TIME, STRUCTURE AND FLUCTUATIONS

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1. INTRODUCTION

The problem of time in physics and chemistry is closely related to the formulation of the second law of thermodynamics. Therefore another possible title of this lecture could have been: "the macroscopic and microscopic aspects of the second law of thermodynamics".

It is a remarkable fact that the second law of thermodynamics has played in the history of science a fundamental role far beyond its original scope. Suffice it to mention Boltzmann's work on kinetic theory, Planck's discovery of quantum theory or Einstein's theory of spontaneous emission, which were all based on the second law of thermodynamics.

It is the main thesis of this lecture that we are only at the beginning of a new development of theoretical chemistry and physics in which thermodynamic concepts will play an even more basic role. Because of the complexity of the subject we shall limit ourselves here mainly to conceptual problems. The conceptual problems have both macroscopic and microscopic aspects. For example, from the macroscopic point of view classical thermodynamics has largely clarified the concept of equilibrium structures such as crystals.

Thermodynamic equilibrium may be characterized by the minimum of the Helmholtz free energy defined usually by

$$F = E - TS \tag{1.1}$$

Are most types of "organisations" around us of this nature? It is enough to ask such a question to see that the answer is negative. Obviously in a town, in a living system, we have a quite different type of functional order. To obtain a thermodynamic theory for this type of structure we have to show that that non-equilibrium may be a *source of order*. Irreversible processes may lead to a new type of dynamic states of matter which I have called "dissipative structures". Sections 2-4 are devoted to the thermodynamic theory of such structures.

These structures are today of special interest in chemistry and biology. They manifest a coherent, supermolecular character which leads to new, quite spectacular manifestations; for example in biochemical cycles involving oscillatory enzymes.

How do such coherent structures appear as the result of reactive collisions. This question is briefly discussed in Section 5. We emphasize that conventional chemical kinetics corresponds to a "mean field" theory very similar to the Van der Waals theory of the equation of state or Weiss' theory of ferromagnetism. Exactly as in these cases the mean field theory breaks down near the instability where the new dissipative structures originate. Here (as in equilibrium theory) fluctuations play an essential role.

In the last two sections we turn to the microscopic aspects. We briefly review the recent work done by our group in this direction. This work leads to a microscopic definition of irreversible processes. However this is only possible through a transformation theory which allows one to introduce new non-unitary equations of motion that explicitly display irreversibility and approach to thermodynamic equilibrium.

The inclusion of thermodynamic elements leads to a reformulation of (classical or quantum) dynamics. This is a most surprising feature. Since the beginning of this century we were prepared to find new theoretical structures in the microworld of elementary particles or in the macroworld of cosmological dimensions. We see now that even for phenomena on our own level the incorporation of thermodynamic elements leads to new theoretical structures. This is the price we have to pay for a formulation of theoretical methods in which time appears with its full meaning associated with irreversibility or even with "history", and not merely as a geometrical parameter associated with motion.

2. ENTROPY PRODUCTION

At the very core of the second law of thermodynamics we find the basic distinction between "reversible" and "irreversible processes" (1). This leads ultimately to the introduction of entropy S and the formulation of the second law of thermodynamics. The classical formulation due to Clausius refers to isolated systems exchanging neither energy nor matter with the outside world. The second law then merely ascertains the existence of a function, the entropy S, which increases monotonically until it reaches its maximum at the state of thermodynamic equilibrium,

$$\frac{dS}{dt} \geqslant 0. \tag{2.1}$$

It is easy to extend this formulation to systems which exchange energy and matter with the outside world. (see fig. 2.1).

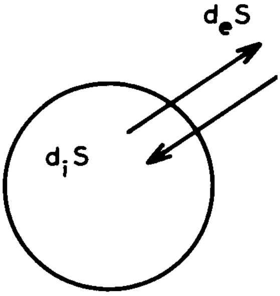


Fig. 2.1. The exchange of entropy between the outside and the inside.

We have then to distinguish in the entropy change dS two terms: the first, d_eS is the transfer of entropy across the boundaries of the system, and the second d_iS, is the entropy produced within the system. The second law assumes then that the entropy production inside the system is positive (or zero)

$$d_iS \geqslant 0. \tag{2.2}$$

The basic distinction here is between "reversible processes" and "irreversible processes". Only irreversible processes contribute to entropy production. Obviously, the second law expresses the fact that irreversible processes lead to one-sidedness of time. The positive time direction is associated with the increase of entropy. Let us emphasize the strong and very specific way in which the one-sidedness of time appears in the second law. According to its formulation it leads to the existence of a function having quite specific properties as expressed by the fact that for an isolated system it can only increase in time. Such functions play an important role in modern theory of stability as initiated by the classic work of Lyapounov. For this reason they are called Lyapounov functions (or functionals).

The entropy S is a Lyapounov function for isolated systems. As shown in all textbooks thermodynamic potentials such as the Helmholtz or Gibbs free energy are also Lyapounov functions for other "boundary conditions" (such as imposed values of temperature and volume).

In all these cases the system evolves to an equilibrium state characterized by the existence of a thermodynamic potential. This equilibrium state is an "attractor" for non-equilibrium states. This is an essential aspect which was rightly emphasized by Planck (1).

However thermodynamic potentials exist only for exceptional situations. The inequality (2.2), which does not involve the total differential of a function, does not in general permit one to define a Lyapounov function. Before we come back to this question let us emphasize that one hundred fifty years after its formulation, the second law of thermodynamics still appears more as a program than a well defined theory in the usual sense, as nothing precise (except the sign) is said about the entropy production. Even the range of validity of this inequality is left unspecified. This is one of the main reasons why the applications of thermodynamics were essentially limited to equilibrium.

To extend thermodynamics to non-equilibrium processes we need an explicit expression for the entropy production. Progress has been achieved along this line by supposing that even outside equilibrium entropy depends only on the same variables as at equilibrium. This is the assumption of "local" equilibrium (2). Once this assumption is accepted we obtain for P, the entropy production per unit time,

$$P = \frac{d_iS}{dt} = \sum_{\rho} J_\rho X_\rho \geqslant 0 \tag{2.3}$$

where the J_ρ are the rates of the various irreversible processes involved (chemical reactions, heat flow, diffusion. . .) and the X_ρ the corresponding generalized forces (affinities, gradients of temperature, of chemical potentials . . .). This is the basic formula of macroscopic thermodynamics of irreversible processes.

Let us emphasize that we have used supplementary assumptions to derive the explicit expression (2.3) for the entropy production. This formula can only be established in some neighborhood of equilibrium (see Ref. 3). This neighborhood defines the region of "local" equilibrium, which we shall discuss from the point of view of statistical mechanics in Section 7.

At thermodynamic equilibrium we have simultaneously for all irreversible processes,

$$J_\rho = 0 \quad \text{and} \quad X_\rho = 0. \tag{2.4}$$

It is therefore quite natural to assume, at least near equilibrium, linear homogeneous relations between the flows and the forces. Such a scheme automatically includes empirical laws such as Fourier's law, which expresses that the flow of heat is proportional to the gradient of temperature, of Fick's law for diffusion, which states that the flow of diffusion is proportional to the gradient of concentration. We obtain in this way the linear thermodynamics of irreversible processes characterized by the relations (4),

$$J_\rho = \sum L_{\rho\rho'} X_{\rho'}. \tag{2.5}$$

Linear thermodynamics of irreversible processes is dominated by two important results. The first is expressed by the Onsager reciprocity relations (5), which state that

$$L_{\rho\rho'} = L_{\rho'\rho}. \tag{2.6}$$

When the flow J_p, corresponding to the irreversible process p, is influenced by the force $X_{\rho'}$ of the irreversible process ρ', then the flow $J_{\rho'}$ is also influenced by the force X_ρ through the same coefficient.

The importance of the Onsager relations resides in their generality. They have been submitted to many experimental tests. Their validity has for the first time shown that nonequilibrium thermodynamics leads, as does equilibrium thermodynamics, to general results independent of any specific molecular model. The discovery of the reciprocity relations corresponds really to a turning point in the history of thermodynamics.

A second interesting theorem valid near equilibrium is the theory of minimum entropy production (6). It states that for steady states sufficiently close to equilibrium entropy production reaches its minimum. Time-dependent states (corresponding to the same boundary conditions) have a higher entropy production. It should be emphasized that the theorem of minimum entropy production requires even more restrictive conditions than the linear relations (2.5). It is valid in the frame of a "strictly" linear theory in which the deviations from equilibrium are so small that the phenomenological coefficients $L_{\rho\rho'}$ may be treated as constants.

The theorem of minimum entropy production expresses a kind of "inertial" property of nonequilibrium systems. When given boundary conditions prevent the system from reaching thermodynamic equilibrium (that is, zero entropy production) the system settles down to the state of "least dissipation".

It was clear since the formulation of this theorem that this property is strictly valid only in the neighborhood of equilibrium. For many years great efforts were made to generalize this theorem to situations further away from equilibrium. It came as a great surprise when it was finally shown that far from equilibrium the thermodynamic behavior could be quite different, in fact, even opposite to that indicated by the theorem of minimum entropy production.

It is remarkable that this new type of behavior appears already in typical situations studied in classical hydrodynamics. The example which was first analyzed from this point of view is the so-called "Bénard instability". Consider a horizontal layer of fluid between two infinite parallel planes in a constant gravitational field, and let us maintain the lower boundary at temperature T_1 and the higher boundary at temperature T_2 with $T_1 > T_2$. For a sufficiently large value of the "adverse" gradient $(T_1 - T_2)/(T_1 + T_2)$, the state of rest becomes unstable and convection starts. The entropy production is then increased as the convection provides a new mechanism of heat transport. Moreover the state of flow, which appears beyond the instability, is a state of organization as compared to the state of rest. Indeed a macroscopic number of molecules have to move in a coherent fashion over macroscopic times to realize the flow pattern.

We have here a good example of the fact that non-equilibrium may be a source of order. We shall see in Sections 3 and 4 that this situation is not limited to hydrodynamic situations but also occurs in chemical systems when well-defined conditions are imposed on the kinetic laws.

It is interesting to notice that Boltzmann's order principle as expressed by the canonical distribution would assign almost zero probability to the occurrence of Bénard convection. Whenever new coherent states occur far from equilibrium, the very concept of probability, as implied in the counting of number of complexions, breaks down. In the case of Bénard convection, we may imagine that there are always small convection currents appearing as fluctuations from the average state; but below a certain critical value of the temperature gradient, these fluctuations are damped and disappear. However, above some critical value certain fluctuations are amplified and give rise to a macroscopic current. A new supermolecular order appears which corresponds basically to a giant fluctuation stabilized by exchanges of energy with the outside world. This is the order characterized by the occurrence of "dissipative structures".

Before we discuss further the possibility of dissipative structures, let us briefly review some aspects of thermodynamic stability theory in relation to the theory of Lyapounov functions.

3. THERMODYNAMIC STABILITY THEORY

The states corresponding to thermodynamic equilibrium, or the steady states corresponding to a minimum of entropy production in linear non-equilibrium thermodynamics, are automatically stable. We have already introduced in Section 2 the concept of a Lyapounov function. According to the theorem of minimum entropy production the entropy production is precisely such a Lyapounov function in the strictly linear region around equilibrium. If the system is perturbed, the entropy production will increase, but the system reacts by coming back to the minimum value of the entropy production.

Similarly, closed equilibrium states are stable when corresponding to the maximum of entropy. If we perturb the system around its equilibrium value, we obtain

$$S = S_0 + \delta S + \tfrac{1}{2}\delta^2 S. \tag{3.1}$$

However, because the equilibrium state was a maximum, the first order term vanishes, and therefore the stability is given by the sign of the second order term $\delta^2 S$.

As Glansdorff and the author have shown $\delta^2 S$ is a Lyapounov function in the neighborhood of equilibrium *independently of the boundary conditions (7).*

Classical thermodynamics permits us to calculate explicitly this important expression. One obtains (8)

$$T\ \delta^2 S = -\left[\frac{C_v}{T}(\delta T)^2 + \frac{\rho}{\varkappa}(\delta v)^2_{N_\gamma} + \sum_{\gamma\gamma'} \mu_{\gamma\gamma'}\,\delta N_\gamma\,\delta N_{\gamma'}\right] < 0. \tag{3.2}$$

Here ρ is the density, $v = 1/\rho$ the specific volume (the index N_γ means that composition is maintained constant in the variation of v) $\varkappa$ the isothermal compressibility, N_γ the mole fraction of component γ and $\mu_{\gamma\gamma'}$ the derivative

$$\mu_{\gamma\gamma'} = \left(\frac{\partial\mu_\gamma}{\partial N_{\gamma'}}\right)_{pT}. \tag{3.3}$$

The basic stability conditions of classical thermodynamics first formulated by Gibbs are:

$C_v > 0$ (thermal stability),
$\varkappa > 0$ (mechanical stability),
$\sum_{\gamma\gamma'} \mu_{\gamma\gamma'}\,\delta N_\gamma\,\delta N_{\gamma'} > 0$ (stability with respect to diffusion).

These conditions imply that $\delta^2 S$ is a negative quadratic function. Moreover it can be shown by elementary calculations that the time derivative of $\delta^2 S$ is related to the entropy production P through (7) (see 2.3),

$$\frac{1}{2}\frac{\partial}{\partial t}\delta^2 S = \sum J_\rho X_\rho = P > 0. \tag{3.4}$$

It is precisely because of inequalities (3.2) and (3.4) that $\delta^2 S$ is a Lyapounov function. Its existence ensures the damping of all fluctuations. That is the reason why near equilibrium a macroscopic description for large systems is sufficient. Fluctuations can only play a subordinate role, appearing as corrections to the macroscopic laws which can be neglected for large systems.

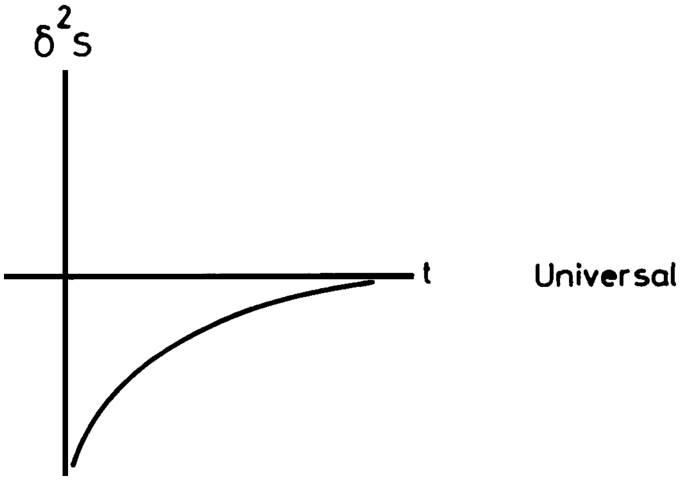


Fig. 3.1. Time evolution of second-order excess entropy ($\delta^2 S$) around equilibrium.

We are now prepared to investigate the fundamental questions: Can we extrapolate this stability property further away from equilibrium? Does $\delta^2 S$ play the role of a Lyapounov function when we consider larger deviations from equilibrium but still in the frame of macroscopic description? We again calculate the perturbation $\delta^2 S$ but now around a nonequilibrium state. The inequality (3.2) still remains valid in the range of macroscopic description. However, the time derivative of $\delta^2 S$ is no longer related to the total entropy production as in (3.4) but to the perturbation of this entropy production. In other words we now have (9),

$$\frac{1}{2}\frac{\partial}{\partial t}\delta^2 S = \sum \delta J_\rho \, \delta X_\rho . \tag{3.5}$$

The right-hand side is what we called the "excess entropy production". Let us again emphasize that the δJ_ρ and δX_ρ are the deviations from the values J_ρ and X_ρ at the stationary state, the stability of which we are testing through a perturbation. Now contrary to what happens for equilibrium or near-equilibrium situations, the right-hand side of (3.5) corresponding to the excess entropy production has generally not a well-defined sign. If for all t larger than t_0, where t_0 is the starting time of the perturbation we have,

$$\sum_\rho \delta J_\rho \, \delta X_\rho \geqslant 0, \tag{3.6}$$

then $\delta^2 S$ is indeed a Lyapounov function and stability is ensured (see fig. 3.2). Note that in the linear range the excess entropy production has the same sign as the entropy production itself and we recover the same result as with the theorem of minimum entropy production. However the situation changes in the far-from-equilibrium range. There the form of chemical kinetics plays an essential role.

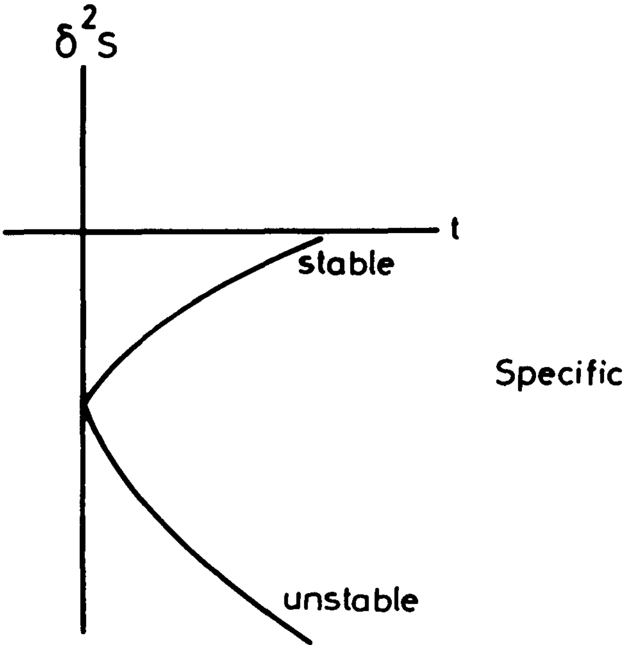


Fig. 3.2. Time evolution of second-order excess entropy ($\delta^2 S$) in case of (asymptotically) stable, marginally stable, and unstable situations.

In the next section we shall consider a few examples. For appropriate types of chemical kinetics the system may become unstable. This shows that there is an essential difference between the laws of equilibrium and the laws far away from equilibrium. The laws of equilibrium are universal. However, far from equilibrium the behavior may become very specific. This is of course a welcome circumstance, because it permits us to introduce a distinction in the behavior of physical systems which would be incomprehensible in an equilibrium world.

Note that all these considerations are very general. They may be extended to systems in which macroscopic motion may be generated or to problems involving surface tension or the effect of external field (10). For example in the case in which we include macroscopic motion we have to consider the expression (see Glansdorff and Prigogine (9)),

$$\delta^2 Z = \delta^2 S - \frac{1}{2}\int \frac{\rho u^2}{T}\, dV \leqslant 0, \tag{3.7}$$

where u are the macroscopic convection velocities. We have integrated over the volume to take into account the space dependence of all u. We may again calculate the time derivative of $\delta^2 Z$ which takes now a more complicated form. As the result may be found elsewhere (9) we shall not reproduce it here. Let us only mention that spontaneous excitation of internal convection cannot be generated from a state at rest which is at thermodynamic equilibrium. This applies of course as a special case to the Bénard instability we have mentioned in Section 2.

Let us now return to the case of chemical reactions.

4. APPLICATION TO CHEMICAL REACTIONS

A general result is that to violate inequality (3.6) we need autocatalytic reactions. More precisely autocatalytic steps are necessary (but not sufficient) conditions for the breakdown of the stability of the thermodynamical branch. Let us consider a simple example. This is the so-called "Brusselator", which corresponds to the scheme of reactions (11),

$$\begin{array}{rcll} A & \rightarrow & X & \text{(a)} \\ 2X+Y & \rightarrow & 3X & \text{(b)} \\ B+X & \rightarrow & Y+D & \text{(c)} \\ X & \rightarrow & E & \text{(d)} \end{array} \qquad (4.1)$$

The initial and final products are A, B, D, E, which are maintained constant while the concentrations of the two intermediate components, X and Y, may change in time. Putting the kinetic constants equal to one, we obtain the system of equations,

$$\frac{dX}{dt} = A + X^2Y - BX - X$$

$$\frac{dY}{dt} = BX - X^2Y, \qquad (4.2)$$

which admits the steady state

$$X_0 = A, \qquad Y_0 = \frac{B}{A} \qquad (4.3)$$

Using the thermodynamic stability criterion or normal mode analysis we may show that solution (4.3) becomes unstable whenever

$$B > B_c = 1 + A^2 \qquad (4.4)$$

Beyond this critical value of B we have a "limit cycle", that is, any initial point in the space X, Y tends to the same periodic trajectory. The important point is therefore that in contrast with oscillating chemical reactions of the Lotka-Volterra type the frequency of oscillation is a well defined function of the macroscopic variables such as concentrations, temperatures . . . The chemical reaction leads to coherent time behavior; it becomes a chemical clock. In the literature this is often called a Hopf bifurcation.

When diffusion is taken into account the variety of instabilities becomes quite amazing and for this reason the reaction scheme (4.1) has been studied by many authors over the past years. A special name has even been introduced - it is generally called the Brusselator. In the presence of diffusion, equations (4.2) now become

$$\frac{\partial X}{\partial t} = A + X^2Y - BX - X + D_X \frac{\partial^2 X}{\partial r^2},$$

$$\frac{\partial Y}{\partial t} = BX - X^2Y + D_Y \frac{\partial^2 Y}{\partial r^2}. \qquad (4.5)$$

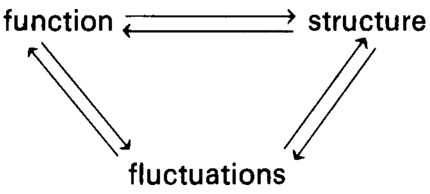
In addition to the limit cycle we have now the possibility of nonuniform steady states. We may call it the "Turing bifurcation" as Turing was the first to notice the possibility of such bifurcations in chemical kinetics in his classic paper on morphogenesis in 1952 (12). In the presence of diffusion the limit cycle may also become space dependent and lead to chemical waves.

Some order can be brought into the results by considering as the "basic solution" the one corresponding to the thermodynamic branch. Other solutions may then be obtained as successive bifurcations from this basic one, or as higher order bifurcations from a non-thermodynamic branch, taking place when the distance from equilibrium is increased.

A general feature of interest is that dissipative structures are very sensitive to global features which characterize the environment of chemical systems, such as their size and form, the boundary conditions imposed on their surface and so on. All these features influence in a decisive way the type of instabilities which lead to dissipative structures.

Far from equilibrium, there appears therefore an unexpected relation between chemical kinetics and the "space-time structure" of reacting systems. It is true that the interactions which determine the values of the relevant kinetic constants and transport coefficients result from short range interactions (valency forces, hydrogen bonds, Van der Waals forces). However, the solutions of the kinetic equations depend in addition on global characteristics. This dependence, which on the thermodynamic branch, near equilibrium, is rather trivial, becomes decisive in chemical systems working under far-from-equilibrium conditions. For example, the occurrence of dissipative structures generally requires that the system's size exceeds some critical value. The latter is a complex function of the parameters describing the reaction-diffusion processes. Therefore we may say that chemical instabilities involve long range order through which the system acts as a whole.

There are three aspects which are always linked in dissipative structures: the function as expressed by the chemical equations, the space-time structure, which results from the instabilities, and the fluctuations, which trigger the instabilities. The interplay between these three aspects



leads to most unexpected phenomena, including "order through fluctuations" which we shall analyze in the next sections.

Generally we have successive bifurcations when we increase the value of some characteristic parameter (like B in the Brusselator scheme).

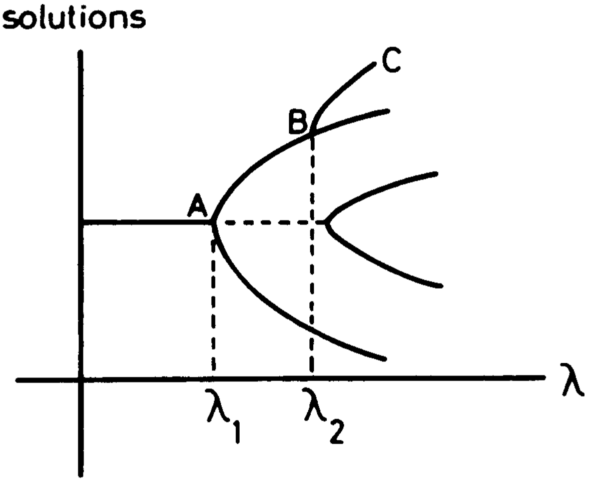


Fig. 4.1. Successive bifurcations.

On the Fig. 4.1. we have a single solution for the value λ_1, but multiple solutions for the value λ_2.

It is interesting that bifurcation introduces in a sense "history" into physics. Suppose that observation shows us that the system whose bifurcation diagram is represented by Fig. 4.1 is in the state C and came there through an increase of the value of λ. The interpretation of this state X implies the knowledge of the prior history of the system, which had to go through the bifurcation points A and B. In this way we introduce in physics and chemistry an "historical" element, which until now seemed to be reserved only for sciences dealing with biological, social, and cultural phenomena.

Every description of a system which has bifurcations will imply both deterministic and probabilistic elements. As we shall see in more detail in Section 5, the system obeys deterministic laws, such as the laws of chemical kinetics, between two bifurcations points, while in the neighborhood of the bifurcation points fluctuations play an essential role and determine the "branch" that the system will follow.

We shall not go here into the theory of bifurcations and its various aspects such as, for example, the theory of catastrophes due to René Thorn (13). These questions are discussed in my recent monograph in collaboration with G. Nicolis (11). We shall also not enumerate the examples of coherent structures in chemistry and biology which are at present known. Again many examples may be found in Ref. 11.

5. THE LAW OF LARGE NUMBERS AND THE STATISTICAL DESCRIPTION OF CHEMICAL REACTIONS

Let us now turn to the statistical aspects of the formation of dissipative structures. Conventional chemical kinetics is based on the calculation of the average number of collisions and more specifically on the average number of reactive collisions. These collisions occur at random. However, how such a chaotic behaviour can ever give rise to coherent structures? Obviously a new feature has to come in. Briefly, this is the breakdown of the conditions of validity of the law of large numbers; as a result the distribution of reactive particles near instabilities is no more at random.

Let us first indicate what we mean by the law of large numbers. To do so we consider a typical probability description of great importance in many fields of science and technology, the Poisson distribution. This distribution involves a variable X which may take integer values X = 0, 1,2,3, . . . According to the Poisson distribution the probability of X is given by

$$\mathrm{pr}(X) = e^{-<X>} \frac{<X>^{X}}{X!} \qquad (5.1)$$

This law is found to be valid in a wide range of situations such as the distribution of telephone calls, waiting time in restaurants, fluctuations of particles in a medium of given concentration. In Eq. (5.1), <X> corresponds to the average value of X. An important feature of the Poisson distribution is that <X> is the only parameter which enters in the distribution. The probability distribution is entirely determined by its mean.

From (5.1), one obtains easily the so-called "variance" which gives the dispersion around the mean

$$<(\delta X)^2> = <(X - <X>)^2>. \qquad (5.2)$$

The characteristic feature is that according to the Poisson distribution the dispersion is equal to the average itself,

$$<(\delta X)^2> = <X>. \qquad (5.3)$$

Let us consider a situation in which X is an extensive quantity proportional to the number of particles N (in a given volume) or to the volume V. We then obtain for the *relative* fluctuations the famous square root law

$$\frac{\sqrt{<(\delta X)^2>}}{<X>} = \frac{1}{\sqrt{<X>}} \sim \frac{1}{\sqrt{N}} \text{ or } \frac{1}{\sqrt{V}}. \qquad (5.4)$$

The order of magnitude of the relative fluctuation is inversely proportional to the square root of the average. Therefore, for extensive variables of order N we obtain relative deviations of order $N^{-1/2}$ This is the characteristic feature of the law of large numbers. As a result we may disregard fluctuations for large systems and use a macroscopic description.

For other distributions the mean square deviation is no more equal to the average as in (5.3). But whenever the law of large numbers applies, the order of magnitude of the mean square deviation is still the same, and we have

$$\frac{<(\delta X)^2>}{V} \sim \text{finite for } V \to \infty. \qquad (5.5)$$

Let us now consider a stochastic model for chemical reactions. As has been done often in the past, it is natural to associate a Markov chain process of the "birth and death" type to a chemical reaction (14). This leads immediately to a Master Equation for the probability $P(X, t)$ of finding X molecules of species X at time t,

$$\frac{dP(X, t)}{dt} = \sum_r W(X - r \rightarrow X)\, P(X - r, t) - \sum_r W(X \rightarrow X + r)\, P(X, t). \quad (5.6)$$

On the right-hand side we have a competition between "gain" and loss terms. A characteristic difference with the classical Brownian motion problem is that the transition probabilities, $W(X - r \rightarrow X)$ or $W(X \rightarrow X + r)$, are non-linear in the occupation numbers. Chemical games are non-linear and this leads to important differences. For example it can be easily shown that the stationary distribution of X corresponding to the linear chemical reaction

$$A \rightleftharpoons X \leftrightharpoons F, \quad (5.7)$$

is given by a Poisson distribution (for given average values of A and F) (15). But it came as a great surprise when Nicolis and the author showed in 1971 (16) that the stationary distribution of X which appears as an intermediate in the chain,

$$\begin{aligned} A + M &\rightarrow X + M \\ 2X &\rightarrow E + D, \end{aligned} \quad (5.8)$$

is no more given by the Poisson distribution,

This is very important from the point of view of the macroscopic kinetic theory. Indeed, as has been shown by Malek-Mansour and Nicolis (17), the macroscopic chemical equations have generally to be corrected by terms associated with deviations from the Poissonian. This is the basic reason why today so much attention is devoted to the stochastic theory of chemical reactions.

For example the Schlögl reaction (18),

$$\begin{aligned} A + 2X &\leftrightharpoons 3X \\ X &\leftrightharpoons B, \end{aligned} \quad \mathbf{(5.9)}$$

has been studied extensively by Nicolis and Turner (19) who have shown that this model leads to a "non equilibrium phase transition" quite similar to that described by the classical Van der Waals equation. Near the critical point as well as near the coexistence curve the law of large numbers as expressed by (5.5) breaks down, as $<(\delta X)^2>$ becomes proportional to a higher power of the volume. As in the case of equilibrium phase transitions, this breakdown can be expressed in terms of critical indices.

In the case of equilibrium phase transitions, fluctuations near the critical point have not only a large amplitude but they also extend over large distances. Lemarchand and Nicolis (20) have investigated the same problem for non-equilibrium phase transitions. To make the calculations possible, they considered a sequence of boxes. In each box the Brusselator type of reaction (4.1) is taking place. In addition, there is diffusion between one box and the other.

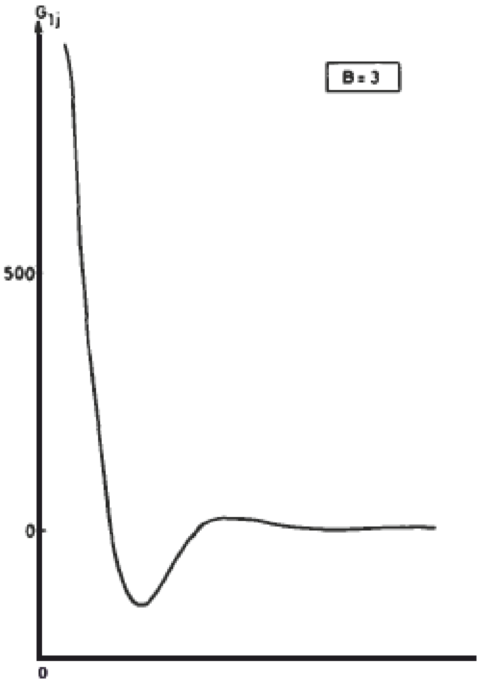


Fig. 5.1. Distance dependence of spatial correlation function Gi, j well below critical point. A = 2, $d_1 = 1$, $d_2 = 4$

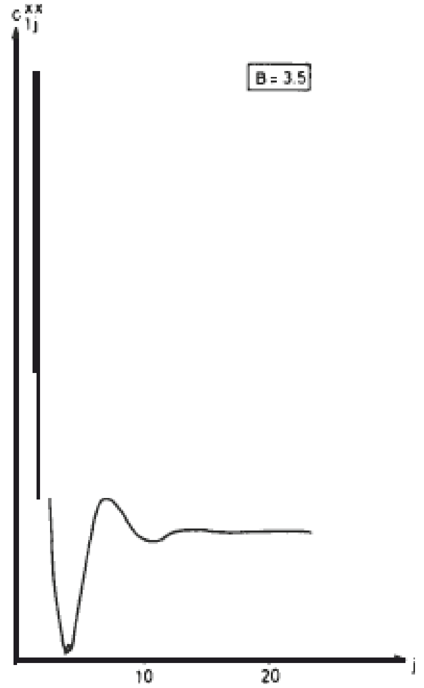


Fig. 5.2. As bifurcation parameter approaches critical value, range of Gi, j increases slightly with respect to behavior shown in Figure 5.1.

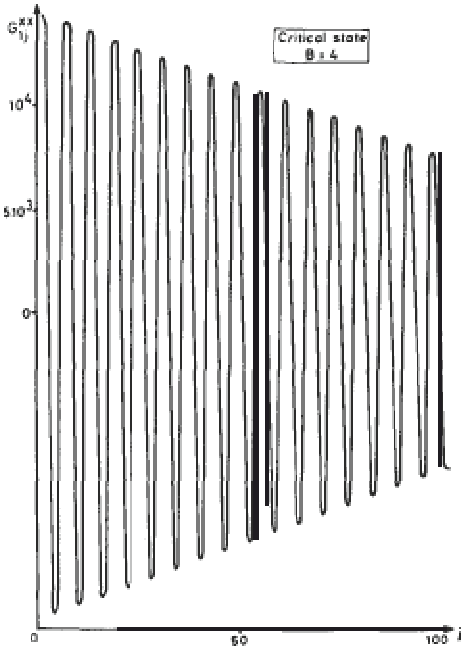


Fig. 5.3. Critical behavior of spatial correlation function Gi, j for same values of parameters as in Fig. 5.1. Correlation function displays both linear damping with distance and spatial oscillations with wavelength equal to that of macroscopic concentration pattern.

Using the Markov method they then calculated the correlation between the occupation numbers of X in two different boxes. One would expect that chemical inelastic collisions together with diffusion would lead to a chaotic behavior. But that is not so. In Figures 5.1-5.3, the correlation functions for below and near the critical state are represented graphically. It is clearly seen that near the critical point we have long range chemical correlations. Again the system acts as a *whole* inspite of the short-range character of the chemical interactions. Chaos gives rise to order. Moreover numerical simulations indicate that it is only in the limit of number of particles, $N \rightarrow \infty$, that we tend to "long range" temporal order.

To understand at least qualitatively this result let us consider the analogy with phase transitions. When we cool down a paramagnetic substance, we come to the so-called Curie point below which the system behaves like a ferromagnet. Above the Curie point, all directions play the same role. Below, there is a privileged direction corresponding to the direction of magnetization.

Nothing in the macroscopic equation determines which direction the magnetization will take. In principle, all directions are equally likely. If the ferromagnet would contain a finite number of particles, this privileged direction would not be maintained in time. It would rotate. However, if we consider an infinite system, then no fluctuations whatsoever can shift the direction of the ferromagnet. The long-range order is established once and for all.

There is a striking similarity with the case of oscillating chemical reactions. When we increase the distance from equilibrium, the system begins to oscillate. It will move along the limit cycle. The phase on the limit cycle is determined by the initial fluctuation, and plays the same role as the direction of magnetization. If the system is finite, fluctuations will progressively take over and perturb the rotation. However, if the system is infinite, then we may obtain a long-range temporal order very similar to the long-range space order in the ferromagnetic system. We see therefore, that the appearance of a periodic reaction is a time-symmetry breaking process exactly as ferromagnetism is a space-symmetry breaking one.

6. THE DYNAMIC INTERPRETATION OF THE LYAPOUNOV FUNCTION

We shall now consider more closely the dynamic meaning of the entropy and more specifically of the Lyapounov function $\delta^2 S$ we have used previously.

Let us start with a very brief summary of Boltzmann's approach to this problem. Even today Boltzmann's work appears as a milestone. It is well known that an essential element in Boltzmann's derivation of the *H*-theorem was the replacement of the exact dynamic equations (as expressed by the Liouville equation to which we shall come back later) by this kinetic equation for the velocity distribution function f of the molecules,

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} = \int dw\, dv \quad \sigma[f'f'_1 - f f_1] \tag{6.1}$$

where the notation is standard.

Once this equation is admitted it is easy to show that Boltzmann's H quantity,

$$H = \int dv\, f \log f, \tag{6.2}$$

satisfies the inequality

$$\frac{dH}{dt} < 0, \tag{6.3}$$

and plays therefore the role of a Lyapounov function.

The progress achieved through Boltzmann's approach is striking. Still many difficulties remain (21). First we have "practical difficulties", as for example the difficulty to extend Boltzmann's results to more general situations (for example dense gases). Kinetic theory has made striking progress in the last years; yet when one examines recent texts on kinetic theory or non-equilibrium statistical mechanics one does not find anything similar to Boltzmann's H-theorem which remains valid in more general cases. Therefore Boltzmann's result remains quite isolated, in contrast to the generality we attribute to the second law of thermodynamics.

In addition we have "theoretical difficulties". The most serious is probably Loschmidt's reversibility paradox. In brief, if we reverse the velocities of the molecules, we come back to the initial state. During this approach to the initial state Boltzmann's H-theorem (6.3) is violated. We have "anti-thermodynamic behavior". This conclusion can be verified, for example by computer simulations.

The physical reason for the violation of Boltzmann's H-theorem lies in the long-range correlations introduced by the velocity inversion. One would like to argue that such correlations are exceptional and may be disregarded. However, how should one find a criterion to distinguish between "abnormal" correlations and normal correlations especially when dense systems are considered ?

The situation becomes even worse when we consider, instead of the velocity distribution, a Gibbs ensemble corresponding to phase density ρ. Its time evolution is given by the Liouville equation,

$$i\,\frac{\partial \rho}{\partial t} = L\rho, \tag{6.4}$$

where

$$L\rho \begin{cases} \text{Poisson bracket } i\{H, \rho\} \text{ in classical dynamics} \\ \text{the commutator } [H, \rho] \text{ in quantum mechanics.} \end{cases} \tag{6.4'}$$

If we consider positive convex functionals such as

$$\Omega = \int \rho^2\, dp\, dq > 0, \tag{6.5}$$

or in quantum mechanics,

$$\Omega = \mathrm{tr}\ \rho^{+} \rho > 0, \tag{6.6}$$

it is easily shown that, as a consequence of Liouville's equation (6.4),

$$\frac{d\Omega}{dt} = 0. \tag{6.7}$$

Therefore, Ω as defined in (6.5) or (6.6) is not a Lyapounov function, and the laws of classical or quantum dynamics seem to prevent us from constructing at all a Lyapounov functional which would play the role of the entropy.

For this reason it has often been stated that irreversibility can only be introduced into dynamics through supplementary approximation such as coarse-graining added to the laws of dynamics (22).

I have always found it difficult to accept this conclusion especially because of the constructive role of irreversible processes. Can dissipative structures be the result of mistakes?

We obtain a hint about the direction in which the solution of this paradox may lie by inquiring why Boltzmann's kinetic equation permits one to derive an *H*-theorem while Liouville equation does not. Liouville's equation (6.4) is obviously Lt-invariant. If we reverse both the sign of L (this can be done in classical dynamics by velocity inversion) and the sign oft, the Liouville equation remains invariant. On the other hand, it can be easily shown (21) that the collision term in the Boltzmann equation breaks the Lt-symmetry as it is even in L. We may therefore rephrase our question by asking: How can we break the Lt-symmetry inherent in classical or quantum mechanics? Our point of view has been the following: The dynamical and thermodynamical descriptions are, in a certain sense, "equivalent" representations of the evolution of the system connected by a non-unitary transformation. Let us briefly indicate how we may proceed. The method which we follow has been developed in close collaboration with my colleagues in Brussels and Austin (23, 24, 25).

7. NON-UNITARY TRANSFORMATION THEORY

As the expression (6.6) has proved inadequate we start with a Lyapounov function of the form,

$$\Omega = \mathrm{tr}\ \rho^{+} \mathbf{M} \rho \geqslant 0, \tag{7.1}$$

(where **M** is a positive operator), with a non-increasing time derivative,

$$\frac{d\Omega}{dt} \leqslant 0 \tag{7.2}$$

This is certainly not always possible. In simple dynamical situations when the motion is periodic either in classical or quantum mechanics, no Lyapounov function may exist as the system returns after some time to its initial state. The existence of M is related to the type of spectrum of the Liouville operator. In the frame of classical ergodic theory this question has been recently studied by Misra (26). Here we shall pursue certain consequences of the possible existence of the operator M in (7.1) which may be considered as a "microscopic representation of entropy". As this quantity is positive, a general theorem permits us to represent it as a product of an operator, say Λ^{-1}, and its hermitian conjugate $(\Lambda^{-1})^+$ (this corresponds to taking the "square root" of a positive operator),

$$M = (\Lambda^{-1})^+ \Lambda^{-1}. \tag{7.3}$$

Inserting this in (7.1) we get,

$$\Omega = \mathrm{tr}\, \tilde{\rho}^+ \tilde{\rho}, \tag{7.4}$$

with

$$\tilde{\rho} = \Lambda^{-1} \rho. \tag{7.5}$$

This is a most interesting result, because expression (7.4) is precisely of the type that we were looking for in the first place. But we see that this expression can only exist in a "new" representation related to the preceding by the transformation (7.5).

First let us write the new equations of motion. Taking into account (7.5), we obtain

$$i \frac{\partial \tilde{\rho}}{\partial t} = \Phi \tilde{\rho}, \tag{7.6}$$

with

$$\Phi = \Lambda^{-1} L \Lambda. \tag{7.7}$$

Now let us use the solution of the equations of motion (6.4). We may replace (7.1) and (7.2) by the more explicit inequalities

$$\Omega(t) = \mathrm{tr}\, \rho^+(o) e^{iLt} M e^{-itL} \rho(o) \leqslant 0, \tag{7.8}$$

$$\frac{d\Omega}{dt} = -\,\mathrm{tr}\, \rho^+(o)^{iLt}\, i(ML - LM) e^{-iLt} \rho(o) \leqslant 0. \tag{7.9}$$

The microscopic "entropy operator" M may therefore not commute with L. The commutator represents precisely what could be called the "microscopic entropy production".

We are of course reminded of Heisenberg's uncertainty relations and Bohr's complementarity principle. It is most interesting to find here also a non-commutativity, but now between dynamics as expressed by the operator L and "thermodynamics" as expressed by M. We therefore have a new and most interesting type of complementarity between dynamics, which implies the knowledge of trajectories or wave functions, and thermodynamics, which implies entropy.

When the transformation to the new representation is performed, we obtain for the entropy production (7.9),

$$\frac{d\Omega}{dt} = -\mathrm{tr}\ \tilde{\rho}^{+}(o)\ e^{i\Phi^{+}t}\ i(\Phi - \Phi^{+})\ e^{-i\Phi t}\ \tilde{\rho}(o) \leqslant 0. \tag{7.10}$$

This implies that the difference between Φ and its hermitian adjoint Φ^{+} does not vanish,

$$i(\Phi - \Phi^{+}) \geqslant 0 \tag{7.11}$$

Therefore we reach the important conclusion that the new operator of motion which appears in the transformed Liouville equation (7.6) can no longer be hermitian as was the Liouville operator L. This shows that we have to leave the usual class of unitary (or anti-unitary) transformations and to proceed to an extension of the symmetry of quantum mechanical operators. Fortunately, it is easy to determine the class of transformations which we have to consider now. Average values can be calculated both in the old and the new representation. The result should be the same; in other words, we require that

$$<A> = \mathrm{tr}\ A^{+}\ \rho = \mathrm{tr}\ \tilde{A}^{+}\ \tilde{\rho}. \tag{7.12}$$

Moreover, we are interested in transformations which will depend explicitly on the Liouville operator. This is indeed the very physical motivation of the theory. We have seen, that the Boltzmann type equations have a broken Lt-symmetry. We want to realize precisely this new symmetry through our transformation (23). This can only be done by considering L-dependent transformations $\Lambda(L)$. Using finally the fact that the density ρ and the observables have the same equations of motion, but with L replaced by $-L$, we obtain the basic condition,

$$\Lambda^{-1}(L) = \Lambda^{+}(-L), \tag{7.13}$$

which replaces here the usual condition of unitarity imposed on quantum mechanical transformations.

It is not astonishing that we do find a non-unitary transformation law. Unitary transformations are very much like changes in coordinates, which do not affect the physics of the problem. Whatever the coordinate system, the physics of the system remains unaltered. But here we are dealing with quite a different problem. We want to go from one type of description, the dynamic one, to another, the "thermodynamic" one. This is precisely the reason why we need a more drastic type of change in representation as expressed by the new transformation law (7.13).

We have called this transformation a "star-unitary" transformation and introduced the notation,

$$\Lambda^{*}(L) = \Lambda^{+}(-L). \tag{7.14}$$

We shall call Λ^{*} the "star-hermitian" operator associated to Λ (star always means the inversion $L \rightarrow -L$). Then (7.13) shows that for star-unitary transformations, the inverse of the transformation is equal to its star-hermitian conjugate.

Let us now consider (7.7). Using the fact that L as well as (7.13) and (7.14), are hermitian, we obtain

$$\Phi^* = \Phi^+(-L) = -\Phi(L) \tag{7.15}$$

or

$$(i\Phi)^* = i\Phi \tag{7.16}$$

The operator of motion is "star-hermitian". This is a most interesting result. To be a star-hermitian, an operator may be either even under L-inversion (that is, it does not change sign when L is replaced by $-L$) or anti-hermitian and odd (odd means that it changes sign when L is replaced by $-L$). A general star-hermitian operator can therefore be written as,

$$i\Phi = \overset{e}{(i\Phi)} + \overset{o}{(i\Phi)}. \tag{7.17}$$

Here the superscripts e and o refer respectively to the even and the odd part of the new time evolution operator Φ. The condition of dissipativity (7.11), which expresses the existence of a Lyapounof function Ω, now becomes

$$i\overset{e}{\Phi} > 0. \tag{7.18}$$

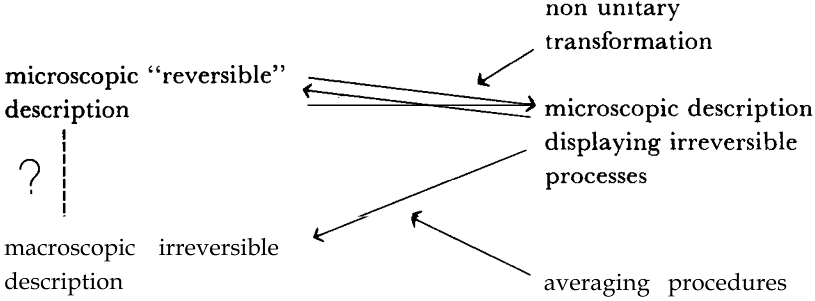
It is the even part which gives the "entropy production".

Let us summarize what has been achieved. We obtain a new form of microscopic equation (as is the Liouville equation in classical or quantum mechanics), but which displays explicitly a part which may be associated to a Lyapounov function. In other words, the equation

$$i\frac{\partial\tilde{\rho}}{\partial t} = (\overset{o}{\Phi} + \overset{e}{\Phi})\tilde{\rho} \tag{7.19}$$

contains a "reversible" part $\overset{o}{\Phi}$ and an "irreversible" part $\overset{e}{\Phi}$. The symmetry of this new equation is exactly the one of Boltzmann's phenomenological kinetic equation, as the flow term is odd and the collision term even in L-inversion.

The macroscopic thermodynamic distinction between reversible and irreversible processes has in this way been transposed into the microscopic description. We have obtained what could be considered as the "missing link" between microscopic reversible dynamics and macroscopic irreversible thermodynamics. The scheme is as follows:



The effective construction of the Lyapounov function Ω, (7.1), through the transformation Λ involves a careful study of the singularities of the resolvent corresponding to the Liouville operator (24).

For small deviations from thermodynamical equilibrium it can be shown, as has been done recently together with Grecos and Theodosopulu (27), that the Lyapounov functional Ω, (7.1), reduces precisely to the macroscopic quantity $\delta^2 S$, (3.2), when in addition only the time evolution of conserved quantities is retained. We therefore have now established in full generality the link between non-equilibrium thermodynamics and statistical mechanics at least in the linear region. This is the extension of the result which was obtained long time ago in the frame of Boltzmann's theory, valid for dilute gases (28).

8. CONCLUDING REMARKS

Now a few 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.

One of the most important aspects of Einstein's theory of relativity is that we cannot discuss the problems of space and time independently of the problem of the velocity of light which limits the speed of propagation of signals. Similarly the elimination of "unobservable" has played an important role in the basic approach to quantum theory initiated by Heisenberg.

The analogy between relativity and thermodynamics has been often emphasized by Einstein and Bohr. We cannot propagate signals with arbitrary speed, we cannot construct a *perpetuum mobile* forbidden by the second law.

From the microscopic point of view this last interdiction means that quantities which are well defined from the point of view of mechanics cannot be observables if the system satisfies the second law of thermodynamics.

For example the trajectory of the system as a whole cannot be an observable. If it would, we could at every moment distinguish two trajectories and the concept of thermal equilibrium would lose its meaning. Dynamics and thermodynamics limit each other.

It is interesting that there are other reasons which at the present time seem to indicate that the relation between dynamic interaction and irreversibility may play a deeper role than was conceived till now.

In the classical theory of integrable systems, which has been so important in the formulation of quantum mechanics, all interactions can be eliminated by an appropriate canonical transformation. Is this really the correct prototype of dynamic systems to consider, especially when situations involving elementary particles and their interactions are considered? Do we not have first to go to a non-canonical representation which permits us to disentangle reversible and irreversible processes on the microscopic level and then only to eliminate the reversible part to obtain well defined but still interacting units?

These questions will probably be clarified in the coming years.

But already now the development of the theory permits us to distinguish various levels of time: time as associated with classical or quantum dynamics, time associated with irreversibility through a Lyapounov function and time associated with "history" through bifurcations. I believe that this diversification of the concept of time permits a better integration of theoretical physics and chemistry with disciplines dealing with other aspects of nature.

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ABSTRACT

We have dealt with the fundamental conceptual problems that arise from the macroscopic and microscopic aspects of the second law of thermodynamics. It is shown that non-equilibrium may become a source of order and that irreversible processes may lead to a new type of dynamic states of matter called “dissipative structures”. The thermodynamic theory of such structures is outlined. A microscopic definition of irreversible processes is given and a transformation theory is developed that allows one to introduce non-unitary equations of motion that explicitly display irreversibility and approach to thermodynamic equilibrium. The work of the Brussels group in these fields is briefly reviewed. We believe that we are only at the beginning of a new development of theoretical chemistry and physics in which thermodynamics concepts will play an ever increasing role.

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