NONLINEAR ROTATIONAL MODES IN MOLECULAR CHAINS

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ABSTRACT

The continual nonlinear wave equations are derived for the rotational excitations of the molecules in wide energy interval: from equilibrium through rotational melting point to rotational disordered phase. Dispersion is considered to be small. Nonlinear oscillations are described by the coordinate along the "valleys" of the effective potential. Local normal coordinates are introduced. Linear equation describes waves of the stiffer normal mode. Nonlinear Sin-Gordon type equation is derived for waves of the softer mode in wide energy interval. The nonlinear wave solutions are analyzed.

INTRODUCTION

An analytical description of the molecular rotor chain dynamics and thermodynamics is developed for low and high energy intervals [1]. The problem is to create theoretical description in the middle range of energies, especially in the vicinity of the point of orientational melting.

Adsorbates [2] or crystals with low-dimensional motives are real 1D and 2D structures. Chain models are necessary stage of investigation of dynamics and thermodynamics of crystals [3], nonlinear lattices [4]. Complexity of models even for 1D linear molecular chain requires some approximations: a model potential and 1D rotation and very hard translational potential, so translation vibrations are frozen and they can be neglected [2,5]. The potential energy of the molecular chain with realistic quadrupolar potential [5] can be written as [6-9]:

$$U_{ch} = \Gamma\{a_0 N + \sum_{i=1}^{N}[a(\cos 2\phi_i + \cos 2\phi_{i+1}) + b\cos 2(\phi_i - \phi_{i+1}) + c\cos 2(\phi_i + \phi_{i+1})]\}$$

$$\Gamma = 3Q^2/4R^5; \; a_0 = 3/4; \; a = 5/4; \; b = 3/8; \; c = 35/8 \tag{1}$$

Here Q is a quadrupolar moment of a molecule, R is a distance between molecules, ϕ_m is an angle between the principal axis of a molecule and the chain axis. The chain energy (1) has minimum [6,7] for the molecules' alternating ordering (two sublattices) at the angles:

$$\phi_{2n} = \frac{\pi}{2} + \pi j; \phi_{2n+1} = \pi j; \qquad \text{or} \qquad \varphi_{2n} = \pi j; \varphi_{2n+1} = \frac{\pi}{2} + \pi j \tag{2}$$

where $j,m,n=0, \pm1, \pm2,...$, index $m=2n$ $(m=2n+1)$ defines even (odd) site.

Lagrangian of the system is $L=K-U$. Here U and $K = \frac{1}{2}\sum_{m=1}^{N} J_i \dot{\varphi}_i^2$ are potential and kinetic energies of the chain, a molecule has a moment of inertia J_i and an angle velocity $\dot{\phi}_i$. Then the Lagrangian variation yields system of equations for chain motion:

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$$J_i \ddot{\phi}_i - 2\Gamma\{2a\sin\phi_i + b[\sin 2(\phi_i - \phi_{i-1}) + \sin 2(\phi_i - \phi_{i+1})] +$$
$$+ c[\sin 2(\phi_i + \phi_{i-1}) + \sin 2(\phi_i + \phi_{i+1})]\} = 0 \tag{3}$$

Let us rewrite these equations for two sublattices that have different equilibrium state (2) in the long-wave limit [8] and introduce new variables for even (ϕ) and odd (ψ) sites. More convenient for further analysis is following form of the equations and variables

$$\ddot{p} - 8\{a\sin p\cos m + c\sin 2p\} = 0$$
$$\ddot{m} - 8\{a\sin m\cos p + b\sin 2m\} = 0 \tag{4}$$
$$m = \phi - \psi; \quad p = \phi + \psi \tag{5}$$

Here dimensionless time and characteristic frequency are introduced: $t \to \tau = t\omega_0$, $\omega_0^2 = \Gamma/J_0$, $J_i = J_0$. Integral of the rotational motion for the molecular chain can be found [8] for the system (4): $W_{ef} = W_k + W_p$. The integral includes "kinetic" W_k and "potential" W_p contributions:

$$W_k = \frac{1}{2}(\dot{p}^2 + \dot{m}^2); \quad W_p = 4[2a\cos p\cos m + b\cos 2m + c\cos 2p] \tag{6}$$
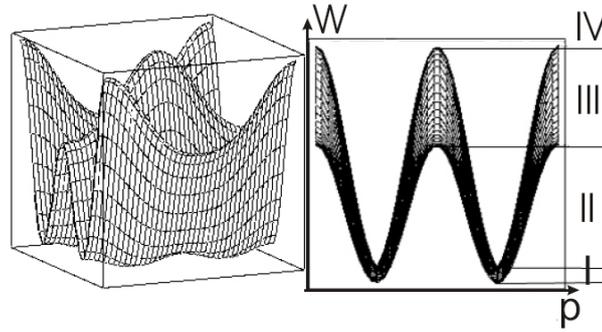

Fig. 1. *The potential relief W_p in a quadrupolar molecular chain. (left) 3D image. (right) View along a valley. (I) Ordered phase. (II) Phase of correlated movements when p is finite, m is infinite. (III) Phase of correlated movements when both p and m are infinit. (IV) Completely disordered phase.*

The rotational excitations demonstrate strong anisotropy in the angle space, easy directions ("valleys" on the potential) exist [8] (see fig. 1). Excitations that spread along "valleys" do not destroy correlation between molecules but a structural data can show rotational disorder (melting). We used the strong anisotropy ('valleys') and the normal modes to split equations for linear and nonlinear (softer mode) molecular chain oscillations [9]. Nonlinear Schrodinger equation was derived for the softer mode, its wave solutions were obtained.

In the present work, the continual nonlinear wave equations are derived for the rotational excitations of the molecules with quadrupolar interaction in wide energy interval: from equilibrium through rotational melting point to disordered phase. Nonlinear oscillations are described by the coordinate along the "valleys". Local normal coordinates are introduced. Linear equation describes waves of the stiffer normal mode. Sin-Gordon equation is derived for the softer mode in wide energy interval, their wave solutions are analyzed.

1. DERIVATION OF THE CONTINUAL EQUATIONS FOR AN INHOMOGENEOUS CHAIN.

The system of equations (3) is a strongly nonlinear and differential-difference. Let us rewrite these equations for two sublattices which have different equilibrium state (2), and introduce new variables for even (ϕ_{2m}) and odd (ϕ_{2m+1}) sites:

$$\ddot{\varphi}_i - 2\{2a\sin\varphi_i + b[\sin2(\varphi_i - \psi_{i-1}) + \sin2(\varphi_i - \psi_{i+1})] +$$
$$+c[\sin2(\varphi_i + \psi_{i-1}) + \sin2(\varphi_i + \psi_{i+1})]\} = 0$$

$$\ddot{\psi}_{i+1} - 2\{2a\sin\psi_{i+1} + b[\sin2(\psi_{i+1} - \varphi_i) + \sin2(\psi_{i+1} - \varphi_{i+2})] +$$
$$+c[\sin2(\psi_{i+1} + \varphi_i) + \sin2(\psi_{i+1} + \varphi_{i+2})]\} = 0$$

$$(7)$$

Here the new variables for even (φ_{2m}) and odd (φ_{2m+1}) sites are introduced. Orientation difference in the same sublattice is distinguished by account of a site number.

Let us introduce more convenient variables instead of (5) to account the sites difference:

$$m_i = \phi_i - \psi_{i+1}; \, p_i = \phi_i + \psi_{i+1} \qquad (8)$$

With purpose to organize these variations let us find sum (for p) and difference (for m) of equations (7), then write expansion for variables ϕ and ψ around values which form p_i and m_i. After grouping we obtain the continual variables $p \equiv p_i$ and $m \equiv m_i$. Then we hold the lowest derivations (no more than the second derivation or multiplication of the first ones). As a result the system of dynamical nonlinear continual differential equations can be yielded:

$$\begin{cases} \ddot{p} = 2\{4a\sin p\cos m - 4b[(m' + p'')\cos2m - 2m'p'\sin2m] + \\ \qquad 4c[(m' + p'')\cos2p + (1 - m'^2 - p'^2)\sin2p]\} \\ \ddot{m} = 2\{4a\sin m\cos p + 4b[(p' + m'')\cos2m + (1 - m'^2 - p'^2)\sin2m] - \\ \qquad 4c[(p' + m'')\cos2p - 2m'p'\sin2p]\} \end{cases} \qquad (9)$$

Here we introduce dimensionless coordinate: $\xi = x/R_0$. Derivations are $p' = \partial p/\partial\xi$ and $p'' = \partial^2 p/\partial\xi^2$, and the same formulae for m, m'. We suppose that derivations are relatively small: $p'' \ll p' \ll p; \, m'' \ll m' \ll m; \, p \ll m$. The attractive feature of the system (9) is symmetry on the coordinates p, m and the interaction parameters over pair exchange:

$$p, c \longleftrightarrow m, b \qquad (10)$$

Let us discuss general properties of the yielded system of equations (9). It was obtained in continuum approximation and describes any nonlinear time-dependent processes in the molecular chain. The system has too complicated construction as over the generalized angle coordinates p and m as their derivations. In comparison with Landau-Lifshits nonlinear equations that describe ferromagnets [10] the space derivations are distributed by especially complicated way: dispersion and nonlinear terms are entangled. Integral of the system (9) is.

$$\frac{1}{2}(\dot{p}^2 + \dot{m}^2) + 4[2a\cos p\cos m + b(1 + p'^2 - m'^2)\cos2m + c(1 - p'^2 + m'^2)\cos2p] = C \quad (11)$$

This integral has the same symmetry (10) as the original system of the equations. The integral includes only the first derivations in the second powers. This integral can be applied to investigation of any nonlinear processes in the molecular chains with alternating ordering.

2. LOCAL NORMAL COORDINATES AND VARIABLES SPLITTING.

The integral (11) is not enough for integration of the considered two-dimensional system in stationary case. We need two integrals of motion and a set of boundary conditions [11]. Nevertheless there is another way to reach integrability. It is the way of the probe orbits [12] when two variables are connected by some kind of dependence and energy minimum is reached under some parameters' value. Generally, integration in spaces with dimension more than 1 requires excluding of extra coordinates. Choice of an orbit is many variant procedure even for power potential [12]. Here we have more complicated case when potential consist of trigonometric functions of the variables. Therefore

we have to elect some path in the p-m plane that seems to provide minimum of the inhomogeneous behavior of the interacting molecular system. This way is not better or worse in comparison with construction of a domain wall in ferromagnetic materials [10] in the cases of Bloch (magnetic moment rotates in the DW plane) or Neel (magnetic moment rotates at right angle to the DW plane).

According to topological analysis in long-wave case [8] the potential relief of 1D chain has very low narrow valleys. We propose the orbit which coincides with the valley bottom, see Fig.2. General equation for the 'valley's' bottom can be obtained from (4):

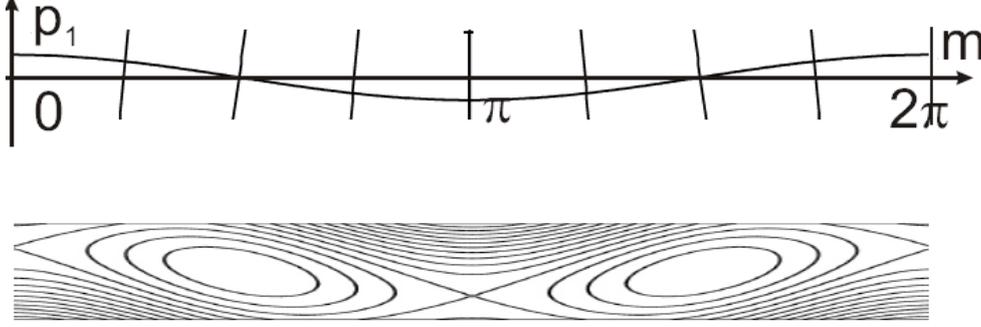$$\cos p = -\beta \cos m; \ \beta = \frac{a}{2c} = \frac{1}{7} \tag{12}$$

Fig.2. Local normal coordinates (curve close to a sinusoid and rectilinear) and relief of a bottom of a valley. The scales on axis are identical.

Accounting values of a and c we have $|\cos p| \leq \beta \ll 1$. So condition $p \simeq \pi/2 + \pi j \simeq const$ is satisfied at any 'valley's' bottom. For b and c evaluation gives $b/c = 3/35 \ll 1$. Other small terms contain $\alpha = a^2/4c^2 \ll 1$. Relation (12) allows rewrite terms containing variable p through m. So the final form of the system (9) of differential equations can be written as:

$$8cm'' - \dot{m} + 8(b - 4\alpha c)\sin 2m = 0$$
$$\ddot{p}_1 + 16cp_1 + 8cp_1'' = 8\{\pm a \cos m - m'(c + b\cos 2m)\} \tag{13}$$

After the variable transformation we obtain dimension form of equation (c_0 and λ_0 are characteristic velocity and length) which coincides with canonical sin-Gordon equation [13]:

$$\frac{\partial \varphi^2}{\partial x^2} - \frac{1}{c_0^2}\frac{\partial \varphi^2}{\partial t^2} = \frac{1}{\lambda_0^2}\sin\varphi; \ \ \varphi = 2m - \pi$$
$$\lambda_0^2 = \frac{cR_0^2}{2(b - 4\alpha c)}; c_0^2 = 8c\omega_0^2 R_0^2 \tag{14}$$

3. THE CHAIN DYNAMICS IN THE MIDDLE ENERGY INTERVAL.

Equation (14) has two big classes of stationary solutions $\varphi(\theta)$, $\theta = x - x_0 - Vt$ which move with velocity V [13]. 1) spacelike $1 - V^2/c_0^2 > 0$; 2) timelike $1 - V^2/c_0^2 < 0$. They are related to the magnetic (spacelike) or electric (timelike) states in a Josephson contact (or the spacelike or timelike intervals in the relativity theory).

For the spacelike solutions the equation (14) has integral of motion E; and for the timelike solutions these equations have another integral of motion B:

$$(1 - \frac{V^2}{c_0^2})(\varphi')^2 = \frac{2}{\lambda_0^2}(E - \cos\varphi) \ ; \ E \geq -1 \tag{15}$$

$$(\frac{V^2}{c_0^2} - 1)(\varphi')^2 = \frac{2}{\lambda_0^2}(B + \cos\varphi) \ ; \ B \geq -1 \tag{16}$$

The integral B in (16) has meaning of mechanical energy of a reversible pendulum with length $l=1$, φ has meaning of angle of vertical deflection of a pendulum rode. At $-1 < B < 1$ the pendulum oscillates near equilibrium position $\varphi = 0$. At $B>1$ the pendulum rotates around the suspending point, the rotation direction is topological invariant $\sigma = \pm 1$. The same is true for the integral of motion E. The only difference is equilibrium position $E = -1$ at $\varphi = \pi$. At $-1 < E < 1$ the pendulum executes an oscillating movement near equilibrium position.

3.1 The spacelike solutions $(V<c_0)$

At $|E|<1$ stationary solution of (14) describes space oscillations near equilibrium position:

$$m(\theta) = \frac{\pi}{2} + \sin^{-1}[dn(\xi_v, k)] \; ; \; \xi_v = \frac{\theta}{\lambda_0 \sqrt{1 - V^2 / c_0^2}} \; ; \; \theta = x - Vt \tag{17}$$

Here $dn^{(\xi_v, k)}$ is Jakobi elliptic function with elliptic module k which is defined by relation $k^2 = (E+1)/2; \; 0 \le k \le 1$. In the limit case $k \to 0$ the periodic function transforms into small oscillations. In the limit case $k \to 1$ the periodic function transforms into solitary peak.

At $E=1$ stationary solution (14) describes domain wall between two domains (2):

$$m(\theta) = \frac{\pi}{2} + 2\arctan[\sigma \exp \xi_v] \tag{18}$$

3.2 The timelike solutions $(V>c_0)$

At $|B|<1$ continual equation of motion (14) due integral (16) has periodic stationary solution which corresponds to time oscillations near equilibrium position:

$$m(\theta) = \frac{\pi}{2} + \cos^{-1}[dn(\xi_v, k)] \; ; \; \xi_v = \frac{\theta}{\lambda_0 \sqrt{V^2 / c_0^2 - 1}} \tag{19}$$

Here elliptic module k is defined by relation $k^2 = (B+1)/2; \; 0 \le k \le 1$. In the limit $k \to 0$ one has small oscillations. In the limit $k \to 1$ one has periodic peaks.

At $B=1$ stationary solution describes domain wall between time domains:

$$m(\theta) = 2\arctan[\exp \sigma \xi_v] \tag{20}$$
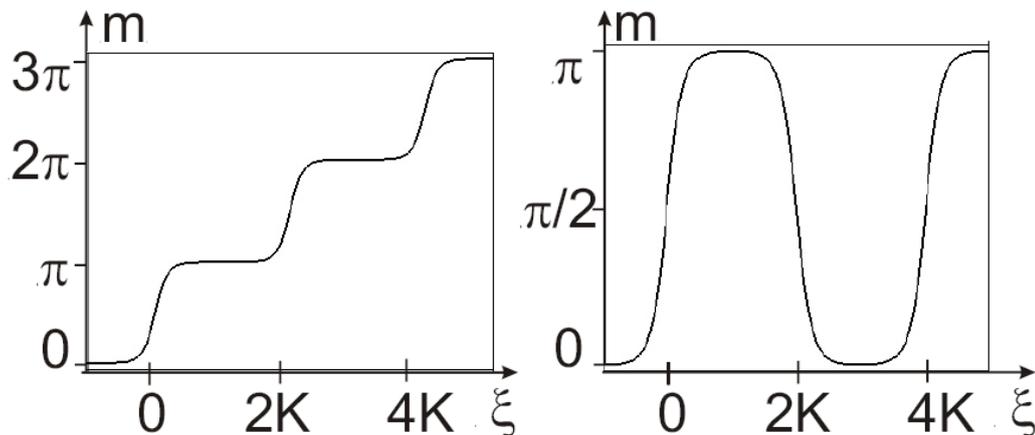

Fig.3. Angles of the molecules orientation in the chain for the timelike solutions (right) according (19) at |B|<1 (oscillations) and (left) according (20) at B>1 (rotation, $\sigma = +1$). Periodic structures at k=0.99 i.e. B=0.996 and B=1.004.

In dependence on topological charge $\sigma = \pm 1$ this solution give kink ($\sigma = +1$, $m(-\infty) = 0$, $m(+\infty) = \pi$) or antikink ($\sigma = -1$, $m(-\infty) = \pi$, $m(+\infty) = 0$) shown in Fig.3.

At $B>1$ continual equation of motion also has periodic stationary solution (time rotation). The solution can be written in following forms:

$$m(x) = \frac{\pi}{2} + \sin^{-1}[\sigma\, sn(\xi_v, k)] \; ; \;\; \xi_v = \frac{\theta}{k\lambda_0\sqrt{V^2/c_0^2 - 1}} \tag{21}$$

Here $sn(\xi_v, k)$ is Jakobi elliptic function with elliptic module k defined by relation $k^2 = 2/(B+1)$; $0 \le k \le 1$. In the limit $k \to 0$ one has homogeneous rotation of the molecules in the chain. In the limit $k \to 1$ the periodic set of kinks (20) arises as in Fig.3.

CONCLUSIONS

The nonlinear excitations of the molecular chain with quadrupolar interaction are considered in the energy range covering the point of the orientational melt. We derive the dynamic continuum equations for the two-sublattice chain with arbitrary nonlinearity and small dispersion. The symmetry of the system of the equations and its integral are found. We used previously found a strong anisotropy of molecular rotation on the angles plane, the 'valley' of the effective potential. To integrate the equations on the plane the trial trajectory (orbit) was introduced, it coincides with the bottom of the valley. Construction of the normal curvilinear coordinates on the plane makes it possible to uncouple the equations for linear and nonlinear vibrations. Linear oscillations are perpendicular to the valley and meet more rigid subsystem. Nonlinear oscillations are along the valley and correspond to a soft subsystem, so unstable state is easily achieved. For the nonlinear subsystem the sine-Gordon equation is derived, one allows to describe the vibration modes around the equilibrium position in the ordered phase and the transition states. Scope of applicability of the description extends from the point of equilibrium to the vicinity of the upper saddle point, i.e. within the valley effective potential (phases I and II in Figure 1). This range of energies in the order of magnitude larger than the region of existence of orientationally ordered phase. To date, dynamical models of molecular chains described only states with small or large energies [1].

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