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Stability, Bifurcation and Transitions of the Nonlinear Molecular Chain In Electric Field

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Abstract

The rotational dynamics of molecular adsorbed chain in longitudinal electric field is studied theoretically. The nonlinear dynamic equations are obtained with accounting of quadrupolar interactions between molecules. A new dimensionless parameter (relation of electric and intermolecular interactions) is introduced in the system of the dynamical equations. It is shown that topology of the energy relief on the angle space is transformed in dependence on the electric intensity. The rotational reordering in electric field is complex phenomenon that have several stages. One of the intermediate states is an indifferent equilibrium net (orientation melting). The stable state is found in strong electric fields.

Keywords
molecular chain oscillation, electric field, topology reconstruction

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Introduction

Low dimensional systems are very important both for modeling and for applications. Real objects can be adsorbed structures [1] or crystals with low-dimensional motives. Studying chains is a necessary stage of investigation of dynamics and thermodynamics of more complex systems: crystals [2], nonlinear dynamics of atomic and molecular lattices [3]. A chain model is used for description of linear lattice dynamics and thermodynamics of molecular cryocrystals [4]. Complexity of models even for 1D molecular chain requires some approximation to be used in order to simplify the system description. Such approximations are model potential and 1D rotation in nonlinear consideration [1,4]. The small oscillations [5] and nonlinear large amplitude ones with topological transitions [6,7] were considered in 1D molecular chain with quadrupolar interaction. In 2D molecular layers with quadruple interaction the orientation small vibrations [8] and nonlinear rotational dynamics [9] were considered. We found the linear oscillation spectrum; the effective potential relief and its topology are reconstructed in dependence on the anisotropy parameter of adsorbed lattice.

In the present work we study the topological reconstruction in the nonlinear molecular chain under an external electric field presence. We introduce the energy of the molecular chain in the electric field and derive corresponding dynamical equations. We find that the stationary solutions have new features and the topology of the effective potential of the system has bifurcation points and transitions in dependence on electric field value.

1. Derivation of dynamic equations for the molecular chain in electric field

We consider linear molecules which consist of two or three atoms (N_2, CO_2, H_2). They cannot have intrinsic electric dipole moment as sequence of symmetry; a quadrupolar moment is the lowest electric one. The molecules can have induced electric dipole moment only: $d_{ind} = \alpha_{\parallel} E_{\parallel} + \alpha_{\perp} E_{\perp}$; $E_{\parallel} = E \cos\phi$; $E_{\perp} = E \sin\phi$. Here $\alpha_{\parallel}$ and $\alpha_{\perp}$ are longitudinal (along molecule axis) and transverse electric polarizability, $E_{\parallel}$ and $E_{\perp}$ are longitudinal and transverse components of electric field intensity, ϕ is angle between the molecular axis and vector ***E***. Potential energy of an induced dipole is $-\vec{E}\vec{d}_{ind}/2$. Substitution of the vectors components yields after simple transformation the potential energy of a molecule in external electric field. For situation when adsorbed molecules could rotate in the plane of substrate only [1], they have only one degree of freedom. Translational degrees of freedom are frozen by substrate. In these suppositions, which were considered in details in articles [5-7], and accounting the electric field contribution, the potential energy of molecules rotational interaction in the chain can be written as:

$$\begin{aligned}
&U_{chE} = \Gamma\{a_0 N + \sum_{i=1}^{N}[-\varkappa_{0i} - 2\varkappa_i \cos 2\phi_i + a(\cos 2\phi_i + \cos 2\phi_{i+1}) + \\
&b\cos 2(\phi_i - \phi_{i+1}) + c\cos 2(\phi_i + \phi_{i+1})]\}) \qquad (1)\\
&\Gamma = 3Q^2/4R^5;\ a_0 = 3/4;\ a = 5/4;\ b = 3/8;\ c = 35/8
\end{aligned}$$

Here new dimensionless parameters of the system related to electric field effect arise:

$$\varkappa_{0i} = \frac{E_i^2}{4\Gamma}(\alpha_{\parallel} + \alpha_{\perp});\ \ \varkappa_i = \frac{E_i^2}{8\Gamma}(\alpha_{\parallel} - \alpha_{\perp}) \qquad (2)$$

They describe isotropic and anisotropic contributions respectively. Each parameter gives relation of a molecule potential energy in electric field and in the chain molecular field. ϕ_i is an angle between the principal axis of corresponding molecule and direction of radius-vector that connects centers of inertia of the molecules in sites *i* and *i*+1, the electric field intensity is oriented along the chain. Rest parameters describe quadrupolar contributions: *Q* is a quadrupolar moment of a molecule, ***R*** is a distance between molecules. Potential energy (1) is obtained in supposition of the nearest neighbors interact only. Without electric field only three symmetric ordering can be constructed [5,6], they provide minimum of the chain potential energy.

Minimum of the energy is reached for the molecules' alternating ordering in the chain that defines even (odd) sites. Stability of this structure was confirmed by small oscillation and their normal coordinates investigation [5] and plotting of the effective potential relief for long wave excitations [5-7].

Lagrangian of the system is *L=K-U* where *U* and $K = \frac{1}{2}\sum J_i\dot{\phi}_i^2$ are potential and kinetic energies of a molecule with moment of inertia J_i=J_0 and angle velocity $\dot{\phi}_i$. Then system of equations for chain motion in electric field is obtained. Let us remember that minimum of the energy without presence of electric field is reached for the molecules' alternating ordering even ϕ and odd ψ. We suppose keeping of the dividing onto two sublattices in an external field. Then these motion equations can be written for two sublattices in the long-wave limit for arbitrary amplitudes and nonlinearity. All even or odd sites are equivalent and the differential-difference sets of equations are transformed into a system of differential equations. The dimensionless time is introduced by relation $t \to \tau = t\omega_0$ where $\omega_0^2 = \Gamma/J_0$. Further analysis will be more convenient with the following change of variables:

$$\begin{cases} m = \phi - \psi; \\ p = \phi + \psi \end{cases} \qquad (3)$$

The system of equations can be rewritten in new more convenient variables:

$$\begin{cases} \ddot{p} - 2\{4(a - \varkappa)\sin p\cos m + 4c\sin 2p\} = 0; \\ \ddot{m} - 2\{4(a - \varkappa)\sin m\cos p + 4b\sin 2m\} = 0. \end{cases} \qquad (4)$$

Integral of the rotational motion of the molecular chain can be obtained: W_{ef}=W_k+W_p. It includes "kinetic" W_k and "potential" W_p contributions:

$$\begin{cases} W_k = \frac{1}{2}(\dot{p}^2 + \dot{m}^2); \\ W_p = 4[2(a - \varkappa)\cos p \cos m + b\cos 2m + c\cos 2p]. \end{cases} \tag{5}$$

Potential relief for W_p over the space of angles is shown on fig. 1. High density of energetic equidistant counters corresponds to high gradient. The fine structure of valley or low energy region is shown as a function of coordinates *m* and *p*. In the right panel the isoenergetic counters are boundaries of the following regions. 1) Region of finite oscillations near equilibrium state. 2) Low separatrix separates regions of finite and infinite motion (rotation). 3) Region of finite variation of p and infinite variation of m variables. Analysis of linear oscillations with arbitrary dispersion [5,6] demonstrates strong relief dependence on wave number however for not large *k* topological properties of the relief remain.

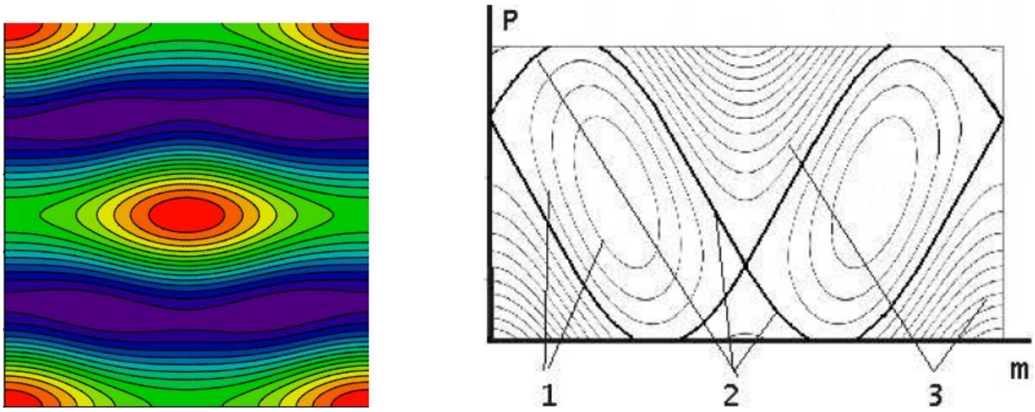

Figure 1. The chain without influence of electric field: *E*=0, $\varkappa = 0$. Left panel. The potential relief W_p (5) as a counter plot without presence of electric field. Variable m changes in range $[-\pi; +\pi]$. Right panel. Detail view of valley $p \simeq -\pi/2$. See details in text.

2. Positions and Energies of Stationary Points

The stationary points of the equations can be determined by conditions $\dot{m} = 0$ and $\dot{p} = 0$. Then the set of equations (1) can be rewritten in the following form:

$$\begin{cases} \sin p\ [(a - \varkappa)\cos m + 2c\cos p] = 0; \\ \sin m[(a - \varkappa)\cos p + 2b\cos m] = 0 \end{cases} \tag{6}$$

Let us rename the factors in the system (6). Then we transform the system to the following form:

$$\begin{cases} ef = 0; \\ gh = 0. \end{cases} \tag{7}$$

Strings in eqs (6,7) coincide, the second factors *f, h* are corresponding square brackets and the first factors *e, g* are corresponding sine functions. Solutions of equations (6) satisfy to several simpler systems.

1) The first of them is *f=0; h=0*. It yields solutions

$$m_{1-1,2} = \pm\pi/2 + 2\pi j; p_{1-1,2} = \pm\pi/2 + 2\pi n \tag{8}$$

that deliver minimum of the chain energy and coincides with equations without electric field $\varkappa = 0$ [5].

2) The second simple system is *f=0; g=0,* it has solutions

$$\begin{cases} p_{2-1} = \pm\arccos(-\dfrac{a-\varkappa}{2c}) + 2\pi n; \;\; m_{2-1} = 2\pi j; \\ p_{2-2} = \pm\arccos(+\dfrac{a-\varkappa}{2c}) + 2\pi n; \;\; m_{2-2} = \pi + 2\pi j. \end{cases} \tag{9}$$

The last stationary points correspond to low saddle ones without electric field [5]. Dependence on electric field arises.

3) The third simple system is *e=0; g=0*. This system has two kinds of solutions. The first kind of solutions coincide with condition E=0 and correspond to the higher saddle points without electric field [5]. The second kind of solutions corresponds to peaks of the effective potential without electric field.

$$\begin{cases} m_{3-1} = \pi + 2\pi j; \;\; p_{3-1} = 2\pi n \\ m_{3-2} = 2\pi j; \qquad p_{3-2} = \pi + 2\pi n \end{cases} \tag{10}$$

4) The forth simple system of equations is *e=0; h=0*. It has no solution without presence of electric field [5-7] with accounting relation between coefficients *a* and *b* in the interaction. Electric field can change relation between parameters and deliver a new solution to the system of equations

$$\begin{cases} m_{4-1} = \pm\arccos(-\dfrac{a-\varkappa}{2b}); \;\; p_{4-1} = 2\pi j \\ m_{4-2} = \pm\arccos(+\dfrac{a-\varkappa}{2b}); \;\; p_{4-2} = \pi + 2\pi j \end{cases} \tag{11}$$

Therefore, complete set of the special points for the system of equation (6) or more convenient one (7) could be obtained from the solutions of the simpler systems pointed above. Without electric fields the potential relief W_p over the space of angles is shown on fig.1 following to [5-7]. Existence of only one motion integral means that the system is not integrable. Nevertheless, it is possible to obtain qualitative consequences about its behavior. Several intervals of energy with qualitatively different character of motion can be pointed out [5]. We can find the effective potential (5) in the stationary points (8-11) and then analyze topology evolution in dependence on electric field.

1) The first simple system solutions give the following value of the effective potential (5) of the molecular chain:

$$W_1 = W_p(m_1, p_1) = 4[2(a-\varkappa)\cos p \cos m + b\cos 2m + c\cos 2p] \tag{12}$$

These solutions correspond to minimums of the effective potential on fig.1.

2) The second simple system delivers the effective potential value:

$$\begin{cases} W_{2-1} = 4[-\dfrac{(a-\varkappa)^2}{2c} + b - c] \\ W_{2-2} = 4[-\dfrac{3(a-\varkappa)^2}{4c} + b - c] \end{cases} \tag{13}$$

The lower separatrix (curve of the type 2 on fig.1) coincides with energy of the low saddle point W_{SL}.

3) The third simple system has two types of solutions. The first solution corresponds to the higher saddle points (higher separatrix with energy W_{SH}) of the effective potential without electric fields. The second solution corresponds to the top points of the effective potential without electric fields.

$$\begin{cases} W_{3-1} = 4[-2(a-\varkappa)+b+c] \\ W_{3-2} = 4[+2(a-\varkappa)+b+c] \end{cases} \tag{14}$$

4) The forth simple system has two solutions (11) which give the following value of the effective potential (5) of the molecular chain:

$$\begin{cases} W_{4-1} = 4[-\dfrac{(a-\varkappa)^2}{2b} - b + c] \\ W_{4-2} = 4[-\dfrac{3(a-\varkappa)^2}{4b} - b + c] \end{cases} \tag{15}$$

At the first glance we can note some features of the stationary point's behavior in dependence on electric field parameter $\varkappa$ which is defined in (2). The first stationary points m_1, p_1 and theirs energy do not depend on electric field. The second and forth sets of stationary points m_2, p_2 and m_4, p_4 positions and theirs energies both depend on electric field. The third stationary points m_3, p_3 positions do not depend on electric field nevertheless theirs energies depend on one.

Therefore, the system of equation which describes the molecular chain rotational dynamic, evolution of all stationary points comes by unique way in dependence on electric field intensity. Further investigation will consider this evolution and changes of phases in the chain.

3. Transitions of the stationary points in electric field and topology transformation

The special points of the effective potential can have the same energy. The equality of the different special point energies $W_m=W_n$ defines the critical value of electric field parameter: κ_{cm-n}. This value corresponds to critical change in the system topology.

Let us range all the critical electric field parameters from minimal to maximal values. These critical values are defined by the following relations

$$\begin{cases} 1)\varkappa_{cc1} = \varkappa_{c4-1} = a - 2b = 0.5; \\ 2)\varkappa_{cc2} = \varkappa_{c1min} = \varkappa_{c3} = \varkappa_{c4mid} = a = 1.25; \\ 3)\varkappa_{cc3} = \varkappa_{c3-24} = \varkappa_{c4-2} = a + 2b = 2; \\ 4)\varkappa_{cc4} = \varkappa_{c1-2} = a + 2\sqrt{bc} = 3.812; \\ 5)\varkappa_{cc5} = \varkappa_{c3-21} = +a + b + c = 6; \\ 6)\varkappa_{cc6} = \varkappa_{c2} = \varkappa_{3-22} = a + 2c = 10. \end{cases} \tag{16}$$

Now we plot the graphic presentation of the special points of the effective potential. First of all the third type stationary points do not change their positions, however their energies (14) change considerably. As the result the third type stationary points take part in the most bifurcation points (16). We can conclude again that, with electric field increasing, the third type stationary points of two kinds change their energies in opposite directions. Namely, the former higher saddle points of the effective potential increase their energy, and the former top points decrease one. This stationary point's energy decreases with electric field increasing. The new forth type stationary points of two kinds give them know at $\kappa=0.5$ (higher saddle points splitting) and $\kappa=2$ (peaks joint into new higher saddle points).

At field $\kappa=1.25$ two kinds of the third type stationary points change their types: the former higher saddle points are transformed into new top points of the effective potential, and the former top

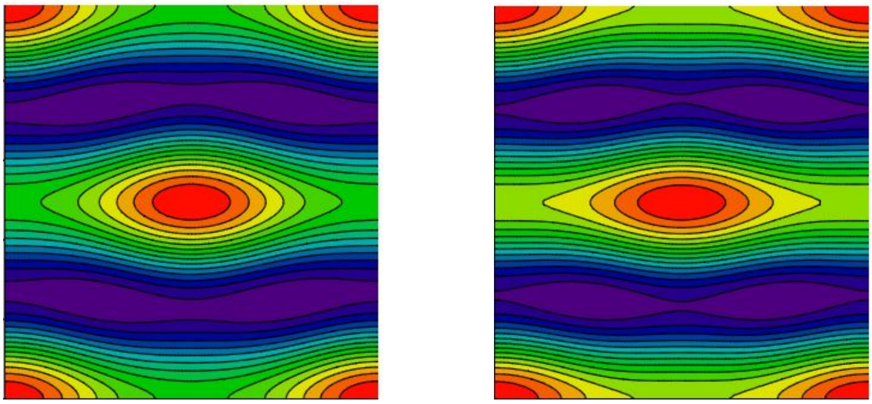

Figure 2. Left panel. The initial topology of the potential relief under: E=0, κ=0.
Right panel. The higher saddle points are splitting. New peaks are ready to arise. E>0, κ=0.5.

points are transformed into new higher saddle points. At fields κ=1.25 the effective potentials go in opposite direction very far and have different signs. The evolution of the high energy region in electric fields is shown on Fig. 3.

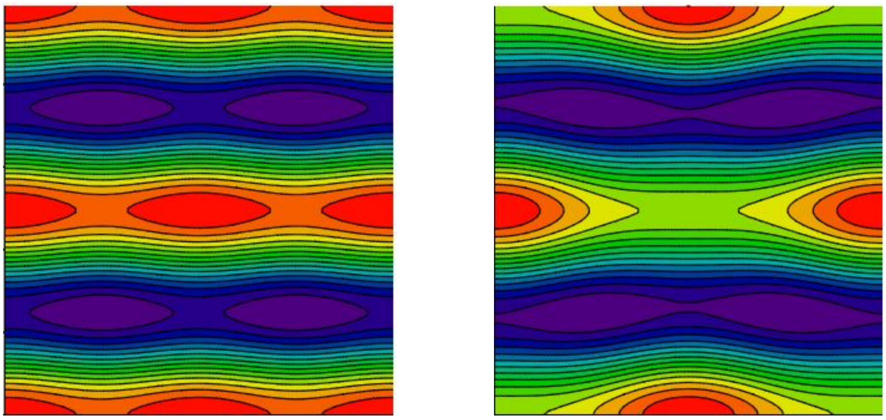

Figure 3. Left panel. New and old peaks are equal: E>0, κ =1.25.
Right panel. The old peaks transform into new higher saddle points. E>0, κ= 2.0.

The first type stationary point energy can be reached. Coordinates of the both stationary points are stable. Especially interesting fact is that these values of energy are reached simultaneously by the formerly lowest and highest points of the effective potential relief (without electric fields). It means that as the bottom of 'valley' as the high energy region are reconstructed qualitatively in the electric field.

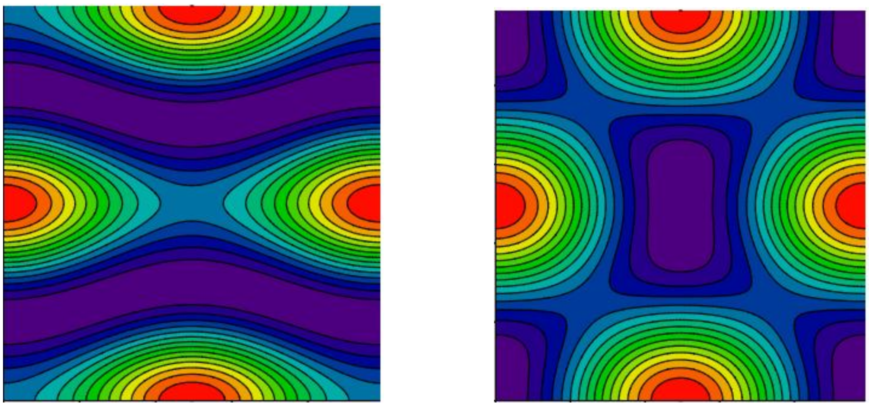

Figure 4. Left panel. The old top points and minima transform into new saddle points: E>0, κ =6.0.
Right panel. The old top points transform into new minima. κ= 10.0.

Conclusions

The dynamical analysis of long-wave motion of the molecular chain leads to conclusion that the reordering process has complex picture. The topological analysis of the effective potential shows that under influence of temperature disordering comes in several steps [5-7] and four qualitatively different dynamic phases exist. Without electric field (fig. 1), the first phase corresponds to oscillations near equilibrium alternatively ordered state. The second one corresponds to low-energy rotational excitations along 'valleys' (easy directions of the effective potential) that do not destroy strong correlation between molecules but a structural data show rotational disorder (melting). The third one corresponds to energies that are enough to produce travel between the 'valleys' and some 'islands' in the angle space are forbidden due to the correlations.

Accounting presence of external electric field equations of the molecules' motion are derived and integral of motion is obtained in the long-wave limit. Depending on the external electric field value the topology of the effective intermolecular potential is transformed in several steps (figs. 2-4). Initially the most stable alternative ordering (figs. 1, 2) of the molecules in the chain is finally transformed into the linear ordering in strong electric field (fig. 4). Rebuilding of the initial order goes firstly under high energy values and could be corresponded to the fourth phase change (fig. 2). The topology of the low energy states changes under higher electric field values (figs 3,4). Initially the valleys change their shape and the saddle points height (fig. 3). Then we have rotate disorder state with an indifferent equilibrium (fig. 4, left panel) and new equilibrium state (fig. 4, right panel). The initial peak point is transformed into the saddle point and then into the energy minimum. The initial minima points are transformed into the indifferent equilibrium lines and then into the low saddle points. The initial higher saddle point splits in two ones and move into initial maxima positions, their initial position become final maxima. The initial lower saddle point splits in two ones and move into initial minima positions, their initial positions joint and become final minima.

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