Journal of Statistical Physics, Vol. 50, Nos. 5/6, 1988

Measure of Irreversibility and Entropy Production in Open Quantum Systems

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Received July 20, 1987

A new concept of a measure of irreversibility for quantum dynamics in open systems is introduced as a suitably regularized substitute for the common notion of entropy production, which, unfortunately, yields infinite values for so many irreversible processes of physical relevance.

KEY WORDS: Irreversible processes; entropy production; open quantum systems; quantum dynamical semigroups.

The notion of entropy production has been introduced in the phenomenological description of nonequilibrium processes[1] as a key concept, and far-reaching consequences have been attributed to it, ranging from "weakly irreversible" processes in the vicinity of thermodynamic equilibrium of ordinary physical systems up to "strongly irreversible" processes very far from equilibrium even in living systems. Attempts to derive the assertions of the phenomenological approach from first principles within the context of quantum theory have proven to be extremely difficult and have left open many relevant questions, particularly the appropriate definition of entropy itself for general nonequilibrium[2-5] as well as the underlying dynamical laws for time evolution.[6-8] Although there are many different definitions of entropy,[4,9] it is reasonable to give preference to the von Neumann entropy

$$S(\rho) \triangleq -\mathrm{Tr}\{\rho \ln \rho\} \tag{1}$$

(ρ a density operator) because of its outstanding properties,[4,9,10] culminating in strong subadditivity, as proven by Lieb and Ruskai,[11] and

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0022-4715/88/0300-1103$06.00/0

in particular also because of its information-theoretic interpretation and obvious significance.[9,12,13] In addition, a measure for the entropy of a state ρ relative to another state σ can be derived from S and has become known as relative entropy,[4,5,9]

$$R(\rho/\sigma) \triangleq \mathrm{Tr}\{\rho \ln \rho - \rho \ln \sigma\} \tag{2}$$

Finally, R has been used by Spohn and Lebowitz[14,15] for a definition of entropy production ψ under the assumption that time evolution

$$\rho \xrightarrow[(t \to \infty)]{\Lambda_t} \sigma$$

is given by a uniquely relaxing and completely positive quantum dynamical semigroup Λ_t. However, the obtained result,

$$\psi\left(\frac{\rho}{\sigma}\right) \triangleq -\left[\frac{d}{dt} R(\rho_t/\sigma)\right]_{t=0}, \qquad \rho_t = \Lambda_t \rho \tag{3}$$

(σ an invariant state: $\Lambda_t \sigma = \sigma$) is only of very limited usefulness, since for most pairs $\{\rho, \sigma\}$ one finds $\psi = \infty$ even in finite-dimensional Hilbert spaces $\mathscr{H}$ and the same is true[14,16] for R. This is extremely unsatisfactory in view of the general bounds $0 \leqslant S \leqslant \ln\{\dim \mathscr{H}\}$. Furthermore, the definition of ψ can evidently be reasonable only for processes with monotonic behavior of S as a function of time, since otherwise the derivative taken at $t = 0$ cannot be a characteristic quantity for the entire time evolution. Of course, for thermodynamic situations close to equilibrium involving faithful states Eq. (3) is appropriate.[15] But the possibilities admitted by the properties of Λ_t for time evolution are much more general and include, just to quote one extreme example, situations such as spontaneous photon emission from a pure initial to a pure final state. Again, for this case, $R = \psi = \infty$, but any reasonable physical thinking would suggest a result somehow proportional to the inverse lifetime.

It will be our intention in the following to construct a measure (or degree) of irreversibility, denoted by P, well-defined for all pairs $\{\rho, \sigma\}$ of state space, in such a way that it is closely analogous to ψ whenever the latter makes sense, but extends successfully to all other cases, too. The relevant problems can be explained for $\dim \mathscr{H} = N < \infty$, whereas extension of the results to $N = \infty$ will be discussed at the end.

In order to have a mathematically safe basis, let us consider the wide class of open systems whose time evolution is given by a quantum dynamical semigroup Λ_t, $t \geqslant 0$, with its dual Λ_t^* completely positive mappings (in the sense of Stinespring[7,8]) of the C^*-algebra of observables. Then, the dynamical law for state changes is a master equation,

$$\dot{\rho}_t = \mathscr{L}\rho_t, \qquad \rho_t = \mathbb{V}^{(M)}, \quad t \geqslant 0 \tag{4}$$

for a time-dependent $N \times N$ density matrix, where $\mathscr{L}$ is the infinitesimal Kossakowski generator of $\Lambda_t = \exp\{\mathscr{L}t\}$ with known structure[7,17,18] and $\mathbb{V}^{(M)}$ is the state space, i.e., a convex subset of a real vector space of dimension $M = N^2 - 1$. To replace R, a suitable relative measure $\mathscr{M}(\rho/\sigma)$ is defined as follows. Consider, first, an operator-valued function $f(\rho, \sigma)$ with the following properties:

$$\begin{aligned} &\text{(a)} \quad f(\rho, \sigma) = f(\sigma, \rho) \geqslant 0, f = 0 \text{ iff } \rho = \sigma, \ \forall \{\rho, \sigma\} \in \mathbb{V}^{(M)} \\ &\text{(b)} \quad f(U\rho U^*, U\sigma U^*) = Uf(\rho, \sigma)\, U^*, \ UU^* = \mathbb{1}_N \\ &\text{(c)} \quad f(\tilde{\rho}, \sigma) = f(\rho, \sigma) \text{ iff } \tilde{\rho} = \rho \\ &\text{(d)} \quad \pi\{f(\rho, \sigma)\} \subset [0, 1], \ \pi \text{ the spectrum} \end{aligned} \tag{5}$$

Since $S(\rho)$ measures the information on $\pi(\rho)$, we define $\mathscr{M}$ by performing the same operation on $\pi(f)$,

$$\mathscr{M}(\rho/\sigma) \mathrel{\hat{=}} -2\,\mathrm{Tr}\{f(\rho, \sigma) \ln f(\rho, \sigma)\} \tag{6}$$

where the factor of 2 is a matter of convenience. Note the change in interpretation when comparing $\mathscr{M}$ with S: whereas $S(\rho)$ measures the information of a state ρ with respect to the central state $\zeta = (1/N)\,\mathbb{1}_N$ ($\mathbb{1}_N$ the unit in N dimensions), in that S attains its maximum for the latter (uniform probability $\leftrightarrow$ minimum information) but its minimum with $S = 0$ for pure states (maximum information), the definition of $\mathscr{M}$ implies maximum information ($\mathscr{M} = 0$) for $\rho = \sigma$ and $\mathscr{M} > 0$ otherwise. Thus, one can say that in $\mathscr{M}$ the final destination states σ play the same role as the pure states do in S. Or, more precisely, if time evolution carries ρ into σ via $\rho_t = \Lambda_t \rho$ ($\forall \rho \in \mathbb{V}^{(M)}$), the quantity $\mathscr{M}(\rho_t/\sigma)$ contains the time-dependent information about the approach to stationarity, since $\mathscr{M}$ is large for ρ_t "far apart" from σ, but is zero if one knows with certainty that the final state has been reached. This is the case in the asymptotic time limit ($t \to \infty$); at no intermediate times ($0 \leqslant t < \infty$) can $\rho_t = \sigma$ hold,[17] as follows basically from the linearity of (4).

A convenient realization of f used for the following examples is given by

$$f_0(\rho, \sigma) = \tfrac{1}{2}(\rho - \sigma)^2 \tag{7}$$

where the first three properties in (5) are trivial and (d) follows from

$\{\rho, \sigma\} \geqslant 0$, $\operatorname{Tr} \rho = \operatorname{Tr} \sigma = 1$, $\operatorname{Tr} \rho^2 \leqslant 1$, $\operatorname{Tr} \sigma^2 \leqslant 1$ and $0 \leqslant \operatorname{Tr}(\rho\sigma) \leqslant 1$. The latter bounds are obtained after applying the Schwartz inequality to[19]

$$\operatorname{Tr}(\rho\sigma) = \sum_{i,k=1}^{N} |(\mathbf{a}^{(i)} \cdot \mathbf{b}^{(k)})|^2 \lambda_i \mu_k$$

where $\rho \mathbf{a}^{(i)} = \lambda_i \mathbf{a}^{(i)}$, $\sigma \mathbf{b}^{(k)} = \mu_k \mathbf{b}^{(k)}$, and, $\|\mathbf{a}^{(i)}\| = \|\mathbf{b}^{(k)}\| = 1$, $\forall i, k$. In order to appreciate an important property of $\mathscr{M}_0$ shared by neither S nor by R, we consider a very simple model for spontaneous emission of a two-level atom[20] with time-dependent state

$$\rho_t = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + (e^{-\gamma t} - \tfrac{1}{2})\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad 0 \leqslant t \leqslant \infty \tag{8}$$

Obviously, $\rho = \left(\begin{smallmatrix} 1 & 0 \\ 0 & 0 \end{smallmatrix}\right)$ and $\sigma = \left(\begin{smallmatrix} 0 & 0 \\ 0 & 1 \end{smallmatrix}\right)$, $S(\rho) - S(\sigma) = 0$, and $R(\rho/\sigma) = \infty$. In contrast, one finds for $\mathscr{M}$ on use of (7) the value $\mathscr{M}_0 = 2 \ln 2$, which seems to reflect the history of the unorthodox time evolution $\rho \to \zeta \to \sigma$, where the central state

$$\zeta = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$$

with maximum $S(\zeta) = \ln 2$ is passed at time $t_\zeta = (\ln 2)/\gamma$. Note that $\mathscr{M}_0$ takes on the above value in any dimension N provided $\rho \neq \sigma$, $[\rho, \sigma] = 0$, $\rho^2 = \rho$, and $\sigma^2 = \sigma$. It is also obvious that $\mathscr{M}_0(\rho_t/\sigma)$ is a well-behaved non-negative function of t, integrable (w.r.t. dt) on $[0, \infty)$, and, therefore, its complete integral $\int_0^\infty \mathscr{M}_0(\rho_t/\sigma)\, dt$ keeps track of the system's history of time evolution along the trajectory through state space and provides information quite analogous to entropy production if divided by the square of a characteristic lifetime τ of the system as a whole. Physically, τ should be identical to the common lifetime of a decaying upper state for two-level systems, but should, of course, comprise all relevant relaxation constants in more general situations.[18] Based on these ideas we are now in position to give a final definition:

For an irreversible process

$$\rho \xrightarrow{\Lambda_t} \sigma$$

described by a uniquely relaxing, completely positive quantum dynamical semigroup Λ_t with Kossakowski generator $\mathscr{L}$, the measure (or degree) of irreversibility P is defined by

$$P \mathrel{\hat{=}} \frac{1}{\tau^2} \int_0^\infty \mathscr{M}(\rho_t/\sigma)\, dt \tag{9}$$

where the characteristic lifetime τ is defined through

$$\tau \triangleq \left[\int_0^\infty \operatorname{Tr}(\mathscr{L}\Lambda_t \rho)^2 \, dt \right]^{-1} \tag{10}$$

Two proofs are necessary regarding the existence of the integrals in (9) and (10), with the result that $0 < P < \infty$ for $N < \infty$. This follows essentially from the spectral properties of the evolution matrix[17,18] associated to $\mathscr{L}$, but the details must be given elsewhere.[21]

Let us now consider two illustrative applications of practical importance, the first for the model given by Eq. (8) and the second for a more general process with two relaxation times as frequently used to describe free induction decay (FID) in terms of Bloch's equations.[22] First, for spontaneous emission one obtains $\tau = \gamma^{-1}$ and $P = \gamma(1 + \ln 2)$. In a geometrical interpretation initial and final states are represented by two diametrical points on the Bloch sphere of maximum radius and time evolution traces a straight trajectory connecting both of them through the center. The value of P will be reduced if the initial state is a mixed state (a point inside the sphere) and for such situations ψ in (3) is also finite and can be compared with P. As a matter of fact, both almost coincide, and this again emphasizes the analogy of P with the conventional notion of entropy production.

Second, let us turn to a class of special solutions of the traditional optical or magnetic Bloch equations,

$$\rho_t = \frac{1}{2} \begin{pmatrix} 1 - w[1 - \exp(-\gamma_1 t)] & 2u \exp[-(\gamma_2 - i\omega)\, t] \\ 2u \exp[-(\gamma_2 + i\omega)\, t] & 1 + w[1 - \exp(-\gamma_1 t] \end{pmatrix} \tag{11}$$

where $0 \leqslant u \leqslant 1/2$, $0 \leqslant w \leqslant 1$, and complete positivity of time evolution is guaranteed[7,18,23] by the semi-inequality $\gamma_1 \leqslant 2\gamma_2$. The analytic solutions of Eqs. (9) and (10) using (7) yield a characteristic time scale

$$\tau = 4[\gamma_1 w^2 + (4u^2/\gamma_2)(\gamma_2^2 + \omega^2)]^{-1} \tag{12}$$

and the representation

$$\begin{aligned} \tau^2 P = {} & \frac{1}{8\gamma_1 \gamma_2^2} (\gamma_2^2 + 4u^2 \gamma_1^2) - \frac{1}{8\gamma_1 \gamma_2} (\gamma_2 + 4u^2 \gamma_1) \ln \left(\frac{1 + 4u^2}{8} \right) \\ & + \frac{2u^2}{\gamma_1 b} F(1, b; b+1; -4u^2) + \frac{8u^4}{\gamma_2 (b+1)} F(1, b+1; b+2; -4u^2) \end{aligned} \tag{13}$$

where F is the Gaussian hypergeometric function[24] and $b = \gamma_2/(\gamma_2 - \gamma_1)$. When applying this result to an ideal FID experiment we can set $u = 1/2$,

$w=1$ and with the special ratio $\gamma_2/\gamma_1=2$ chosen for simplicity, Eq. (13) reduces to

$$P=\frac{\gamma_2}{128}(7+\ln 2)\left[\frac{3}{2}+\left(\frac{\omega}{\gamma_2}\right)^2\right]^2 \tag{14}$$

where ω now has the meaning of the frequency offset. Recall that the lineshape for this decay process[25] is inversely proportional to $[1+(\omega/\gamma_2)^2]$. Thus, P is a minimum at the linecenter (on resonance) and increases toward the wings.

Coming back to the general formula (9), some comments should now be made about the extension to infinite dimensions. If the open system is described in a separable Hilbert space $\mathscr{H}$ ($\dim \mathscr{H}=\infty$) and associated state space $T_+(\mathscr{H})$, the positive cone of trace-class operators on $\mathscr{H}$, a bounded infinitesimal generator $\mathscr{L}$ of a norm-continuous completely positive quantum dynamical semigroup Λ_t has been derived by Lindblad.[26] Consequently, the problem of formulating time evolution in analogy to $N<\infty$ is definitely settled for $N=\infty$. Regarding the existence of $\mathscr{M}(\rho_t/\sigma)$, a sufficient condition will be provided by processes with $S(\Lambda_t\rho)<\infty (t\geqslant 0)$ and integrability, i.e., existence of τ and P is most probably guaranteed if the evolution matrix[17] corresponding to $\mathscr{L}$ contains at most finite-dimensional Jordan blocks. This, however, will need further investigations and rigorous proofs, of course.

In conclusion, one can say that the quantity P contains the following important information on the dynamics of a system: if time evolution changes the state ρ_t such that $S(\rho_t)$ is strongly (weakly) varying on the characteristic timescale τ, the value of P will be large (small). This allows a suitable comparison of different processes according to their "strength" of irreversibility, as is also the case with ψ in (3) whenever the latter is well-defined. Of course, one should remark that ψ provides the much simpler concept in that it is given already in terms of the semigroup generator[15,17] $\mathscr{L}$ only, whereas the determination of P involves the full dynamics Λ_t. Despite of this apparent shortcoming, this seems, in general, unavoidable in view of the possibly complicated solutions[17] of (4), which imply in many cases that the relevant state changes need not necessarily occur in the neighborhood of $t=0$. Thus, definition (9) is of the desired general validity.

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