex j one associates a Cartesian coordinate system: The x axis joins the $j-2$ and j vertices, the y and z axes are, respectively, in and orthogonal to the j , $j-1$, $j-2$ plane.

The equations for the harmonic motion of the vertices

⁵ D. E. Witenhafer and J. L. Koenig, *Bull. Am. Phys. Soc.* **11**, 232 (1966).

* Work partially supported by the National Science Foundation.

¹ B. Wunderlich, *J. Chem. Phys.* **37**, 1203 (1962).

² W. Myers, G. C. Summerfield, and J. S. King, *J. Chem. Phys.* **44**, 184 (1966).

³ A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press, New York, 1963), pp. 137, 178.

⁴ P. Dean, *Proc. Phys. Soc. (London)* **73**, 413 (1959).

are written in internal coordinates. For the bending mode, the passage from Cartesian displacement x to internal displacement l is illustrated in Fig. 2. Similar transformations define s and t in:

$$\begin{aligned}
 m\ddot{l}_j &= -\gamma_6 \cos\beta_{j-2}l_{j-2} + 2\gamma_6 l_j - \gamma_6 \cos l_{j+2} \text{ (bending),} \\
 m\ddot{s}_j &= -\gamma_s \cos 2\alpha s_{j-1} + 2\gamma_s s_j - \gamma_s \cos 2\alpha s_{j+1} \text{ (stretching),} \\
 m\ddot{t}_j &= -\gamma_t |\cos\phi_{j-2}| t_{j-2} + 2\gamma_t t_j - \gamma_t |\cos\phi_{j+2}| t_{j+2} \\
 &\quad \text{(out of plane). (1)}
 \end{aligned}$$

A conformation is given by a sequence $\{\phi_i\}$, $i = 1, \dots, N$. The effect of a change in conformation is to modify the orientation of the interatomic forces; we assume, however, that the magnitude of binary interaction is invariant under changes in conformations. We consider two cases: (1) ϕ_i can have one of the two values, 0 or $\bar{\phi}$, and (2) ϕ_i can have any value in the interval $(0, 2\pi)$. In case (1) we expect results analogous to single mass defects and binary alloys. In case (2) we expect results similar to level distributions for a random matrix.⁶

When every ϕ_i is zero, the chain is extended. When only one element is different from zero, it is called singly folded. When more than one element is different from zero, it is called multiply folded.

II. CALCULATIONS FOR SINGLY FOLDED CHAINS

If $M_0(\omega^2) = A_0 - \omega^2 I$, where A_0 is the dynamical matrix of the extended structure with cyclic boundary

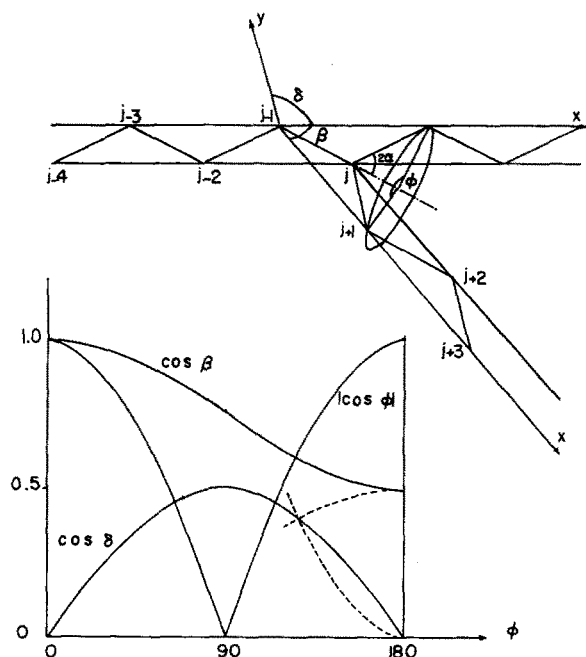


FIG. 1. Trans- and gauche conformations of the carbon skeleton for $2\alpha = 60^\circ$. The diagram at the bottom is the variation of force orientations as a function of internal rotation angle; the dotted lines are drawn symmetrically to $\cos\beta$ and $|\cos\phi|$, respectively, and intersect on the $\cos\delta$ curve.

⁶ C. E. Porter, *Statistical Theories of Spectra: Fluctuations* (Academic Press, New York, 1965), pp. 239, 298.

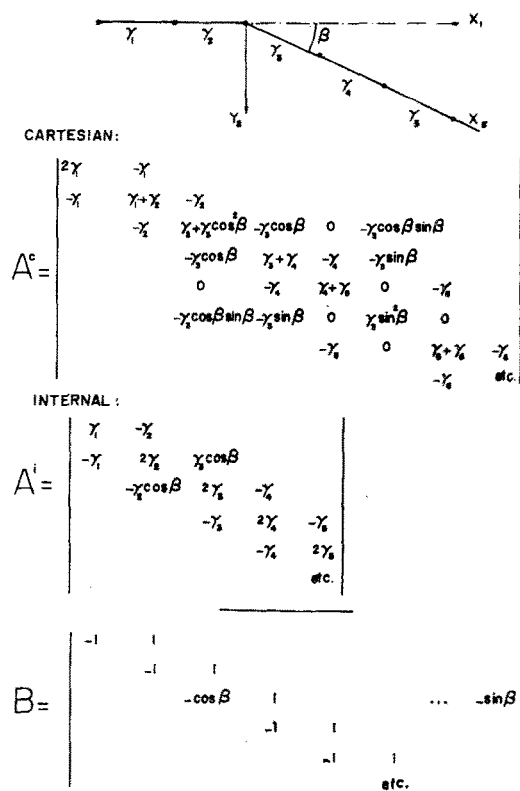


FIG. 2. Dynamical matrix in Cartesian and internal displacements coordinates for the bending motion. B matrix.

conditions, there corresponds to the singly folded chain a matrix M which, according to the Green's function method, is written as

$$M(\omega^2) = M_0(I + M_0^{-1}D).$$

The frequencies are the roots of

$$|I + M_0^{-1}(\omega^2)D| = 0. \tag{2}$$

In our approximation the "defect" matrix has the form

$$D = \begin{pmatrix} \dots & \vdots & \vdots & \dots \\ \dots & 0 & d_{j-1,j} & \dots \\ \dots & d_{j,j-1} & 0 & \dots \\ \dots & \vdots & \vdots & \dots \end{pmatrix}. \tag{3}$$

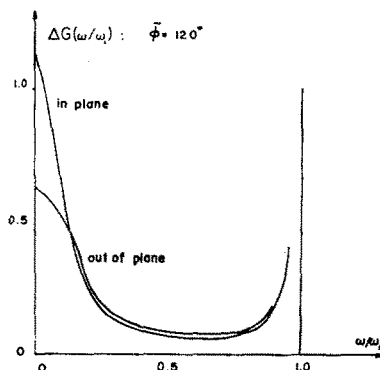
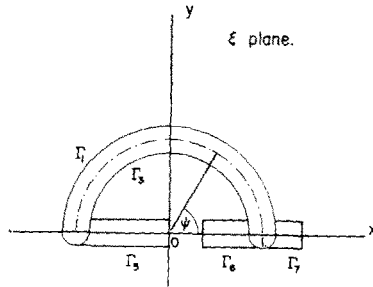


FIG. 3. Correction to the extended frequency distribution for a singly folded chain. The exact normalization of these curves is given by Eq. (7).

FIG. 4. Integration contour for Eq. (11).



For the bending mode:

$$d_{j-1,j} = d_{j,j-1} = \gamma_b(1 - \cos\beta_j).$$

For the transverse mode, this matrix element is

$$d_{j-1,j} = d_{j,j-1} = \gamma_t(1 - |\cos\phi_j|).$$

The stretch mode is not affected by changes in conformation in this model. The dependance of the stretch frequency on a valence-angle defect is given later. The elements of the matrix are the Green's function of the extended conformation; they are written:

$$M_{0ij}^{-1} = g(n), \quad n = |i - j|.$$

In this case,

$$g(n) = \begin{cases} \frac{\cotg N\theta/4}{2\gamma_b \sin\theta} \cos n\theta/2 - \frac{\sin |n|\theta/2}{2\gamma_b \sin\theta}, & n \text{ even} \\ 0, & n \text{ odd} \end{cases} \quad (4)$$

$$\sin^2\theta/2 = \omega^2/\omega_L^2; \quad \omega_L^2 = 4\gamma.$$

For the bending and out-of-plane modes, the frequency distribution for the extended structure is

$$G_0(\omega) = \sum_{mr} G_0^{mr}, \quad (5)$$

where m is the index of the mode (in and out of plane), and r is the index of the row (upper and lower).

$$G_0^{mr} = 1/\omega_L(1 - \omega^2/\omega_L^2)^{1/2}. \quad (6)$$

A single fold introduces a correction to the frequency distribution of the form:

$$\Delta G^{mr}(\omega) = f_{ms} G_0^{mr} - (\omega/N) [\delta(\omega^2 - \omega_2^2) + \delta(\omega^2)] + \begin{cases} 0, & \nu < 0 \\ \frac{2\omega(1+\nu)}{N} \delta\{\omega^2 - (\omega_2^2/2)[1 + (1+\nu/2)(1+\nu)^{-1}]\}, & \nu > 0, \end{cases} \quad (7)$$

so that the frequency distribution of a singly folded chain excluding the stretch mode is

$$G(\omega) = G_0 + \sum_{mr} \Delta G^{mr}, \quad (8)$$

TABLE I. Correspondence between ω and ξ .

ω^2	ξ	Contour
0 to $(\omega_L^2/2)(1 - \cos 2\alpha)$	$1/\cos 2\alpha \pm (1/\cos^2 2\alpha - 1)$ to 1	Γ_6, Γ_7
$(\omega_L^2/2)(1 - \cos 2\alpha \cos \psi)$ $(\omega_L^2/2)(1 + \cos 2\alpha)$ to ∞	$e^{i\psi}; 0 \leq \psi \leq \pi$ -1 to 0 ⁻	$\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$ Γ_5

where

$$f_{mr} = -(1 + \nu/2)\nu/N\pi [\nu^2 + 32(\omega^2/\omega_L^2)(1 - \omega^2/\omega_L^2)] \quad (9)$$

and

$$\nu = -\sin^2\alpha(1 - \cos\phi)[2 - \sin^2\alpha(1 - \cos\phi)]$$

for bending motion, and

$$\nu = \cos^2\phi - 1$$

for transverse motion. In all cases $\nu \leq 0$.

The effect of folding is to reduce the singularities of $G(\omega^2)$ at $\omega = 0$ and $\omega = \omega_L$, and to raise the frequency distribution in the central part of the $(0, \omega_L)$ interval (Fig. 3).

For the transverse mode, this effect reaches a maximum at $\phi = \pi/2$; the left and right branches move independently. For the bend mode the effect is greatest at $\phi = \pi$.

The effect of a valence-angle defect on the stretch mode is determined in a similar way; the defect matrix elements are

$$d_{j-1,j} = d_{j,j-1} = \gamma_s(\cos 2\alpha - \cos 2\alpha'),$$

where α' is the "defect" value.

Relations (2) and (3) remain valid. The Green's function, however, has an additional factor $\cos 2\alpha$ in the denominator which modifies the integration path given in Mahanty *et al.*⁷

The Fourier transform of the square frequency distribution is determined in this reference from

$$\Delta F(\alpha) = \int_c e^{i\alpha\omega^2 d} \ln |I + M_0^{-1}D|. \quad (10)$$

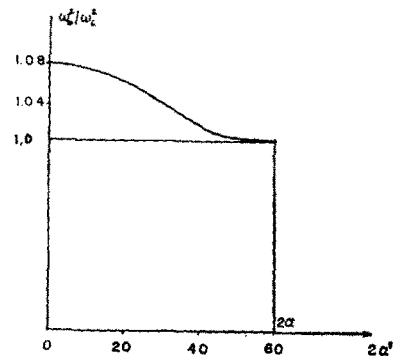


FIG. 5. Separation of the out-of-band stretching modes from the continuum as a function of valence-angle defect. See Eq. (14).

⁷J. Mahanty, A. A. Maradudin, and G. H. Weiss, *Progr. Theoret. Phys. (Kyoto)* **20**, 369 (1958).

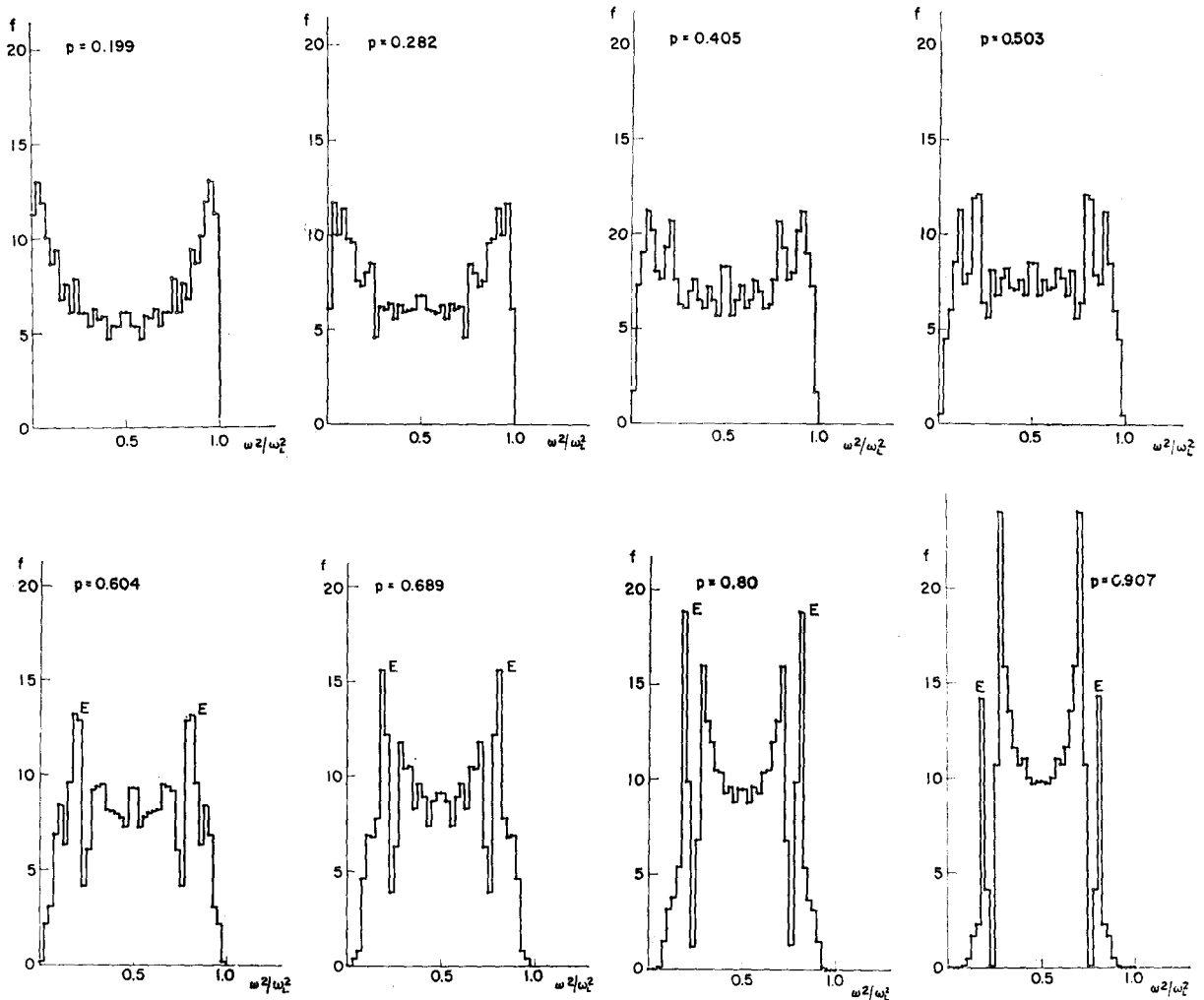


FIG. 6. Frequency distribution for several concentrations of randomly distributed gauche conformations.

The appropriate change of variable is here

$$\omega^2 = (\omega_L^2/4)[2 - \cos 2\alpha(\xi - \xi^{-1})]. \quad (11)$$

The correspondence is given in Fig. 4 and Table I.

The out-of-band mode above the continuum arises in the Γ_6 integration, and the out-of-band mode below the continuum arises in the Γ_6 integration. Thus the

Green's function is

$$g(n) = \begin{cases} -(1/\gamma_s \cos 2\alpha)[\xi^n/(\xi - \xi^{-1})], & |\xi| < 1 \\ -(1/\gamma_s \cos 2\alpha)[\xi^{-n}/(\xi^{-1} - \xi)], & |\xi| > 1. \end{cases} \quad (12)$$

The frequency distribution of the unperturbed chain is

$$G_{0s} = (\omega/\pi\omega_L^2)[\cos^2 2\alpha - (1 - 2\omega^2/\omega_L^2)^2]^{-1/2}. \quad (13)$$

The additional term due to the defect is

$$\Delta G_s(\omega) = fG_{0s} - \frac{\omega}{2N} \left\{ \delta \left[\omega^2 - \omega_L^2(1 + \cos 2\alpha) \right] + \delta \left[\omega^2 - \frac{\omega_L^2}{2}(1 - \cos 2\alpha) \right] \right\} \quad (14)$$

$$+ \begin{cases} 0, & \mu < 0 \\ \frac{2\omega(1+\mu)}{N} \left(\delta \left[\omega^2 - \frac{\omega_L^2}{2} [1 + \cos 2\alpha(1 + \mu/2)(1 + \mu)^{-1/2}] \right] + \delta \left[\omega^2 - \frac{\omega_L^2}{2} [1 - \cos 2\alpha(1 + \mu/2)(1 + \mu)^{-1/2}] \right] \right), & \mu > 0 \end{cases}$$

$$f = (1 + \mu/2)2\mu/N[\mu^2 + (8/\cos^2 2\alpha)][\cos^2 2\alpha - (1 - 2\omega^2/\omega_L^2)^2]$$

$$\mu = \cos^2 2\alpha' / \cos^2 2\alpha - 1. \quad (15)$$

Then the contribution to the frequency distribution from the stretch mode for a singly folded chain is

$$G_s(\omega) = G_{0s} + \Delta G_s.$$

For $\alpha' < \alpha$, the valence defect reduces the singularities at $(\omega_L/2)(1 \pm \cos 2\alpha)$. In the range $\alpha' > \alpha$, the singularities are "enhanced." Also, two out-of-band modes appear: one lower than the lowest, the other higher than the greatest unperturbed modes.⁸ The separations $(\omega_0/\omega_L)^2$ are given as a function of α' in Fig. 5.

III. CALCULATIONS FOR MULTIPLY FOLDED CHAINS

Our model includes only nearest-neighbor forces and we neglect interactions between modes. Consequently, the dynamical matrix for any conformation is in tri-diagonal form (Fig. 2). The eigenvalue distribution f of such matrices is known to be easily calculated by use of Sturm sequences. This method is explained in detail

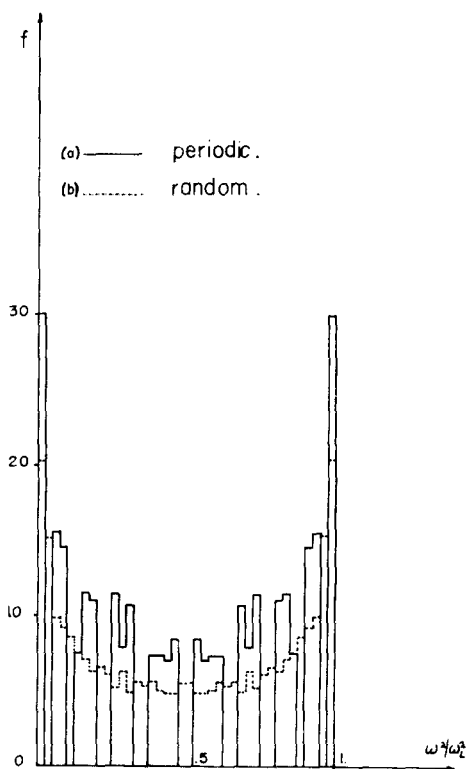


FIG. 7. Comparison of frequency distributions for (a) regularly spaced folds (ten $\phi_i = 0$ followed by one $\phi_i = 120^\circ$) and (b) a random distribution of 120° folds occurring with a frequency $p = 0.089$.

It is interesting to note that if we had used fixed, rather than cyclic, boundary conditions, we would have obtained two extra out-of-band modes. Both of these modes appear well separated from and below the continuum and they appear even for the extended conformation. Fixed boundary conditions correspond to an infinite mass defect; and it is well known⁹ that this defect does not produce out-of-band modes above the continuum. However due to the zigzag geometry, we have two modes below the continuum. If we use free boundary conditions, we get no extra out-of-band modes.

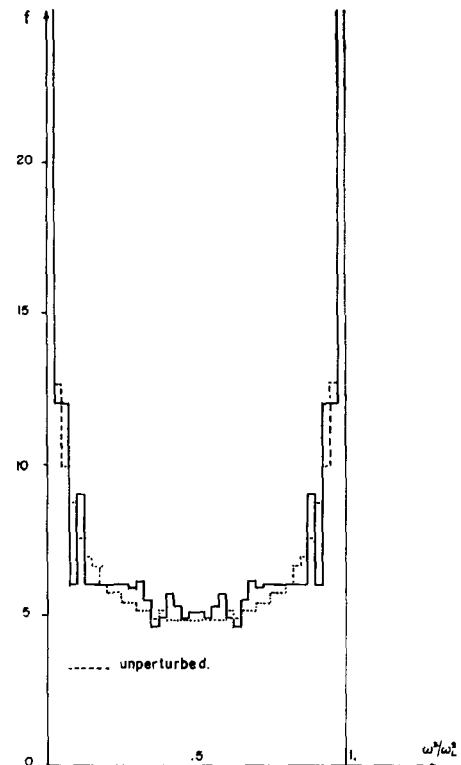


FIG. 8. Frequency distribution for a periodically folded chain one-hundred $\phi_i = 0$ followed by five $\phi_i = 120^\circ$.

elsewhere,⁴ and we do not go into the details of its application. However, it simply is a method of computing the number of eigenvalues of the dynamical matrix in an interval of the variable ω^2 , in terms of the principal determinants evaluated at the end points of the interval.

We first consider the case where ϕ_i takes one of the two values 0 and $\tilde{\phi}$; we chose $\tilde{\phi} = 120^\circ$, corresponding to "gauche" conformations. We define the concentration p as the number of internal rotation angles different from zero, divided by the total number of angles. We shall determine the frequency distribution of the transverse mode for various values of p . Another parameter is the order in which the ϕ_i are distributed along the chain; we have considered two extreme cases, namely, random and periodic distribution.

Figure 6 shows the spectrum for the out-of-plane mode for eight concentrations of gauche conformations, randomly distributed. We can recognize the inverse square law in the vicinities $p = 0$ and $p = 1$. Also recognizable is the occurrence of the sequences $\tilde{\phi}, \tilde{\phi}, \tilde{\phi}, 0, \tilde{\phi}, \tilde{\phi}, \tilde{\phi}$ in the diagrams for $p > 0.5$, by the peaks labeled E ; this is done according to the analysis of Ref. 4. It would be interesting to identify the island $0, 0, 0, \tilde{\phi}, 0, 0, 0$, and others by a similar technique.

The effects of ordered sequences of angles 0 and $\tilde{\phi}$ are shown in Figs. 7 and 8. In Fig. 7(a), we show the frequency distribution for the out-of-plane mode for repeated sequences of ten zero angles followed by one $\tilde{\phi}$. Comparing this to Fig. 7(b) for $p = 0.089$, we see that

there is a considerable difference between random and regular ordering of defects. This certainly suggests an investigation of the frequency distribution for Markov chains.

In Fig. 8, we show the out-of-plane frequency distribution for an ordered sequence of one-hundred zero angles followed by five $\phi=120^\circ$. This configuration should correspond to the folding of chains in crystallites. While there are differences between this frequency distribution and the frequency distribution for the extended chain, it seems unlikely that an experiment could be devised to measure the differences.

In Fig. 9, we show the frequency distribution for the out-of-plane and bending modes for a random distribution of the values of the ϕ 's in the interval zero to 2π . These frequency distributions are considerably different from both the ordered and disordered sequences of trans- and gauche angles. They also show a characteristic difference among themselves; this is to be expected since the matrix elements for in- and out-of-plane motions do not have the same dependence on the internal rotation angle.

IV. DISCUSSION

Using a simple model for the motions of the carbon skeleton of a polyethylene chain, we have computed the frequency distribution as a function of chain conformation. For this model there are variations in the frequency distribution that should be observable experimentally. For example, one could distinguish between certain conformations in the variation of the specific heat¹ or the neutron-scattering cross section.²

Our model is certainly too simple to describe the detailed nature of the frequency distribution as a function of chain conformation. However, the model does give the general features of the frequency distribution quite well for the extended chain. Certainly the ease with which calculations can be made for this model makes it at least a good starting point for more detailed and realistic calculations.

We have not attempted a detailed calculation of any measurable quantities such as the specific heat or neutron cross section. We have limited ourselves here to examining the variation of the frequency distribution for various chain conformations and, in particular, which of these should be differentiable experimentally.

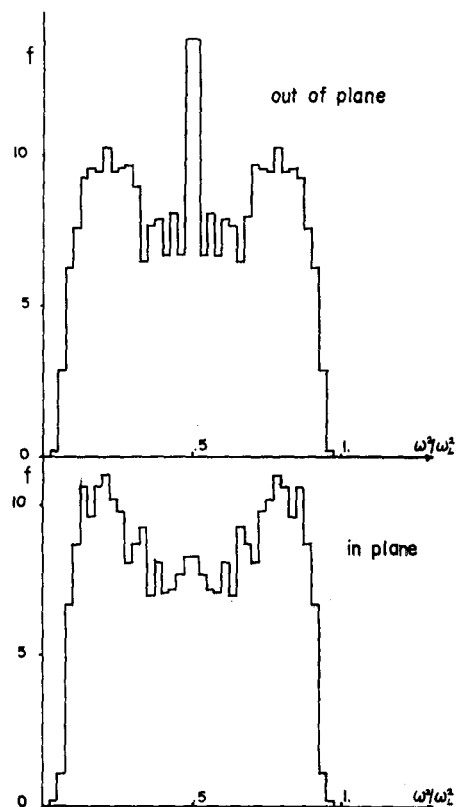


FIG. 9. Frequency distributions for in-plane bending and out-of-plane motions for a random distribution of angles in the range $(0, 2\pi)$.

From these results we would expect to find a measurable difference in the specific heats and neutron cross sections for certain conformations. In a future work, we will perform an analysis of neutron-scattering data and specific heats to distinguish between the various possibilities.

Insertion of the neglected interactions due to the folding itself may well modify the present results. Other effects such as change of magnitude of binary forces may also have a nonnegligible contribution.

However, we have shown that each conformation has a typical frequency distribution. If a more rigorous correspondence could be established between conformations and frequency distributions, it could help to decide such questions as structures of crystallite, amorphous, and intermediate regions.