THE DESCRIPTION OF POLYETHYLENE CRYSTAL AS A CONTINUUM WITH INTERNAL DEGREES OF FREEDOM

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Abstract—Polyethylene crystal is described in terms of a continuum with internal degrees of freedom. The motion equations are derived from "first principles" i.e. from the molecular potentials of interaction. The asymptotic decomposition of appropriate motion equations is provided, the main asymptotic boundary problems are formulated, the vibration spectra and the elastic moduli of the crystal are prescribed.

INTRODUCTION

The model of a continuum with internal degrees of freedom is well known in mechanics [see e.g. Kunin (1975)]. This model is important in describing media with sophisticated microstructure, especially for the cases of fast and small-range loading.

The elastic continuum in this sort of theory is characterized by two types of variables: (i) the displacement vector of the mass centre of the elementary cell, which is responsible for the conventional world of theory of elasticity, and (ii) internal variables—rotations and deformations of the cell, responsible for the microstructure. The elastic constants connected with these internal variables are usually introduced phenomenologically [see Kunin (1975)].

As far as we know this kind of elasticity theory has not yet been applied for the description of polymer crystals, although these systems seem to be a natural field for application of the models of elastic continuum with microstructure. These crystals usually have a complicated type of lattice with the possibility of rotations and intercellular deformations. The elastic constants for these systems may be obtained from widely studied and well-known molecular potentials of interaction.

The development of such a theory for polymer crystals seems to be useful for several reasons. The first and obvious one is the necessity of prediction of vibration spectra of the system. The analytic accomplishment of such prediction requires the solution of a complete system of dynamics equations. The second reason is that in order to obtain the expressions for macroscopic elastic constants (even for the case of the usual theory of elasticity) we also need to take into account the internal degrees of freedom.

The systems of equations of nonlocal theories are often hardly tractable analytically because of complexity and large number of variables. It turns out not to be the case for polymer crystals. Strong anisotropy which is the peculiarity of these systems gives an opportunity to apply the asymptotic approach and thus to obtain approximate solutions for the elastic problems.

In this paper we attempt to provide the analysis described for the crystal of orthorombic polyethylene. The structure of the paper is as follows. In the first part the model of crystal with potentials of interaction is introduced and discrete nonlinear equations of motion are obtained. In the second part these equations are continualized and linearized. In the third part of the paper the asymptotic analysis of the equations obtained is provided. In the fourth and the fifth parts the theory-of-elasticity limit is analyzed and vibration spectra incorporated with elastic modules are calculated and compared with experimental data.

1. THE MOTION EQUATIONS OF POLYETHYLENE CRYSTAL

Here we are going to use the conventional model of orthorombic polyethylene crystal presented in Fig. 1. As elementary cell we may choose two fragments of neighbouring chains as presented in Fig. 2. The axial directions are also indicated there.

We choose the model of polyethylene chain with CH_2-groups being considered as single particles. Such a consideration implies neglecting high-frequency vibration modes of CH_2-groups. These vibrations seem not to affect essentially the elastic behaviour and nonlinear dynamics of PE crystal and their elimination is commonly accepted.

The deformation energy connected with a certain configuration of crystal thus may be written down as

$$E_{def} = \sum_{kij} E_{intra} + \frac{1}{2}\sum_{kij} E_{inter} \tag{1}$$

where E_{intra} is intramolecular energy and E_{inter} is intermolecular energy of interaction if taking into account all possible pairs of chains. The subscripts i and j denote the numbers of chains in X and Y directions respectively, the subscript k is the number of segments in the chain.

The first problem to be solved is that of appropriate choice of intramolecular potential of interaction. We use here the data presented in Noid $et\ al.$ (1991):

$$E_{intra} = V_b + V_{val} + V_{conf} \tag{2}$$

where

$$V_b = D(1 - \exp(-\alpha(|r_k - r_{k+1}| - r_0))) \tag{3}$$

where $D = 334.72$ kJ mol^{-1}, $\alpha = 19.1$ nm^{-1}, $r_0 = 0.153$ nm, r_k, r_{k+1} are the positions of neighboring groups in the chain,

$$V_{val} = \frac{1}{2}\gamma(\cos\theta - \cos\theta_0)^2 \tag{4}$$

with $\gamma = 130.122$ kJ mol^{-1}, $\theta_0 = 113°$ is the valence angle potential, θ being the valence angle;

$$V_{conf} = 8.37 + 1.6754\cos\phi + 6.695\cos 3\phi \tag{5}$$

is the potential of conformation, all numbers having the dimension kJ mol^{-1}, ϕ is the conformation angle.
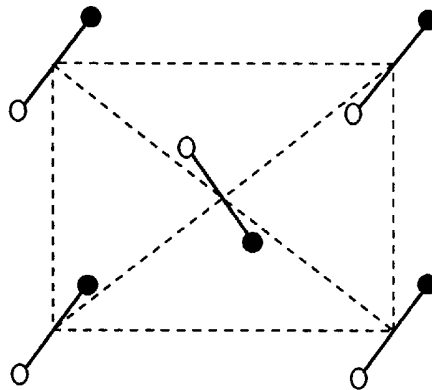

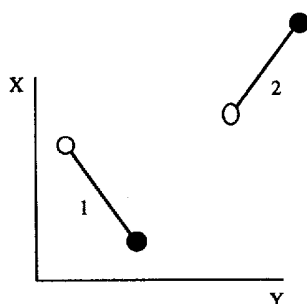Fig. 1. The astructure of orthorombic polyethylene crystal.

Fig. 2. The elementary cell of the crystal (x and y are the crystalline axes).

The intermolecular energy of interaction is calculated as sum of pairs of Lennard–Jones potentials in three neighbouring layers:

$$E_{inter} = \tfrac{1}{2}\sum V(_\alpha\mathbf{r}_s^1 - _\beta\mathbf{r}_t^2).\tag{6}$$

Here $\mathbf{r}$ is the position vector of the appropriate CH_2-group, the superscripts 1 and 2 denote two macromolecules, the subscripts α and β sign all possible combinations of R and L (see Fig. 2) and subscripts s and t vary from $k-1$ to $k+1$. In the sum (1) the summation in the second term is implied for all the crystal. The pair potential of interaction $V(\mathbf{r})$ is supposed of Lennard–Jones type. We restrict ourselves by consideration of pair potential only because the nonlocal effects (e.g. the dependence on more than two interacting particles positions) is not peculiar for noncovalent bonds in this type of molecular systems.

The potentials considered give us an opportunity to write down the motion equations of PE crystal. In order to formulate the model potentials and to obtain the results in tractable analytical form we introduce variables describing the crystal configuration as:

$$_\alpha\mathbf{R}_k = \tfrac{1}{2}(\mathbf{r}_k + \mathbf{r}_{k+1})\tag{7}$$

which is the position of centre of masses in the fragment, the subscript α being connected with the number of chains in the cell;

$$_\alpha\varphi_k = (\mathbf{r}_k - \mathbf{r}_{k+1}) \cdot \mathbf{m}/cl\tag{8}$$

is the rotation of the chain, $\mathbf{m}$ being the unit vector normal to the chain plane, $c = \cos(\theta_0/2)$, l is the length of undisturbed bond (see Fig. 3).

The next problem to be solved here is to define the tractable model potential of intermolecular interaction, because potential (2), though being physically correct and reasonable, is obviously intractable analytically. The model potential is to satisfy the following conditions: it is to give correct values of elastic moduli and to correspond to the
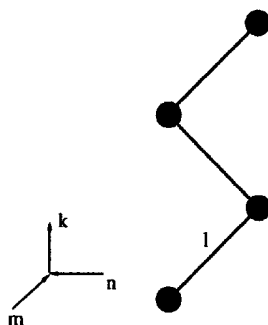

Fig. 3. The structure of polyethylene chain.

symmetry of our crystal. We may present it as the first terms of Fourier series of the potential (6):

$$V_{\text{inter}} = \sum_{mnk} \sum \{ \Upsilon(_k\rho_{mn}) + B\cos (_k\varphi_m - _k\varphi_n)$$

$$+ C[\cos (_{k+1}\varphi_m - _k\varphi_n) \cos (^1_k\Delta_{mn}) + \cos (_k\varphi_m - _{k+1}\varphi_n) \cos (^2_k\Delta_{mn})]$$

$$+ A_1 \cos (_k\varphi_m + _k\varphi_n) + A_2 \cos 2(_k\varphi_m + _k\varphi_n) + D_k\rho_{mn} \sin_k \varphi_m \}   \quad (9)$$

where $_k\rho_{mn} = _k\mathbf{l}_{mn} \cdot (\delta_k\mathbf{R}_m - \delta_k\mathbf{R}_n)$, $_k\mathbf{l}_{mn}$ being the vector of respective position of two chains denoted by subscripts m and n, $\delta_k\mathbf{R}_j$ denotes the displacement of the j-th chain from equilibrium position,

$$^1_k\Delta_{mn} = \pi[(_{k+1}W_m - _kW_n)/ls + v(_{k+1}y_m - _ky_n)],$$

$$^2_k\Delta_{mn} = \pi[(_kW_m - _{k+1}W_n)/ls + v(_ky_m - _{k+1}y_n)],$$

$$_kW_m = \mathbf{k}\delta_k\mathbf{R}_m, S = \sin (\theta_0/2), _ky_m = _k\mathbf{l}_{mn} \cdot \delta_k\mathbf{R}_m, _ky_n = _k\mathbf{l}_{mn} \cdot \delta_k\mathbf{R}_n,$$

Υ being the Lennard–Jones potential, and the last term appearing due to interaction between translational and rotational motions in the system. The subscript k is the number of segments in the chain.

It is possible now to write down the discrete equations describing the motion of PE crystal. We take into account the intermolecular interaction with its six nearest neighbours. The motion of the elementary cell is described by 12 variables (three variables corresponding to each atom which participates in the cell). We use here the following variables to characterize the motion: two displacement vectors of centres of masses (6 variables), two rotations of the chain, the bond and valence angle deformations of each chain. We take into account the intermolecular interaction by defining the equations governing the displacements and rotations only. Four other degrees of freedom are connected with excitation of optical modes of vibrations with large energy if compared with the intermolecular one. So these degrees of freedom may be accounted in single chain approximation.

The discrete nonlinear equations describing the dynamics of PE crystal may be written as:

$$\frac{\mu \partial^2 _{mn}\mathbf{R}_k}{\partial t^2} = - \frac{\partial(V_b + V_{\text{val}} + V_{\text{conf}})}{\partial_{mn}\mathbf{R}_k} - \frac{\partial V_{\text{inter}}}{\partial_{mn}\mathbf{R}_k}   \quad (10)$$

where $\mu = 28$ atomic units of mass;

$$\frac{J \partial^2_{mn}\varphi_k}{\partial t^2} = - \frac{\partial(V_{\text{val}} + V_{\text{conf}} + V_{\text{inter}})}{\partial_{mn}\varphi_k}   \quad (11)$$

where $J = \mu l^2 c^2/4$. The potential of valence bonds is absent here because they are not involved in the rotation. The valence and conformation angles may be represented as:

$$\cos \theta_k = \frac{(\mathbf{r}_k - \mathbf{r}_{k-1}) \cdot (\mathbf{r}_k - \mathbf{r}_{k+1})}{|\mathbf{r}_k - \mathbf{r}_{k-1}||\mathbf{r}_k - \mathbf{r}_{k+1}|}   \quad (12)$$

and

$$\cos \phi_k = \frac{[(\mathbf{r}_k - \mathbf{r}_{k-1}) \times (\mathbf{r}_k - \mathbf{r}_{k+1})] \cdot [(\mathbf{r}_k - \mathbf{r}_{k+1}) \times (\mathbf{r}_{k+1} - \mathbf{r}_{k+2})]}{|(\mathbf{r}_k - \mathbf{r}_{k-1}) \times (\mathbf{r}_k - \mathbf{r}_{k+1})||(\mathbf{r}_k - \mathbf{r}_{k+1}) \times (\mathbf{r}_{k+1} - \mathbf{r}_{k+2})|}.   \quad (13)$$

2. THE CONTINUALIZATION AND LINEARIZATION OF MOTION EQUATIONS

We start with the linearization of intramolecular interactions and writing down appropriate equations. These equations are important while studying processes with small intramolecular and large intermolecular perturbations such as collective twist. They are written as follows [for one-chain approximation see Kirkwood (1939), Pitzer (1940)]:

$$\frac{\partial^2}{\partial t^2}\xi_n + \alpha[s^2(2\xi_n - \xi_{n+1} - \xi_{n-1}) + (-1)^n cs(\eta_{n+1} - \eta_{n-1})]$$

$$+ \beta[c^2(2\xi_n - \xi_{n+2} - \xi_{n-2}) + (-1)^n cs(\eta_{n+2} - \eta_{n-2} - 2\eta_{n+1} + 2\eta_{n-1})]$$

$$+ \sum_6 \left(\frac{\partial V_{inter}}{\partial W_k}\right) = 0 \quad (14)$$

$$\frac{\partial^2}{\partial t^2}\eta_n + \alpha[c^2(2\eta_n - \eta_{n+1} - \eta_{n-1}) + (-1)^n cs(\xi_{n+1} - \xi_{n-1})]$$

$$+ \beta[s^2(6\eta_n - 4\eta_{n+1} - 4\eta_{n-1} + \eta_{n+2} + \eta_{n-2}) - (-1)^n cs(\xi_{n+2} - \xi_{n-2}$$

$$+ 2\xi_{n+1} - 2\xi_{n-1})] + \sum_6 \left(\frac{\partial V_{inter}}{\partial u_k}\right) = 0 \quad (15)$$

$$\frac{\partial^2}{\partial t^2}Z_n + \gamma(4Z_n - Z_{n-1} - Z_{n+1} - 2Z_{n-2} - 2Z_{n+2} + Z_{n+3} + Z_{n-3}) + \sum_6 \left(\frac{\partial V_{inter}}{\partial Z_n}\right) = 0. \quad (16)$$

In these formulae $\xi_n = \mathbf{k} \cdot \delta \mathbf{r}_n, \eta_n = \mathbf{m} \cdot \delta \mathbf{r}_n, Z_n = \mathbf{n} \cdot \delta \mathbf{r}_n, u_k = \mathbf{m} \cdot \delta \mathbf{R}_k, k = 2n$. The summation is extended over the six nearest neighbours of the chain. The constants α, β, and γ are the rigidities of valence bonds, valence angles and torsional angles respectively in linear approximation.

The next step is the continualization of motion equations in their part corresponding to intramolecular interaction while leaving the intermolecular part in discrete form. This approximation is important because excitations with small intramolecular and large intermolecular gradients are possible in PE crystal because of large difference of corresponding energies in the case of comparable deformations. The strict continualization of equations (14–16) needs, however, the consideration of several limit cases which correspond to wavenumbers close to zero and to π. By presenting the variables in exponential form (without account of intermolecular interaction) we obtain well-known relations [Kirkwood (1939), Pitzer (1940)]:

$$\xi_n = \xi\exp(i(\omega_1 t - \vartheta n)), \eta_n = \eta(-1)^n\exp(i(\omega_1 t - \vartheta n)), \quad Z_n = Z(-1)^n\exp(i(\omega_2 t - \vartheta n))$$

$$\omega_1^2 = \omega_0^2 \pm (\omega_0^4 - \omega_*^4)$$

$$\omega_0^2 = \alpha[1 + \cos\vartheta(c^2 - s^2)] + 2\beta 1 + \cos\vartheta)[1 - \cos\vartheta(c^2 - s^2)]$$

$$\omega_*^4 = 8\alpha\beta(1 + \cos\vartheta)\sin^2\vartheta;$$

$$\omega_2^2 = \gamma(4 + 2\cos\vartheta - 4\cos 2\vartheta - 2\cos 3\vartheta). \quad (17)$$

The first limit case to be regarded here is that of $\vartheta \ll \pi$. The dispersive relations give for this case:

$$\omega_1^2 \approx 2[\alpha(1+c^2-s^2)+4\beta(1+s^2-c^2)] - \frac{8\alpha\beta\vartheta^2}{\alpha(1+c^2-s^2)+4\beta(1+s^2-c^2)} \quad \text{(optical branch)}$$

$$\omega_1^2 = \frac{8\alpha\beta\vartheta^2}{\alpha(1+c^2-s^2)+4\beta(1+s^2-c^2)} \quad \text{(acoustic branch)}$$

$$\omega_2^2 = 16\gamma\vartheta^2. \tag{18}$$

For the other limit case (close to π) we introduce the new wavenumber $\chi = \pi - \vartheta$ and thus obtain:

$$\omega_1^2 = \frac{2\beta\chi^4}{1+s^2-c^2} \quad \text{(acoustic branch)}$$

$$\omega_1^2 = 2\alpha(1+s^2-c^2) - \frac{2\beta\chi^4}{1+s^2-c^2} \quad \text{(optical branch)}$$

$$\omega_2^2 = \tfrac{4}{3}\gamma\chi^4. \tag{19}$$

We don't take into account the optical branches of vibrations because of their high energy.

Thus for each case we may write down the "main" equations describing the behaviour of the chain. Each dispersive relation corresponds to a certain motion equation for "leading" mode of motion. For the case of small wavenumbers these leading degrees of freedom are the displacement in direction of chain axis and the rotation. For the variables introduced before we obtain from eqns (14) and (16)-(18):

$$\frac{\partial^2}{\partial t^2}W_k - T\frac{\partial^2}{\partial z^2}W_k + \sum_6 \left(\frac{\partial V_{\text{inter}}}{\partial W_k}\right) = 0$$

$$\frac{\partial^2}{\partial t^2}\varphi_k - 16\gamma\frac{\partial^2}{\partial z^2}\varphi_k + \sum_6 \left(\frac{\partial V_{\text{inter}}}{\partial \varphi_k}\right) = 0$$

$$T = \frac{8\alpha\beta}{\alpha(1+c^2-s^2)+4\beta(1+s^2-c^2)}. \tag{20}$$

The second system of equations corresponding to wavenumbers close to π may be presented as follows:

$$\frac{\partial^2}{\partial t^2}u_k + \frac{2\beta}{1+s^2-c^2}\frac{\partial^4}{\partial z^4}u_k + \sum_6 \left(\frac{\partial V_{\text{inter}}}{\partial u_k}\right) = 0$$

$$\frac{\partial^2}{\partial t^2}v_k + \tfrac{4}{3}\gamma\frac{\partial^4}{\partial z^4}v_k + \sum \left(\frac{\partial V_{\text{inter}}}{\partial v_k}\right) = 0. \tag{21}$$

The accompanying "optical" deformations (which correspond to relatively small deformations of valence bonds and antiphase deformations of valence angles) in these approximations may be directly calculated from the solution for "main" displacements.

Here we have obtained that the motion of polyethylene crystal in long-wave limit (which corresponds to the conventional theory of elasticity) is described by two systems of equations which are not connected in the single chain limit. The connection exists due to intermolecular interaction which is much weaker than intramolecular. The natural way for solution of such a system is the procedure of subsequent approximations when the

approximation of zero order corresponds to crystal deformation without X and Y gradients. The details of such a procedure will be presented further.

The next step of our investigation is the linearization of motion equations (20)–(21) with intermolecular potential (9) in the form (the terms other then the quadratic ones are omitted):

$$V_{\text{inter}} = \sum_{mnk}\sum \{K(_k\rho_{mn})^2 - \tfrac{1}{2}B(_k\varphi_m - _k\varphi_n)^2$$

$$-\tfrac{1}{2}C[(_{k+1}\varphi_m - _k\varphi_n)^2 + (_k^1\Delta_{mn})^2 + (_k\varphi_m - _{k+1}\varphi_n)^2 + (_k^2\Delta_{mn})^2]$$

$$-A_1(_k\varphi_m + _k\varphi_n)^2 - 2A_2(_k\varphi_m + _k\varphi_n)^2 + D_k\rho_{mnk}\varphi_m\}. \quad (22)$$

This potential function gives an opportunity to write down the motion equations explicitly. This system connects eight equations according to number of variables. For the projection of motion equations on Z axis we thus obtain:

$$\frac{\partial^2}{\partial t^2}\,_{ij}^1 W_k = T\frac{\partial^2}{\partial Z^2}\,_{ij}^1 W_k$$

$$-8\frac{\pi}{ls}C(_k^1\Delta_{ij} - _{k-1}^2\Delta_{ij} + _k^1\Delta_{i-1j} - _{k-1}^2\Delta_{i-1j} + _k^1\Delta_{ij-1} - _{k-1}^2\Delta_{ij-1} + _k^1\Delta_{i-1j-1} - _{k-1}^2\Delta_{i-1j-1})$$

$$-8\frac{\pi}{ls}C^*(_k\Delta_{i-1j}^* - _{k-1}\Delta_{i-1j}^* + _k\Delta_{i+1j}^* - _{k-1}\Delta_{i+1j}^*).$$

$$\frac{\partial^2}{\partial t^2}\,_{ij}^2 W_k = T\frac{\partial^2}{\partial Z^2}\,_{ij}^2 W_k$$

$$-8\frac{\pi}{ls}C(_k^2\Delta_{ij} - _{k-1}^1\Delta_{ij} + _k^2\Delta_{i+1j} - _{k-1}^1\Delta_{i+1j} + _k^2\Delta_{ij+1} - _{k-1}^1\Delta_{ij+1} + _k^2\Delta_{i+1j+1} - _{k-1}^1\Delta_{i+1j+1})$$

$$-8\frac{\pi}{ls}C^*(_k^*\Delta_{i-1j} - _{k-1}^*\Delta_{i-1j} + _k^*\Delta_{i+1j} - _{k-1}^*\Delta_{i+1j}). \quad (23)$$

In this system of equations the values denoted by * correspond to interactions between two chains which are of the same type and are neighbours with respect to the X axis. The star in the right side of Δ corresponds to interaction between type 1 chains and in the left to type 2 chains.

The second pair of equations determine the rotation motion:

$$\frac{\partial^2}{\partial t^2}\,_{ij}^1\varphi_k = 16\gamma\frac{\partial^2}{\partial z^2}\,_{ij}^1\varphi_k + 4B[(_k^1\varphi_{ij} - _k^2\varphi_{ij}) + (_k^1\varphi_{ij} - _k^2\varphi_{i-1j}) + (_k^1\varphi_{ij} - _k^2\varphi_{ij-1}) + (_k^1\varphi_{ij} - _k^2\varphi_{i-1j-1})]$$

$$+8C[(_k^1\varphi_{ij} - _{k+1}^2\varphi_{ij}) + (_k^1\varphi_{ij} - _{k+1}^2\varphi_{i-1j}) + (_k^1\varphi_{ij} - _{k+1}^2\varphi_{ij-1}) + (_k^1\varphi_{ij} - _{k+1}^2\varphi_{i-1j-1})$$

$$+(_k^1\varphi_{ij} - _{k-1}^2\varphi_{ij}) + (_k^1\varphi_{ij} - _{k-1}^2\varphi_{i-1j}) + (_k^1\varphi_{ij} - _{k-1}^2\varphi_{ij-1}) + (_k^1\varphi_{ij} - _{k-1}^2\varphi_{i-1j-1})]$$

$$+2B^*[(_k^1\varphi_{ij} - _k^1\varphi_{i-1j}) + (_k^1\varphi_{ij} - _k^1\varphi_{i+1j})] + 2C^*[(_k^1\varphi_{ij} - _{k+1}^1\varphi_{i-1j}) + (_k^1\varphi_{ij} - _{k+1}^1\varphi_{i+1j})$$

$$+(_k^1\varphi_{ij} - _{k-1}^1\varphi_{i-1j}) + (_k^1\varphi_{ij} - _{k-1}^1\varphi_{i+1j})] + 4(A_1 + 4A_2)_{ij}^1\varphi_k - D\sum_4\rho_{mn} - D^*\sum_2\rho_{mn}$$

$$\frac{\partial^2}{\partial t^2}\,_{ij}^2\varphi_k = 16\gamma\frac{\partial^2}{\partial z^2}\,_{ij}^2\varphi_k + 4B[(_k^2\varphi_{ij} - _k^1\varphi_{ij}) + (_k^2\varphi_{ij} - _k^1\varphi_{i+1j}) + (_k^2\varphi_{ij} - _k^1\varphi_{ij+1}) + (_k^2\varphi_{ij} - _k^1\varphi_{i+1j+1})]$$

$$+8C[(_k^2\varphi_{ij} - _{k+1}^1\varphi_{ij}) + (_k^2\varphi_{ij} - _{k+1}^1\varphi_{i+1j}) + (_k^2\varphi_{ij} - _{k+1}^1\varphi_{ij+1}) + (_k^2\varphi_{ij} - _{k+1}^1\varphi_{i+1j+1})$$

$$+(_k^2\varphi_{ij} - _{k-1}^1\varphi_{ij}) + (_k^2\varphi_{ij} - _{k-1}^1\varphi_{i+1j}) + (_k^2\varphi_{ij} - _{k-1}^1\varphi_{ij+1}) + (_k^2\varphi_{ij} - _{k-1}^1\varphi_{i+1j+1})]$$

$$+2B^*[(^2_k\varphi_{ij}-^2_k\varphi_{i-1j})+(^2_k\varphi_{ij}-^2_k\varphi_{i+1j})]+2C^*[(^2_k\varphi_{ij}-^2_{k+1}\varphi_{i-1j})+(^2_k\varphi_{ij}-^2_{k+1}\varphi_{i+1j})$$

$$+(^2_k\varphi_{ij}-^2_{k-1}\varphi_{i-1j})+(^2_k\varphi_{ij}-^2_{k-1}\varphi_{i+1j})]+4(A_1+4A_2)^2_{ij}\varphi_k-D\sum_4\rho_{mn}-D^*\sum_2\rho_{mn}. \qquad (24)$$

Two other pairs of equations correspond to the projections of the motion equations on the directions of X and Y axes respectively. This is in fact the linearization of eqns (21). Here we introduce

$$_{ij}X_k = u_k \text{ for the cell with number } i,j$$
$$_{ij}Y_k = v_k \text{ for the cell with number } i,j$$

and therefore obtain from (21):

$$\frac{\partial^2}{\partial t^2}{}^1_k X_{ij}+\kappa_1\frac{\partial^4}{\partial z^4}{}^1_k X_{ij}+\kappa_z\frac{\partial^4}{\partial z^4}{}^1_k Y_{ij}$$

$$-4K(a/L^2)\{a[(^1_k X_{ij}-^2_k X_{ij})+(^1_k X_{ij}-^2_k X_{i-1j})+(^1_k X_{ij}-^2_k X_{ij-1})+(^1_k X_{ij}-^2_k X_{i-1j-1})]$$

$$+b[(^1_k Y_{ij}-^2_k Y_{ij})+(^1_k Y_{ij}-^2_k Y_{i-1j})+(^1_k Y_{ij}-^2_k Y_{ij-1})+(^1_k Y_{ij}-^2_k Y_{i-1j-1})]\}$$

$$+K^*[(^1_k X_{ij}-^1_k X_{i-1j})+(^1_k X_{ij}-^1_k X_{i+1j})]+32Da^1_k\varphi_{ij}/L^2+4D^{*1}_k\varphi_{ij}/a$$

$$+8vCa/L(^1_k\Delta_{ij}-^2_{k-1}\Delta_{ij}+^1_k\Delta_{i-1j}-^2_{k-1}\Delta_{i-1j}+^1_k\Delta_{ij-1}-^2_{k-1}\Delta_{ij-1}+^1_k\Delta_{i-1j-1}-^2_{k-1}\Delta_{i-1j-1})$$

$$+8v^*C^*(_k\Delta^*_{i-1j}-_{k-1}\Delta^*_{i-1j}+_k\Delta^*_{i+1j}-_{k-1}\Delta^*_{i+1j}) = 0$$

$$\frac{\partial^2}{\partial t^2}{}^2_k X_{ij}+\kappa_1\frac{\partial^4}{\partial z^4}{}^2_k X_{ij}+\kappa_z\frac{\partial^4}{\partial z^4}{}^2_k Y_{ij}$$

$$-4K(a/L^2)\{a[(^2_k X_{ij}-^1_k X_{ij})+(^2_k X_{ij}-^1_k X_{i+1j})+(^2_k X_{ij}-^1_k X_{ij+1})+(^2_k X_{ij}-^1_k X_{i+1j+1})]$$

$$+b[(^2_k Y_{ij}-^1_k Y_{ij})+(^2_k Y_{ij}-^1_k Y_{i+1j})+(^2_k Y_{ij}-^1_k Y_{ij+1})+(^2_k Y_{ij}-^1_k Y_{i+1j+1})]\}$$

$$+K^*[(^2_k X_{ij}-^2_k X_{i-1j})+(^2_k X_{ij}-^2_k X_{i+1j})]+32Da^2_k\varphi_{ij}/L^2+4D^{*2}_k\varphi_{ij}/a$$

$$+8vCa/L(^2_k\Delta_{ij}-^1_{k-1}\Delta_{ij}+^2_k\Delta_{i+1j}-^1_{k-1}\Delta_{i+1j}+^2_k\Delta_{ij+1}-^1_{k-1}\Delta_{ij+1}+^2_k\Delta_{i+1j+1}-^1_{k-1}\Delta_{i+1j+1})$$

$$+8v^*C^*(^*_k\Delta_{i-1j}-^*_{k-1}\Delta_{i-1j}+^*_k\Delta_{i+1j}-^*_{k-1}\Delta_{i+1j}) = 0. \qquad (25)$$

The second pair of equations for this asymptotic limit, corresponding to the projections on the Y axis, is written as:

$$\frac{\partial^2}{\partial t^2}{}^1_k Y_{ij}+\kappa_1\frac{\partial^4}{\partial z^4}{}^1_k Y_{ij}+\kappa_2\frac{\partial^4}{\partial z^4}{}^1_k X_{ij}$$

$$-4K(b/L^2)\{a[(^1_k X_{ij}-^2_k X_{ij})+(^1_k X_{ij}-^2_k X_{i-1j})+(^1_k X_{ij}-^2_k X_{ij-1})+(^1_k X_{ij}-^2_k X_{i-1j-1})]$$

$$+b[(^1_k Y_{ij}-^2_k Y_{ij})+(^1_k Y_{ij}-^2_k Y_{i-1j})+(^1_k Y_{ij}-^2_k Y_{ij-1})+(^1_k Y_{ij}-^2_k Y_{i-1j-1})]\}+32Db^1_k\varphi_{ij}/L^2$$

$$+8vCb/L(^1_k\Delta_{ij}-^2_{k-1}\Delta_{ij}+^1_k\Delta_{i-1j}-^2_{k-1}\Delta_{i-1j}+^1_k\Delta_{ij-1}-^2_{k-1}\Delta_{ij-1}$$

$$+^1_k\Delta_{i-1j-1}-^2_{k-1}\Delta_{i-1j-1}) = 0$$

$$\frac{\partial^2}{\partial t^2}{}^2_k Y_{ij}+\kappa_1\frac{\partial^4}{\partial z^4}{}^2_k Y_{ij}+\kappa_2\frac{\partial^4}{\partial z^4}{}^2_k X_{ij}$$

$$-4Kb/L^2\{a[(^2_k X_{ij}-^1_k X_{ij})+(^2_k X_{ij}-^1_k X_{i+1j})+(^2_k X_{ij}-^1_k X_{ij+1})+(^2_k X_{ij}-^1_k X_{i+1j+1})]$$

$$+b[(^2_k Y_{ij}-^1_k Y_{ij})+(^2_k Y_{ij}-^1_k Y_{i+1j})+(^2_k Y_{ij}-^1_k Y_{ij+1})+(^2_k Y_{ij}-^1_k Y_{i+1j+1})]\}+32Db^2_k\varphi_{ij}/L^2$$

$$+8vCb/L(^2_k\Delta_{ij}-^1_{k-1}\Delta_{ij}+^2_k\Delta_{i+1j}-^1_{k-1}\Delta_{i+1j}+^2_k\Delta_{ij+1}$$

$$-^1_{k-1}\Delta_{ij+1}+^2_k\Delta_{i+1j+1}-^1_{k-1}\Delta_{i+1j+1})=0. \tag{26}$$

In these equations X is the displacement of certain chain in X direction and Y in y direction; κ_1 and κ_2 are the factors of bending stiffness and may be easily expressed with parameters α and β; $L=(a^2+b^2)^{1/2}$.

The next step needs full continualization of the motion equations. If considering the smooth change rates of variables and if introducing the cell variables

$$U_1=(X_1+X_2)/2, \quad u_1=(X_1-X_2)/2$$

$$U_2=(Y_1+Y_2)/2, \quad u_2=(Y_1-Y_2)/2$$

$$U_3=(W_1+W_2)/2, \quad u_3=(W_1-W_2)/2$$

$$\Phi=(\varphi_1+\varphi_2)/2, \quad \Psi=(\varphi_1-\varphi_2)/2 \tag{27}$$

we thus obtain for rotations:

$$\frac{\partial^2}{\partial t^2}\Phi=E_{14}\frac{\partial^2}{\partial x^2}\Phi+E_{24}\frac{\partial^2}{\partial y^2}\Phi+E_{34}\frac{\partial^2}{\partial z^2}\Phi+M\left(ab\frac{\partial^2}{\partial x\partial y}\Phi+2a\frac{\partial}{\partial x}\Psi+2b\frac{\partial}{\partial y}\Psi\right)$$

$$+J_{11}\frac{\partial^2}{\partial x^2}U_1+J_{12}\frac{\partial^2}{\partial y^2}U_1+J_{21}\frac{\partial^2}{\partial x^2}U_2+J_{22}\frac{\partial^2}{\partial y^2}U_2$$

$$+H_1\left[2\left(a\frac{\partial}{\partial x}u_1+b\frac{\partial}{\partial y}u_1\right)+ab\frac{\partial^2}{\partial x\partial y}U_1\right]+H_2\left[2\left(a\frac{\partial}{\partial x}u_2+b\frac{\partial}{\partial y}u_2\right)\right.$$

$$\left.+ab\frac{\partial^2}{\partial x\partial y}U_2\right]-Q_1\Phi;$$

$$\frac{\partial^2}{\partial t^2}\Psi=E_{15}\frac{\partial^2}{\partial x^2}\Psi-E_{24}\frac{\partial^2}{\partial y^2}\Psi+E_{35}\frac{\partial^2}{\partial z^2}\Psi-M\left(ab\frac{\partial^2}{\partial x\partial y}\Psi+2a\frac{\partial}{\partial x}\Phi+2b\frac{\partial}{\partial y}\Phi\right)$$

$$+L_{11}\frac{\partial^2}{\partial x^2}u_1-J_{12}\frac{\partial^2}{\partial y^2}u_1+L_{21}\frac{\partial^2}{\partial x^2}u_2-J_{22}\frac{\partial^2}{\partial y^2}u_2$$

$$-H_1\left[2\left(a\frac{\partial}{\partial x}U_1+b\frac{\partial}{\partial y}U_1\right)+ab\frac{\partial^2}{\partial x\partial y}u_1\right]-H_2\left[2\left(a\frac{\partial}{\partial x}U_2+b\frac{\partial}{\partial y}U_2\right)+ab\frac{\partial^2}{\partial x\partial y}u_2\right]$$

$$-Q_2\Psi+Z(au_1+bu_2). \tag{28}$$

For the displacement in Z direction:

$$\frac{\partial^2}{\partial t^2}U_3=A_{31}\frac{\partial^2}{\partial x^2}U_3+A_{32}\frac{\partial^2}{\partial y^2}U_3+E_{33}\frac{\partial^2}{\partial z^2}U_3+K_{13}\frac{\partial^2}{\partial x\partial z}U_1+K_{23}\frac{\partial^2}{\partial y\partial z}U_2$$

$$+I_{33}\left[2\left(a\frac{\partial}{\partial x}u_3+b\frac{\partial}{\partial y}u_3\right)+ab\frac{\partial^2}{\partial x\partial y}U_3\right];$$

$$\frac{\partial^2}{\partial t^2}u_3=-8I_{33}u_3+A^*_{31}\frac{\partial^2}{\partial x^2}u_3-A_{32}\frac{\partial^2}{\partial y^2}u_3+E^*_{33}\frac{\partial^2}{\partial z^2}u_3+K^*_{13}\frac{\partial^2}{\partial x\partial z}u_1$$

$$-K_{23}\frac{\partial^2}{\partial y\partial z}u_2-I_{33}\left[2\left(a\frac{\partial}{\partial x}U_3+b\frac{\partial}{\partial y}U_3\right)+ab\frac{\partial^2}{\partial x\partial y}u_3\right]. \tag{29}$$

This system of equations connects the internal and external variables for the case of small wavenumbers. For the case of wavenumbers close to π the behaviour of crystal for low-frequency vibrations is governed by other systems:

$$\frac{\partial^2}{\partial t^2} U_1 = -\kappa_1 \frac{\partial^4}{\partial x^4} U_1 - \kappa_2 \frac{\partial^4}{\partial y^4} U_2 + E_{11} \frac{\partial^2}{\partial x^2} U_1 + A_{12} \frac{\partial^2}{\partial y^2} U_1 + A_{13} \frac{\partial^2}{\partial z^2} U_1$$

$$+ K_{13} \frac{\partial^2}{\partial x \partial z} U_3 + K_{12} \frac{\partial^2}{\partial x \partial y} U_2 + I_{11} \left[2\left(a \frac{\partial}{\partial x} u_1 + b \frac{\partial}{\partial y} u_1 \right) + ab \frac{\partial^2}{\partial x \partial y} U_1 \right] + I_{14} \Phi;$$

$$\frac{\partial^2}{\partial t^2} u_1 = -\kappa_1 \frac{\partial^4}{\partial x^4} u_1 - \kappa_2 \frac{\partial^4}{\partial y^4} u_2 + E_{11}^* \frac{\partial^2}{\partial x^2} u_1 - A_{12}^* \frac{\partial^2}{\partial y^2} u_1 + A_{13} \frac{\partial^2}{\partial z^2} u_1$$

$$+ K_{13}^* \frac{\partial^2}{\partial x \partial z} U_3 - K_{12} \frac{\partial^2}{\partial x \partial y} U_2 - I_{11} \left[2\left(a \frac{\partial}{\partial x} U_1 + b \frac{\partial}{\partial y} U_1 \right) + ab \frac{\partial^2}{\partial x \partial y} u_1 \right]$$

$$+ I_{14} \Psi - 8 I_{11} u_1. \tag{30}$$

The equations for direction of Y axis and appropriate internal degree of freedom are written as:

$$\frac{\partial^2}{\partial t^2} U_2 = -\kappa_1 \frac{\partial^4}{\partial x^4} U_2 - \kappa_2 \frac{\partial^4}{\partial y^4} U_1 + A_{12} \frac{\partial^2}{\partial x^2} U_2 + E_{22} \frac{\partial^2}{\partial y^2} U_2 + A_{23} \frac{\partial^2}{\partial z^2} U_2$$

$$+ K_{23} \frac{\partial^2}{\partial y \partial z} U_3 + K_{12} \frac{\partial^2}{\partial x \partial y} U_1 + I_{22} \left[2\left(a \frac{\partial}{\partial x} u_2 + b \frac{\partial}{\partial y} u_2 \right) + ab \frac{\partial^2}{\partial x \partial y} U_2 \right] + I_{24} \Phi;$$

$$\frac{\partial^2}{\partial t^2} u_2 = -\kappa_1 \frac{\partial^4}{\partial x^4} u_2 - \kappa_2 \frac{\partial^4}{\partial y^4} u_1 - A_{12} \frac{\partial^2}{\partial x^2} u_2 - E_{22} \frac{\partial^2}{\partial y^2} u_2 - A_{23} \frac{\partial^2}{\partial z^2} u_2$$

$$- K_{23} \frac{\partial^2}{\partial y \partial z} u_3 - K_{12} \frac{\partial^2}{\partial x \partial y} u_1 - I_{22} \left[2\left(a \frac{\partial}{\partial x} U_2 + b \frac{\partial}{\partial y} U_2 \right) + ab \frac{\partial^2}{\partial x \partial y} u_2 \right] + I_{24} \Psi - 8 I_{22} u_2.$$

$$\tag{31}$$

The notions of continuous functions correspond to appropriate rotations and displacements. For expressions for the constants see the Appendix.

Here we have obtained the asymptotic equations describing the motion of PE crystal. However these equations are rather complicated and for practical purposes may be simplified by further asymptotic reduction. This is the subject of the next section.

3. THE ASYMPTOTIC ANALYSIS OF LINEARIZED EQUATIONS

In order to simplify the equations and to obtain the approximate solutions two asymptotic procedures are used here. The first is connected with the consideration of a small wavelength limit for excitations with frequencies close to gap values in the vibration spectrum. In the general case [see e.g. Kunin (1975)] this approach gives an opportunity to define for each limit case the equation for "leading" degree of freedom and to calculate the values of other variables.

The second procedure is applied for the analysis of the most important limit case—the conventional theory of elasticity. The asymptotic decomposition of this system is based on the small parameter connected with strong anisotropy of the system (Manevitch et al., 1982).

We start from the continualized system of equations obtained in the second chapter. Several peculiarities of the general system considered are to be mentioned. First, the

equations of U_j evolution do not contain terms proportional to the variables which appear with time derivatives. The other five equations contain such terms. This means that for small wavenumbers three branches of dispersional curves tend to zero and the others tend to finite frequencies and thus cause gaps in the vibrational spectra.

The smallness of wavenumbers supposed, when proceeding with the continualization, gives us an opportunity to elucidate the relationship between internal and external degrees of freedom. In order to provide such an analysis we introduce the small parameter related to the smallness of wavenumbers.

$$a\,\partial/\partial x \sim b\,\partial/\partial y \sim d\,\partial/\partial z \sim \delta \ll 1.$$

There exist several possibilities for the frequency of excitation for small wavenumbers. Let us first take into account one significant for the theory of elasticity limit, the case of small frequencies and thus let us suppose $\omega\,\partial/\partial t \sim \delta$ for all characteristic frequencies of this system. The only non-contradictory relationships possible for this system are:

$$G_j/U_j \sim \delta, \quad j = 1, 2, 3, \quad \Phi/U \sim \delta^2, \quad \Psi/U \sim \delta^3. \tag{32}$$

The appropriate equations may be written as:

$$\frac{\partial^2}{\partial t^2} U_1 = -\kappa_1 \frac{\partial^4}{\partial z^4} U_1 - \kappa_2 \frac{\partial^4}{\partial z^4} U_2 + C_{11} \frac{\partial^2}{\partial x^2} U_1 + C_{12} \frac{\partial^2}{\partial y^2} U_1 + C_{13} \frac{\partial^2}{\partial z^2} U_1$$

$$+ K_{13} \frac{\partial^2}{\partial x\,\partial z} U_3 + K_{12} \frac{\partial^2}{\partial x\,\partial y} U_2;$$

$$\frac{\partial^2}{\partial t^2} U_2 = -\kappa_1 \frac{\partial^4}{\partial z^4} U_2 - \kappa_2 \frac{\partial^4}{\partial z^4} U_1 + C_{12} \frac{\partial^2}{\partial x^2} U_2 + C_{22} \frac{\partial^2}{\partial y^2} U_2$$

$$+ C_{23} \frac{\partial^2}{\partial z^2} U_2 + K_{23} \frac{\partial^2}{\partial y\,\partial z} U_3 + K_{12} \frac{\partial^2}{\partial x\,\partial y} U_1;$$

$$\frac{\partial^2}{\partial t^2} U_3 = C_{13} \frac{\partial^2}{\partial x^2} U_3 + C_{23} \frac{\partial^2}{\partial y^2} U_3 + C_{33} \frac{\partial^2}{\partial z^2} U_3 + K_{13} \frac{\partial^2}{\partial x\,\partial z} U_1 + K_{23} \frac{\partial^2}{\partial y\,\partial z} U_2;$$

$$u_1 = -\frac{1}{4}\left(a\frac{\partial}{\partial x}U_1 + b\frac{\partial}{\partial y}U_1\right)$$

$$u_2 = -\frac{1}{4}\left(a\frac{\partial}{\partial x}U_2 + b\frac{\partial}{\partial y}U_2\right)$$

$$u_3 = -\frac{1}{4}\left(a\frac{\partial}{\partial x}U_3 + b\frac{\partial}{\partial y}U_3\right)$$

$$\Phi = F_{11}\frac{\partial^2}{\partial x^2}U_1 + F_{12}\frac{\partial^2}{\partial y^2}U_1 + F_{21}\frac{\partial^2}{\partial x^2}U_2 + F_{22}\frac{\partial^2}{\partial y^2}U_2$$

$$\Psi = F_{11}^*\frac{\partial^2}{\partial x^2}G_1 + F_{12}^*\frac{\partial^2}{\partial y^2}G_1 + F_{21}^*\frac{\partial^2}{\partial x^2}G_2 + F_{22}^*\frac{\partial^2}{\partial y^2}G_2. \tag{33}$$

For the expressions for F_{ij} see the Appendix.

The first three equations of this system constitute the conventional theory of elasticity, the other formulae express the relations between internal and external degrees of freedom. The existence of internal degrees of freedom changes here the values of elastic constants only. The role of terms with fourth derivatives will be elucidated in the next section.

Table 1.

Modulus	Numerical simulation* (GPa)	Present result
C_{11}	20.5	19.1
C_{22}	15.5	17.1
C_{33}	338.0	349.0
C_{12}	11.0	12.3
C_{13}	5.4	5.88
C_{23}	3.30	3.51
K_{12}	6.88	6.59
K_{13}	3.68	3.59
K_{23}	1.95	1.76

* The data of extrapolation to zero temperature.

The expressions for the components of elastic moduli tensor C_{ij} are written as follows:

$$C_{11} = E_{11} - a^2 I_{11}/2 + I_{14}F_{11},$$

$$C_{22} = E_{22} - b^2 I_{22}/2 + I_{24}F_{22}$$

$$C_{33} = E_{33}$$

$$C_{21} = A_{12} - b^2 I_{11}/2 + I_{14}F_{12}$$

$$C_{23} = A_{23}, \quad C_{31} = A_{13}$$

$$K_{12} = -16a^2 b^2 (K + 4Cv)/L^2$$

$$K_{13} = 32\pi da(Cva/L + C^*v^*)/ls$$

$$K_{23} = 32\pi dbCv/ls. \tag{34}$$

These expressions constitute the solution for the problem of analytical prediction of polyethylene crystal elastic moduli. The natural test for these expressions is comparison with the data of numerical simulations (Bacon *et al.* 1983). The results of such comparison are presented in Table 1. Nine elastic moduli of PE crystal calculated in Bacon *et al.* (1983) by means of numerical simulation are compared with the values calculated from expression (34). The constants in these expressions were estimated from the model potentials (3), (4), (9). In the paper of Bacon *et al.* (1983) the data concerning the elastic moduli were presented for several values of temperature above zero. We estimate the moduli for zero temperature with the help of an extrapolation procedure. The correlation is satisfactory, taking account of the inaccuracy of the extrapolation procedure and the approximations made.

The other variables also may be chosen as the "leading" ones [see Kunin (1975)] and a similar asymptotic procedure may be performed. The case of small wavenumbers and frequencies close to the frequency of free vibrations of Φ variable is of physical significance. Let us regard

$$(w^2 \, \partial^2/\partial t^2 + Q_1) \sim \delta^2. \tag{35}$$

This supposition leads us to following system of equations:

$$\left(\frac{\partial^2}{\partial t^2}\Phi + Q_1 \right) = C_{14}\frac{\partial^2}{\partial x^2}\Phi + C_{24}\frac{\partial^2}{\partial y^2}\Phi + C_{34}\frac{\partial^2}{\partial z^2}\Phi$$

$$\Psi = -\frac{1}{4}\left(a\frac{\partial}{\partial x}\Phi + b\frac{\partial}{\partial y}\Phi \right)$$

$$U_1 = a_1\Phi$$

$$u_1 = a_1\Psi$$

$$U_2 = a_2 \Phi$$

$$u_2 = a_2 \Psi$$

$$U_3 = k_{13} \frac{\partial^2}{\partial x \partial z} \Phi + k_{12} \frac{\partial^2}{\partial x \partial y} \Phi$$

$$u_3 = k_{13}^* \frac{\partial^2}{\partial x \partial z} \Psi + k_{12}^* \frac{\partial^2}{\partial x \partial y} \Psi. \tag{36}$$

The analogous expressions may be received for each degree of freedom. However the system under consideration gives an opportunity to carry out one more procedure of asymptotic analysis and to simplify significantly the equations obtained.

4. THE ASYMPTOTIC ANALYSIS FOR LOW FREQUENCY CASE

The last step in order to obtain the asymptotic equations describing the elastic behaviour of polyethylene crystal is the asymptotic analysis of elasticity equations on the base of natural hierarchy of interactions in this crystal. We undertake here the analysis for the first three equations of system (33) only. A similar procedure may be performed for all other cases.

According to the magnitude of interaction potentials we may choose the orders of elastic moduli as follows:

(a) $C_{33} \sim \varepsilon^0$—as connected with the deformation of valent angles (the value of this constant is about 350 GPa);

(b) $C_{13}, C_{23}, K_{3i}, \sim \varepsilon^2$—as they are connected with constants of "diagonal" LJ bonds only. Their value is of order 2–5 GPa (see Table 1) and so they are about two orders of magnitude less than C_{33}. The "starred" constants denoted in the same way are of the same order.

(c) All the other constants are considered to be of order ε—as they are connected with nearest-neighbour LJ interaction and are of order 10–20 GPa.

In order to solve the problem we suppose that the orders of magnitude of the derivatives and variables may be estimated as follows:

$$\omega \partial/\partial t \sim \varepsilon^\beta, \quad a \partial/\partial x \sim \varepsilon^{\alpha_1}, \quad b \partial/\partial y \sim \varepsilon^{\alpha_2}, \quad d \partial/\partial z \sim \varepsilon^{\alpha_3}, \quad U_1 \sim \varepsilon^\gamma, \quad U_2 \sim \varepsilon^\delta, \quad U_3 \sim 1.$$

$$\tag{37}$$

If substituting these estimations into the system (33) we may obtain several non-contradictory solutions for the orders of magnitude for our variables. The first series being physically significant is written as:

$$\alpha_1 = -1/2, \quad \alpha_2 = -1/2, \quad \alpha_3 = 1/2, \quad \beta = 1/2, \quad \gamma = 2, \quad \delta = 2.$$

The appropriate (i.e. with the highest order terms remaining) system of equations accompanying these estimations is written as:

$$\frac{\partial^2}{\partial t^2} U_3 = C_{13} \frac{\partial^2}{\partial x^2} U_3 + C_{23} \frac{\partial^2}{\partial y^2} U_3 + C_{33} \frac{\partial^2}{\partial z^2} U_3$$

$$0 = C_{11} \frac{\partial^2}{\partial x^2} U_1 + C_{12} \frac{\partial^2}{\partial y^2} U_1 + K_{13} \frac{\partial^2}{\partial x \partial z} U_3 + K_{12} \frac{\partial^2}{\partial x \partial y} U_2$$

$$0 = C_{12}\frac{\partial^2}{\partial x^2}U_2 + C_{22}\frac{\partial^2}{\partial y^2}U_2 + K_{23}\frac{\partial^2}{\partial y\,\partial z}U_3 + K_{12}\frac{\partial^2}{\partial x\,\partial y}U_1. \qquad (38)$$

This system of equations describes the solution of a certain boundary problem for U_3 and determines the functions U_1 and U_2 from this solution. It is possible to satisfy the boundary conditions for these variables by solving an additional system governed by asymptotic estimation:

$$\alpha_1 = 1/2, \quad \alpha_2 = 1/2, \quad \alpha_3 = 0, \quad \beta = 1, \quad \gamma = -5/2, \quad \delta = -5/2.$$

The appropriate equations are written as:

$$\frac{\partial^2}{\partial t^2}U_1 = C_{11}\frac{\partial^2}{\partial x^2}U_1 + C_{12}\frac{\partial^2}{\partial y^2}U_1 + C_{13}\frac{\partial^2}{\partial z^2}U_1 + K_{12}\frac{\partial^2}{\partial x\,\partial y}U_2$$

$$\frac{\partial^2}{\partial t^2}U_2 = C_{12}\frac{\partial^2}{\partial x^2}U_2 + C_{22}\frac{\partial^2}{\partial y^2}U_2 + C_{23}\frac{\partial^2}{\partial z^2}U_2 + K_{12}\frac{\partial^2}{\partial x\,\partial y}U_1$$

$$0 = C_{33}\frac{\partial^2}{\partial z^2}U_3 + K_{13}\frac{\partial^2}{\partial x\,\partial z}U_1 + K_{23}\frac{\partial^2}{\partial y\,\partial z}U_2. \qquad (39)$$

This system gives an opportunity to satisfy the boundary conditions for U_1 and U_2. It is the first approximation for the asymptotic procedure which gives the series for each function with respect to parameter ε. This procedure is analogous to the solutions in Manevitch *et al.* (1982) for other systems.

Two systems of equations (38)–(39) demonstrate the idea of asymptotic procedure for the solution of the orthotropic elasticity problem for the case of strong anisotropy mentioned above. Let us now introduce the formal consideration of the problem.

For the elastic moduli we introduce:

$$C_{11} = \varepsilon c_{11}, \quad C_{21} = \varepsilon c_{21}, \quad C_{31} = \varepsilon^2 c_{31}, \quad C_{22} = \varepsilon c_{22}, \quad C_{32} = \varepsilon^2 c_{32}, \quad C_{33} = c_{33},$$

$$K_{31} = \varepsilon^2 k_{31}, \quad K_{32} = \varepsilon^2 k_{32}, \quad K_{21} = \varepsilon k_{21}.$$

All components of the symmetric tensors c_{ij} and k_{ij} are of the same order of magnitude (the squared velocity of longitudinal sound in the polyethylene chain).

We look for the solution of the boundary problem for equations (33) in the form:

$$U_1 = \varepsilon^2 u_1 + u_2$$

$$U_2 = \varepsilon^2 v_1 + v_2$$

$$U_3 = w_1 + \varepsilon^{5/2} w_2 \qquad (40)$$

accompanying it with anzats

$$\xi_1 = \varepsilon^{-1} x, \quad \zeta_1 = \varepsilon^{-1} y, \quad \eta_1 = z$$

for the problem concerning the variables subscripted by 1 and

$$\xi_2 = \varepsilon^{1/2} x, \quad \zeta_2 = \varepsilon^{1/2} y, \quad \eta_2 = z$$

for the problem concerning the variables subscripted by 2.

The first system of equations is written as follows:

$$\frac{\partial^2}{\partial t^2}w_1 = c_{13}\frac{\partial^2}{\partial x^2}w_1 + c_{23}\frac{\partial^2}{\partial y^2}w_1 + c_{33}\frac{\partial^2}{\partial z^2}w_1 + \varepsilon^3\left(k_{13}\frac{\partial^2}{\partial x\,\partial z}u_1 + k_{23}\frac{\partial^2}{\partial y\,\partial z}v_1\right)$$

$$\varepsilon^2\frac{\partial^2}{\partial t^2}u_1 = c_{11}\frac{\partial^2}{\partial x^2}u_1 + c_{12}\frac{\partial^2}{\partial y^2}u_1 + k_{13}\frac{\partial^2}{\partial x\,\partial z}w_1 + k_{12}\frac{\partial^2}{\partial x\,\partial y}v_1 + \varepsilon^3c_{13}\frac{\partial^2}{\partial z^2}u_1$$

$$\varepsilon^2\frac{\partial^2}{\partial t^2}v_1 = c_{12}\frac{\partial^2}{\partial x^2}v_1 + c_{22}\frac{\partial^2}{\partial y^2}v_1 + k_{23}\frac{\partial^2}{\partial y\,\partial z}w_1 + k_{12}\frac{\partial^2}{\partial x\,\partial y}u_1 + \varepsilon^3c_{23}\frac{\partial^2}{\partial z^2}v_1. \tag{41}$$

The second system, which satisfies the boundary conditions for U_1, U_2 is written as:

$$\frac{\partial^2}{\partial t^2}u_2 = c_{11}\frac{\partial^2}{\partial x^2}u_2 + c_{12}\frac{\partial^2}{\partial y^2}u_2 + c_{13}\frac{\partial^2}{\partial z^2}u_2 + k_{12}\frac{\partial^2}{\partial x\,\partial y}v_2 + \varepsilon^3k_{13}\frac{\partial^2}{\partial x\,\partial z}w_2$$

$$\frac{\partial^2}{\partial t^2}v_2 = c_{12}\frac{\partial^2}{\partial x^2}v_2 + c_{22}\frac{\partial^2}{\partial y^2}v_2 + c_{23}\frac{\partial^2}{\partial z^2}v_2 + k_{12}\frac{\partial^2}{\partial x\,\partial y}u_2 + \varepsilon^3k_{23}\frac{\partial^2}{\partial y\,\partial z}w_2$$

$$\varepsilon\frac{\partial^2}{\partial t^2}w_2 = c_{33}\frac{\partial^2}{\partial z^2}w_2 + k_{13}\frac{\partial^2}{\partial x\,\partial z}u_2 + k_{23}\frac{\partial^2}{\partial y\,\partial z}v_2 + \varepsilon^3\left(c_{13}\frac{\partial^2}{\partial x^2}w_2 + c_{23}\frac{\partial^2}{\partial y^2}w_2\right). \tag{42}$$

We find the solutions of these systems as asymptotic series:

$$u_i = \sum_{m=0}^{\infty}\varepsilon^m u_i^{(m)}, \quad v_i = \sum_{m=0}^{\infty}\varepsilon^m v_i^{(m)}, \quad w_i = \sum_{m=0}^{\infty}\varepsilon^m w_i^{(m)}.$$

The asymptotic procedure for determination of each approximation is obvious.

Let us now consider the structure of higher approximations for these asymptotic systems. Considering the case of solutions independent of the Y variable the equations are reduced to the following form:

$$\frac{\partial^2}{\partial t^2}w_1 = c_{13}\frac{\partial^2}{\partial x^2}w_1 + c_{33}\frac{\partial^2}{\partial z^2}w_1 + \varepsilon^3k_{13}\frac{\partial^2}{\partial x\,\partial z}u_1$$

$$\varepsilon^2\frac{\partial^2}{\partial t^2}u_1 = c_{11}\frac{\partial^2}{\partial x^2}u_1 + k_{13}\frac{\partial^2}{\partial x\,\partial z}w_1 + \varepsilon^3c_{13}\frac{\partial^2}{\partial z^2}u_1$$

$$\varepsilon^2\frac{\partial^2}{\partial t^2}v_1 = c_{12}\frac{\partial^2}{\partial x^2}v_1 + \varepsilon^3c_{23}\frac{\partial^2}{\partial z^2}v_1 \tag{43}$$

and

$$\frac{\partial^2}{\partial t^2}u_2 = c_{11}\frac{\partial^2}{\partial x^2}u_2 + c_{13}\frac{\partial^2}{\partial z^2}u_2 + \varepsilon^3k_{13}\frac{\partial^2}{\partial x\,\partial z}w_2$$

$$\varepsilon\frac{\partial^2}{\partial t^2}w_2 = c_{33}\frac{\partial^2}{\partial z^2}w_2 + k_{13}\frac{\partial^2}{\partial x\,\partial z}u_2 + \varepsilon^3c_{13}\frac{\partial^2}{\partial x^2}w_2$$

$$\frac{\partial^2}{\partial t^2}v_2 = c_{12}\frac{\partial^2}{\partial x^2}v_2 + c_{23}\frac{\partial^2}{\partial z^2}v_2. \tag{44}$$

Two first equations of each system constitute the asymptotic equations for a plane orthotropic body. The static version of these equations was studied in Manevitch *et al.* (1982) and it was shown that if we introduce the following anzats:

$$\zeta_1 = \varepsilon^{-1} x, \quad \eta_1 = z \sum_{m=0}^{\infty} \varepsilon^{3m} \alpha_m$$

$$\zeta_2 = \varepsilon^{1/2} x \sum_{m=0}^{\infty} \varepsilon^{3m} \beta_m, \quad \eta_2 = z \tag{45}$$

the coefficients α_m, β_m may be chosen so as to reduce the main equation in each pair for all orders of approximation to Laplace form. For our plane dynamics system the analogous statement is valid: the same anzats reduce the main equations to the form of the usual wave equation.

As for the 3D case, the problem may be treated by considering the transversely isotropic continuum as first approximation for the system considered. Such analysis may give reliable predictions because the anisotropy in the plane transversal to the chains is negligible compared to the main one. The details of the asymptotic procedure are presented in Manevitch *et al.* (1982).

The analysis remains incomplete if we don't elucidate the role of bending terms in equations (33). For the estimations

$$\partial/\partial z \sim \partial/\partial y \sim \partial/\partial x, \quad U_1 \sim U_2 \sim U_3$$

the initial system of equations is reduced in the main approximation to the form

$$\frac{\partial^2}{\partial t^2} U_1 = -\kappa_1 \frac{\partial^4}{\partial z^4} U_1 - \kappa_2 \frac{\partial^4}{\partial z^4} U_2$$

$$\frac{\partial^2}{\partial t^2} U_2 = -\kappa_1 \frac{\partial^4}{\partial z^4} U_2 - \kappa_2 \frac{\partial^4}{\partial z^4} U_1$$

$$0 = C_{33} \frac{\partial^2}{\partial z^2} U_3. \tag{46}$$

All the variables are only z-dependent and the system of equations obtained constitutes the description of the single-chain limit, i.e. the intermolecular interaction here may be neglected. The results proven here are obvious from the physical viewpoint: for the system considered the intermolecular interaction is negligible for comparatively large wavenumbers in the z direction. Thus it is possible to formulate the applicability condition for the conventional elasticity approach if concerning the polyethylene crystal:

$$k_z \ll (C/\kappa) \tag{47}$$

where C is the characteristic value of intermolecular moduli, κ is bending rigidity. In usual crystals these values are of the same order and the validity of the conventional approach is determined by the applicability of the continualization procedure only.

Such an analysis is possible for each limit case and gives an opportunity to solve the elastic problems for various boundary conditions with the help of comparatively simple equations.

5. THE VIBRATION SPECTRA OF THE CRYSTAL

The last natural test in order to evaluate the applicability of equations obtained for the description of dynamics of polyethylene crystal is the comparison of dispersion relations derived from these equations to the experimental spectra of the crystal. The equations (36) (43), (44) give an opportunity to describe certain branches of vibration spectra; eqns (43), (45) lead to three dispersion relations describing approximately three branches of spectra in the region of small wavenumbers K_x, K_y, $K_z \to 0$ and small frequencies $\Omega \to 0$:
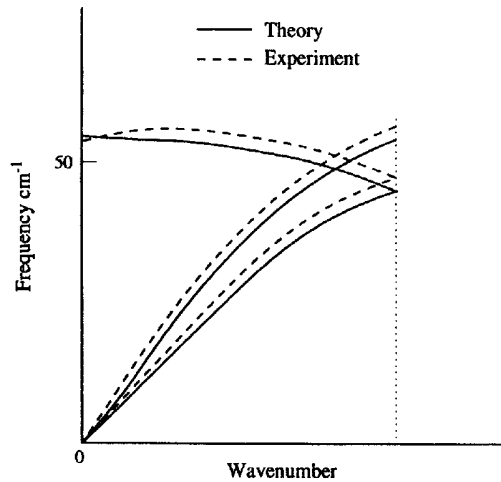
Fig. 4. Dispersion curves correspondent to wavevector K_x ($K_y = K_z = 0$).

$$\text{(a)}\ \Omega_1^2 = C_{13}K_x^2 + C_{23}K_y^2 + C_{33}K_z^2$$

$$\text{(b)}\ \Omega_2^2 = C_{11}K_x^2 + C_{13}K_z^2$$

$$\text{(c)}\ \Omega_3^2 = C_{22}K_y^2 + C_{23}K_z^2.$$

The equation (36) leads to the relation describing the other branch of vibration spectrum for K_x, K_y, $K_z \to 0$ and $\Omega \to (Q_1)^{1/2}$:

$$\text{(d)}\ \Omega_4^2 = Q_1 + C_{14}K_x^2 + C_{24}K_y^2 + C_{34}K_z^2.$$

These expressions give satisfactory coincidence with the experimental data [see also Ginzburg *et al.* (1989) for detailed comparison in the case of $K_x = K_y = 0$].

In Fig. 4 we present the comparison of our results with experimental data (Painter *et al.* 1986) for two branches with $K_y = K_z = 0$.

It is to be mentioned that the expressions for close to π and zero wavenumbers may be obtained also for the other branches with the help of a similar procedure. Outside this region the expressions lose their validity because the continualization procedure becomes illegal. But for this region we may restrict ourselves by considering the single chain limit because for comparatively large K_z the intramolecular energy exceeds the intermolecular (as was demonstrated above for the case of bending). Various numerical simulation studies [see, e.g. Wozny *et al.* (1994)], concerning the investigation of PE spectra, deal with this limit and give reliable predictions even for systems with hydrogen atoms, but their application for 3D crystal seems to be rather complicated. This field appears to be advantageous for asymptotic analytical methods.

It is worth while also to notice that the approach developed should be valid also for other polymer crystals. The reason is that the long-wave approach being developed here takes into account the number of degrees of freedom and the "topology" of interactions only. Thus neither more sophisticated microstructure nor the spiraling of the crystal affect the applicability of this approach. However they certainly affect the values of elastic moduli of the crystal.

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APPENDIX

In this Appendix the expressions for coefficients in equations are presented:

(a) *The elastic moduli:*

$$C_{11} = E_{11} - a^2 I_{11}/2, \quad C_{21} = A_{12} - b^2 I_{11}/2, \quad C_{31} = A_{31}$$

$$C_{22} = E_{22} - b^2 I_{22}/2, \quad C_{23} = A_{12} - a^2 I_{22}/2, \quad C_{33} = E_{33}$$

$$K_{12} = -16 a^2 b^2 (K + 4Cv)/L^2$$

$$K_{13} = 32\pi da (Cva/L - C^*v^*)/ls, \quad K_{23} = -32\pi db^2 Cv/Lls.$$

(b) *The moduli of rotational equation:*

$$E_{14} = -a^2 (4B + 16C + 2B^* + 2C^*), \quad E_{24} = -b^2 (4B + 16C),$$

$$E_{34} = 16\gamma - d^2 (32C + 2C^*), \quad Q_1 = -4(A_1 + 4A_2).$$

(c) *The other constants:*

$$E_{35} = -16\gamma + d^2 (32C - 2C^*), \quad E_{15} = a^2 (4B + 16C - 2B^* - 2C^*),$$

$$M = 4B + 16C, \quad H_1 = Da/L, \quad H_2 = Db/L, \quad Z = -8D/L,$$

$$Q_2 = -(4(A_1 + 4A_2) + 32B + 128C), \quad J_{11} = -Da^3/L - D^*a^2, \quad L_{11} = Da^3/L - D^*a^2,$$

$$J_{12} = -Dab^2/L, \quad J_{21} = -Dba^2/L, \quad J_{22} = -Db^3/L,$$

$$A_{31} = -8(\pi/ls)^2 a^2 (C + C^*), \quad A_{31}^* = 8(\pi/ls)^2 a^2 (C - C^*), \quad A_{32} = -8(\pi/ls)^2 Cb^2,$$

$$E_{33} = T - 8d^2 (\pi/ls)^2 (4C + C^*), \quad E_{33}^* = T + 8d^2 (\pi/ls)^2 (4C - C^*),$$

$$K_{13} = -32\pi da (Cva/L + C^*v^*)/ls, \quad I_{33} = 16(\pi/ls)^2 C,$$

$$E_{11} = 4a^4 (-4K + 8Cv^2 + 8C^*v^{*2})/L^2, \quad E_{11}^* = -4a^4 (-4K + 8Cv^2 - 8C^*v^{*2})/L^2,$$

$$A_{12} = 4a^2 b^2 (-4K + 8Cv^2)/L^2, \quad A_{13} = -32v^2 a^2 d^2 C/L^2 + 8v^{*2} C^*d^2, \quad A_{13}^* = 32v^2 a^2 d^2 C/L^2 + 8v^{*2} C^*d^2,$$

$$K_{13}^* = 32\pi ad (Cva/L - C^*v^*)/L, \quad I_{11} = 4a^2 (K + 4Cv^2)/L^2, \quad I_{14} = 32Da/L^2 + 4D^*/a,$$

$$E_{22} = 4b^4 (-4K + 8Cv^2), \quad I_{22} = 4b^2 (K + 4Cv^2)/L^2, \quad I_{14} = 32Db/L^2.$$