Proc. Natl. Acad. Sci. USA Vol. 74, No. 10, pp. 4152–4156, October 1977 Physics

Microscopic theory of irreversible processes

(Friedrichs model/statistical mechanics/nonequilibrium entropy)

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Contributed by I. Prigogine, July 11, 1977

The microscopic theory of irreversible pro-ABSTRACT cesses that we developed is summarized and illustrated, using as a simple example the Friedrichs model. Our approach combines the Poincaré's point of view (dynamical interpretation of irreversibility) with the Gibbs-Einstein ensemble point of view. It essentially consists in a nonunitary transformation theory based on the symmetry properties of the Liouville equation and dealing with continuous spectrum. The second law acquires a microscopic content in terms of a Liapounov function which is a quadratic functional of the density operator. In our new representation of dynamics, which is defined for a restricted set of observables and states, this functional takes a universal form. We obtain, in this way, a semi-group description, the generator of which contains a part directly related to the mi-croscopic entropy production. The Friedrichs model gives us a simple field theoretical example for which the entropy pro-duction can be evaluated. The thermodynamical meaning of life-times is explicitly displayed. The transition from pure states to mixtures, as well as the occurrence of long tails in thermodynamic systems, are also briefly discussed.

1. Introduction

Is there a microscopic theory of irreversible processes? Since the very formulation of the second law, this question remains a widely discussed problem in theoretical physics. The aim of this article is to indicate why an affirmative answer can now be given to this question and to provide a simple example for which such a microscopic theory can be constructed. A few historical remarks will help to put the problem in the proper perspective.

The simplest dynamic realization of entropy would be a microscopic phase function, say N(q,p). However, Poincaré (1) has shown, in the frame of classical mechanics, that such a phase function, with the necessary properties, does not exist. In contrast to Poincaré, Boltzmann turned to probabilistic assumptions to derive his celebrated H-theorem. Some of the difficulties inherent to Boltzmann's approach are well known (the classical 'paradoxes'') and have been discussed elsewhere (2). In addition, the computer results by Wainwright et al. (3) for the Green-Kubo integrand of the self-diffusion coefficient clearly show the inadequacy of Boltzmann's equation in this context. Instead of the expected exponential decay, one finds a "long tail" depending on the dimensionality of the system. The interpretation of this effect in terms of mode-mode coupling theories has been abundantly discussed in the literature (4). We shall come back to this effect later on and indicate why our approach bypasses this difficulty.

To avoid the shortcomings of Boltzmann's approach, Gibbs (see ref. 2 for a recent discussion) has introduced an ensemble approach in terms of the distribution function in phase space (or density operator in quantum language). The evolution of ρ is given by the so-called Liouville-von Neumann equation

$$i\frac{\partial\rho}{\partial t} = L\rho \qquad [1.1]$$

where the Liouville superoperator L is either the Poisson bracket $i\{H, \}$ or the commutator $[H,]_{-}$ with the hamiltonian H.

The entropy would be related to a convex functional of the distribution function. However, any *universal* functional Ω of ρ (i.e., which does not explicitly depend on the dynamic characteristics of the system) may be shown, under quite general conditions, to remain constant in time

$$\frac{d\Omega}{dt} = 0.$$
 [1.2]

(Examples of such functionals are the Gibbs entropy $-k \int \rho \ln \rho d\Gamma$ and $-k \int \rho^2 d\Gamma$.)

As a result, most subsequent attempts have been based on the replacement of ρ by some "coarse grained" distribution, or the projection of the ρ -state into some subspace. This idea has not been successful, as its meaning is not clear: no unambiguous prescription for the operation of "coarse graining" has ever been formulated.

The point of view taken by our group is different. It combines a strictly dynamic point of view (temporal group property, no stochastic assumptions) with the ensemble point of view of Gibbs. Because of the linear form of the Eq. 1.1 for the distribution function, we look for a quadratic functional

$$\Omega = \operatorname{Tr} \rho^+ M \rho > 0 \qquad [1.3]$$

with a nonincreasing time derivative

$$\frac{d\Omega}{dt} \le 0.$$
 [1.4]

The most important and somewhat unexpected result is that the hermiticity of the dynamic operator L does not preclude the validity of [1.4]. In this way dynamics and thermodynamics become compatible. Of course the existence of the superoperator M requires conditions on the *dynamics* of the system.[†] For example, if the Liouville superoperator L has a purely discrete spectrum, no functional Ω of this type can exist.

This procedure may also be considered as the natural extension of the "direct method of Liapounov" (5) to partial differential equations with continuous spectrum. Therefore, we shall call Ω a Liapounov functional. Its existence is closely tied to the microscopic formulation of the second law.

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[†] The relation between the construction of *M* and classical ergodic theory has been investigated recently by B. Misra (unpublished), who has shown that mixing is a necessary and *K*-flow a sufficient condition for the existence of at least one superoperator *M*. However, the situations studied by our group do not refer to ergodic systems which we consider as too restrictive to be of physical interest.

The quadratic character of the functional [1.3] permits us to link the construction of M to the determination of a new representation for the distribution function ρ . Because the superoperator M is positive, we may express it as the product of a superoperator Λ^{-1} [we use the notations used in our earlier works (2, 6, 7)] and its hermitian conjugate

$$M = (\Lambda^{-1})^+ \Lambda^{-1}.$$
 [1.5]

Inserting Eq. 1.5 in Eq. 1.3, we get

$$\Omega = \operatorname{Tr} \tilde{\rho}^+ \tilde{\rho} \quad \text{with} \quad \tilde{\rho} = \Lambda^{-1} \rho.$$
 [1.6]

In the new representation, we obtain therefore a universal expression for the Liapounov function. Dynamics enters only in the transformation Λ^{-1} . We recover in this way the basic features of the approach pioneered by Boltzmann and Gibbs. As the consequence of [1.4], and assuming the existence of the inverse transformation Λ , we have also in this representation a *contractive semi-group* (instead of a group) corresponding to the equation of motion

$$i\frac{\partial\tilde{\rho}}{\partial t} = \Phi\tilde{\rho}$$
 [1.7]

with

$$\Phi = \Lambda^{-1} L \Lambda.$$
 [1.8]

The mathematical problem involved in this approach is therefore to relate a group to a semi-group through a (nonunitary) similitude. The general requirements discussed in Section 2 will further restrict the class of nonunitary transformations to the so-called starunitary transformations. For the dynamical systems and the class of states (and observables, we discuss this further in Section 2) for which such a Liapounov function can be constructed, there exists a long-time distribution (the equilibrium distribution) which acts as an attractor for the initial distribution function. The existence of such an attractor gives, of course, its very meaning to the entropy (8, 9). Therefore, our construction establishes a relation between entropy and the microscopic superoperator M.[‡] The second law then acquires a purely dynamical content. Though our approach has been presented elsewhere (2, 7), we find it useful to summarize in Section 2 some of the basic problems involved, with the emphasis on Liapounov functions. We then in Section 3 consider, as an explicit example, the so-called Friedrichs model. This model, which has been extensively studied (10-13), provides us with an example of a quantum system for which the second law can be formulated in microscopic terms. Our method also permits us to discuss the meaning of quantization and the definition of quantum states for unstable particles. However, this aspect will not be treated here, but in a separate paper. In Section 4, we turn then to a few general conclusions and discuss the relevance of our result to the basic problems of the distinction between pure states and mixtures in quantum mechanics (14).

In summary, our approach seems to us to provide the "missing link" between *microscopic reversible* dynamics and *macroscopic irreversible* thermodynamics, in accordance with the scheme:

Microscopic reversible dynamics $(\text{group}) \rightleftharpoons \text{microscopic}$ ic dynamics including irreversibility (semi-group) \rightleftharpoons macroscopic irreversible thermodynamics.

2. General requirements on the Liapounov functional

Let us consider the expression [1.3] for the Liapounov functional. Using the formal solution of the Liouville equation [1.1] we require that the following inequalities are satisfied:

$$\Omega(t) = \mathrm{Tr} \left[\rho^+(0) e^{iLt} M e^{-iLt} \rho(0) \right] > 0 \qquad [2.1]$$

and

$$\frac{d\Omega}{dt} = -\text{Tr} \left[\rho^+(0) e^{iLt} i (ML - LM) e^{-iLt} \rho(0) \right] \le 0. \quad [2.2]$$

The microscopic "entropy superoperator" M can therefore not commute with L. The superoperator

$$D \equiv i(ML - LM) \ge 0 \qquad [2.3]$$

represents the microscopic "entropy production."

When the transformation to the new representation is performed (using Eqs. 1.6 and 1.8), we obtain for the entropy production

$$\frac{d\Omega}{dt} = -\operatorname{Tr}\left[\tilde{\rho}^+(0)e^{i\Phi^+t}i(\Phi-\Phi^+)e^{-i\Phi t}\tilde{\rho}(0)\right] \le 0. \quad [2.4]$$

This implies that

$$i(\Phi - \Phi^+) \ge 0.$$
 [2.5]

We observe that the existence of a Liapounov function requires the nonhermiticity of the dynamic operator Φ . Therefore, the transformation Λ cannot be unitary. To make the problem of the determination of Λ more definite, we introduce two more requirements (2, 7): (a) For the observable A, the transformation has to preserve the average value $\langle A \rangle$, for states ρ that are in the domain of Λ^{-1} . In other words, we require that

$$\langle A \rangle = \operatorname{Tr} A^+ \rho = \operatorname{Tr} \tilde{A}^+ \tilde{\rho}.$$
 [2.6]

Using Eq. 1.6, this implies

$$A = (\Lambda^{-1})^+ \tilde{A}$$
 [2.7]

and the observable A must be in the range of $(\Lambda^{-1})^+$. For these observables, states satisfying Eq. 2.6 will be the ones that give rise to a decreasing Liapounov functional and therefore are in the domain of attraction of the asymptotic equilibrium distribution. Note that our transformation theory is based on the invariance [2.6], which is a weaker requirement than the invariance of $\operatorname{Tr} |\alpha\rangle \langle \alpha | \cdot | \beta \rangle \langle \beta | = |\langle \alpha | \beta \rangle|^2$, where $|\alpha\rangle$ and $|\beta\rangle$ are arbitrary state vectors in a Hilbert space. Therefore, we are not confined within the limits of unitary (or anti-unitary) transformations (15, 16). (b) We admit transformations that are functionals of the operator L. The reason is the following. Eq. 1.1 has the L-t symmetry: if we change both L into -L and t into -t, Eq. 1.1 remains invariant. [In classical systems the transformation $L \rightarrow -L$ corresponds to velocity inversion (2).] On the contrary, all phenomenological equations describing approach to equilibrium present a broken L-t symmetry. § Λ , which connects the group [1.1] to the semi-group [1.7], must permit the symmetry-breaking. Now the evolution in time can be formulated in terms of the state, Eq. 1.1, or alternatively in terms of observables, following the equation

$$i\frac{dA}{dt} = -LA \qquad [2.8]$$

which differs from Eq. 1.1 by L-inversion. To preserve the

[‡] To relate Ω to "thermodynamic" entropy, supplementary conditions have to be required (2) (such as additivity and relation between equilibrium entropy and phase).

[§] This is easily seen on the simplest examples such as the relaxation equation for the one-particle distribution function $(\partial f/\partial t) + v(\partial f/\partial x) = -(f - f^0)/(\tau), \tau > 0$ where the right-hand side is invariant in respect to L-inversion, while the left-hand side is not.

equivalence between the two descriptions, we require that to each transformation $\Lambda(L)$ on ρ , there corresponds a transformation $\Lambda(-L)$ on A (7, 17). Combining this with Eq. 2.7 we deduce

$$(\Lambda^{-1}(L))^+ = \Lambda(-L)$$
[2.9]

or

$$\Lambda(L)\Lambda^{+}(-L) = 1.$$
 [2.10]

This condition replaces the usual conditions of unitarity for a change of representation.

In earlier works (2, 6, 7) we have introduced the abbreviation

$$\Lambda^* \equiv \Lambda^+(-L)$$
 [2.11]

and called Λ a "starunitary" transformation. Eq. **2.10** then defines the subclass of nonunitary transformations to which Λ belongs.

It can now be verified easily that the operator [1.8] is star *hermitian* (6), that is,

$$(i\Phi)^* \equiv [i\Phi(-L)]^+ = i\Phi.$$
 [2.12]

The starhermiticity of an operator can be realized in two ways; the operator may be hermitian and even under *L*-inversion (superscript e) or antihermitian and odd (superscript o). It can thus be written

$$i\Phi = (i\Phi) + (i\Phi)$$
 [2.13]

and the condition of dissipativity [2.5] becomes

$$(i \Phi) \ge 0.$$
 [2.14]

This even part gives directly the "entropy production," [2.4] or [2.2].

The evolution generator at the microscopic level is now split, in Eq. 1.7,

$$\frac{\partial \tilde{\rho}}{\partial t} = -[(i \Phi) + (i \Phi)]\tilde{\rho} \qquad [2.15]$$

into a reversible part, which does not contribute to the change of the Liapounov functional and an irreversible part, which determines this change. As mentioned in Section 1, we obtain a microscopic formulation of dynamics (at the level of distribution functions or states) that displays *explicitly* irreversibility (semi-group property).

In addition, the operators of motion appearing in the phenomenological equations have in common that they derive from *star hermitian* superoperators. For example, the flow term in the Boltzmann equation corresponds to a star hermitian superoperator which is antihermitian and odd under L-inversion and the collision term to a superoperator which is hermitian and even.

There are of course other important aspects of transformation theory that we do not include here (for example, preservation of hermiticity; see refs. 2 and 7). Let us now turn to an example.

3. Example: The Friedrichs model

We shall now consider a simple model for which the transformation Λ leading from a group to a semi-group description has been explicitly constructed. Our aim here is not to present calculations (see refs. 10–12), but to discuss qualitatively some of the characteristic features of the construction of Λ without entering into problems of a more technical nature. The hamiltonian in second quantization formalism is

$$H = \omega_1 a_1^{+} a_1 + \sum_k \omega_k a_k^{+} a_k + \lambda \sum_k (V_k a_1^{+} a_k + V_k^{cc} a_k^{+} a_1).$$
 [3.1]

 a^+,a are the usual creation and destruction operators. The interaction V_k is assumed to be of order $L^{-3/2}$, where L^3 is the volume of the quantization box. In the infinite volume limit, the ω_k spectrum becomes continuous $(0, \infty)$ and ω_1 lies within the continuum $(\omega_1 > 0)$. The strength of the interaction is such that, in the one particle sector we restrict ourselves to, there is no bound state. The system is fully determined when the behavior of the various matrix elements of the states ρ and observables A in the infinite volume limit is specified:

$$\begin{array}{ll} \rho_{11}, A_{11}, A_{kk} & \text{are taken independent of the volume } L^3 \\ \rho_{1k}, A_{1k} & \text{behave like } L^{-3/2} \\ \rho_{kk}, \rho_{kk'}, A_{kk'} & \text{are of order } L^{-3}. \end{array}$$

This volume dependence is preserved in time by the Liouville equation [1.1] and all the terms appearing in Tr $A^+\rho$ (Eq. 2.6) are finite in the limit $L^3 \rightarrow \infty$.

The Green's function of the particle 1

$$\left(\frac{1}{z-H}\right)_{11} \equiv \frac{1}{\eta(z)}$$
 [3.2]

where

$$\eta(z) = z - \omega_1 - \sum_k \frac{|V_k|^2}{(z - \omega_k)}$$
 [3.3]

is of particular importance since, as well known, it is associated with the dispersion equation. In the infinite volume limit, the function $\eta^{-1}(z)$ is analytic except for a cut along the positive real axis. $\eta^{+}(z)^{-1}/\eta^{-}(z)^{-1}$, its analytic continuations in the lower/upper half plane, have conjugate poles $\omega_1 + \zeta/\omega_1 + \zeta^{cc}$ which go to ω_1 when $\lambda \rightarrow 0$. We call $\mathcal{A}_1/\mathcal{A}_1^{cc}$ the residues of the Green's function at these poles. The matrix elements of the superoperators Λ and Λ^{-1} are obtained (see refs. 10–12) in terms of $\zeta, \zeta^{cc}, \mathcal{A}_1, \mathcal{A}_1^{cc}, \eta(z)$, and other simple functions, as well as various distributions defined through their analytic continuations. In this construction no claim of strict unicity is made. There may be other starunitary transformations but the qualitative remarks we shall present apply as well to them.

The explicit form of the matrix elements of $\tilde{\rho}(0)$ in terms of $\rho(0)$ can be obtained, and also the evolution operator Φ [1.8]. Eq. 1.7 is easily solved to give $\tilde{\rho}(t)$ in terms of $\tilde{\rho}(0)$. The important point is that *each* element of $\tilde{\rho}(t)$ that contributes, in the construction of the Liapounov function [1.6], has an exponential time dependence of the form

$$e^{(ia+b)t} \qquad [3.4]$$

with a, b real, $b \leq 0$. To get this time dependence, we have to add elements of ρ weighted by suitable coefficients (given precisely by the transformation operator Λ^{-1}). Such expressions for $\tilde{\rho}$ can only be obtained if *suitable restrictions* on $\rho(0)$ are imposed. In the limit of a large volume, as summations over k become integrations, we have integrals of Cauchy's type

$$\int_0^\infty \frac{V(k)\rho_1(k)}{z+\omega_1-\omega_k} dk \qquad [3.5]$$

computed for Im z > 0 and continued analytically through the cut, to ζ in the lower complex plane. This procedure requires well-known conditions on the smoothness of $V(k)\rho_1(k)$ and on its behavior at infinity (18).

In the case of classical mechanics, such conditions rule out

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delta-like distribution functions representing single trajectories. It isn't hard to conceive that indeed a single trajectory for Hamiltonian systems could not be associated with a Liapounov functional.

Similar restrictions apply to the construction of observables \tilde{A} in the new representation (see Eq. 2.7). Therefore, the equivalence condition [2.6] can only hold for a restricted class of states and observables.

Now the Liapounov functional

$$\Omega(t) = \tilde{\rho}_{11}(t)^2 + 2\sum_k |\tilde{\rho}_{k1}(t)|^2 + \sum_{kk'} |\tilde{\rho}_{kk'}(t)|^2 \quad [3.6]$$

takes the form

$$\Omega(t) = e^{-2i(\zeta - \zeta^{cc})t} u_1 + 2e^{-i(\zeta - \zeta^{cc})t} u_2 + u_3 \qquad [3.7]$$

 u_1, u_2, u_3 being positive quantities.

In the particular case in which, at the initial time, we have a pure state corresponding to the "bare" particle, $\rho_{11}(0)$ is unity and all other components for the initial density matrix in the original representation vanish.

Then u_1, u_2, u_3 can be easily computed to give

$$u_1 = \mathcal{A}_1 \mathcal{A}_1^{cc} \qquad [3.8]$$

$$u_2 = (\mathcal{A}_1 \mathcal{A}_1^{cc})^{1/2}$$
 [3.9]

$$u_3 = 1.$$
 [3.10]

We have simply

$$\Omega(t) = (|\mathcal{A}_1|e^{-\gamma t} + 1)^2$$
 [3.11]

where $\gamma = i(\zeta - \zeta^{cc})$ is the inverse of the lifetime of the particle. If the particle would be stable, $|\mathcal{A}_1|$ would be the square of the usual "renormalization constant" of the particle, i.e., the probability of finding the bare particle in the physical one-particle state. But, in that case, the expressions for u_{2,u_3} are no longer given by Eqs. 3.8 and 3.9 and $\Omega(t)$ reduces to unity.

The purely exponential decay of the Liapounov functional is due to its definition [3.6] and to the exponential time dependence [3.4] which is ultimately linked to the roots of the dispersion equation.

On the other hand, if we compute averages $\langle A \rangle$ in the new representation, we can expect, in general, a nonexponential behavior. Indeed, for instance, $\Sigma_k \tilde{\rho}_{1k}(t)\tilde{A}_{k1}$ leads to

$$\int_0^\infty e^{-i(\omega_1+\zeta-\omega_k)t}f(k)dk \qquad [3.12]$$

the long time dependence of which is determined by the precise form of f(k) for small wave-numbers k.

A specific feature of the Friedrichs model is that the damping is wave-number independent. This contrasts with collective phenomena as encountered in hydrodynamics, where, for long wavelength modes, the damping is proportional to k^2 . Then the summation in [3.6] would give rise to the well-known long tails discovered by Wainwright *et al.* (3).

Of importance is the following remark discussed in more detail elsewhere (M. de Haan, C. George, and F. Mayné, unpublished data): while the transformation operator Λ or the generator of the semi-group $i\Phi$ n.ay, under suitable conditions, be expanded in powers of the coupling parameter λ , M cannot be obtained in a straightforward way as the product of the perturbation expansions of $(\Lambda^{-1})^+$ and (Λ^{-1}) (see Eq. 1.5). This is essentially due to the fact that Λ contains distributions and the product of the perturbation expansions appearing in $(\Lambda^{-1})^+\Lambda^{-1}$ is ill defined as long as no partial resummation is performed.

As an example, the explicit expression of the matrix element $M_{11,11}$ of the microscopic entropy operator (see Eq. 1.5) is (see Eqs. 3.7-3.10)

$$M_{11,11} = u_1 + 2u_2 + u_3 = (|\mathcal{A}_1| + 1)^2.$$
 [3.13]

This expression, in the limit $\lambda \rightarrow 0$, takes the value 4. In contradistinction $(\Lambda^{-1})^+$ and Λ^{-1} being unity in that limit, their product would give $M_{11,11} = 1$, but each successive power in the development in λ would be divergent.

The even part of $i\Phi$ is directly related to the entropy production (see Eqs. 2.4 and 2.5). It has a simple physical meaning in the Friedrichs model, since it is due to the decay of the unstable particle.[¶] There appears therefore a simple relationship between decay and entropy, as we have (see Eq. 3.11)

$$(i \Phi)_{11,11} = \gamma = \frac{1}{i} \Lambda^{+}_{11,ij} [LM - ML]_{ij,i'j'} \Lambda_{i'j',11} \quad [3.14]$$

The lifetime $\tau = \gamma^{-1}$ is determined by the commutator of L with the microscopic "entropy" superoperator M.

Let us now discuss a few features that are of general interest.

4. Duality of dynamic description

Approach to equilibrium always involves in some way or other the occurrence of a mixture [think about the canonical ensemble, even if we would start with a pure state (19)]. Is this statement in contradiction to the basic quantum mechanical result that a pure state is preserved by the Schrödinger equation ("linearity" of quantum mechanics, see ref. 14)? This question can be reformulated as follows: to what extent is the existence of an entropy production linked to the appearance of a mixture? A first interesting observation is that, in going to the semi-group description, no distinction between pure states and mixtures has to be made as the relation $\rho^2 = \rho$ is not conserved by the nonunitary and *nonfactorizable* transformation Λ .

Note, however, that starting at the initial time with a bare particle pure state, we can obtain $\tilde{\rho}(0)$, and use the semi-group equation [1.7]. At any time t > 0, we may go back to $\rho(t)$ and verify that it is still a pure state. This is in fact a general feature which illustrates the completeness of the starunitary transformation theory. The "equivalence" between the two representations (as long as the states and observables belong, respectively, to the domain of Λ^{-1} and Λ^+) applies for all times, however large but finite. That $\rho(t)$ is still a pure state is in agreement with the quantum mechanical result. Now the variables (states and observables) to be considered in the theory form a restricted set. In the case of the Friedrichs model, we had to require "Cauchy integrality." It is only in connection with this specific set that we can speak of irreversibility (in the sense of the existence of a Liapounov function). Indeed, the asymptotic limit can be properly defined in the new representation and obeys $\Phi \tilde{\rho} = 0$. The asymptotic state $\tilde{\rho}^{as}$ serves as an attractor for various initial states that were pure states or mixtures in the original representation. There is no reason for the asymptotic state to be a pure state in this original representation.

We believe that this scheme can be extended to situations more general than the Friedrichs model. These remarks are of obvious importance for the theory of quantum mechanical measurement ("reduction of the wave packet") (see refs. 14 and 20), but will not be pursued further here. Let us now turn to thermodynamic systems. As a characteristic feature, they admit both a dynamic description in terms of the Liouville-von

¹ There is also a contribution to entropy production due to scattering (10), which can be neglected in the limit of infinite volume.

Neumann equation [1.1] and a semi-group description [1.7]. The important point is that we can go from one description to the other through the transformation Λ . This is of special interest for computer simulation problems (3), where the initial condition is given in the dynamic description while the time evolution is ultimately described in terms of thermodynamic concepts [as, for instance, in mode-mode coupling theories (4)].

Here the weakness of the usual Boltzmann-type approach becomes manifest. The notion of collision requires the semigroup description. Boltzmann's equation or similar master equations are at most approximations (21, 22) for the evolution of the diagonal components of $\tilde{\rho}$ (we note $\tilde{\rho}_0$ these elements) and say nothing about correlations (the off-diagonal components). Now, for the complete dynamic description, the complete $\tilde{\rho}$ is needed. Even if one starts in the original representation with a ρ that is assumed to be diagonal, in the new representation all correlations are excited, because L and M cannot be simultaneously diagonal (see Eq. 2.2) and Λ^{-1} connects diagonal and off-diagonal components of the density matrix. This is true whatever the coupling constant λ or the concentration. So, even for simple dynamic situations, we have to take into account all components of $\tilde{\rho}$. That leads to nonexponential behaviors in $\langle A \rangle$ and long tails.

We believe that these considerations [together with the fact that we can easily deal with the classical "paradoxes" (2)] show that our microscopic derivation of irreversibility goes far beyond any method using a probabilistic approach.

There appears to be a complete similarity between the meaning of irreversibility on the macroscopic level and its meaning on the microscopic level. To the forgetting of initial macroscopic conditions resulting from the semi-group properties of macroscopic equations (such as Fourier's equation) corresponds the forgetting of initial microscopic conditions on distribution functions or observables through the microscopic semi-group equations which form the essential content of our theory.

Here we have mainly emphasized "thermodynamic" considerations. There are other equally interesting aspects related to the very definition of unstable particles, a problem which attracts, today, a great deal of interest. We shall treat this aspect in a separate paper where we shall show that dynamics incorporating explicitly irreversible processes leads to a physically most appealing new formulation of quantum field theory. This is not so astonishing because at the very start of quantum mechanics, particles or quanta of energy have been introduced in correspondence with the approach of physical systems to thermodynamic equilibrium (23, 24).

We acknowledge stimulating discussions with Profs. Henin, Misra, Grecos, and Sudarshan. This work has been partially supported by the Welch Foundation of Houston, Texas, and the Belgian Government: Actions de Recherches Concertées, Convention 76/81 II.3.

- Poincaré, M. (1889) C.R. Hebd. Seances Acad. Sci. 108, 550– 553.
- Prigogine, I., George, C., Henin, F. & Rosenfeld, L. (1973) Chem. Scr. 4, 5–32.
- Wainwright, T., Alder, B. & Gass, D. (1971) Phys. Rev. A 4, 233-237.
- 4. Pomeau, Y. & Résibois, P. (1975) Phys. Rep. 19c, 64-139.
- 5. Hahn, W. (1967) Stability of Motion (Springer-Verlag, New York).
- George, C. (1974) 1971 Austin Lectures in Statistical Physics (Springer-Verlag, New York), Vol. 28, pp. 53-77.
- 7. George, C. (1973) Physica 65, 277-302.
- 8. Glansdorff, P. & Prigogine, I. (1971) Thermodynamic Theory of Structure, Stability and Fluctuations (Wiley-Interscience, New York).
- 9. Edelen, D. G. B. (1975) Adv. Chem. Phys. 33, 399-442.
- 10. de Haan, M. & Henin, F. (1973) Physica 67, 197-237.
- 11. de Haan, M. (1977) Bull. Cl. Sci. Acad. R. Belg. 63, 69-93.
- 12. de Haan, M. (1977) Bull. Cl. Sci. Acad. R. Belg. 63, 317-340.
- 13. Grecos, A. & Prigogine I. (1972) Physica 59, 77-96.
- d'Espagnat, B. (1977) Conceptual Foundations of Quantum Mechanics (Benjamin Addison Wesley, Boston, MA), 2nd ed.
- Wigner, E. P. (1954) Group Theory and Its Application to Quantum Mechanics of Atomic Spectra (Academic Press, New York).
- Emmerson, J. M. (1971) Symmetry Principles in Particle Physics (Clarendon Press, Oxford).
- 17. George, C. & Prigogine, I. (1974) Int. J. Quantum Chem. Symp. 8, 335-346.
- Smirnov, V. (1964) A Course of Higher Mathematics (Pergamon Press, Oxford).
- Prigogine, I., Grecos, A. & George, C. (1976) Proc. Natl. Acad. Sci. USA 73, 1802–1805.
- George, C., Prigogine, I. & Rosenfeld, L. (1972) Det Kongelige Danske Videnskabernes Selskab Matematisk-fysiske Meddelelser 38, 12, 1-44.
- 21. Van Hove, L. (1955) Physica, 21, 517-540.
- 22. Prigogine, I. (1962) Non Equilibrium Statistical Mechanics (Interscience, New York).
- 23. Einstein, A. (1916) Verh. Dtsch. Phys. Ges. 18, 316-320.
- 24. Planck, M. (1900) Verh. Dtsch. Phys. Ges. 2, 239-241.