The 1977 Nobel Prize in Chemistry

The classical subject of thermodynamics is normally taught in a self-contained and complete manner; however, it continues to be at the forefront of research in nearly all fields of science. The 1977 Nobel Prize in Chemistry, awarded to Professor Ilya Prigogine of the Free University of Brussels, Belgium, acknowledges his central role in the advances made in irreversible thermodynamics over the last three decades. Prigogine was awarded the prize for "his contributions to nonequilibrium thermodynamics, particularly the theory of dissipative structures."

The subject of the properties of systems far from equilibrium is a fascinating one. There exist a variety of phenomena not possible near or at equilibrium, including chemical systems with multiple stationary states, chemical hysteresis, nucleation processes which give rise to transitions between multiple stationary states, oscillatory systems, the formation of stable and oscillatory macroscopic spatial structures, chemical waves, and the critical behavior of fluctuations. These topics are receiving increasing attention by scientists in many fields, such as mathematics, physics, chemistry, biology, ecology, population dynamics, and sociology.

To appreciate the advances made by Prigogine and his co-workers, in particular P. Glansdorff, G. Nicolis, and R. Lefever, we need to recall some essentials of classical thermodynamics. Since Boltzmann's time it has been customary to identify entropy as a measure of disorder and thus to interpret the second law of thermodynamics as a principle of increasing disorder. Isolated systems—as well as equilibrium systems, which may exchange energy and matter with the surroundings—attain maximum disorder, subject to the imposed constraints, such as constant temperature. In equilibrium systems there may appear structures, such as a crystal, which one characterizes by an extremum in the appropriate thermodynamic potential. All equilibrium structures are stable to small perturbations. The classical Gibbs-Duhem stability theory applies to equilibrium structures and predicts that any spontaneous fluctuation regresses in time and disappears.

Since the turn of the century, examples of phenomena have been found which appear to be in conflict with the principle of maximum disorder. In 1898 R. E. Liesegang discussed a periodic precipitation phenomenon which occurs when a concentrated salt solution, such as lead nitrate, diffuses into an aqueous medium (often with a lyophilic gel such as agar-agar) containing, for example, potassium iodide. The resulting precipitate, in this case lead iodide, forms discontinuously in bands parallel to the diffusion front, which are now known as Liesegang rings.

Figure 1 shows a Liesegang ring pattern. An ordered structure forms spontaneously; spatial gradients are initially present, although in fact that condition is not necessary. In an initially homogeneous solution in which the bromination of malonic acid occurs (Belousoff-Zhabotinsky reaction) the patterns shown in Fig. 2 may develop. Both examples are systems initially far from equilibrium; the unconstrained equilibrium probability for the appearance of such a structure is vanishingly small.

In hydrodynamics the Benard problem involves the thermal stability in horizontal layers of fluid heated from below. For some critical value of the Rayleigh number, the state of the fluid at rest becomes unstable and a cellular convection structure of macroscopic dimensions appears.

Biological systems show a high degree of organization and order. In a remarkable article published in 1952, A. Turing proposed a model for the structural origin of biomorphogenesis based on a set of hypothetical chemical reactions with nonlinearities and feedback loops coupled to diffusion, and showed thereby the possibility of the formation of macroscopic, spatial structures. However, this work was essentially ignored. It needed the insight and determination of Prigogine and his co-workers to recognize the potential importance of the subject and to stimulate activity in the scientific community. Prigogine started an extensive investigation of the mechanisms that bring about spontaneous organization. Simpler models than those proposed by Turing were devised so that preliminary studies of instabilities could be more easily accomplished. Next Glansdorff and Prigogine turned to thermodynamic issues, in particular the extension of thermodynamic theory to include the possibility of creation of order.

Ilya Prigogine

The departure from classical equilibrium thermodynamics started with two famous papers of L. Onsager published in 1931, for which he was awarded the 1968 Nobel Prize in Chemistry. In these papers Onsager showed that thermodynamic methods can be applied to nonequilibrium situations not too far from equilibrium. The term "not too far" is well defined in the sense that this is the regime where linear relations between fluxes (of heat, matter, and so on) and thermodynamic forces (such as temperature gradients and chemical potential gradients) hold. This relation is represented by the equation

$$J_i = \sum_j L_{ij} X_j$$

where J_i is the ith flux and X_j is the jth thermodynamic force. Onsager proved that the coefficients L_{ij} are symmetric ($L_{ij} = L_{ji}$). This important result, known as Onsager's reciprocal relations, opened the way for an extensive discussion and application of the thermodynamics of near-equilibrium phenomena. Onsager also made a statement concerning the "principle of least dissipation of energy," which applies to stationary states in the linear regime. The statement implies that a physical system open to fluxes evolves until it attains a stationary state where the rate of dissipation is minimal. Prigogine proved this implication with great generality in 1945 and called it the principle of minimum entropy production.

The new discoveries concerning the near-equilibrium regime, important as they were, did not show a radical change with respect to equilibrium theories. Prigogine and his co-workers showed that the very fact that near-equilibrium stationary states are characterized by minimum entropy production renders them uninteresting in a certain sense. The entropy production was proved to be a Lyapounoff function, and therefore the stationary states are always stable. Any spontaneous fluctuation that arises in the system regresses in time and disappears. A system near equilibrium cannot evolve spontaneously to new and interesting structures.

Prigogine and his group, as well as others, started to investigate systems with nonlinearities obtained by autocatalysis or feedback loops in the reaction mechanism driven far from equilibrium. They found radically different behavior and unexpected results. As the system is driven far from equilibrium, it may become unstable and then evolve spontaneously to new structures showing coherent behavior. Prigogine refers to the equilibrium and near-equilibrium states as the thermodynamic branch, whereas the new structures are called dissipative structures. The important point is that beyond the instability of the thermodynamic branch, physical systems show a new type of organization relating the coherent space-time behavior to the dynamical processes inside the system. The dissipative structures can be maintained only through a sufficient flow of energy and matter. The work required to maintain the system far from equilibrium is the source of the formation of order. Fluctuations play a crucial role near the point of instability (in some way similar to critical points in phase transitions); they become large on a macroscopic scale and are built up by the nonlinear behavior of the system into dissipative structures.

The central question concerns the conditions of instability of the thermodynamic branch. The theory of stability of ordinary differential equations is well established. The problem that confronted Prigogine and his collaborators was to develop a thermodynamic theory of stability that spans the whole range of equilibrium and nonequilibrium phenomena. In 1971 Glansdorff and Prigogine published a monograph on a thermodynamic theory of stability in which the key concept is again related to the entropy production. It is assumed that there exists a local entropy, and expansion of the deviation of that quantity yields the "excess entropy" $\delta^2 S$

$$\Delta S = (\delta S) + \frac{(\delta^2 S)}{2} + \ldots$$

which is a quadratic negative definite expression. Moreover, the time derivative of 1/2 $[\delta^2 S]$ is the entropy production. Whenever $\partial\delta^2 S/\partial t > 0$ the excess entropy is a Lyapounoff function and the state is stable. A sufficient condition of instability is therefore $\partial\delta^2 S/\partial t < 0$. This important result is limited to small fluctuations because higher-order terms were neglected in the expansion of the entropy, but this is adequate for an instability condition. Further, the sufficient condition for instability applies to time-independent boundary conditions. The extension to more general situations remains to be done.

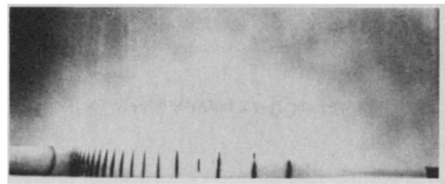

Fig. 1. Leisegang ring pattern in PbI_2. [From Flicker and Ross (*1*)].

Fig. 2. Spiral wave patterns in the Zhabotinsky reaction. [From A. T. Winfree, Purdue University]

The thermodynamics of processes far from equilibrium provides an important framework for analyzing the consequences of the onset of instability. Given the deterministic equations of motion (kinetics and diffusion, for instance), one can of course determine the onset of instability by linearization techniques. However, evaluation of the developed dissipative structure requires solution of the full nonlinear equations. Much theoretical work has been done by the Brussels group and others on systems with multiple stationary states, the formation of macroscopic spatial structures, chemical waves, and the character of fluctuations far from equilibrium. The concept of instability in reaction mechanisms has been developed in some detail for an analysis of prebiotic evolution.

The possibility of building order through fluctuations under extreme nonequilibrium conditions has implications for biomorphology, embryology, and evolution. The maintenance of highly ordered structures requires exchange of energy and matter with the surroundings, and only this constant flux supports the high degree of organization needed for existence. The concept of dissipative structures provides a model construct for the analysis of these difficult problems.

The ideas of self-organization are not limited to chemical and biological systems. Similar phenomena occur in population dynamics, meteorology, chemical engineering, and economics. Prigogine likes to point out the analogy to urban existence. A big town can survive only as long as food, fuel, and other vital commodities flow in while products and wastes flow out.

The commonality of problems in many different fields has led Prigogine to stress the philosophical implication of his studies. He points out that the 19th century saw the idea of evolution emerging with apparently two different implications. In thermodynamics the second law appears as the evolution law of continuous disorganization, or the disappearance of structure introduced by the initial conditions. In biology or in sociology, the idea of evolution is, on the contrary, related to the increase in organization, resulting in structure whose complexity is ever increased. Thus the classical thermodynamic point of view indicated that chaos is progressively taking over, whereas biology points in the opposite direction. Are there two different sets of physical laws that need to be involved to account for such differences in behavior? The general conclusion of Prigogine's work is that there is only one type of physical law, but different thermodynamic situations: near and far from equilibrium. Destruction of structure is the typical behavior in the neighborhood of thermodynamic equilibrium. Creation of structure may occur, when nonlinear kinetic mechanisms operate beyond the stability limit of the thermodynamic branch. All these various situations obey the dicta of the second law of thermodynamics.

The study of nonlinear phenomena is at present an open and live field. Many questions of great interest need to be answered. Experimental efforts lag behind theoretical advances. It is gratifying that the Nobel Prize has been awarded to the man who set an important and promising field in motion. With extraordinary enthusiasm and drive, Prigogine has established a school of thermodynamics that has stimulated and influenced scientists in many fields around the world.

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