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Frequency Distribution, Specific Heat, and Young's Moduli of Orthorhombic Polyethylene with Skeletal Approximation

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In preliminary studies on the frequency distribution, specific heat and Young's moduli of the orthorhombic polyethylene crystal, methylene groups were treated as single dynamic units. Inter-methylene force constants were estimated from the intermolecular potential function of methane and from deBoer's potential function. Dynamical matrices of acoustic vibrations were constructed. A practical method was worked out for deriving the frequency distribution of acoustic vibrations from the volume enclosed in constant-frequency surfaces in a three-dimensional phase-difference space. With reference to specific heat in the lowest temperature region, inter-methylene force constants were adjusted. An efficient method was used for calculating the frequency distribution of crystal vibrations of chain-polymers. The frequency distribution of orthorhombic polyethylene crystal and specific heats in low temperature region were calculated in agreement with experimental results. A simple approximate method was used for treating Young's moduli of orthorhombic chain-polymer crystals. Applicability of the skeletal approximation is discussed.

Experimental specific heat[1-4] of polyethylene with various degree of crystallinity was extrapolated to 100% crystallinity and specific heat of the crystalline region and amorphous region was obtained by Wunderlich.[5] Stockmeyer and Hecht[6] treated the lattice dynamics of a model crystal with anisotropic force field in a tetragonal lattice. Tarasov[7] treated a chain-polymer crystal model as elastic rods with weak inter-rod interactions. These over-simplified models might be useful in studying temperature dependence of specific heat. However, these models are not applicable for analysing spectroscopic data including infrared and Raman frequencies.

For polymer-chain crystals, the specific heat of the crystalline region is proportional to the third power of absolute temperature in the lowest temperature region, but is nearly proportional to temperature at intermediate temperatures below 70°K. Thus, experimental specific heat may be reproduced[5] by adjusting characteristic frequencies (ν_{D3} and ν_{D1}) of a combination of the three-dimensional and one-dimensional Debye models. However, if the frequency distribution of the combined Debye models is quite different from the actual distribution, the physical meaning of characteristic frequencies (especially ν_{D1}) is not clear.

Specific heat of crystalline material is due to the frequency distribution of crystal vibrations which depend upon the force field. The intramolecular force field of polyethylene[8] and hydrocarbon molecules[9-11] were studied and a general theory of polymer-chain vibrations was derived.[12-14] However, for the purpose of studying frequency distribution, specific heat or neutron-scattering cross sections theoretically, normal vibrations of acoustic branches and optical branches of the three-dimensional crystal need be treated.

A general method of group-theoretical analysis of crystal vibrations was reported previously[15] for orthorhombic crystals. Furthermore, general matrix methods were derived for studying molecular crystals and chain-polymer crystals and for

1) I. V. Sochara, *Dokl. Akad. Nauk SSSR*, **130**, 126 (1960).
2) F. S. Daiton, D. M. Evans, F. E. Hoare and T. P. Melia, *Polymer*, **3**, 277 (1962).
3) L. L. Isaacs and C. W. Garland, *J. Phys. Chem. Solids.*, **23**, 311 (1962).
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6) W. H. Stockmeyer and C. E. Hecht, *J. Chem. Phys.*, **21**, 1954 (1953).
7) V. V. Tarasov, *J. Chem. Phys.* (USSR), **24**, 111 (1950); *J. Amer. Chem. Soc.*, **80**, 5052 (1958).
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9) T. Shimanouchi, *Pure Appl. Chem.*, **7**, 261 (1962).
10) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).
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12) P. Higgs, *Proc. Roy. Soc.* (London), **220**, 472 (1953).
13) T. Miyazawa, *J. Chem. Phys.*, **35**, 693 (1961).
14) H. Sugeta and T. Miyazawa, *ibid.*, **47**, 2034 (1967).
15) T. Kitagawa and T. Miyazawa, This Bulletin, **42**, 3437 (1969).

approximately calculating the frequency distribution of low frequency lattice vibrations. In the present study, a practical method of calculating frequency distributions of chain-polymer crystals was developed and frequency distribution, specific heat and Young's moduli of polyethylene crystal were treated. Methylene groups were approximately regarded as single dynamic units since internal vibrations of methylene groups lie above 700 cm^{-1} and thus contribute little to specific heat below 150°K. The present study has been reported in a short communication.[16]

Force Field of Polyethylene Crystal

Crystal Structure. The X-ray diffraction of the orthorhombic polyethylene crystal (P_{nam}) was analysed by Bunn.[17] Two molecular chains pass through a unit cell along the c axis and there are four methylene groups per unit cell. Lattice constants at room temperature are $a_0=7.40$, $b_0=4.93$ and $c_0=2.54$ Å, with the bond length of 1.53 Å (C–C) and the bond angle of 112°(C–C–C). The setting angle of the main-chain plane (angle α in Fig. 1) is 48.7°.

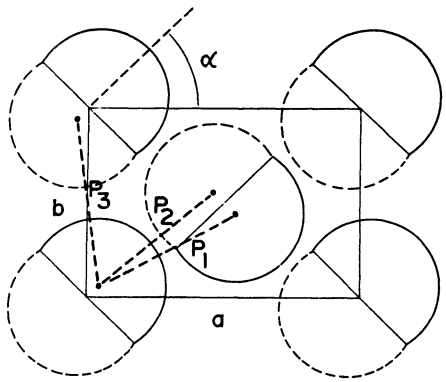

Fig. 1. Interchain potential of polyethylene crystal (skeletal approximation).

Intrachain Force Field. For normal vibration treatment, the force field of the polyethylene crystal was expressed as the sum of the intrachain terms and interchain terms.

$$V(\text{crystal}) = V(\text{intrachain}) + V(\text{interchain}) \quad (1)$$

The intrachain force field used was the Urey-Bradley force field,[9]

$$V(\text{intrachain}) = \frac{1}{2}\sum[K_r(\Delta r)^2 + K_\phi(\Delta\phi)^2 + K_q(\Delta q)^2 + K_t(\Delta t)^2] \quad (2)$$

where K_r, K_ϕ, K_q and K_t are force constants associated with the bond-stretching (Δr), angle-bending ($\Delta\phi$), repulsion (Δq) and internal-rotation coordinates (Δt). The values of intrachain force constants were adjusted (Table 1) so as to reproduce the frequency-dispersion curves of the isolated polyethylene chain.[8] The number of each type of terms per unit cell is listed in Table 1.

Table 1. Force constants and equilibrium distances

	N	d(Å)	Force constant
K_r	4	1.53	4.0 md/Å
K_q	4	2.5	0.35 md/Å
P_1	4	4.12	0.025 md/Å
P_2	8	4.18	
P_3	4	4.51	0.003 md/Å
K_t	4		0.047 md·Å
K_ϕ	4		0.59 md·Å

N; number of potential terms per unit cell.

Interchain Force Field. There are three types of close contacts (p_1, p_2 and p_3 in Fig. 1) between methylene groups of neighboring chains. Accordingly, the interchain force field was expressed as

$$V(\text{interchain}) = \frac{1}{2}\sum[P_1(\Delta p_1)^2 + P_2(\Delta p_2)^2 + P_3(\Delta p_3)^2] \quad (3)$$

where P_1, P_2, and P_3 are the force constants associated with the intermethylene stretching coordinates Δp_1, Δp_2 and Δp_3. These force constants were adjusted with reference to the experimental specific heat[18] at temperatures below 10°K where P_1 and P_2 were taken equal (intermethylene distances are nearly equal).

Acoustic Branches and Specific Heat

Normal Vibration Treatments. For an orthorhombic crystal, normal modes are specified with phase-difference vector $\boldsymbol{\delta}(\delta_a,\delta_b,\delta_c)$, whose components are phase differences of atomic displacements between adjacent unit cells along the a, b, and c axes. A group-theoretical method for constructing symmetry coordinates of orthorhombic crystals was described previously.[15]

For orthorhombic polyethylene, there are four methylene groups per unit cell. If methylene groups are treated as single dynamic units, there are twelve vibrational modes for any given phase-difference vector. Twelve Cartesian symmetry coordinates were described.[15] In the present study, dynamical matrices were diagonalized with a NEAC 2201 electronic computer.

16) T. Miyazawa and T. Kitagawa, *J. Polym. Sci., Part B*, **2**, 395 (1964).
17) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).
18) W. Reese and J. E. Tucker, *J. Chem. Phys.*, **43**, 105 (1965).

Acoustic Branches. Specific heat of a crystal in the lowest temperature region is due to acoustic vibrations of lowest frequencies. Since the frequency distribution of these acoustic vibrations is proportional to the second power of frequency, the specific heat is proportional to the third power of absolute temperature. For a chain-polymer crystal, the coefficient may be derived as a function of interchain force constants.

For an orthorhombic crystal, three acoustic vibrations are reduced, in the limit of $\boldsymbol{\delta}\to 0$, to translations (B_{1u}, B_{2u}, B_{3u}) along the a, b, and c axes. Actually, however, three frequencies are degenerate and accordingly the eigenvector matrix ($\boldsymbol{L}_S$) of the dynamical matrix ($\boldsymbol{D}_S$) is not uniquely determined. The eigenvector matrix $\boldsymbol{L}_S(0)$ may be obtained approximately after diagonalization of $\boldsymbol{L}_S(\boldsymbol{\delta}_0)$ for a very small $\boldsymbol{\delta}_0$.

The eigenvector matrix $\boldsymbol{L}_S(0)$ may be used in deriving the dynamical matrix $\boldsymbol{H}(\boldsymbol{\delta})$ of acoustic vibrations. Thus, elements of the dynamical matrix $\boldsymbol{D}_S(\boldsymbol{\delta})$ [12×12] are expanded up to second power of δ_a, δ_b and δ_c and subsequently are subjected to the orthogonal transformation with $\boldsymbol{L}_S(0)$. In the transformed matrix, cross terms for overall-rotational modes (about the chain axis) and translatory acoustic modes are proportional to the first power of δ_a, δ_b and δ_c. Thus, the second-order perturbation treatment is applied for obtaining the dynamical matrix $\boldsymbol{H}(\boldsymbol{\delta})$ of translatory acoustic modes along the a, b and c axes, respectively,

$$\left.\begin{aligned} H_{11} &= A_1\delta_a^2 + B_1\delta_b^2 + C_1\delta_c^2 \\ H_{22} &= A_2\delta_a^2 + B_2\delta_b^2 + C_2\delta_c^2 \\ H_{33} &= A_3\delta_a^2 + B_3\delta_b^2 + C_3\delta_c^2 \\ H_{23} &= D_1\delta_b\delta_c \\ H_{13} &= D_2\delta_a\delta_c \\ H_{12} &= D_3\delta_a\delta_b \end{aligned}\right\} \quad (4)$$

For the orthorhombic crystal of polyethylene, the coefficients A, B, C and D were obtained as functions of interchain force constants (Table 2). The diagonal element H_{33} is associated with the translatory mode along the c axis and accordingly is independent of P_1 since the contact line (p_1) is perpendicular to the axis. Also, the translatory mode along the c axis involves intrachain distortions and accordingly C_3 is a sum of interchain terms (P_2 and P_3), and a constant intrachain term of 0.0620. It may be mentioned also that C_1, C_2 and C_3 are independent of P_1 because the contact p_1 is between adjacent chains in the ab plane (perpendicular to the c axis). Similarly, A_1, A_2 and A_3 are independent of P_3 because the contact p_3 is between adjacent chains along the b axis (perpendicular the to a axis).

TABLE 2. THE COEFFICIENTS (A, B, C AND D) OF DYNAMICAL MATRIX ELEMENTS FOR ACOUSTIC MODES

H_{11}	A_1	$= 0.0143P_1 + 0.0201P_2$
	B_1	$= 0.0143P_1 + 0.0201P_2 + 0.0110P_3$
	C_1	$= 0.0201P_2 + 0.0003P_3$
H_{22}	A_2	$= 0.0035P_1 + 0.0124P_2$
	B_2	$= 0.0035P_1 + 0.0124P_2 + 0.0646P_3$
	C_2	$= 0.0124P_2 + 0.0161P_3$
H_{33}	A_3	$= 0.0033P_2$
	B_3	$= 0.0033P_2 + 0.0056P_3$
	C_3	$= 0.0033P_2 + 0.0014P_3 + 0.0620$
H_{23}	D_1	$= 0.0127P_2 + 0.0191P_3$
H_{13}	D_2	$= 0.0162P_2$
H_{12}	D_3	$= 0.0142P_1 + 0.0315P_2$

Constant-frequency Surfaces. Frequencies [$\nu_i(\boldsymbol{\delta})$] of three acoustic vibrations may be obtained from eigenvalues [$\lambda_i(\boldsymbol{\delta})$] of a dynamical matrix $\boldsymbol{D}(\boldsymbol{\delta})$,

$$\lambda_i(\boldsymbol{\delta}) = [2\pi c\nu_i(\boldsymbol{\delta})]^2 \quad (5)$$

If off-diagonal terms are negligible as compared with diagonal terms, then eigenvalues (λ_i) approximate to diagonal elements (H_{ii}) and constant-frequency surfaces of acoustic vibrations are ellipsoids in the phase-difference space. The sum of volumes enclosed in three constant-frequency surfaces is given as

$$v(\nu) = (4\pi/3)\times 8\pi^3c^3\nu^3\sum_{i=1}^{3}(A_iB_iC_i)^{-1/2} \quad (6)$$

Actually, however, off-diagonal elements of dynamical matrices are not negligible as compared with diagonal elements, and accordingly diagonalization of dynamical matrices is required. In practical treatments, it may be recalled that all elements of dynamical matrices Eq. (4) are given as quadratic forms of components (δ_a, δ_b, δ_c) of phase-difference vector ($\boldsymbol{\delta}$). Accordingly with the use of spherical polar coordinates[19] in $\boldsymbol{\delta}$ space, phase-differences are now written as

$$\left.\begin{aligned} \delta_a &= |\boldsymbol{\delta}|\cdot\sin\theta\cos\phi \\ \delta_b &= |\boldsymbol{\delta}|\cdot\sin\theta\sin\phi \\ \delta_c &= |\boldsymbol{\delta}|\cdot\cos\theta \end{aligned}\right\} \quad (7)$$

where $|\boldsymbol{\delta}|$ is the length of a phase-difference vector $\boldsymbol{\delta}$. Substituting Eq. (7) into Eq. (4), it may be seen that frequencies (ν_i) of acoustic vibrations are proportional to $|\boldsymbol{\delta}|$ and ratios

$$\rho_i(\theta,\ \phi) = |\boldsymbol{\delta}|/\nu_i(\boldsymbol{\delta}) \quad (8)$$

depend upon the angles θ and ϕ in $\boldsymbol{\delta}$ space. Accordingly, dynamical matrices are now expressed as $\boldsymbol{H}(|\boldsymbol{\delta}|, \theta, \phi)$ and are diagonalized for a given $|\boldsymbol{\delta}|$ but for many samples of θ and ϕ. Then for the ith acoustic branch, the constant-frequency (ν) surfaces may be obtained by numerical calculation of ratios $\rho_i(\theta,\phi)$ as functions of θ and ϕ. The volume enclosed in a constant-frequency (ν) surface of the ith branch is given as

$$v_i(\nu) = (8\nu^3/3)\int_0^{\pi/2}\int_0^{\pi/2}[\rho_i(\theta,\ \phi)]^3\sin\theta\,d\theta\,d\phi \quad (9)$$

19) W. V. Houston, *Rev. Mod. Phys.*, **20**, 161 (1948).

since, for orthorhombic crystals, the irreducible zone of the $\boldsymbol{\delta}$ space is one-eighth of the first Brillouin zone.[15] In practical calculation, numerical integration is carried out with divisions of $\Delta\theta=\pi/90$ and $\Delta\phi=\pi/36$ (confirmed to be sufficiently fine). The sum of volumes enclosed in constant-frequency surfaces of three acoustic vibrations is given as

$$v(\nu) = (8\nu^3/3)\sum_{i=1}^{3}\sum_{\phi}\sum_{\theta}[\rho_i(\theta,\ \phi)]^3 \sin\theta\cdot\Delta\theta\Delta\phi \qquad (10)$$

$$\theta = \pi/180,\ 3\pi/180,\cdots,\ 89\pi/180$$

$$\phi = \pi/72,\ 3\pi/72,\cdots,\ 35\pi/72$$

Frequency Distribution. Under the cyclic boundary condition, allowed phase-difference vectors are distributed uniformly in the first Brillouin zone. Accordingly the number (per unit cell) of acoustic vibrations lying below a given frequency (ν) is given as $v(\nu)/8\pi^3$ since the total volume of the first Brillouin zone is $8\pi^3$. For an orthorhombic crystal containing n equivalent groups (or molecules), the normalized fraction of the number of acoustic vibrations lying between ν and $\nu+d\nu$ is given as $g(\nu)d\nu$, where $g(\nu)$ is obtained by differentiation.

$$g(\nu) = d[v(\nu)/8\pi^3 n]/d\nu = \gamma\nu^2 \qquad (11)$$

$$\gamma = \{\sum_{i=1}^{3}\sum_{\phi}\sum_{\theta}[\rho_i(\theta,\ \phi)]^3 \sin\theta\}\times(\Delta\theta\Delta\phi/n\pi^3) \qquad (12)$$

For the orthorhombic crystal of polyethylene, the number of methylene groups per unit cell is $n=4$.

Specific Heat. The specific heat of a crystal is given as the sum of terms due to crystal vibrations,

$$C_v/R = \sum_{\nu} G(\nu)u^2 \exp(-u)[1-\exp(-u)]^{-2} \qquad (13)$$

$$u = hc\nu/kT \qquad (14)$$

where $G(\nu)$ is the normalized distribution (histogram at ν) of vibrational frequencies. In the lowest temperature region, the specific heat is primarily due to the frequency distribution of acoustic vibrations [Eq. (11)]. Accordingly, $G(\nu)$ in Eq. (13) is replaced with $g(\nu)d\nu$ and the integration is carried out yielding

$$C_v/R = \gamma(k/hc)^3T^3\int_0^{\infty} u^4\exp(-u)[1-\exp(-u)]^{-2}du$$

$$= 25.98\,\gamma\,(k/hc)^3T^3 \qquad (15)$$

The value of C_v/RT^3 is therefore proportional to γ which depends upon interchain force constants.

For orthorhombic polyethylene, inter-methylene force constants may be estimated from the intermolecular potential function of methane or from deBoer's potential function (to be discussed later). If estimated values of three constants (P_1, P_2 and P_3) are adjusted under fixed relative ratios, the value of γ is nearly proportional to $P^{-3/2}$. For polyethylene, the value of $10^5C_v/RT^3$ is experimentally obtained as 1.9 (by Isaacs[3]) or as 1.68 (by Tucker and Reese[18]). In the present study, intermethylene force constants were adjusted to $P_1=P_2=0.025$ and $P_3=0.003$ md/Å so that $10^5C_v/RT^3$ is calculated as 1.86.

Frequency Distribution and Specific Heat

Factor-group Modes. For the orthorhombic crystal of polyethylene, there are five lattice modes with $\boldsymbol{\delta}=0$ (factor-group modes, Fig. 2). The B_{2u}, B_{1u} and A_u modes are antiparallel translatory modes along a, b and c axes and A_g and B_{3g} are rotatory modes around the chain axis.[20] These frequencies were calculated as 153, 104 and 47 cm^{-1} and 97 and 100 cm^{-1} with the intermethylene force constants (Table 1).

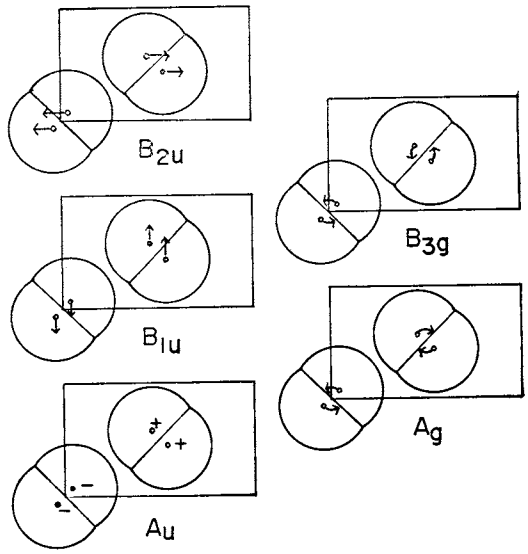

Fig. 2. Lattice vibrations ($\boldsymbol{\delta}=0$) of orthorhombic polyethylene.

Dispersion Curves. For any given phase-difference vector $\boldsymbol{\delta}$, there are eight vibrations of polyethylene below 700 cm^{-1}. Frequencies of these vibrations vary with $\boldsymbol{\delta}$. As an example, the dispersion curves are shown in Fig. 3 for $\boldsymbol{\delta}=(0,0,0)\rightarrow(0,0,\pi)$. It may be noted that, as $\boldsymbol{\delta}\rightarrow 0$, five optical branches become the factor-group modes (Fig. 2) and three acoustic branches are reduced to overall translations along the a, b and c axes. Symmetry assignments (Δ_1—Δ_4) of dispersion curves were made by a group-theoretical treatment.[15] Dispersion curves of the same symmetry species do not intersect one another.

Sampling of Phase-difference Vectors. The frequency distribution of a crystal may be calculated after normal-coordinate treatments of crystal vibrations with all possible phase-difference vectors. Under the cyclic boundary condition, phase-difference components along the a, b or c axis are

20) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).

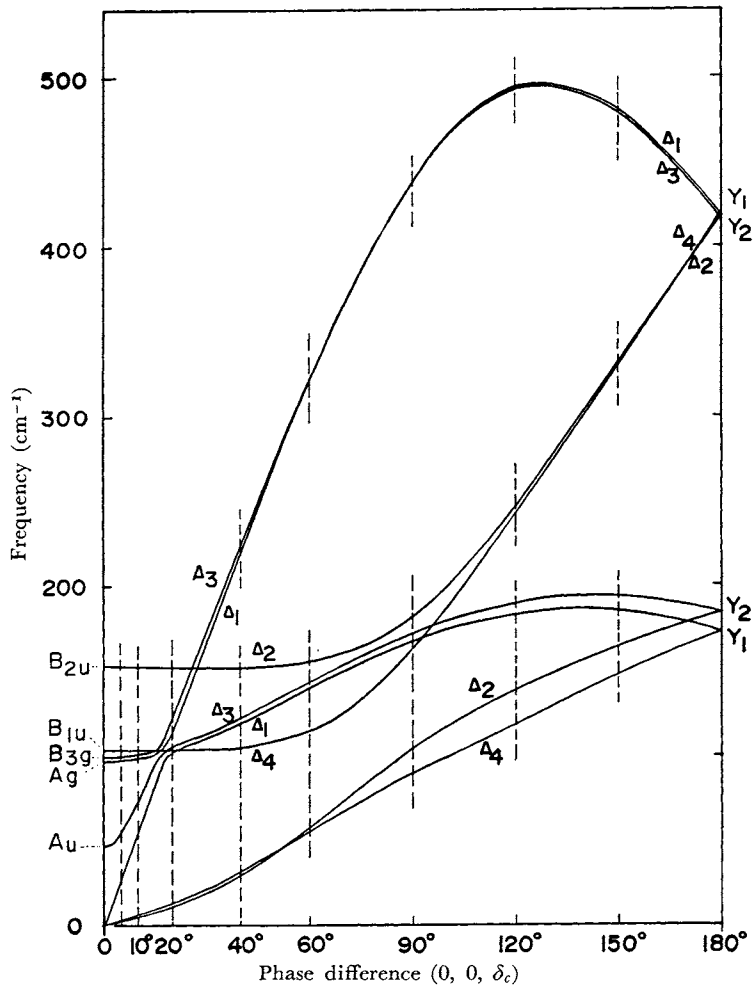

Fig. 3. Dispersion curves [$\boldsymbol{\delta}=(0, 0, 0)\rightarrow(0, 0, \pi)$] of vibrational frequencies of orthorhombic polyethylene (skeletal approximation).

uniformly distributed in the region $-\pi<\delta\leqq\pi$. For an orthorhombic crystal, however, the irreducible volume in $\boldsymbol{\delta}$ space is one eighth ($0\leq\delta\leq\pi$) of the first Brillouin zone.[15]

Vibrational frequencies of chain-polymer crystals change little with δ_a or δ_b, because the interchain force field is much weaker than the intrachain force field. On the other hand, vibrational frequencies change sensitively with δ_c and accordingly it is advisable to take many more values of δ_c than of δ_a or δ_b.

In the present study on polyethylene, the phase-differences of δ_a or δ_b were given nine values (10, 30, 50, ..., 150, and 170°) at an interval of 20°. On the other hand, the phase-difference of δ_c were given 540 values (1/6, 3/6, 5/6, 7/6,..., 1077/6, and 1079°/6 at an interval of 1°/3, yielding a total of 43,740 δ vecotrs in the irreducible volume. However, computation of vibrational frequencies for these many δ vectors is not practical and accordingly it was desirable to use an interpolation method. Thus, for every set of δ_a and δ_b, dynamical matrices were diagonalized to yield vibrational frequencies only for each of ten values of δ_c (0, 5, 10, 20, 40, 60, 90, 120, 150, and 180°). These δ_c values were selected nonuniformly so as to reproduce low-frequencies satisfactorily for small δ_c values (Fig. 3).

Interpolation. For frequency-interpolation, a cubic equation was constructed as

$$\nu(\delta_c) = \mathrm{d}_0 + \mathrm{d}_1\delta_c + \mathrm{d}_2\delta_c^2 + \mathrm{d}_3\delta_c^3 \qquad (16)$$

which satisfies frequencies (ν_1, ν_2, ν_3, and ν_4) for successively selected values of $\delta_c=\delta_1$, δ_2, δ_3 and δ_4. Equation (12) may be used for $\delta_2<\delta_c<\delta_3$ and is applicable to δ_c values of 5—150°. However, the equation for $\delta_1=90°$, $\delta_2=120°$, $\delta_3=150°$ and $\delta_4=180°$ was also used for δ_c values of 150—180°. In practical computation, Eq. (16) was rewritten as

$$\nu(\delta_c) = (\nu_1\ \nu_2\ \nu_3\ \nu_4)\cdot\boldsymbol{w}_\delta \qquad (17)$$

$$\boldsymbol{w}_\delta = \begin{bmatrix} 1 & 1 & 1 & 1 \\ \delta_1 & \delta_2 & \delta_3 & \delta_4 \\ \delta_1^2 & \delta_2^2 & \delta_3^2 & \delta_4^2 \\ \delta_1^3 & \delta_2^3 & \delta_3^3 & \delta_4^3 \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ \delta_c \\ \delta_c^2 \\ \delta_c^3 \end{bmatrix} \tag{18}$$

and the $\boldsymbol{w}_\delta$ vector was used commonly for any set of δ_a and δ_b. For the δ_c values of 0—5°, a quartic equation was constructed as

$$\nu(\delta_c) = d_0' + d_2'\delta_c^2 + d_4'\delta_c^4 \tag{19}$$

which satisfies frequencies for $\delta_c=0$, 5 and 10°. Vibrational frequencies thus calculated with the interpolation method were confirmed to agree, better than ± 0.7 cm^{-1}, with those calculated with diagonalization of dynamical matrices. Thus, the computation time consumed in frequency calculations for 43740 $\boldsymbol{\delta}$ vectors was drastically reduced.

Frequency Distribution. The frequencies of a total of 349920 vibrations of orthorhombic polyethylene were collected. The frequency distribution was constructed with the frequency interval of 1 cm^{-1} and was then normalized to the vibrational degree of freedom of a methylene group below 700 cm^{-1},

$$\sum_\nu G(\nu) = 2 \tag{20}$$

The frequency distribution histogram of polyethylene crystal (skeletal approximation) is shown in Fig. 4 with a frequency interval of 5 cm^{-1}. Two peaks appear at about 500 and 200 cm^{-1}, as expected previously from dispersion curves of an isolated chain of polyethylene.[8] Existence of these peaks was confirmed by scattering experiments of thermal neutron from crystalline polyethylene.[21,22]

Specific Heat. The normalized frequency distribution $G(\nu)$ [Eq.(20)] was substituted into

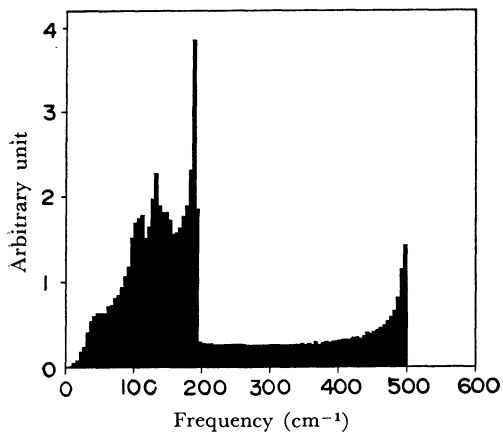

Fig. 4. The frequency distribution histogram of orthorhombic polyethylene crystal (skeletal approximation).

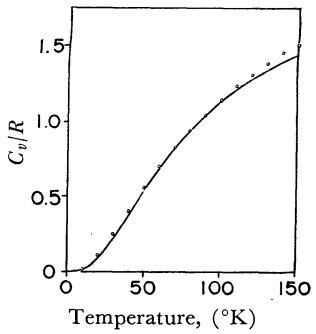

Fig. 5. Specific heat (C_v/R) of orthorhombic polyethylene crystal; open circles: experimental,[5] solid line: calculated with the skeletal approximation.

Eq. (13) and the specific heat at constant volume was obtained as shown in Fig. 5. At temperatures above ~15°K, calculated values of C_v/R gradually deviate from the T^3 law and then become nearly proportional to T, in good agreement with experimental values.[5] The specific heat (C_v/R) due to internal modes of methylene groups was estimated as small as 0.002 at 100°K and as 0.038 at 150°K.

Young's Moduli

Chain-polymer Crystal. For chain-polymer crystals, Young's modulus along the chain direction (c axis) depends primarily upon the intrachain force field whereas Young's moduli along the a or b axes depend primarily upon the interchain force field. Comparison of the calculated and experimental values of Young's moduli (a or b axes) serves as a check on calculated force constants of the interchain force field.

Intrachain forces of chain-polymer crystals are much stronger than interchain forces. Accordingly, in treating Young's moduli along the a or b axes, intrachain displacements (Δc) may well be neglected. Under homogeneous deformation, the potential energy of orthorhombic chain-polymer crystals may be written with two external-deformation coordinates (Δa and Δb) and an internal-deformation coordinate ($\Delta\alpha$) [Fig. 1],

$$V = \frac{1}{2}\tilde{\boldsymbol{\beta}}\boldsymbol{C}\boldsymbol{\beta} \tag{21}$$

$$\tilde{\boldsymbol{\beta}} = (\Delta a\ \Delta b\ \Delta\alpha) \tag{22}$$

where $\boldsymbol{C}$ is the elastic stiffness constant matrix. Then, in equilibrium, the tension (f_a) along the a axis is balanced with $-\partial V/\partial \Delta a$ and the tension (f_b) along the b axis is balanced with $-\partial V/\partial \Delta b$, but the internal tension (f_α) is always equal to zero so that $\partial V/\partial \Delta\alpha=0$. Under homogeneous deformation, therefore,

$$\boldsymbol{\beta} = \begin{bmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{bmatrix} \begin{bmatrix} f_a \\ f_b \\ 0 \end{bmatrix} \tag{23}$$

21) H. R. Danner, G. J. Safford, H. Boutin and M. Berger, *J. Chem. Phys.*, **40**, 1417 (1964).
22) W. R. Myers, J. L. Donovan and J. S. King, *ibid.*, **42**, 4299 (1965).

where $S(=C^{-1})$ is the elastic compliance matrix. From Eq. (23) Young's moduli along the a and b axes are derived as

$$\left.\begin{aligned} E_a &= a_0/b_0c_0S_{11} \\ E_b &= b_0/a_0c_0S_{22} \end{aligned}\right\} \quad (23)$$

Relative ratio of external and internal deformations $[(\Delta a/a_0) : (\Delta b/b_0) : \Delta\alpha]$ is equal to $[(S_{11}/a_0) : (S_{21}/b_0) : S_{31}]$ under the tension of f_a, but is equal to $[(S_{12}/a_0) : (S_{22}/b_0) : S_{32}]$ under the tension f_b.

Polyethylene. Young's moduli (in unit of 10^{11} dyne/cm^2) of orthorhombic polyethylene crystal were calculated as $E_a=0.9$ and $E_b=0.3$, from the interchain force constants at lowest temperatures. In comparison, experimental values[23] at room temperature are $E_a=0.4$ and $E_b=0.3$.

Discussions

Intermethylene Force Constants. Effective force constants of $CH_2\cdots CH_2$ contacts (p) are useful for studying crystal vibrations and solid state properties of hydrocarbon polymers. Intermethylene force constants may be transferred from the second derivative (kcal/Å^2) of intermolecular potential (V) of methane,[24]

$$d^2V/dp^2 = 2.008\times10^9/p^{14} - 1.630\times10^5/p^8 \quad (25)$$

Thus for intermethylene contacts of $p_1=4.12$, $p_2=4.18$ and $p_3=4.51$ Å, intermethylene force constants at room temperature were calculated as $P_1=0.018$, $P_2=0.015$ and $P_3=0.002$ md/Å, respectively. If these intermethylene constants at room temperature are used, the specific heats at temperatures below 10°K are calculated slightly larger than the experimental data, indicating that intermethylene constants at <10°K should be larger than those at room temperature. In fact, at lower temperatures, intermethylene contacts become shorter and intermethylene force constants are expected to become larger than those at room temperature.

In treating elastic constants of polyethylene crystal, interchain force constants were derived by Odajima and Maeda[25] from deBoer's repulsive potential function[26] for H$\cdots$H contacts (x). Force constants (in unit of md/Å) are given as

$$d^2V/dx^2 = 150\cdot\exp(-3.53x) \quad (26)$$

In the present study, Eq.(26) was transferred to the case of intermethylene force constants. Actual intermethylene contacts (p) were converted to corresponding H$\cdots$H contacts (x),

$$x = (r_H/r_{CH_2})p \quad (27)$$

where r_H and r_{CH_2}, are van der Waals' radii[27] of hydrogen (1.2Å) and methylene group (2.0Å). Thus, from intermethylene contacts, force constants of orthorhombic polyethylene crystal were estimated as $P_1=0.024$, $P_2=0.022$, and $P_3=0.003$ md/Å. With reference to experimental specific heats at temperatures below 10°K, these values of force constants were only slightly adjusted to yield the final set of force constants as listed in Table 1. Equations (26) and (27) were also used for estimating effective interchain force constants of orthorhombic polyoxymethylene crystal.[28]

Constant-frequency Surfaces. In the dynamical matrices of acoustic vibrations of polyethylene crystal, off-diagonal elements may not be neglected as compared with diagonal elements. Accordingly, constant-frequency surfaces of polyethylene are much distorted from ellipsoidal surfaces. However, if off-diagonal elements are neglected, constant-frequency surfaces become ellipsoidal, and the specific heat ($10^5C_v/RT^3$) in the lowest temperature region is calculated as 1.02, that is much smaller than the theoretically correct value of 1.86. Accordingly, off-diagonal elements of dynamical matrices can not be neglected, and the volume enclosed in constant-frequency surfaces need be numerically integrated with Eqs. (7)—(10).

Frequency Distribution. The prominent peaks of the frequency distribution (Fig. 4) at 500 and 200 cm^{-1} correspond to the maximum frequencies of the dispersion curves of the C–C–C bending branches and C–C internal-rotation branches around δ_c values of 120—150° (Fig. 3). In the region 450—200 cm^{-1}, four dispersion curves of the C–C–C bending branches are almost straight and depend little upon δ_a or δ_b. Accordingly, the frequency distribution is nearly constant in the region 450—200 cm^{-1}, as expected similarly for Debye's one-dimensional elastic continuum.[29]

In the frequency distribution of polyethylene (Fig. 4), there is a peak at the high-frequency cut-off of 500 cm^{-1} but, with Tarasov's model, no peak is expected to appear at the one-dimensional characteristic frequency (ν_{D1}). With the three-dimensional Debye model, a peak is expected to appear at the cut-off frequency (ν_{D3}) below which the frequency distribution is proportional to ν^2. In the frequency distribution of polyethylene (Fig. 4), a ν_{D3} peak can not be identified uniquely among several peaks due to low-frequency optical modes. The characteristic frequencies were adjusted[5] to $\nu_{D1}=375$ cm^{-1} and $\nu_{D3}=85$ cm^{-1} so as to reproduce experimental specific heat. However, these can not be identified uniquely in the frequency

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distribution of polyethylene (Fig. 4).

Skeletal Approximation. In the normal vibration treatment of orthorhombic polyethylene crystal by Tasumi and Shimanouchi,[30] hydrogen atoms as well as carbon atoms were treated as single dynamic units and the factor group frequencies were calculated as 134(A_g), 109(B_{3g}), 99(B_{2u}), 71(B_{1u}), and 55 cm^{-1}(A_u). It may be remarked that the requencies of the rotatory modes (A_g and B_{3g}) are higher than the frequencies of the translatory modes (B_{2u} and B_{1u}). In the present study, the lattice dynamics of polyethylene was studied where methylene groups were treated as single dynamic units at sites of carbon atoms. With this skeletal approximation, the frequencies of the rotatory modes are lower than the frequencies of the translatory modes.

In the rotatory modes of polyethylene chain about the axis, displacements of carbon atoms are much smaller than those of hydrogen atoms. Accordingly, changes in intermethylene contacts are much smaller than in inter-hydrogen contacts. Therefore, the rotatory frequencies calculated with the skeletal approximation are lower than those calculated by Tasumi.[30]

On the other hand, in the translatory modes of polyethylene chain, displacements of carbon atoms are equal to displacements of hydrogen atoms. Accordingly, changes in intermethylene contacts do not differ much from changes in inter-hydrogen contacts and the skeletal approximation is fairly applicable. In fact, intermethylene force constants estimated from deBoer's potential function were only slightly adjusted so as to reproduce experimental specific heat in the lowest temperature region.

30) M. Tasumi and T. Shimanouchi, *J. Chem. Phys.*, **43**, 1245 (1965).