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# Simple lattice-dynamical model of polymers

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A simple rigid-molecule model of polymer chains and crystals which utilizes the extended-point-mass (EPM) approximation is proposed for the analysis of normal mode vibrations of polymers. The EPM approximation introduces the concept of an effective size for the rigid molecular units and considerably simplifies the calculations of libration-libration and libration-translation force constants. The proposed model has been applied successfully to the lattice-dynamics calculations of polyethylene. The unknown force-constant parameters are determined from fitting the measurements of long-wavelength frequencies and the elastic constants. The model imposes restrictions on the relative values of normal-mode vibrations which make the present assignments of $\nu_5^b(0)$ and $\nu_7^b(0)$ frequencies unacceptable. The present calculations of polyethylene dispersion curves are the only calculations which exhibit the two features of symmetry about the $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and $\frac{1}{2}\overline{\frac{1}{2}}0$ points in the Brillouin zone as well as showing three acoustic dispersion branches. These features are not observed in any of the previous calculations of polyethylene dispersion curves.

## I. INTRODUCTION

The complexity of the lattice-dynamical analysis of a crystalline solid intensifies with increasing number of atoms in the primitive unit cell. Among crystalline solids, polymers present the most difficult situation because of their low symmetry and the large number of atoms per unit cell. For polymers, a Born—von Kármán-type[1] study based on atom-atom interactions would result in a very large number of force constant parameters which could make the calculations prohibitive or meaningless depending on the number of available experimental data and the procedure employed for fitting the force constants to observed properties.

A theoretical interpretation of the mechanical and thermal properties of crystalline polymers would be more successful if the model development utilizes simplifications available from the already known characteristics of inter- and intramolecular forces in a polymer crystal. The lattice dynamics of polymers would simplify considerably when the differences between the internal, external, and lattice modes of vibration are incorporated into the theoretical analysis. This three-tiered structure of forces in polymers essentially allows isolation of each group almost independently of the others and hence immensely simplifies the calculations.

For polymer crystals, because of stronger intrachain interactions, the normal modes of the isolated chain can be studied relatively independently of the low-frequency lattice modes. The intrachain frequencies consist of the two groups of external and internal modes of vibration. The external modes include translational and librational modes which involve rigid motions of the molecular units as a whole, and hence can be studied independently of the internal modes through a rigid-molecule approximation.

Normal mode vibrations in polymer crystals have not been investigated using a rigid-molecule approximation, and so far, the studies have utilized atom-atom interactions and Wilson's $F$ and $G$ matrix method.[2] Using this method, which becomes relatively complex for polymers and generally involves a large number of force constants, the lattice dynamics of polyethylene[3–5] and polytetrafluoroethylene[6] have been studied.

The rigid-molecule approximation[7] has been extensively and successfully applied to a number of molecular solids such as hexamethylenetetramine,[8,9] urea,[10] ammonium chloride,[11,12] and sodium azide.[13] Although the rigid-molecule approximation is a significant step from atom-atom interaction models in reduction of the number of force constants, it still involves the relatively difficult problem of calculating the libration-libration and libration-translation force constants of interacting rigid molecules. A further simplification of the rigid molecular treatment can be accompanied through the extended-point-mass (EPM) approximation[14] which expresses the libration-

libration and libration-translation force constants in terms of translation-translation force constants and a new parameter which relates to the effective sizes of the interacting rigid molecules.

In order to illustrate the special features of the EPM approximation as applied to polymer solids, we have elected to study polyethylene as an example. Polyethylene is the simplest polymer structure and hence becomes the ideal subject for demonstrating various characteristics of any theoretical model. The lattice dynamics of polyethylene, using Wilson's $F$ and $G$ matrix method, has been studied employing atom-atom interactions,[3] dipole-dipole interactions[4] and noncentral interaction potentials.[5] These calculations, in general, are complex and involve a relatively large number of parameters fitted to the observed frequencies.[15]

In this study we are presenting a rigid-molecule treatment of crystalline polymers based on the EPM approximation. The model calculations will consider lattice dynamics of polyethylene in order to illustrate various features of the model when applied to complex polymer structures. In Sec. II the EPM approximation is briefly introduced. Section III considers the lattice dynamics of an isolated polyethylene chain. In Sec. IV the force constants of the isolated chain and a two-parameter analytical interaction potential for intermolecular forces are used in the lattice-dynamics analysis of an orthorhombic polyethylene crystal. Section V includes discussion and concluding remarks.

## II. THEORETICAL MODEL

In a polymer crystal the molecular units, i.e., the combinations of atoms that can be treated as a rigid entity translating and librating as a whole, are designated by the index $k$ in unit cell $l$. Each molecule makes the displacement $\vec{u}(lk)$ and the librations $\vec{\theta}(lk)$ from its equilibrium configuration. Writing the force and torque equations for molecules of mass $m$ and moment of inertia $\underline{I}$, and assuming traveling wave solutions of $\omega(\vec{q})$ and wave vector $\vec{q}$, we get

$$\omega^2 \begin{bmatrix} \underline{m} & \underline{0} \\ \underline{0} & \underline{I} \end{bmatrix} \begin{bmatrix} \vec{U} \\ \vec{\Theta} \end{bmatrix} = \underline{D} \begin{bmatrix} \vec{U} \\ \vec{\Theta} \end{bmatrix}, \tag{1}$$

where $\underline{D}$ is the dynamical matrix defined by

$$\underline{D}(\vec{q},kk') = \sum_{l'} \underline{\phi}(l',kk') e^{i\vec{q}\cdot[\vec{r}(k)-\vec{r}(l'k')]} . \tag{2}$$

The dynamical matrix has the order of $6n \times 6n$ where $n$ is the number of molecules per unit cell. The force constant matrix $\underline{\phi}$ is of the form

$$\underline{\phi} = \begin{bmatrix} \phi_{xx} & \phi_{xy} & \phi_{xz} & \phi_{x\alpha} & \phi_{x\beta} & \phi_{x\gamma} \\ \phi_{yx} & \phi_{yy} & \phi_{yz} & \phi_{y\beta} & \phi_{y\beta} & \phi_{y\gamma} \\ \phi_{zx} & \phi_{zy} & \phi_{zz} & \phi_{z\alpha} & \phi_{z\beta} & \phi_{z\gamma} \\ \phi_{\alpha x} & \phi_{\alpha y} & \phi_{\alpha z} & \phi_{\alpha\alpha} & \phi_{\alpha\beta} & \phi_{\alpha\gamma} \\ \phi_{\beta x} & \phi_{\beta z} & \phi_{\beta z} & \phi_{\beta\alpha} & \phi_{\beta\beta} & \phi_{\beta\gamma} \\ \phi_{\gamma x} & \phi_{\gamma y} & \phi_{\gamma z} & \phi_{\gamma\alpha} & \phi_{\gamma\beta} & \phi_{\gamma\gamma} \end{bmatrix} \tag{3}$$

$$= \begin{bmatrix} \underline{\phi}^{(1)} & \underline{\phi}^{(2)} \\ \underline{\phi}^{(3)} & \underline{\phi}^{(4)} \end{bmatrix} , \tag{4}$$

where $\underline{\phi}^{(4)}$ is the libration-libration, $\underline{\phi}^{(3)}$ and $\underline{\phi}^{(2)}$ the libration-translation, and $\underline{\phi}^{(1)}$ the translation-translation force constants.

Using the EPM approximation, the expressions for the force constants become

$$\begin{aligned} \phi_{xy}(l',kk') &= \phi_{xy}(l',kk') , \\ \phi_{x\beta}(l',kk') &= \phi_{xy}(l',kk')\epsilon_{y\beta\nu}R_\nu(l'k'/k) , \\ \phi_{\alpha y}(l',kk') &= \phi_{xy}(l',kk')\epsilon_{x\alpha\nu}R_\nu(k/l'k') , \\ \phi_{\alpha\beta}(l',kk') &= \phi_{xy}(l',kk')\epsilon_{x\alpha\mu}\epsilon_{y\beta\delta} \\ &\quad \times R_\delta(l'k'/k)R_\mu(k/l'k') . \end{aligned} \tag{5}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol and $\vec{R}(lk/l'k')$ is the effective size of the molecular unit $lk$ located at the origin and interacting with molecule $l'k'$. Using the intrinsic symmetry in a crystalline structure, it can be shown that

$$\vec{R}(lk/l'k') = -\vec{R}(l'k'/lk) . \tag{6}$$

Calculations on hexamine[14] and $NaN_3$ (Ref. 13) have shown that for noncovalent bonding the assumption of hard-sphere contact provides satisfactory results for the determination of the effective molecular sizes. For polymer solids, we propose that the effective sizes of interacting molecules bonded by covalent forces be determined, using the assumption of hard-sphere contact, from the coordinates of the point halfway between the centers of mass of the interacting molecules. The effective size of a molecule depends on the orientation of the interacting molecules, and hence, is direction dependent. It can be shown that the number of effective size vectors of a rigid molecule varies directly with the number of its neighboring interactions.

The application of the EPM approximation to crystalline polymers will utilize the following two-tiered analysis based on the observed differences between internal, external, and lattice modes of vibration:

(1) The EPM approximation will be applied to selected rigid molecule units in the isolated chain and the force constants governing the librational and translational motions of the external modes will be calculated.

(2) The lattice dynamics of the crystalline polymer will be analyzed using the EPM approximation. The force-constant values of the isolated chain, determined previously, and a two-body interaction potential of Lennard-Jones form will be used for calculating the force constants of the polymer crystal. The interchain force constants are calculated from the Lennard-Jones potential using the relationship

$$\phi_{xy}(l',kk') = \left[-\delta_{xy} + \frac{r_x r_y}{r^2}\right]\frac{1}{r}\frac{dV}{dr} - \frac{r_x r_y}{r^2}\frac{d^2V}{dr^2}\,, \qquad (7)$$

where $V$ is the Lennard-Jones interaction potential given by

$$V(r) = 4\epsilon\left[\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right]. \qquad (8)$$

$\sigma$ and $\epsilon$ are the unknown potential parameters and $r = |\vec{r}(k) - \vec{r}(l'k')|$.

With the simple theoretical model as outlined above, the lattice-dynamics analysis of a crystalline polymer is reduced to the solution of a two-parameter dynamical matrix, hence considerably simplifying and streamlining the normal mode calculations. In Secs. III and IV we will demonstrate the strength of this simple model in application to polyethylene crystal.

## III. POLYETHYLENE CHAIN

The polyethylene chain has a $D_{2h}$ point group in a planar zigzag chain, shown in Fig. 1, which includes two molecular $CH_2$ units per primitive cell of the linear lattice. Labeling the two $CH_2$ units by $k=1$ and 2 and utilizing the symmetry operations of the chain, it can be shown that

$$\underline{\phi}(12+) = \begin{bmatrix} \phi_{xx} & 0 & \phi_{xz} & 0 & \phi_{x\beta} & 0 \\ 0 & \phi_{yy} & 0 & \phi_{y\alpha} & 0 & \phi_{y\gamma} \\ \phi_{xz} & 0 & \phi_{zz} & 0 & \phi_{z\beta} & 0 \\ 0 & -\phi_{y\alpha} & 0 & \phi_{\alpha\alpha} & 0 & \phi_{\alpha\gamma} \\ -\phi_{x\beta} & 0 & -\phi_{z\beta} & 0 & \phi_{\beta\beta} & 0 \\ 0 & -\phi_{y\gamma} & 0 & \phi_{\alpha\gamma} & 0 & \phi_{\gamma\gamma} \end{bmatrix}, \qquad (9)$$

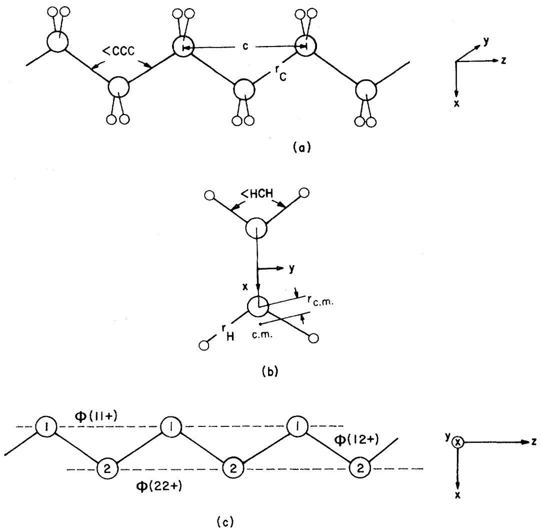

FIG. 1. (a) Definitions of structural parameters and the Cartesian reference axes for polyethylene chain. (b) Definition of the center of mass of rigid $CH_2$ molecule with $X_{c.m.} = \pm 2m_H r_H \cos(\angle HCH)/(2m_H + m_C)$, $Y_{c.m.} = Z_{c.m.} = 0$ relative to the position of carbon atom. (c) Definition of rigid-molecule designations for nearest, 12, and next-nearest, 11 and 22, interactions.

where the + sign refers to the 12 interaction in the positive $z$ axis direction. The translation-libration and libration-libration force constants are given in EPM approximation by

$$\begin{aligned}
&\phi_{x\beta}(12+) = -R_z(1/2+)\phi_{xx} + R_x(1/2+)\phi_{xz}\,, \\
&\phi_{y\alpha}(12+) = R_z(1/2+)\phi_{yy}\,, \\
&\phi_{y\gamma}(12+) = -R_x(1/2+)\phi_{yy}\,, \\
&\phi_{z\beta}(12+) = -R_z(1/2+)\phi_{xz} + R_x(1/2+)\phi_{zz}\,, \\
&\phi_{\alpha\alpha}(12+) = -R_z^2(1/2+)\phi_{yy}\,, \\
&\phi_{\beta\beta}(12+) = -R_z^2(1/2+)\phi_{xx} - R_x^2(1/2+)\phi_{zz} \\
&\qquad\qquad + 2R_x(1/2+)R_z(1/2+)\phi_{xz}\,, \\
&\phi_{\gamma\gamma}(12+) = -R_x^2(1/2+)\phi_{yy}\,, \\
&\phi_{\alpha\gamma}(12+) = R_x(1/2+)R_z(1/2+)\phi_{yy}\,.
\end{aligned} \qquad (10)$$

The $\underline{\phi}(12-)$ force constants are obtained from $\underline{\phi}(12+)$ through the $xy$ plane reflection symmetry operation. It can be shown that $\underline{\phi}(11+)$ has a similar force-constant matrix form as given in Eqs. (9) and (10) except for

$$R_x(1/1+) = 0$$

and (11)

$$\phi_{xz}(11+) = 0\,.$$

$\underline{\phi}(11-)$ is obtained from $\underline{\phi}(11+)$ through reflection symmetry, and $\underline{\phi}(22+)$ is determined from $\underline{\phi}(11+)$ through the inversion symmetry operation. The effective sizes $\vec{\text{R}}(1/2+)$ and $\vec{\text{R}}(1/1+)$ are graphically illustrated in Fig. 2.

Using the above force-constant matrices, the self terms $\underline{\phi}(0,kk)$ are calculated using the relations

$$\begin{aligned}
\phi_{ij}^{(1)}(0,kk) &= -\sum_{l'k'}{}'\,\phi_{ij}^{(1)}(l',kk')\ ,\\
\phi_{ij}^{(2)}(0,kk) &= -\sum_{l'k'}{}'\,\phi_{ij}^{(2)}(l',k'k)\ ,\\
\phi_{ij}^{(3)}(0,kk) &= -\sum_{l'k'}{}'\,\phi_{ij}^{(3)}(l',kk')\ ,\\
\phi_{i\alpha}^{(4)}(0,kk) &= -\sum_{l'k'}{}'\,[-\phi_{i\beta}^{(3)}r_z(l'k')\\
&\qquad +\phi_{i\gamma}^{(3)}r_y(l'k')+\phi_{i\alpha}^{(4)}]\ ,\\
\phi_{i\beta}^{(4)}(0,kk) &= -\sum_{l'k'}{}'\,[\phi_{i\alpha}^{(3)}r_z(l'k')\\
&\qquad -\phi_{i\gamma}^{(3)}r_x(l'k')+\phi_{i\beta}^{(4)}]\ ,\\
\phi_{i\gamma}^{(4)}(0,kk) &= \sum_{l'k'}{}'\,[-\phi_{i\alpha}^{(3)}r_y(l'k')\\
&\qquad +\phi_{i\beta}^{(3)}r_x(l'k')+\phi_{i\gamma}^{(4)}]\ .
\end{aligned} \tag{12}$$

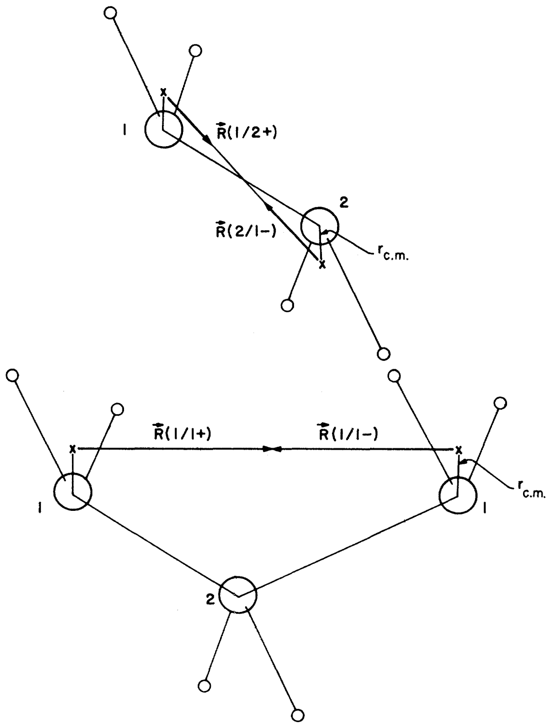

FIG. 2. The effective sizes of 12 and 11 molecular interactions. The centers of mass of the interacting $CH_2$ molecules are identified by ×. The effective size vectors are directed along the line joining the centers of mass of the interacting molecules.

In the above equations only $i,j=x,y,z$ are variable indices.

The dynamical matrix is formed according to Eq. (2) and the dynamical matrix elements are summarized in the Appendix. The first interesting feature of the dynamical matrix is that the $12\times 12$ matrix has a structure consisting of two independent $6\times 6$ matrices, one for the in-plane and the other for the out-of-plane modes of vibration. The $6\times 6$ in-plane matrix includes translational motions along the $x$ and $z$ axes, and $\beta$ librations in the $xz$ plane about the $y$ axis. The $6\times 6$ out-of-plane matrix includes translational modes along the $y$ axis coupled with out-of-plane $\alpha$ (about the $x$ axis in the $yz$ plane) and $\gamma$ (about the $z$ axis in the $xy$ plane) librational modes. The decoupling of in-plane and out-of-plane modes is only dependent on the rigid-molecule approximation and is independent of any assumptions that can be made for the nature of the intermolecular forces and the range of neighboring interactions. For polyethylene, the rigid-$CH_2$ approximation is a highly plausible assumption, since the forces holding the C—H bond (frequencies of $\sim 3000\ \text{cm}^{-1}$) are considerably stronger than the forces holding the C—C bond (frequencies of $\sim 1000\ \text{cm}^{-1}$).

In order to determine values of the unknown parameters the dynamical matrix is studied in the long-wavelength, $\vec{q}=0$, limit. At $\vec{q}=0$ the two $6\times 6$ matrices can be reduced to explicit expressions for almost all of the normal mode frequencies. Defining

$$\begin{aligned}
&\alpha_1=\phi_{xx}(12+)\ ,\ \ \alpha_2=\phi_{xx}(11+)\ ,\\
&\beta_1=\phi_{yy}(12+)\ ,\ \ \beta_2=\phi_{yy}(11+)\ ,\\
&\gamma_1=\phi_{zz}(12+)\ ,\ \ \gamma_2=\phi_{zz}(11+)\ ,\\
&\nu_1=\phi_{xz}(12+)\ ,\ \ R_{z_2}=R_z(1/1+)\ ,\\
&R_{z_1}=R_z(1/2+)\ ,\\
&R_{x_1}=R_x(1/2+)\ ,
\end{aligned} \tag{13}$$

and

$$\underline{M}=\begin{bmatrix}\underline{m} & \underline{0}\\ \underline{0} & \underline{I}\end{bmatrix}^{-1}\underline{D}\ , \tag{14}$$

where $\underline{D}$ is defined in Eq. (2), and using normal mode designations of Tasumi and Shimanouchi,[3] it can be shown that

$$
\begin{aligned}
\omega^2(\nu_4^a(0)) &= [M_{xx}(11)-M_{xx}(12)]_{\vec{q}=0} = -\frac{4\alpha_1}{2m_\mathrm{H}+m_\mathrm{C}} \;, \\
\omega^2(\nu_8^b(0)) &= [M_{\alpha\alpha}(11)-M_{\alpha\alpha}(12)]_{\vec{q}=0} = -\frac{2}{I_{xx}}[R_{z_1}\beta_1(\tfrac{1}{2}c-2R_{z_1})+cR_{z_1}\beta_2] \;, \\
\omega_2(\nu_7^a(\pi)) &= [M_{\alpha\alpha}(11)+M_{\alpha\alpha}(12)]_{\vec{q}=0} = -\frac{2c}{I_{xx}}(\tfrac{1}{2}R_{z_1}\beta_1+R_{z_2}\beta_2) \;, \\
\omega^2(\nu_3^a(0)) &= [M_{\beta\beta}(11)-M_{\beta\beta}(12)]_{\vec{q}=0} \\
&= -\frac{2}{I_{yy}}\{-\tfrac{1}{2}c(R_{z_1}\alpha_1-R_{x_1}\nu_1)+(R_{z_1}\nu_1-R_{x_1}\gamma_1)[r_\mathrm{C}\cos(\angle\mathrm{CCC})+2r_\mathrm{c.m.}] \\
&\qquad +2R_{z_1}^2\alpha_1+2R_{x_1}^2\gamma_1-4R_{x_1}R_{z_1}\nu_1-cR_{z_2}\alpha_2\} \;, \\
\omega^2(\nu_8^a(\pi)) &= [M_{\gamma\gamma}(11)-M_{\gamma\gamma}(12)]_{\vec{q}=0} \\
&= \frac{2}{I_{zz}}\{-R_{x_1}\beta_1[r_\mathrm{C}\cos(\angle\mathrm{CCC})+2r_\mathrm{c.m.}]+2R_{x_1}^2\beta_1\} \;,
\end{aligned}
\tag{15}
$$

where ∠CCC represents the angle formed by the three carbon atoms in the backbone and the subscript c.m. denotes center of mass. For $\omega^2(\nu_7^b(0))$ and $\omega^2(\nu_5^b(0))$ we get

$$
\begin{vmatrix} 2M_{yy}(11)-\omega^2 & -2M_{y\gamma}(11) \\ -2M_{y\gamma}(11) & M_{\gamma\gamma}(11)+M_{\gamma\gamma}(12)-\omega^2 \end{vmatrix}_{\vec{q}=0} = 0 \;, \tag{16}
$$

and for $\omega^2(\nu_3^b(\pi))$ and $\omega^2(\nu_4^b(\pi))$ we get

$$
\begin{vmatrix} 2M_{zz}(11)-\omega^2 & -2M_{z\beta}(11) \\ -2M_{z\beta}(11) & M_{\beta\beta}(11)+M_{\beta\beta}(12)-\omega^2 \end{vmatrix}_{\vec{q}=0} = 0 \;. \tag{17}
$$

From Eqs. (16) and (17) we can get

$$
\begin{aligned}
\omega^2(\nu_7^b(0))+\omega^2(\nu_5^b(0)) &= [M_{\gamma\gamma}(11)+M_{\gamma\gamma}(12)+2M_{yy}(11)]_{\vec{q}=0} \\
&= -\frac{2}{I_{zz}}R_{x_1}\beta_1[r_\mathrm{C}\cos(\angle\mathrm{CCC})+2r_\mathrm{c.m.}]-\frac{4\beta_1}{2m_\mathrm{H}+m_\mathrm{C}} \\
\omega^2(\nu_3^b(\pi))+\omega^2(\nu_4^b(\pi)) &= [M_{\beta\beta}(11)+M_{\beta\beta}(12)+2M_{zz}(11)]_{\vec{q}=0} \\
&= \frac{2}{I_{yy}}\{-\tfrac{1}{2}c(R_{z_1}\alpha_1-R_{x_1}\nu_1)-cR_{z_2}\alpha_2 \\
&\qquad +(R_{z_1}\nu_1-R_{x_1}\gamma_1)[r_\mathrm{C}\cos(\angle\mathrm{CCC})+2r_\mathrm{c.m.}]\}-\frac{4\gamma_1}{2m_\mathrm{H}+m_\mathrm{C}} \;.
\end{aligned}
\tag{18}
$$

An early assessment gives a total of ten unknown force constants and effective size parameters for polyethylene. The number of finite frequencies at $\vec{q}=0$ is nine, and hence our analysis may appear to be a case of abundant parameters available for fitting the frequencies. However, not all of the unknown parameters are independent, and not all of the long-wavelength normal mode frequencies have been measured and assigned.

Going back to the assumptions of the EPM approximation, the value of $R_{z_2}$ is determined by the hard-sphere radius of contact of interacting molecules and is given by

$$
R_{z_2}=r_\mathrm{C}\sin(\angle\mathrm{CCC}) \;. \tag{19}
$$

$R_{x_1}$ and $R_{z_1}$ are related by the condition that the effective size vectors are directed along the line connecting the centers of mass of the two interacting molecules and hence

$$
R_{x_1}=\left[\frac{r_\mathrm{C}\cos(\angle\mathrm{CCC})+2r_\mathrm{c.m.}}{r_\mathrm{C}\sin(\angle\mathrm{CCC})}\right]R_{z_1} \;. \tag{20}
$$

The force constant $\gamma_2$ does not appear in the expressions for the frequencies at $\vec{q}=0$, and therefore, the total number of the independent parameters that can be fitted to the known long wavelength frequencies is seven.

Only eight of the nine frequencies of polyethylene normal mode vibrations at $\vec{q}=0$ have been measured and assigned. Table I summarizes the available experimental data and their corresponding assignments for polyethylene. From Eqs. (15) and (18) it is observed that the in-plane frequencies $\nu_3^b(\pi),\nu_3^a(0),\nu_4^a(0),\nu_4^b(\pi)$ can be fitted to the force constants $\alpha_1$, $\alpha_2$, $\nu_1$, and $\gamma_1$ leaving the unknown parameters $R_{z_1}$, $\beta_1$, and $\beta_2$ for fitting the out-of-plane frequencies $\nu_7^a(\pi)$, $\nu_7^b(0)$, $\nu_8^a(\pi)$, and $\nu_8^b(0)$.

Our first attempt at fitting the three parameters to the four out-of-plane frequencies was unsuccessful. We considered the possibility of adding extra parameters to make the fit possible. The simplest choice was to allow variations in $R_{z_2}$. However, a study of the equations reveals that $R_{z_2}$ and $\beta_2$ always appear in the combination $R_{z_2}\beta_2$ and hence $R_{z_2}$ could not be used as an independent parameter for long-wavelength frequencies. The second alternative was to allow independent variations of $R_{z_1}$ and $R_{x_1}$. This flexibility, however, did not produce any improvements in the fit. Our final alternative was to extend the range of interactions to include third and even fourth nearest neighbors. Observations on metallic hydrides[19] have indicated that under certain circumstances the weak next-nearest neighbor force constants could have significant influence on the dispersion curves. This exercise, however, proved futile and even with inclusion of three to five additional parameters of third or fourth nearest neighbors no satisfactory fit to the observed frequencies and their corresponding polarization vectors could be obtained.

A closer study of the $2\times2$ dynamical matrix of $\nu_5^b(0)$ and $\nu_7^b(0)$ reveals a very interesting structure. It can be shown that regardless of the range of molecular interactions included in the calculations, this matrix has the general form of

$$\left[\sum_{l'k'}\phi_{y\gamma}\right]\begin{bmatrix} -\dfrac{4}{m}P & -\dfrac{4}{(I_{zz}m)^{1/2}} \\ -\dfrac{4}{(I_{zz}m)^{1/2}} & \dfrac{2}{I_{zz}}[r_{\mathrm{C}}\cos(\angle\mathrm{CCC})-2r_{\mathrm{c.m.}}] \end{bmatrix}, \tag{21}$$

TABLE I. Normal-mode frequencies of polyethylene chain.

| Mode designations | | Observations | | | | |
|---|---|---|---|---|---|---|
| Ref. 3 | Ref. 17 | Ref. 3 | Ref. 16 | Ref. 17 | Ref. 18 | Frequencies used in present calculations |
| $\nu_3^b(\pi)$ | $\omega(CH_2)$ | 1415 | 1370 | 1372 | 1370 | 1370 |
| $\nu_3^a(0)$ | $\omega(CH_2)$ | 1175 | 1176 | 1176 | 1176 | 1176 |
| $\nu_7^b(0)$ | $\rho(CH_2)$ | 1157 | 1168 | 1170 | 1170 | |
| $\nu_8^a(\pi)$ | $\rho(CH_2)$ | 721 | 725 | 721 | | 725 |
| $\nu_7^a(\pi)$ | $\tau(CH_2)$ | 1295 | 1295 | 1295 | 1295 | 1295 |
| $\nu_8^b(0)$ | $\tau(CH_2)$ | 1050 | 1050 | 1050 | 1050 | 1050 |
| $\nu_4^a(0)$ | $\nu_s(C-C)$ | 1131 | 1131 | 1131 | 1063 | 1131 |
| $\nu_4^b(\pi)$ | $\nu_{as}(C-C)$ | 1061 | 1061 | 1064 | 1128 | 1061 |

where

$$P=\frac{\sum_{l'k'}\phi_{yy}}{\sum_{l'k'}\phi_{y\gamma}}\ ,\quad m=2m_{\rm H}+m_{\rm C}\ . \tag{22}$$

The $2\times2$ dynamical matrix in Eq. (21) is dependent only on the rigid-molecule approximation and is independent of EPM approximation and the nature or range of interaction forces. Hence, the frequencies $\nu_5^b(0)$ and $\nu_7^b(0)$ are seen to be dependent only on one single parameter, $P$, defined in Eq. (22). It can be shown that regardless of the values that $P$ may assume, the normal modes of vibration will always obey the relation

$$\nu_5^b(0)>\nu_7^b(0)\quad \text{at } \vec{q}=0\ . \tag{23}$$

This conclusion contradicts past assignments[3,4] of the observed and calculated frequencies of these modes.

A similar study of the expressions governing $\nu_7^b(0)$ and $\nu_8^a(\pi)$ shows that for all parametric variations we will have

$$\nu_7^b(0)\le\nu_8^a(\pi)\ , \tag{24}$$

which indicates $\nu_8^a(\pi)$ acting as a ceiling for the value of $\nu_7^b(0)$. Contrary to our findings, the traditional assignment for $\nu_7^b(0)$ is 1170 $\text{cm}^{-1}$ which is greater than the value of 725 $\text{cm}^{-1}$ for $\nu_8^a(\pi)$. A measurement of $\nu_5^b(0)$ frequency is not available from infrared and Raman spectroscopy. Analysis[20] based on an extremely simplified picture of interactions as homogeneous and isotropic elastic rods has suggested a value of about 200 $\text{cm}^{-1}$ for $\nu_5^b(0)$.

Based on our theoretical calculations we conclude that the existing assignments of frequencies to $\nu_5^b(0)$ and $\nu_7^b(0)$ are unacceptable, and that the following relations must be satisfied:

$$\nu_7^b(0)\le 725\ \text{cm}^{-1}$$

and (25)

$$\nu_5^b(0)>\nu_7^b(0)\ ,$$

Hence, in our fitting procedure we assume $\nu_7^b(0)$ to be an unknown property to be determined from calculations. Therefore, the three frequencies of $\nu_7^a(\pi)$, $\nu_8^b(0)$, and $\nu_8^a(\pi)$ are fitted to be three unknown parameters $R_{z_1}$, $\beta_1$, and $\beta_2$.

The value of the force constant $\gamma_2$ cannot be determined from the long-wavelength frequencies since it does not appear in any of the expressions at $\vec{q}=0$. We calculate $\gamma_2$ from information available on polyethylene elastic constants. The derivation of expressions for the elastic constants of polyethylene is simplified by neglecting the contribution of the librational modes to the elastic constant values. Using the method of long waves[1] it can be shown that

$$\begin{aligned}
C_{33}&=A_1\left[2\gamma_1+8\gamma_2-\frac{2\nu_1^2}{\alpha_1}\right],\\
C_{44}&=A_1(2\beta_1+8\beta_2)\ ,\\
C_{55}&=A_1\left[2\alpha_1+8\alpha_2-2\frac{\nu_1^2}{\gamma_1}\right],
\end{aligned} \tag{26}$$

with

$$A_1=-\frac{\rho}{2}\,\frac{[r_{\rm C}\sin(\angle{\rm CCC})]^2}{2m_{\rm H}+m_{\rm C}}\ , \tag{27}$$

where $\rho$ is the polyethylene density taken as 0.997 $\text{g/cm}^3$.

From measurements of the elastic constants of polyethylene[21-23] we have the following:

$$C_{33}=2.4\times10^{12}\ , \tag{28}$$

in units of $\text{dyn/cm}^2$. This information is used for determining the value of $\gamma_2$. Calculations of $C_{44}$ and $C_{55}$ from Eq. (26) yield

$$\begin{aligned}
C_{44}&=1.92\times10^{12}\ ,\\
C_{55}&=0.78\times10^{12}
\end{aligned} \tag{29}$$

(again, in units of $\text{dyn/cm}^2$) for the single chain elastic constants.

The values of the force constants and the effective size parameters are summarized, respectively, in Tables II and III. These values are used in calculation of the dispersion curves of polyethylene chain along the $[00\xi]$ direction with the results given in Fig. 3. The two major features of the calculated dispersion curves are their symmetry about $00\frac{1}{2}$ and the existence of three acoustic dispersion curves. It is of interest to note that none of these

TABLE II. Force-constant parameters of polyethylene chain (in $10^4$ dyn/cm).

| | |
|---|---|
| $\alpha_1$ | $-26.44$ |
| $\beta_1$ | $-28.02$ |
| $\gamma_1$ | $-23.30$ |
| $\nu_1$ | $-19.34$ |
| $\alpha_2$ | $-0.237$ |
| $\beta_2$ | $-0.0487$ |
| $\gamma_2$ | $-6.475$ |

TABLE III. Effective size parameters of polyethylene chain (in Å).

| | |
|---|---|
| $R_{x_1}$ | 0.173 |
| $R_{z_1}$ | 0.213 |
| $R_{z_2}$ | 1.270 |

two features exists in any of the previous lattice-dynamics calculations of polyethylene.[3-5] Our experience shows that both the symmetry and the acoustic branches could be distorted and lost if self terms are not properly calculated. The self terms essentially ensure invariance conditions[24] under which the chain properties remain the same under whole-body translation or rotation.

The dispersion curves are calculated using the structural data of Mathisen, Norman, and Pedersen[30] for polyethylene. The calculations of the dispersion curves were repeated for different sets of polyethylene structural parameters, summarized in Table IV. It is observed that the calculations are not sensitive to any special set of parameters given in Table IV.

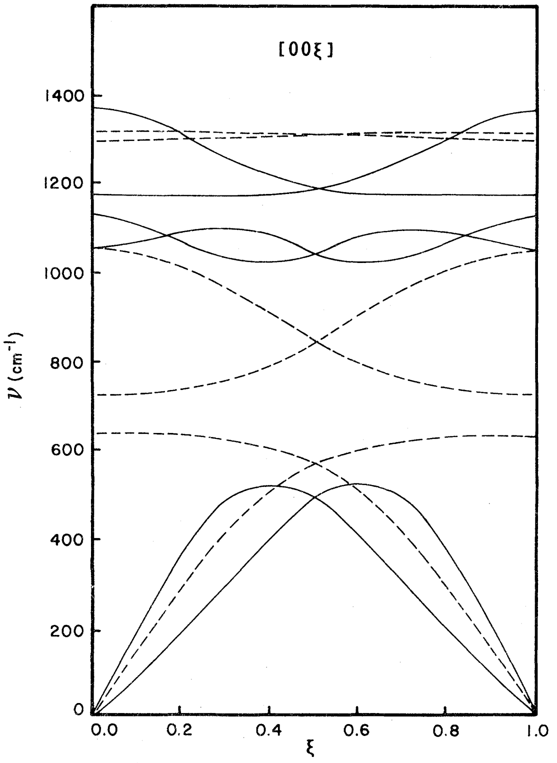

FIG. 3. Dispersion curves of polyethylene chain along [00ξ] direction. The in-plane modes of vibration are given as dashed lines and the out-of-plane modes as solid lines.

## IV. ORTHORHOMBIC POLYETHYLENE CRYSTAL

The orthorhombic unit cell of polyethylene contains two chains each contributing two $CH_2$ groups. The chains' axes are coincident with the $c$ axis direction and the planes of the chains make an angle with respect to the longer lateral, $a$ axis, basis vector which is defined as the setting angle $\varphi$. Various measurements of the setting angle have arrived at the values of 41°,[31] 42°,[32] and 48°.[33,34] We will utilize both 41° and 48° setting angles in the calculation of the dispersion curves of crystalline polyethylene. The orthorhombic lattice parameters are[31]

$$a = 7.161 \ , \quad b = 4.866 \ , \quad c = 2.5412 \ , \tag{30}$$

in units of Å.

The dynamical matrix of polyethylene crystal includes all interactions within a 6-Å radius. All interchain translation-translation force constants de-

TABLE IV. Various sets of structural parameters used in the calculation of polyethylene normal-mode frequencies.

| Reference | C–C bond (Å) | C–H bond (Å) | ∠CCC | ∠HCH |
|---|---|---|---|---|
| 25 | 1.533 | 1.07 | 111°54′ | 107° |
| 26 | 1.54 | 1.093 | 109°28′ | 109°28′ |
| 27 | 1.54 | 1.1 | 112° | 110° |
| 28 | 1.54 | 1.09 | 111°47′ | 109°27′ |
| 29 | 1.5423 | 1.1147 | 113°52′ | 106°8′ |
| 30 | 1.532 | 1.058 | 112°1′ | 109°18′ |

pend only on the two parameters, $\sigma$ and $\epsilon$, of the Lennard-Jones interaction potential. The interchain translation-libration and libration-libration force constants are determined from translation-translation force constants and the effective size parameters which are calculated from the coordinates of the halfway point between the centers of mass of the interacting molecules.

The four $CH_2$ molecules in the unit cell are designated by $k=1$ and 2 in the chain which has the same $xyz$ coordinates as the isolated chain of Fig. 1. The two $CH_2$ units in the second chain are designated by $k=3$ and 4. The intrachain 11, 22, and 12 interaction force constants are identical to those of the isolated chain. The 33, 44, and 34 interaction force constants are related to the 11, 22, and 12 force constant matrices through the axes transformation matrix

$$\begin{bmatrix} \cos 2\varphi & \sin 2\varphi & 0 \\ -\sin 2\varphi & \cos 2\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{31}$$

where $\varphi$ is the setting angle.

In order to determine the unknown Lennard-Jones potential parameters, the measurements of long-wavelength lattice modes of polyethylene are utilized. The far-infrared spectrum of crystalline polyethylene shows two bands of 73 and 94 $cm^{-1}$ at room temperature. These two frequencies are assigned[35–38] as $\nu_5^b(\pi)=94$ $cm^{-1}$ and $\nu_5^a(\pi)=73$ $cm^{-1}$. These two well-established assignments are used in calculation of the Lennard-Jones interaction potential parameters. Table V summarizes the values of $\sigma$ and $\epsilon$ for two setting angles of 41° and 48°.

From values of $\sigma$ and $\epsilon$ in Table V the frequency of the remaining lattice mode, $\nu_9^b(0)$, is calculated and compared with the available neutron scattering data[39,40] in Table VI. From Table VI it appears that a setting angle of 41° provides better agreement with the observed frequencies as compared to the setting angle of 48°. Table VII summarizes the comparison of the calculated single chain normal mode frequencies with those of the crystalline polyethylene for the setting angle of 41°.

The dispersion curves of crystalline polyethylene are calculated along $[00\xi]$, $[\xi\xi 0]$, and $[\xi\bar{\xi}0]$ directions and given in Figs. 4 and 5 for 41° setting angle. Similar calculations using the 48° setting angle give negative eigenvalues for the dynamical matrix along $[\xi\xi 0]$ and hence are unacceptable as viable solutions. Our calculations of crystalline polymers, hence, favor the recent measurements[31,32] of the setting angle of about 41°.

Except for small values of $\xi$, the dispersion curves of polyethylene chain and crystal along $[00\xi]$ are very similar. For all practical purposes, it seems that the chain provides a good approximation to the normal modes of the crystal with the wave vector along the chain axis. Considering the weak nature of the interchain van der Waals forces, this observation could have been made without any calculations. It is also interesting to note that along $[\xi\xi 0]$ and $[\xi\bar{\xi}0]$ directions the optical modes remain essentially at constant frequencies with very little dispersion. This characteristic is based on the fact that the high frequency intrachain optical modes are not influenced by weak van der Waals forces of interchain interactions.

## V. DISCUSSION

A simple lattice-dynamics model of crystalline polymers which uses the EPM approximation is proposed and applied to the study of normal mode vibrations of polyethylene chain and crystal. The calculations of normal mode frequencies for polyethylene involve only a limited number of adjustable parameters, but more importantly, they show the model to be capable of reaching generalizations about the relative values of the normal mode fre-

TABLE V. Intermolecular Lennard-Jones potential parameters as a function of setting angle. Lattice frequencies used for fitting the potential parameters are also given.

| Setting angle | 41° | 48° |
|---|---|---|
| $\nu_5^b(\pi)$ ($cm^{-1}$) | 94 | 94 |
| $\nu_5^a(\pi)$ ($cm^{-1}$) | 73 | 73 |
| $\epsilon/k_B$ (K) | 180 | 589 |
| $\sigma$ (Å) | 3.510 | 3.364 |

TABLE VI. Comparison of the calculated values of $\nu_9^b(0)$ with the experimental data.

| | Frequency ($cm^{-1}$) |
|---|---|
| Calculated, $\varphi=41°$ | 39 |
| Calculated, $\varphi=48°$ | 58 |
| Observed, Ref. 39 | 39 |
| Observed, Ref. 40 | 46 |

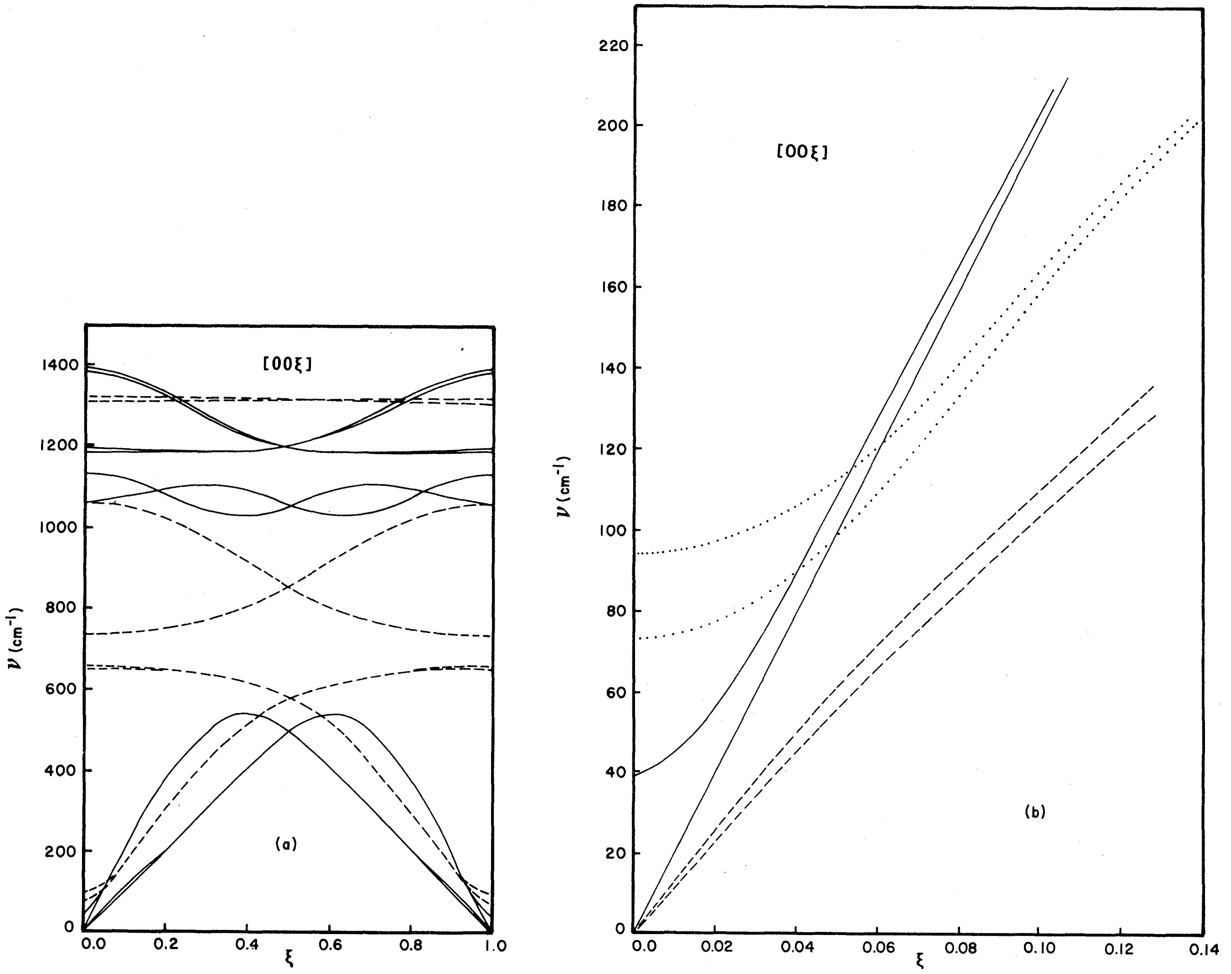

FIG. 4. Dispersion curves of orthorhombic polyethylene crystal along $[00\xi]$ direction; (a) including all modes of vibration, (b) showing details of low frequency modes of vibration.

quencies without making any parametric calculations. This was specifically illustrated for $\nu_7^b(0)$.

The simplicity of the proposed model and the limited number of available force constants greatly reduce the possibility of forcing a fitting of parameters to the experimental data. In this analysis, it is shown that regardless of the range and nature of forces assumed for intermolecular interactions, there is no way of fitting the $\nu_7^b(0)$ mode to its previously assigned frequency value, and hence modifications in this assignment are necessary. The calculations, without any parametrization of values, show that $\nu_7^b(0)$ must be smaller than 725 $\text{cm}^{-1}$ and our results give a value of 641 $\text{cm}^{-1}$ as compared to a previous assignment of 1170 $\text{cm}^{-1}$.

Another interesting feature of our simple calculations is the appearance of three acoustic modes, and the symmetry of the dispersion curves about $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and $\frac{1}{2}\bar{\frac{1}{2}}0$ points in the Brillouin zone. None of these features which are essential and independent of the lattice dynamical model is observed in other more complex calculations[3-5] on polyethylene.

We believe that the proposed model provides a high degree of simplification which is especially useful when the polymer chain becomes more complex in structure. The significance of this simple model lies in its application to biopolymers where there is considerable interest in the study of low frequency vibrations of biological substances.

## APPENDIX

The dynamical matrix elements for the isolated chain are as follows:

$$M_{xx}(11)=A_M[2\alpha_2(\cos 2\pi\xi-1)-2\alpha_1]\equiv f_1(\alpha_1,\alpha_2)\ ,$$

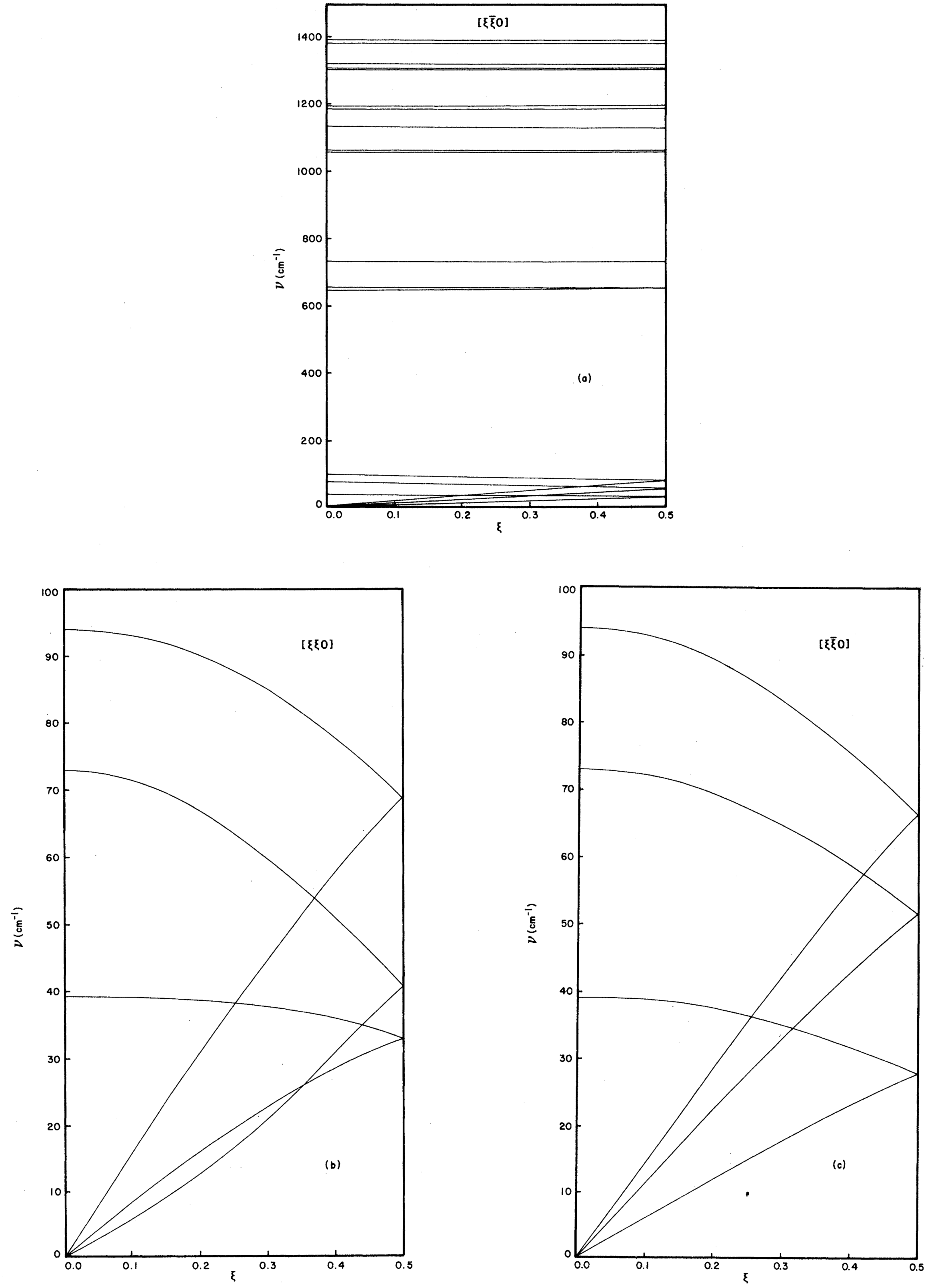

FIG. 5. Dispersion curves of orthorhombic polyethylene crystal (a) all modes of vibration along $[\xi\bar{\xi}0]$, (b) details of low frequency modes along $[\xi\xi0]$, and (c) details of low-frequency modes of vibration along $[\xi\bar{\xi}0]$.

$$M_{yy}(11)=f_1(\beta_1,\beta_2)\ ,$$

$$M_{zz}(11)=f_1(\gamma_1,\gamma_2)\ ,$$

$$M_{x\beta}(11)=-i\,2A_yR_{z_2}\alpha_2\sin 2\pi\xi\equiv f_2(\alpha_2,A_y)\ ,$$

$$M_{y\alpha}(11)=-f_2(\beta_2,A_x)\ ,$$

$$M_{y\gamma}(11)=-2A_zR_{x_1}\beta_1\ ,$$

$$M_{z\beta}(11)=-2A_y(R_{z_1}\nu_1-R_{x_1}\gamma_1)\ ,$$

$$M_{\alpha y}(11)=-M_{y\alpha}(11)\ ,$$

$$M_{\beta x}(11)=-M_{x\beta}(11)\ ,$$

$$M_{\beta z}(11)=M_{z\beta}(11)\ ,$$

$$M_{\gamma y}(11)=M_{y\gamma}(11)\ ,$$

$$\begin{aligned}M_{\alpha\alpha}(11)=-2[&R_{z_2}^2\beta_2(\cos 2\pi\xi-1)+R_{z_1}\beta_1(R_1-R_{z_1})\\&+2R_{z_2}R_1\beta_2]/I_{xx}\ ,\end{aligned}$$

$$\begin{aligned}M_{\beta\beta}(11)=2[&-R_{z_2}^2\alpha_2(\cos 2\pi\xi-1)\\&-R_1(R_{z_1}\alpha_1-R_{x_1}\nu_1)+R_2(R_{z_1}\nu_1-R_{x_1}\gamma_1)\\&+R_{z_1}^2\alpha_1+R_{x_1}^2\gamma_1\\&-2R_{x_1}R_{z_1}\nu_1-2R_1R_{z_1}\alpha_2]/I_{yy}\ ,\end{aligned}$$

$$M_{\gamma\gamma}(11)=2\beta_1R_{x_1}(R_{x_1}-R_2)/I_{zz}\ ,$$

$$M_{xy}(22)=M_{xy}(11)\ ,\quad x,y\equiv\text{all } x,\ y,\ \text{and } z$$

$$M_{\alpha\beta}(22)=M_{\alpha\beta}(11)\ ,\quad \alpha,\beta\equiv\text{all } \alpha,\ \beta,\ \text{and } \gamma$$

$$M_{x\beta}(22)=M_{x\beta}(11)\ ,$$

$$M_{y\alpha}(22)=M_{y\alpha}(11)\ ,$$

$$M_{y\gamma}(22)=-M_{y\gamma}(11)\ ,$$

$$M_{z\beta}(22)=-M_{z\beta}(11)\ ,$$

$$M_{\alpha y}(22)=-M_{y\alpha}(22)\ ,$$

$$M_{\beta x}(22)=-M_{x\beta}(22)\ ,$$

$$M_{\beta z}(22)=M_{z\beta}(22)\ ,$$

$$M_{\gamma y}(22)=M_{y\gamma}(22)\ ,$$

$$M_{xx}(12)=2A_M\alpha_1\cos\pi\xi\equiv f_3(\alpha_1)\ ,$$

$$M_{yy}(12)=f_3(\beta_1)\ ,$$

$$M_{zz}(12)=f_3(\gamma_1)\ ,$$

$$M_{xz}(12)=i\,2A_M\nu_1\sin\pi\xi\ ,$$

$$M_{zx}(12)=M_{xz}(12)\ ,$$

$$M_{\alpha\alpha}(12)=-2R_{z_1}^2\beta_1\cos\pi\xi/I_{xx}\ ,$$

TABLE VII. Comparison of the calculated normal mode frequencies of single chain and crystalline polyethylene.

| Single chain mode | Single chain frequency (cm$^{-1}$) | Crystalline frequency (cm$^{-1}$) |
|---|---|---|
| $\nu_3^a(0)$ | 1176 | 1194<br>1183 |
| $\nu_3^b(\pi)$ | 1370 | 1390<br>1380 |
| $\nu_4^a(0)$ | 1131 | 1133<br>1132 |
| $\nu_4^b(\pi)$ | 1061 | 1062<br>1062 |
| $\nu_5^b(0)$ | 1318 | 1322<br>1319 |
| $\nu_5^a(\pi)$ | 0 | 73 |
| $\nu_5^b(\pi)$ | 0 | 94 |
| $\nu_7^b(0)$ | 641 | 654<br>648 |
| $\nu_7^a(\pi)$ | 1295 | 1305<br>1301 |
| $\nu_8^b(0)$ | 1050 | 1059<br>1054 |
| $\nu_8^a(\pi)$ | 725 | 733<br>732 |
| $\nu_9^b(0)$ | 0 | 39 |

$$M_{\beta\beta}(12)=-2(R_{z_1}^2\alpha_1+R_{x_1}^2\gamma_1-2R_{x_1}R_{z_1}\nu_1)\cos\pi\xi/I_{yy}\ ,$$

$$M_{\gamma\gamma}(12)=-2R_{x_1}^2\beta_1\cos\pi\xi/I_{zz}\ ,$$

$$M_{\alpha\gamma}(12)=i\,2R_{x_1}R_{z_1}\beta_1\sin\pi\xi/(I_{xx}I_{zz})^{1/2}\ ,$$

$$M_{\gamma\alpha}(12)=M_{\alpha\gamma}(12)\ ,$$

$$M_{x\beta}(12)=i\,2A_y(-R_{z_1}\alpha_1+R_{x_1}\nu_1)\sin\pi\xi\ ,$$

$$M_{y\alpha}(12)=i\,2A_xR_{z_1}\beta_1\sin\pi\xi\ ,$$

$$M_{y\gamma}(12)=-2A_zR_{x_1}\beta_1\cos\pi\xi\ ,$$

$$M_{z\beta}(12)=2A_y(-R_{z_1}\nu_1+R_{x_1}\gamma_1)\cos\pi\xi\ ,$$

$$M_{\alpha y}(12)=-M_{y\alpha}(12)\ ,$$

$$M_{\beta x}(12)=-M_{x\beta}(12)\ ,$$

$$M_{\beta z}(12)=-M_{z\beta}(12)\ ,$$

$$M_{\gamma y}(12)=-M_{y\gamma}(12)\ ,$$

where

$$A_M = \frac{1}{2m_{\mathrm{H}} + m_{\mathrm{C}}} , \quad A_i = \frac{1}{(I_{ij} A_M)^{1/2}} , \quad j = x,y,z$$

$$R_1 = r_{\mathrm{C}} \sin(\angle \mathrm{CCC}) ,$$

$$R_2 = r_{\mathrm{C}} \cos(\angle \mathrm{CCC}) + \frac{4m_{\mathrm{H}} r_{\mathrm{H}} \cos(\angle \mathrm{HCH})}{2m_{\mathrm{H}} + m_{\mathrm{C}}} ,$$

and

$$q_z = \frac{2\pi\xi}{c} , \quad 0 \le \xi \le 1 .$$

All other elements of the dynamical matrix have a value of zero.

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[1] M. Born and K. Huang, *Dynamical Theory of the Crystal Lattices* (Clarendon, Oxford, England, 1954).

[2] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[3] M. Tasumi and T. Shimanouchi, J. Chem. Phys. 43, 1245 (1965).

[4] M. Tasumi and S. Krimm, J. Chem. Phys. 46, 755 (1967).

[5] M. Kobayashi, J. Chem. Phys. 70, 4797 (1979).

[6] L. Piseri, B. M. Powell, and G. Dolling, J. Chem. Phys. 58, 158 (1973).

[7] For a comprehensive review see G. Venkataraman and V. C. Sahni, Rev. Mod. Phys. 42, 409 (1970).

[8] H. Hahn and W. Biem, Phys. Status Solidi 3, 1911 (1963).

[9] W. Cochran and G. S. Pawley, Proc. R. Soc. (London) Ser. A 280, 1 (1964).

[10] J. Lefebvre, M. More, R. Fouret, B. Hennion, and R. Currat, J. Phys. C 8, 2011 (1975).

[11] K. Parlinski, Acta Phys. Pol. 34, 1019 (1968); 35, 223 (1969).

[12] C. H. Kim, H. A. Rafizadeh, and S. Yip, J. Chem. Phys. 57, 2291 (1972).

[13] H. A. Rafizadeh, S. Yip, and H. Prask, J. Chem. Phys. 56, 5377 (1972).

[14] H. A. Rafizadeh and S. Yip, J. Chem. Phys. 53, 315 (1970).

[15] For a review see J. Barnes and B. Fanconi, J. Phys. Chem. Ref. Data 7, 1309 (1978).

[16] T. Shimanouchi, *Tables of Molecular Vibrational Frequencies,* NSRDS-NBS-39 (U. S. GPO, Washington, D.C., 1970), Vol. I.

[17] P. J. Hendra, H. P. Jobic, and P. Marsden, Spectrochim. Acta 33, 445 (1977).

[18] J. Maxfield, R. S. Stein, and M. C. Chen, J. Polym. Sci. 16, 37 (1978).

[19] H. A. Rafizadeh, Phys. Rev. B 23, 1628 (1981).

[20] C. Y. Liang, S. Krimm, and G. B. B. M. Sutherland, J. Chem. Phys. 25, 543 (1956).

[21] I. Sakurada and Y. Nukushina, J. Polym. Sci. 57, 651 (1962).

[22] I. Sakurada and K. Kaji, J. Polym. Sci. C 31, 57 (1970).

[23] S. L. Hsu and S. Krimm, J. Appl. Phys. 48, 4013 (1977).

[24] R. Geick, Z. Phys. B 32, 5 (1978).

[25] P. W. Teare, Acta Crystallogr. 12, 294 (1959).

[26] R. G. Snyder, J. Chem. Phys. 47, 1316 (1967).

[27] T. P. Lin and J. L. Koening, J. Mol. Spectrosc. 9, 228 (1962).

[28] T. Kitagawa and T. Miyazawa, Polym. J. 1, 471 (1970).

[29] M. J. S. Dewar, Y. Yamaguchi, and S. H. Suck, Chem. Phys. Lett. 51, 175 (1977).

[30] H. Mathisen, N. Norman, and B. F. Pedersen, Acta Chem. Scand. 21, 127 (1967).

[31] G. Avitabile, R. Napolitano, B. Pirozzi, K. D. Rouse, M. W. Thomas, and B. T. M. Willis, J. Polym. Sci. B 13, 351 (1975).

[32] R. G. Snyder, J. Mol. Spectros. 7, 116 (1961).

[33] W. Bunn, Trans. Faraday Soc. 35, 842 (1939).

[34] P. W. Teare, Acta Crystallogr. 12, 294 (1959).

[35] S. Krimm and M. J. Bank, J. Chem. Phys. 42, 4059 (1965).

[36] J. W. Fleming, G. W. Chantry, P. A. Turner, E. A. Nicol, H. A. Willis, and M. E. A. Cudby, Chem. Phys. Lett. 17, 84 (1972).

[37] G. J. Davies and J. Haigh, Infrared Phys. 14, 183 (1974).

[38] J. Zirke and M. Meissner, Infrared Phys. 18, 871 (1978).

[39] G. J. Safford, A. W. Naumann, and F. T. Simon, J. Chem. Phys. 45, 3787 (1966).

[40] J. F. Twisleton and J. W. White, *Neutron Inelastic Scattering, 1972,* Proceedings of the Symposium on Neutron Inelastic Scattering, Grenoble, 1972 (IAEA, Vienna, 1972), p. 301.