Nonlinear model dynamics for closed-system, constrained, maximal-entropy-generation relaxation by energy redistribution

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We discuss a nonlinear model for relaxation by energy redistribution within an isolated, closed system composed of noninteracting identical particles with energy levels e_i with $i=1,2,\ldots,N$. The time-dependent occupation probabilities $p_i(t)$ are assumed to obey the nonlinear rate equations $\tau \, dp_i/dt = -p_i \ln p_i - \alpha(t)p_i - \beta(t)e_i p_i$ where $\alpha(t)$ and $\beta(t)$ are functionals of the $p_i(t)$'s that maintain invariant the mean energy $E = \Sigma_{i=1}^{N} e_i p_i(t)$ and the normalization condition $1 = \Sigma_{i=1}^{N} p_i(t)$. The entropy $S(t) = -k_B \Sigma_{i=1}^{N} p_i(t) \ln p_i(t)$ is a nondecreasing function of time until the initially nonzero occupation probabilities reach a Boltzmann-like canonical distribution over the occupied energy eigenstates. Initially zero occupation probabilities, instead, remain zero at all times. The solutions $p_i(t)$ of the rate equations are unique and well defined for arbitrary initial conditions $p_i(0)$ and for all times. The existence and uniqueness both forward and backward in time allows the reconstruction of the ancestral or primordial lowest entropy state. By casting the rate equations in terms not of the p_i's but of their positive square roots $\sqrt{p_i}$, they unfold from the assumption that time evolution is at all times along the local direction of steepest entropy ascent or, equivalently, of maximal entropy generation. These rate equations have the same mathematical structure and basic features as the nonlinear dynamical equation proposed in a series of papers ending with G. P. Beretta, Found. Phys. **17**, 365 (1987) and recently rediscovered by S. Gheorghiu-Svirschevski [Phys. Rev. A **63**, 022105 (2001); **63**, 054102 (2001)]. Numerical results illustrate the features of the dynamics and the differences from the rate equations recently considered for the same problem by M. Lemanska and Z. Jaeger [Physica D **170**, 72 (2002)]. We also interpret the functionals $k_B\alpha(t)$ and $k_B\beta(t)$ as nonequilibrium generalizations of the thermodynamic-equilibrium Massieu characteristic function and inverse temperature, respectively.

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I. INTRODUCTION

Much work has appeared in recent years on the study of entropy-generating irreversible nonequilibrium dynamics. Limited discussion of previous work is found in [1–3] and references therein, but no thorough critical review of the subject is available, although it would be very helpful to provide proper acknowledgement of pioneering work, avoid "rediscoveries" such as in [4], and outline the different frameworks, motivations, approaches, and controversial aspects. To be sure, recent discussions [2,4–6] on possible fundamental tests of standard unitary quantum mechanics, related to the existence of "spontaneous decoherence" at the microscopic level, and on understanding and predicting decoherence in important future applications [7] involving nanometric devices, fast switching times, clock synchronization, superdense coding, quantum computation, teleportation, quantum cryptography, etc., show that the subject of irreversible nonequilibrium dynamics is by no means settled.

It is not the purpose of this paper to attempt such a difficult review, nor to address the related fundamental issues lurking beneath interpretation (see, e.g., [8–10]). Rather we wish to address the model problem recently outlined in [1].

This model may prove useful to complement various historical and contemporary efforts to extend linear Markovian theories of dissipative phenomena and relaxation based on master equations, the Lindblad and Langevin equations, to the nonlinear and far nonequilibrium domain. For example, spectroscopic studies of the effects of vibrational relaxation on line shapes of two-level electronic transitions cannot be regularized under the Markovian approximations so that various nonlinear approaches are being developed and tested [11] in some cases at the expense of giving up preservation of (complete) positivity [12] or Hermiticity [13] of the (reduced) density operator.

Again, it is not our purpose here to review the literature of these specific potential applications of our model dynamics, nor to apply it explicitly to particular examples. Rather we wish to focus on illustrating its general features (including preservation of positivity and Hermiticity at all times, even backward) that make it a good candidate (that is, compatible with all reasonable requirements imposed by thermodynamic principles [14]) of extensions of the traditional linear master equations for open-system dynamics, capable of including the description of nonlinear spontaneous relaxation within the system (even if isolated) by energy redistribution between the occupied levels.

We consider an isolated, closed system composed of noninteracting identical particles with single-particle energy levels e_i with $i=1,2,\ldots,N$ where N is assumed finite for simplicity and the e_i's are repeated in case of degeneracy. We restrict our attention to the class of dilute-Boltzmann-gas states in which the particles are independently distributed among the N (possibly degenerate) one-particle energy eigenstates. In density operator language, this is tantamount

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to restricting attention to the subset of one-particle density operators that are diagonal in the representation which diagonalizes the one-particle Hamiltonian operator. We denote by p_i the occupation probability of the ith eigenstate, so that the per particle mean energy, normalization, and entropy functionals are given by the relations

$$E(\mathbf{p}) = \sum_{i=1}^{N} e_i p_i, \quad U(\mathbf{p}) = \sum_{i=1}^{N} p_i,$$

$$S(\mathbf{p}) = -k_B \sum_{i=1}^{N} p_i \ln p_i, \tag{1}$$

where $\mathbf{p}$ denotes the vector of p_i's, the Boltzmann constant k_B may be used to nondimensionalize S (or we may assume for simplicity $k_B = 1$ unit of entropy), and of course $U(\mathbf{p}) = 1$ for any normalized distribution $\mathbf{p}$.

As is well known, for a given value of E, the thermodynamic-equilibrium canonical distribution

$$p_j^{\mathrm{se}}(E) = \frac{\exp[-\beta^{\mathrm{se}}(E)e_j]}{\sum_{i=1}^{N} \exp[-\beta^{\mathrm{se}}(E)e_i]} \tag{2}$$

has inverse temperature $\beta^{\mathrm{se}}(E) = 1/k_B T(E)$ and maximal entropy $S^{\mathrm{se}}(E) = -k_B \Sigma_{i=1}^{N} p_i^{\mathrm{se}}(E) \ln p_i^{\mathrm{se}}(E)$.

We are interested in studying the dynamics of a nonequilibrium distribution obtained, for example, by exciting some energy eigenstates. As suggested in [1], a way to alter the distribution is to repopulate (e.g., by selective laser heating) or depopulate (in principle, by selective cooling or resonance fluorescence) a subset of eigenstates. This is described by multiplying each p_j by a perturbation factor $f_j \geq 0$ (with $j = 1, 2, \ldots, N$) (repopulation $f_j > 1$, depopulation $f_j < 1$) and then renormalizing, to yield the perturbed nonequilibrium distribution

$$\tilde{p}_j = \frac{f_j p_j^{\mathrm{se}}(E)}{\sum_{i=1}^{N} f_i p_i^{\mathrm{se}}(E)}. \tag{3}$$

Of course, in general the perturbed distribution has a different mean energy $\tilde{E} = \Sigma_{i=1}^{N} e_i \tilde{p}_i$ and different entropy $\tilde{S} = -k_B \Sigma_{i=1}^{N} \tilde{p}_i \ln \tilde{p}_i$. However, a proper choice of the perturbation factors f_i may maintain $\tilde{E} = E$, in which case $\tilde{S} < S^{\mathrm{se}}(E)$ (see Sec. VII).

To describe the relaxation toward the new target canonical equilibrium distribution $\mathbf{p}^{\mathrm{se}}(\tilde{E})$, the dynamical equation proposed in [1] is, for $j = 1, 2, \ldots, N$,

$$\frac{dp_j}{dt} = -\upsilon[\ln p_j + a_L(\mathbf{p}) + b_L(\mathbf{p})e_j], \tag{4a}$$

where

$$a_L(\mathbf{p}) = \frac{\sum_i e_i \sum_j e_j \ln p_j - \sum_i \ln p_i \sum_j e_j^2}{N \sum_i e_i^2 - \left(\sum_i e_i\right)^2}, \tag{4b}$$

$$b_L(\mathbf{p}) = \frac{\sum_i \ln p_i \sum_j e_j - \sum_i e_i \ln p_i}{N \sum_i e_i^2 - \left(\sum_i e_i\right)^2}. \tag{4c}$$

This equation does have the capability of continuously rearranging the distribution so that the perturbed distribution evolves toward the maximal entropy target distribution given by Eq. (2) with energy $\tilde{E}$. However, in the far nonequilibrium region it has the defect of implying the unphysical feature that an initially unpopulated eigenstate gets populated at an infinite rate. This feature is in contrast with a wealth of successful models of physical systems in which by limiting our attention to a subset of relevant single-particle eigenstates we get good results that are relatively robust with respect to adding to the model other less relevant, unpopulated or little populated eigenstates. According to Eq. (4), instead, distributions where some eigenstates are very little populated would survive only for extremely short times.

The equation of motion that we propose for the time evolution of the perturbed distribution is, for $j = 1, 2, \ldots, N$,

$$\frac{dp_j}{dt} = -\frac{1}{\tau}[p_j \ln p_j + \alpha(\mathbf{p})p_j + \beta(\mathbf{p})e_j p_j], \tag{5a}$$

where

$$\alpha(\mathbf{p}) = \frac{\sum_i e_i p_i \sum_j e_j p_j \ln p_j - \sum_i p_i \ln p_i \sum_j e_j^2 p_j}{\sum_i e_i^2 p_i - \left(\sum_i e_i p_i\right)^2}, \tag{5b}$$

$$\beta(\mathbf{p}) = \frac{\sum_i p_i \ln p_i \sum_j e_j p_j - \sum_i e_i p_i \ln p_i}{\sum_i e_i^2 p_i - \left(\sum_i e_i p_i\right)^2}. \tag{5c}$$

We show in Sec. II that the apparently slight modification with respect to Eq. (4) not only fixes the cited defect, while maintaining the relevant overall features of conserving energy, normalization, nonnegativity of the probabilities, and maintaining the entropy generation rate nonnegative. It also features the existence and uniqueness of the solutions of the Cauchy problem for all times $-\infty < t < +\infty$, and entails a large class of partially canonical equilibrium distributions that are unstable, as well as a single conditionally stable canonical equilibrium distribution for each value of the energy, as required by a well-known statement of the second law of thermodynamics [15,16].

We show in Sec. II that the structure of Eq. (5) is the same as that of the general nonlinear quantum equation we discuss in a series of papers written over 20 years ago [17–21] in which we develop and propose a nonlinear quantum dynamics in an attempt to unite ordinary quantum mechanics and

general equilibrium and nonequilibrium thermodynamics. As acknowledged also in [2,22], the nonlinear quantum dynamical law first proposed by this author [23] does have very intriguing and appealing mathematical features. We must admit, however, that the physical interpretation, motivation, and context of our pioneering scheme is still considered "adventurous" [24] by most of the physical community, although we would prefer to term it "revolutionary" in the sense of Kuhn [25]. For this reason, in this paper we do not pursue such controversial interpretation, but we wish to emphasize that—leaving aside its interpretation and focusing attention only on its mathematics—our previous work represents to our knowledge the first time that the steepest-entropy-ascent (or maximal-entropy-generation) ansatz has been explicitly formulated and implemented in a general dynamical law capable of describing the relaxation of arbitrary nonequilibrium states toward thermodynamic equilibrium.

In Sec. III we provide a derivation of Eq. (5) from the assumption that the occupation probability distribution evolves along the steepest-entropy-ascent trajectory in the state space defined in terms not of the p_i's but of their positive square roots $\sqrt{p_i}$'s. In Sec. IV we derive a fluctuation-dissipation formulation of the equation and in Sec. V a variational formulation.

In Sec. VI we discuss the simplest degenerate case in which the relaxation equation admits an analytical solution, and we compare results with those numerically derived from the natural extension of Eq. (4) to such a case. Finally, in Sec. VII we show some numerical results that illustrate the general features of the proposed nonlinear relaxation equation.

II. MAIN FEATURES OF THE ASSUMED NONLINEAR RELAXATION EQUATION

By analogy with the dynamical law introduced in [17,19,23,26], Eq. (5) may also be written as a ratio of determinants in the form

$$\frac{dp_j}{dt} = -\frac{1}{\tau} \frac{\begin{vmatrix} p_j \ln p_j & p_j & e_j p_j \\ \sum p_i \ln p_i & 1 & \sum e_i p_i \\ \sum e_i p_i \ln p_i & \sum e_i p_i & \sum e_i^2 p_i \end{vmatrix}}{\begin{vmatrix} 1 & \sum e_i p_i \\ \sum e_i p_i & \sum e_i^2 p_i \end{vmatrix}}, \quad (6)$$

where $|\cdot| = \det[\cdot]$, and τ is assumed constant [27] and may be used to nondimensionalize time (or we may assume $\tau = 1$ unit of time).

The resulting rate of entropy generation may be written as a ratio of Gram determinants in the form

$$\frac{dS}{dt} = \frac{k_B}{\tau} \frac{\begin{vmatrix} \sum p_i (\ln p_i)^2 & \sum p_i \ln p_i & \sum e_i p_i \ln p_i \\ \sum p_i \ln p_i & 1 & \sum e_i p_i \\ \sum e_i p_i \ln p_i & \sum e_i p_i & \sum e_i^2 p_i \end{vmatrix}}{\begin{vmatrix} 1 & \sum e_i p_i \\ \sum e_i p_i & \sum e_i^2 p_i \end{vmatrix}}$$
$$\geqslant 0, \quad (7)$$

where the nonnegativity follows from the well-known properties of Gram determinants (see also Sec. III).

Equation (5) or the equivalent Eq. (6) is well behaved in the sense that the following general features can be readily verified (detailed proofs in [4,17]).

(1) It conserves the normalization of the distribution and the mean energy E along the entire time evolution.

(2) It preserves the nonnegativity of each p_i.

(3) It maintains the rate of entropy generation nonnegative at all times.

(4) It maintains unoccupied all the initially unoccupied eigenstates; in other words, given a distribution p_i and defining the vector $\boldsymbol{\delta}(\mathbf{p})$ of δ_i's such that, for each $i = 1, 2, \ldots, N$, $\delta_i = 0$ if $p_i = 0$ or $\delta_i = 1$ if $p_i \neq 0$, the vector $\boldsymbol{\delta}$ is time invariant.

(5) It drives any arbitrary initial distribution $\mathbf{p}(0)$ toward the partially canonical (or canonical, if $\delta_i = 1$ for all p_i's) equilibrium distribution, reached as $t \to \infty$,

$$p_j^{\mathrm{pe}}(E, \boldsymbol{\delta}) = \frac{\delta_j \exp[-\beta^{\mathrm{pe}}(E, \boldsymbol{\delta})e_j]}{\displaystyle\sum_{i=1}^{N} \delta_i \exp[-\beta^{\mathrm{pe}}(E, \boldsymbol{\delta})e_i]}, \quad (8)$$

where, of course, $\boldsymbol{\delta} = \boldsymbol{\delta}(\mathbf{p}(0))$ and the value of β^{pe} is determined by the initial state through the relation $\sum_{i=1}^{N} e_i p_i^{\mathrm{pe}}(E, \boldsymbol{\delta}) = E = E(\mathbf{p}(0))$. Distributions (8) are those for which $d\mathbf{p}/dt = 0$, i.e., that satisfy the equilibrium condition $p_i \ln p_i = -\alpha p_i - \beta e_i p_i$ for all i's and some scalars α and β.

Moreover, Eq. (6) is well behaved not only in forward time but also in backward time, consistently with the strongest form of the principle of causality, by which future states of a strictly isolated system should unfold deterministically from initial states along smooth unique trajectories in state domain, defined for all times (future as well as past). Indeed, for any given arbitrary "initial" distribution $\mathbf{p}(0)$ we can follow the unique trajectory $\mathbf{p}(t)$ for $-\infty < t < +\infty$. In forward time the target distributions of all trajectories are given by Eq. (8), $\mathbf{p}(+\infty) = \mathbf{p}^{\mathrm{pe}}(E(\mathbf{p}(0)), \boldsymbol{\delta}(\mathbf{p}(0)))$. The backward-time earliest (or "primordial") lowest-entropy distribution $\mathbf{p}(-\infty)$ is also uniquely identified by the given initial distribution $\mathbf{p}(0)$ through Eq. (6), but it is harder to characterize analytically in general. Depending on the given $\mathbf{p}(0)$, the redistribution among energy eigenstates may affect some of the occupation numbers in a nonmonotonic way. In the limit as $t \to -\infty$, however, all dp_j/dt's [the right-hand side of each of Eqs. (6)] become sign definite; for example, they may become all positive except for a particular one which tends to

$p_{\bar{k}}(-\infty)=1$, so that all others tend to zero, $p_{j\neq\bar{k}}(-\infty)=0$ [this can happen only if the mean energy $E(\mathbf{p}(0))$ is exactly equal to the $\bar{k}$th energy level, i.e., only if $E(\mathbf{p}(0))=e_{\bar{k}}$], or they may all tend to zero except for two particular p_j's, say $p_{\bar{j}}$ and $p_{\bar{k}}$ which tend to finite values, clearly with $p_{\bar{j}}+p_{\bar{k}}=1$ (examples in Sec. VII).

Because the model equation maintains the rate of entropy generation nonnegative, the entropy functional S [Eq. (1)] is an S function [16] and, therefore, every thermal-like canonical equilibrium distribution (8) is $\boldsymbol{\delta}$-E-conditionally stable, that is, stable with respect to perturbations that do not alter the mean value E of the energy and the set of unoccupied energy eigenstates (described by the zeros in vector $\boldsymbol{\delta}$). These distributions constitute the "target" highest-entropy states compatible with the mean value of the energy and the invariant subset of unoccupied eigenstates. These distributions, however, are not E-conditionally stable, that is, stable with respect to all perturbations that do not alter the mean value E. Indeed, starting from a distribution (8), a perturbation that changes a zero probability to an infinitesimal value, makes the perturbed distribution proceed in time by amplifying that probability until a new, different, and higher-entropy target canonical distribution is reached. For a given mean energy E, the only canonical distribution that is E-conditionally stable is the one for which all energy eigenstates are occupied, i.e., the maximal-entropy canonical distribution (2).

By interpreting the entropy S as a measure of how "well" the energy is distributed among the available energy eigenstates, the proposed nonlinear dynamics describes a spontaneous internal redistribution of the energy along the path of maximal entropy increase leading toward an "optimally" distributed (highest-entropy) state compatible with the condition of maintaining unoccupied the initially unoccupied energy eigenstates.

III. CONSTRUCTION OF THE EQUATION FROM THE STEEPEST-ENTROPY-ASCENT ANSATZ

In this section, we provide a brief derivation of Eq. (6) from the assumption that the occupation probability distribution evolves along the steepest-entropy-ascent trajectory in the proper state space. We also discuss an important degenerate case.

For the purpose of this derivation, instead of working with the vector $\mathbf{p}$ of the occupation probabilities, we work in terms of their positive square roots [28], $y_i=\sqrt{p_i}$, and the corresponding vector $\mathbf{y}$. We rewrite the mean energy, normalization, and entropy functionals as

$$E(\mathbf{y})=\sum_{i=1}^{N} e_i y_i^2, \quad U(\mathbf{y})=\sum_{i=1}^{N} y_i^2,$$

$$S(\mathbf{y})=-k_B\sum_{i=1}^{N} y_i^2 \ln y_i^2 \qquad (9)$$

where, of course, $U(\mathbf{y})=1$ for any $\mathbf{y}$. The ith components of the gradients of these functionals are, respectively,

$$e_i'=2e_i y_i, \quad u_i'=2y_i, \quad s_i'=-2k_B(y_i \ln y_i^2 + y_i) \quad (10)$$

and, therefore, the time-rate-of-change functionals may be written as

$$\dot{E}=(\dot{\mathbf{y}},\mathbf{e}'), \quad \dot{U}=2(\dot{\mathbf{y}},\mathbf{y}),$$

$$\dot{S}=(\dot{\mathbf{y}},\mathbf{s}'), \qquad (11)$$

where $(\cdot,\cdot)$ denotes the scalar product of two vectors [e.g., the normalization condition $U(\mathbf{y})=1$ may be rewritten as $(\mathbf{y},\mathbf{y})=1$], and the energy and entropy gradient vectors $\mathbf{e}'$ and $\mathbf{s}'$ are defined by the components in (10), while we choose to substitute immediately the obvious relation $\mathbf{u}'=2\mathbf{y}$.

In order to maintain $(\dot{\mathbf{y}},\mathbf{y})=0$ and $(\dot{\mathbf{y}},\mathbf{e}')=0$ the vector $\dot{\mathbf{y}}$ must be orthogonal to the linear manifold spanned by $\mathbf{y}$ and $\mathbf{e}'$.

For unconstrained maximal-entropy generation, $\dot{\mathbf{y}}$ would be in the direction of the gradient $\mathbf{s}'$ of the entropy functional $S(\mathbf{y})$; in this case, however, because $\mathbf{s}'$ is almost never orthogonal to the $\mathbf{y}\mathbf{e}'$ manifold, in general $U(\mathbf{y})$ and $E(\mathbf{y})$ would not remain time invariant. Instead, we assume constrained—constant $E(\mathbf{y})$ and $U(\mathbf{y})$—maximal-entropy generation. We obtain it by taking $\dot{\mathbf{y}}$ in the direction of the component of $\mathbf{s}'$ orthogonal to the $\mathbf{y}\mathbf{e}'$ manifold. Denoting such component by $\mathbf{s}'_{\perp\mathbf{y}\mathbf{e}'}$ we therefore assume

$$\dot{\mathbf{y}}=\frac{1}{4k_B\tau(\mathbf{y})}\mathbf{s}'_{\perp\mathbf{y}\mathbf{e}'}, \qquad (12)$$

where $\tau(\mathbf{y})$ may be any positive definite functional of $\mathbf{y}$ with dimensions of time, which determines the time rate at which $\mathbf{y}$ evolves along the path of constrained steepest entropy ascent. For simplicity, and for the purpose of comparison with [1], we assume τ a positive constant as done in our first proposal of this equation of motion in [17,20,21,23].

Using the well-known theory of Gram determinants, we can write an explicit expression for $\mathbf{s}'_{\perp\mathbf{y}\mathbf{e}'}$. If $\mathbf{y}$ and $\mathbf{e}'$ are linearly independent, we have

$$\mathbf{s}'_{\perp\mathbf{y}\mathbf{e}'}=\frac{\begin{vmatrix} \mathbf{s}' & \mathbf{y} & \mathbf{e}' \\ (\mathbf{s}',\mathbf{y}) & (\mathbf{y},\mathbf{y}) & (\mathbf{e}',\mathbf{y}) \\ (\mathbf{s}',\mathbf{e}') & (\mathbf{y},\mathbf{e}') & (\mathbf{e}',\mathbf{e}') \end{vmatrix}}{\begin{vmatrix} (\mathbf{y},\mathbf{y}) & (\mathbf{e}',\mathbf{y}) \\ (\mathbf{y},\mathbf{e}') & (\mathbf{e}',\mathbf{e}') \end{vmatrix}}. \qquad (13a)$$

If instead $\mathbf{y}$ and $\mathbf{e}'$ are linearly dependent, i.e., if $\mathbf{e}'=2e\mathbf{y}$ for some scalar e, the expression is

$$\mathbf{s}'_{\perp\mathbf{y}\mathbf{e}'}=\begin{vmatrix} \mathbf{s}' & \mathbf{y} \\ (\mathbf{s}',\mathbf{y}) & (\mathbf{y},\mathbf{y}) \end{vmatrix} \Big/ (\mathbf{y},\mathbf{y})=\mathbf{s}'-(\mathbf{s}',\mathbf{y})\mathbf{y},$$

$$(13b)$$

where we use $(\mathbf{y},\mathbf{y})=1$. In either case, we readily verify that

$$\dot{E}=(\dot{\mathbf{y}},\mathbf{e}')=0, \quad \dot{U}=2(\dot{\mathbf{y}},\mathbf{y})=0,$$

$$\dot{S} = (\dot{\mathbf{y}}, \mathbf{s}') = 4\pi k_B(\dot{\mathbf{y}}, \dot{\mathbf{y}}), \tag{14}$$

from which we see that the rate of entropy generation is related to the norm of $\dot{\mathbf{y}}$ and is positive definite.

Combining Eqs. (12) and (13a) we find

$$4k_B\tau\dot{\mathbf{y}} = \mathbf{s}' - a(\mathbf{y})\mathbf{y} - b(\mathbf{y})\mathbf{e}', \tag{15a}$$

where

$$a(\mathbf{y}) = \frac{(\mathbf{s}',\mathbf{y})(\mathbf{e}',\mathbf{e}') - (\mathbf{s}',\mathbf{e}')(\mathbf{e}',\mathbf{y})}{(\mathbf{y},\mathbf{y})(\mathbf{e}',\mathbf{e}') - (\mathbf{y},\mathbf{e}')(\mathbf{e}',\mathbf{y})}, \tag{15b}$$

$$b(\mathbf{y}) = \frac{(\mathbf{s}',\mathbf{e}')(\mathbf{y},\mathbf{y}) - (\mathbf{s}',\mathbf{y})(\mathbf{y},\mathbf{e}')}{(\mathbf{y},\mathbf{y})(\mathbf{e}',\mathbf{e}') - (\mathbf{y},\mathbf{e}')(\mathbf{e}',\mathbf{y})}, \tag{15c}$$

and, setting $p_i = y_i^2$ and $\dot{p}_i = 2y_i\dot{y}_i$ we readily obtain Eq. (5) and the identities $\alpha(\mathbf{p}) = 1 + a(\mathbf{y})/2k_B$ and $\beta(\mathbf{p}) = b(\mathbf{y})/k_B$.

Similarly, combining Eqs. (12) and (13b) we find

$$4k_B\tau\dot{\mathbf{y}} = \mathbf{s}' - (\mathbf{s}',\mathbf{y})\mathbf{y} \tag{16a}$$

and, therefore, in the degenerate case of $\mathbf{y}$ and $\mathbf{e}'$ linearly dependent, the relaxation equations are, for $j = 1, 2, \ldots, N$,

$$\frac{dp_j}{dt} = -\frac{1}{\tau}\left[p_j \ln p_j - p_j\left(\sum_i p_i \ln p_i\right)\right], \tag{16b}$$

or, equivalently,

$$\frac{dp_j}{dt} = -\frac{1}{\tau}\begin{vmatrix} p_j \ln p_j & p_j \\ \sum_i p_i \ln p_i & 1 \end{vmatrix}. \tag{16c}$$

In this case, the rate of entropy generation may be written as

$$\frac{dS}{dt} = \frac{k_B}{\tau}\begin{vmatrix} \sum_i p_i(\ln p_i)^2 & \sum_i p_i \ln p_i \\ \sum_i p_i \ln p_i & 1 \end{vmatrix} \geq 0, \tag{17}$$

where the nonnegativity follows from the well-known properties of Gram determinants.

Equation (16c) substitutes for Eq. (6) when $\mathbf{e}' = 2e\mathbf{y}$ for some scalar e or, equivalently, when $e_i p_i = e p_i$ for every i, that is, when the populated eigenstates all correspond to the same energy level. If satisfied at one instant in time this condition is satisfied at all times, both forward and backward in time. It follows that in such degenerate cases the entire time evolution is governed by Eq. (16b). In the general nondegenerate cases, i.e., when at one time (and, hence, at all times) $e_i p_i \neq E p_i$ for two or more i's, where E is the mean energy, the time evolution is entirely governed by Eq. (5) [or, equivalently, (6) or (15)]. This also implies that the denominators of $\alpha(\mathbf{p})$ and $\beta(\mathbf{p})$ [or, equivalently, of $a(\mathbf{y})$ and $b(\mathbf{y})$] remain positive definite at all times and, hence, the entire time evolution is well defined.

As stated above, the feature that unpopulated eigenstates remain unpopulated is extremely important as it is compatible, for example, with the widely accepted and successful possibility to describe real systems by means of simplified models with a limited number of relevant energy eigenstates.

The same feature does not hold for Eq. (4), because it implies that an initially unpopulated eigenstate gets popu-lated at an infinite rate. For the same reason, Eq. (4) does not allow tracing the time evolution backward in time beyond the instant when the first eigenstate becomes unpopulated, for at earlier times the condition $p_i \geq 0$ is not satisfied.

IV. FLUCTUATION-DISSIPATION FORMULATION

It is noteworthy that Eq. (6) admits a general fluctuation-dissipation formulation and interpretation. To see this, we introduce the energy and entropy fluctuation functionals as follows:

$$\langle\Delta E\Delta E\rangle(\mathbf{p}) = \sum_i p_i[e_i - E(\mathbf{p})]^2 = \sum_i p_i e_i^2 - \left(\sum_i p_i e_i\right)^2$$

$$= \frac{1}{4}\begin{vmatrix} (\mathbf{y},\mathbf{y}) & (\mathbf{e}',\mathbf{y}) \\ (\mathbf{y},\mathbf{e}') & (\mathbf{e}',\mathbf{e}') \end{vmatrix}, \tag{18}$$

$$\langle\Delta S\Delta S\rangle(\mathbf{p}) = \sum_i p_i[-k_B \ln p_i - S(\mathbf{p})]^2$$

$$= k_B^2\sum_i p_i(\ln p_i)^2 - k_B^2\left(\sum_i p_i \ln p_i\right)^2, \tag{19}$$

$$\langle\Delta E\Delta S\rangle(\mathbf{p}) = \sum_i p_i[e_i - E(\mathbf{p})][-k_B \ln p_i - S(\mathbf{p})], \tag{20}$$

and rewrite functionals $\beta(\mathbf{p})$ and $\alpha(\mathbf{p})$ as

$$\beta(\mathbf{p}) = \frac{1}{k_B}\frac{\langle\Delta E\Delta S\rangle(\mathbf{p})}{\langle\Delta E\Delta E\rangle(\mathbf{p})}, \tag{21}$$

$$\alpha(\mathbf{p}) = \frac{S(\mathbf{p})}{k_B} - \beta(\mathbf{p})E(\mathbf{p}). \tag{22}$$

At the thermodynamic-equilibrium distribution with energy E, $\mathbf{p}^{\text{se}}(E)$, we have

$$k_B\beta(\mathbf{p}^{\text{se}}(E)) = k_B\beta^{\text{se}}(E) = 1/T(E), \tag{23}$$

$$k_B\alpha(\mathbf{p}^{\text{se}}(E)) = k_B\alpha^{\text{se}}(E) = S^{\text{se}}(E) - E/T(E), \tag{24}$$

and in Eq. (24) we recognize the thermodynamic-equilibrium Massieu characteristic function [15]

$$M^{\text{se}} = S - E/T. \tag{25}$$

It is therefore natural, in this framework, to adopt the following generalization of the Massieu function to arbitrary nonequilibrium distributions:

$$M(\mathbf{p}) = k_B\alpha(\mathbf{p}) = S(\mathbf{p}) - k_B\beta(\mathbf{p})E(\mathbf{p}), \tag{26}$$

with $\beta(\mathbf{p})$ given by Eq. (21). The corresponding fluctuation functional is

$$\langle\Delta M\Delta M\rangle(\mathbf{p}) = \sum_i p_i[-k_B \ln p_i - k_B\beta(\mathbf{p})e_i - M(\mathbf{p})]^2. \tag{27}$$

We can readily verify that [Eq. (7)] may be rewritten as

$$\frac{dS}{dt} = \frac{1}{k_B\tau}\langle\Delta M\Delta M\rangle \qquad (28)$$

and, therefore, the rate of entropy generation is directly proportional to the fluctuations of our generalized Massieu function [29]. Such fluctuations are related to entropy and energy fluctuations through functional $k_B\beta(\mathbf{p})$ as follows:

$$\langle\Delta M\Delta M\rangle(\mathbf{p}) = \langle\Delta S\Delta S\rangle(\mathbf{p}) - k_B^2\beta(\mathbf{p})^2\langle\Delta E\Delta E\rangle(\mathbf{p}), \quad (29)$$

and become zero at every canonical thermodynamic-equilibrium distribution $\mathbf{p}^{\mathrm{se}}(E)$, Eq. (2), and at every partially canonical equilibrium distribution $\mathbf{p}^{\mathrm{pe}}(E,\boldsymbol{\delta})$, Eq. (8), as well.

It is noteworthy that the functional $k_B\beta(\mathbf{p})$, which is well defined by Eq. (21) only for distributions with $\langle\Delta E\Delta E\rangle \neq 0$, may be interpreted in this framework as a natural generalization to nonequilibrium of the inverse temperature, at least insofar as for $t\to+\infty$ it tends to the thermodynamic-equilibrium inverse temperature $k_B\beta^{\mathrm{se}}$ of distribution (2) or the partial equilibrium inverse temperature $k_B\beta^{\mathrm{pe}}$ of distribution (8).

The special case of distributions with $\langle\Delta E\Delta E\rangle = 0$ happens if and only if $\mathbf{e}' = 2e\mathbf{y}$ for some scalar e (see Sec. III). In such a special degenerate case, $\langle\Delta E\Delta E\rangle$ remains zero along the entire time evolution, which is given by Eq. (16b), and the role of the Massieu function is taken up by the entropy S, for both equilibrium and nonequilibrium distributions. The fluctuation-dissipation form of the rate of entropy generation [Eq. (17)] becomes the following:

$$\frac{dS}{dt} = \frac{1}{k_B\tau}\langle\Delta S\Delta S\rangle, \qquad (30)$$

and in this special degenerate case the canonical and partially canonical equilibrium distributions all have $\langle\Delta S\Delta S\rangle = 0$, for they consist of $N_{\boldsymbol{\delta}} = (\boldsymbol{\delta},\boldsymbol{\delta})$ probabilities p_i all equal to $1/N_{\boldsymbol{\delta}}$ and of $N-N_{\boldsymbol{\delta}}$ all equal to zero.

As regards the fluctuation-dissipation relations, the various well-formulated arguments, derivations and interpretations discussed for Eq. (4) by Englman in the Appendix of Ref. [1] and based on the steepest-entropy-ascent ansatz—introduced in quantum thermodynamics by the present author [19]—apply with minor modifications also for our better-behaved dynamical equation Eq. (5). In addition, we prove in [26] that Eq. (5) implies a generalized Onsager reciprocity theorem.

V. VARIATIONAL FORMULATION

In terms of the $y_i = \sqrt{p_i}$ notation, we can derive our equation of motion also as a result of the following equivalent variational formulation (along the lines recently proposed in [4]):

$$\max_{\dot{\mathbf{y}}} \dot{S} = (\dot{\mathbf{y}},\mathbf{s}') \quad \text{subject to } \dot{E} = (\dot{\mathbf{y}},\mathbf{e}') = 0,$$

$$\dot{U} = (\dot{\mathbf{y}},\mathbf{y}) = 0, \quad \text{and } (\dot{\mathbf{y}},\dot{\mathbf{y}}) = \xi(\mathbf{y}), \qquad (31)$$

where the last constraint implies that we maximize the entropy generation rate only with respect to the "direction" of

$\dot{\mathbf{y}}$, i.e., at every given $\mathbf{y}$ we select the maximizing $\dot{\mathbf{y}}$ among a subset of vectors that share the same (but otherwise arbitrary) norm $\xi(\mathbf{y})$. For $\mathbf{y}$ and $\mathbf{e}'$ linearly independent, using the standard method, we associate the Lagrange multipliers a, b, and $4k_B\tau$ with the constraints, and from Eq. (14) and the necessary Euler-Lagrange conditions

$$\frac{\partial}{\partial\dot{\mathbf{y}}}[(\dot{\mathbf{y}},\mathbf{s}') - a(\dot{\mathbf{y}},\mathbf{y}) - b(\dot{\mathbf{y}},\mathbf{e}') - 4k_B\tau(\dot{\mathbf{y}},\dot{\mathbf{y}})] = 0, \quad (32)$$

we readily obtain Eq. (15) as well as, upon substitution into the constraints, the multipliers given by Eqs. (15b) and (15c), and the square norm of $\dot{\mathbf{y}}$,

$$\xi(\mathbf{y}) = \frac{\dot{S}}{4k_B\tau} = \frac{1}{16k_B^2\tau^2}\frac{\Gamma(\mathbf{s}',\mathbf{y},\mathbf{e}')}{\Gamma(\mathbf{y},\mathbf{e}')}$$

$$= \frac{1}{16k_B^2\tau^2}\frac{\begin{vmatrix} (\mathbf{s}',\mathbf{s}') & (\mathbf{y},\mathbf{s}') & (\mathbf{e}',\mathbf{s}') \\ (\mathbf{s}',\mathbf{y}) & (\mathbf{y},\mathbf{y}) & (\mathbf{e}',\mathbf{y}) \\ (\mathbf{s}',\mathbf{e}') & (\mathbf{y},\mathbf{e}') & (\mathbf{e}',\mathbf{e}') \end{vmatrix}}{\begin{vmatrix} (\mathbf{y},\mathbf{y}) & (\mathbf{e}',\mathbf{y}) \\ (\mathbf{y},\mathbf{e}') & (\mathbf{e}',\mathbf{e}') \end{vmatrix}}, \qquad (33)$$

where Γ denotes the Gram determinant of the argument vectors.

Similarly, for the degenerate cases with $\mathbf{y}$ and $\mathbf{e}'$ linearly dependent, the normalization and constant energy conditions collapse into a unique constraint with which we associate the Lagrange multiplier c, and by the same standard procedure we obtain Eq. (16a) and, upon substitution into the constraints, the multiplier $c = (\mathbf{s}',\mathbf{y})$, and the square norm of $\dot{\mathbf{y}}$,

$$\xi(\mathbf{y}) = \frac{\dot{S}}{4k_B\tau} = \frac{1}{16k_B^2\tau^2}\Gamma(\mathbf{s}',\mathbf{y}) = \frac{1}{16k_B^2\tau^2}\begin{vmatrix} (\mathbf{s}',\mathbf{s}') & (\mathbf{y},\mathbf{s}') \\ (\mathbf{s}',\mathbf{y}) & (\mathbf{y},\mathbf{y}) \end{vmatrix}. \qquad (34)$$

VI. SIMPLEST CASE: TWO-LEVEL PARTICLES WITH DEGENERATE EIGENSTATES

The simplest mathematical form of the model equation that derives from the equation of motion proposed in the previous sections is obtained when we have an isolated, closed gas composed of noninteracting identical two-level particles with degenerate energy levels, such as electronic spins in the absence of an applied magnetic field. Then for $N=2$, both levels have energy $e_1 = e_2 = e$, the occupation probabilities of the two corresponding eigenstates are $p_1 = 1-p$ and $p_2 = p$, respectively, and the model equation (16c) for redistribution among the two eigenstates becomes

$$\frac{dp}{dt} = p(1-p)\ln\frac{1-p}{p}, \qquad (35)$$

where we set $\tau = 1$. The rate of entropy generation ($k_B = 1$) is

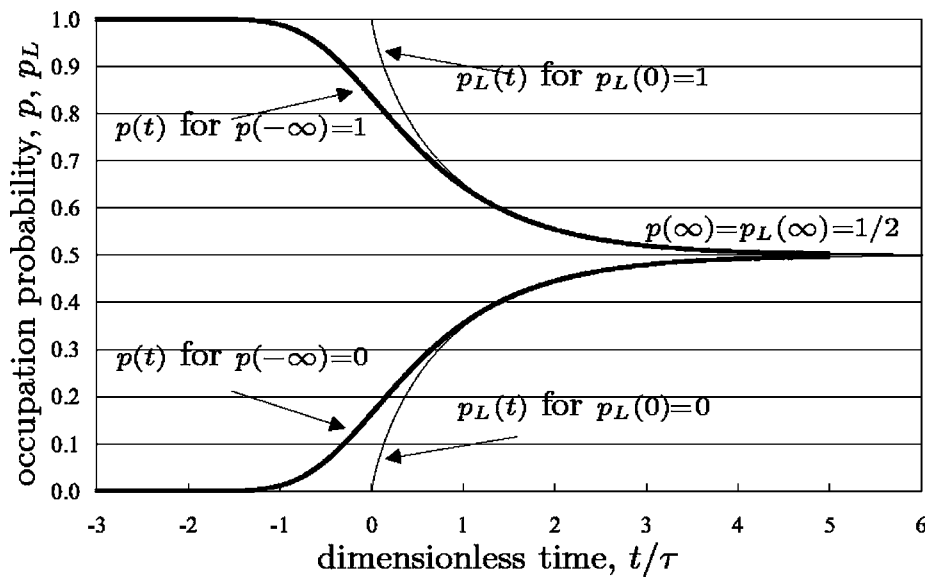$$\dot{S} = p(1-p)\left(\ln\frac{1-p}{p}\right)^2. \qquad (36)$$

FIG. 1. Comparison of the time dependences $p(t)$ and $p_L(t)$, respectively, implied by the rate equation (35) that we propose and the rate equation (40) discussed in [1].

Not only is Eq. (35) well behaved at all times [existence and uniqueness of the solution for any initial $p(0)$ with $0 \leqslant p(0) \leqslant 1$], but it can also be integrated to yield

$$t = \int_{p(0)}^{p(t)} \frac{dp}{p(1-p)\ln \frac{1-p}{p}} = \ln \frac{\ln \frac{1-p(0)}{p(0)}}{\ln \frac{1-p(t)}{p(t)}}, \quad (37)$$

or, equivalently,

$$p(t) = \frac{1}{1 + \left(\frac{1-p(0)}{p(0)}\right)^{\exp(-t/\tau)}} \quad (38a)$$

$$= \frac{1}{2} + \frac{1}{2}\tanh\left(-\frac{1}{2}\exp(-t/\tau)\ln\frac{1-p(0)}{p(0)}\right), \quad (38b)$$

from which we readily find $p(\infty) = 1/2$ and

$$p(-\infty) = \frac{1}{1 + \left(\frac{1-p(0)}{p(0)}\right)^{\infty}} = \begin{cases} 0 & \text{for } p(0) < 1/2, \\ 1 & \text{for } p(0) > 1/2. \end{cases} \quad (39)$$

By analogy, the extension to this degenerate case of the model equation proposed in [1] is $dp_j/dt = v(-\ln p_j + a_L)$ with $2a_L = \Sigma_{i=1}^{2}\ln p_i = \ln p + \ln(1-p)$, that is (setting $v = 1/2$ and adding, for clarity, the subscript L),

$$\frac{dp_L}{dt} = \frac{1}{4}\ln\frac{1-p_L}{p_L}, \quad (40)$$

which yields the entropy generation rate

$$\dot{S}_L = \frac{1}{4}\left(\ln\frac{1-p_L}{p_L}\right)^2. \quad (41)$$

Figure 1 shows a comparison between the time dependence (38) implied by our rate equation (35) and that obtained by numerical solution (by a standard Runge-Kutta

method) of the rate equation (40), for both $p(-\infty) = 0 = p_L(0)$ and $p(-\infty) = 1 = p_L(0)$. For the purpose of comparison, time $t = 0$ is selected where $p_L(0) = 0$ or 1 and the initial state $p(0)$ is selected so as to emphasize that in the limit as $t \to +\infty$ we have $p(t) \approx p_L(t)$. In fact, we readily verify from both Eqs. (35) and (40) that the two time dependences have the same asymptotic behavior as they approach the equilibrium distribution, that is,

$$\frac{dp}{dt} \approx \frac{1}{2} - p \quad \text{and} \quad \dot{S} \approx 4\left(\frac{1}{2} - p\right)^2. \quad (42)$$

This simplest case brings out the evident different behavior at early times and the unphysical feature of the solution of Eq. (40) at $p_L = 0$ where the repopulation rate is infinite, implying that no unpopulated eigenstate can survive unpopulated. Instead, our Eq. (35) maintains unpopulated any initially unpopulated eigenstate, and it also maintains relatively little populated an initially little populated eigenstate for a lapse of time that is quantified by Eq. (37) and depends on how close the initial value $p(0)$ is to zero. For example, the time required to take $p(0) = 10^{-2n}$ to $p(t) = 10^{-2}$ is $t \approx \ln n$ (that is, $t \approx \tau \ln n$).

Figure 2 shows a plot of the entropy generation rate $\dot{S}$ versus p obtained from Eq. (36) compared with $\dot{S}_L$ versus p_L as obtained from Eq. (41), where again the essential differences for small values of p and $1 - p$ are singled out.

VII. NUMERICAL RESULTS

The energy versus entropy diagram introduced by Gibbs represents the intersection with the E-S plane of the E-S-V-$\mathbf{n}$ surface representing the stable thermodynamic-equilibrium states of a system, assuming that the energy eigenvalues depend on the volume V and the amounts of constituents $\mathbf{n}$, so that the surface is represented by the so-called fundamental relation $S = S(E, \{e_j(V, \mathbf{n})\})$. In [15] the use of such a diagram has been extended to include the projection onto the E-S plane of all other states, i.e., not only the stable
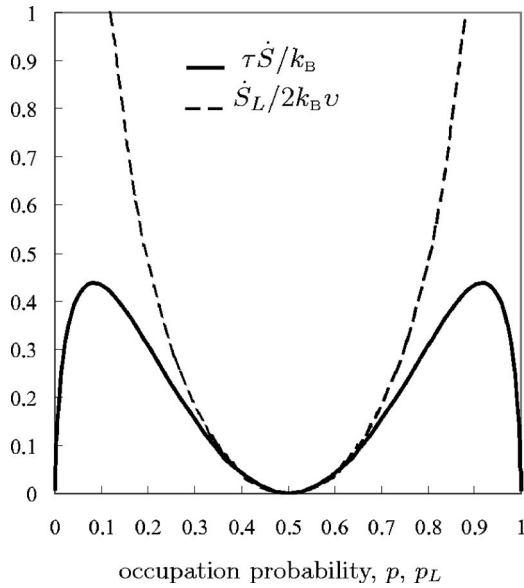
FIG. 2. Comparison between the entropy generation rate $\dot{S}$ versus p as given by Eq. (36) for $k_B=1$ and $\tau=1$ and $\dot{S}_L$ versus p_L as given by Eq. (41) for $k_B=1$ and $\upsilon=1/2$.

equilibrium states but also the nonequilibrium and the non-stable equilibrium states, with given fixed values of V and $\mathbf{n}$ and, therefore, a given fixed set of energy eigenvalues. On such a diagram, therefore, one point represents in general a multitude of distributions, except at every point of maximal entropy for each given value of E (V and $\mathbf{n}$ are fixed) which corresponds to a unique canonical distribution (2), i.e., a unique stable thermodynamic-equilibrium state.

For a four-level nondegenerate system, Fig. 3 represents on the diagram the families of possible canonical (2) and
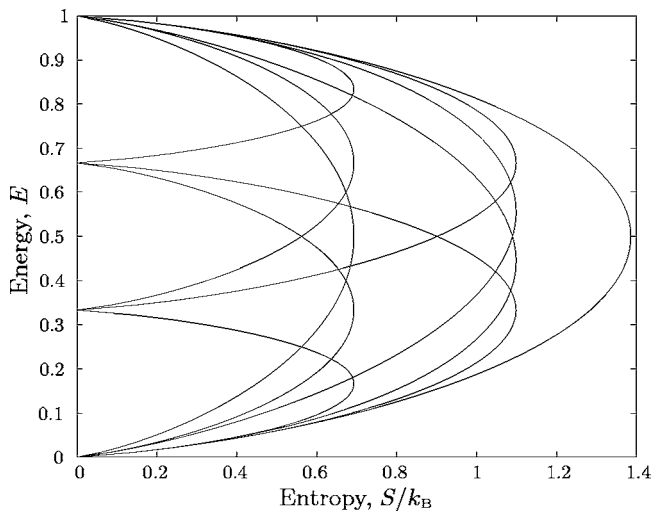

FIG. 3. Representation on an energy versus entropy diagram (for $N=4$ and nondegenerate eigenstates with energies $\mathbf{e}=[0,1/3,2/3,1]$) of the families of possible canonical and partially canonical equilibrium distributions which in our dynamics are the only ones with zero entropy generation rate. For example, a horizontal line at $E=0.4$ intersects seven different families of partially canonical states.
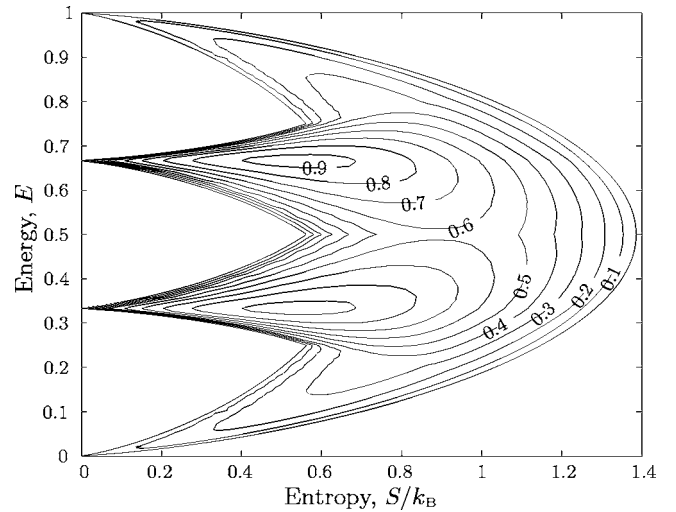

FIG. 4. Representation on an energy versus entropy diagram (for $N=4$ and nondegenerate eigenstates with energies $\mathbf{e}=[0,1/3,2/3,1]$) of the iso-$\dot{S}_{\max}$ contour curves where $\dot{S}_{\max}$ represents at each point in the diagram the highest value of the rate of entropy generation dS/dt according to Eq. (6) among all the possible distributions represented by that point.

partially canonical (8) equilibrium distributions which in our dynamics are the only ones with zero entropy generation rate. We recall that the slope of these curves is related to the parameter $\beta^{\mathrm{pe}}(E,\boldsymbol{\delta})$ because $\partial S^{\mathrm{pe}}(E,\boldsymbol{\delta})/\partial E|_{\boldsymbol{\delta}}=k_B\beta^{\mathrm{pe}}(E,\boldsymbol{\delta})$, which for the canonical distribution (all δ_i's equal to unity) is $\partial S(E)/\partial E=k_B\beta(E)=1/T(E)$.

The number of possible distributions that share a given pair of values of E and S is in general an $(N-3)$-fold infinity except at maximal entropy for each value of E, where the distribution is unique, and at few other notable exceptions such as at minimal entropy for each given E where the distribution may be unique or sometimes manyfold. For all possible distributions represented by a given point on the E-S diagram, we may evaluate the rate of entropy generation dS/dt according to Eq. (6) and select the highest value, that we denote by $\dot{S}_{\max}(E,S)$. The result of this numerical computation is sketched in Fig. 4 where the iso-$\dot{S}_{\max}$ contour curves are plotted on the entire allowed domain on the energy versus entropy diagram (of course, under the restriction to the subset of states specified in the Introduction).

The next figures show typical time dependences of the occupation probabilities that result from the numerical integration (by means of a standard Runge-Kutta algorithm) of Eq. (6) in both forward and backward time. All trajectories in these figures refer to a system with $N=4$ and nondegenerate eigenstates with $\mathbf{e}=[0,1/3,2/3,1]$, and all have the same mean energy $E=2/5$; they all tend, of course, to the canonical distribution $\mathbf{p}^{\mathrm{se}}(2/5)=[0.3474,0.2722,0.2133,0.1671]$ that has inverse temperature $\beta^{\mathrm{se}}(2/5)=0.7321$. They are obtained by assuming for all cases an initial distribution $\mathbf{p}(0)$ obtained by perturbing the canonical distribution $\mathbf{p}^{\mathrm{se}}(E)$ [Eq. (2)] according to Eq. (3) with the energy-preserving perturbing factors defined as follows, for $j=1,2,\ldots,N$:
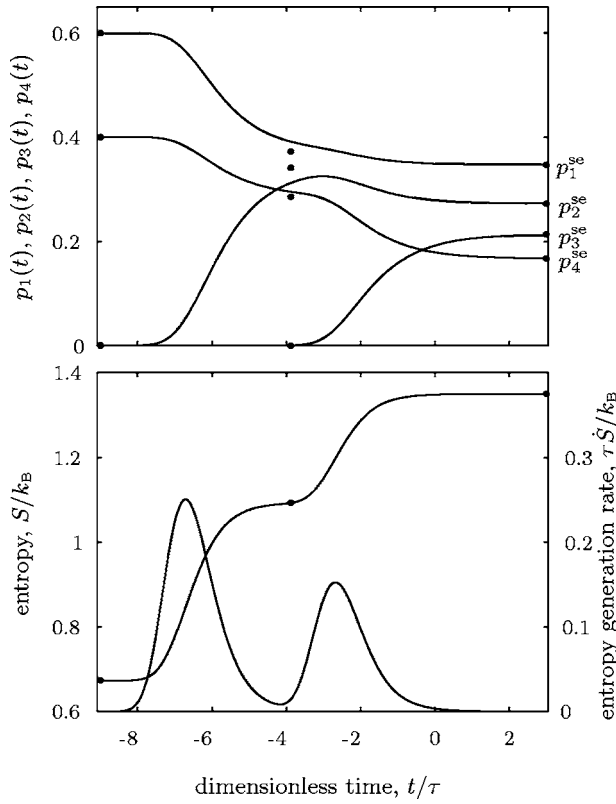
FIG. 5. Top: typical time dependences of the occupation probabilities that result from the numerical integration of Eq. (6) both forward and backward in time, for $N=4$, $\mathbf{e}=[0,1/3,2/3,1]$, energy $E=2/5$, initial state at $t=0$ from Eq. (44) with $\lambda=0.9$ and $\boldsymbol{\delta}=[1,1,0,1]$. The dots on the right represent the maximal-entropy distribution; the dots at the left represent the lowest-entropy or primordial distribution; the dots in the middle represent the $\mathbf{p}^{\mathrm{pe}}(E,\boldsymbol{\delta})$ distribution used in Eq. (44) to select the $t=0$ state, plotted at the instant in time when the entropy of the time-varying trajectory is equal to the entropy of the $\mathbf{p}^{\mathrm{pe}}(E,\boldsymbol{\delta})$ distribution. Bottom: the corresponding time dependence of the entropy (left axis) and the entropy generation rate (right axis).

$$f_j = 1 - \lambda + \lambda \frac{p_j^{\mathrm{pe}}(E,\boldsymbol{\delta})}{p_j^{\mathrm{se}}(E)} \quad \text{with } 0 < \lambda < 1, \qquad (43)$$

where λ is otherwise arbitrary, and also $\boldsymbol{\delta}$ is arbitrarily chosen among the possible vectors of 0's and 1's compatible with the given value of E and form (8) of the distribution $\mathbf{p}^{\mathrm{pe}}(E,\boldsymbol{\delta})$ (see Fig. 3), where $\beta^{\mathrm{pe}}(E,\boldsymbol{\delta})$ is computed by solving the relation $\Sigma_i e_i p_i^{\mathrm{pe}}(E,\boldsymbol{\delta})=E$. For all subsequent figures we use $\lambda=0.9$.

Figure 5 shows the time dependence of the occupation probabilities that results under the assumptions just cited using $E=2/5$, $\lambda=0.9$, and $\boldsymbol{\delta}=[1,1,0,1]$ in Eq. (43) and subsequently substituting in Eq. (3), that is,

$$\mathbf{p}(0) = \lambda \mathbf{p}^{\mathrm{pe}}(E,\boldsymbol{\delta}) + (1-\lambda)\mathbf{p}^{\mathrm{se}}(E). \qquad (44)$$

It is noteworthy that when the trajectory gets very close to the partially canonical unstable-equilibrium distribution $\mathbf{p}^{\mathrm{pe}}(E=2/5, \boldsymbol{\delta}=[1,1,0,1])$ the entropy surface presents a local "plateaux" and the entropy generation rate drops almost
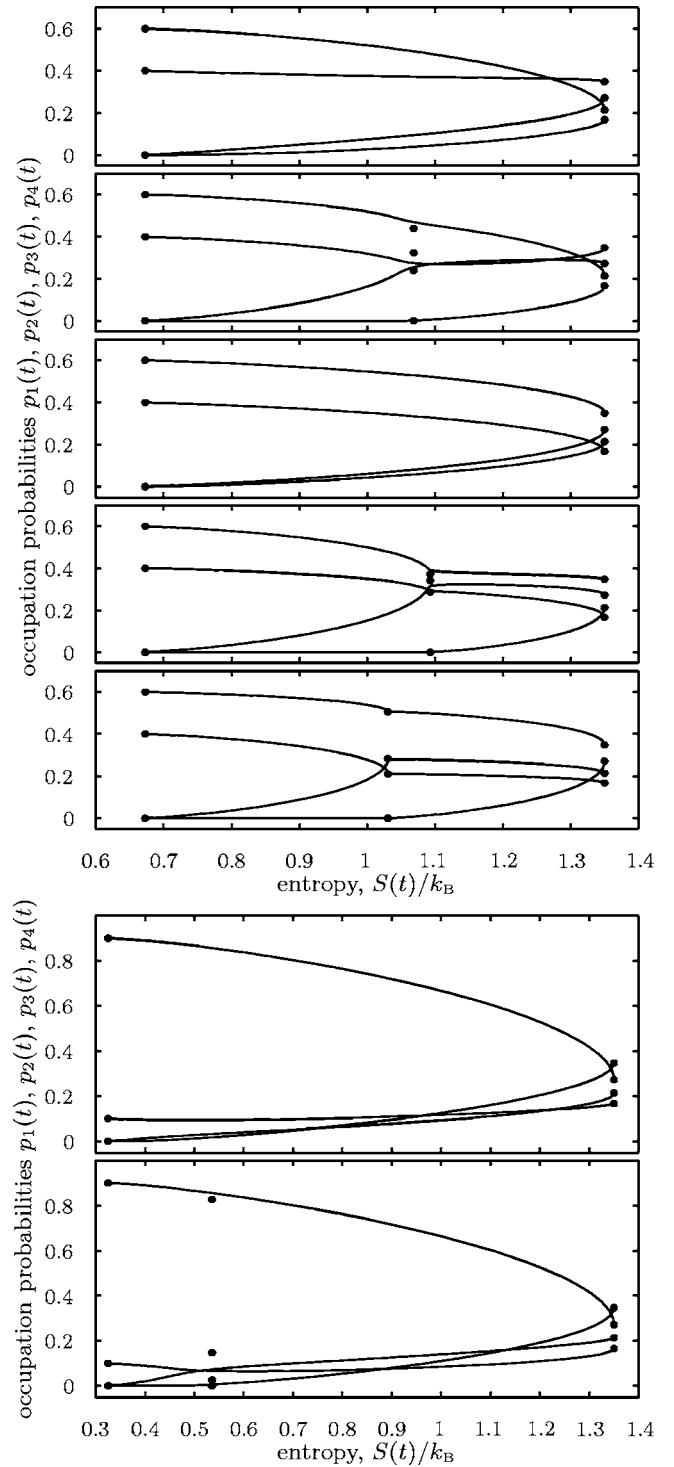

FIG. 6. Plots of $p_i(t)$ versus $S(t)$ for seven sample time dependences of the occupation probabilities that result from the numerical integration of Eq. (6) both forward and backward in time, for different initial distributions.

to zero, but shortly after the trajectory bends in a direction of steeper slope that drives the generation up again until the canonical distribution $\mathbf{p}^{\mathrm{se}}(E)=[0.3474, 0.2722, 0.2133, 01671]$ is finally approached, with inverse temperature $\beta^{\mathrm{se}}(2/5)=0.7321$. Of course, the entropy is a monotonically increasing function of time along the entire trajectory.
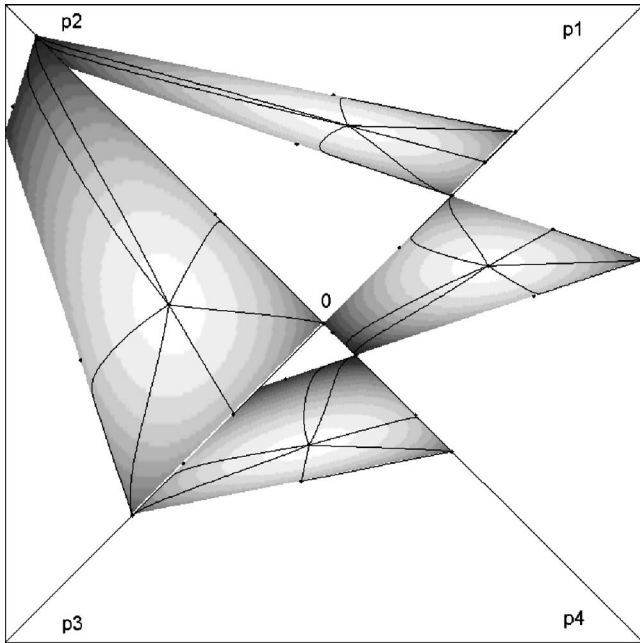
FIG. 7. Each rotated quadrant of the graph represents, for the corresponding pair of occupation probabilities, a plot of the seven trajectories shown in Fig. 6 drawn over contour plots of the entropy surface.

Figure 6 shows the same trajectory as well as six other trajectories, but instead of plotting the time dependence of the occupation probabilities we plot them against entropy. The initial (time $t=0$) distributions used to obtain these seven sample trajectories are obtained from Eq. (44) with $E=2/5$, $\lambda=0.9$, and each of the seven partially canonical states corresponding to the given value of the energy. These seven states are easily identified on the E-S diagram in Fig. 3 by drawing a horizontal line at $E=0.4$. For the first, third, and sixth trajectories we use the $\mathbf{p}^{\mathrm{pe}}(E,\boldsymbol{\delta})$ states with $\boldsymbol{\delta} =[1,0,1,0]$, $[1,0,0,1]$, and $[0,1,0,1]$, respectively, which (as apparent from the subsequent Fig. 7) are lowest-entropy boundary points of the entropy surface for the given energy, and turn out to be also the primordial states of the corresponding trajectories. For the remaining trajectories we use the $\mathbf{p}^{\mathrm{pe}}(E,\boldsymbol{\delta})$ states with $\boldsymbol{\delta}=[1,1,1,0]$, $[1,1,0,1]$, $[1,0,1,1]$, and $[0,1,1,1]$, respectively. These too are boundary points of the entropy surface, but they correspond to partial maxima (over the subset of distributions with one unoccupied eigenstate as specified by the corresponding zero element of $\boldsymbol{\delta}$). It is seen that these partial maxima affect the trajectories passing nearby by acting as partial attractors especially in the initial phase of the time evolution.

Figure 7 is a more elaborate representation of the same seven trajectories. They are shown four times from different perspectives on the background of contour plots of the entropy surface, for four pairs of occupation probabilities. Indeed, for $N=4$ and fixed energy E, the number of independent occupation probabilities is 2. Thus for four pairs of probabilities (p_1-p_2, p_2-p_3, p_3-p_4, p_4-p_1), we draw the contour plot of the entropy surface over the entire domain of allowed values (which of course are contained in a triangular region of the first quadrant), and over this plot we draw the seven trajectories (and the seven partially canonical states used to choose them). To save space, we then rotate each of the four graphs (respectively by 45°, 135°, 225°, 315°) and combine them on the same graph in Fig. 7. The figure visualizes clearly that the trajectories indeed follow paths of locally-steepest-entropy ascent and unfold smoothly also backward in time to the primordial states. We also note that these lowest-entropy states exhibit a singular behavior in that, for example, state $[2/5,0,3/5,0]$ is the primordial state for two entirely different trajectories, state $[3/5,0,0,2/5]$ for three others, and state $[0,9/10,0,1/10]$ for the remaining two. Moreover, the partially canonical states appear as partial attractors of trajectories passing nearby, as seen quite clearly for the second, fourth, and fifth trajectories of Fig. 6, which are partially attracted by the partially canonical states with $\boldsymbol{\delta}=[1,1,1,0]$, $[1,1,0,1]$, and $[1,0,1,1]$, respectively.

VIII. CONCLUSIONS

The model we propose for the description of the time evolution of the occupation probabilities of a perturbed, isolated, physical system with single-particle eigenstates with energies e_i for $i=1,2,\ldots,N$, is in good agreement with general thermodynamic requirements such as energy conservation, conservation of normalization, and nonnegativity of the probabilities, entropy nondecrease, E-conditional stability of the maximal-entropy canonical equilibrium states, E-conditional nonstability of each non-maximal-entropy partially canonical equilibrium states, and existence and uniqueness of solutions for all initial perturbed distributions, in both forward and backward time. As in our previous work [17,19,20,23,26], the proposed rate equations implement the fundamental ansatz that nonequilibrium time dependence follows the path of steepest entropy ascent (or, using the terminology adopted in [2,4], maximal-entropy generation).

The model can be readily generalized to include additional constraints and therefore adapted to other physical and nonphysical (e.g., information theoretical, biological) problems that obey the same maximal-entropy formalism and the maximal-entropy generation rate ansatz. Using the formalism developed in Sec. III it can even be readily generalized to different entropy functionals or nonlinear objective functionals that may be relevant in many other contexts that share with the present the basic mathematical framework.

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[27] That the relaxation time τ need not be constant (as was initially assumed in [17,18,20,21,23] as well as in [1]) but may be any positive functional of **p** was realized in [26]. See also G. P. Beretta, e-prints quant-ph/0112046 and quant-ph/0511091.

[28] The $\rho = \gamma\gamma^\dagger$ formalism proposed by B. Reznik [Phys. Rev. Lett. **76**, 1192 (1996)] and adopted by Gheorghiu-Svirschevski [4] does extend the $\rho = (\sqrt{\rho})^2$ formalism introduced in [23,17,19] in an interesting and elegant way; however, it is not necessary to derive our nonlinear equation. Moreover, it may be conceptually troublesome because it leaves unspecified the choice of γ for a given ρ, and thus risks to imply the existence of yet unidentified, (hidden?) physical observables that would render the operator ρ an insufficient state descriptor.

[29] As we discuss in a forthcoming paper to be published elsewhere, the important relation (28) holds also for the quantum equation proposed in [23,4,17], i.e., also when the restriction $[H, \rho] = 0$, which defines the class of distributions considered in the present paper, is removed.