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From Nonequilibrium Thermodynamics to Nonlinear Dynamics

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Abstract—Systems with more than one steady state are used as an example to highlight the differences between the thermodynamic and kinetic approaches to systems analysis. As follows from the comparison of approaches, only the kinetic approach is an appropriate tool for describing such systems.

Key words: nonlinear dynamics, self-organization, far-from-equilibrium thermodynamics

For many of us, the book *Problems of Biological Physics* written by Lev A. Blumenfeld [1] has become a turning point in thinking. Reading of this book predetermined for many years our ways in science and the approaches that we used to study live matter. Very few authors manage to achieve such impact in their books. Therefore, all Blumenfeld's books inspired much interest and stirred vigorous debate. His last book [2] was not an exception. It was on the day of his death that he signed its proofs. Blumenfeld wrote in that book: "A physicist beginning to study biological objects usually gets a feeling of something miraculous. Spatially and temporally ordered processes of, for example, mitosis and meiosis are so different from the processes observed in ordinary physical experiments that the question unavoidably arises whether we need some special physics of live matter, with laws different from those taught in schools and universities." This passage is imbued with pessimism. Blumenfeld had always been solid in the view that biological processes can be explained by natural laws (laws of physics), without invoking supernatural forces. We see that the last move of his thought has brought this postulate into challenge. We do not share his pessimism. In our opinion, the capacities of physics for explaining biological phenomena are far from being exhausted. This article was inspired by our frequent discussions with Blumenfeld and presents our arguments in these discussions.

What was the cause of Blumenfeld's pessimism? What gave rise to his hesitation? He answered these questions in the paragraph following immediately the cited passage: "In one of my books on biophysical problems [1], I wrote 'In principle, the known basic laws of physics are sufficient for describing and understanding the structure and function of all the existing biological systems.' Today I am not that certain."

Presumably, Blumenfeld's doubts and hesitations were largely related to the futile attempts at tackling biological problems with thermodynamics. It is mandatory to take into account the dynamic properties of biological systems and their being far from equilibrium. Neither can be neglected; otherwise, we lose the ability to understand what is going on in biological systems. However, thermodynamics is a static science. Blumenfeld put it as follows: "The term of time interval is somewhat alien in the context of thermodynamics. Formally, neither thermodynamics nor equilibrium static mechanics make any use of the concept of time."

Thermodynamic views are so universally valid and all-encompassing that they have determined an era in natural sciences, not only in physics. The basics of modern thermodynamics were formulated by Gibbs

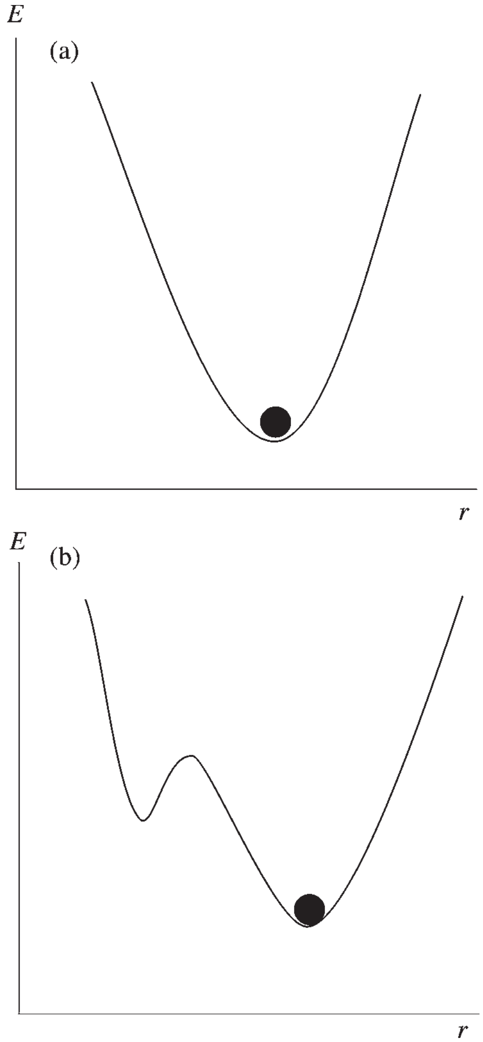

Fig. 1. Examples of a ball in a potential well.

more than a century ago. Blumenfeld, who was an expert in this field, used the formalism of thermodynamics throughout his life to work in biology, to understand how biological molecules act, and to analyze the mechanisms of biological processes. And he saw clearer than anybody else did that the success of this approach was limited. Yet thermodynamics has been so overwhelming as to spawn quite a number of delusions.

For example, everybody believes that, being left to its own, any substance will spread uniformly and isotropically throughout the available space. However, whenever and wherever we turn, we find nothing isotropic around. Nevertheless, we are unassailably convinced that this statement is correct despite what we see with our own eyes. Analogous longstanding misbeliefs concerning chemical reactions have been demolished in studies promoted by the discovery made by B.P. Belousov.

As early as, presumably, the 1920s, it became clear that equilibrium thermodynamics did not do well in describing the surrounding world. Attempts were undertaken to improve the situation. The first step was made by Onsager, who coined the term "nonequilibrium thermodynamics". This line of research, which is based on approximating the solution to a nonlinear system by expanding nonlinear functions into series, has been pursued for more than 50 years. However, nothing more efficient than the formalism of classical thermodynamics has been proposed. All the approaches developed have serious flaws. In effect, these additions to classical thermodynamics make little sense. Therefore, it is obvious that we have to pose limits on the range of its applicability and use thermodynamics only within these limits. Where thermodynamics does not work, we are compelled to use theories and descriptions in which time is present in the explicit form, that is, dynamics proper.

Consider a trivial example of a ball in a potential well (Fig. 1a). This may be a description of a physical pendulum, which is easy to imagine and known to everybody. Equilibrium thermodynamics states that the ball would lie at the bottom of the well. The equilibrium behavior of such a ball or many such balls in their respective wells can be perfectly described within the framework of thermodynamics.

Let now the ball be out of equilibrium. If the deviation from equilibrium is small, we can use the laws describing dynamic behavior of linear systems. Such laws are very similar mathematically in different divisions of physics. It is generally accepted that linear approximation (nonlinear thermodynamics is a linear approximation to the equilibrium, linear movement around the equilibrium) works fine as long as deviations are small. In fact, the point is not in how large deviations are. The approximation may appear to be good despite large deviations and poor even when deviations are small. Its goodness depends on the potential well shape and on the size of the part of the well that is in use during functioning of the system. Let us consider the situation in more detail taking again a ball in a potential well as an example. The dynamics of this system is given by equations of the following type:

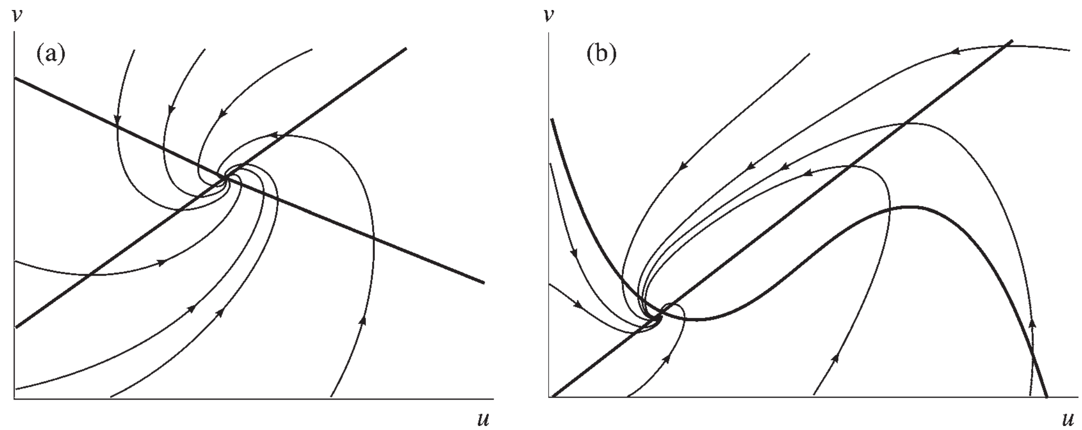

Fig. 2. Phase portraits of (a) a linear and (b) nonlinear systems with one stable state.

$$\begin{cases} \dfrac{du}{dt} = a_{11}(u - u^*) + a_{12}(v - v^*) \\ \dfrac{dv}{dt} = a_{21}(u - u^*) + a_{22}(v - v^*). \end{cases}$$

It is convenient to use phase space in qualitative analysis of the dynamic behavior described by sets of ordinary differential equations. Phase space is another mathematical tool for describing dynamic systems. Interestingly, this tool was developed in classical mechanics and statistic physics also at the end of the nineteenth century and the beginning of the twentieth century. Its development proceeded concurrently with but absolutely independently of classical thermodynamics. In the phase space, the state of the system is depicted with a point. Changes in the state of the system with time (real motion of the system) correspond to the movement of that point along a line called phase trajectory.

By way of example, let us consider the phase portrait of a harmonic oscillator (Fig. 2a). It is well known that a harmonic oscillator can be described with two variables, of which on is coordinate and the other is velocity. Suppose that the variables depicted in Fig. 2 are the dimensionless coordinate and the dimensionless velocity of a harmonic oscillator in some coordinate system. In this case, the phase space is a plane, which is often called phase portrait. The phase portrait of this system looks as follows. The system has one fixed point, which corresponds to the lowest position of the ball in the potential well. Any deviations from this position result in that linear forces arise that return the ball to the bottom of the well. In mechanics and many other sciences, it is shown that, if forces arising in a potential field are proportional to displacements (i.e., are linear), the energy is a quadratic function, as that shown in Fig. 1a.

The simple relationship between the type of the potential function and the dynamics of the system is a great virtue of this approach, created mainly by efforts of Poincaré more than 100 years ago. Even a greater virtue is that it allows us to analyze the dynamics of any systems, be they linear or to whatever extent nonlinear. We can do it qualitatively and need not care that the majority of equations that we write in any science, especially in biology, are highly nonlinear.

Thus, inspecting the behavior of a ball in a potential well qualitatively, one may infer that the linear and nonlinear systems are not very different. For example, if we find that a linear approximation is insufficient, we can expand any function into a Taylor series and take a higher-order approximation.

What does it mean according to Poincaré? It is generally known that the potential well for a linear system is described with a parabola, i.e., a quadratic function. Hence, if the potential is a quadratic function, the system is strictly linear. If the system is nonlinear, it seems that it can be described with a sum of quadratic and higher-order terms. If the higher-order terms are small, their addition does not make the problem more difficult to solve. It simply means that for each next approximation we shall solve, in effect, also a linear problem. The procedure of solving the problem, in which the potential is of the type shown in Fig. 1a but highly nonlinear, does not change dramatically. From the standpoint of a qualitative theory, all such solutions are similar. The theory tells us a quite obvious thing: the closer we are to the equilibrium point, the more accurate is the linear description. Hence there is no reason to expect significant

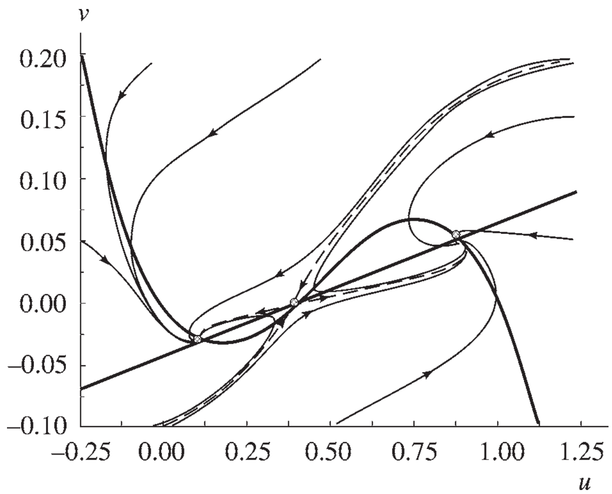

Fig. 3. Phase portrait of model (1) with two stable states for $\varepsilon = 0.02$, $a = 9.3995$, $b = -0.405$, and $n = 0.4$. Shown are the nullclines of both equations and phase trajectories. Dashed lines depict the separatrices of the saddle. Coordinates of the upper, intermediate, and lower fixed points are (0.88; 0.051); (0.395; –0.001), and (0.12; –0.0299), respectively.

differences for nonlinear systems with potentials of the type shown in Fig. 1a.

The situation changes dramatically and becomes really nonlinear when the potential well has more than one minimum (Fig. 1b). It is impossible to understand how to perform series expansion in this case. Previously, the potential was expanded around the equilibrium position (in the vicinity of the bottom of the well). Now, there are two equilibrium positions, and the system can pass from one to the other. Thermodynamics fails to consider such transitions. Thermodynamics postulates that wells are filled according to their depth, so that deeper wells contain more objects. However, this postulate holds if the dynamics of the process is such that there are objects that tend necessarily to one of the equilibrium positions. This is the case near the equilibrium and if there is just one equilibrium position. However, most of the systems we deal with are different. They spend much energy and receive much energy from somewhere. They are far from the position of thermodynamic equilibrium. Being far from equilibrium does not mean the absence of other potential wells (local minima). They may have several local minima. This statement fully applies to biological systems, which owe their existence to intense energy flux through them. The situation changes dramatically. Analysis of systems with two or even more local minima (i.e., steady states) shows that they do not live always in one steady state; rather, they make transitions between them.

Consider a well-known set of nonlinear equations with a cubic nonlinearity:

$$\begin{cases} \dfrac{du}{dt} = -u(u-1)(u-n) - v, \\ \dfrac{dv}{dt} = \varepsilon[u - av + b]. \end{cases} \quad (1)$$

At some parameter values, this model has only one steady state (Fig. 2b) and its phase portrait resembles the phase portrait of a harmonic oscillator. The resemblance is especially close in the vicinity of the steady state. However, at slightly different parameter values [3], one more steady state emerges in the phase portrait (Fig. 3). After its emergence, the system has two steady states, and none of them is more probable than the other. This situation is realistic in systems with large energy flows through them. Qualitatively new things arise, which cannot be described by approximation techniques. This system is bistable. The space of initial conditions for the variables becomes separated in two parts (dashed line in Fig. 3). If we start from some initial conditions in one half of the plane, we shall settle in one well. If we choose the initial conditions in the other half, we arrive at the other steady state (potential well). The height of the barrier between the wells determines the probability of transition between the states. These transitions are not prohibited, but imply the existence of a threshold that should be overcome. Obviously, the system consists essentially of two attraction basins. This situation is impossible to obtain by step-by-step approximations, because they always lead to one steady state. The existence of many basins of attraction, even so simple as the two in Fig. 3, is something qualitatively new. Such a phase space results in intricate behavior of the system. Moreover, when one of the states disappears, the behavior of the system remains complex. A limit cycle (undamped oscillations) may arise, a situation that is absolutely inconsistent with the thermodynamic approach. This is why the history of oscillatory chemical reactions (e.g., the Belousov–Zhabotinsky reaction) was so dramatic. Over a long time, they had been dismissed as artifacts.

In analysis of systems with complex phase space and many steady states (especially when there are quasi-steady states corresponding to extinct attractors), our physical intuition fostered in the spirit of classical thermodynamics blinds us and leads to confusion. We cannot guess how the system would behave in one or another case.

Until now, we considered the dynamics of the systems in which time was the only independent variable. Actually, there may also be other variables (moreover, this is a more common case, which, as it turned out, is of prime importance in nonlinear dynamics). We mean spatial variables. The basically new behavior of the system, very different from what the thermodynamic concepts predict, is most conspicuous in situations when we deal with spatial phenomena. Let us consider several examples. The first theoretical considerations of the Belousov reaction mentioned above and some other close examples began with very simple models. In these simple models, qualitatively new phenomena were discovered.

One of the phenomena disclosed in those simple models is a trigger wave. This term describes a transition of a medium (system) from one state to another in response to a perturbation applied at one point. Consider a homogeneous medium, in which some reactions, say, chemical, are possible. Let there be exchange of reactants between its points. Adding diffusion terms into model (1) with the parameters at which two stable states exist, we would observe waves:

$$\begin{cases} \dfrac{du}{dt} = -u(u-1)(u-n) - v + D_u \Delta u, \\ \dfrac{dv}{dt} = \varepsilon[u - av + b] + D_v \Delta v. \end{cases} \quad (2)$$

Figure 4 shows such a trigger wave. This trigger wave is the simplest one. Its propagation brings the medium from its initial trivial (or lower) spatially homogeneous steady state to the nontrivial (or upper) steady state.

In addition to trigger waves, autowaves were detected in such systems (Fig. 5). In this case, excitation of a medium at a point gives rise to a wave that runs to infinity without damping. It does not stop; its speed and amplitude remain constant. An important property of such waves is that their collision results in annihilation instead of interference. In other words, when two autowaves collide, both simply perish (Fig. 6).

Yet another simple well-known example is dissipative structures, or Turing structures. In this case, the isotropic spatial distribution of matter appears to be unstable. After a transient process, alternating high- and low-density regions fill the entire space (Fig. 7).

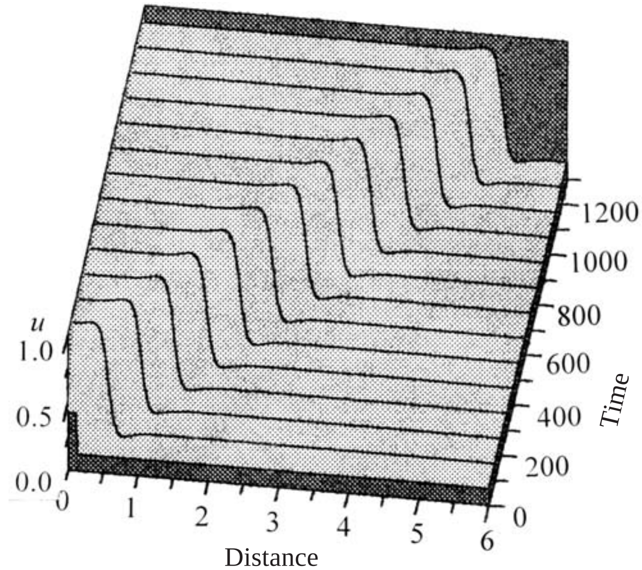

Fig. 4. A trigger wave in a bistable described by model (1) with added diffusion terms. Wave propagation brings the medium from its initial trivial (or lower) spatially uniform steady state to the nontrivial (or upper) one. The parameters are as in Fig. 3; D_u (diffusion coefficient for activator) = 0.001; and D_v (diffusion coefficient for inhibitor) = 0.005.

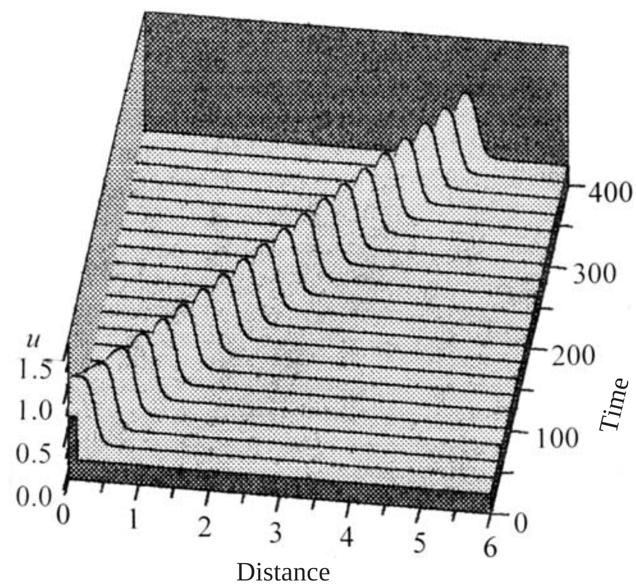

Fig. 5. An autowave (ε = 0.008, a = 5.18, b = –0.275, n = 0.4; D_u = 0.001, D_v = 0).

These strange wave and structures are far from normal behavior of diffusion media obeying classical thermodynamics. According to the latter, a diffusion

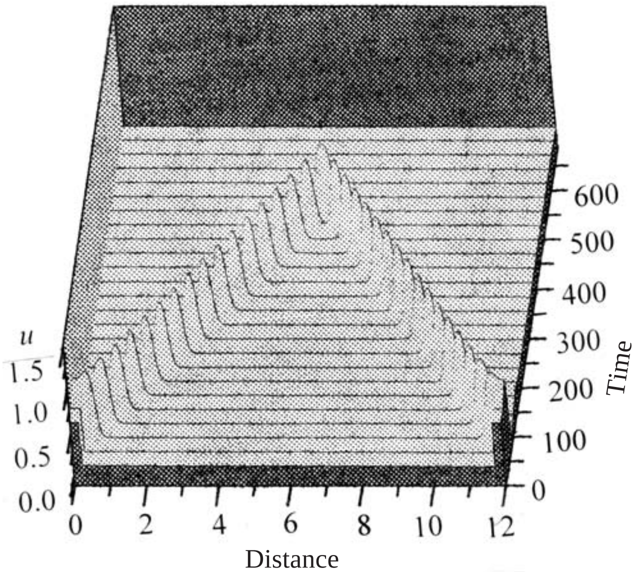

Fig. 6. Interaction of two autowaves. For parameter values, see Fig. 5.

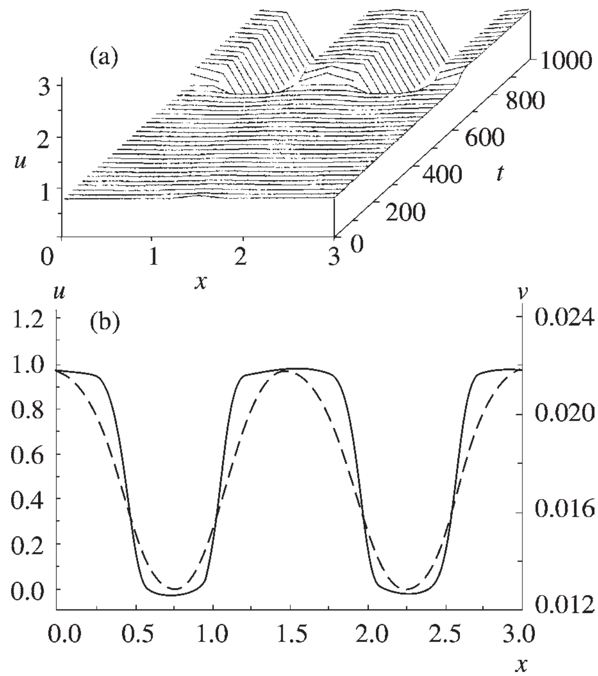

Fig. 7. Dissipative structures in model (2): (a) formation of a Turing structure by variable u (activator) and (b) spatial profiles of activator u and inhibitor v (solid and dashed lines, respectively) at time $t = 1000$. In computations, $\varepsilon = 0.01$, $a = 4$, $b = -0.48$, $n = 0.4$, $D_u = 0.001$, and $D_v = 0.07$. The model was solved on a segment $[0, L]$. The initial conditions were set as a small local rise of u at the center of the segment; the system was in the steady state corresponding to the fixed point ($u = 0.742$; $v = 0.065$).

medium tends to attenuate waves and pass into an isotropic state. From the early 1960s though the mid-1990s, the general view was that behavior of far-from-equilibrium systems is limited to the few unusual examples described above. Thermodynamics seemed to encompass all but a small area where anomalies, such as dissipative structures and autowaves, can occur.

However, during the last decade this field has been experiencing a revolution by sly degrees. More and more new types of behavior are discovered in various systems.

Really weird things have been detected. When we see the space filled in the Turing model with a kind of standing waves, we still retain the ability to imagine how catalysis coupled to diffusion produces a spatially inhomogeneous concentration distribution. It is not so in the following example. Imagine a vessel filled with a well-stirred solution of some reactants. Let a small perturbation be applied at some point of this isotropic medium in the vessel. After some time, a peak is formed in response to this perturbation (Fig. 8). The activator concentration is high in the peak and close to zero outside. This nonuniform distribution does not dissipate for whatever long time, in apparent contradiction to what we used to intuitively think about solutions. When solutions of some substances are placed in a vessel, we expect that their distributions will eventually become uniform, even if the substances react with one another. The result contradicts the expectations. It looks as if it were natural for a substance to concentrate in one place. It can be compared to a chair that makes a sudden jump without any external forcing. Such solitary structures can be standing or can travel throughout the space. One traveling peak was described by A.N. Zaikin. He is among those modest people who work without rushing for sensation. In their comprehensive studies, many unusual patterns have been detected.

In recent years, more sophisticated models have been proposed, in which new dynamic patterns have been revealed. We have developed a model of blood clotting [4], which reads

$$\begin{cases} \dfrac{\partial u_1}{\partial t} = D\dfrac{\partial^2 u_1}{\partial x^2} + K_1 u_1 u_2 (1 - u_1)\dfrac{(1 + K_2 u_1)}{(1 + K_3 u_3)} - u_1, \\ \dfrac{\partial u_2}{\partial t} = D\dfrac{\partial^2 u_2}{\partial x^2} + u_1 - K_4 u_2, \\ \dfrac{\partial u_3}{\partial t} = D\dfrac{\partial^2 u_3}{\partial x^2} + K_5 u_1^2 - K_6 u_3. \end{cases} \qquad (3)$$

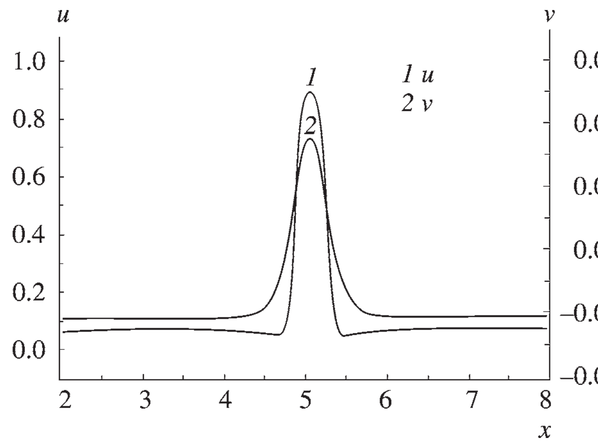

Fig. 8. Established spatial profiles of (*1*) activator *u* and (*2*) inhibitor *v* for a peak. In computations, $\varepsilon = 0.02$, $a = 9.3995$, $b = -0.2637$, $n = 0.4$, $D_u = 0.001$, and $D_v = 0.05$. No dependence on the segment length *L* was found.

In this model, one can observe a multitude of patterns—a whole zoo. Here, we mention just a few of them. One example is a peak arising from an initially isotropic medium (Fig. 9). This peak is remarkable not only in that it breaks the spatial isotropy, but also in that it is nonstationary. Its amplitude varies with time. Another example is something resembling an autowave (Fig. 10). On average, its speed and amplitude are constant. However, as it moves, its amplitude oscillates. Strictly speaking, this pattern is not an autowave.

Consider other, more intricate wave patterns arising in this model. We have not only standing localized peaks (which can vary in amplitude or not) and running solitary waves whose amplitudes oscillate or remain constant, but also waves that can divide, reproducing themselves and filling the entire space (Fig. 11). They can propagate in such a way: first, no activity is observed, then one burst occurs and moves somewhere, divides, and generates new bursts. However, even far behind the propagating wave, some activity remains. At first glance, the entire medium begins to fluctuate chaotically.

We also detected hybrids between standing structures and autowaves. For example, a standing peak arises not at the site of activation, but away of it (Fig. 12). Immediately after activation, something like an autowave arises, runs for a while, and then stops propagating, converting to a standing peak. The distance it runs depends on the model parameters. This dependence affords a possibility of remote control

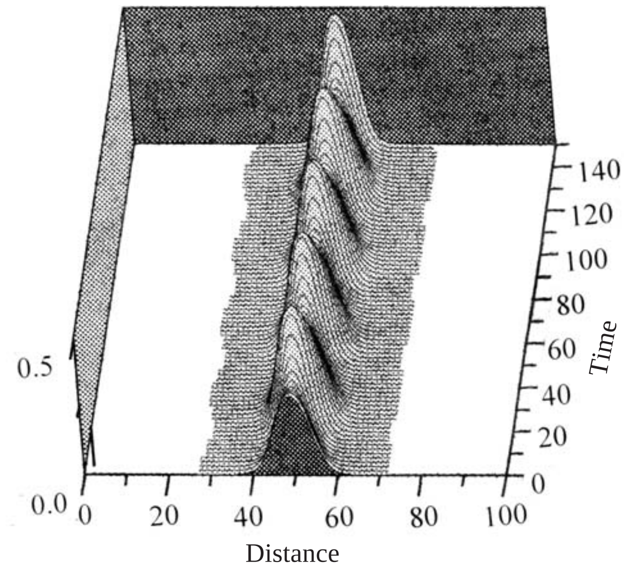

Fig. 9. A spatially localized oscillating structure (peak) in model (3). In computations, $D = 1$, $K_1 = 6.85$, $K_2 = 6.62$, $K_3 = 2.36$, $K_4 = 0.1$, $K_5 = 14.0$, and $K_6 = 0.0725$.

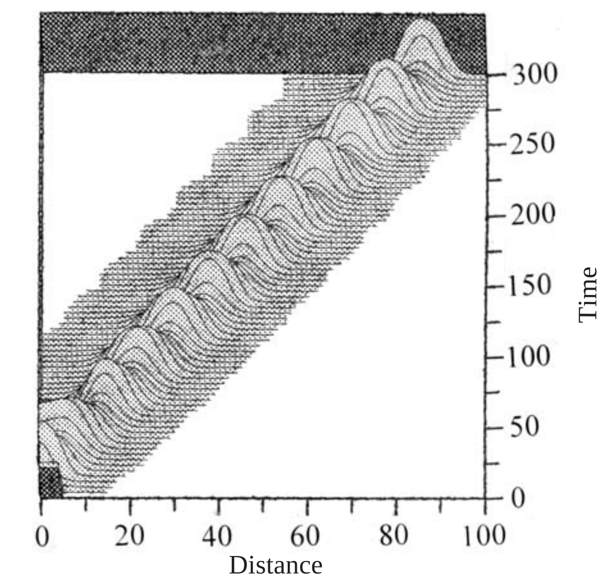

Fig. 10. A thrombin wave with oscillating amplitude. In computations, $K_2 = 4$ and $K_6 = 0.0715$. Other constants are as indicated in Fig. 9.

over generation of barriers and boundaries away from the signal source.

The examples presented are not exhaustive. For a long time, we knew only autowaves and Turing structures. At present, the number of possible spatiotemporal patterns is rapidly increasing. Presumably, some psychological barrier has been overcome. Even in the models where only autowaves were known previously, much more complex modes are now disclosed.

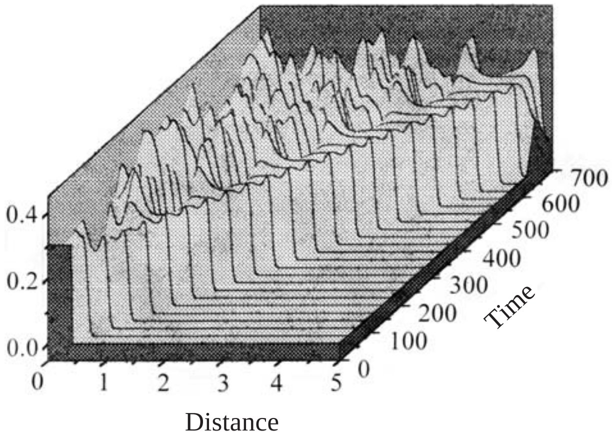

Fig. 11. Chaotic activity in the medium after passage of a thrombin wave. In computations, $D = 2.6 \cdot 10^{-4}$, $K_1 = 6.85$, $K_2 = 4.0$, $K_3 = 2.36$, $K_4 = 0.087$, $K_5 = 17.0$, and $K_6 = 0.09$.

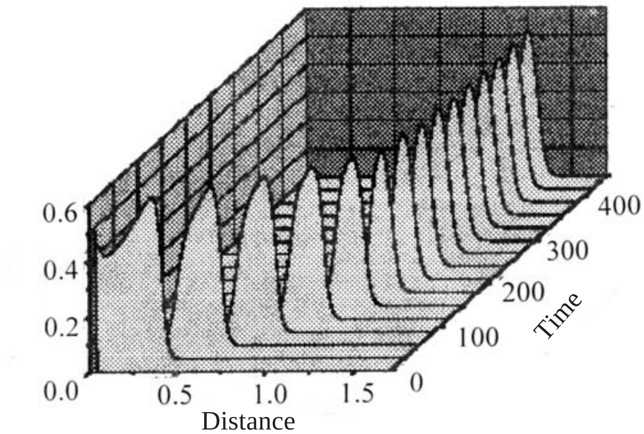

Fig. 12. A thrombin wave that stops propagating at some distance from the site of activation and forms a standing nonuniform structure. In computations, $K_2 = 11$ and $K_6 = 0.066$. Other constants are as indicated in Fig. 11.

In addition, studies and modeling of particular systems, especially biological systems, lead to new equations, sometimes relatively simple, which also give rise to new modes and new phenomena. As the repertoire of dynamic modes expands, a new world—a world of nonlinear dynamic patterns—emerges. They are so diverse and unpredictable that our classical thermodynamic intuition just gives up. With the classical approach, the outcome of an experiment was intuitively predictable on the grounds of physical logic. In contrast, classical physical reasoning can lead us into a pitfall when we are dealing with new dynamical systems. We are compelled to elaborate new common sense, also physical thinking but taking in systems that are far from thermodynamic equilibrium and essentially nonlinear.

In our opinion, Blumenfeld's pessimism was related to the transient nature of the few recent years. Regretfully, Blumenfeld has not lived to see the rise of the new—dynamic—era, which is obviously taking over now and would dominate in all natural sciences. We can ask why this era begins now rather than 100 year ago, when Poincaré and his followers laid the foundations of the qualitative analysis of dynamical systems. However, this question is of only philosophical interest.

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