

# Polymer Crystallization as the Self-Organization of Chain Macromolecules

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MD simulation is used to investigate the self-organization exhibited by a chain of atoms with strong interaction between nearest neighbours and weak interaction between more distant atoms. It is shown that the supermolecular structure is formed in several steps: at first, an initially straight chain becomes zigzag-shaped, then the zigzag ribbon folds, producing regions of crystalline and amorphous structure; after that the system contracts into a globe, the amorphous-structure regions transforming into crystalline ones by a reptile like motion. A simple analytical description of such polymer structuring is also given.

## 1. Introduction

Some polymer crystals can be formed by fold packing of linear macromolecules [1, 2]. The existing models of folding are quite convincing in spite of the fact that they are mostly based on indirect experiments and speculative conclusions. Unfortunately, these models cannot answer important questions such as why the folding occurs and why macromolecular self-organization leads to the appearance of crystalline structure. Well-developed traditional methods of theoretical physics are of little use in this case because this many-body problem is nonlinear. Therefore recourse to computer simulation is warranted [3].

The first efforts in this field were made in terms of solid state physics reformulated for polymer physics [3, 4]. However, the shortcoming of this approach is that the initial polymer structure was specified in advance. In our preliminary computer experiments [5] we have tried to avoid this drawback and to receive crystalline structure automatically from a linear anharmonic chain of atoms as a consequence of self-organization. We attempted to understand how interatomic potentials predestine self-organization. In spite of the small number of atoms (40–80), we observed coiling of one and two parallel anharmonic chains which finally crystallized.

In this paper we consider the self-organization of 500 atoms. We also give a simple analytical description of the reasons for polymer structuring.

## 2. Calculation Procedure

In our numerical experiment we investigated the two-dimensional crystallization of chain of 500 atoms strongly interacting by a Morse potential between the nearest neighbours. The pair interaction between more distant atoms in the chain was assumed to be weak by reducing of the depth of the potential well by a factor of 25. The reasons of this choice, discussed at full length in [6, 7] and briefly in [8], consist in the following.

The total macromolecular energy incorporates many terms [9]. The main term is the bond potential (strong interaction); e.g. the energy of a carbon-carbon bond is 2.6 eV [10]. The second term is the bond-angle potential, which is by one order of magnitude smaller in organic molecules [11], molecular crystals [12], and polymers [2, 13]. The energy of all other interactions, including intermolecular interactions [2, 14] is one or two orders of magnitude smaller in the case of organic polymers. Hence the scaling factor of the potential-well depths for all atom pairs which are not nearest neighbours (weak interaction) lies between 1/100 and 1/10 compared to the strong interaction.

It should be emphasized that the precise form of the atom-atom potentials has no pronounced effect on the molecular conformation [12]. Moreover, not only the conformations but also the dynamic properties of polymer systems are insensitive to the anharmonic potentials used; one can take Morse, Mie, Lennard-Jones or Buckingham potentials and receive similar results [3]. This is because the anharmonicity parameters of these potentials do not differ much [15, 16].

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In our previous numerical experiments we have used two-different scaling factors, namely, 1/10 in [17–19] and 1/25 in [4, 5]. We have not found any special features in the dynamical behaviour of the system studied which might be ascribed to the difference in the scaling factors. For this reason we have chosen in this investigation the scaling factor 1/25 for all the weak interactions. Besides, we have chosen one and the same potential curve, namely the Morse potential for all the interactions (strong or weak). Such approach permits to use the minimum number of arbitrary parameters.

In molecular dynamics experiments there is no need to introduce special entropic effects because they originate automatically from the fluctuations of kinetic and potential energy. This problem was investigated thoroughly in our previous works by computer simulations [3, 8, 16, 20–30] as well as analytically [15–17, 20, 31–36]. The magnitude of the entropic factors depends strongly on the strain energy and temperature of a system studied, i.e. on an initial state. In the present work a straight chain was brought to a state of thermodynamic equilibrium at  $T = 10$  K. This means that the initial velocities of atoms are selected at random from the Maxwellian distribution corresponding to a predetermined temperature in such a way that  $E_{\text{kin}}^x = E_{\text{kin}}^y$ . Here,  $E_{\text{kin}}^i$  is the kinetic energy of the atomic motion along the  $i$ -axis.

The equations of motion are integrated numerically by the Nordsieck method to the fifth degree of accuracy. All the calculations are made on an IBM PC AT 386 computer, the computing time was less than 500 min for one evolution history which comprises approximately 1200–1400 periods of atom vibrations. In other respects the calculation procedure is similar to that used previously by Govorov [4].

### 3. Results of Modeling

We present and discuss only one evolution history because other evolution histories were similar.

Figures 1–10 show the evolution dynamics of an initially straight chain of atoms. The temperature of the system is illustrated by Figure 11. The chain begins to coil from the free ends (Figure 1). There appear embryos of a zigzag structure in the uncoiled part of the chain which are distributed randomly (Figure 2). The zigzag regions grow through all the chain whereas the coiled ends rearrange themselves forming a tri-

angular crystal lattice (Figure 3). All the processes considered lead to heating the system until the temperature reaches a maximum (Fig. 11, I). The originally straight chain transforms completely into a zigzag ribbon (Fig. 4). Therefore, the first stage of the evolution may be called “formation of a secondary macromolecular structure”.

Then the temperature begins to drop and during this temperature fall (Fig. 11, II) the zigzag ribbon folds (Figs. 4, 5) creating an amorphous structure in the middle of the former chain (Fig. 6). During this stage the system becomes completely two-dimensional. This means that up to this time, the system can be treated as if it were a set of quasilinear zigzag-ribbon-segments whose interaction may be neglected (see the Discussion). Thereupon, any theoretical consideration of the evolution problem is complicated because it is necessary to deal with the two-dimensional system as a whole [37]. For this reason the second stage may be called “dimensional transformation”.

After that, the system contracts into a two-dimensional cluster and begins to rotate around its centre of gravity (Figure 7), the amorphous part transformed into a crystalline one (Fig. 8) and the temperature decreases very quickly (Fig. 11, III). It should be noted that rotational forces do not influence the folding of the chain, at least in the first and second stages where the system remains quasi one-dimensional. However, these forces can exert some action on the further evolution of the two-dimensional structure formed. Stage III may be called “formation of a supermolecular structure”. Towards the end of this stage the structure becomes completely crystalline but contains many defects.

The following change is connected with ordering of the crystalline structure (Figs. 9, 10) initiated by reptile motion of different parts of the macromolecule in the regions with bad short-range order. During this “ordering stage” the temperature is decreasing very slowly (Fig. 11, IV).

Here we would like to put emphasis on the principal difference between ordinary and polymer crystals. In a two-dimensional ordinary crystal, all the six nearest neighbours are equivalent because the potential relief is one and the same; in a polymer crystal, only two nearest neighbours from the six ones are connected with the atom considered by strong bonds (along the chain) whereas the four other nearest neighbours are connected with this atom by weak interactions. As a

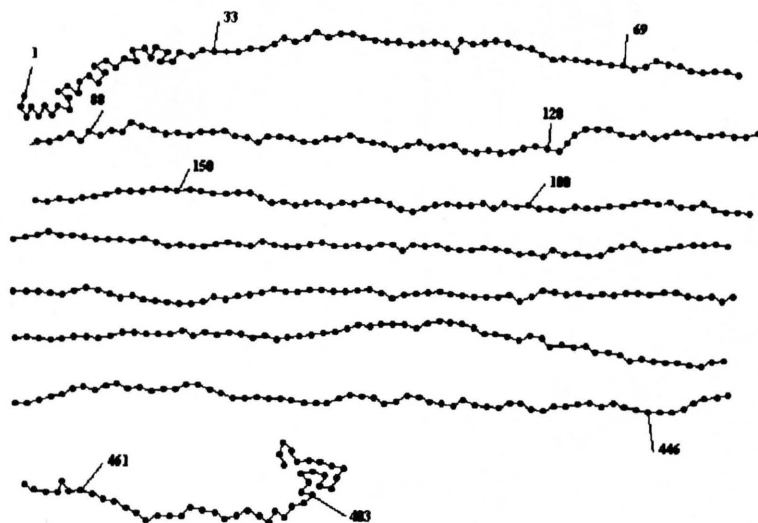


Fig. 1. Coiling begins from the free ends of a chain. Here and in the next figures, the numbers of some atoms are given by numerals for convenience.

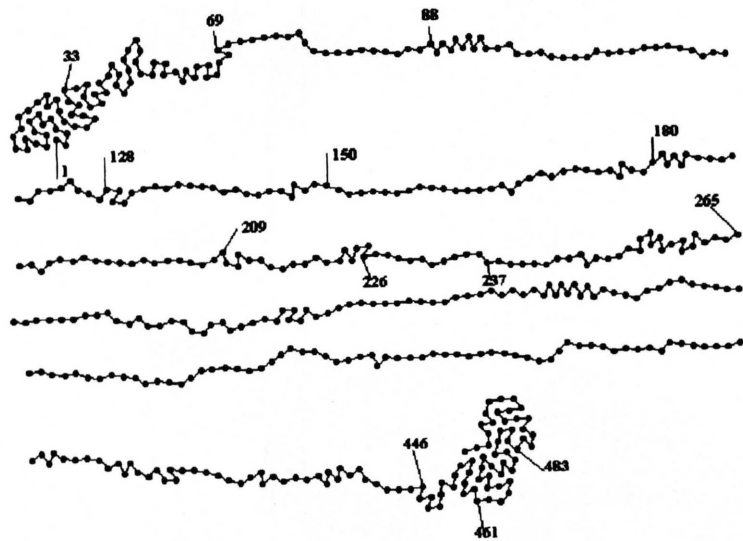


Fig. 2. Appearance of zigzag embryos inside a chain.

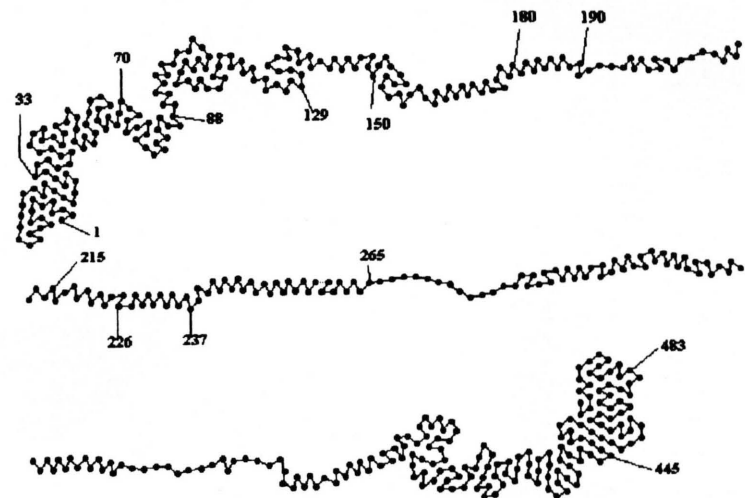


Fig. 3. Growth of zigzag regions and formation of crystalline structure at the ends of chain.

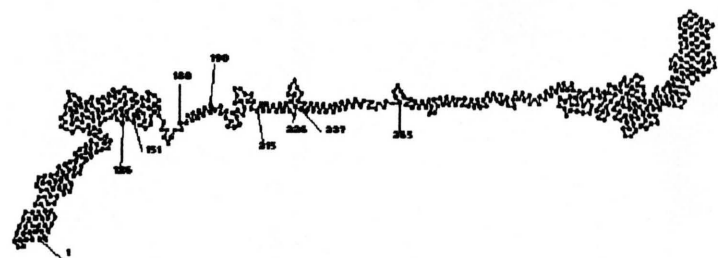


Fig. 4. Folding of zigzag regions. Transformation of the chain into a ribbon is ended.

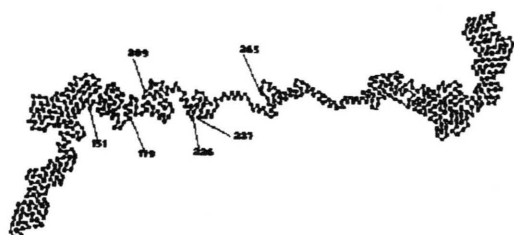


Fig. 5. Ribbon folding continues.

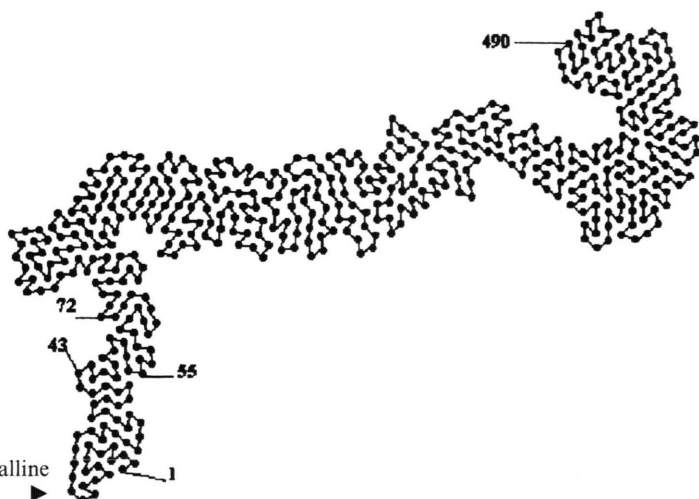


Fig. 6. End of folding. The system consists of two crystalline parts (ends) and one amorphous (middle). ▶

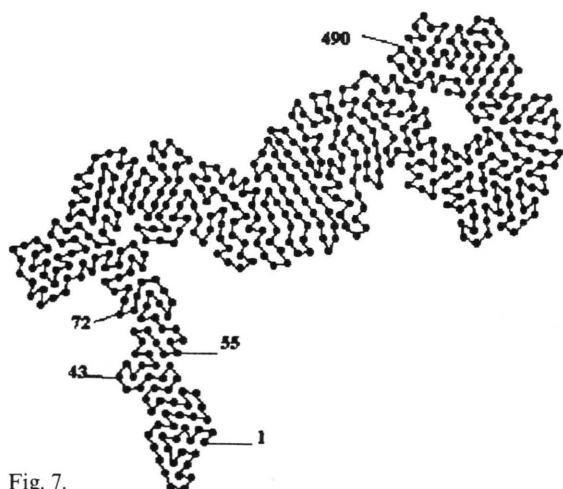


Fig. 7.

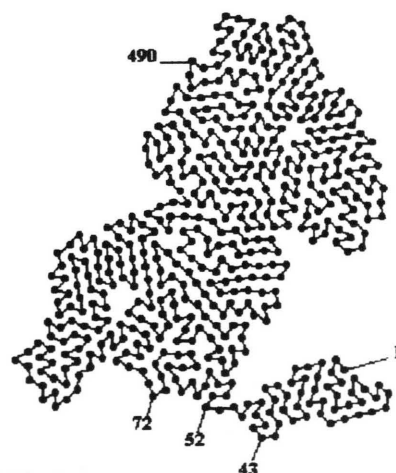


Fig. 8.

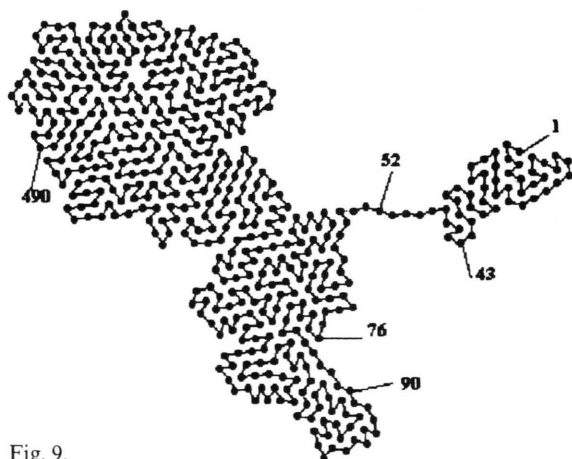


Fig. 9.

Fig. 7. Contraction due to rotation around a gravity centre.

Fig. 8. Transformation of the amorphous middle into a crystalline structure under rotational contraction and tearing off part of the crystalline region.

Fig. 9. Removal of defects from the crystalline phase due to reptile motion.

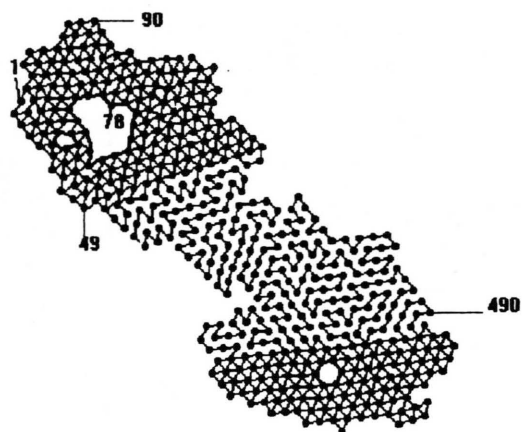


Fig. 10. End of self-organization. The final crystalline structure contains a vacancy (bottom), two dislocations and a void (top). The defects are mainly formed in consequence of the reunification with the torn-off part shown in Fig. 9.

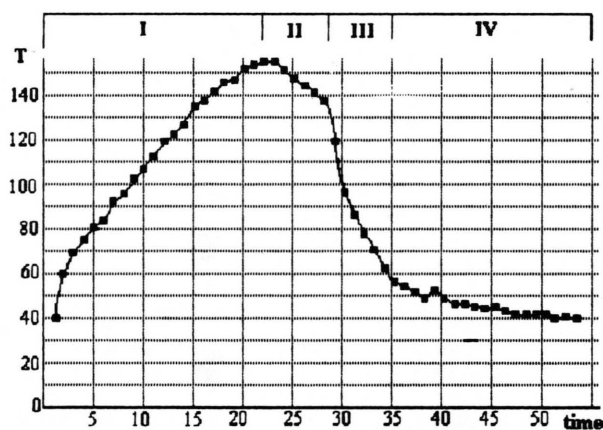


Fig. 11. The four temperature-stages.

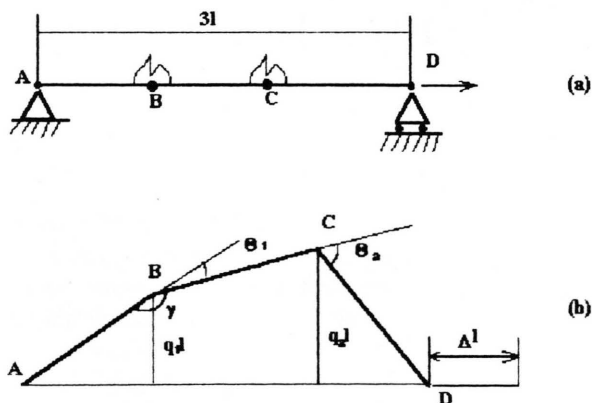


Fig. 12. Elementary cell in the initial state (a) and during the formation of zigzag embryos (b).

result, each atom resides in a strongly anisotropic potential relief, but it is precisely this relief which makes possible the reptile motion.

It should also be remarked that in two-dimensional computer simulation there is no point in introducing special criteria, such as a pair correlation function, structure factor and so on, to distinguish amorphous and crystalline structure because a short-range and/or long-range order can be seen in computer-simulation-snapshots at once. However, in three-dimensional experiments such criteria are needed [7, 38].

#### 4. Discussion

To understand the mechanism of the self-organization, consider the potential energy of the atomic chain during the formation of the secondary macromolecular structure (the first stage of the evolution). For this purpose, divide the chain into the overlapping elementary cells of four atoms (Figure 12a). Let the distance between the boundary atoms of the straight cell be equal to  $3l$ . As the potential well for the nearest neighbours is much deeper than for atoms which are not nearest neighbours, we can assume that our elementary cell consists of three rigid rods of length  $l$  which are hinged together. The left-edge rod can rotate around the fixed point A, the second rod around the first edge, and so forth. The right-and-left-edge rods are bound with the middle rod by hinge springs in the points B and C. Elastic resistance in these points caused by the hinge springs simulates the weak interaction between nonnearest neighbour atoms. This interaction is just the one known in mechanics of crystal lattices as the noncentral interaction of the nearest pairs of atoms [39]. The hinge springs are fully straightened when the rods lie along a straight line between the edges and a definite force is applied in the point D. The straight line configuration can be disturbed under a vertical displacement of any internal atom.

Further we shall follow the approach developed by Thompson [40] who analyzed the instability of a three-links rod under the action of a compressing force. However, we must reformulate Thompson's model for our problem. As the system considered has two degrees of freedom, let us denote the vertical displacement of atoms B and C by symbols  $q_1 l$  and  $q_2 l$ , respectively, where  $q_n$  are generalized coordinates,  $n = 1, 2$ .

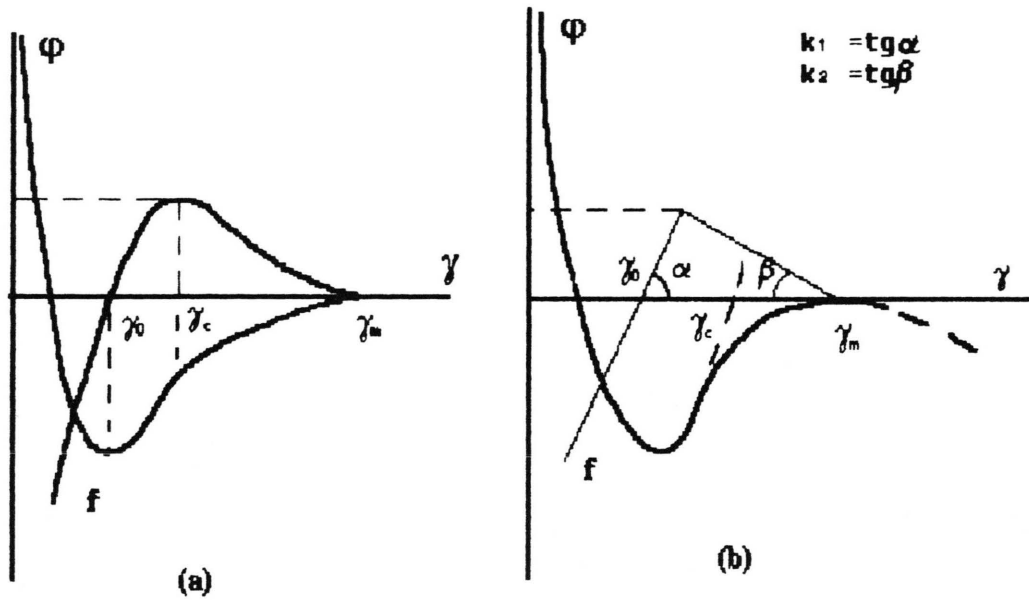


Fig. 13. Comparison of a real anharmonic interatomic potential (a) with the corresponding spline potential (b).

In harmonic approximation, the elastic energy of the elementary cell takes the form

$$U = \frac{K}{2} \sum_{n=1}^2 (\theta_n - \theta)^2, \quad (1)$$

where  $K$  is the elastic module of the hinge spring,  $\theta = \pi - \gamma_0$  the equilibrium valence angle.

From Fig 12 b, it follows that

$$\begin{aligned} \theta_1 - \theta &= \arcsin q_1 - \arcsin q - \arcsin(q_2 - q_1), \\ \theta_2 - \theta &= \arcsin q_2 - \arcsin q + \arcsin(q_2 - q_1), \end{aligned} \quad (2)$$

where  $q = \sin \theta$  is the equilibrium generalized coordinate. Let  $q_n - q$  be small, then

$$\begin{aligned} \theta_1 - \theta &= (q_1 - q) - (q_2 - q_1), \\ \theta_2 - \theta &= (q_2 - q) - (q_2 - q_1). \end{aligned} \quad (3)$$

Introducing the generalized displacements

$$\eta_n = q_n - q \quad (4)$$

we can always decompose arbitrary displacements into symmetric and asymmetric ones,

$$\eta_s = \frac{\eta_1 + \eta_2}{2}, \quad \eta_a = \frac{\eta_2 - \eta_1}{2} \quad (5)$$

and write down the elastic energy in the diagonal form

$$U = \frac{K}{2} (2\eta_s^2 + 18\eta_a^2). \quad (6)$$

If the cell shortens in the horizontal direction by

$$\begin{aligned} \Delta l &= l(3 - \sqrt{1 - \eta_1^2} - \sqrt{1 - \eta_2^2} - \sqrt{1 - (\eta_2 - \eta_1)^2}) \\ &\cong l(\eta_s^2 + 3\eta_a^2), \end{aligned} \quad (7)$$

the elastic energy of the cell is decreased by the work  $f\Delta l$  which was made during stretching the cell from  $3l - \Delta l$  to  $3l$ . Therefore the new elastic energy of the cell is

$$\begin{aligned} U &= \frac{1}{2} (2K - 2fl) \eta_s^2 + \frac{1}{2} (18K - 6fl) \eta_a^2 \\ &= \frac{1}{2} C_s \eta_s^2 + \frac{1}{2} C_a \eta_a^2, \end{aligned} \quad (8)$$

where

$$C_s = 2(K - fl), \quad C_a = 6(3K - fl) \quad (9)$$

are the stability coefficients.

Up to this point, we suppose that the coefficients  $K$  and  $f$  are constants. However, for semiempirical anharmonic potentials such as Morse, Lennard-Jones, etc. which are widely used in condensed matter physics [3], the coefficients  $K$  and  $f$  are, actually, non-linear functions of the valence angle  $\gamma$  (Figure 13 a). To simplify the consideration, let us approximate the real interatomic potential by the spline potential [15],

which in our case has the form

$$\varphi(\gamma) = \begin{cases} \frac{K_1}{2} (\gamma - \gamma_0)^2 - \varphi_0, & 0 < \gamma < \gamma_0, \\ -\frac{K_2}{2} (\gamma - \gamma_m)^2, & \gamma_c < \gamma < \gamma_m, \\ 0, & \gamma > \gamma_m. \end{cases} \quad (10)$$

Here  $K_1 > K_2 > 0$  are the elastic moduli,  $\gamma_0$  is the equilibrium valence angle which was accepted to be  $\pi/3$  in our calculations,  $\varphi_0$  and  $\gamma_0$  are the well depth and the inflection point of a real anharmonic potential, respectively,  $\gamma_m$  is the cut-off angle equal to  $\pi$ . The spline potential consists of two parabolas joined together in an inflection point of a real potential. It is very useful for the analysis of processes in solids [15] because the dependence of the force on the argument is very simple (Figure 13 b). Using the spline potential, we have only one variable coefficient, viz.  $f(\gamma)$ .

Let us decrease the valence angle  $\gamma$  from  $\pi$  to  $\gamma_0$ . It can be seen from Fig. 13 b that the force will increase on diminishing the elastic energy of the cell in such a way that, at first, the symmetric stability coefficient becomes zero at  $f_s = K_2/l$  and then the asymmetric one at  $f_a = 3K_2/l$ . This means that in our case, for the initial supermolecular structure the symmetric mode of instability is softer than the asymmetric one. However, it should be emphasized that if the valence-angle-force is in the interval  $f_s < f(\gamma) < f_a$ , we have  $C_s < 0$  and  $C_a > 0$ , so the cell energy has only a local minimum. The global minimum can be got if both  $C_s$  and  $C_a$  are negative. As a result, there appears mostly a zigzag structure (asymmetric mode) sometimes containing "symmetric" cells which can be considered as coiling faults. Therefore the formation of the secondary macromolecular zigzag structure is connected with the instability of the primary macromolecular straight structure which was formed, as suggested, during the synthesis of a macromolecule.

As for the dimensional-transformation-stage which leads to the appearance of a real two-dimensional

structure and is initiated by folding the zig-zag ribbon under the action of self-compression, this process can be treated, in principle, in just the same way as the zigzag formation. For example, it can be seen from Figs. 3 and 4 that folding the ribbon between atoms 190 and 215 is caused by the asymmetric mode of instability, whereas folding the ribbon between atoms 226 and 237 is due to the symmetric one. The dynamic theory of this stage is given in [37].

## 5. Conclusion

We have considered the self-organization of a macromolecule taking as a start an initially straight anharmonic chain with a strong and a weak interaction between atoms. The strong interaction determines the primary structure of a macromolecule, the weak interactions create secondary and tertiary macromolecular structures. Here, we use the structure hierarchy which is accepted in biophysics [13]. In a fully straight chain obtained as a result of a synthesis, the weak interaction is absent. However, immediately after the synthesis the weak interaction comes into play leading to self-organization.

It should be noted that the self-organization observed is obtained in the framework of classical physics almost from the first principles because in the MD approach, only the equations of motion and interatomic interactions are given a priori but different supermolecular structures are created automatically. Therefore the allegation that classical physics gives a rather poor description of the evolution [41] may be questioned. To our mind, the microscopic approach based on molecular dynamics schemes is more promising, at least at the first stage, for investigation of self-organization and irreversibility [3] than the more formal methods using kinetics, thermodynamics, or other hypotheses sometimes written in the form of nonlinear differential equations [41–43].

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