

THE NONLINEAR MODEL OF THE LIBRATIONAL DYNAMICS OF THE PARAFFIN CRYSTAL

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Abstract. In our work we consider the librational dynamics of the chains in paraffin crystals. We consider the paraffin chains being completely rigid and only inter-chain potential is taken into account. To study the possible change in the dynamics with the increase of the temperature, i.e. when the system achieves the vicinity of the rotation phase transition we consider the model without restrictions on the amplitudes of the rotational angles. The nonlinear spectra of the system are studied.

Keywords: librational dynamics; oscillatory chains; nonlinear normal modes; dispersion relation.

1. Introduction

Dynamics of the strongly nonlinear materials is a very important field of Material science and Physics in the last decades. Many nonlinear effects play a crucial role in the processes of phase transitions and heat transport, also they can strongly influence the dynamical properties of the materials. In particular, dynamics of paraffin crystals and crystalline polyethylene attracts the attention of many scientists since decades [1-5]. The structure of the crystalline n-alkanes and their phase transitions are studied in experiments and with use of molecular dynamics modelling [6,7,8]. The phase transitions of the typical crystalline n-alcane with the increase of the temperature of the sample includes the appearance of the so-called rotation phase with almost free rotational motions of the chains along their long axes and then transition to the liquid phase [9]. Very good results for the modelling of the dynamics are obtained using the united-atoms approximate model of the polyethylene [10,11] which compiles both nano-scale interactions with the micro-scale effects and gives the base for the phase-transitions study. There are many theoretical works on the nonlinear dynamics, excitations and phase transitions in the crystalline polyethylene [12,13,14]. However, the theoretical works considering short-chain librational dynamics specific for crystalline paraffins are still lacking. As a first step of the consideration we develop a simple nonlinear model qualitatively describing the inter-chain interaction and analyze the nonlinear spectra appearing in the high-amplitude dynamics also when the amplitudes of the librational motions are not supposed to be small.

2. Model and its reduction

To study the librational motions of the paraffin chains, we consider the model of the paraffin in the crystalline phase using the united atoms approximation [8,10]. The model describes methylene groups as collective grain with effective interaction potential, and without any internal degrees of freedom. The simplification allows study the carbon backbone dynamics without high-frequency degrees of freedom motions which are not significant for our goal. This approximation was thoroughly checked and shows all the possible crystalline phases of the

n-alkanes: monoclinic, triclinic and orthorhombic ones [6]. The model also shows realistic density and crystals cell parameters.

Our model considers the paraffin chains as trans-zigzag chains of the limited length ordered in accordance with the triclinic crystal symmetry. In the case all the chains are parallel, in one of the directions orthogonal to the chain axes they compose an “anti-ferromagnetic” row, when all the neighbors have the rotational phase-shift equal π . In the other direction they do not have a shift and compose a “ferromagnetic” state. We are interested in the consideration of motions concerning only the librational dynamics of the paraffin chains, therefore we assume the valent C-C bonds and C-C-C back-bone angles being completely rigid and not disturbed. This assumption can be applicable for the short-chain paraffins, which demonstrate in experiments the triclinic crystalline phase, because their length is less or equal to the length of torsion localized excitations in the full-atoms molecular-dynamics experiments [15].

For simplicity we assume that the wave-number only in one of the crystalline directions (i.e. “anti-ferromagnetic” one) is not equal to zero. This assumption is based on the consideration that the inter-chain interaction in this direction is the most intensive and the possible excitations evolution is expected along this crystal axis.

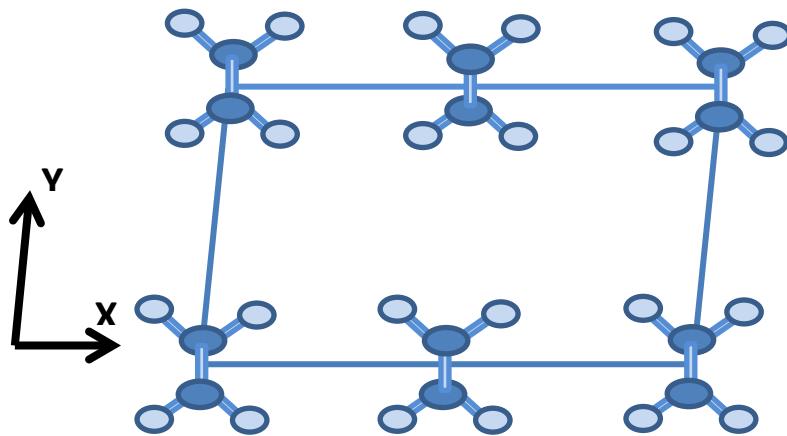


Fig. 1. Scheme of the triclinic-crystal of the n-paraffin, the light-blue color defines the hydrogen atoms, while the blue color defines the carbon atoms; the view of the one atomic layer.

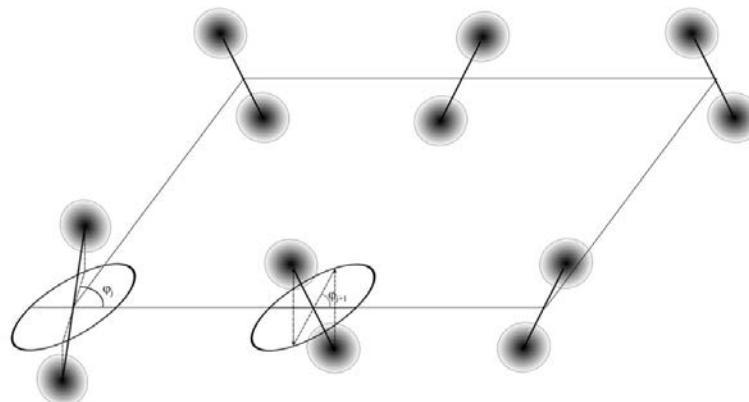


Fig. 2. Angle variables of the united-atoms model of the zigzag chain for the different components of Furrier series of inter-chain potential.

The inter-chain interaction is described by the van der Waals potential. The typical representation has the form of the Lennard-Jones potential with the parameters taken same as for the polyethylene in [8,10]:

$$V_{LJ} = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right), \quad (1)$$

$\epsilon=0.961$ kJ/mole, $\sigma=3.5$ Å. According to modelling by Zubova and coauthors [8,10] the parameters of the crystal are to be taken as follows: length of the bonds between the two neighboring beads in one chain $L=2.085$ Å, angle between the two bonds in one zig-zag chain $\theta=75$ grad, distance between the two chains along the X direction (see Fig.2). The inter-chain potential is approximated as the first terms of Fourier series of the potential (1) when the configuration of the crystal (see Fig. 1, Fig. 2) is taken into account:

$$V_{\text{inter}} = V_0 - \sum_{m,n,k} \{ A_k \cos(k\varphi_m + k\varphi_n) + B_k \cos(k\varphi_m - k\varphi_n) - C_k \cos(k\varphi_m - k\varphi_n) \cos(k\varphi_m + k\varphi_n) + \dots \}, \quad (2)$$

where index k defines the different atomic layers, while m, n define the interacting centers in different chains, the summation is over all the interacting centers.

The first terms of the Fourier expansion provide qualitative agreement with the structure of the full Lennard-Jones potential of the chains interaction (see Fig. 3).

We study the dynamics of the system in the case when the wave number in only one of the directions (0,1,0) is not equal to zero, therefore the equations of motion for angular variables look as follows:

$$\frac{d^2\varphi_j}{dt^2} + A(\sin(\varphi_j + \varphi_{j+1}) + \sin(\varphi_j + \varphi_{j+1})) - B(\sin(\varphi_{j+1} - \varphi_j) - \sin(\varphi_j - \varphi_{j-1})) + C \sin(2\varphi_j) = 0. \quad (3)$$

The model is reduced to quasi-one-dimensional case, which describes the dynamics of the chain in the rigid form with potential of interaction V_{inter} in the configuration analogous to the “anti-ferromagnetic” state, when the neighboring elements have the phase shift of π . The time-variable is rescaled to unity.

In the models of the crystalline lattices very often the continualized equations are considered [16,17,18]. However, we concentrate our study on the discrete model, taking into account the fact, that continualization of the equation (3) will not allow to describe adequately the effects of gradient type of the nonlinearity.

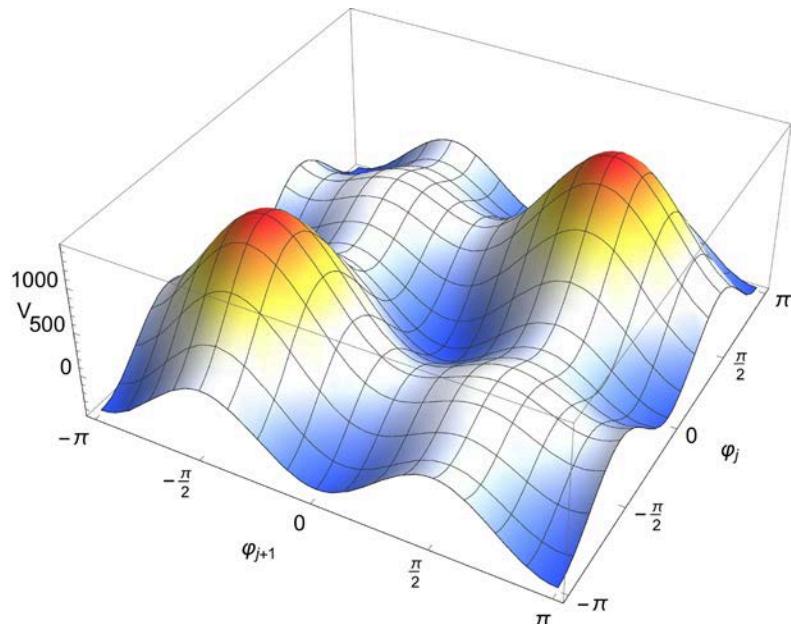


Fig. 3. Form of the asymptotic potential (2) for $V_0=261$, $A_1=261$, $B_1=239$, $C_1=676$.

3. Asymptotic analysis

We intend to study the nonlinear oscillations without restrictions to the rotational amplitudes, therefore a quasilinear approximation cannot be applied. Our problem is significantly nonlinear and there is no evident small parameter to be introduced. To study the dynamics of the system we use the introduced earlier by us semi-inverse method [19,20]. The method allows to separate slow and fast dynamics of the system supposing that the frequencies of the resonating nonlinear normal modes (NNMs) [21] are close to the gap frequency.

We introduce new complex variables:

$$\psi_j = \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{\omega}} \dot{\phi}_j + i\sqrt{\omega} \phi_j \right), \quad \psi_j^* = \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{\omega}} \dot{\phi}_j - i\sqrt{\omega} \phi_j \right), \quad (4)$$

and implement two-scale asymptotic procedure:

$$\frac{d}{dt} = \frac{\partial}{\partial \tau_1} + \varepsilon \frac{\partial}{\partial \tau_2}, \quad \psi_k = \phi_k(\tau_2) e^{i\omega\tau_1}. \quad (5)$$

In the main asymptotic approximation we obtain equation in the following form:

$$\begin{aligned} i \frac{d\phi_j}{d\tau_2} &= \left(\frac{\omega}{2} \right) \phi_j - \frac{A}{\sqrt{2\omega}} \left(J_1 \left(\sqrt{\frac{2}{\omega}} |\phi_j + \phi_{j+1}| \right) \frac{(\phi_j + \phi_{j+1})}{|\phi_j + \phi_{j+1}|} + J_1 \left(\sqrt{\frac{2}{\omega}} |\phi_j + \phi_{j-1}| \right) \frac{(\phi_j + \phi_{j-1})}{|\phi_j + \phi_{j-1}|} \right) + \\ &\quad \frac{B}{\sqrt{2\omega}} \left(J_1 \left(\sqrt{\frac{2}{\omega}} |\phi_{j+1} - \phi_j| \right) \frac{(\phi_{j+1} - \phi_j)}{|\phi_{j+1} - \phi_j|} - J_1 \left(\sqrt{\frac{2}{\omega}} |\phi_j - \phi_{j-1}| \right) \frac{(\phi_j - \phi_{j-1})}{|\phi_j - \phi_{j-1}|} \right) - \frac{C}{\sqrt{2\omega}} J_1 \left(\sqrt{\frac{2}{\omega}} |2\phi_j| \right) \frac{(2\phi_j)}{|2\phi_j|}. \end{aligned} \quad (6)$$

We look for the stationary solutions: $\phi_j = \sqrt{X} e^{ikj}$

$$\begin{aligned} \left(\frac{\omega}{2} \right) - \frac{A}{\sqrt{2\omega X}} J_1 \left(\sqrt{\frac{2X}{\omega}} \cos \left(\frac{k}{2} \right) \right) \cos \left(\frac{k}{2} \right) + \\ - \frac{B}{\sqrt{2\omega X}} J_1 \left(\sqrt{\frac{2X}{\omega}} \sin \left(\frac{k}{2} \right) \right) \sin \left(\frac{k}{2} \right) - \frac{C}{\sqrt{2\omega X}} J_1 \left(\sqrt{\frac{2X}{\omega}} \right) = 0. \end{aligned} \quad (7)$$

Introducing initial excitation of one element and using (4) we obtain:

$$X = \frac{Q^2 \omega}{2}. \quad (8)$$

Using this result we get the dispersion relation:

$$\omega^2 = \frac{2}{Q} \left(2AJ_1 \left(2Q \cos \left(\frac{k}{2} \right) \right) \cos \left(\frac{k}{2} \right) + 2BJ_1 \left(2Q \sin \left(\frac{k}{2} \right) \right) \sin \left(\frac{k}{2} \right) + CJ_1(2Q) \right). \quad (9)$$

We obtained a degenerated spectrum with only $N/2+1$ lines for the N chains in the domain. The “width” of the spectrum for the low-amplitude case is defined by the relation between B and A parameters of the model. To check the spectrum obtained we compare our results with the exact solutions of the initial equation (3) for the two limiting cases when the equations can be solved exactly as equation of a pendulum: homogeneous mode with $k=0$ (in-phase mode) and π -mode (antiphase mode, $k=N/2$). The frequencies of in-phase and antiphase modes in the asymptotic system are:

$$\omega_{in}^2 = \frac{4(A + C/2)}{Q} J_1(2Q), \quad (10)$$

$$\omega_a^2 = \frac{4(B + C/2)}{Q} J_1(2Q). \quad (11)$$

If we introduce the condition of the in-phase motion to the initial system (6), we obtain the equation of the pendulum:

$$\frac{d^2\varphi}{dt^2} + 2(A + C/2) \sin(2\varphi) = 0, \quad (12)$$

which can be solved exactly; the frequency is:

$$\omega_m^2 = \frac{\pi\sqrt{(A+C/2)}}{K(\sin(Q))}. \quad (13)$$

The same procedure can be repeated for the anti-phase mode with the wave number $k=N/4$, N - number of the interacting chains in the domain:

$$\omega_a^2 = \frac{\pi\sqrt{(B+C/2)}}{K(\sin(Q))}. \quad (14)$$

The dependence of the frequency on the amplitude of the initial excitation Q and on the wave-number is presented on the Fig. 4 and Fig.5 correspondingly. The amplitude-frequency evolution is compared with the analytical results for the initial equation (13) and (14). We see that for lower amplitude values the frequency of the homogeneous NNM has the lowest value, while the frequency of the π -mode has the highest value. When the value of the amplitude is close to the $\pi/2$ the inversion of the spectrum occurs: the frequency of the π -mode approaches the value of the frequency of the homogeneous one, while all the other frequencies have higher values.

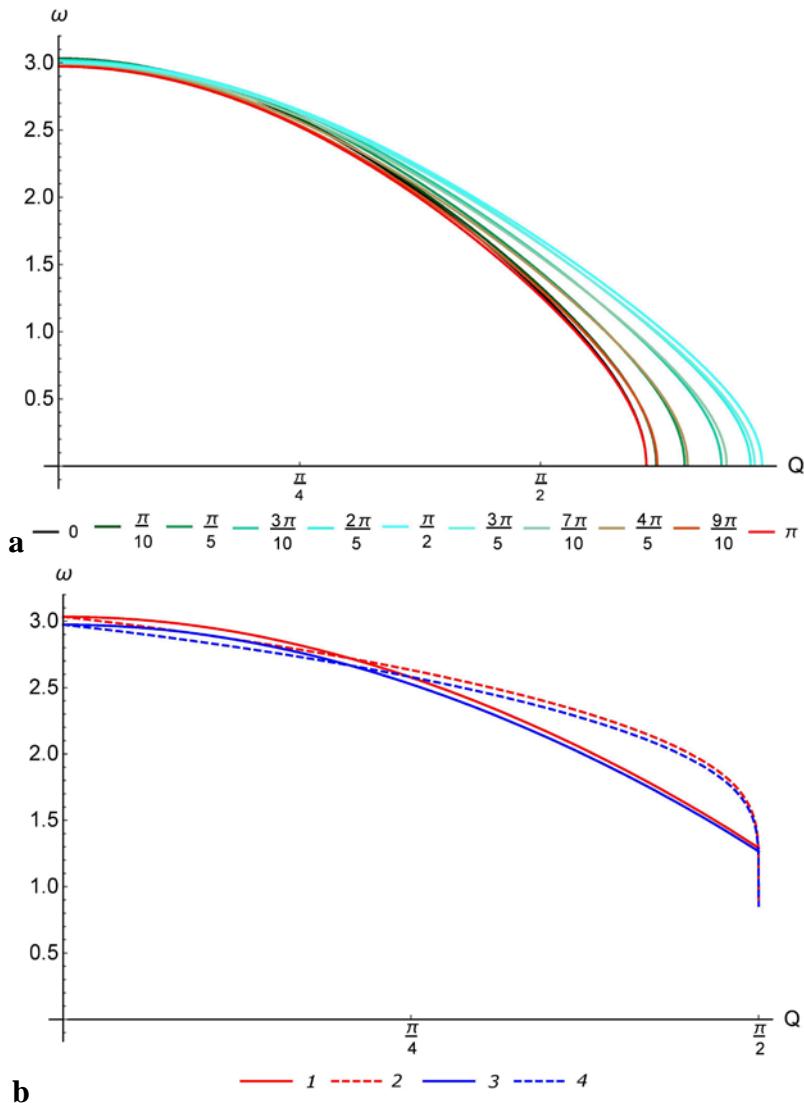


Fig. 4. a) Dependence of the NNM frequency on the amplitude of the excitation, different colors denote different wave-numbers; b) comparison of the asymptotic values with the exact solution for two limiting cases: red line denotes the homogeneous NNM, blue line denotes the π -mode, solid line denotes the asymptotic solutions, dashed line denotes the exact solutions, $A=1$, $B=0.91$, $C=2.6$.

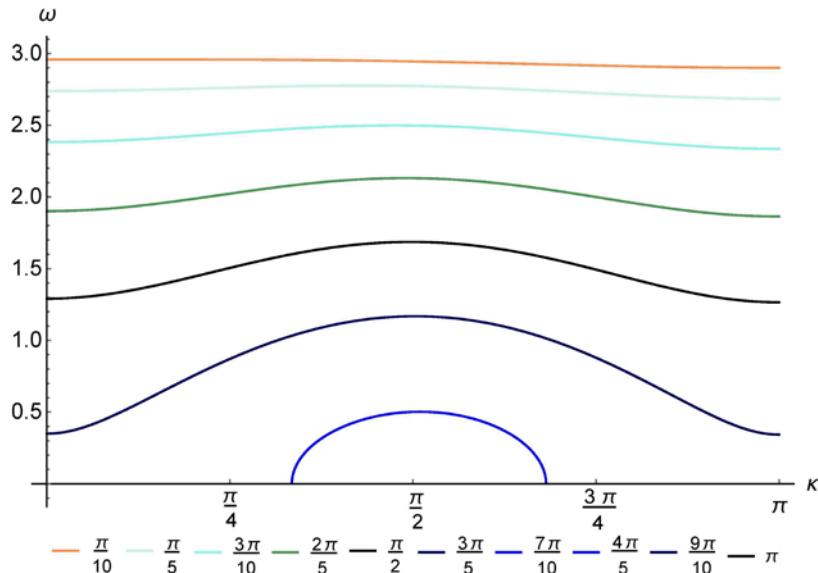


Fig. 5. Dispersion relation of the asymptotic system (9), $A=1$, $B=0.91$, $C=2.6$, different colors denote different values of excitation.

4. Conclusions

We have developed a simple model describing the high-amplitude librational dynamics of the chains in the crystalline paraffins with triclinic symmetry. We considered the simplest case when the wave-vector only in one direction is not equal to zero. Using the semi-inverse method approximation we investigated the nonlinear spectra of the chains dynamics and found them to be in a very good agreement with the exact solutions in the simplest cases of the homogeneous and π -mode. We have also found an inversion of the spectrum with the growth of the amplitude of excitation.

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