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A brief tale on how chemical oscillations became popular: an interview with Anatol Zhabotinsky

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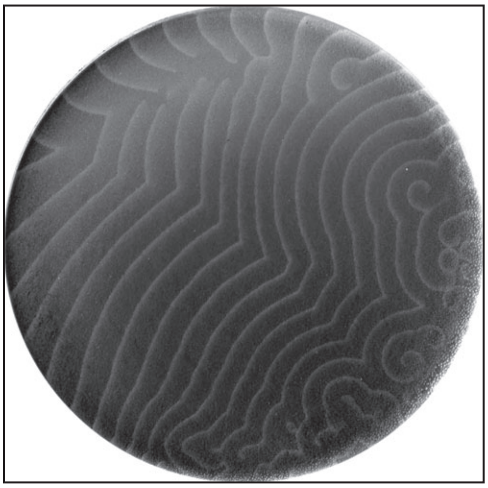
INTRODUCTION

Nowadays everyone who deals with complexity, both in science and in humanistic disciplines, has heard about the 'Belousov–Zhabotinsky (BZ) reaction'. This reaction represents, without any doubt, one of the most cited examples of a self-organizing chemical system, and at present over 1,500 papers have been published on the BZ reaction. But it was not always so, and in this respect the BZ reaction represents a good (though maybe not the most important) example of how reluctant academia can be to recognize observations that do not seem to fit into existing theories.

The first observation of an oscillating chemical reaction in liquid phase was made in 1921 by Bray [1], who observed periodic variations in iodine concentrations during decomposition of hydrogen peroxide catalyzed by the iodate ion. The scientific community considered this behavior as contradicting the second law of thermodynamics and attributed the oscillations to unknown impurities. It was quite odd that scientists spent more time trying to explain why this reaction was supposed to be impossible than in seriously attempting to understand what was going on.

Despite the theoretical work of Prigogine about oscillations in far from equilibrium systems (1955), the myth that chemical oscillations in homogeneous systems were impossible, because they contradict the second law of thermodynamics, persisted until the mid-1960s (what Anatol Zhabotinsky calls the Dark Age [2]).



One of the most fascinating manifestations of the BZ reaction is its capability to self-organize in spatio-temporal patterns. The picture shows spatially extended structures of a ferroin-catalyzed BZ reaction. Oxidizing chemical waves evolve on a reduced medium forming spirals, pacemaker structures, and other interesting patterns.

Nevertheless, a crucial discovery was made by the Russian chemist, B.P. Belousov, in 1951, which led the way toward the future development of nonlinear dynamics in chemistry. He observed oscillation of the solution color during the oxidation of citric acid by bromate catalyzed by ceric ions. Even though Belousov carried out a qualitative analysis of the system and found the conditions for stable oscillations, his results were rejected by all the chemical journals to which he submitted them, and he eventually published a report of his discovery only in 1959 in an obscure booklet printed by his own institute [3]. The final chapter of this story (or the first, depending on the point of view) was written by Anatol Zhabotinsky. After his graduation from Moscow State University, he started to study the Belousov reaction on the advice of his former professor Simon Shnol. In 1962, he sent his first paper on chemical oscillations in a modified Belousov reaction to the Russian journal *Biofizika* [4]. After understanding the principal mechanism of this oscillating reaction [5], Zhabotinsky switched his attention to one of its most fascinating aspects: the capability to produce chemical waves.

Thanks to Zhabotinsky's work and the future work that it inspired, the existence of chemical oscillations in homogeneous systems was fully accepted by the scientific community and the misunderstandings in theory regarding the second law of thermodynamics were removed. Now the activity related with BZ reaction is still strong and it remains a useful tool in many scientific fields, from nonlinear kinetic theory to biological disciplines.

INTERVIEW

Federico Rossi (FR): How did you become aware of Belousov's work, and why did you decide to go on with it? What aspect of the reaction raised your interest? Were you aware at the beginning of your work of the impact that the reaction would have on the scientific community?

Anatol Zhabotinsky (AZ): After graduation from the Department of Biophysics at Moscow State University School of Physics, I got a job at a cancer research institute. My superiors were satisfied with my performance but the research itself was not interesting for me. I had a lot of free time and decided to do some study on the periodic forcing of glycolytic oscillations. I showed the project to my former biochemistry professor, Simon Shnol, who told me that the project was very interesting but impossible to complete because of the lack of necessary reagents, which could be bought only with hard currency. He suggested that instead I should study an oscillating reaction discovered by Boris Belousov. I agreed, and after a while Shnol gave me Belousov's recipe with a small amount of reagents. I mixed the reagents according to the recipe and observed oscillations in the solution color. Then I started altering the recipe to improve recordings of the oscillations and obtain as stable oscillations as possible. The substitution of malonic acid for citric acid resulted in a major improvement. I did what every researcher does, tried to render a phenomenon as clear as possible and to understand its mechanism. I knew that it was a rather unusual phenomenon but I could not foresee that it would attract so much attention.

FR: Many years passed from the discovery of the reaction to its full acceptance by the scientific community. In the meantime, Belousov abandoned his studies of the reaction. Nevertheless some events led the scientific community to fully accept the existence of chemical oscillators in a homogeneous phase. In our opinion, among these events, the contributions of Ilya Prigogine and the Brussels school were of particular relevance. How did the theory of far from equilibrium systems and the concept of 'dissipative structures' in particular, influence your work?

AZ: Prigogine has shown that for chemical oscillations to emerge the system must be far from equilibrium that is outside the Onsager domain. That led to a much better understanding of the nature of such types of oscillations. However, homogeneous and heterogeneous systems are not different from the thermodynamic point of view. So, there is some sort of irony in the development of the field because before the BZ reaction became known there was a lot of talk about homogeneity and heterogeneity, but after the BZ reaction became popular, nobody was interested to know whether it was truly homogeneous. I have shown that the BZ reaction was a homogeneous one, but my data has been published only in my book *Concentration Self-Oscillations* in Russian, and, I guess, remained more or less unknown. I never saw a serious discussion of the homogeneity of the BZ reaction.

FR: The impact of the BZ reaction on the scientific world goes beyond a purely mechanistic interest, a merely chemical–physics point of view. We can find the BZ reaction cited in many philosophic essays, treated as one of the most important examples of complex systems. Do you think that the characteristics of the BZ reaction justify such a large interest, even in not strictly scientific fields? In your opinion, what are the aspects of the BZ reaction that made it so famous outside the laboratory?

AZ: From the scientific point of view the BZ reaction is the simplest closed macroscopic system that can be maintained far from equilibrium by an internal source of free energy homogeneously distributed in space. For students and nonscientists the BZ reaction makes it possible to see the development of complex patterns without any devices by naked eye on a very convenient time scale of the order of minutes and a space scale of several millimeters.

FR: Prigogine says about self-organization:

> *[…] when a system is pushed far from thermodynamic equilibrium, an instability appears. This instability often leads the system to an internal self-organization (e.g. Turing structures). Probably also Life itself is the result of spontaneous self-organization processes.*

Do you think that the BZ reaction, and its self-organizing capability, could indeed be a valid model for studying living systems?

AZ: The observation of spiral waves in the BZ reaction–diffusion system helped significantly to prove that the same type of waves is responsible for the emergence of cardiac arrhythmias. However, in general, I do not think it is a good model of life processes. The BZ reaction is much simpler than any real-life process. First, it has a much smaller number of time scales. Second, in the heart of the BZ reaction one finds the replication of a pair of autocatalytic species, while in the heart of any living system you find the replication of a genetic code, which is quite complex and capable of mutations.

FR: What are, in your opinion, the most important contributions deriving from your reaction to the various scientific fields (chemistry, physics, biology, etc.)?

AZ: I think that the study of the BZ reaction was the nucleation process for the emergence of nonlinear chemical dynamics as an independent field of physical chemistry. In the field of pattern formation, the BZ reaction–diffusion system is one of the richest sources of various spatio-temporal patterns.

FR: What do you think are the most exciting current and future directions in this area of research?

AZ: I think that self-organization in biology, especially in development and the activity of the brain remains and will remain for long time the most exciting and important area of study of complex systems. In nanotechnology, controlled self-organization under nonequilibrium conditions promises new effective ways for the self-assembly of complex nanodevices.

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