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Dilip Kondepudi
Wake Forest University

Tomio Petrosky
The University of Texas at Austin

John A. Pojman
Louisiana State University

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Dilip Kondepudi, Tomio Petrosky and John A. Pojman

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Dissipative structures and irreversibility in nature: Celebrating 100th birth anniversary of Ilya Prigogine (1917–2003)

Dilip Kondepudi,[1] Tomio Petrosky,[2] and John A. Pojman[3]
[1]Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109, USA
[2]Center for Studies in Complex Quantum Systems, The University of Texas at Austin, Austin, Texas 78712, USA
[3]Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, USA

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Friends and colleagues who knew Ilya Prigogine well called him "A poet of thermodynamics." It is an apt description. When Prigogine talked about thermodynamics and irreversible processes, one had the sense he understood or knew more than what his words conveyed. Natural processes all around us are irreversible; it is a fact. Their consequence is not merely to increase the entropy of the universe and destroy order. They can also do the opposite: create highly ordered complex structures with extraordinary properties and create life itself. Prigogine saw this as a profound aspect of nature that thermodynamics has revealed. When he came across the famed South Indian sculpture of Nataraja, the dancing Shiva, that depicts as a cosmic dance the perfect balance between creation and destruction that originate from the same source, he made sure he had a bronze statue of Nataraja of highest artistic quality in his art collection. A picture of it became the cover art for the book *Thermodynamic Theory of Structure Stability and Fluctuations*,[1] that he coauthored with Paul Glansdorff. It was poetry of thermodynamics, creation and destruction emerging from a common source, a perfectly balanced cosmic dance. One could surmise all this from Prigogine's discourses on thermodynamics.

Dissipative structures was the name Prigogine coined, nearly 50 years ago, for the complex structures created by irreversible processes. As this special issue celebrating the hundredth anniversary of his birth shows (Prigogine was born on January 25, 1917) the study of dissipative structures is still a very active subject that is advancing into new areas. If we pursue the study of dissipative structures, we might be led to more insights, perhaps even new laws or principles that give us a better understanding of how complex structures come about spontaneously, their responses to changes in physical parameters, and their collective behavior. These advances, among other things, are also a quest for a thermodynamic understanding of processes we see in organisms and even those that created life.

Convinced of the centrality of irreversible processes in nature and the reality of the arrow of time, Prigogine had to confront a vexing duality of physics. From the point of view of time-reversible mechanics, motion—and hence all transformations of matter—into the future or into the past had no fundamental distinction. Irreversibility and the arrow of time could not be real, it must be an illusion. It must be an illusion created by us, macroscopic living beings, due to the limitations of our faculties. Prigogine's rejection of this view of irreversibility and the arrow of time was unequivocal. Many a time, we have witnessed him say, with much passion and certainty, in lectures and in conversations in cafes, "Irreversible processes created us, we did not create them." At times, his assertion was more literary: "We are the children, and not the progenitors, of the arrow of time, of evolution."

It was mechanics that had to be modified, or its formulation extended, to come to terms with the reality of irreversible processes and the arrow of time. To this end, he promoted the development of the theory of non-unitary transformation. In his 1977 Nobel Lecture,[2] he noted in his concluding remarks, "The inclusion of thermodynamic irreversibility through a non-unitary transformation theory leads to a deep alteration of the structure of dynamics. We are led from groups to semigroups, from trajectories to processes. This evolution is in line with some of the main changes in our description of the physical world during this century." This theory continues to make progress. Several articles in this issue are on this topic.

Prigogine's scientific contributions could be broadly grouped into three periods: (i) the early period in which he reformulated thermodynamics as a science of irreversible processes, thus changing it from a theory of states as it was formulated in the 19th century, (ii) the period in which his Brussels-Austin group formulated the theory of dissipative structures and conducted extensive studies of diverse systems, and (iii) the later period in which his group focused on making irreversibility a fundamental part of physics by extending the formulation of mechanics.

In the first phase of his work, synthesizing the concepts developed by his mentor Theophile DeDonder, and others such as Duhem, Natanson, Jaumann, and Onsager, Prigogine fundamentally changed the formulation of thermodynamics by making it a theory of processes, not a theory of states.

As it was formulated in the 19th century, thermodynamics identified two fundamental functions of state, energy and entropy, the former associated with the First Law and the latter associated with the Second Law of thermodynamics. In this theory, calculation of changes in entropy could only be done for an idealized, infinitely slow, reversible process in which $dS = dQ/T$. The theory did not have a formulation that related the changes in entropy to real processes in nature that are irreversible and took place at a non-zero rate.

For irreversible processes, it was only stated that $dS > dQ/T$. That left irreversible processes outside the domain of the theory, but the theory was still very powerful because one could use the concept of reversible processes to compute the difference in entropy between two states. Additionally, since calculations of changes in entropy were confined to infinitely slow reversible processes, the classical thermodynamics did not have a way to compute the rate of change of entropy, dS/dt, and relate it to irreversible processes. In his 1943 monograph, *The Nature of Thermodynamics*, Bridgman described the state of 19th century classical thermodynamics thus:[3] "It is almost always emphasized that thermodynamics is concerned with reversible processes and equilibrium states and that it can have nothing to do with irreversible processes or systems out of equilibrium in which changes are progressing at a finite rate. The reason for the importance of equilibrium states is obvious enough when one reflects that temperature itself is defined in terms of equilibrium states. But the admission of general impotence in the presence of irreversible processes appears on reflection to be a surprising thing. Physics does not usually adopt such an attitude of defeatism."

Following the advances made by Lars Onsager in the 1930s, Prigogine introduced a formulation of thermodynamics[4–6] as a theory of irreversible processes. Crucial to this theory was the concept of *local equilibrium* in which it was assumed that, in an elemental volume at each location, the system existed in a state of equilibrium. Thus, temperature and other state variables became functions of position, and the system as a whole was inhomogeneous. The idea of local equilibrium was supported by statistical physics, which showed that, locally, Maxwell distribution of velocities was reached very rapidly, establishing a well-defined concept of temperature at each position. As for entropy, the formalism defines a change in the entropy of a system, dS, in a time interval dt, as

$$dS = d_iS + d_eS, \tag{1}$$

in which d_iS is the entropy produced by irreversible processes and d_eS is the change in entropy due to exchange of energy and matter with system's exterior. The explicit relation between d_iS and irreversible processes is expressed in terms of thermodynamic forces, F_k, and thermodynamic flows, J_k

$$\frac{d_iS}{dt} = \sum_k F_k J_k. \tag{2}$$

If this expression is taken to define the rate of entropy change in each elemental volume, it is straightforward to write the appropriate densities and integrals for the all thermodynamic quantities for the entire inhomogeneous system. This is the modern formalism that has given us a broader understanding of thermodynamics. One could now compute the rates of entropy production in terms of rates of irreversible processes such as chemical reaction and heat conduction. In the modern formalism, the Second Law is stated as: $d_iS \geq 0$.

Under Prigogine's leadership, an active Brussels School of thermodynamics and statistical mechanics flourished and resulted in the publication of highly successful monographs,[7–9] which were published in many languages. Today, new developments of thermodynamics are taking place spurred by nano- and other technologies.

In the late 1950s and early 1960s with the realization that nonequilibrium conditions could produce chemical oscillation, a new phase of activity began. It had its origins in the realization that, when far from thermodynamic equilibrium, irreversible processes can drive the system to organized states; the phenomenon of *self-organization* came to light. Irreversible processes generated entropy, which was thought of as disorder. Yet, the same irreversible processes also produced self-organization, thus began the study of dissipative structures. Here was the key to understand the origin of order and the vast diversity of form and function we see in nature. It also gave rise to new questions regarding the stability of nonequilibrium states,[1] the consequences of nonlinearity of equations that described systems far from thermodynamics equilibrium and discovery of many self-organizing systems.

In 1967, when Prigogine accepted the directorship of the Center for the Study of Statistical Mechanics and Thermodynamics at the University of Texas in Austin, his group expanded and became the Brussels-Austin group. The study of dissipative structures entered a new phase drawing researchers from around the world. As a result, the Noble Prize for Chemistry was awarded to Prigogine in 1977 for his contributions to thermodynamics. The book he coauthored with Grégoire Nicolis that summarizes much of the work on dissipative structures at that time also appeared in the same year.[10] A few years later, a broader picture of Prigogine's view of time, complexity, and the role of irreversible processes appeared in his book *La Nouvelle Alliance*, in French, and *Order out of Chaos*, in English.[11] This book was translated into 18 languages and is widely read. Subsequently, Prigogine wrote several books for the general reader about the arrow of time and complexity. The study of dissipative structures is still a flourishing field of research.

At the time Prigogine received the Nobel Prize in Chemistry, at the age of 60, he was already thinking about how mechanics needs to be modified to make irreversible process and the arrow of time intrinsic to it, thus began the third phase of his research. But this problem has vexed many before him, including such people as Henri Poincaré, and it goes to the core of dynamical systems. Poincaré's classification of dynamical systems as integrable and nonintegrable systems was an important ingredient of Prigogine's thinking. Poincaré proved that in nonintegrable systems, it is not possible to construct a canonical or unitary transformation that generates new invariants of motion by acting on the corresponding unperturbed invariants. Prigogine saw a connection between this result and irreversibility. In addition, in "chaotic systems," which show that dynamics is not a science that gives us the ability to predict the future behavior indefinitely, he saw the limitation of mechanics and the need for its extension to make probability and irreversibility a

fundamental outcome of this extension. To this end, he and his collaborators began formulating a theory of non-unitary transformations in which probability emerges not as a result of our inability to specify microscopic state but rather as a dynamical consequence of resonance singularities in nonintegrable systems. He continued working on this theory until he passed away in the year 2003. This subject too continues to make advances today.

The articles in this special issue can be related broadly to the three major phases of Prigogine's contributions. The following articles are related to the first phase. Nicolis and De Decker's article[12] "Stochastic approach to irreversible thermodynamics" show how the formulation of thermodynamics is extended to explicitly include fluctuations of macroscopic observables. In this overview, the authors present a formalism that relates fluctuations and irreversibility and the contribution of fluctuations to entropy production. In the article[13] titled "The underdamped Brownian duet and stochastic linear irreversible thermodynamics," Proesmans and Van den Broeck discuss the key features of stochastic thermodynamics such as the fluctuation theorem, fluctuation-dissipation relations, and efficiencies when fluctuations are involved. The discussion is presented with a concrete example of a Brownian particle driven by periodic forces. A critical review of the fluctuation theorem is contained in the article[14] titled "Fluctuation theorem: A critical review" by Malek-Mansour and Baras. The theorem has many subtle features and had unfortunately led to articles that claimed the Second Law can be violated. Quoting Max Planck, the authors rightly remind the reader that the Second Law is a macroscopic law, stated as the impossibility of the perpetual motion machine of the second kind, that it is either valid in all systems or it is valid in none, there is no third possibility. The article notes several aspects of the fluctuation theorem that needs to be carefully considered for its applicability.

Articles on dissipative structures are a major part of this special issue. Albert Goldbeter, whose contributions to the field of biochemical oscillations are well known, presents an excellent and stimulating review in the article, "Dissipative structures and biological rhythms."[15] A table in this article presents the remarkable range of periodicity in the cellular and supra-cellular levels. In the same field, is an article[16] by Amemiya *et al.* titled "Primordial oscillations in life: Direct observation of glycolytic oscillations in individual HeLa cervical cancer cells." In it one finds an overview of the role of glycolytic oscillation in cellular rhythms and cancer cells. The authors also discuss the topics of self-assembly and its relation to dissipative structures: dissipative structure-assisted self-assembly and self-assembly-assisted dissipative structures. The relevance of dissipative structures in understanding organisms is the topic of the article[17] by Kondepudi, Kay and Dixon. "Dissipative structures, machines and organisms: A perspective" presents a voltage-driven system that remarkably shows behavior which is similar to that we see in an organism. They show that almost all the different aspects of the complex behavior observed in this system can be characterized as an evolution to states with higher rates of entropy production. A perspective on the fundamental difference between machines and organisms can also be found in this article.

One of the most celebrated aspects of dissipative structure is explaining how patterns can form in chemical systems far from equilibrium. Burdoni and De Wit discuss the how the interplay between reactions and diffusion can create local spatiotemporal patterns when separate reactants are placed in contact in their article titled "Dissipative structures: from reaction-diffusion to chemo-hydrodynamic patterns."[18] They used the Brusselator model and found localized waves, Turing patterns and reaction-diffusion patterns. In the article "Chlorine dioxide-induced and Congo red-inhibited Marangoni effect on the chlorite- trithionate reaction front," Liu *et al.* studied the effect of Marangoni convection on propagating fronts in the chlorite-trithionate reaction.[19] Chlorine dioxide produced in the reaction changes the surface tension, causing a fluid flow. However, the addition of the indicator Congo red created an oscillatory front while bromophenol blue resulted in multiple vortices. Biria *et al.* reviewed optical waves in photoreactive systems.[20] Their article, "Coupling nonlinear optical waves to photoreactive and phase-separating soft matter: Current status and perspectives," discusses how nonlinear optical dynamics can couple with phase separation to create remarkable pattern formation with practical uses. In their article "Effect of pseudo-gravitational acceleration on the dissolution rate of miscible drops," Viner *et al.* considered how the rotational acceleration in a spinning drop tensiometer affects the dissolution of miscible drops.[21] The high rotation rate in the tensiometer creates a pseudo-gravitational field that creates an opposing force (barodiffusion) to dissolution but also creates a buoyancy-driven flow that increases dissolution. Bunton *et al.* studied the modulation of pattern formation in viscous fingering of miscible fluids in a Hele-Shaw cell by a crosslinking reaction of a thiol with an acrylate which they present in their article titled "The effect of a crosslinking chemical reaction on pattern formation in viscous fingering of miscible fluids in a Hele–Shaw cell."[22] They found that the patterns could be changed by the adjusting the rate of the reaction.

Papers related to the third phase analyze irreversible process of Hamiltonian system for open dynamical systems with infinitely many degrees of freedom and analyze chaotic systems and a nonlinear process in the quantum optics. "Microscopic description of irreversibility in quantum Lorentz gas by complex spectral analysis of the Liouvillian outside the Hilbert space" by Petrosky *et al.*[23] discusses an application of the complex spectral analysis of the Liouvillian. Prigogine had developed this type of analysis with his Austin-Brussels group. For a quantum Lorentz gas, they show that irreversible process of a Hamiltonian system is obtained on a purely dynamical basis in all space and timescale including the microscopic atomic interaction range without relying upon any phenomenological operations. The article "Irreversibility and the breaking of resonance-antiresonance symmetry" by Ordonez and Hatano[24] presents an interesting time-reversal symmetric resolution of unity to describe irreversible process of open quantum systems for a simple model of a single-site coupled to two leads in a

lattice. "A wave-function model for the CP-violation in mesons" by Fathi *et al.*[25] discusses CP symmetry violation in mesons by using the two-level Friedrichs Hamiltonian model. The Friedrichs model has been one of the prototypical models Prigogine and his coworkers have analyzed. In this model, the dynamical origin of irreversibility through the resonance singularity that appears in the solution of the fundamental equation of motion that is symmetric with the direction of time is described. An article titled, "Generalized second law for a simple chaotic system" by Hasegawa *et al.*[26] discuss a generalization of the Second Law (nonequilibrium maximum work formulation) for a simple chaotic system. They show the thermodynamic entropy can increase even for a system in which Gibbs-Shannon entropy is conserved. "Signatures of chaos in the Brillouin zone" by Barr *et al.*[27] discuss also the chaotic behavior of a quantum billiards tiled on an infinite plane. They show that energy sheets of the Brillouin zone begin to mix as the classical dynamics of the billiard changes from regular to chaotic behavior. Finally, in "Semiconductor surface emitting lasers for photon pairs generation" Vanbever *et al.*[28] discuss a nonlinear process in quantum optics. This nonlinear process has been one of Prigogine's favorite subjects. They study the feasibility of generating photon pairs in a resonant Vertical-Cavity Surface-Emitting Laser (VCSEL) as a result of a third-order nonlinear, four wave mixing interaction.

We remember Ilya Prigogine not only as a dynamic and inspiring colleague but also as a very kind and generous person. He enjoyed people and arranged for dinners with his colleagues frequently. Throughout his life, he welcomed visitors to his group and provided them with generous support. He was an ardent art collector with a museum quality collection of pre-Columbian art. In his younger years, he was also an accomplished keyboard musician. His epitaph reads:

> *L'ÉTONNEMENT EST SOURCE DE CRÉATIVITÉ*
> (ASTONISHMENT IS THE SOURCE OF CREATIVITY).

EDITORS' RECOLLECTIONS

Ilya Prigogine was Dilip Kondepudi's Ph.D. advisor. Kondepudi continued working with him for many years after obtaining his doctorate and they published many article together. In 1998, they authored a textbook titled *Modern Thermodynamics: From Heat Engines to Dissipative Structures* that was published in six languages and is used in over 25 countries. He shares a much cherished memory of Prigogine:

> When I was at the University of Texas at Austin, there were times when Prigogine came by my office and said "Dilip, let us go and have some coffee… if it is ok," characteristically patting his chest lightly with his left hand. I took it to mean he wanted to get away from his office and talk about some idea he wanted to clarify in his mind. I loved those informal discussions with him. It was my chance to see him develop an idea through discussion, to know what he thought of an idea I was pursuing and to ask him to clarify something he said at a recent lecture that I did not understand. We often went to a small bakery near the university with a long name, "Captain Quackenbush's Intergalactic Dessert Company and Espresso Café" There we sat, with a cup of good European coffee, and he often talked about how physics had to be altered to make irreversibility fundamental to it. I can still hear his voice in my mind, "It is so amazing, people are so believing in time reversibility." I made it a point to take pad and pen with me to these coffee chats. One day, he wrote an outline of how he thought general theory of relativity and thermodynamics can be combined to make irreversibility fundamental. I saw a grand plan in it, and I kept that piece of paper. I still have it in my folder of Prigogine memorabilia.

Tomio Petrosky met Ilya Prigogine in 1980 and worked closely with him and was one of his closest colleagues towards the end of Prigogine's life. They authored many papers together. He also often went to the bakery "Quackenbush" mentioned above by Kondepudi for chatting on any kind of subjects with Prigogine. His recollections:

> Occasionally we heard words of wisdom from Prigogine. He said, "There were two most important things in my life. The one is encounter with people. The other is discussion with my colleagues. If you do not discuss, you can get only the result you wish." Once at a press conference in Japan, Prigogine was asked what the source of his drive and motivation to continue scientific work are. He replied, "It is dissatisfaction! It seems to me that many scientists are satisfied with the present explanation of basic laws in physics, especially those concerning time. I feel something is unsatisfactory. To remove this dissatisfaction is my strong motivation to continue science."

John Pojman was a graduate student at Texas from 1984–1988 and he recalls how Prigogine affected his career:

> I became interested in chemical self-organization my senior year at Georgetown University. I spoke with Professor Joseph Earley, who had demonstrated the Belousov-Zhabotinsky reaction in my general chemistry class three years earlier, and he said I should go to graduate school at the University of Texas at Austin and work with Professor Prigogine. I applied to UT and visited Austin in the Spring of 1984. I had written a letter to Professor Prigogine and arranged an appointment to meet him. He met me in the lobby of his apartment building, wearing slippers and invited me to come up to his apartment. He was very gracious, stating "I have a half an hour, what would you like to talk about?" I do not remember what I replied but he proceeded to give a lecture on the arrow of time and how empires not only decline and fall but also rise. I was enthralled by his approach and ultimately attended UT where I worked jointly with Professor Prigogine and Professor James Whitesell in Chemistry. I met with Prigogine twice a year during his visits to UT, and he continued to inspire

my interests in self organization. Although my de facto advisor was Dilip Kondepudi, who was then a postdoc, Professor Prigogine supported my study of polymer interchange reactions as a Maxwell-Boltzmann gas.

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