

NONLINEAR ROTOR DYNAMICS OF 2D MOLECULAR ARRAY: TOPOLOGY RECONSTRUCTION

V.A. Lykah¹ and E.S. Syrkin^{2*}

¹National Technic University "Kharkov Polytechnic Institute", 61002, Kharkov, Ukraine

²B. Verkin Institute for Low Temperature Physics and Engineering NAN, 61103, Kharkov, Ukraine

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Molecular layers with rotational degrees of freedom and quadrupolar interaction between linear molecules are investigated theoretically. We found earlier that alternative orientation of the molecules along and perpendicular to an axis of the rectangular lattice is preferable. Here we find the integral of motion and give the topology analysis of the possible dynamical phases and special points in the long-wave limit. We find the strong anisotropy in the angle space: directions of easy excitation ("valleys") exist. We show the potential relief reconstruction in dependence on the adsorbed lattice anisotropy.

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1. INTRODUCTION

Low dimensional systems are objects of a great interest either as models or as description of real objects. 1D and 2D models are a necessary stage of investigation of dynamics and thermodynamics of more complex systems: crystals, atomic and molecular lattices [1–3]. 1D chain models are applied to the description of linear lattice dynamics and thermodynamics of molecular cryocrystals [4, 5] (that can be generalized into 3D systems [4, 6]) in order to investigate nonlinear dynamics [7] and thermoconductivity [8]. Real objects where 1D and 2D models can be applied to are adsorbed structures [9] or crystals with low-dimensional motives. Some approximations are necessary to simplify system's description because of the complexity of models even for 1D molecular chain. For linear models such approximations are a force matrix (harmonic expansion near equilibrium position) instead of parameters of interaction between molecules, and given parallel ordering of molecules [4–6]. In nonlinear consideration such approximations are a model potential and 1D rotation [7–9]. In articles [10, 11] the equilibrium state, oscillation spectrum and density of states were found for 1D and 2D molecular array with quadrupolar interaction.

In this paper we use approximations of one degree of freedom for every molecule as in [7–9] and very stiff translation potential as in [7, 8], so translation vibrations can be neglected. In this model for 1D [10] and 2D [11] adsorbed molecular systems, the structures with alternative orientation ordering are stable and are observed experimentally [9]. The article is constructed as follows. In the second section the potential energy is derived for the orientation interaction of the molecules placed in a rectangular lattice on

an adsorbing plane and rotated in this plane. In the third section the dynamic equations of the molecular orientation oscillations are developed. In conclusion we consider the whole picture of oscillations.

2. ENERGIES AND EQUATIONS OF MOTION

In this paper we consider nonlinear rotational dynamics of molecular 2D layer with realistic quadrupolar interaction between two linear molecules [4].

There are another several contributions to the interaction between the molecules. These contributions have the same structure of terms [4] but their coefficients depend on the distance between molecules and molecules' parameters. Therefore, the model with quadrupolar interaction between the molecules is the simplest one but it reflects the most essential features of real interactions and classical dynamics of the linear adsorbed molecules.

Let us consider the most realistic situation when the adsorbed molecules rotate in the plane of the substrate. Then the potential energy of the orientational part of interaction between the molecules in the 2D layer should be written [11]. Several symmetric orderings that can provide minimum of the orientation potential energy in the adsorbed molecular layer with rectangular lattice were considered in the work [11]. The absolute minimum of the potential energy is reached for the alternative ordering of the molecules for both directions in the layer:

$$\begin{aligned} \phi_{2n,2m} = 0; \phi_{2n,2m+1} = \pi/2; \phi_{2n+1,2m} = \pi/2; \\ \text{or } \phi_{2n,2m} = \pi/2; \phi_{2n,2m+1} = 0; \phi_{2n+1,2m} = 0. \end{aligned} \quad (1)$$

It means that each molecule has the nearest neighbors that are oriented perpendicularly to it. Stability of this structure was confirmed by investigation of small

*Corresponding author E-mail address: syrkin@ilt.kharkov.ua

oscillations [11]. It is important that these structures are observed in the experiments [9].

Let us consider oscillations of the adsorbed molecular layer. Lagrangian of the system is $L = K - U$ where U and $K = \frac{1}{2} \sum J_{i,j} \dot{\phi}_{i,j}^2$ are the total potential and kinetic energies that are obtained as the sum of the energies for the $\{i, j\}$ -th molecule with the moment of inertia $J_{i,j} = J_0$ and angle velocity $\dot{\phi}_{i,j}$. Then the system of Lagrange equations of the motion is [11]:

$$\begin{aligned} J_0 \ddot{\phi}_{i,j} = & 2\Gamma \{ a \sin 2\phi_{i,j} \\ & + b[\sin 2(\phi_{i,j} - \phi_{i+1,j}) + \sin 2(\phi_{i,j} - \phi_{i-1,j})] \\ & + c[\sin 2(\phi_{i,j} + \phi_{i+1,j}) + \sin 2(\phi_{i,j} + \phi_{i-1,j})] \} \\ & + 2\Gamma \rho^{-5} \{ -a \sin 2\phi_{i,j} \\ & + b[\sin 2(\phi_{i,j} - \phi_{i,j+1}) + \sin 2(\phi_{i,j} - \phi_{i,j-1})] \\ & + c[\sin 2(\phi_{i,j} + \phi_{i,j+1}) + \sin 2(\phi_{i,j} + \phi_{i,j-1})] \}. \end{aligned} \quad (2)$$

Here $\phi_{i,j}$ is the angle between the molecular axis in the site i, j and axis Ox of rectangular lattice of the molecules. The parameters of the interaction are:

$$\Gamma = \frac{3Q^2}{4R_{0a}^5}; \quad a_0 = \frac{3}{4}; \quad a = \frac{5}{4}; \quad b = \frac{3}{8}; \quad c = \frac{35}{8}; \quad \rho = \frac{R_{0b}}{R_{0a}} \quad (3)$$

where Q is the quadrupolar moment of a molecule, ρ is the parameter of anisotropy, the lattice constants are R_{0a} and R_{0b} . Condition $\rho \geq 1$ is applied only to meet the requirement of crystallography where inequality $R_{0b} \geq R_{0a}$ is generally used.

The obtained system of equations (2) is nonlinear and differential-difference. It is naturally to begin its investigation starting with the linear approximation for 1D [10] and for 2D rectangular [11] lattices. Long-wave limit for arbitrary amplitudes and nonlinearity for 1D case was investigated in [12]. We will consider the long-wave limit for the 2D rectangular lattice.

Let us rewrite equations (2) for two sublattices. They are caused by separating the molecules into two subsystems in equilibrium state for even ($\phi_{2m,2n}$) and odd ($\psi_{2m\pm 1,2n}$ or $\psi_{2m,2n\pm 1}$) sites. Then the sites of the same type are equivalent and the set of equations can be transformed into a system of differential equations. Then we introduce more convenient variables

$$m = \phi - \psi; \quad p = \phi + \psi \quad (4)$$

and dimensionless time $t \rightarrow \tau = t\omega_0$; $\omega_0^2 = \Gamma/J_0$. Then the system of the equations can be written as

$$\begin{aligned} \ddot{p} - 8 \{ (1 - \frac{1}{\rho^5}) a \cos m \sin p + (1 + \frac{1}{\rho^5}) c \sin 2p \} &= 0; \\ \ddot{m} - 8 \{ (1 - \frac{1}{\rho^5}) a \cos p \sin m + (1 + \frac{1}{\rho^5}) b \sin 2m \} &= 0. \end{aligned} \quad (5)$$

3. TOPOLOGY. SPECIAL POINTS

Very important information about dynamics of the system can be obtained from the special (stationary or fixed) points of the equations that are determined

by conditions $\dot{\psi} = 0, \ddot{\psi} = 0$ and $\dot{\phi} = 0, \ddot{\phi} = 0$. Then the set of equations (5) can be rewritten as:

$$\begin{aligned} \sin p [a(1 - \frac{1}{\rho^5}) \cos m + 2c(1 + \frac{1}{\rho^5}) \cos p] &= 0; \\ \sin m [a(1 - \frac{1}{\rho^5}) \cos p + 2b(1 + \frac{1}{\rho^5}) \cos m] &= 0, \end{aligned} \quad (6)$$

Solutions of equations (6) can be obtained by solving several simple systems. The first simple system is

$$\cos m = 0; \quad \cos p = 0. \quad (7)$$

Its solution $m_1 = \pi/2 + \pi j$; $p_1 = \pi/2 + \pi n$ coincides with conditions (1) of energy minimum of the molecular array. It coincides with the chain case.

The second simple system is

$$\begin{aligned} a(1 - \frac{1}{\rho^5}) \cos m + 2c(1 + \frac{1}{\rho^5}) \cos p &= 0; \\ \sin m = 0. \end{aligned} \quad (8)$$

It yields solutions

$$m_2 = \pi j; \quad p_2 = \arccos(\pm \frac{a(\rho^5 - 1)}{2c(\rho^5 + 1)}); \quad (9)$$

where sign + is for $j = 2n + 1$ and sign - is for $j = 2n$. As we can see below these stationary points correspond to low saddle points. As the system approaches a square lattice of the molecules ($\rho \rightarrow 1$) the deviation from the values $p = \pi/2 + \pi j$ vanishes.

The third simple system of equations is

$$\sin p = 0; \quad \sin m = 0. \quad (10)$$

Its solutions are $m_3 = \pi j$; $p_3 = \pi n$. When $j + n = 0, \pm 2, \pm 4, \dots$ the solutions correspond to peaks of the effective potential. The solutions of the type $j + n = 2i + 1$ correspond to the high saddle points. These solutions coincide for 1D and 2D lattices.

The fourth simple system of equations

$$\begin{aligned} \sin p = 0; \\ a(1 - \frac{1}{\rho^5}) \cos p + 2b(1 + \frac{1}{\rho^5}) \cos m = 0; \end{aligned} \quad (11)$$

has solutions

$$p_4 = \pi j; \quad m_4 = \arccos(\pm \frac{a(\rho^5 - 1)}{2b(\rho^5 + 1)}). \quad (12)$$

The system (11) is not satisfied for the chain ($\rho \rightarrow \infty$) because of $|\cos m_4| = a/2b > 1$. The rectangular lattice yields new solutions at condition $|\cos m| \leq 1$ or

$$\begin{aligned} \rho_{bs} \leq \rho \leq \rho_{bg}; \\ \rho_{bs}^5 = \frac{a - 2b}{a + 2b} = \frac{1}{4}; \quad \rho_{bg}^5 = \frac{a + 2b}{a - 2b} = 4. \end{aligned} \quad (13)$$

The rectangular array of the molecules has solutions on condition $|\cos m| = 1$, which coincide with (10). It means that at conditions $\rho = \rho_{bg}$ or $\rho = \rho_{bs}$ the peaks and the high saddle points of the effective potential change their behavior.

Therefore all special points of the system of equations could be obtained from the solutions of the more simple systems. This is the complete set of the special points of the system.

4. INTEGRAL OF MOTION AND PHASES

We obtain integral of the rotational motion of the molecular array: $W_{ef} = W_k + W_p$. It includes “kinetic” W_k and “potential” W_p contributions:

$$W_k = \frac{1}{2}(\dot{m}^2 + \dot{p}^2);$$

$$W_p(m, p) = 4\left\{\left(1 - \frac{1}{\rho^5}\right)2a \cos m \cos p + \left(1 + \frac{1}{\rho^5}\right)[b \cos 2m + c \cos 2p]\right\}. \quad (14)$$

Potential relief for W_p over the space of angles is shown in Fig. 1. Analysis of linear oscillations with arbitrary dispersion [10, 11] has demonstrated strong dependence of the relief on dispersion (wave number) but for not large k the relief do not change strongly. Existence of only one motion integral means that the system is not integrable, nevertheless it is possible to obtain some qualitative consequences about its behavior. Motion of a molecular chain and rectangular array is stochastic in space of angles because of complex potential [13]. An excitation energy is determined by temperature or by diffracting particles (electrons, neutrons etc.) in structure experiments. We can point out several intervals of energy with qualitatively different character of motion of the molecules (dynamical phases) that can be related to different structural phases.

1) The phase I ($W_{min} \leq W_{ef} < W_{SL}$) is a region of finite rotating oscillations of the molecules near equilibrium positions m_1, p_1 (7):

$$W_{min} = W_p(m_1, p_1) = -4\left(1 + \frac{1}{\rho^5}\right)(b + c). \quad (15)$$

They are ellipses' centers at valley bottoms in Fig. 1a – e. The molecular configuration is shown in Fig. 1f. A structural data show the rotational arrangement. High boundary of this region is energy of lower separatrix W_{SL} .

2) $W_{ef} \simeq W_{SL}$ is a narrow region of motion with energy of the low separatrix that coincides with energy of the low saddle points m_2, p_2 in points (8):

$$W_{SL} = 4\left\{-\frac{a^2(\rho^5 - 1)^2}{2c(\rho^5 + 1)\rho^5} + \left(1 + \frac{1}{\rho^5}\right)(b - c)\right\}; \quad (16)$$

The low separatrix separates a finite and infinite motion (rotation) of the molecules in the chain or 2D array. All thermodynamic characteristics have a peculiarity because of high density of states [1] and the order-disorder phase transition at this energy.

3) The phase II ($W_{SL} < W_{ef} < W_{SH}$) is a region of finite variation of p and infinite variation of m between the lower separatrix W_{SL} and higher separatrix W_{SH} . A low-energy excitations along $p \simeq \pi/2 + \pi j$ ('valleys' on the potential) exist for the chain or 2D array. Excitations along 'valleys' do not destroy strong correlation between rotating molecules so that $p \simeq \pi/2 + \pi j$ along j -th 'valleys'. The molecular motion is limited in the angle space by the higher separatrix curves. Structural data for this phase show rotational disorder (melting).

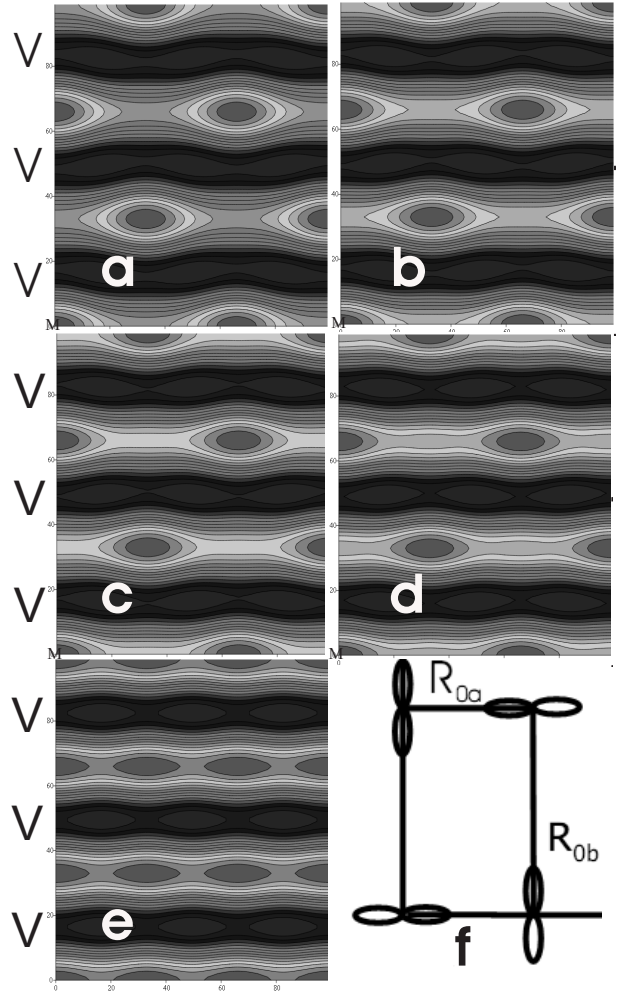


Fig. 1. The effective potential W_p (14) relief (normalized height) as a contour plot function of coordinates $m = \phi - \psi$ (horizontal) and $p = \phi + \psi$ (vertical). Variables change in range $[0; +3\pi]$. High density of equidistant contours corresponds to high gradient. The letter V points out 'valley' of W_p . The parameter of the lattice anisotropy takes values $\rho^5 = 10; 4; 3; 2; 1$ at a – e panels. Panel f shows elementary cell of the lattice

4) $W_{ef} \simeq W_{SH}$ is a narrow region of motion with energy of high separatrix that coincides with energy of higher saddle point $m_3 = \pi j, p_3 = \pi n$ at $j + n = 2i + 1$ (10):

$$W_{SH} = 4\left\{-\left(1 - \frac{1}{\rho^5}\right)2a + \left(1 + \frac{1}{\rho^5}\right)[b + c]\right\}. \quad (17)$$

The high separatrix separates a finite and infinite motion (rotation) over p coordinate. All thermodynamic characteristics have a peculiarity at this energy.

5) The phase III ($W_{SH} < W_{ef} < W_T$) is a region of infinite variation of p and m coordinates but some regions (islands) of angles near the peaks of the effective potential W_T are forbidden. At these energies the transitions between 'valleys' are possible when the system passes above the high separatrix.

6) $W_{ef} \simeq W_T$ is narrow region of motion with mean energy near the tops $m_3 = \pi j, p_3 = \pi n$ at

$j + n = 2i$ of the effective potential (10):

$$W_T = 4\left\{\left(1 - \frac{1}{\rho^5}\right)2a + \left(1 + \frac{1}{\rho^5}\right)[b + c]\right\}. \quad (18)$$

At this energy all thermodynamic characteristics usually have a peculiarity because of high density of states. The system undergoes the phase transition into completely disordered phase.

7) The phase IV ($W_T \leq W_{ef}$) corresponds to completely disordered phase.

All these stationary points and corresponding energy intervals give qualitatively the same behaviour for the chain and 2D array of the adsorbed molecules. In the chain case ($\rho \rightarrow \infty$), the fine structures of the valleys, top and saddle points as well as corresponding molecules' orderings are shown in figures in [12].

5. THE TOPOLOGY RECONSTRUCTION

Significant changes in the topology appear due to the extreme points connected with solutions p_4, m_4 (12) of the fourth simple system (11). These solutions exist at $\rho_{bs} \leq \rho \leq \rho_{bg}$ (13) and give two kinds of the new saddle points with energy

$$W_N = W_p(p_4; m_4) = 4\left\{-\frac{a^2(\rho^5 - 1)^2}{2b(\rho^5 + 1)\rho^5} + \left(1 + \frac{1}{\rho^5}\right)[-b + c]\right\}. \quad (19)$$

When parameter ρ decreases, these solutions arise at $\rho = \rho_{bg}$ and the new saddle points coincide with the old saddle points (17)

$$W_N = W_{SH} = 4\frac{-6ab + 2ac}{a + 2b}.$$

As ρ decreases, pairs of new saddle points split around a position ($m = -\pi j, p = \pi$) ($m = \pi, p = \pi$), ($m = 0, p = \pi$). The old saddle points turn out into peaks meanwhile the old peaks keep their positions and role. At $\rho = \rho_{bs}$ either positions or energies of the new saddle points coincide with the old top points values. Further system evolution goes with the old peaks and saddle points that keep their positions but change their functions. In the limit case $\rho = 1$ the old and the new local peaks have equal height $W_{Np} = W_T$. The new saddle points come to the middle position between the old and the new peaks.

To describe these changes of the system graphically, we find the effective potential cross-sections along the lines of the peaks and higher saddle points $p = 0; \pi$. One of them is shown in top panel in Fig. 2.

The first equation in the second simple system (8) is also the equation of the valley bottom. So one can exclude the variable p . The cross-sections along the valley bottom of the effective potential (14)

$$W_p(m) = 4\left\{-\frac{a^2(\rho^5 - 1)^2}{2c(\rho^5 + 1)\rho^5} \cos^2 m + \left(1 + \frac{1}{\rho^5}\right)[b \cos 2m - c]\right\} \quad (20)$$

are shown in bottom panel in Fig. 2. We can see that the bottom part of the effective potential changes only quantitatively.

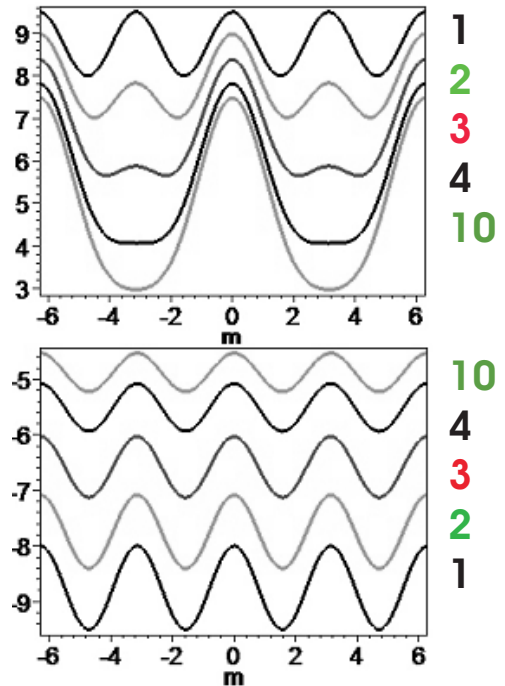


Fig. 2. Potential relief W_p (14) cross-sections at different values of lattice anisotropy parameter ρ (the same values ρ^5 as in Fig. 1 are denoted at right edge of each panel). Top panel shows cross-section along top and high saddle points of the potential. Bottom panel shows cross-section along bottom of the valley

6. CONCLUSIONS

We considered the molecular adsorbed layer of linear molecules with quadrupolar interaction. The molecules have only one rotational degree of freedom in the plane of adsorbing surface. In this model, the alternative ordering of the molecules along and perpendicular to the axes of the rectangular unit cell is most stable. This structure has two physically different sites per unit cell (two different molecules' orientation) and doubled lattice constants. The theoretically found equilibrium state coincides with experimentally observed structures. Equations of motion are derived in long-wave limit. Their motion integral has been obtained. The topological analysis of the system gives the following results.

In the bottom the topology of the effective potential completely coincides with the case of the molecular chain. The difference between 1D and 2D molecular structures consists in the dependence on the ratio of the lattice constants in 2D case. The square molecular lattice has the most stable equilibrium structure (wide interval of the phase I in bottom at Fig. 2). As the ratio of the lattice constants is growing the spectrum is softening and the chain limit comes quickly.

The top part of the effective potential considerably changes its topology at $\rho^5 = 4$, as ratio of the lattice constants goes to 1 starting from the chain case ($\rho \gg 1$). The square molecular lattice has i) the most drastic changes of the topology, ii) the most wide energy interval of the phase II and the most narrow interval of the phase III (see top panel in Fig. 2).

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НЕЛИНЕЙНАЯ РОТАЦИОННАЯ ДИНАМИКА 2D МАССИВА МОЛЕКУЛ: РЕКОНСТРУКЦИЯ ТОПОЛОГИИ

В.А. Лыках, Е.С. Сыркин

Теоретически исследованы молекулярные слои с вращательными степенями свободы и квадрупольным взаимодействием между линейными молекулами. Мы нашли ранее, что предпочтительным является альтернативное упорядочение молекул с ориентацией вдоль и перпендикулярно оси прямоугольной решетки. Выведены уравнения движения, найден их интеграл и проведен топологический анализ возможных динамических фаз и особых точек в длинноволновом пределе. Показана сильная анизотропия в плоскости углов: существуют направления легкого возбуждения ("долины"). Мы показываем реконструкции потенциального рельефа в зависимости от анизотропии адсорбированной решетки.

НЕЛІНІЙНА РОТАЦІЙНА ДИНАМІКА 2D МАСИВУ МОЛЕКУЛ: РЕКОНСТРУКЦІЯ ТОПОЛОГІЇ

В.О. Луках, Є.С. Сиркін

Теоретично досліджені молекулярні шари з обертальними ступенями свободи і квадрупольною взаємодією між лінійними молекулами. Ми знайшли раніше, що кращим є альтернативне впорядкування молекул з орієнтацією вздовж і перпендикулярно осі прямокутної ґратки. Виведено рівняння руху, знайдено їх інтеграл і проведено топологічний аналіз можливих динамічних фаз і особливих точок для довгохвильової межі. Показано сильну анизотропію в площині кутів: існують напрями легкого збудження ("долини"). Ми показуємо реконструкцію потенційного рельєфу в залежності від анизотропії адсорбованої решітки.