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The second law as a selection principle: The microscopic theory of dissipative processes in quantum systems

(entropy/semigroups/superposition principle)

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ABSTRACT **The second law of thermodynamics, for quantum systems, is formulated, on the microscopic level. As for classical systems, such a formulation is only possible when specific conditions are satisfied (continuous spectrum, nonvanishing of the collision operator, etc.). The unitary dynamical group can then be mapped into two contractive semigroups, reaching equilibrium either for $t \to +\infty$ or for $t \to -\infty$. The second law appears as a symmetry-breaking selection principle, limiting the observables and density functions to the class that tends to thermodynamic equilibrium in the *future* (for $t \to +\infty$). The physical content of the dynamical structure is now displayed in terms of the appropriate semigroup, which is realized through a nonunitary transformation. The superposition principle of quantum mechanics has to be reconsidered as irreversible processes transform pure states into mixtures and unitary transformations are limited by the requirement that entropy remains invariant. In the semigroup representation, interacting fields lead to units that behave incoherently at equilibrium. Inversely, nonequilibrium constraints introduce correlations between these units.**

1. Introduction

There is today a widespread interest in irreversible processes, specially in the field of quantum systems (measurement theory, unstable particles, etc.). In macroscopic physics, irreversibility is introduced in connection with the second law of thermodynamics (see ref. 1).

The first attempt in the direction of a microscopic theory of irreversible processes was, of course, due to Boltzmann (2). As well known, Boltzmann's basic idea was to describe as stochastic the dynamical processes which occur in a system. As the consequence, time going on, the probability of the state tends to its maximum. In this way, Boltzmann has definitively linked *irreversibility and probability* (see refs. 3 and 4).

Recently, it was shown (refs. 5–7; S. Martinez and E. Tirapegui, personal communication) that, among the so-called classical "dynamical systems" (such as K flows, Bernoulli schemes, etc.), there exists a class of systems, characterized by a high degree of instability, for which Boltzmann's program can be rigorously enforced. Indeed, in sufficiently unstable systems, the motion becomes so "stochastic" that we may introduce a nonunitary equivalence between the dynamical unitary group $U(t)$ and a semigroup description $\Sigma(t)$ corresponding to a Markov process. Such systems may be called "intrinsically random." For $t \geq 0$, this implies the condition

$$\Lambda^{-1} U(t) = \Sigma(t) \Lambda^{-1}. \qquad [1.1]$$

However, there remains a degeneracy. If Eq. 1.1 is meaningful, there exists (because of the time-reversal symmetry of the motion) a second operator Λ' that mediates the transition from the dynamical group to a Markov process for $t \leq 0$. To raise this degeneracy, a supplementary restriction has to be introduced on the type of initial states that can be observed or prepared. As the admissible states are not invariant in respect to velocity inversion, this restriction expresses a kind of intrinsic polarization of dynamical systems, so that intrinsically random systems become "intrinsically irreversible." "Irreversibility" is thus a stronger property than "randomness," which itself implies "instability."

The second law appears therefore as a "selection principle" propagated by the dynamics of the system. An infinite entropy "barrier" separates the states that are permitted from the states that are prohibited. This is in complete agreement with the macroscopic meaning of the second law, which also limits our action on the macroscopic variables of the system. Irreversibility arises only starting with a "minimum of complexity" of the dynamical description: there must exist representations of the unitary group, each of which, taken separately, breaks the time-reversal symmetry [the so-called "fibers" in the K flows (5, 6)].

In the present paper, we turn to the microscopic theory of irreversibility in quantum systems (see also refs. 3 and 4).

Let us first comment why a quantum theory of irreversible processes seems to us of fundamental importance for the very structure of quantum theory. In classical dynamics, if a trajectory would be a meaningful concept for all dynamical systems, there would be no place for irreversibility. Similarly, in quantum theory irreversibility implies limitations of the concept of wave function. Quantum theory was built by using as a model the Hamilton–Jacobi theory. Today we understand better the limitations inherent to this approach.

We therefore expect drastic changes in the structure of quantum mechanics of systems involving irreversible processes and specially in the transformation theory (8–10). In particular, the role of the "normal," diagonal form of the hamiltonian reached after a unitary transformation has to be reconsidered.

We know from previous work that irreversible processes in quantum mechanics are only possible in the limit of a continuous spectrum (11). This means that we have to consider the limit of an infinite number of degrees of freedom as studied in field theory or in nonequilibrium statistical mechanics. This situation leads to mathematical questions that cannot be treated at the same level of rigor as for classical systems with a few degrees of freedom.

We shall concentrate here on the basic physical questions

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involved. Proofs will be included elsewhere.

2. Dynamics of correlations

The appropriate formulation of dynamics, for the class of systems we are interested in, starts with the Liouville–von Neumann equation for the classical distribution function or the quantum density matrix ρ (3, 4, 12–14):

$$i\frac{\partial \rho}{\partial t} = L\rho, \qquad [2.1]$$

where L is the Liouville operator.

In this formalism, the description of the time evolution of states or observables can be presented as a *dynamics of correlations*. As a first step, it is useful to introduce a pair of complementary orthogonal projection operators P and Q: $P^2 = P$; $Q = 1 - P$. We often use the notations: $P\rho = \rho_0$, $Q\rho = \rho_c$. When ρ_0 corresponds to the momentum or energy distribution, ρ_c then describes spatial correlations. Therefore, ρ_0 is also called the "vacuum of correlations." By using this decomposition of unity, $P + Q = 1$, Eq. **2.1** is split into a set of coupled differential equations:

$$i\partial_t \rho_0 = PLP\,\rho_0 + PLQ\,\rho_c. \qquad [2.2]$$

$$i\partial_t \rho_c = QLP\,\rho_0 + QLQ\,\rho_c. \qquad [2.3]$$

Correlations ρ_c can thus be created from the vacuum through QLP, propagate through QLQ, and be destroyed through PLQ. This description is only meaningful if we start with a representation of the hamiltonian H (or the liouvillian), which contains both a P and a Q part (the P part is usually the "unperturbed energy" and the Q part, the interaction energy). There may be various choices of P and Q. (See Section 7.)

Eqs. **2.2** and **2.3** may be solved in various ways, starting with given conditions for ρ_0 and ρ_c at some instant. A convenient procedure for discussing them involves the resolvent of L: $(z - L)^{-1}$. Values of z in the upper-half plane (Im $z > 0$) are associated with positive times, and values in the lower-half plane (Im $z < 0$), with negative times.

As usually, we decompose the resolvant of L as a sum of partial resolvents, corresponding to the decomposition of unity into P and Q:

$$(z - L)^{-1} =$$

$$(P + \mathscr{C}(z))\,(z - PLP - \Psi(z))^{-1}\,(P + \mathscr{D}(z)) + \mathscr{P}(z). \qquad [2.4]$$

In this way, we introduce basic operators of the kinetic description—namely, the propagation $\mathscr{P}(z) = (z - QLQ)^{-1}Q$, destruction $\mathscr{D}(z) = PLQ\,\mathscr{P}(z)$, creation $\mathscr{C}(z) = \mathscr{P}(z)QLP$, and collision $\Psi(z) = PLQ\,\mathscr{P}(z)QLP$ operators. This terminology stems from the fact that, for specific systems, the "asymptotic (future) collision operator"

$$\Psi(+iO) = \lim_{z \to +iO} \Psi(z) \qquad [2.5]$$

describes the effect of collision processes. An example is the case of a dilute (classical) gas, where two-particle collisions dominate. $\Psi(+iO)$, up to the first order in density, corresponds to the collision operator of the Boltzmann equation. Furthermore, the decay of initial correlations—i.e., off-diagonal elements of the density matrix—depends on the properties of $\mathscr{P}(z)$, while fresh correlations, created in the system because of interactions, are characterized by $\mathscr{C}(z)$.

In terms of these definitions, it is easy to derive the so-called "generalized master equation:"

$$i\partial_t \rho_0(t) =$$

$$PLP\,\rho_0(t) + \int_0^t dt'\,\hat{\Psi}(t - t')\,\rho_0(t') + \hat{\mathscr{D}}(t)\,\rho_c(0), \qquad [2.6]$$

where the kernel $\hat{\Psi}(t)$, for instance, is given by the inverse Laplace transform of the collision operator $\Psi(z)$. The duality between collisions and correlations clearly appears in Eq. **2.6**: the rate of evolution of the vacuum component $\rho_0(t)$ at some instant t, positive, is influenced by its value at earlier times $\rho_0(t')$ (in a nonmarkovian way), but by the correlations $\rho_c(0)$ at the initial time *only*. Such correlations can be termed *precollisional* correlations, as they are present before any collision, represented by the operator Ψ, can take effect. Similarly, fresh correlations can be born through $\mathscr{C}$, from the vacuum of correlation at earlier times, $\rho_0(t')$, but such *postcollisional* correlations do not, in any way, influence the evolution of the uncorrelated part, $\rho_0(t)$. If, in the generalized master equation (Eq. **2.6**), the memory of the initial correlations fades away, time going on, the evolution will be asymptotically dominated by the effect of collisions. Then, as we shall see in Section 3, the system may reach thermodynamical equilibrium.

The distinction between pre- and postcollisional correlations plays a decisive role in the analysis of the Loschmidt paradox (3, 4). A simpler example corresponds to scattering. We have then two effects: the collision process disperses the particles (i.e., it makes the velocity distribution more symmetrical) and, in addition, correlations are produced between the scattered particles and the scatterer. The appearance of correlations can be made explicit by performing a *velocity inversion* (i.e., placing, at some finite distance, a spherical mirror, with the target as center). Briefly speaking, the role of scattering is the following: in the direct process, it makes the velocity distribution more symmetrical and creates correlations; in the inverse process, the velocity distribution becomes less symmetrical and correlations disappear. Therefore, it is through the consideration of correlations that a physical distinction can be introduced between the *direct process* (the sequence collisions ⟶ correlations) and the *inverse process* (the sequence correlations ⟶ collisions).

As indicated by the generalized master equation (Eq. **2.6**), the long time behavior is closely related to the preparation of the initial state. It has to be understood that, for the systems of interest, initial conditions cannot be arbitrarily chosen, according to the will of the experimenter or the observer: the initial conditions have to be themselves the outcome of some previous dynamical evolution. It therefore becomes quite natural to formulate a selection principle on the initial states, asserting that *only transient precollisional correlations can be prepared or observed in nature.*

3. Instability

The condition a constant of motion ϕ has to satisfy is

$$L\phi = 0. \qquad [3.1]$$

The dynamical system will admit a number of conserved quantities, such as energy, total momentum, etc., which we shall call *"regular invariants."* In addition, as the result of the continuity of the spectrum of L, there may be other invariants we call *"singular invariants"* (15).

Using the projections P and Q, as well as the notations introduced in Section 2, we obtain from Eq. **3.1**:

$$(PLP + \Psi(z))\,\phi_0 + z\mathscr{D}(z)\phi_c = 0 \qquad [3.2]$$

and

$$\phi_c = \mathscr{C}(z)\phi_0 + z\mathscr{P}(z)\phi_c. \quad [3.3]$$

For all nonreal z, any constant of the motion satisfies the above relations, and conversely, any function satisfying these equations is invariant.

In the limit $z \to +iO$ (which corresponds to $t \to +\infty$), we may classify the constants of the motion as follows: when the condition

$$\lim_{z \to iO} z\mathscr{D}(z)\ \phi_c = 0 \quad [3.4]$$

is satisfied, Eq. **3.2** implies

$$(PLP + \Psi(+iO))\ \phi_O = 0. \quad [3.5]$$

The P component, ϕ_O, of such an invariant ϕ is a *"collisional invariant."*

Furthermore, if the stronger condition

$$\lim_{z \to +iO} z\,\mathscr{P}(z)\ \phi_c = 0 \quad [3.6]$$

holds, the Q component, ϕ_c, of the invariant is a functional of its P component—namely:

$$\phi_c = \mathscr{C}(+iO)\ \phi_O, \quad [3.7]$$

and the invariant is called a regular invariant. We may indeed verify that conserved quantities, such as functions of H only, obey both conditions **3.4** and **3.6**. In this context, if, for a given invariant, one of the conditions (**3.4** or **3.6**) does not hold, we call it a singular invariant.

The basic difference between regular and singular invariants is that singular invariants necessarily involve *persistent correlations*. On the contrary, regular invariants are maintained as the result of the collisions. The nonvanishing of the asymptotic collision operator $\Psi(+iO)$, as it appears in Eq. **3.5**, is thus of fundamental importance. When this is so, and

$$\lim_{\varepsilon \to 0} \mathscr{D}\ (+i\varepsilon)\ \rho_c = \text{finite}, \quad [3.8]$$

where ρ_c is the correlated part at some initial instant, the distribution function will lead to a collisional invariant for $t \to +\infty$. Indeed, the initial correlations are then forgotten, and the asymptotic state is determined by the collision operator. Similarly, the condition

$$\lim_{\varepsilon \to 0} \mathscr{D}(-i\varepsilon)\ \rho_c = \text{finite} \quad [3.9]$$

implies that the distribution function leads to a collisional invariant for $t \to -\infty$.

Regular invariants belong to a subspace E of the Liouville space, which corresponds to thermodynamic equilibrium. The nonvanishing of $\Psi(+iO)$ expresses therefore an instability of the dynamical evolution. The subspace E is then reached for $t \to +\infty$ if the initial distribution corresponds to precollisional correlations, having only a temporary character. However, if the possibility of persistent correlations is taken into account, the conditions **3.8** and **3.9** are not necessarily satisfied. If we would limit our systems to distributions that tend to regular invariants for $t \to \pm\infty$, we could not distinguish the two directions of time. There are however distributions that tend to a regular invariant for $t \to +\infty$ and to a singular one for $t \to -\infty$, as well as distributions that go to equilibrium in the far past and to a singular invariant in the far future. Each of them (they are velocity inverses of each other) corresponds to a realization of dynamics that has a broken time symmetry, as in each of them, $t \to -\infty$ and $t \to +\infty$ play different roles. This emphasizes the importance of singular invariants in our discussion. If we add the distributions that do not asymptotically tend to equilibrium in either time directions, we obtain four situations, as schematically represented in Fig. 1.

4. Asymptotic time behavior of distribution functions

Let us illustrate the general discussion of Section 3. We consider a "regular" distribution function, ρ_n, which, both for $t \to +\infty$ and $t \to -\infty$, approaches a regular invariant. Let us then take, at time $t = 0$, a state that has evolved from this normal state ρ_n, for a positive time interval $\tau > 0$:

$$\rho(t = 0) = U(\tau)\rho_n. \quad [4.1]$$

Note that, in the time evolution of ρ towards the past, we expect to find an "abnormal" behavior, during the time interval between zero and $-\tau$. Indeed, in the evolution to the past, we shall, during this period of time, destroy precollisional correlations. We may now consider a superposition of initial conditions of the form **4.1**, involving arbitrary times. As an example, we may consider the initial state

$$\rho^{(+)}(0) = \rho_n + \lim_{T \to \infty} \int_0^T d\tau\ U(\tau)\varphi \quad [4.2]$$

or, similarly, the initial state

$$\rho^{(-)}(0) = \rho_n + \lim_{T \to \infty} \int_{-T}^0 d\tau U(\tau)\varphi. \quad [4.3]$$

In the first case (**4.2**) we expect abnormal behavior when we go to the past and in the second (**4.3**), when we go to the future.

The distribution function φ has to be submitted to various conditions: preservation of the trace and maintenance of the positive character of the distribution functions $\rho(\pm)$. We shall also assume that φ is orthogonal to the subspace E of regular invariants, $E\varphi = 0$.

The long time behavior of the singular contributions $\rho_s^{(\pm)}$ to $\rho^{(\pm)}$ can easily be studied. We find for ρ_s^-

$$\lim_{t \to +\infty} \rho_s^-(t) = 2\Pi\ \delta(L)\varphi \quad [4.4]$$

$$\lim_{t \to -\infty} \rho_s^-(t) = 0. \quad [4.5]$$

Similar results are valid for ρ_s^+:

$$\lim_{t \to +\infty} \rho_s^+(t) = 0 \quad [4.6]$$

$$\lim_{t \to -\infty} \rho_s^+(t) = 2\Pi\ \delta(L)\varphi. \quad [4.7]$$

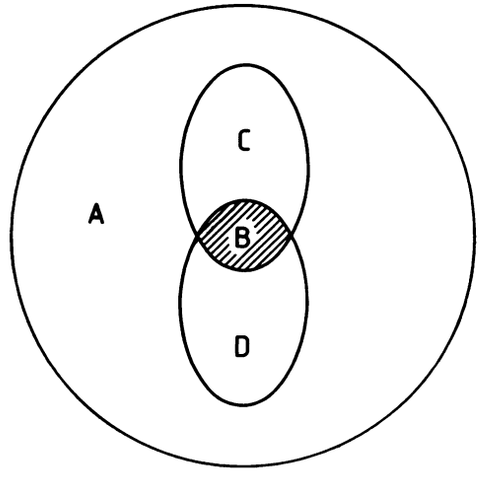

FIG. 1. Classification of states (see text).

This example shows how easy it is to transform a normal distribution ρ_n into an *"oriented" distribution*, which reduces to a singular invariant only in the future, or only in the past.

5. The second law as a selection principle

We may now formulate the second law of thermodynamics on the microscopic level: only distribution functions that tend to equilibrium for $t \to +\infty$ can be observed in nature (or prepared in the laboratory). In reference to Fig. 1, this statement means that only situations B and C are to be considered. Therefore, according to this interpretation of the second law, only precollisional correlations of *limited range* would exist in dynamical systems. Note that nothing can be said about postcollisional correlations, but they cannot prevent the approach to equilibrium in the future. The microscopic content of the second law appears as expressing a limit to observations and manipulations, exactly as does the second law on the macroscopic level. Correlations cannot be controlled to an extent that they undo the effect of collisions. The probabilistic interpretation of entropy, which *presupposes* a direction of time, becomes only possible as a consequence of this *negative* statement.

We have now to prove that the selection principle that we have introduced is propagated by dynamics. This requires the *theory of subdynamics* (3).

Through the extraction of suitable singularities of the resolvent, in the neighborhood of $z = iO$, we may define the "future-oriented" operator Π, which has the following properties: Π is an idempotent operator $\Pi^2 = \Pi$ (for this reason, we also call it a "projection" operator) and Π commutes with the Liouville operator: $[\Pi, L]_- = 0$. Through the same procedure, but by considering the neighborhood of $z = -iO$, we define the "past-oriented" operator Π', which shares the properties: $\Pi'^2 = \Pi'$, $[\Pi', L]_- = 0$. Π' can be obtained from Π through some conjugation that we call L inversion. The Π and Π' operators are different ($\Pi' \neq \Pi$), but they are related however. Indeed, neither Π nor Π' is a hermitian operator ($\Pi \neq \Pi^+$; $\Pi' \neq \Pi'^+$) but they are "star-hermitian"—i.e., they remain invariant when one performs both a hermitian conjugation and an L inversion—i.e.,

$$\Pi = \Pi'^+ \equiv \Pi^*. \qquad [5.1]$$

Π and Π' enjoy other symmetry properties (3), which will not be used here. The form of Π has been studied repeatedly. The important point here is that, when acting on distribution functions ρ, it contains the quantity $D\,\rho_c = \lim_{z \to +iO} \mathcal{D}(z)\,\rho_c + \ldots$. We see therefore by comparison with Eqs. **3.8** and **3.9**, that $\Pi\rho$ will not be well defined for all distribution functions ρ that do not go to regular invariants for $t \to +\infty$. Similarly, $\Pi'\rho$ is not well defined for all ρ that do not go to a regular invariant for $t \to -\infty$.

We have summarized the situation in Fig. 1, with its various regions corresponding to the various behaviors. The C region represents the domain of Π, the D region, the domain of Π', the B region, the domain common to Π and Π'.

Let us briefly compare our statements with Boltzmann's original formulation (2, 4). Boltzmann considered initial conditions without correlations—i.e., having only a P component (this would correspond to molecular chaos). Such a distribution corresponds to the domain common to Π and Π' (the shaded region in Fig. 1). Although Boltzmann's revolutionary idea, of singling out a specific class of initial conditions, appears more important than ever, his own realization of this idea was not satisfactory. Indeed, P does not commute with L, $[P, L]_- \neq 0$, and therefore, time going on, any distribution function will acquire a Q component. Moreover, P is invariant in respect to the L inversion, $P = P'$ and Boltzmann's considerations could thus not lead to a preferred direction of time.

6. Nonunitary transformation and contractive semigroup

The transition from the dynamical group to a semigroup (16) may be mediated through an operator Λ such that

$$\Pi = \Lambda P \Lambda^{-1} \quad \text{with} \quad \Pi(\lambda \to 0) = P, \qquad [6.1]$$

where λ is the coupling constant in the hamiltonian ($H = H_o + \lambda V$).

The explicit construction of the Λ transformation (3, 17) requires the knowledge not only of the operator Π but also of the complete decomposition of its orthogonal complement $\hat{\Pi}$,

$$\hat{\Pi} = 1 - \Pi = \sum_{(v)}{}' \overset{(v)}{\Pi} \qquad [6.2]$$

in a set of orthogonal projection operators $\overset{(v)}{\Pi}$, each of which commutes with L: $[\overset{(v)}{\Pi}, L]_- = 0$. These operators are obtained through the extraction of singularities of the resolvent of L, in the neighborhood of the eigenvalues of QLQ in the limit $\lambda \to 0$, following a suitable procedure of analytic continuation.

By using the symmetry properties of P and Π, recalled in Section 5, it is possible to show that the Λ operator is starunitary—i.e.,

$$\Lambda^{-1} = \Lambda^*, \qquad [6.3]$$

where Λ^* is the operator obtained from Λ by performing both a hermitian conjugation and an L inversion. Similarly, the past-oriented projection operator Π' is also related to the (same) P-projection operator through a similitude Λ', obtained from Λ through an L inversion. Note that Λ and Λ' are different.

We therefore have a pair of nonunitary transformations, Λ and Λ', which lead, respectively, to *two different "physical" representations*,

$$^{(p)}\rho \equiv \Lambda^{-1}\rho \quad \text{and} \quad ^{(p')}\rho \equiv \Lambda'^{-1}\rho. \qquad [6.4]$$

Then, for $t > 0$,

$$i\partial_t^{(p)}\rho = \Phi^{(p)}\rho \quad \text{with} \quad \Phi = \Lambda^{-1} L \Lambda, \qquad [6.5]$$

while, for $t < 0$,

$$-i\partial_t^{(p')}\rho = \Phi'^{(p')}\rho \quad \text{with} \quad \Phi' = -\Lambda'^{-1} L \Lambda'. \qquad [6.6]$$

To each semigroup, we may associate a Lyapunov function, which corresponds to a microscopic formulation of the second law. We may take, for instance (3, 18),

$$\Omega = (^{(p)}\rho, {}^{(p)}\rho) = (\rho, \Lambda^{-1+}\Lambda^{-1}\rho) = (\rho, M\rho) \qquad [6.7]$$

with

$$M \equiv \Lambda'\Lambda^*. \qquad [6.8]$$

M is thus the microscopic expression of the entropy operator. Ω evolves *monotonously* towards its minimum value at equilibrium, when $t \to +\infty$. Similarly, we could define Ω' for the semigroup associated with $^{(p')}\rho$. The regions of Fig. 1 thus admit another interpretation: the unitary evolution $U(t)$ is defined on all regions, the regions C and D correspond to the domains of Λ^{-1} and Λ'^{-1}, respectively, and the region B, to the domain common to Λ^{-1} and Λ'^{-1}.

In complete analogy with classical mechanics, we may introduce a classification of dynamical systems according to the following criteria: (*a*) instability (nonvanishing of the asymptotic collision operator); (*b*) "intrinsic randomness" (existence of the transformations Λ and Λ', leading from the unitary equations

of motion to the semigroup description); and (*c*) "intrinsic irreversibility" (raising of the degeneracy through the exclusion of one of the semigroups).

Well-documented examples of those systems are known: Laurent matrices correspond to quantum unstable systems (15); the Friedrichs model or quantum electrodynamics (18) lead to intrinsically irreversible systems.

7. Some basic properties of dissipative quantum systems

We shall now indicate some fundamental properties of dissipative quantum systems. We have noticed that such systems have always to be considered in the limit of a continuous spectrum. As we always work in the space of density operators, which is a product space, in comparison with the usual Hilbert space of quantum mechanics, rather delicate questions related to the *product* of distributions have to be examined. We have shown previously, using general arguments (3, 11), that the existence of the microscopic entropy operator M necessarily leads to the loss of the basic distinction between pure states and mixtures.

Some of the more striking properties of dissipative quantum systems are the following:

(*a*) The whole procedure rests on the introduction of P and Q, but, as mentioned previously, alternative decompositions are possible. Of course, formula **6.7** can be seen in a different representation $\rho = U\tilde{\rho}$, $\tilde{M} = U M U^{-1}$. However, we may also ask which are the representations that appear as symmetries of entropy in the sense that they leave Ω invariant. Obviously, all of the transformations U which commute with M form the group of "permitted" transformations compatible with the second law.

(*b*) We may only formulate the second law if we start with H containing both P and Q parts. If we first perform a transformation that diagonalizes H (hence, L), no distinction can be made between regular and singular invariants. This transformation does not commute with M and is therefore excluded. Moreover, in the situation in which we can construct the nonunitary transformation operator Λ, the transformation operator U leading to the diagonalization of L becomes ill defined.

For systems with discrete spectrum and restricted classes of systems with continuous spectrum, the normal form of dynamics remains the "diagonalized" one. On the contrary, for systems for which the second law of thermodynamics is meaningful, the choice of representation is severely restricted (note that the transition to large systems already breaks the canonical invariance), and the normal form is obtained after the starunitary transformation. This corresponds to a change of observables: in dissipative systems, other observables, like lifetimes and cross sections (which are not included in the diagonal form), now play an essential role.

(*c*) In addition to the restriction on the unitary transformation, there appears another limitation of the superposition principle, which leads to a severe limitation of the concept of wave function itself. Let us write Eq. **6.5** as

$$\rho(t) = \Lambda\, e^{-i\Phi t}\, \Lambda^{-1}\, \rho(0). \qquad [7.1]$$

Suppose we start with a pure state at $t = 0$. The semigroup operator Φ generates exponential damping terms. When they are taken into account, a pure state is transformed into a mixture. Of course, if we could invert "time," we could reconstruct the pure state, but because of the second law this requires an entropy cost (6), which, after sufficiently long times, goes beyond any permitted transfer of "information."

(*d*) As a result of the selection rule introduced in the second law, the permitted ρ's are separated from the prohibited ones by an infinite entropy barrier. Indeed, take a density operator that goes to a singular invariant for $t \to +\infty$; we may still apply Eq. **7.1**. However, $\Lambda^{-1}\,\rho(0)$ becomes ill defined [the products of distributions involved in Λ^{-1} and $\rho(0)$ lead to divergent terms]; these divergences are cancelled by Λ. [Note however that, in such a case, $\Lambda'^{-1}\,\rho(0)$ is well defined.]

The formulation of a microscopic theory of irreversible processes opens new possibilities for the definition of "quantized units." It always appeared difficult to accommodate physical "interacting" units, including lifetimes and cross sections, in the frame of the unitary scheme (see ref. 19) as well as Haag's theorem (20). We may now define the quantized units as the ones that appear in the contractive semigroup incorporating the second law. These units will behave incoherently at thermodynamical equilibrium (where the entropy is maximum). An example has been studied recently by Henin (21).

On the contrary, nonequilibrium will introduce correlations between them. This vision of matter that becomes coherent under nonequilibrium constraints is in agreement with the picture that emerges from nonequilibrium thermodynamics and nonequilibrium fluctuation theory.

The outstanding contribution of quantum theory from the epistemological point of view was to show that even at the basic level, probabilities were unavoidable. In our opinion, we have to go one step further: even at the basic microscopic level, irreversibility and the second law play an essential role.

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