thermodynamic theory of
structure, stability and fluctuations

P. Glansdorff · I. Prigogine

Thermodynamic Theory of
STRUCTURE, STABILITY
AND FLUCTUATIONS

P. GLANSDORFF

and

I. PRIGOGINE

Université Libre de Bruxelles, Brussels, Belgium,
and University of Texas, Austin, Texas

Introduction

The basic description of a mechanical system is in terms of the coordinates and the momenta of the molecules, or in terms of its wave function. However such a description when applied to systems of interest in chemical physics, hydrodynamics or biology leads to great practical and conceptual difficulties. Even if we could conceive computers big enough to study the molecular dynamics of say 10^{23} molecules in a macroscopic system, the knowledge of their positions and their velocities would be of little interest as we would never be able to repeat an experiment involving the same initial state.

The great importance of thermodynamic and hydrodynamic methods is that they provide us with a 'reduced description', a 'simplified language' with which to describe macroscopic systems. In many cases of interest such a reduced description is all that is needed. For instance, to predict the temperature evolution of some piece of metal it is sufficient to solve the Fourier equation with appropriate initial and boundary conditions. The temperature at every point is an average taken over a large number of molecules. The agreement between the predictions of the Fourier equation and experiment shows that a more detailed study of the evolution in terms of mechanical quantities is not required. It is not the purpose of this monograph to analyse the relation between the mechanical and the macroscopic descriptions. This can only be done with the help of statistical mechanics of many-body systems. Here we shall be concerned solely with macroscopic methods.

How far can we proceed with such methods? What is the class of phenomena which may be investigated? These are some of the problems we shall deal with in this book.

It is well known that once the second law is formulated, classical thermodynamics concentrates essentially on the study of equilibrium states. Classical thermodynamics concentrates on the properties of systems which have reached thermodynamic equilibrium (e.g. Schottky, 1929). It is mainly during the last twenty years that we have witnessed the rapid growth of thermodynamics of irreversible processes. The great importance of this development lies in the fact that it makes possible the application of macroscopic methods outside

equilibrium (for a short history of this subject see I. Prigogine, 1947). However this development was essentially limited to the *near-equilibrium* region. In this region, the thermodynamic forces (such as temperature gradient, chemical affinities, . . .) and the thermodynamic flows (such as flow of heat, chemical reactions rates, . . .) are linked by linear relations.

The Onsager reciprocity relations (1931) and the Theorem of Minimum Entropy production (1945) both belong to this *Linear Non-Equilibrium Thermodynamics*.

Today this branch of Thermodynamics of irreversible processes, is a classical subject and is adequately treated in many monographs (especially de Groot and Mazur, 1961).

Is it necessary to go further? Some examples will suffice to stress the interest of an extension of thermodynamics into the non-linear region. Let us first consider the case of chemical reactions. It is well known that if the reaction rate is sufficiently slow not to perturb to an appreciable extent the Maxwell equilibrium distribution of each component, a macroscopic description in terms of average concentrations of the components is possible (for more details, see e.g. Prigogine, 1967). Still the relations between chemical rates and affinities are in general *non-linear*.

Another important field of research where macroscopic methods have been applied with success is *hydrodynamics*. Of special interest for us will be the theory of hydrodynamic stability. It is well known that some simple patterns of flow (such as the Poiseuille flow) are realized only for certain ranges of parameters. Beyond these ranges they become unstable.

As a simple example we may consider the thermal stability in horizontal layers of a fluid heated from below. This is the so-called Bénard problem which we shall study in detail in Chapters XI and XII of this monograph (Chandrasekhar, 1961). For some critical value of a dimensionless parameter called the Rayleigh number, the state of the fluid at rest becomes unstable and cellular convection sets in. Now both below and beyond this instability a macroscopic description of the fluid is possible. Thermodynamic considerations should then be of great importance to understand the location and the meaning of the instability.

Our central problem is thus the following: can we extend the methods of thermodynamics to treat the entire range of phenomena starting from equilibrium and including non-linear situations and instabilities?

We shall see that this extension is indeed possible for the whole class of situations for which the local entropy may be expressed in terms of the *same independent variables* as if the system were at equilibrium. This is the assumption of 'local equilibrium', the validity of which implies the dominance of collisional effects which tend to restore thermodynamic equilibrium. In other words, at no moment molecular distribution functions of velocities or of relative positions, may deviate strongly from their equilibrium form (Chapter II, §2). This condition should be considered here as a *sufficient* condition for the application of thermodynamic methods. It is quite possible that a unified thermodynamic approach could be set up under less restrictive conditions. However, we do not explore this possibility here.

Even so restricted, the extension referred to above, leads to a substantial increase of the power of macroscopic methods. Various problems treated till now by quite different methods may be approached in a new unified way; even some problems of classical equilibrium thermodynamics find their natural answer once formulated in the frame of a more general approach.

Any theory whose aim is to include the possibility of new organization of matter in far from equilibrium conditions such as those applying beyond an unstable transition, has to face the problem of fluctuations. A purely causal description is no longer sufficient even for systems involving a large number of degrees of freedom. As an illustration consider a typical problem in hydrodynamics: the stability of the laminar flow of a fluid. Suppose a small fluctuation δE_{kin} appears in the kinetic energy. To this fluctuation will correspond some small 'hump' in the velocity profile, as shown on the figure.
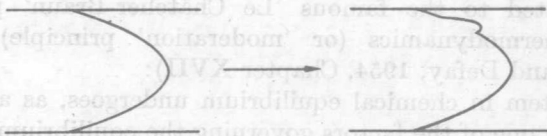
Fluctuation in the velocity profile

If δE_{kin} vanishes everywhere for $t \to \infty$, the flow is stable. On the contrary, if δE_{kin} increases with time, then a new state of flow will be reached. As well known from classical hydrodynamics, this will be the case if the Reynolds number lies beyond a critical value corresponding to turbulence.

The main point is therefore the following: a new 'structure' is always the result of an instability. It originates from a fluctuation. Whereas a fluctuation is normally followed by a response that brings the system back to the unperturbed state, on the contrary, at the point of formation of a new structure, fluctuations are amplified. This idea is of course the basis of classical stability theory derived from normal mode analysis (e.g. Chandrasekhar, 1961). One considers small perturbations around a steady state which satisfy linear equations of evolution. The time dependence of each normal mode is of the form $exp\, \omega\, t$ where ω is in general a complex quantity $\omega_r + i\, \omega_i$. The stability condition implies then that for each normal mode:

$$\omega_r < 0 \qquad (1)$$

One of our main objects will be to relate stability theory to the thermodynamics of irreversible processes in order to obtain as much information as possible, independently of a detailed normal mode analysis. Clearly, we must then in some way incorporate in our thermodynamic description, the response of the system to fluctuations. In other words we have to build a *generalized thermodynamics* which will also include a macroscopic theory of fluctuations.

Let us emphasize that the fluctuations may have either an external or an internal origin. They may result for example, from a temporary disturbance of the boundary conditions. However, the existence of many degrees of freedom in a macroscopic system automatically implies spontaneous *fluctuations*. The stability conditions of a given process then become the conditions for the *regression of fluctuations*.

The problem of the response to spontaneous fluctuations is also closely related to the famous 'Le Châtelier-Braun' principle of classical thermodynamics (or 'moderation' principle). It states (Prigogine and Defay, 1954, Chapter XVII):

'Any system in chemical equilibrium undergoes, as a result of a variation in one of the factors governing the equilibrium, a compensating change in a direction such that, had this change occurred alone it would have produced a variation of the factor considered in the *opposite* direction'.

For equilibrium situations, the moderation principle when applied to intensive variables (pressure, temperature, mole fractions) can easily be proved.

But what happens when we apply the moderation principle to non-equilibrium situations?

A step towards the discussion of such problems was the proof of the theorem of minimum entropy production (I. Prigogine, 1945). When a steady state is characterized by the minimum of entropy production, fluctuations will regress exactly as in thermodynamic equilibrium and the moderation principle will be satisfied.

The very existence of hydrodynamic instabilities shows that this is no longer necessarily so for situations *far* from equilibrium. We come to one of the most basic questions of macroscopic physics: *Under which conditions may we extrapolate results obtained by equilibrium thermodynamics or by linear non-equilibrium thermodynamics to far from equilibrium conditions?* More specifically: What is the generality of instability phenomena? What is the possibility of their occurrence in purely dissipative systems? And how is a system being organized beyond such a transition?

Classical thermodynamics had solved the problem of the competition between randomness and organization for equilibrium systems. But what happens far from equilibrium? Can we find there new organizations, new structures stabilized through the interaction with the outside world?

From a macroscopic point of view it is necessary to distinguish between two types of structure:

(a) equilibrium structures;

(b) dissipative structures.

Equilibrium structures may be formed and maintained through *reversible* transformations implying no appreciable deviation from equilibrium. A crystal is a typical example of an equilibrium structure. Dissipative structures have a quite different status: they are formed and maintained through the effect of exchange of energy and matter in non-equilibrium conditions. The formation of cell patterns at the onset of free convection (Chapter XI) is a typical example of a dissipative structure. We may consider a convection cell as a *giant fluctuation* stabilized by the flow of energy and matter prescribed by the boundary conditions.

As we shall see, such dissipative structures may, under well defined conditions, exist also for open systems involving chemical reactions (especially Chapters VII, XIV–XVI).

A hint towards a thermodynamic theory which would also include a macroscopic theory of fluctuations, is provided by the Einstein

theory of fluctuations. More precisely a generalization of Einstein's theory which may be applied both to equilibrium and non-equilibrium macroscopic evolutions (Chapter VIII) indicates that the basic quantity to consider is the 'curvature' $\delta^2 S$ of the entropy. For isolated systems and small fluctuations, this quantity is identical to the entropy change considered by Einstein. But the important feature is that $\delta^2 S$ retains a simple physical meaning under much more general conditions.

In the whole range of macroscopic physics for which the local equilibrium assumption remains valid, $\delta^2 S$, or its straightforward generalization involving inertial effects, is a negative definite quadratic function.

The problem of the regression of fluctuations, or equivalently of the validity of a moderation principle, leads to the study of the time evolution of $\delta^2 S$. This approach corresponds clearly to the basic ideas of Liapounoff's stability theory (e.g. La Salle and Lefshetz, 1961, Pars, 1965).

As well known non-equilibrium thermodynamics is based on the balance equation for entropy:

$$dS = d_e S + d_i S \tag{2}$$

with

$$d_i S \geqslant 0 \tag{3}$$

Here $d_e S$ denotes the contribution of the outside world (entropy flow) and $d_i S$, the entropy production due to the irreversible processes inside the system. This term $d_i S$, may be expressed in terms of the rates of the irreversible processes and the corresponding forces. We wish now to go beyond equation (2) and to establish *a new balance equation for* $\delta^2 S$, giving $d\delta^2 S$. The corresponding source term, which we call the '*excess entropy production*', is of fundamental importance. Whenever its sign is positive, the system is stable. One finds that near equilibrium this condition is identically satisfied. The Le Châtelier–Braun principle is then also satisfied and fluctuations regress. However far from equilibrium this is no longer so. At the marginal state, corresponding to the transition between stability and instability, the excess entropy production vanishes. In this way the physical meaning of instabilities can be studied with great generality†.

† At least as long as both the unperturbed and perturbed states may be described macroscopically.

We see that the method followed here combines various points of view: the emphasis on balance equations (as in linear non-equilibrium thermodynamics), the classical thermodynamic stability theory, Liapounoff's stability theory and an extension of Einstein's fluctuation formula. All of them contribute to achieve a unified treatment of macroscopic physics, involving both reversible and irreversible processes in both the near and far from equilibrium situations.

It is worth noting that in a very interesting paper, G. N. Lewis (1931) proposed to unify fluctuation theory and thermodynamics. However, he was concerned only with equilibrium situations, where the effect of fluctuations is generally negligible (with the exception of critical phenomena).

Before we comment on the organization of this monograph, we would like to mention another major result of our approach. We derive a very general inequality valid for any evolution of a macroscopic system under fixed boundary conditions. Because of this high degree of generality, we call this inequality the *'universal'* evolution criterion (Chapter IX). Usually this criterion appears in the form of a non-exact differential which means that no thermodynamic potential in the classical sense, can be associated with this criterion. Still the criterion may be used to obtain a *generalization* of the concept of thermodynamic potential. This is 'local potential' (Chapter X). The main feature of the local potential is that each unknown function (e.g. the distribution of temperature in the non-linear heat conduction problem) appears *twice*: once as an average quantity and once as a fluctuating quantity. This then leads to a generalization of classical variational techniques valid for non-self-adjoint problems. The local potential presents a minimum (in the functional sense) when the average quantity coincides with the most probable one.

Applications of the local potential method to the convergence of successive approximations are presented in Chapter X, while a few examples of its use for the solution of stability problems are studied in Chapter XII.

In order to obtain a self-contained text we have reformulated in Chapters I–IV a number of important results of equilibrium thermodynamics as well as of linear non-equilibrium thermodynamics. This includes the conservation laws, the second law of thermodynamics, the basic theorems of linear non-equilibrium thermodynamics such as the Onsager relations, the theorem of minimum entropy

production, and finally the classical Gibbs–Duhem stability theory. These elements are presented here in a form which should permit the reader to understand the more recent developments without having to refer elsewhere.

Chapters V–VII are devoted to an extension of classical thermodynamic stability theory to general equilibrium and non-equilibrium conditions. It is interesting to note that even for equilibrium conditions, the classical theory was restricted to the few cases where the minimum of a thermodynamic potential exists (for example systems of given volume and temperature). In many cases what is given are well defined *boundary conditions* and not the values of some thermodynamic variables *inside* the system. As a rule, no minimum property of a thermodynamic potential is then available and we had first to develop a new approach to the stability problem (Chapter V) which could then be extended to non-equilibrium situations. As already mentioned the essential result of this approach is the introduction of the so-called 'excess entropy production'. The sign of this quantity is directly related to the stability of a non-equilibrium process in respect to its fluctuations.

The extension of Einstein's fluctuation theory is discussed in Chapter VIII. In a macroscopic theory such as the one considered in this monograph, fluctuations are introduced in a somewhat *ad hoc* manner to test stability. This method of treatment has some serious draw-backs. For instance, it cannot lead to an estimate of the time delay which may be involved in the transition from one stable state to another. Also 'average equations' such as the equations of chemical kinetics may correspond only to a first approximation, in the vicinity of such a transition point, as the fluctuations are then likely to increase much beyond their normal level.

These are very interesting questions and we are actively involved in the study of some of these aspects. In the near future publications, we hope to go beyond the few preliminary results stated in Chapters VIII, XIV–XVI.

We have already mentioned in this introduction the concepts of 'universal evolution criterion' and of 'local potential' studied in Chapter IX and X.

Chapters XI–XVI are devoted to applications. Because of the variety of problems to which the theory may be applied we wished only to present a few examples to illustrate some characteristic features. We begin in Chapter XI with stability problems for fluid layers such as the problem of thermal instability (Bénard problem).

Our thermodynamic stability criterion then leads directly to the variational principles for the Bénard problem as derived from the normal mode analysis by Chandrasekhar and others (Chandrasekhar, 1961). In our opinion, this illustrates the degree of unification achieved in our approach between thermodynamic and hydrodynamic methods.

In Chapter XII, we deal with more complicated stability problems for fluid layers, such as laminar flow instability, and the mutual influence of flow and thermal gradients on stability. This also provides typical illustrations of the local potential technique.

A quite different type of problem is studied in Chapter XIII where we deal mainly with the stability of finite amplitude wave propagation in ideal fluids. The interesting point is that in general the excess entropy production (more exactly its generalization including inertial effects) appears as either a positive *definite* or a negative *definite* function. As a consequence the stability problem can then be solved without any reference to the properties of the marginal state. We have here examples of *time-dependent* evolutions which may be unstable (compression waves). There exist therefore situations where a solution of the partial differential equations of macroscopic physics (here of wave propagation) while correct, does not correspond to stable physical situations.

Chapters XIV–XVI are devoted to the investigation of open chemical systems. It seems to us that such a study presents a special interest due to a number of unexpected features and the direct relevance of the results to biological problems.

Far from equilibrium we may then have oscillations in time around the steady state. We may have also either instabilities, or multiple steady states each being stable in some range. The problem of oscillations is studied in Chapter XIV. The first models for chemical oscillations were introduced a long time ago initially by Lotka (1920) and Volterra (1931). But it is only in recent years, especially in the domain of biochemical reactions, that a considerable amount of data on low frequency chemical oscillations has become available.

As pointed out in Chapter XIV there are two types of chemical oscillations: the first corresponds to oscillations on the 'thermodynamic branch'. This is the situation realized in the Lotka–Volterra model. More precisely this model corresponds to the limit of infinite chemical affinity. The other type corresponds to oscillations beyond the marginal stability of the thermodynamic branch. This leads

then to the concept of 'limit cycle' introduced by Poincaré in theoretical mechanics (1892). These limit cycles are of great interest, as they provide us with a beautiful example of time order generated by irreversible processes.

Chemical instabilities which lead to space organization are studied in Chapter XV. Such 'symmetry breaking instabilities' are of special interest as they lead to a spontaneous 'self organization' of the system both from the point of view of its *space order* and its *function*. We have here typical examples of what we have called dissipative structures corresponding to a low entropy value. Such situations may arise in systems which are able to use part of the energy or matter exchanged with the outside world to establish a macroscopic internal order.

The existence of these dissipative structures has now been confirmed both by computer and laboratory experiments (Büsse 1969, Herschkowitz, 1970). In far from equilibrium conditions, chemical reactions may compensate the effect of diffusion, and lead to organized structures on a macroscopic level. This is a fact of primary importance and is likely to open new perspectives in classical thermodynamics.

Moreover the requirements necessary to obtain an instability in far from equilibrium conditions are compatible with the mechanisms of some of the most important biochemical reactions responsible for the maintainance of biological activity (Prigogine, Lefever, Goldbeter and Herschkowitz, 1969).

Another interesting point is that the variety of steady states accessible to an open system may become much larger in far from equilibrium conditions. Examples are studied in Chapter XVI. Again, this enlarged variety of possibilities has important biological implications. As an illustration we study a model of membrane excitation due to Blumenthal, Changeux and Lefever (1969) in which co-operative behaviour together with irreversible processes far from equilibrium lead to a new type of 'dissipative' phase transition.

All these results indicate that dissipation may indeed be a source of order both in time and space. It is difficult to avoid the feeling that such considerations may ultimately contribute to narrow the gap which still exists today between biology and theoretical physics. Far from equilibrium and beyond the instability we have really a new state of matter induced by a prescribed flow of free energy. Do biological processes belong to this state? This is quite a challenging problem which still requires a considerable amount of thought and

study. At least what seems henceforth certain is that important biological processes involve situations beyond the instability and consequently, can not be accounted for by mere extrapolation from thermodynamic equilibrium.

This monograph comprises three distinct parts, the first (Chapters I–IX), is devoted to the general theory, the second (Chapters X–XIII), to the variational techniques and hydrodynamic applications, and finally the third (Chapters XIV–XVII), to instabilities in chemical systems. Readers particularly interested in the last part, which contains a discussion about the possible application to biology, may leave out Part II.

The french philosopher Heuri Bergson (1907) called the second law of thermodynamics the most 'metaphysical' of all laws of nature. Whether a compliment or a criticism, this applies also to the 'generalized thermodynamics' we develop in this monograph.

Classical thermodynamics is essentially a theory of *'destruction of structure'*. One may even consider the entropy production as a measure of the 'rate' of this destruction. But in some way such a theory has to be completed by a theory of *'creation of structure'*, lacking in classical thermodynamics.

We have seen that in addition to the entropy production this approach introduces the *'excess entropy production'* which seems to be the basic quantity whose behaviour characterizes the occurrence of new structures and their stability. In the case of chemical reactions we shall see that the stability is determined by a rather complex inter-play of both kinetic and thermodynamic quantities. No statements completely independent of kinetics can be made at present. Specific classes of chemical reactions have to be considered (e.g., systems of monomolecular reactions, cross-catalytic reactions). As a consequence there exists a whole wealth of possibilities. This contrasts with the *universal* character of the statements made by classical thermodynamics about systems approaching equilibrium.

But this multiplicity of possibilities seems precisely necessary to describe the various far from equilibrium situations. A flow of energy may organize systems and *decrease* their entropy (as in the case of symmetry breaking instabilities referred to before). In other cases it may *increase* their entropy. Likewise it may also increase their entropy production as in the Bénard instability by adding a new mechanism of dissipation, or it may decrease it. We shall study examples of all these situations in this monograph.

The importance of stability theory has been emphasized in a wide

range of fields of research such as biology, economics, sociology. To quote P. Weiss (1968): 'Considering the cell as a population of parts of various magnitude, the rule of order is objectively described by the fact that the resultant behaviour of the population as a whole is infinitely less variant from moment to moment than are the momentary activities of its parts'.

This statement applies as well to the cell as to a human population. In spite of this stability property, a modification of the state variables may lead to a new pattern of organization.

Now in all these cases we basically deal with situations which correspond much more closely to the non-equilibrium conditions than to the situations studied by classical equilibrium thermodynamics. Whichever we consider, a cell or a society, it interacts with its medium and the exchange of energy and matter is an essential element of its very existence.

Therefore we may hope that the far from equilibrium approach we develop in this book may act as an element of unification bringing closer problems belonging to a wide range of disciplines.

It is well known that the most detailed analysis of 'order' made in physics refers to equilibrium situations. But here we have to extend this concept to non-equilibrium situations. To borrow an expression introduced by P. Weiss (1968), we must study 'molecular ecology', analyse the order in terms of population dynamics and compare it with the order in equilibrium systems. The relation between this order and probability is a completely different one than that of equilibrium. In the cell pattern corresponding to thermal instabilities, a macroscopic number of molecules has a coordinated motion over macroscopic times. This would correspond for equilibrium situations to a probability smaller than anything we could imagine.

But even the time evolution of such systems has to be described in new terms. We have already emphasized the relation between fluctuations and instabilities. Therefore the evolution of the system now involves both deterministic and statistical aspects and from the macroscopic point of view at least, contains some essential indeterministic features.

Already classical thermodynamics had added a new element to the concept of time through distinction between reversible and irreversible processes. Now still another element is added; the history of successive instabilities. In this way such systems acquire a 'historical' dimension. Their state can no longer be characterized by the value of variables at a given moment, but in addition we need

to know the succession of instabilities which have occurred in the past. Biological systems carry with them their information. Is this information not at least related to the 'historical dimension'?

These are fascinating questions, and we feel that we are only at the very beginning. Still, as we shall see, specific examples may already be discussed along these lines.

Certainly one of the most attractive features of thermodynamics has always been its power of unification, its reduction of a large variety of phenomena to a few basic ideas. This is the tradition we have tried to follow in this monograph.

P. GLANSDORFF
I. PRIGOGINE

Contents

v

Contents