THERMODYNAMIC THEORY OF STABILITY, STRUCTURE AND FLUCTUATIONS

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ABSTRACT

The development of the thermodynamics of irreversible processes is outlined with a review of recent work and a discussion of the application of these concepts to physicochemical, biological and hydrodynamic phenomena. The extension of local thermodynamics to include a theory of stability and of fluctuations receives attention. The author concludes with remarks on the stability properties of chemical reactions in open systems and comments on the possible implications of results in the interpretation of fundamental biological phenomena.

1. INTRODUCTION

Classical thermodynamics deals with transformations involving equilibrium states. Once the validity of the second law is admitted, one considers exclusively systems which have already reached thermodynamic equilibrium. The behaviour of these systems is then completely described in terms of a set of state functions, the *thermodynamic potentials*, whose extremal properties determine both the equilibrium state itself and its stability properties[1].

Many attempts to enlarge equilibrium thermodynamics in order to include irreversible changes have been made since the second law was formulated in the middle of the previous century. The early considerations were, however, restricted to the treatment of very special irreversible processes, such as thermoelectric effects. In addition, although a number of scientists such as P. Duhem[2] had already conceived the beginnings of a macroscopic physics embracing both equilibrium and non-equilibrium phenomena, it was only recently, and particularly during the last twenty years, that we have witnessed the firm foundations and the rapid growth of the thermodynamics of irreversible processes. The present object will be to present a review of recent developments in irreversible thermodynamics and to discuss the application of these concepts to the study of physicochemical, biological and hydrodynamic phenomena. The first point to explore will therefore be the following. Is it possible to extend the methods of classical thermodynamics to treat all possible phenomena starting from close to equilibrium states and including arbitrary non-linear situations? In fact we will answer this question by defining a set of conditions which will guarantee a first extension of thermodynamics to non-equilibrium situations. It is not claimed that these conditions apply to all irreversible changes and it is quite possible that

a consistent thermodynamic theory could be set up under less restrictive conditions.

Let any given thermodynamic system be divided into microscopically large but macroscopically small subsystems each having a given volume V. We also assume that it is meaningful to specify at any given moment in the subsystem the internal energy content, E and the mole fractions, n_i of species i. At equilibrium the thermodynamic quantities such as temperature T, pressure p, chemical potential μ_i of component i, entropy S, are well-defined quantities depending on E, V and n_i. If now equilibrium does not hold, it is necessary to re-define all these quantities. We assume that T, p, μ_i and S for each subsystem of a globally non-equilibrium system depend on E, V and n_i in exactly the same way as in equilibrium. In other terms, one proceeds as if equilibrium prevailed in each subsystem separately. This is known as the assumption of *local equilibrium*. Analytically, this implies first that a local formulation of non-equilibrium thermodynamics is possible. And secondly, that in this formulation the local entropy will be expressed in terms of the same independent variables as if the system were at equilibrium. In other words, if ns is the entropy density, ne the energy density, and v the specific volume the well-known Gibbs relation will hold locally:

$$s = s(ne, v, n_i)$$
$$T\, d(s) = d(e) + p\, dv - \sum_i \mu_i\, dn_i \tag{1}$$

The local formulation of irreversible thermodynamics based on equation 1 has been worked out systematically by Prigogine[3]. A few years later the same author established the domain of validity of this local equilibrium assumption by showing that it implies the dominance of dissipative processes over purely mechanical processes. In more specific terms, at a given point, the molecular distribution functions of velocities and relative positions may only deviate slightly from their equilibrium forms[4].

In his original work Prigogine considered the case of weakly coupled systems (behaving as systems of non-interacting degrees of freedom at equilibrium). For such systems entropy may be defined in terms of the local molecular distribution function $f_1(\mathbf{x}, \mathbf{v}, t)$ ($\mathbf{x}$ is the position, $\mathbf{v}$ the velocity of a particle) through the Boltzmann relation

$$ns = -k \int d\mathbf{v} f_1 \ln f_1 \tag{2}$$

where k is Boltzmann's constant.

The extension of Prigogine's results to the case of strongly coupled systems is not trivial, due to difficulties in defining entropy for such systems in terms of the molecular distribution functions. Recently, however, Prigogine and co-workers have elaborated a quasi-particle representation of statistical mechanics which permits description of the thermodynamic properties of strongly coupled systems in terms of new entities, the dressed particles. In this representation ns takes the form

$$ns = -k \int d\mathbf{v} \tilde{f}_1 \ln \tilde{f}_1 \tag{3}$$

where $\tilde{f}_1$ is now the one quasi-particle distribution function. In general $\tilde{f}_1$ is a complicated functional of f_1 due to the interactions. Using now this entropy

definition J. Wallenborn, M. G. Velarde and the author have extended Prigogine's conclusions to strongly coupled systems[5]. Again it was necessary to assume that the (quasi-particle) distribution function may only deviate slightly from its equilibrium form.

Clearly this is a sufficient condition which guarantees the applicability of the thermodynamic methods. It is conceivable that an irreversible thermodynamics may be constructed based on more general conditions. For instance, Coleman[6] has recently worked out a non-local theory adapted to the study of materials with memory. We do not discuss this approach here but only focus attention on the local formulation.

It should be pointed out that the local equilibrium assumption permits treatment of a great variety of problems corresponding to situations far removed from complete thermal equilibrium. For instance very complicated chemical reaction schemes with extremely large affinities may be treated adequately provided that they are not too fast. Similarly all effects described by the Stokes–Navier equations, including hydrodynamic instabilities, are within the domain of the local equilibrium theory.

Here we discuss the applications of the theory to non-equilibrium situations with special emphasis on typically non-linear problems which cannot even be formulated within the framework of classical thermodynamics. We first present in section 2 a brief review of the general theory and of its applications in the linear region. We then discuss, in section 3, the extension of irreversible thermodynamics arbitrarily far from equilibrium and sketch a unified approach to problems as different as non-linear transport phenomena, hydrodynamic instabilities and so on. In section 4 we discuss an extension of local thermodynamics to include a theory of fluctuations. This is necessary, especially for a theory seeking to describe unstable situations. The final sections 5 and 6 are devoted to the study of chemical reactions in open systems and to comments on the possible implications of the results in the understanding of fundamental biological phenomena.

2. GENERAL FORMALISM—THE LINEAR REGION

The starting point is of course the second law of thermodynamics which deals with the entropy change, dS in a system. Let dS be split into two parts[3]. We denote by d_eS the flow of entropy due to interactions with the external world and by d_iS the change in S due to processes inside the system, or *entropy production*. We have

$$dS = d_eS + d_iS \tag{4}$$

The second law refers to d_iS only and reads

$$d_iS \geqslant 0 \tag{5}$$

where the equality applies for reversible changes.

Using the local equilibrium assumption we may now proceed in the calculation of the entropy production per unit time and volume, σ, defined by

$$P = \frac{d_iS}{dt} = \int dV \sigma \tag{6}$$

$$\sigma \geqslant 0$$

381

The calculation consists of developing equation 4 using the Gibbs equation 1 and then substituting de, dv, dn_i from the balance equations of mass, momentum and energy. The final result is[3]

$$\sigma = \sum_i J_i X_i \tag{7}$$

σ is therefore a bi-linear form summed over all irreversible processes i, of suitably defined flows, J_i, associated with these irreversible processes, and of generalized forces X_i giving rise to these flows.

It is clear that, as long as the flows are parameters not related to the corresponding forces, the equations of thermodynamics do not permit the explicit study of the evolution of a system subject to well-defined boundary conditions. It is therefore necessary to combine the general balance equations with additional, phenomenological laws relating Js and Xs. Now experiment shows that at thermal equilibrium there is no macroscopic transport of mass, momentum or energy; as a result all currents J_i vanish. On the other hand the conditions of thermal equilibrium imply the absence of constraints such as systematic temperature gradients etc. Therefore the generalized forces X_i vanish at the same time as J_i do. It is thus quite natural to assume that, in the neighbourhood of equilibrium, linear laws between flows and forces will constitute a good first approximation. The phenomenological laws will therefore take the form

$$J_i = \sum_j L_{ij} X_j \tag{8}$$

where the sum is over (coupled) irreversible processes and the phenomenological coefficients $\{L_{ij}\}$ are in general functions of the thermodynamic state variables T, p etc. Equations 6 define the linear domain of irreversible processes[7, 8].

The coefficients $\{L_{ij}\}$ cannot be arbitrary. It has been known for a long time that the diagonal coefficients are non-negative. On the contrary, it was only in 1931 that Onsager established the first general relations between the non-diagonal coefficients[9]. He showed that it is always possible to choose the flows and forces such that the matrix $[L_{ij}]$ be symmetrical

$$L_{ij} = L_{ji} \tag{9}$$

These are the celebrated Onsager reciprocity relations which were later generalized by Casimir to a wider class of irreversible phenomena[10].

The proof followed by Onsager relates concepts as different at first sight as fluctuations and macroscopic transport phenomena. This was a very important first step towards a justification of irreversible thermodynamics. It is remarkable that more recent work on the foundations of thermodynamics has fully justified the original Onsager relations. At the same time these works, which are based principally on non-equilibrium statistical mechanics, have established the domain of validity of equations 8 and 9 to be the domain of small deviations of the momentum distribution functions from their equilibrium values[11].

The phenomenological laws 8 together with Onsager's relations 9 constitute a convenient framework within which one can study a great number of irreversible phenomena in linear approximation[7, 8]. Interesting as it is, this

approach is, however, only a particular aspect of irreversible thermodynamics. The local formulation of irreversible thermodynamics has been developed in yet another direction—the search for variational principles. The question one asks is whether there exists a general principle—other than the second law—characterizing non-equilibrium states themselves independently of the details of phenomena occurring in the system. In order to formulate this question quantitatively it is necessary to analyse in some detail the character of a non-equilibrium state in thermodynamics. In an isolated system one has $d_eS = 0$ and the second principle implies that entropy increases until it reaches its maximum value. The system thus tends more or less rapidly to a uniquely determined permanent state which is the state of thermodynamic equilibrium. Consider now instead of an isolated system a closed system which can exchange energy with the external world, or an open system which can exchange both energy and matter. In this case, and provided the external reservoirs are sufficiently large to remain in a time-independent state, the system may tend to a permanent régime other than the equilibrium one. This will be a *steady non-equilibrium state*. Now this régime is no longer characterized by a maximum of entropy (as $d_eS \neq 0$) or by a minimum of free energy. In other terms, the variational principles valid in thermal equilibrium cannot be extended beyond this state. It is therefore necessary to look for new principles which generalize the concept of a thermodynamic potential to steady (or slowly varying in time) non-equilibrium states. To this end we subdivide the domain of non-equilibrium phenomena into two parts: the region close to equilibrium and the region of states arbitrarily far from equilibrium. Here we deal only with the first region, i.e. the linear domain of irreversible processes, and we only consider systems in mechanical equilibrium.

In his classical work on reciprocity relations[9] Onsager had already proposed a variational principle for such non-equilibrium states which he called the *principle of least dissipation of energy*. In this principle it is understood that the thermodynamic forces remain fixed and only the macroscopic currents may vary.

On the other hand Prigogine has shown[3, 7] that steady states close to equilibrium are also characterized by an entirely different variational principle according to which, at the steady state, the entropy production per unit time is a minimum

$$d_iS/dt = \text{minimum} \qquad (10)$$

The interest of this principle is that it implies the existence of a thermodynamic potential, the entropy production, as a non-equilibrium state function. The physical interpretation of this principle is therefore quite different from Onsager's variational principle. In addition, in the least dissipation principle the flows vary but the forces are fixed, whereas in the minimum entropy production principle the flows vary at the same time with the forces and are only subject to the boundary conditions imposed on the system.

Certainly, both principles determine correctly at the steady state the distribution of currents and forces in the system. However, we mainly deal here with the consequences of the minimum entropy production principle

which was the only one to have been extended beyond the linear domain. Before we discuss non-linear problems let us outline some interesting aspects of this principle.

In the first place, it is important to realize that it provides a general *evolution criterion*. Indeed, the validity of the theorem of minimum entropy production together with the second law implies that a physical system will necessarily evolve to the steady non-equilibrium state and that the latter corresponds to a stable situation. On the other hand it can be shown[7] that, under certain conditions, the steady state which, by the theorem, is characterized by a minimum of dissipation or so to say by a maximum of efficiency, is also characterized by a lower value of entropy than at equilibrium: increased efficiency is thus combined with an increasing complexity of structure (as measured by the entropy reduction). In this way the theorem of minimum entropy production provides a link between the concept of '*structure*' and of '*evolution*' towards a dissipative state[12].

The interest of these concepts and the possibility of a connection between them might seem academic in the framework of a linear description of irreversible processes but it acquires a fundamental importance in the non-linear region.

3. NON-LINEAR THERMODYNAMICS

For a long time non-equilibrium thermodynamics was confined to the study of linear problems. There exist, however, a large number of important and even quite frequently occurring phenomena which cannot be described by the methods of linear thermodynamics even in a first approximation. For instance, with chemical reactions it is often necessary to adopt non-linear phenomenological laws. Also whenever a system is not at mechanical equilibrium the coupling between dissipative and convective processes leads to effects of a new type which cannot be treated by the methods of linear theory.

The extension of the local formulation of thermodynamics to the non-linear region has been achieved during the last fifteen years by Glansdorff and Prigogine[7, 13, 14]. In its present form it comprises three essential aspects: (i) the derivation of general evolution criteria for steady states far from equilibrium, (ii) the search of thermodynamic potentials characterizing these states, (iii) the study of stability of these states. We shall now briefly comment on each of these points separately.

(i) The problem of evolution criteria was solved in two steps, the first involving a discussion of purely dissipative processes[15] the second providing an extension to systems involving mechanical motion[13, 16, 19]. The final result is as follows. In the whole domain of phenomena which are adequately described by a local theory it is possible to construct a differential expression $d\Phi$ depending on the state variables such that

$$d\Phi/dt \leqslant 0 \qquad (11)$$

the equality being applicable at the stationary state. $d\Phi$ is a combination of dissipative and convective processes. In the absence of convective motion it can be shown that[15]

$$d\Phi = \int dV \sum_i J_i dX_i \equiv d_x \mathscr{P} \qquad (12)$$

i.e. $d\Phi$ is the variation of entropy production per unit time due to a change in the generalized forces. As in the general case the flows J_i are complicated functions of X_is it follows that in principle $d\Phi$ *is a non-total differential*; in other words $d\Phi$ does not represent the variation of a thermodynamic state function. It is only in the limit of linear phenomena and of validity of the Onsager relations that it becomes the differential of a state function, the entropy production. In this case the evolution criterion can be reduced to the theorem of minimum entropy production.

(ii) The fact that $d\Phi$ is not a total differential in the general case gives rise to the problem of the search for a variational principle. This is a very complicated problem which has only recently been properly formulated. The main point is to realize that, except in a number of exceptional cases where suitable integrating factors or suitable classes of transformations make $d\Phi$ a total differential[7, 14], it becomes necessary to formulate an *extended variational principle*. This novel point of view gives rise to a function Ψ, the *local potential* according to the terminology introduced by Glansdorff and Prigogine[16], which shares some of the properties of the potentials of classical thermodynamics. However, it is necessary to look at Ψ as a functional of two sets of functions, average ones corresponding to (quasi-steady) solutions of the macroscopic equations and fluctuating quantities. The extended variational principle has therefore to be understood in terms of fluctuation theory. The Euler–Lagrange equations corresponding to Ψ can be reduced then in the average to the equations of macroscopic physics, i.e. provided at the very end the fluctuating functions are set equal to their average values.

Certainly, the property of the first variation of Ψ to generate the equations of evolution is also shared by functionals other than the local potential. For instance for an equation of evolution

$$L(u) = 0 \tag{13a}$$

defined in a domain V of the independent variable x, the functional

$$\Psi_1 = \int_V \mathrm{d}x u L(\bar{u}) \tag{13b}$$

(where u and $\bar{u}$ are respectively the fluctuating and average values of u) gives rise to equation 13a by means of an ordinary variational procedure. If now the unknown functions u in the local potential and in the functional 13b are approximated, e.g. by a series expansion, the variational equations resulting from the local potential or from 13b are both identical to the equation obtained when 13a is approximately solved by the well-known Galerkin method[13, 14].

As a result the Galerkin method gives the same approximations as those based on the local potential. It can be shown, however, that the extended variational procedure is supplemented by *a minimum property* expressing that the excess local potential is positive definite around the non-fluctuating state. This fundamental property which is largely responsible for the physical significance of Ψ has permitted us to establish convergence of the variational procedure[17]. It also made it possible to treat in a unified way many interesting non-linear hydrodynamic and stability problems[18, 19].

(iii) The property of $d\Phi$ not to be a total differential and the lack of a true variational principle also imply that steady states far from equilibrium are

no longer characterized by the minimum of a thermodynamic potential. As a result *the stability of these states is not always ensured.* This separation between evolution and stability leads thus to the search for independent stability criteria for states far from equilibrium. Recently a complete *infinitesimal* stability theory of non-equilibrium states has been worked out[14,20-22]. The main result is as follows. Within the domain of validity of the local formulation of thermodynamics it is possible to construct a negative definite quadratic form

$$\delta^2 z = \delta^2 s - (\delta v)^2/T < 0 \qquad (14)$$

where s is the specific entropy, v the average hydrodynamic velocity and δ denotes the variation of the corresponding quantity as a result of a fluctuation. It can be shown that whenever the equilibrium stability conditions are satisfied[1], $\delta^2 s$ is itself a negative semi-definite quadratic form even around states far from thermodynamic equilibrium

$$\delta^2 s \leqslant 0 \qquad (15)$$

Moreover, in the limit of small fluctuations,

$$(\partial/\partial t)\,\delta^2 z > 0 \qquad (16)$$

in all cases the non-equilibrium state is stable. Clearly this formulation is closely related to the ideas underlying Lyapounov's stability theory[23].

The important point is, however, that equations 14 to 16 constitute *a thermodynamic stability criterion.* Let us emphasize once more that in order to derive this criterion it has been necessary to go beyond the fundamental equation 7 and establish excess balance equations for the quadratic fluctuations, $\delta^2 s$ and $(\delta v)^2$, of entropy and kinetic energy.

Equation 16 contains a complicated interplay between purely dissipative and convective processes. In the neighbourhood of equilibrium it can be shown that the stability criterion is trivially fulfilled once $\delta^2 s < 0$. Alternatively, the existence of thermodynamic potentials guarantees the stability of near-equilibrium states except in the neighbourhood of phase transition points. Moreover, it follows from equations 14 to 16 that internal convection processes can never arise in this limit[13]. Far from equilibrium, however, relation 16 does not follow from 14 and 15 and therefore the stability of the system may be compromised even when the equilibrium state is perfectly stable. If an instability occurs the system necessarily tends to a new régime which may correspond to a completely different state of organization of matter. Since equilibrium remains stable we may say that unlike what happens close to equilibrium, this new régime is not a continuous extrapolation of the equilibrium behaviour.

4. FLUCTUATIONS

At this point the problem of the behaviour of fluctuations becomes quite essential. In a system characterized by a large number of degrees of freedom, such as a typical macroscopic body, fluctuations are always present. Therefore at each moment the system is in a kind of 'dynamical equilibrium' which is determined by the response to its own spontaneous fluctuations.

Usually the fluctuations give rise to a response which brings the system back to the reference state. On the contrary, at the point of an unstable transition fluctuations are amplified and give rise to observable effects. Therefore a new structure which may arise beyond an instability always originates in a fluctuation. As a result a purely deterministic description of the system is no longer sufficient and it becomes necessary to extend irreversible thermodynamics in order to include a macroscopic theory of fluctuations.

Let us recall how this problem is solved at equilibrium. In an isolated system Boltzmann's relation defining entropy in terms of number of states available may be inverted to give rise to the classical Einstein formula giving the probability of fluctuations around a *macroscopic* (equilibrium) state[1,23].

$$P \propto \exp [\Delta S/k] \qquad (17)$$

where ΔS is the entropy change around equilibrium ($\Delta S < 0$ for a fluctuation) and k Boltzmann's constant. For small fluctuations ΔS may be expanded to second order quantities. Since for an isolated system at equilibrium S is a maximum, equation 17 can be reduced to the second variation term

$$P \propto \exp [\delta^2 S/k] \qquad (18)$$

What is the generalization of expression 18 to non-equilibrium situations? As we say in section 3 the basic property $\delta^2 S < 0$ which is responsible for the validity of expression 18 is also shared by fluctuations around non-equilibrium states provided the local equilibrium assumption is made. It is therefore tempting to build a non-equilibrium fluctuation theory based, in a first approximation, on expression 18, wherein the excess quantities are calculated around *a non-equilibrium reference state*[25-27]. If this conjecture is justified one will be able to predict the behaviour of fluctuations by studying $\delta^2 S$ and the way it evolves in time and obtain therefore a relation between stability properties and fluctuations.

Attempts to justify the local equilibrium fluctuation theory have been made by Lax[28]. More recently Babloyantz and the author have developed a master equation approach to fluctuations which is applicable to systems arbitrarily far from equilibrium and to the study of arbitrarily large fluctuations[29-31]. In all cases treated the extension of expression 18 to non-equilibrium situations was recovered in the limit of stable systems and small fluctuations, provided some well-defined conditions on the relaxation times were satisfied. These conditions refer to a large separation of time scales between the fluctuating system and the external world. They require the former to be much shorter than the latter so that the state of the environment shall not be influenced by the fluctuating system. This condition is in agreement with the idea that in order to maintain a non-equilibrium macroscopic state one should impose a set of given boundary conditions.

The examples studied by Babloyantz and Nicolis refer mostly to chemical reactions in open systems[29,31] and to energy transfer in a system at mechanical equilibrium[30]. At present our group is involved in work on the stochastic theory of fluctuations in the neighbourhood of unstable transitions. It is expected that this work will permit a clarification of the mechanism of establishment of an instability and of the structure of the final state

beyond the transition point. Indeed, it is the initial fluctuation which will determine the type of future situation. The macroscopic time evolution assumes therefore an essentially statistical aspect.

5. DISSIPATIVE STRUCTURES

In equilibrium thermodynamics instabilities only occur at phase transition points. The new phase beyond instability has a markedly different structure; in particular it may correspond to a more ordered state. For instance at the paraferromagnetic transition at the Curie point a system exhibiting spherical symmetry is replaced by a new one having a lesser cylindrical symmetry. Consequently the ferromagnet which is being formed has a much higher degree of 'organization'. Such structures, however, are completely independent of the external world. Once they are formed they are self-maintained and do not require an exchange of energy or matter with the environment.

In systems far from equilibrium a new type of instability appears, due to the existence of constraints which are responsible for the maintenance of a steady non-equilibrium state. Can one associate with these instabilities the formation of ordered structures of a new type? Such non-equilibrium structures would differ from equilibrium ones in that their maintenance would necessitate the continuous exchange of energy and matter with the outside world. For this reason Prigogine, who first suggested the existence of these states, has called them *dissipative structures*[32, 33].

Let us formulate the problem in thermodynamic terms in its most general form. Consider a non-isolated system (closed or open) subject to constraints which give rise to a steady non-equilibrium state. In this state the values of different thermodynamic variables such as flows etc. depend parametrically on a number of quantities, $\{X\}$ measuring the deviation of the system from equilibrium. For instance, X may be a gradient of temperature or composition, the overall affinity of a set of coupled chemical reactions, and so on. Let us adopt the convention that the state $\{X = 0\}$ is the state of thermodynamic equilibrium. For $\{X \neq 0\}$ but small the equilibrium régime is continued · by the steady states close to equilibrium whose stability is guaranteed once equilibrium is stable. On the contrary, for $\{X \neq 0\}$ and arbitrarily large, although it is always possible to define a continuous extrapolation of the equilibrium régime, the stability of the states belonging to this branch, which will be referred to as *thermodynamic branch*, is no longer ensured automatically. In addition, the uniqueness property of the equilibrium state is not applicable in this case and the system may present more than the stationary state, provided it obeys non-linear laws. One of these stationary states belongs to the thermodynamic branch but is not necessarily stable. It is therefore possible, *a priori*, to have a number of new effects, for instance: the system may not decay monotonically to the steady state belonging to the thermodynamic branch, once it is perturbed from it; in the limit it may even never return to this state but evolve to a time-dependent régime: under similar conditions it may finally deviate and evolve to a new stationary régime corresponding to a branch different from the thermodynamic one. This transition will manifest itself abruptly as an *instability*, i.e. as a fundamentally discontinuous process.

This situation is frequently met in hydrodynamics. In this domain the problem of instabilities is a classical one which has been studied thoroughly since the early years of the present century[13, 36]. Recently Glansdorff and Prigogine have shown that the general formulation of non-linear thermodynamics provides a framework which permits a thermodynamic analysis of such instability phenomena. They have also been able to formulate their conclusions in terms very similar to phase transitions. Amongst the different problems treated let us quote: the onset of thermal convection in a horizontal fluid layer heated from below (Bénard problem); stability of waves and the formation of shocks and detonations; stability of parallel flows; and so on[13, 14, 16, 18].

The occurrence of instabilities and the subsequent formation of structures is a much less obvious effect for purely dissipative systems, i.e. systems without mechanical motion. In fact, it is only during the last few years that this possibility has been studied systematically and a theory of dissipative structures has been set up for such systems[32, 33, 35–37]. The types of problems which were studied most actively refer to open systems undergoing chemical reactions.

This problem presents a special interest because of the possible implications of the results in the understanding of biological phenomena. Indeed, typical biological processes appear to happen under open system conditions (exchange of ions through membrane processes, ADP ⇆ ATP transformations inside the cell and so on). It is therefore tempting to associate biological structures with dissipative structures arising beyond a chemical instability.

Let us first analyse the non-equilibrium phenomena which may arise in open systems in the neighbourhood of instabilities. We may distinguish between three possible types of situation: (i) oscillations around steady states, (ii) symmetry-breaking instabilities and (iii) multiple steady states.

(i) Although oscillations were suggested a long time ago by Lotka and Volterra[38], it is only during the last few years that there has been a great accumulation of data on the occurrence of time oscillations in systems of chemical reactions. Even more interesting, biochemical reactions of fundamental importance have been shown to exhibit oscillatory behaviour in time. Let us quote for example: oscillations in metabolic reactions comprising activation or inhibition (glycolysis[39, 40]); oscillations in protein synthesis in the cellular level (β-galactosidase synthesis in *Escherichia coli*[41] and so on[42]). These phenomena have recently been investigated from a thermodynamic standpoint. It has been necessary to distinguish between two fundamentally different types of behaviour: oscillations having the same character as those occurring in conservative systems (Volterra–Lotka type oscillations[42]) and oscillations beyond a chemical instability[44]. At present it appears that oscillation in metabolic reactions can best be explained by the second type of mechanism. In other words, a biochemical oscillating system would be a dissipative structure.

(ii) This conjecture, which suggests the fundamental importance of the concept of dissipative structure, is also substantiated by the study of symmetry-breaking instabilities[32, 33, 35, 36, 45–47]. This term refers to the spontaneous appearance of spatial structure in a previously homogeneous system. The important point is that this spontaneous self-organization has

interesting implications from the point of view of both the *space order* and the *function* of the system. Systems which are able to transform part of the energy or matter received from the outside world into macroscopically distinguishable internal order may well exhibit this type of phenomenon and therefore be typical examples of dissipative structures. Again biological systems certainly belong to this category. It is therefore very tempting to associate biological structures with chemical instabilities leading to a spontaneous self-organization[47].

(iii) A change in functional behaviour may also arise in systems which keep their macroscopic space order unchanged. As an example a system may flip-flop between two simultaneously stable steady states which differ only in the levels of concentration of different constituents. It is well known that the classical Jacob–Monod model of regulation in protein synthesis gives rise to such types of transitions which may be associated with 'mutations'[48]. Another very interesting application is in the functioning of excitable membranes. Roughly speaking, a biological excitable membrane may exist in two permanent states: one polarized (associated with the maintenance of different ionic concentrations in the two sides) and one depolarized state derived from the former upon passage of a pulse or upon a change in permeability. It has been shown that this depolarization process may be quantitatively interpreted as a transition arising beyond the point of instability of the polarized state. This instability is due to the difference in the ionic concentrations which here plays the role of the constraint keeping the system in a far from equilibrium state[49].

Summarizing, we may say that instabilities in the thermodynamic branch of solutions can lead to time or space organization and to a change in functional behaviour in open systems undergoing chemical reactions. These instabilities can only arise at a finite distance from thermodynamic equilibrium, i.e. their occurrence necessitates a minimum level of dissipation. Structure and dissipation appear therefore to be intimately connected far from equilibrium. At the same time the system becomes more 'flexible' in this region as it can now occur in a multitude of stable states. This is a very important property which may well be the basis for a thermodynamic theory of evolution in biology.

Computer and laboratory experiments have now confirmed the existence of dissipative structures in certain models[45,46] and also in particular biochemical[39,40] and organic[50,51] reactions. Of course, much remains to be done before it becomes possible to evaluate the full impact of the theory in the interpretation of fundamental biological phenomena.

All these complicated new effects can be and have been analysed within the framework of non-linear thermodynamics outlined in sections 3 and 4[14,32,33,43-47,49]. In addition, the stability conditions 14 and 15 provide sufficient criteria for the types of processes which may give rise to dissipative structures. Aside from the condition of finite distance from equilibrium it is shown that non-linear reaction schemes are necessary for the occurrence of instabilities. This certainly covers the most important biochemical reactions where non-linearity appears through cross-catalysis, autocatalysis, activation or inhibition. Additional new information given by the thermodynamic evolution and stability criteria include: fixation of the direction of rotation

in cyclic processes around the steady state; hints about the relative increase of dissipation and energy transfer at the unstable transition point; and so on.

6. CONCLUSIONS

We have seen that, even beyond the linear domain, thermodynamics may yield interesting results concerning the evolution of systems to steady non-equilibrium states and the stability properties of the latter. Non-linear thermodynamics constitutes a framework for a unified study of phenomena as different at first sight as hydrodynamic instabilities and the formation of spatial or temporal structures in chemistry.

One of the most important features of dissipative structures analysed in the previous section is that they are separated from the thermodynamic branch by an instability. One can say that there exists a real threshold for organization of matter determined by a minimum value of the thermodynamic constraint keeping the system out of equilibrium, which value depends in an intrinsic way upon the parameters descriptive of the system (kinetic constants, diffusion coefficients etc.).

It would thus be very tempting to think that dissipative instabilities act as a kind of phase transition leading to *a new state of matter*. In this new state we have essentially novel properties of the large-scale system, although the laws referring to the molecular level may remain unchanged.

It is exciting to realize that the analogy between dissipative and biological structures may lead to the idea that life and absence of life are just two states of matter separated by a chemical instability. This point of view implies that life follows the laws of thermodynamics appropriate to far from equilibrium conditions. It may therefore help to reconcile the duality between the living and the inanimate world with the unity of the laws of nature.

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