NONLINEAR TORSION DYNAMICS OF THE N-PARAFFIN CRYSTAL

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Abstract. The nonlinear dynamical equations, which describe the torsion oscillations of the n-paraffin (alkanes) crystal have been derived in the framework of the coarse-grain model. The essentially nonlinear discrete equations reflect the influence of the internal multi-well conformation potential of the paraffin chain as well as the symmetry of the molecular field of the chain environment at the arbitrary large oscillation amplitudes.
Keywords: n-paraffin; torsion oscillations; nonlinear dynamics; coarse-grain model.

1. Introduction

During the period of nanoscale materials and devices progress, the development of the theoretical models of media becomes the extremely important problem from the viewpoint of atomic description of the nanoscale processes as well as the expansion of these models onto the meso- and micro-levels. Due to that, the construction of the coarse-grain models of the complex objects has the obvious advantages in saving the computational resources and simplification of the analytical description. This allows also to build a bridge to the continual description of the media. In such a case the realistic analytical model should reflect the essential peculiarities of the coarse-grain model, in particular, the nonlinear processes, which are specific for the nanoscale objects. The appearance of the nonlinear dynamics at the nano scale results from the defectless structure of the nanoobjects, e.g. the carbon nanotubes, that permits large elastic deformations without significant rearrangement of the initial structure. In particular, the rotational dynamics in some molecular crystals is the large amplitude motion, which needs in the nonlinear description and occurs without destruction of the crystal order. The n-alkanes (paraffin) are the most well known examples of the molecular crystals, where the rotational phases were observed.

The n-alkanes are the low molecular-weight homologies of the most widespread polymer – polyethylene (PE) [1-6]. In spite of the long history of investigations, some significant questions concerning the PE crystal structure and phase transitions are discussed up to date. In particular, the existence of the rotational state and its possible modifications were considered in [7,8] (see also references herein). The rotational phase in the n-alkanes is the thermodynamically stable state, which is specified by the rotation of the macromolecules as whole about their axes with preservation of the crystal structure in the plane, which is perpendicular to this axis. There are some modifications of the rotational phase, which are differed mainly by the molecule arrangement and the parameters of the crystal cell. The phase transitions between these modifications occurs with changing the temperature. The typical sequence of the phase transitions is *C->RPs->IL*, where *C*, *RPs* and *IL* identify the Crystal state, Rotational Phases and Isotropic Liquid, respectively.

It is obvious that the transition from the crystal state into the rotational phase should be forestalled by the large amplitude torsion oscillations of the alkane molecules. In such a case we need in the analytical model, which can describe these oscillations. However, the essentially

nonlinear models of the dynamical processes are very complex for the analytical solution. In this work, we present the asymptotic analysis of the torsion dynamics of the n-alkane crystal. The model of the torsion dynamics is restricted with the rotation degree of freedom without deformation of the valence bonds or valence angles in the framework of the coarse-grain model of the PE crystal [9]. The coarse-grain model assumes that the CH_2-group is considered as a single object without any internal degrees of freedom. It was shown that such a model allows us to reproduce three crystal arrangement, which are specific for the PE crystal – triclinic, monoclinic and orthorhombic [10]

2. The chain model in the crystal environment

The n-alkane molecule is the chain of carbon atoms, which are arranged as the nodes of the planar zigzag line with the angle between valence bonds $\angle CCC = 112^0$. The valence bond length is equal to 1.54Å. Two hydrogen atoms are in the plane, which is perpendicular to the zigzag plane. The length of C-H bond is equal to 1.10Å. and the angle between them $\angle HCH = 109.5^0$ (see fig.1).
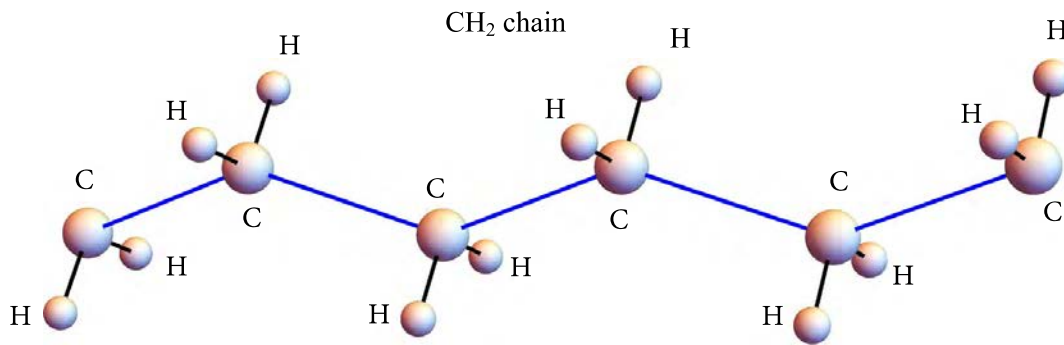

Fig. 1. Fragment of the n-alkane chain.

If we are interested in the vibrations of the chain backbone (skeletal oscillations), which have been described by Kirkwood [11] for the first time, it is naturally to change the CH_2-group by an "united atom" (UA) with the mass $m_a=m_C+2m_H$ (m_C and m_H are the masses of carbon and hydrogen atoms, respectively) and the center of the forces, which is inside the HCH triangle. In the recent paper [9] such an effective roughening has been proposed.

The internal energy of the chain deformation is the sum of several types of interactions:

$$E = E_{cc} + E_{CCC} + E_{CCCC}, \tag{1}$$

where E_{cc}, E_{CCC} and E_{CCCC} are the energies of valence bond, valence angle and conformational /torsion/ angle deformations, respectively. The latter is measured as the dihedral angle between the planes, which contain two neighboring triads of the united atoms. It is very important, that the values of mentioned energies are essentially differed. The rigidity of valence bonds exceeds 10^3 kJ/mol/Å, while the rigidity of the valence angle is specified by the value ~ 167 kJ/mol/grad, and the rigidity of the torsion energy can be estimated as ~ 35 kJ/mol/ rad. Consequently, considering the torsion vibrations of the alkane chain we can assume that only torsion energy E_{CCCC} is important for the rotational motion of the molecule backbone, while the deformations of the valence bonds and angles are negligible. There is one more peculiarity of the torsion potential E_{CCCC} (fig.2). This is the existence of three equilibrium states, which are slightly differed in the energy, but can appear at the normal conditions. They have the values of the torsion angle $\psi = 180^0, \pm120^0$. The first value corresponds to the planar chain (trans-conformation) and the second lead to the rotation of the chain plane on the angle $+120^0$ (gauche+) and -120^0 (gauche–). In the basic state of the alkane crystal all the chains are in the trans conformations and any gauche conformation is a structural defect.
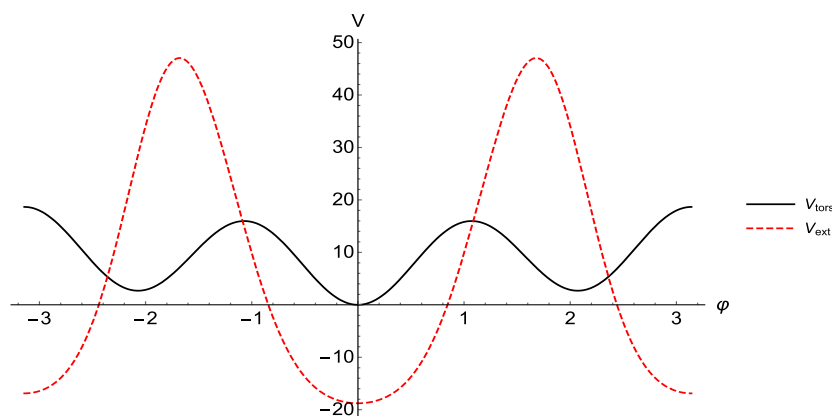
Fig. 2. Torsion (black solid line) and molecular field (red dashed curve) potentials.

So, we will consider the torsion oscillations of the $(CH_2)_n$ molecule in the alkane crystal in the framework of mentioned coarse-grain model. We assume that the C-C valence bonds and C-C-C valence angles are infinitely rigid but we should take into account the crystal environment, which forms the "external" field. This field is generated by the non-covalent Van der Waals interactions between the united atoms of the considered chain and its nearest environment. The energy of non-covalent interaction is traditionally described by the Lennard-Jones potential:

$$E_{VdW} = \epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right), \tag{2}$$

where r is the distance between atoms, and ϵ and σ specify the depth and the position of the potential well, respectively. For the considered system $\epsilon = 0.96 \ kJ/mol$ and $\sigma = 3.5$Å. In spite of that potential function (2) describes the infinite-range interaction, the main contribution in the molecular field is made by the nearest neighbors. It can be shown that the cutoff radius $r \sim 10.5$ Å is the well-defined value for the estimation of the molecular field. Fig. 3 shows the fragment of the alkane crystal, which contributes into the molecular field for the rotational degree of freedom of the central chain. So, the external (on-site) potential for the rotation can be written as follows:

$$E_{ext} = \sum_{n,m,j} E_{VdW}(r_{n,m,j}), \tag{3}$$

where the sum is taken over the sphere with radius $R_{cut} \sim 10.7$ Å and centered on the considered united atom. The result of such estimation is shown in fig. 2 as the function of the rotational angle φ. One can see that the on-site potential is the periodic function and we estimated the rigidity of it as $15.452 \ kJ/mol/\ rad$.
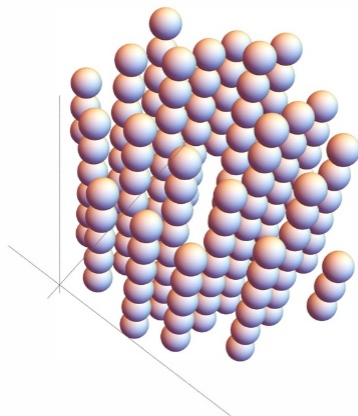

Fig. 3. Fragment of the united atom crystal. The atoms, which effectively participate in the covalent interactions, are shown.

Keeping in mind the analytical description of the torsion dynamics of the chain, we will approximate E_{ext} by the sum of its Fourier expansion terms. One can show that the leading term in the Fourier expansion of E_{ext} is the second harmonic one.

$$E_{ext} \approx \sum_k \gamma_k cosk\varphi \qquad (4)$$

The values of the Fourier expansion coefficient are presented in the Table 1.

Table 1. Fourier coefficients for molecular field (3).

k	0	1	2	3	4	5	6
γ_k (kJ/mol)	7.597	-3.833	-31.421	4.241	6.318	-1.631	-0.275

Resuming all of mentioned above one can write the potential energy of alkanes chain in the crystal as follows:

$$E_{rot} = \sum_{n=1}^{N} \beta_1(1 - \cos(\varphi_{n+1} - \varphi_n)) + \beta_3(1 - \cos 3(\varphi_{n+1} - \varphi_n)) + \sum_k \gamma_k cosk\varphi_n , \qquad (5)$$

where N is the length of the alkane chain. For the best of our knowledge, the nonlinear lattices with a similar potential function have been considered for the first time in the works [12].

3. Asymptotic analysis: nonlinear normal modes

The equation of torsion motion of the j-th united atom can be obtained from energy (5) as follows:

$$I\frac{d^2\varphi_j}{dt^2} + \frac{\partial E_{rot}}{\partial \varphi_j} = 0,$$

where $I = m_a\rho^2$ is the inertia moment and ρ is the distance from the axis of the chain to the center of the united atom. The extended representation of the equations of motion is written as:

$$I\frac{d^2\varphi_j}{dt^2} - \beta_1\left(\sin(\varphi_{j+1} - \varphi_j) - \sin(\varphi_j - \varphi_{j-1})\right) - 3\beta_3\left(\sin\left(3(\varphi_{j+1} - \varphi_j)\right) - \right.$$
$$\left. \sin\left(3(\varphi_j - \varphi_{j-1})\right)\right) + \sum_k n\gamma_k \sin k\varphi_j = 0, \ (j = 1, \dots N). \qquad (6)$$

These equations are essentially discrete and nonlinear and, generally speaking, can not be analytically solved. One should note that the traditionally used long wave-length approximation does not conserve the specific structure of the torsion potential. However, using the semi-inverse asymptotic method [13,14] we can obtain the natural frequencies of the nonlinear normal oscillations and investigate the resonant interaction of the nonlinear normal modes. For this aim we introduce the complex representation of the equation of motion, which is written in term of functions:

$$\Psi_j = \frac{1}{\sqrt{2}}\left(\frac{i}{\sqrt{\omega}}\frac{d\varphi_j}{dt} + \sqrt{\omega}\varphi_j\right), \qquad (7)$$

where ω is (unknown yet) frequency. The inverse transformation is written as follows:

$$\varphi_j = \frac{1}{\sqrt{2\omega}}(\Psi_j + \Psi_j^*) \qquad (8)$$

Taking into account expression (8), one can represent the trigonometric functions by their expansion in the Taylor series:

$$\sin \alpha f = \sum_{k=0} \frac{(-1)^k}{(2k+1)!}\left(\frac{\alpha}{\sqrt{2\omega}}\right)^{2k+1}(\Phi + \Phi^*)^{2k+1} ; \qquad (9)$$
$$\Phi = \frac{1}{\sqrt{2}}\left(\frac{i}{\sqrt{\omega}}\frac{df}{dt} + \sqrt{\omega}f\right), f = \{\varphi_n, \varphi_{n+1} - \varphi_n, \dots\}.$$

Substituting this expansion into original equations of motion, we get the complex form of equations:

$$i\frac{d}{dt}\Psi_j - \frac{\omega}{2}(\Psi_j - \Psi_j^*) + \frac{1}{I\sqrt{2\omega}}\sum_{k=0}\frac{(-1)^k}{(2k+1)!}(\frac{1}{\sqrt{2\omega}})^{2k+1}(\frac{\beta_1}{\mu}(\ldots) + 3\frac{\beta_3}{\mu}(\ldots) -$$

$$\sum_n n\frac{\gamma_n}{\mu}(\ldots)) = 0, \tag{10}$$

where omitted terms in the brackets represent the respective combinations of Ψ_j .

We will look for the stationary solutions of equations (10) as follows:

$$\Psi_j = \chi_j e^{-i\omega t}, \tag{11}$$

where the functions χ_j do not depend on the time t.

Substituting (11) into equations above and integrating over the period $2\pi/\omega$, we get following equations from the conditions of the secular terms absence:

$$\frac{\omega}{2}\chi_j + \frac{1}{I\sqrt{2\omega}}[\beta_1\left(J_1\left(\sqrt{\frac{2}{\omega}}|\chi_{j+1} - \chi_j|\right)\frac{\chi_{j+1}-\chi_j}{|\chi_{j+1}-\chi_j|} - J_1\left(\sqrt{\frac{2}{\omega}}|\chi_j - \chi_{j-1}|\right)\frac{\chi_j-\chi_{j-1}}{|\chi_j-\chi_{j-1}|}\right) +$$

$$3\beta_3\left(J_1\left(3\sqrt{\frac{2}{\omega}}|\chi_{j+1} - \chi_j|\right)\frac{\chi_{j+1}-\chi_j}{|\chi_{j+1}-\chi_j|} - J_1\left(3\sqrt{\frac{2}{\omega}}|\chi_j - \chi_{j-1}|\right)\frac{\chi_j-\chi_{j-1}}{|\chi_j-\chi_{j-1}|}\right)] -$$

$$\frac{1}{I\sqrt{2\omega}}\sum_k k\gamma_k J_1(k\sqrt{\frac{2}{\omega}}|\chi_j|) = 0, \tag{12}$$

where J_1 is the Bessel function of the first order.

It is readily checked that the solution of equations (12) is represented as follows:

$$\chi_j = \sqrt{X}e^{i\kappa j} \tag{13}$$

with

$$X = \frac{\omega}{2}Q^2, \tag{14}$$

if the frequency ω satisfies the relation:

$$\omega^2 = \frac{2}{\mu Q}(\sum_n n\gamma_n J_1(nQ) + 2\left[\beta_1 J_1\left(2Q\sin\frac{\kappa}{2}\right) + 3\beta_3 J_1\left(6Q\sin\frac{\kappa}{2}\right)\right]\sin\frac{\kappa}{2}). \tag{15}$$

Here Q is the oscillation amplitude. The relation (14) can be readily derived from expression (7).

So, expression (15) is the dispersion relation for the nonlinear normal modes (13). Fig. 4 shows the dependences of the natural frequencies on the wave number κ and the oscillation amplitude Q (Fig. 4 a and 4 b, respectively).

First of all, one should notice the presence of the imaginary frequencies, the square of which are negative. It means that the respective normal modes do not exist. However, it is not so for the large amplitude oscillations of the chain as whole, i.e. oscillations with wave number $\kappa = 0$. The numerical simulations shows, that such oscillations with large amplitudes exist, but with respect to the equilibrium state $\varphi_0 = \pi$ (in such a case the equations of motion (6) should be written with respect to this equilibrium state).
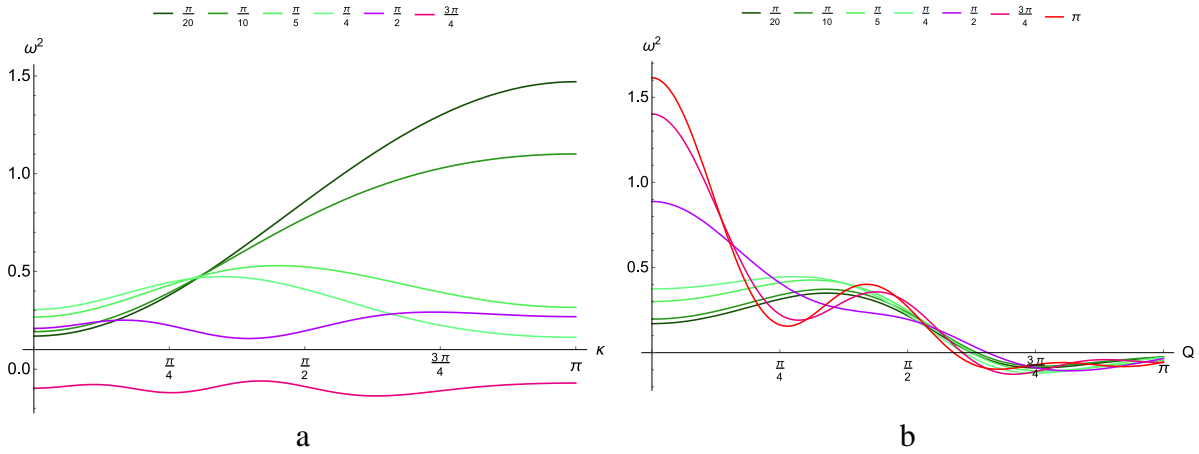
Fig. 4. Dependences of the square of natural frequencies on the wave number κ (a) and oscillation amplitude Q (b). The legends show the values of amplitudes (a) and wave numbers (b), respectively.

The complex structure of the torsion interaction leads to the non-conventional behavior of the oscillation frequencies when the amplitude increases. The dispersion relation in the small amplitude limit is similar to that for the Frenkel-Kontorova model [15], but the dependence $\omega(\kappa)$ becomes almost planar, while the oscillation amplitude rises (Fig. 4 a). It means that the nonlinear normal modes with very different wave numbers may turn out to be under resonant conditions. In contrast to the linear dynamical system, the nonlinear normal modes in the system under consideration can interact effectively if the resonance between them occurs. In such a case, a linear combination of the nonlinear normal modes is a slowly changed function of the time and its scale of variety is determined by the difference between the natural frequencies of the nonlinear normal modes. Their interaction can be studied by the time dependent version of equation (12) [14].

4. Numerical simulations.
In order to verify the dispersion relations obtained above, the numerical simulations of the initial system (6) have been made for the system with 20 united atoms. Because of the definition of the torsion angle needs in coordinates of two united atoms, the system has been divided onto 10 groups with 2 atoms in each. The parameters of torsion interaction (β_1, β_3) have been chosen accordingly to work [9]. Two questions concerning the dynamics of the system under study were of our interest. At first, whether the natural frequencies of the full system are in accordance with the analytically predicted dispersion relations? And second question is: in what degree the modal profile (13) corresponds to the real oscillations? The results are shown in Figs. 5 and 6. Fig. 5 shows the natural frequencies as the functions of the wave number at different oscillation amplitudes inside the range $[0, \frac{\pi}{2}]$. (We did not consider the amplitudes, which exceed the value $\pi/2$ for the reasons mentioned above.) One can see, that the accordance between analytically predicted and numerically measured frequencies is good enough.
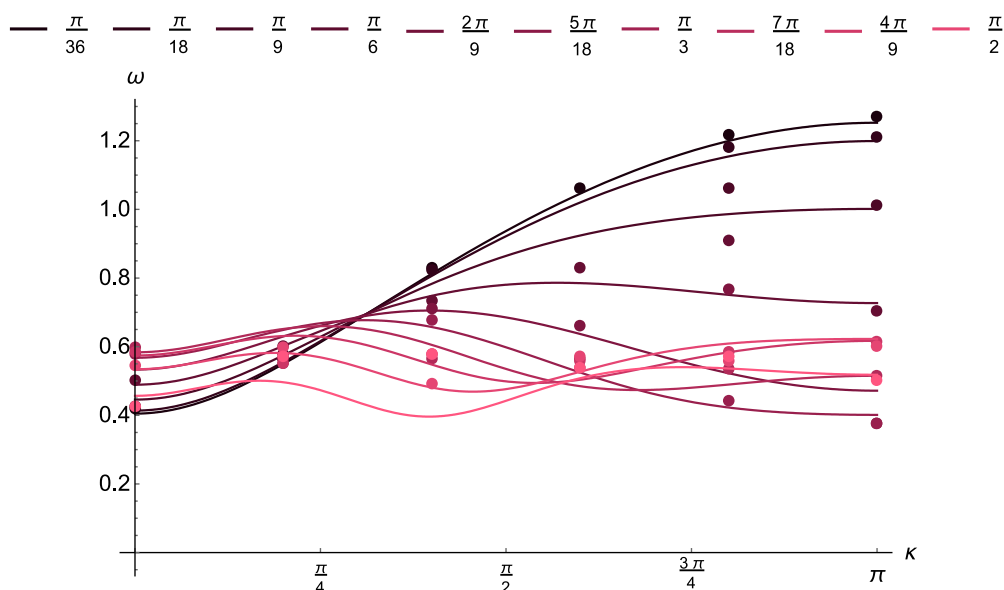
$$\frac{\pi}{36} \quad \frac{\pi}{18} \quad \frac{\pi}{9} \quad \frac{\pi}{6} \quad \frac{2\pi}{9} \quad \frac{5\pi}{18} \quad \frac{\pi}{3} \quad \frac{7\pi}{18} \quad \frac{4\pi}{9} \quad \frac{\pi}{2}$$

Fig. 5. Comparison of analytical (solid lines) and numerically estimated (points) frequencies for the nonlinear normal modes at different oscillation amplitudes. The legend shows the oscillation amplitudes Q.

Numerical simulations show that modes (13) reproduce the oscillation shape for the original system at small-amplitude limit for any wave numbers. This region is shown in Fig. 6 by blue color. However, while the oscillation amplitude grows, the oscillation profile becomes slightly different from simple shape (13), in spite of that the oscillation frequencies correspond to analytical predictions. Such oscillations correspond to yellow region in Fig. 6.
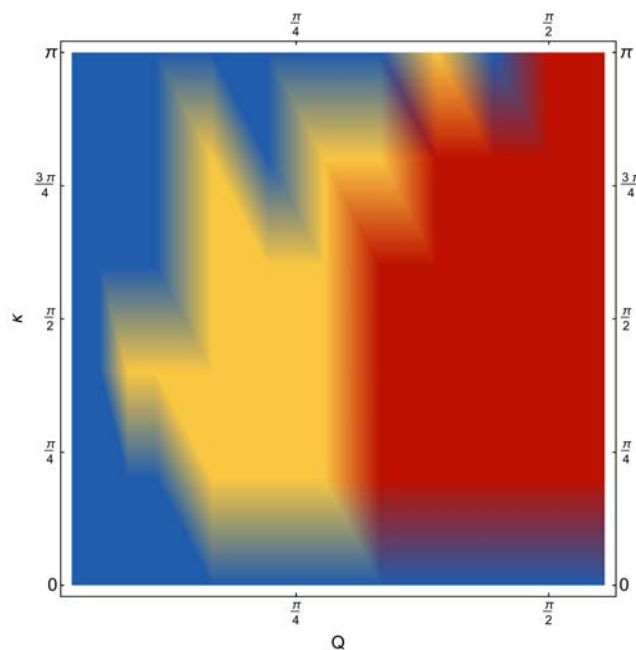
Fig. 6. Map of the normal mode stability. Blue – stable oscillations, yellow – slightly unstable, red – unstable with the local rotations.

The oscillations with the large amplitudes ($\geq \pi/3$) exhibit a trend to the local rotations of some united atoms. Due to periodicity of the potential energy, the chain is not destroyed and the oscillations with respect to "new" equilibrium state occur with the same frequency. The domain of such behavior is marked in Fig. 6 by red color. One should notice that the uniform

mode ($\kappa = 0$) is stable at any amplitude of the oscillations. All mentioned peculiarities are quite expected, if one takes into account the non-monotonic behavior of the potential energy. It is clear that the shape of oscillation with amplitude near the maximum of the potential energy can not be similar to the standing wave like expression (13). In addition, the possible resonant interaction between modes with different wave number can appear as instability of the wave shape. The analysis of the modes' stability under condition of the resonant interaction is a subject of the further study.

5. Conclusion

The analysis of the torsion vibrations of the n-alkane molecule in the crystal field shows that these vibrations can be well described in the framework of asymptotic semi-inverse approach at the small-amplitude limit. The natural frequencies as well as the shapes of oscillations can be represented analytically. While the oscillation amplitude increases the shapes of the oscillations are changed, in spite of the frequencies satisfy the analytical predictions well enough. The further growth of the oscillation amplitude, which occurs while the temperature of the crystal grows, leads to the onset of the local rotations of some CH_2 groups. Generally speaking, the model discussed above is not good approximation of such rotations, because these processes need in the deformations of the valence angles between neighbor C-C bonds. Nevertheless, one should notice that the uniform rotation mode, which is responsible for the rotation state of the n-alkane crystal, preserves its shape up to highest possible oscillation amplitudes. However, the process of the transition into the rotation phase is forestalled by the large amplitude oscillations with the large number of the local rotations.

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