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Discrete model of transition between order and static chaos in peptides and polymers

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In Memory of Professor Henryk Zorski

Biological function of a peptide or properties of a polymer material depend on chemical composition of a macromolecule and on its geometry. A mechanistic model is considered to investigate the factors changing a geometrically ordered macromolecule into a geometrically chaotic one, assuming no chemical change. $2D$ and $3D$ examples show how a small change in interaction between parts of a macromolecule can transform an ordered geometry of the (bio) polymer into a chaotic one. It is mathematically interesting that the systems obey the difference equations, which in the continuum limit lead to differential equations with well-behaving (non-chaotic) solutions, while in certain cases behavior of the difference equations seems to be chaotic.

1. Introduction

Biological function of a peptide depends not only on its chemical composition but also on the geometrical order of the macromolecule. The equilibrium state of peptides' and polymers' macromolecules may be either ordered or chaotic. During the last few years there has been a growing interest in mechanical models of biological macromolecules. The models investigate changes of the shapes molecules and the influence of the shape on the biological properties of the molecules [1–6]. Prof. Henryk Zorski was interested in this type of models and played an active role in developing some of them [7, 8].

Similar to the biological function of a peptide, properties of polymer materials can change drastically with geometry of the macromolecule. For example, a foil obtained from a polymer in such way that all the macromolecules are ordered, may have different mechanical and/or optical properties than a material obtained from the same polymer, but with random geometry of the macromolecules. Conductivity of conducting polymers may drastically change or even be lost if their macromolecules are not properly ordered.

In this paper a simple model of a macromolecule is investigated [5, 8]. The macromolecule is assumed to consist of a large number of identical rigid rods representing the monomers, with elastic joints between them. The set of difference equations, which describe the configuration of the system, is relatively simple thanks to the simplicity of the model; in $2D$ it formally resembles the standard system known from the chaos theory. Natural variables for the difference equations are angles, under which rods are connected in the coordinate space and differences of the consecutive angles. Apparently this model already has sufficient complexity to recreate transition from an ordered to a chaotic structure. Discrete nature is crucial for the systems behavior: a continuum limit of the difference equations leads to differential equations with well-behaving (non-chaotic) solutions. The difference equations contain a parameter reflecting strength of the interaction between monomers. This parameter is a scalar in $2D$ and a two-component vector in $3D$. The strength of interaction can sometimes be changed without change in chemical structure of the macromolecules by a solvent. Equilibrium state of a macromolecule changes from an ordered geometry, observed for small values of the parameter, to a chaotic geometry for the values that are sufficiently large. It means that for very small values of the parameter there are no initial conditions for which system would be chaotic. When the value is growing, there appear small areas of initial conditions in the phase space of the system for which the solutions are chaotic. These areas grow with growing value of the parameter; for sufficiently large value of the parameter all of the solutions are chaotic. Results of several numerical simulations of $2D$ and $3D$ systems are presented, showing how a small change in interaction between parts of a molecule and/or in initial conditions of the system, can transform a geometrically ordered peptide or polymer into a chaotic one. In some cases, a system is ordered if it is considered on the $2D$ plane, but if it is considered in a $3D$ space, it shows chaotic behavior on the other plane.

The solutions discussed in this work are cases of static chaos; the parameter in all the simulations is a varying length of a peptide or polymer chain rather than time. Computer simulations were performed to investigate behavior of the macromolecule. Interaction between monomers is described by the parameter K in the $2D$ case, and by a pair of parameters

$$K = \{K_1, K_2\} \tag{1.1}$$

in the $3D$ case. The interaction depends on the monomers' characteristics, but it is modified by the presence of external potentials such as interaction with solvent molecules, electromagnetic field, etc. Generally, equilibrium state of the macromolecule changes from ordered geometry for small values of K to a chaotic geometry for K sufficiently large. The equilibrium problem is described in terms

of angle(s) between the consecutive rods. In the case of a molecule in the plane ($2D$) there is one angle for each pair of rods. In case of a molecule in $3D$ space there are two angles for each pair of rods. The natural variables for the difference equations describing the equilibrium positions of the molecule are the angles themselves and the differences of consecutive angles. This choice of variables imposes obvious periodicity conditions. The variables give parameterization of the space, which can be named a phase space of the system when a continuous time is the independent variable. The equations written in terms of these variables resemble or, in some special cases, are the same as the standard system. The standard system is known for its chaotic behavior when the values of the parameter $K$are above a certain threshold value. There is an important physical difference between the standard system and its counterparts for the problem of equilibrium configuration. Namely, the discrete independent variable n in case of the standard system is discrete time, while in case of the molecule equilibrium it is the number of the consecutive rod.

It is expected that in $2D$ as well as in the $3D$ case, there are significant areas of chaotic behavior in the system. The $2D$ case was treated earlier [5, 8] and really chaotic behaviors were found in numerical simulations, resembling the known results for a standard model. The $3D$ case leads to a system of equations, a part of which can be represented in the way equivalent to the $2D$ case. These equations can be solved independently of the remaining ones, and show the chaotic behaviors just the same as in a $2D$ case. The remaining variables satisfy a system of equations, which, in addition to looking similar to the $2D$ case, has a factor that couples it to the above system of equations. As a result, the behavior of the former system influences the behavior of the second one. When first system is in its regular, non-chaotic behavior, the second one may be either regular or chaotic, depending on the value of its coupling parameter K_2. On the other hand, chaotic behavior of the first system forces the second one, by the coupling, to be always chaotic too. One can expect that regular (non-chaotic) behavior of the former system will not enforce chaos on the latter system, but it can show such a chaotic behavior by itself. However, if the former system shows a chaotic behavior, this always pumps chaos into the latter system as well. These heuristic considerations were supported by results of simulations shown below in a series of examples of possible equilibrium configurations in the two projection planes of the phase space.

2. Methodology

When a set of discrete equations describing a particular physical system is developed, it is then investigated numerically. Variables in these equations

are all angles or derivatives of angles – this is why dynamical planes that are investigated are compactified. These variables change cyclically from $(-\pi)$ to $(-\pi)$. The same analytical characteristics of the system are of course present when dynamical plane is investigated without compactification, so it is a matter of choice of the graphical representation, which type of dynamical plane, compact or not, the system of equations is numerically investigated on.

The independent, discrete parameter in the systems is the segment number. The parameter is running along the macromolecule. The macromolecule is much longer than an individual unit; this is why it is assumed to be infinite, just to simplify the consideration. Numerical simulations cannot, from their very nature, be run to infinity. The simulations presented here were always performed sufficiently long to make sure that there were no changes in the visual representation of the results even if the simulation was performed for one order of magnitude or two orders of magnitude longer (except of course for the misleading impression that the area becomes completely covered if individual points or lines are represented graphically in large size).

The geometrical configuration of the macromolecule in equilibrium is investigated. The problem is static. Nevertheless, the equations have formal similarity to dynamical equations. The only difference is in what is an independent, running parameter. The parameter is running along the length of the molecule instead along the time of evolution in a typical dynamical system. This difference is important in physical interpretation only. No matter what is the physical interpretation of the running parameter and the dependent variables, and no matter what symbols are assigned to these variables, the mathematical nature of the equations and their solutions do not change. This is why the systems of equations considered in this paper are investigated in the same mathematical/numerical way as the dynamical systems of equations, with which they are formally identical. The same criteria of numerical investigations of the solution are taken into account in numerical distinguishing between the ordered and chaotic solution, as it would be in consideration of a mathematically identical system of dynamical equations.

3. 2D problem: rigid rods with elastic joints

Consideration starts from the simplest possible model. The model consists of an infinite chain of identical rigid rods of length l connected by identical joints. Movement in each joint is parameterized by two angles, θ and ϕ. In this section it is assumed that joints have freedom of movement in θ only, this is why the obtained model is 2D. It will be generalized into $3D$ in the next section. It leads to an assumption for the interaction moments at the n-th joint

The state-of-equilibrium conditions are derived from the $2D$ problem as follows. The assumption for the interaction moments at the joints is:

$$M^{(n)} = -\partial/\partial\theta^{(n)} \left(\frac{1}{2} \Phi_o \left(\theta^{(n)} - \theta^{(n-1)} \right)^2 \right) = -\Phi_o \left(\theta^{(n)} - \theta^{(n-1)} \right).$$

The moment equation at equilibrium has the form:

$$M^{(n+1)} - M^{(n)} + F^{(o)} l \sin\theta^{(n)} = 0 \tag{3.1}$$

i.e.

$$\Delta^2 \theta^{(n)} - K \sin\theta^{(n)} = 0, \tag{3.2}$$

$$K = F^{(o)} l / \Phi_o,$$

where Δ^2 is the second difference. It is a discrete operator, analogous to the second derivative in the differential calculus.

Denoting $\theta^{(n)} = x_n$, $\theta^{(n+1)} - \theta^{(n)} = y_n$, $x_n \in [0, 2\pi)$, $y_n \in [-\pi, \pi)$, we have

$$x_{n+1} = x_n + y_n,$$

$$y_{n+1} = y_n + K \sin x_{n+1},$$

i.e. the standard system. Hence, for sufficiently large K the system of rods exhibits the deterministic chaos. It is interesting to observe that the continuum limit of (3.2) as $l \to 0$ is the pendulum equation

$$\theta'' - K/l^2 \sin\theta = 0$$

known also as the sine-Gordon equation, which is well known and does not exhibit any chaos.

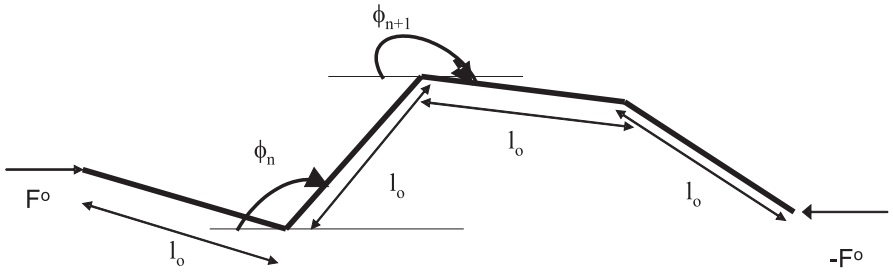

FIG. 1. Scheme of a part of chain in the $2D$ case.

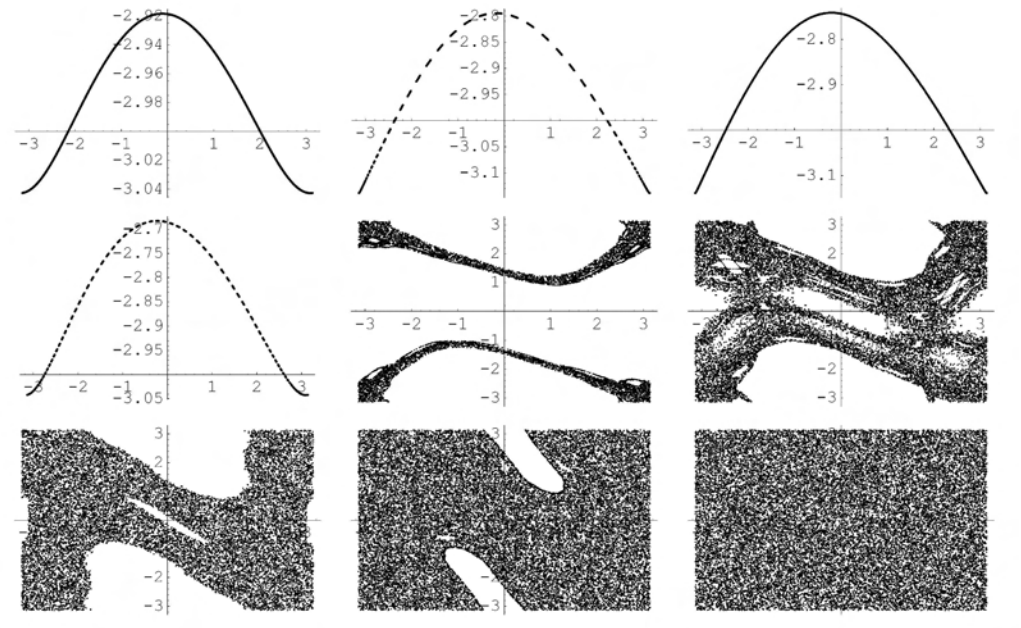

FIG. 2. Numerical solutions of the $2D$ case with parameter k in the consecutive images equal to 0.1, 0.3, 0.4, 0.5, 0.9, 1.3, 2.0, 4.0, 10.0. With growth of the parameter value, the solution changes from deterministic to chaotic, with well visible islands, to a solution plane completely and randomly covered.

4. 3D problem; rigid rods with elastic joints

The condition of the equilibrium for the moments gives:

$$M^{(n+1)} - M^{(n)} + F^{(o)} \times l^{(n)} = 0.$$

Assuming without any loss of generality

$$F^{(o)} = F^{(o)}(1, 0, 0)$$

and setting

$$l^{(n)} = l\left(\cos\theta^{(n)} \sin\phi^{(n)}, \sin\theta^{(n)} \sin\phi^{(n)}, \cos\phi^{(n)}\right),$$

we have

$$M_1^{(n+1)} - M_1^{(n)} = 0,$$

$$M_2^{(n+1)} - M_2^{(n)} - F^{(o)} l \cos\phi^{(n)} = 0,$$

$$M_3^{(n+1)} - M_3^{(n)} + F^{(o)} l \sin\theta^{(n)} \sin\phi^{(n)} = 0.$$

Constitutive assumptions: the two moments depend on angles assigned to the appropriate joints:

$$M_2^{(n)} = \alpha\, \Phi_o(\phi^{(n)} - \phi^{(n-1)}),$$

$$M_3^{(n)} = \beta\, \Phi_o(\theta^{(n)} - \theta^{(n-1)}).$$

In a 3D case, K is a pair of parameters, Eq. (1.1), where

$$K_1 = F^{(o)} l/(\alpha\, \Phi_o) \quad \text{and} \quad K_2 = F^{(o)} l/(\beta\, \Phi_o).$$

Denoting $\Psi^{(n)} = \phi^{(n)} + \pi/2$ we obtain:

$$\Delta^2 \Psi^{(n)} - K_1 \sin \Psi^{(n)} = 0,$$

$$\Delta^2 \theta^{(n)} - K_2 \sin \theta^{(n)} \cos \Psi^{(n)} = 0.$$

The second pair of equations, i.e. the second plane equations of the $3D$ system, is weakly coupled to the first one, which, on the other hand, is completely identical to the $2D$ system considered above. Numerical solutions of the $3D$ system are presented below. In a case of an ordered solution in the first plane, (which is always an equivalent to one of the ordered $2D$ solutions) both ordered and chaotic solutions are always observed in the second plane. The character of these solutions depends on the value of the parameter K_2. On the other hand, in cases when the solution on the first plane is chaotic, only chaotic solutions can be observed on the second plane, independent of the value of the parameter K_2.

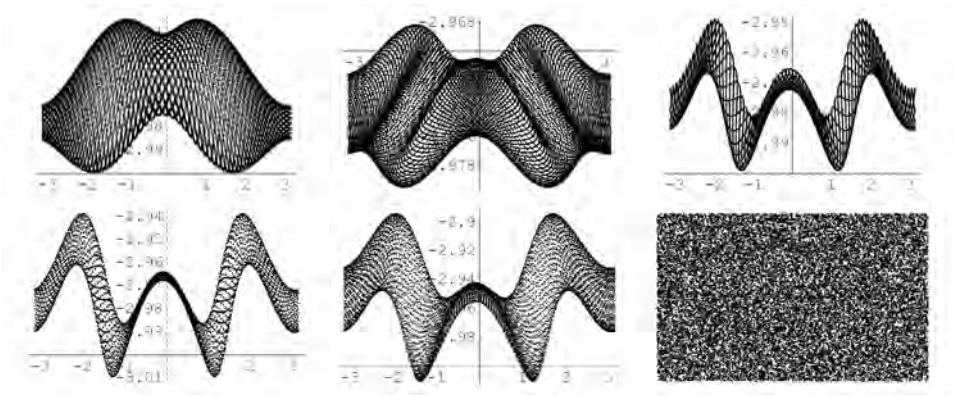

FIG. 3. $3D$ – second plane for parameter $K_1 = 0.1$-ordered solution. The second parameter K_2 is equal: 0.001, 0.0099, 0.01, 0.015, 0.02, 4. Solutions for lower value of K_2, present a clear ordered pattern, while for the ones of high value of K_2, character of the solutions changes visibly.

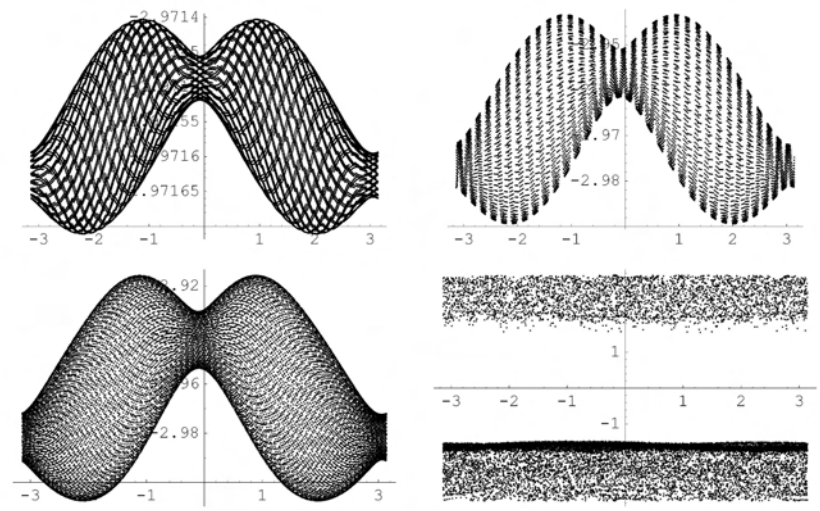

Fig. 4. $3D$- second plane for parameter $K_1 = 0.3$ – ordered solution in the first plane. The second parameter K_2 is equal: 0.0001, 0.015, 0.03, 0.1. Solutions for lower value of K_2 present a clear pattern, while for the ones of high value of K_2, the character of the solutions changes into what looks as chaotic solutions.

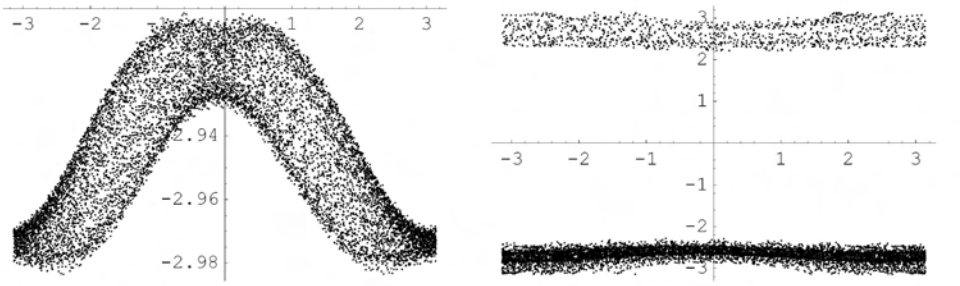

Fig. 5. $3D$- second plane for parameter $K_1 = 0.4$ – ordered solution in the first plane. The second parameter K_2 is equal: 0.01 and 0.05. Character of the solutions is visibly different.

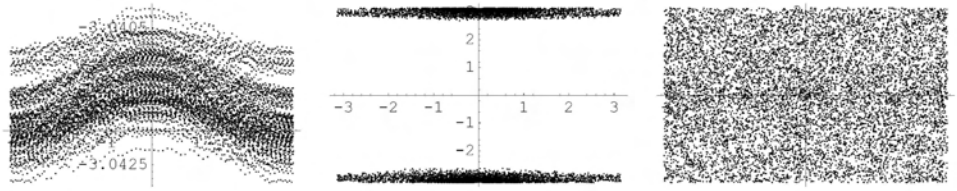

Fig. 6. $3D$ solutions for $K_1 = 1$ – chaotic solution on the first plane the images represent, the second plane for K_2 equal respectively 0.0001, 0.1, and 1. None of the solutions is ordered, and the second plane for K_2 equal 1 is covered randomly, with no visible pattern.

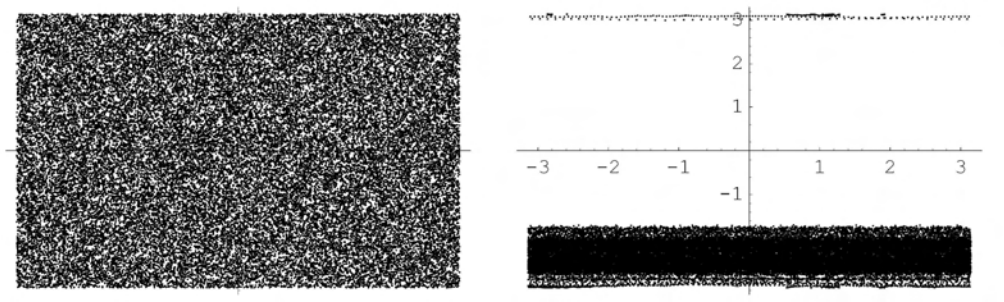

FIG. 7. $3D$ solution, both planes for $K_1 = 10.0$ and $K_2 = 0.0099$. For this value of the parameter K_1, no matter how small is the parameter K_2, the solution would never be ordered.

5. Conclusions

A mechanical model of peptide/polymer macromolecules was considered, aimed at investigating which factors can influence the changes in equilibrium configuration from ordered into chaotic. The reason is that for many macromolecules, both types of equilibrium configurations are observed. The model considered in this paper, an infinite chain of identical rigid rods connected by identical elastic joints, is the simplest one, which recreates changes between the ordered and chaotic equilibrium solutions when the value of the parameter describing interaction between the rods grows. The model was investigated in $2D$ as well as in $3D$. The solutions for different values of the parameter were investigated numerically. It is interesting to mention that the $2D$ set of equations is a discrete version of the well-known sine-Gordon equation, which does not possess any chaotic solutions. Chaotic solutions appear only in a discrete system for such values of the parameter which are sufficiently large. When values of the parameters are sufficiently high, the whole plane of the solution is covered randomly with no structures (islands) observed. It suggests that a discrete structure of a macromolecule, built of rigid mers connected in elastic way, plays an important role in this type of transformation of equilibrium, i.e. energetically preferred, state of a macromolecule. An ordered $2D$ solution, when analyzed in $3D$, has always both the ordered and chaotic solutions in the second plane, in which a pair of equations is weakly coupled to the first pair. It depends on the value of the parameter in the second plane. A chaotic $2D$ solution would always force a solution in the second plane, which is weakly coupled to the first plane, to be chaotic.

The future directions of this research include comparison of these theoretical models with values of the parameter K for real peptides and polymers, as well

as reconstruction of shapes of macromolecules, which correspond to the ordered solutions. There are also some modifications of the equation to be considered, which are equivalent to some modification/complication of the initial model. The majority of them also have both the ordered and chaotic solutions in the discrete/difference version, despite having ordered solutions only in the continuous/differential version of the same equations. It only emphasizes the role of the discrete approach in searching for the chaotic solution.

Acknowledgments

This work was started and the model was proposed by Prof. H. Zorski. He has suggested the main idea and also supervised the work, proposed the equations and discussed the numerical results in the years 1993–95, when the $2D$ model was numerically investigated. He also recognized the solutions as a static chaos. There were also plans for investigation of the $3D$ model, but due to external circumstances this work was put on hold. The sudden death of Prof. H. Zorski finished the collaboration, and this paper is an effort to publish the results as well as show them in a wider perspective, together with the $3D$ numerical solutions which were initially planned.

I would like to thank Dr. T. Lipniacki for his encouragement to finish the work in time for the Conference in memory of Prof. H. Zorski and for interesting discussions.

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