

Steepest entropy ascent model for far-nonequilibrium thermodynamics: Unified implementation of the maximum entropy production principle

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By suitable reformulations, we cast the mathematical frameworks of several well-known different approaches to the description of nonequilibrium dynamics into a unified formulation valid in all these contexts, which extends to such frameworks the concept of steepest entropy ascent (SEA) dynamics introduced by the present author in previous works on quantum thermodynamics. Actually, the present formulation constitutes a generalization also for the quantum thermodynamics framework. The analysis emphasizes that in the SEA modeling principle a key role is played by the geometrical metric with respect to which to measure the length of a trajectory in state space. In the near-thermodynamic-equilibrium limit, the metric tensor is directly related to the Onsager's generalized resistivity tensor. Therefore, through the identification of a suitable metric field which generalizes the Onsager generalized resistance to the arbitrarily far-nonequilibrium domain, most of the existing theories of nonequilibrium thermodynamics can be cast in such a way that the state exhibits the spontaneous tendency to evolve in state space along the path of SEA compatible with the conservation constraints and the boundary conditions. The resulting unified family of SEA dynamical models is intrinsically and strongly consistent with the second law of thermodynamics. The non-negativity of the entropy production is a general and readily proved feature of SEA dynamics. In several of the different approaches to nonequilibrium description we consider here, the SEA concept has not been investigated before. We believe it defines the precise meaning and the domain of general validity of the so-called maximum entropy production principle. Therefore, it is hoped that the present unifying approach may prove useful in providing a fresh basis for effective, thermodynamically consistent, numerical models and theoretical treatments of irreversible conservative relaxation towards equilibrium from far nonequilibrium states. The mathematical frameworks we consider are the following: (A) statistical or information-theoretic models of relaxation; (B) small-scale and rarefied gas dynamics (i.e., kinetic models for the Boltzmann equation); (C) rational extended thermodynamics, macroscopic nonequilibrium thermodynamics, and chemical kinetics; (D) mesoscopic nonequilibrium thermodynamics, continuum mechanics with fluctuations; and (E) quantum statistical mechanics, quantum thermodynamics, mesoscopic nonequilibrium quantum thermodynamics, and intrinsic quantum thermodynamics.

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I. INTRODUCTION

The problem of understanding entropy and irreversibility has been tackled by a large number of preeminent scientists during the past century. Schools of thought have formed and flourished around different perspectives of the problem. Several modeling approaches have been developed in various frameworks to deal with the many facets of nonequilibrium.

In this paper, we show how to construct steepest entropy ascent (SEA) models of nonequilibrium dynamics by adopting a unified mathematical formulation that allows us to do it at once in several different well-known frameworks of nonequilibrium description.

To avoid doing inevitable injustices to the many pioneers of all these approaches and to the many and growing fields of their application, here we skip a generic introduction and given no references nor a review of previous work. Rather, we dig immediately into the mathematical reformulations of the different frameworks in such a way that the construction of the proposed SEA dynamics becomes formally a single geometrical problem that can be treated at once.

Our reformulations here not only allow a precise meaning, general implementation, and unified treatment of the so-called

maximum entropy production (MEP) principle (for a recent review see Ref. [1]) in the various frameworks but also extend to all frameworks an observation that we have been developing in the quantum thermodynamics framework for the past three decades [2–5]. In doing so, we also introduce an important generalization for the quantum thermodynamics modeling framework.

The observation is that we cannot simply maximize the entropy production subject to a set of conservation constraints or boundary conditions, but in order to identify a SEA path in state space we must equip the state space with a metric field with respect to which to compute the distance traveled during the time evolution.

The generalization is as follows. In our previous work, we adopted the proper uniform metric for probability distributions, namely the Fisher-Rao metric, because in quantum thermodynamics the state representative, the density operator, is essentially a generalized probability distribution. In other frameworks, however, the state representative not always is a probability distribution. Moreover, the present application to the framework of mesoscopic nonequilibrium thermodynamics [6,7] shows that standard results such as the Fokker-Planck equation and Onsager theory emerge as straightforward results of SEA dynamics with respect to a metric characterized by a generalized metric tensor that is directly related to the inverse of the generalized conductivity

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tensor. Since the generalized conductivities represent, at least in the near-equilibrium regime, the strength of the system's reaction when pulled out of equilibrium, it appears that their inverse, i.e., the generalized resistivity tensor, represents the metric with respect to which the time evolution, at least in the near equilibrium, is locally SEA.

But the local SEA construction does much more, because it offers a strongly thermodynamically consistent way to extend the well-known near-equilibrium theories to the treatment of nonequilibrium states.

The unified formulation of the local SEA variational problem is as follows and it is not restricted to near equilibrium: The time evolution of the local state is the result of a balance between the effects of transport or Hamiltonian dynamics and the spontaneous and irreversible tendency to advance the local state representative in the direction of maximal entropy production per unit of distance traveled in state space compatible with the conservation constraints.

Geometrically, the measure of distance traveled in state space requires the choice of a local metric tensor. Physically, the local metric tensor contains the full information about the relaxation kinetics of the material. The standard near-equilibrium results obtain when the local metric tensor is proportional to the inverse of the local matrix of generalized conductivities, i.e., to the local generalized resistivity matrix.

The structure of the SEA geometrical construction for the description of highly nonequilibrium dissipative dynamics in the nonlinear domain turns out to be closely related to the formulation of dissipation in the well-known general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) [8–10]. The seeds of SEA and GENERIC developed independently in the early 1980s with different motivations and approaches, but the common general thrust has been, and still is, to impose strong thermodynamic consistency in the dynamical modeling of systems far from stable thermodynamic equilibrium. SEA has focused exclusively on the irreversible entropy-generation component of the time evolution, while GENERIC has emphasized the coupling and interplay between the reversible and irreversible components of the time evolution.

We will show elsewhere [11] that the main technical differences are that (1) SEA chooses a (nondegenerate) Riemannian metric tensor as dissipative structure, while GENERIC chooses two compatible degenerate structures (Poisson and degenerate co-Riemannian), and (2) in the description of a continuum, SEA uses the local entropy density field as potential, while GENERIC uses the global energy and entropy functionals as potentials. Future work is needed to address also the relationships and establish differences and similarities between the SEA description of far from equilibrium dissipation and other closely related approaches, such as the recent contact geometry of mesoscopic thermodynamics and dynamics [12–14], the general ideas of the rate-controlled constrained-equilibrium approach to far-from-local-equilibrium thermodynamics [15,16] and of the quasiequilibrium approximation of invariant manifolds [17], as well as the works of Ziegler [18] and Edelen [19].

The question of what “the physical basis” is for the SEA scheme (or that for the GENERIC scheme) is tricky and philosophically ill posed. It is as if one would ask what the

physical basis is for believing that a classical system should obey Hamilton's equations or the equivalent minimum action principle. The meaning of “physical reality” is well explained in the classic book on this subject by Henry Margenau [20]. There is a level of perceptions, the empirical world, that we try to describe by defining concepts, their relations with the plane of perceptions (operational measurement procedures), and relations among concepts that we call laws or principles (often using the language of mathematics to express them efficiently). The farther the construction goes from the plane of perceptions the more “abstract” it becomes, but the advantage is that more abstraction may allow us to encompass and regularize a broader set of less abstract theories, in short, to unify them. At any level of abstraction, what makes a theory “physical” are its links to the plane of perception, namely the fact that the theory allows us to model some empirical evidence with some reasonable level of approximation.

Paraphrasing the words of Feynman, what makes a particular law or principle “great,” such as the great conservation principles or the second law of thermodynamics, is the fact that they hold for whatever level of description of whatever empirical reality, provided the model has some basic structure and obeys some reasonable conditions, such as those that grant and give meaning to the concept of separability between the object of study and its surroundings. The spirit of the SEA construction is precisely this. We consider a number of frameworks that have successfully modeled nonequilibrium systems at some level of description, we focus on how these successful models of physical reality describe entropy production by irreversibility, and we cast them in a way that allows us to see that they can all be encompassed and regularized by the unifying geometrical SEA construction. The GENERIC construction is even more ambitious in that it attempts to unify at once also the reversible and transport contributions by recognizing their common Hamiltonian structure and their relations with the irreversible aspects of the dynamics.

Being more abstract (i.e., farther from Margenau's plane of perceptions) than the various physical theories they unify, the SEA and GENERIC constructions emerge as general dynamical principles which operate within the same domain of validity of the second law of thermodynamics and, hence, enjoy a similar level of “greatness”, by complementing it with the additional essential and general features of nonequilibrium behavior at all levels of description.

An important fraction of the greatness of the second law of thermodynamics stems from the fact that it supports the operational definition of entropy [21,22] as a property of any well-defined system and in any of its equilibrium and nonequilibrium states. Other good fractions that have direct impact also on the near-equilibrium description of dynamics derive from the stability and maximal entropy features of the equilibrium states.

An important fraction of the importance of the SEA principle stems from the fact that for any well-defined system it supports the operational definition of the metric field \hat{G} over its entire state space, which characterizes even in the far-nonequilibrium domain all that can be said about the spontaneous, irreversible, entropy-generating tendency towards stable equilibrium. Another good fraction derives from the fact that within the SEA construction the MEP

principle acquires a precise and general validity whereby, in any well-defined model, the entropy-producing component of the dynamics effectively pulls the state of the system in the direction of steepest entropy ascent compatible with the metric field \hat{G} and the imposed conservation laws.

The paper is structured as follows. In Sec. II we reformulate several of the well-known approaches for the description of dissipation in nonequilibrium systems to express them all in terms of a common geometrical formulation. In Sec. III we then introduce our steepest-entropy-ascent unified variational formulation of nonequilibrium dissipation and discuss its main general features. In Sec. IV we give a pictorial representation of the same concepts and in Sec. V we draw our conclusions.

II. COMMON STRUCTURE OF THE DESCRIPTION OF DISSIPATION IN SEVERAL NONEQUILIBRIUM FRAMEWORKS

In this section we show that several well-known nonequilibrium frameworks at various levels of description can be recast in slightly nonstandard, but unifying, notation so that they all exhibit as common features the following essential conditions:

C1: the state space, denoted by the symbol \mathcal{L} , is a manifold in a Hilbert space equipped with a suitable inner product $(\cdot|\cdot)$; we denote its elements (the states) by γ or, alternatively, $|\gamma\rangle$;

C2: the system properties (energy, entropy, mass, momentum, etc.) are represented by real functionals $\tilde{A}(\gamma)$, $\tilde{B}(\gamma)$, . . . of γ such that their functional derivatives with respect to γ are also elements of \mathcal{L} ; we denote them by $\delta\tilde{A}(\gamma)/\delta\gamma$ or, alternatively, by $|\delta\tilde{A}(\gamma)/\delta\gamma\rangle$;

C3: if the states are functions of time t only, $\gamma = \gamma(t)$, their time evolution $\gamma(t)$ obeys the equation of motion,

$$|d\gamma/dt\rangle = |\Pi_\gamma\rangle, \quad (1)$$

where $|\Pi_\gamma\rangle$ is also an element of \mathcal{L} such that the rates of change of the entropy $\tilde{S}(\gamma)$ and of any conserved property $\tilde{C}_i(\gamma)$, with i labeling a list of conserved properties, are

$$dS/dt = \Pi_S \quad \text{with} \quad \Pi_S = (\Phi|\Pi_\gamma) \geq 0, \quad (2)$$

$$dC_i/dt = \Pi_{C_i} \quad \text{with} \quad \Pi_{C_i} = (\Psi_i|\Pi_\gamma) = 0, \quad (3)$$

where Π_S and Π_{C_i} are the respective production rates and $|\Phi\rangle = |\delta\tilde{S}(\gamma)/\delta\gamma\rangle$ and $|\Psi_i\rangle = |\delta\tilde{C}_i(\gamma)/\delta\gamma\rangle$ are shorthand for denoting the variational derivatives with respect to γ of the entropy functional $\tilde{S}(\gamma)$ and the conserved functional $\tilde{C}_i(\gamma)$, respectively;

C3': if the states are continuum fields $\gamma = \gamma(t, \mathbf{x})$, where \mathbf{x} is position and t is time, assume that the time evolution obeys the equation of motion,

$$|\partial\gamma/\partial t\rangle + \mathcal{R}_\gamma|\gamma\rangle = |\Pi_\gamma\rangle, \quad (4)$$

where \mathcal{R}_γ is an operator on \mathcal{L} responsible for the description of the local fluxes in the continuum and $|\Pi_\gamma\rangle$ is an element of \mathcal{L} responsible for the description of the local production densities, such that the balance equations for entropy and any conserved property are

$$\partial S/\partial t + \nabla \cdot \mathbf{J}_S = \Pi_S \quad \text{with} \quad \Pi_S = (\Phi|\Pi_\gamma) \geq 0, \quad (5)$$

$$\partial C_i/\partial t + \nabla \cdot \mathbf{J}_{C_i} = \Pi_{C_i} \quad \text{with} \quad \Pi_{C_i} = (\Psi_i|\Pi_\gamma) = 0, \quad (6)$$

where, of course, \mathbf{J}_S and \mathbf{J}_{C_i} are the respective local Lagrangian fluxes and Π_S and Π_{C_i} the respective local production densities.

In the next subsections we introduce the details of the slightly nonstandard notations that allow us to reformulate in the terms just outlined some of the approaches that have been developed over the past several decades to provide thermodynamically consistent theories of nonequilibrium dissipation at various levels of description. This list of approaches is by no means exhaustive and their reformulations have no important elements of novelty. Their presentation here is only intended to explicitly substantiate the above common features in some of the most well-known nonequilibrium modeling frameworks. Perhaps the only major point is that in order to satisfy condition C2 in frameworks (A), (B), (D), and (E), we will borrow from the formalism we originally developed for the quantum framework [2,3] (later introduced also in Refs. [4,23]): the use of square roots of probabilities (instead of the probabilities themselves) as state representatives.

The reader who does not need to be convinced about such details can skip the rest of this section and jump to Sec. III, where we provide the unified construction and implementation of the SEA concept, based only on the general assumptions itemized above.

A. Framework A: Statistical or information-theoretic models of relaxation to equilibrium

Let \mathcal{L} be the set of all n -vectors of real finite numbers $A = \text{vect}(a_j)$, $B = \text{vect}(b_j)$, . . . ($n \leq \infty$), equipped with the inner product $(\cdot|\cdot)$ defined by

$$(A|B) = \text{Tr}(AB) = \sum_{j=1}^n a_j b_j. \quad (7)$$

In information theory [24], the probability assignment to a set of n events, p_j being the probability of occurrence of the j -th event, can be represented by $\rho = \text{vect}(p_j)$. In order to easily impose the constraint of preservation of non-negativity of the probabilities during their time evolution and to obtain condition C2 above, we adopt the description in terms of the square root of ρ that we denote by

$$\gamma = \text{vect}(\gamma_j = \sqrt{p_j}). \quad (8)$$

Typically, we consider a set of conserved expectation values of the process

$$\{\tilde{C}_i(\gamma)\} = \{\tilde{H}(\gamma), \tilde{N}_1(\gamma), \dots, \tilde{N}_r(\gamma), \tilde{I}(\gamma)\}, \quad (9)$$

where $\tilde{H}(\gamma) = \text{Tr}(\gamma^2 H) = \sum_{j=1}^n \gamma_j^2 e_j$ with H denoting the constant vector $H = \text{vect}(e_j)$, for $i = 1, \dots, r$, $\tilde{N}_i(\gamma) = \text{Tr}(\gamma^2 N_i) = \sum_{j=1}^n \gamma_j^2 n_{ij}$ with N_i denoting the constant vector $N_i = \text{vect}(n_{ij})$, and $\tilde{I}(\gamma) = \text{Tr}(\gamma^2 I) = \sum_{j=1}^n \gamma_j^2 = 1$, providing the normalization condition, with $I = \text{vect}(1)$. Notice that the variational derivatives $\delta\tilde{H}/\delta\gamma = \text{vect}(2\gamma_j e_j)$, $\delta\tilde{N}_i/\delta\gamma = \text{vect}(2\gamma_j n_{ij})$, $\delta\tilde{I}/\delta\gamma = 2\gamma$ are vectors in \mathcal{L} , thus satisfying condition C2 above. We denote them collectively by

$$\Psi_i = \delta\tilde{C}_i/\delta\gamma, \quad (10)$$

A time evolution of the square-root probability distribution, $\gamma(t)$, is a solution of the rate equation

$$\frac{d\gamma}{dt} = \Pi_\gamma, \quad (11)$$

where the term Π_γ must be such as to satisfy the constraints of conservation of the expectation values $\tilde{C}_i(\gamma)$, i.e., such that

$$\Pi_{C_i} = \frac{d\tilde{C}_i}{dt} = \frac{d}{dt}\text{Tr}(\gamma^2 C_i) = (\Psi_i | \Pi_\gamma) = 0. \quad (12)$$

The entropy in this context is represented by the Shannon functional

$$\tilde{S}(\gamma) = -k\text{Tr}(\rho \ln \rho) = (-k\gamma \ln \gamma^2 | \gamma) \quad (13)$$

so the rate of entropy production is given by

$$\Pi_S = \frac{d\tilde{S}}{dt} = -k\frac{d}{dt}\text{Tr}(\rho \ln \rho) = (\Phi | \Pi_\gamma), \quad (14)$$

where Φ denotes its variational derivative with respect to γ ,

$$\Phi = \delta\tilde{S}/\delta\gamma = \text{vect}(-2k\gamma_j - 2k\gamma_j \ln \gamma_j^2). \quad (15)$$

It is noteworthy that an advantage of the state representation in terms of square-root probability distributions is that $\delta S/\delta\gamma$ is well defined and belongs to \mathcal{L} for any distribution, even if some of the probabilities p_i are equal to zero, whereas in such cases $\delta S/\delta\rho$ is undefined and does not belong to \mathcal{L} .

In Sec. III we present the SEA construction which in this framework provides a model for the rate term Π_γ whereby Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ and the suitable additional constraint we discuss therein.

An attempt along the same lines has been presented in Ref. [25].

B. Framework B: Small-scale and rarefied gas dynamics

Let Ω_c be the classical one-particle velocity space, and \mathcal{L} the set of real, square-integrable functions A, B, \dots on Ω_c , equipped with the inner product $(\cdot | \cdot)$ defined by

$$(A | B) = \text{Tr}_c(AB) = \int_{\Omega_c} AB \, d\Omega_c, \quad (16)$$

where $\text{Tr}_c(\cdot)$ in this framework denotes $\int_{\Omega_c} \cdot \, d\Omega_c$, with $d\Omega_c = dc_x \, dc_y \, dc_z$.

In the kinetic theory of rarefied gases and small-scale hydrodynamics [26], the probability to find a particle (at position \mathbf{x} and time t) with velocity between \mathbf{c} and $\mathbf{c} + d\mathbf{c}$ [where, of course, $\mathbf{c} = (c_x, c_y, c_z)$] is given by $f(\mathbf{c}; \mathbf{x}, t) \, d\Omega_c / \int_{\Omega_c} f \, d\Omega_c$, where $f(\mathbf{c}; \mathbf{x}, t)$ is the local phase-density distribution which for every position \mathbf{x} and time instant t is a function in \mathcal{L} .

Also in this framework, in order to easily impose the constraint of preservation of the non-negativity of f during its time evolution and, perhaps more importantly, to obtain condition C2, we introduce the local one-particle state representation not by f itself but by its square root, which we assume is also a function in \mathcal{L} that we denote by $\gamma = \gamma(\mathbf{c}; \mathbf{x}, t)$. Therefore, we have

$$\begin{aligned} f &= \gamma^2, & \frac{\partial f}{\partial t} &= 2\gamma \frac{\partial \gamma}{\partial t}, \\ \frac{\partial f}{\partial \mathbf{x}} &= 2\gamma \frac{\partial \gamma}{\partial \mathbf{x}}, & \frac{\partial f}{\partial \mathbf{c}} &= 2\gamma \frac{\partial \gamma}{\partial \mathbf{c}}, \end{aligned} \quad (17)$$

and for any functionals $\tilde{A}_f(f)$ and $\tilde{A}_\gamma(\gamma) = \tilde{A}_f(\gamma^2)$,

$$\frac{\delta \tilde{A}_\gamma(\gamma)}{\delta \gamma} = 2\gamma \left. \frac{\delta \tilde{A}_f(f)}{\delta f} \right|_{f=\gamma^2} \quad (18)$$

Again, among the functionals that represent the one-particle physical observables we focus on the conserved fields, i.e., the collision invariants (mass, momentum, energy), which we denote synthetically by the set

$$\{\tilde{C}_i(\gamma)\} = \{m \tilde{n}(\gamma), \tilde{M}_x(\gamma), \tilde{M}_y(\gamma), \tilde{M}_z(\gamma), \tilde{H}(\gamma)\}, \quad (19)$$

where m is the single-particle mass, $\tilde{n}(\gamma) = \text{Tr}_c(\gamma^2)$ the particle number density field, $\tilde{M}_i(\gamma) = m \text{Tr}_c(\gamma^2 c_i)$ the i -th component of the momentum density field, and the total energy density field $\tilde{H}(\gamma) = \tilde{T}(\gamma) + \tilde{U}(\gamma)$ is, in general, composed of a kinetic energy contribution $\tilde{T}(\gamma) = \frac{1}{2} m \text{Tr}_c(\gamma^2 \mathbf{c} \cdot \mathbf{c})$ and a potential energy contribution $\tilde{U}(\gamma)$, such that at position \mathbf{x} and time t the functional derivative $\delta \tilde{U}(\gamma)/\delta \gamma = 2\gamma \varphi_\gamma(\mathbf{x}, t)$ is a function in \mathcal{L} , thus obeying condition C2 above, where $\varphi_\gamma(\mathbf{x}, t)$ is the single-particle potential field. For example, for a uniform externally applied field in the z direction, $-\nabla \varphi_\gamma(\mathbf{x}) = \mathbf{a} = -a \nabla z$ with a constant. Again, for the Vlasov-Poisson kinetic theory [27], $\tilde{U}(\gamma) = \frac{1}{2} \text{Tr}_c(\gamma^2 \varphi_\gamma)$, where $\varphi_\gamma(\mathbf{x}, t)$ is a nonlocal functional of γ , with $\varphi_\gamma(\mathbf{x}, t) = \int_{\Omega_{x'}} d\Omega_{x'} \int_{\Omega_{x''}} d\Omega_{x''} V(|\mathbf{x} - \mathbf{x}'|) \gamma^2(\mathbf{c}'; \mathbf{x}', t)$ representing a locally averaged mean-field single-particle potential due to the effects of the neighboring particles via the interparticle potential V assumed to be a function of particle distance only.

The dissipative time evolution of the distribution function f is given by the Boltzmann equation or some equivalent simplified kinetic model equation, which in terms of the square-root distribution may be written in the form

$$\frac{\partial \gamma}{\partial t} + \mathbf{c} \cdot \nabla \gamma - \nabla \varphi_\gamma \cdot \frac{\partial \gamma}{\partial \mathbf{c}} = \Pi_\gamma. \quad (20)$$

In order to satisfy the constraints of mass, momentum, and energy conservation, the collision term Π_γ must be such that

$$\Pi_{C_i} = (\Psi_i | \Pi_\gamma) = 0, \quad (21)$$

where

$$\Psi_i = \delta \tilde{C}_i / \delta \gamma. \quad (22)$$

The entropy density field in this context is represented by

$$S(\mathbf{x}, t) = \tilde{S}(\gamma) = -k \text{Tr}_c(\gamma^2 \ln \gamma^2) = (-k\gamma \ln \gamma^2 | \gamma), \quad (23)$$

the rate of entropy production is

$$\Pi_S = (\Phi | \Pi_\gamma), \quad (24)$$

where

$$\Phi = \delta \tilde{S} / \delta \gamma, \quad (25)$$

and the entropy balance equation is

$$-k \frac{\partial \text{Tr}_c(f \ln f)}{\partial t} - k \nabla \cdot \text{Tr}_c(f \mathbf{c} \ln f) = \Pi_S, \quad (26)$$

where $\mathbf{J}_S = -k \text{Tr}_c(f \mathbf{c} \ln f)$ represents the entropy flux field.

In Sec. III, we construct the family of models for the collision term Π_γ such that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ and the suitable additional geometrical constraint we discuss therein.

The resulting family of SEA kinetic models of the collision integral in the Boltzmann equation is currently under investigation by comparing it with standard models such as the well-known Bhatnagar, Gross, and Krook (BGK) model as well as with Monte Carlo simulations of the original Boltzmann equation for hard spheres [28]. In addition to the strong thermodynamic consistency even far from stable equilibrium, Ref. [28] gives a proof that in the near-equilibrium limit the SEA models reduce to the corresponding BGK models.

In a forthcoming paper [11], we work out the explicit relation between SEA and GENERIC and we provide the explicit SEA form of the full Boltzmann collision operator by using its already-available GENERIC form [8,14,29,30].

C. Framework C: Rational extended thermodynamics, macroscopic nonequilibrium thermodynamics, and chemical kinetics

Let \mathcal{L} be the set of all n vectors of real numbers $A = \text{vect}(a_j)$, $B = \text{vect}(b_j)$, \dots ($n \leq \infty$), equipped with the inner product $(\cdot|\cdot)$ defined by

$$(A|B) = \text{Tr}(AB) = \sum_{j=1}^n a_j b_j. \quad (27)$$

In rational extended thermodynamics [31], the local state at position \mathbf{x} and time t of the continuum under study is represented by an element γ in \mathcal{L} , i.e.,

$$\gamma(\mathbf{x}, t) = \text{vect}[\alpha_j(\mathbf{x}, t)]. \quad (28)$$

Thus, $\gamma(\mathbf{x}, t)$ represents a set of extensive underlying fields or internal variables $\alpha_j(\mathbf{x}, t)$ which represent the instantaneous spatial distributions within the continuum of the local densities that define all its other local properties. In particular, for the conserved properties energy, momentum, and mass [32] it is assumed that their local densities and their local (Lagrangian) fluxes are all given by particular functions of γ that we denote synthetically by

$$\{\tilde{C}_i(\gamma)\} = \{\tilde{E}(\gamma), \tilde{M}_x(\gamma), \tilde{M}_y(\gamma), \tilde{M}_z(\gamma), \tilde{m}_k(\gamma)\}, \quad (29)$$

$$\{\mathbf{J}_{C_i}(\gamma)\} = \{\mathbf{J}_E(\gamma), \mathbf{J}_{M_x}(\gamma), \mathbf{J}_{M_y}(\gamma), \mathbf{J}_{M_z}(\gamma), \mathbf{J}_{m_k}(\gamma)\}, \quad (30)$$

so the energy, momentum, and mass balance equations take the form

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{J}_{C_i} = \Pi_{C_i} = 0. \quad (31)$$

Moreover, also for the local entropy density and the local (Lagrangian) entropy flux it is assumed that they are given by particular functions of γ that we denote respectively by

$$S(\gamma) \quad \text{and} \quad \mathbf{J}_S(\gamma), \quad (32)$$

so the entropy balance equation takes the form

$$\frac{\partial S}{\partial t} + \nabla \cdot \mathbf{J}_S = \Pi_S, \quad (33)$$

where Π_S is the local production density.

In general, the balance equation for each of the extensive underlying field properties, i.e., the internal variables, is

$$\frac{\partial \alpha_j}{\partial t} + \nabla \cdot \mathbf{J}_{\alpha_j} = \Pi_{\alpha_j}, \quad (34)$$

where \mathbf{J}_{α_j} and Π_{α_j} are the corresponding flux and production density, respectively. Equivalently, this set of balance equations may be written synthetically as

$$\frac{\partial \gamma}{\partial t} + \nabla \cdot \mathbf{J}_\gamma = \Pi_\gamma, \quad (35)$$

where $\mathbf{J}_\gamma = \text{vect}(\mathbf{J}_{\alpha_j})$ and $\Pi_\gamma = \text{vect}(\Pi_{\alpha_j})$.

It is then further assumed that there exist functions $\Phi_{\alpha_j}(\gamma)$ (Liu's Lagrange multipliers [33]) that we denote here in vector form by

$$\Phi = \text{vect}(\Phi_{\alpha_j}) \quad (36)$$

such that the local entropy production density can be written as

$$\Pi_S = \sum_{j=1}^n \Phi_{\alpha_j} \Pi_{\alpha_j} = (\Phi|\Pi_\gamma) \quad (37)$$

and must be non-negative everywhere.

For our development in this paper we additionally assume that there also exist functions $\Psi_{i\alpha_j}(\gamma)$ that we denote in vector form by

$$\Psi_i = \text{vect}(\Psi_{i\alpha_j}) \quad (38)$$

such that the production density of each conserved property C_i can be written as

$$\Pi_{C_i} = \sum_{j=1}^n \Psi_{i\alpha_j} \Pi_{\alpha_j} = (\Psi_i|\Pi_\gamma). \quad (39)$$

Typically, but not necessarily, the first $4 + n_{\text{sp}} - n_r$ underlying fields $\alpha_j(\mathbf{x}, t)$ for $j = 1, \dots, 4 + n_{\text{sp}} - n_r$ are conveniently chosen to coincide with the energy, momentum, and (independently conserved [32] linear combinations of the) mass densities, where n_{sp} is the number of species and n_r the number of independent reactions, so Eqs. (34) for $j = 1, \dots, 4 + n_{\text{sp}} - n_r$ coincide with Eqs. (31) because $\Pi_{\alpha_j} = 0$ for this subset of conserved fields.

The above framework reduces to the traditional Onsager theory of macroscopic nonequilibrium thermodynamics (NET) [6] if the α_j 's are taken to represent the local deviations of the underlying fields from their equilibrium values. In this context, the usual notation calls the functions Φ_{α_j} the ‘‘thermodynamic forces’’ and Π_{α_j} the ‘‘thermodynamic currents.’’

In Sec. III we construct an equation of motion for γ such that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ plus a suitable additional constraint.

The same framework reduces to the standard scheme of chemical kinetics (CK) if the α_j 's include the local reaction coordinates of each of the n_r steps of the detailed kinetic mechanism, the corresponding Π_{α_j} 's are the local rates of advancement of the reactions, $\Phi_{\alpha_j} = \partial S / \partial \alpha_j = - \sum_{\ell=1}^{n_{\text{sp}}} v_\ell^j \mu_\ell / T$ is the entropic affinity of the j -th reaction step (equal to the de Donder affinity divided by the temperature, see, e.g., Refs. [34,35], where μ_ℓ is the chemical potential of species ℓ), and m_k are the local values of the $n_{\text{sp}} - n_r$ independently conserved linear combinations of the masses of the various species (see Ref. [32] for the precise definition) so $\Pi_{m_k} = 0$ are their local production densities.

In the CK framework, the SEA construction is closely related to the gradient-dynamics formulations of the Guldberg-Waage mass action law as suggested in Refs. [36,37] and more recently in Refs. [38,39].

D. Framework D: Mesoscopic nonequilibrium thermodynamics and continuum mechanics with fluctuations

Let \mathcal{L} be the set of all n vectors $A = \text{vect}(a_j(\boldsymbol{\alpha}))$, $B = \text{vect}(b_j(\boldsymbol{\alpha}))$, ... whose entries $a_j(\boldsymbol{\alpha})$, $b_j(\boldsymbol{\alpha})$, ... are real, square-integrable functions of a set of mesoscopic (internal) variables denoted synthetically by the vector

$$\boldsymbol{\alpha} = \text{vect}(\alpha_1, \dots, \alpha_m), \quad (40)$$

whose m -dimensional range Ω_α is usually called the $\boldsymbol{\alpha}$ space. Let \mathcal{L} be equipped with the inner product $(\cdot|\cdot)$ defined by

$$(A|B) = \sum_{i=1}^n \text{Tr}_\alpha(a_i b_i) = \sum_{i=1}^n \int_{\Omega_\alpha} a_i(\boldsymbol{\alpha}) b_i(\boldsymbol{\alpha}) d\Omega_\alpha, \quad (41)$$

where $\text{Tr}_\alpha(\cdot)$ in this framework denotes $\int_{\Omega_\alpha} \cdot d\Omega_\alpha$, with $d\Omega_\alpha = d\alpha_1 \cdots d\alpha_m$.

In mesoscopic nonequilibrium thermodynamics (MNET) (see, e.g., Refs. [6,40]) the α_j 's are the set of mesoscopic (coarse-grained) local extensive properties assumed to represent the local nonequilibrium state of the portion of continuum under study. Our mesoscopic description of the local state at position \mathbf{x} and time t is in terms of a square-root probability density on the $\boldsymbol{\alpha}$ space Ω_α , which we denote by

$$\gamma(\boldsymbol{\alpha}; \mathbf{x}, t)$$

such that $\gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha$ represents the probability that the values of the underlying fields are between $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha} + d\boldsymbol{\alpha}$. In the standard formulation the state representative is the probability distribution $P(\boldsymbol{\alpha}; \mathbf{x}, t) = [\gamma(\boldsymbol{\alpha}; \mathbf{x}, t)]^2$.

It is assumed that the probability density γ obeys a continuity equation that we may write as follows:

$$\frac{\partial \gamma}{\partial t} + \mathbf{v} \cdot \nabla \gamma = \Pi_\gamma \quad \text{with} \quad 2\gamma \Pi_\gamma = -\nabla_\alpha \cdot \Pi_\alpha, \quad (42)$$

where $\mathbf{v} = \mathbf{v}(\boldsymbol{\alpha})$ is the particle velocity expressed in terms of the underlying fields (usually it is convenient to take the first three α_j 's to coincide with the velocity components), $\mathbf{v} \cdot \nabla \gamma = \nabla \cdot \mathbf{J}_\gamma$, where \mathbf{J}_γ is the flux of square-root probability density, and

$$\Pi_\alpha(\boldsymbol{\alpha}; \mathbf{x}, t) = \text{vect}(\Pi_{\alpha_j}), \quad \nabla_\alpha = \text{vect}\left(\frac{\partial}{\partial \alpha_j}\right), \quad (43)$$

where the Π_{α_j} 's are interpreted as probability weighted components of a streaming flux in Ω_α , i.e., a current in the space of mesoscopic coordinates.

The local densities $C_i(\mathbf{x}, t)$ of the conserved properties are assumed to have an associated underlying extensive property which can be expressed in terms of the mesoscopic coordinates as $c_i(\boldsymbol{\alpha})$ such that

$$C_i(\mathbf{x}, t) = \tilde{C}_i(\gamma) = \int_{\Omega_\alpha} c_i(\boldsymbol{\alpha}) \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha, \quad (44)$$

$$\Psi_i = \delta \tilde{C}_i / \delta \gamma = 2\gamma c_i. \quad (45)$$

They obey the balance equation

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{J}_{C_i} = \Pi_{C_i} = 0, \quad (46)$$

where the local Lagrangian flux $\mathbf{J}_{C_i}(\mathbf{x}, t)$ and the local production density $\Pi_{C_i}(\mathbf{x}, t)$ are defined as follows:

$$\begin{aligned} \mathbf{J}_{C_i}(\mathbf{x}, t) &= \int_{\Omega_\alpha} c_i(\boldsymbol{\alpha}) \mathbf{v}(\boldsymbol{\alpha}) \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \\ \Pi_{C_i}(\mathbf{x}, t) &= (\Psi_i | \Pi_\gamma) \\ &= \int_{\Omega_\alpha} c_i(\boldsymbol{\alpha}) 2\gamma(\boldsymbol{\alpha}; \mathbf{x}, t) \Pi_\gamma(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \\ &= - \int_{\Omega_\alpha} c_i(\boldsymbol{\alpha}) \nabla_\alpha \cdot \Pi_\alpha(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \\ &= \int_{\Omega_\alpha} \Pi_\alpha(\boldsymbol{\alpha}; \mathbf{x}, t) \cdot \nabla_\alpha c_i(\boldsymbol{\alpha}) d\Omega_\alpha \\ &= (\psi_i | \Pi_\alpha), \end{aligned} \quad (47)$$

where in the next-to-last equation we integrated by parts and assumed that currents in $\boldsymbol{\alpha}$ space decay sufficiently fast to zero as the α_j 's $\rightarrow \infty$, and we defined

$$\psi_i(\boldsymbol{\alpha}) = \nabla_\alpha c_i(\boldsymbol{\alpha}). \quad (48)$$

Also the condition of preservation of normalization is written in the same way, by setting $c_0(\boldsymbol{\alpha}) = 1$ so $\Psi_0 = 2\gamma$ and the corresponding balance equation (46) with the condition $\Pi_{C_0}(\mathbf{x}, t) = 0$ yields the following conditions on Π_γ and Π_α :

$$\begin{aligned} \Pi_{C_0}(\mathbf{x}, t) &= (\Psi_0 | \Pi_\gamma) = \int_{\Omega_\alpha} 2\gamma(\boldsymbol{\alpha}; \mathbf{x}, t) \Pi_\gamma(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \\ &= - \int_{\Omega_\alpha} \nabla_\alpha \cdot \Pi_\alpha(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha = 0. \end{aligned} \quad (49)$$

The local entropy density $S(\mathbf{x}, t)$ is expressed in terms of the local square-root probability density as

$$S(\mathbf{x}, t) = \tilde{S}(\gamma) = -k \int_{\Omega_\gamma} \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) \ln \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \quad (50)$$

such that

$$\Phi = \delta \tilde{S} / \delta \gamma = -2k\gamma(\boldsymbol{\alpha}; \mathbf{x}, t) [1 + \ln \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t)], \quad (51)$$

and the entropy balance equation takes the form

$$\frac{\partial S}{\partial t} + \nabla \cdot \mathbf{J}_S = \Pi_S, \quad (52)$$

where the local Lagrangian flux $\mathbf{J}_S(\mathbf{x}, t)$ and the local production density $\Pi_S(\mathbf{x}, t)$ are defined as follows:

$$\begin{aligned} \mathbf{J}_S(\mathbf{x}, t) &= -k \int_{\Omega_\alpha} \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) \mathbf{v}(\boldsymbol{\alpha}) \ln \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \\ \Pi_S(\mathbf{x}, t) &= (\Phi | \Pi_\gamma) \\ &= -k \int_{\Omega_\alpha} [1 + \ln \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t)] \\ &\quad \times 2\gamma(\boldsymbol{\alpha}; \mathbf{x}, t) \Pi_\gamma(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \\ &= k \int_{\Omega_\alpha} \ln \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) \nabla_\alpha \cdot \Pi_\alpha(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \end{aligned}$$

$$\begin{aligned}
 &= -k \int_{\Omega_\alpha} \Pi_\alpha(\boldsymbol{\alpha}; \mathbf{x}, t) \cdot \nabla_\alpha \ln \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t) d\Omega_\alpha \\
 &= (\phi | \Pi_\alpha), \tag{53}
 \end{aligned}$$

where we used the normalization condition (49) and again in the next-to-last equation we integrated by parts and defined

$$\phi(\boldsymbol{\alpha}; \mathbf{x}, t) = -k \nabla_\alpha \ln \gamma^2(\boldsymbol{\alpha}; \mathbf{x}, t). \tag{54}$$

In Sec. III, we construct an equation of motion for γ such that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ and the suitable geometrical constraint we discuss therein. The result, when introduced in Eq. (42), will yield the Fokker-Planck equation for $\gamma(\boldsymbol{\alpha}; \mathbf{x}, t)$, which is also related (see, e.g., Ref. [41]) to the GENERIC structure [8–10]. The formalism can also be readily extended to the family of Tsallis [42] entropies in the frameworks of nonextensive thermodynamic models [43].

E. Framework E: Quantum statistical mechanics, quantum information theory, quantum thermodynamics, mesoscopic nonequilibrium quantum thermodynamics, and intrinsic quantum thermodynamics

Let \mathcal{H} be the Hilbert space ($\dim \mathcal{H} \leq \infty$) associated with the physical system and \mathcal{L} the set of all linear operators A, B, \dots on \mathcal{H} , equipped with the real inner product $(\cdot | \cdot)$ defined by

$$(A | B) = \text{Tr}(A^\dagger B + B^\dagger A)/2, \tag{55}$$

where A^\dagger denotes the adjoint of operator A and $\text{Tr}(\cdot)$ the usual trace functional symbol.

In the quantum frameworks that we consider in this section, the state representative is the density operator ρ , i.e., a unit-trace, self-adjoint, and non-negative-definite element of \mathcal{L} .

Instead, also here we will adopt the state representation in terms of the generalized square root of the density operator that we developed in this context [2–5] in order to easily impose the constraints of preservation of both the non-negativity and the self-adjointness of ρ during its time evolution as well as to satisfy Condition C2. Therefore, we assume that the state representative is an element γ in \mathcal{L} from which we can compute the density operator as follows:

$$\rho = \gamma \gamma^\dagger. \tag{56}$$

In other words, we adopt as state representative not the density operator ρ itself but its generalized square root γ . Therefore, we clearly have

$$\frac{d\rho}{dt} = \gamma \frac{d\gamma^\dagger}{dt} + \frac{d\gamma}{dt} \gamma^\dagger. \tag{57}$$

We then consider the set of operators corresponding to the conserved properties, denoted synthetically as

$$\{C_i\} = \{H, M_x, M_y, M_z, N_1, \dots, N_r, I\}. \tag{58}$$

Here we assume that these are self-adjoint operators in \mathcal{L} , where each M_j and N_i commutes with H , i.e., $H M_j = M_j H$ for $j = x, y, z$ and $H N_i = N_i H$ for $i = 1, \dots, r$, and that I is the identity operator [44].

The semiempirical description of an irreversible relaxation process is done in this framework by assuming an evolution

equation for the state γ given by the equations

$$\frac{d\gamma}{dt} + \frac{i}{\hbar} H \gamma = \Pi_\gamma, \tag{59}$$

$$\frac{d\gamma^\dagger}{dt} - \frac{i}{\hbar} \gamma^\dagger H = \Pi_{\gamma^\dagger}. \tag{60}$$

As a result, it is easy to verify that for the density operator the dynamical equation is

$$\frac{d\rho}{dt} + \frac{i}{\hbar} [H, \rho] = \Pi_\gamma \gamma^\dagger + \gamma \Pi_{\gamma^\dagger}, \tag{61}$$

where $[\cdot, \cdot]$ denotes the commutator. From this we see that in order to preserve hermiticity of ρ the dissipative terms Π_γ and Π_{γ^\dagger} must satisfy the conditions

$$\Pi_{\gamma^\dagger} = \Pi_\gamma^\dagger \quad \text{and} \quad \Pi_\gamma = \Pi_{\gamma^\dagger}^\dagger. \tag{62}$$

In order to satisfy the constraints of conservation of the expectation values $\text{Tr}(\rho C_i)$, each C_i must commute with H ; moreover, the term Π_γ must be such that

$$\begin{aligned}
 \Pi_{C_i} &= \frac{d}{dt} \text{Tr}(\rho C_i) = \text{Tr}(C_i \Pi_\gamma \gamma^\dagger + \gamma \Pi_{\gamma^\dagger} C_i) \\
 &= (2C_i \gamma | \Pi_\gamma) = 0. \tag{63}
 \end{aligned}$$

The entropy functional in this context is represented by

$$\tilde{S}(\gamma) = -k \text{Tr}(\rho \ln \rho) = (-k (\ln \gamma \gamma^\dagger) \gamma | \gamma), \tag{64}$$

so the rate of entropy production under a time evolution that preserves the normalization of ρ is given by

$$\Pi_S = -k \frac{d}{dt} \text{Tr}(\rho \ln \rho) = (-2k (\ln \gamma \gamma^\dagger) \gamma | \Pi_\gamma). \tag{65}$$

In quantum statistical mechanics (QSM) and quantum information theory (QIT), ρ is the von Neumann statistical or density operator which represents the index of statistics from a generally heterogeneous ensemble of identical systems (same Hilbert space \mathcal{H} and operators $\{H, N_1, \dots, N_r\}$) distributed over a range of generally different quantum mechanical states. If each individual member of the ensemble is isolated and uncorrelated from the rest of the universe, its state is described according to quantum mechanics by an idempotent density operator ($\rho^2 = \rho = P_{|\psi\rangle} = \frac{|\psi\rangle\langle\psi|}{\langle\psi|\psi\rangle}$), i.e., a projection operator onto the span of some vector $|\psi\rangle$ in \mathcal{H} . If the ensemble is heterogeneous, its individual member systems may be in different states, $P_{|\psi_1\rangle}$, $P_{|\psi_2\rangle}$, and so on, and the ensemble statistics is captured by the von Neumann statistical operator $\rho = \sum_j w_j P_{|\psi_j\rangle}$. The entropy functional here represents a measure of the informational uncertainty as to which homogeneous subensemble the next system will be drawn from, i.e., as to which will be the actual pure quantum state among those present in the heterogeneous ensemble.

In this framework, unless the statistical weights w_j change for some extrinsic reason, the quantum evolution of the ensemble is given by Eq. (61) with $\Pi_\gamma = 0$ so Eq. (61) reduces to von Neumann's equation of quantum (reversible) Hamiltonian evolution, corresponding to $\rho(t) = \sum_j w_j P_{|\psi_j(t)\rangle}$, where the underlying pure states $|\psi_j(t)\rangle$ evolve according to the Schrödinger equation $d|\psi_j\rangle/dt = -iH|\psi_j\rangle/\hbar$.

In the framework of QSM and QIT, the SEA equation of motion we construct in the next Sec. III for γ and

hence, through Eq. (57), for ρ represents a model for the rates of change of the statistical weights w_j in such a way that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ (and a suitable additional constraint, see Sec. III). This essentially extends to the quantum landscape the same statistical or information-theoretic nonequilibrium problem we defined above as Framework A.

In quantum thermodynamics (QT), instead, the density operator takes on a more fundamental physical meaning. It is no longer related to the heterogeneity of the ensemble, and it is no longer assumed that the individual member systems of the ensemble are in pure states.

The prevailing interpretation of QT (for a recent review see Ref. [45]) is the so-called open-system model whereby the quantum system under study (each individual system of a homogeneous ensemble) is always viewed as in contact (weak or strong) with a thermal reservoir or “heat bath,” and its not being in a pure state is an indication of its being correlated with the reservoir. The overall system-plus-reservoir composite is assumed to be a pure quantum mechanical state in $\mathcal{H} \otimes \mathcal{H}_R$ and reduces to the density operator ρ on the system’s space \mathcal{H} when we partial trace the overall density operator over the reservoir’s space \mathcal{H}_R .

The semiempirical description of an irreversible relaxation process is done in this framework by assuming for Π_ρ in Eq. (61) the Lindblad-Gorini-Kossakowski-Sudarshan (LGKS) form [46,47]

$$\Pi_\rho = \sum_j \left(V_j \rho V_j^\dagger - \frac{1}{2} \{V_j^\dagger V_j, \rho\}_+ \right), \quad (66)$$

where $\{\cdot, \cdot\}_+$ denotes the anticommutator and operators V_j are to be chosen to properly model the system-reservoir interaction. The justification and modeling assumptions that lead to the general form of Eq. (66) are well known.

In the framework of QT the SEA equation of motion we construct in the next section may be useful as an alternative model for Π_ρ (or for a term additional to the LGKS term) such that Π_S is maximal subject to the conservation constraints $\Pi_{C_i} = 0$ (and the suitable additional constraint defined below in Sec. III). In some cases this could be simpler than the LGKS model and it has the advantage of a strong built-in thermodynamics consistency. A similar attempt has been recently discussed in Ref. [48] as an application of the GENERIC scheme.

Mesoscopic nonequilibrium quantum thermodynamics (MNEQT) [7] starts from the formalism of QSM but attempts to extend the Onsager NET theory and MNET to the quantum realm. We will show elsewhere that the present SEA formulation reduces to MNEQT in the near-equilibrium limit and can therefore be viewed as the natural extension of MNEQT to the far-nonequilibrium regime. The essential elements of this proof have actually already been given [4] but only for the particular case corresponding to Eq. (70) below (Fisher-Rao metric).

An even more fundamental physical meaning is assumed within the theory that we originally called quantum thermodynamics [2,3,49–53] but more recently renamed intrinsic quantum thermodynamics (IQT) to avoid confusion with

the more traditional theories of QT such as those just outlined.

IQT assumes that the second law of thermodynamics should complement the laws of mechanics even at the single-particle level [49]. This can be done if we accept that the true individual quantum state of a system, even if fully isolated and uncorrelated from the rest of the universe, requires density operators ρ that are not necessarily idempotent. Over the set of idempotent ρ ’s, QT coincides with quantum mechanics (QM), but it differs fundamentally from QM because it assumes a broader set of possible states, corresponding to the set of nonidempotent ρ ’s. This way, the entropy functional $\tilde{S}(\rho)$ becomes in IQT an intrinsic fundamental property. In a sense IQT with its SEA dynamical law accomplishes the conceptual program, so intensely sought for also by Ilya Prigogine and coworkers [54], of answering the following questions [2]: What if entropy, rather than a statistical, information-theoretic, macroscopic, or phenomenological concept, were an intrinsic property of matter in the same sense as energy is universally understood to be an intrinsic property of matter? What if irreversibility were an intrinsic feature of the fundamental dynamical laws obeyed by all physical objects, macroscopic and microscopic, complex and simple, large and small? What if the second law of thermodynamics, in the hierarchy of physical laws, were at the same level as the fundamental laws of mechanics, such as the great conservation principles? When viewed from such extreme perspective, the IQT conceptual scheme remains today as “adventurous” as it was acutely judged by John Maddox in 1985 [55].

In the framework of IQT the SEA equation of motion (61) for ρ which results from the expression for Π_γ we construct in the next section represents a strong family of implementations of the MEP principle at the fundamental quantum level which contains our original formulation as a special case.

Even the brief discussion above shows clearly that the differences among QSM, QIT, QT, IQT, and MNEQT are important on the interpretational and conceptual levels. Nevertheless, it is also clear that they all share the same basic mathematical framework. Hence, we believe that the SEA dynamical model, which we show here fits their common mathematical basis, can find in the different theories different physical interpretations and applications.

III. STEEPEST-ENTROPY-ASCENT DYNAMICS: UNIFIED VARIATIONAL FORMULATION OF NONEQUILIBRIUM DISSIPATION

In the preceding section we formulated the nonequilibrium problem in various different frameworks in a unifying way that allows us to represent their dissipative parts in a single formal way. In essence, as summarized by conditions C1–C4 above, the state is represented by an element γ of a suitable vector space \mathcal{L} equipped with an inner product $(\cdot | \cdot)$. The term in the dynamical equation for γ which is responsible for dissipative irreversible relaxation and hence entropy generation is another element Π_γ of \mathcal{L} which, together with the variational derivatives Φ and Ψ_i of the functionals $\tilde{S}(\gamma)$ and $\tilde{C}_i(\gamma)$ representing, respectively, the entropy and the constants of motion, determines the rate of entropy production according

to the relation

$$\Pi_S = (\Phi|\Pi_\gamma) \quad (67)$$

and the rates of production of the conserved properties C_i according to the relation

$$\Pi_{C_i} = (\Psi_i|\Pi_\gamma). \quad (68)$$

The formulations in terms of square roots of probabilities in Framework A, of the square root of the phase density in Framework B, of the square-root probability density in Framework D, and of the generalized square root of the density operator in Framework E take care not only of the important condition that for the evolution law to be well defined it must conserve the non-negativity of probabilities, phase densities, and density operators (which must also remain self adjoint) but also of condition C2, namely that functional derivatives of the entropy and the constants of the motion are also elements of the vector space \mathcal{L} .

We are now ready to formulate the SEA construction. We do this by assuming that the time evolution of the state γ follows the path of steepest entropy ascent in \mathcal{L} compatible with the constraints. So, for any given state γ , we must find the Π_γ which maximizes the entropy production Π_S subject to the constraints $\Pi_{C_i} = 0$. But in order to identify the SEA path we are not interested in the unconditional increase in Π_S that we can trivially obtain by simply increasing the “norm” of Π_γ while keeping its direction fixed. Rather, the SEA path is identified by the direction of Π_γ which maximizes Π_S subject to the constraints, regardless of the norm of Π_γ . Hence, we must do the maximization at constant norm of Π_γ .

In the absence of Hamiltonian or transport contributions to the time evolution of γ , the vector Π_γ is tangent to the path $\gamma(t)$. Therefore, the norm of Π_γ represents the square of the distance $d\ell$ traveled by γ in the state space \mathcal{L} in the time interval dt , the square of the “length” of the infinitesimal bit of path traveled in state space in the interval dt . The variational problem that identifies the SEA direction at each state γ looks at all possible paths through γ , each characterized by a possible choice for Π_γ . Among all these paths it selects the one with the highest entropy produced in the interval dt , $\Pi_S dt$ per unit of distance $d\ell$ traveled by γ .

It is therefore apparent that we cannot identify a SEA path until we equip the space \mathcal{L} with a metric field with respect to which to compute the distance $d\ell$ traveled and the norm of Π_γ .

In our previous work [5], we selected the Fisher-Rao metric based on the inner product $(\cdot|\cdot)$ defined on \mathcal{L} . Indeed, in dealing with probability distributions it has been argued by several authors that the Fisher-Rao metric is the proper unique metric for the purpose of computing the distance between two probability distributions (see, e.g., Refs. [56–58]). According to this metric, the distance between two states γ_1 and γ_2 is given by

$$d(\gamma_1, \gamma_2) = \sqrt{2} \arccos(\gamma_1|\gamma_2), \quad (69)$$

which implies that the distance traveled along a trajectory in state space is

$$d\ell = 2\sqrt{(\Pi_\gamma|\Pi_\gamma)} dt. \quad (70)$$

As a result, for Framework E the SEA dynamics we have originally proposed is most straightforward.

However, here we will not adopt *a priori* a specific metric but rather assume a most general metric, which in Framework E generalizes our previous work and in the other frameworks provides the most general formulation. We assume the following expression for the distance traveled along a short bit of trajectory in state space:

$$d\ell = \sqrt{(\Pi_\gamma|\hat{G}(\gamma)|\Pi_\gamma)} dt, \quad (71)$$

where $\hat{G}(\gamma)$ is a real, symmetric, and positive-definite operator on \mathcal{L} that we call the metric tensor field, (super)matrix, or (super)operator depending on the framework. In general, $\hat{G}(\gamma)$ may be a nonlinear function of γ . In Framework E, since \mathcal{L} is the space of operators on the Hilbert space \mathcal{H} of the quantum system, \hat{G} is a superoperator on \mathcal{H} . For example, a simple case is when $\hat{G}|A\rangle = |[G^\dagger, [G, A]]\rangle$ with G some operator in \mathcal{L} .

We may now finally state *the SEA variational problem* and solve it. The problem is to *find the instantaneous “direction” of Π_γ which maximizes the entropy production rate Π_S subject to the constraints $\Pi_{C_i} = 0$* . We solve it by maximizing the entropy production rate Π_S subject to the constraints $\Pi_{C_i} = 0$ and the additional constraint $(d\ell/dt)^2 = \epsilon^2 = \text{prescribed}$. The last constraint keeps the norm of Π_γ constant as necessary in order to maximize only with respect to its direction. From Eq. (71) it amounts to keeping fixed the value of $(\Pi_\gamma|\hat{G}|\Pi_\gamma)$ at some small positive constant ϵ^2 . The solution is easily obtained by the method of Lagrange multipliers. We seek the unconstrained maximum, with respect to Π_γ , of the Lagrangian

$$\Upsilon = \Pi_S - \sum_i \beta_i \Pi_{C_i} - \frac{\tau}{2} (\Pi_\gamma|\hat{G}|\Pi_\gamma), \quad (72)$$

where β_i and $\tau/2$ are the Lagrange multipliers. Like \hat{G} , they must be independent of Π_γ but can be functions of the state γ . Using Eqs. (67) and (68), we rewrite (72) as follows:

$$\Upsilon = (\Phi|\Pi_\gamma) - \sum_i \beta_i (\Psi_i|\Pi_\gamma) - \frac{\tau}{2} (\Pi_\gamma|\hat{G}|\Pi_\gamma). \quad (73)$$

Taking the variational derivative of Υ with respect to $|\Pi_\gamma\rangle$ and setting it equal to zero we obtain

$$\frac{\delta\Upsilon}{\delta\Pi_\gamma} = |\Phi\rangle - \sum_i \beta_i |\Psi_i\rangle - \tau \hat{G}|\Pi_\gamma\rangle = 0, \quad (74)$$

where we used the identity $(\Pi_\gamma|\hat{G} = \hat{G}|\Pi_\gamma\rangle$, which follows from the symmetry of \hat{G} . Thus, we obtain the SEA general evolution equation (the main result of this paper)

$$|\Pi_\gamma\rangle = \hat{L}|\Phi\rangle - \sum_j \beta_j |\Psi_j\rangle, \quad (75)$$

where we define for convenience

$$\hat{L} = \frac{1}{\tau} \hat{G}^{-1}. \quad (76)$$

Since in the various frameworks \hat{L} can be connected with the generalized Onsager conductivity (super)matrix in the near equilibrium regime, we see here that $\tau\hat{L}$ is the inverse of the metric (super)matrix \hat{G} with respect to which the dynamics

is SEA. In other words, denoting the generalized Onsager resistivity (super)matrix by \hat{R} we have $\hat{R} = \tau \hat{G}$. Since \hat{G} is positive definite and symmetric, so are \hat{L} and \hat{R} . In other words, the SEA assumption automatically entails Onsager reciprocity near thermodynamic equilibrium.

Inserting Eq. (75) into the conservation constraints (68) yields the important system of equations which defines the values of the Lagrange multipliers β_j ,

$$\sum_j (\Psi_i | \hat{L} | \Psi_j) \beta_j = (\Psi_i | \hat{L} | \Phi). \quad (77)$$

This system can be readily solved for the β_j 's (for example, by Cramer's rule) because the functionals $(\Psi_i | \hat{L} | \Psi_j)$ and $(\Psi_i | \hat{L} | \Phi)$ are readily computable for the current state γ . Notice that the determinant of the matrix $[(\Psi_i | \hat{L} | \Psi_j)]$ is a Gram determinant and its being positive definite is equivalent to the condition of linear independence of the conservation constraints. When Cramer's rule is worked out explicitly, the SEA equation (75) takes the form of a ratio of determinants with which we presented it in the IQT framework [5,50–53], namely,

$$|\Pi_\gamma\rangle = \frac{\begin{vmatrix} \hat{L}\Phi & \hat{L}\Psi_1 & \cdots & \hat{L}\Psi_n \\ (\Psi_1 | \hat{L} | \Phi) & (\Psi_1 | \hat{L} | \Psi_1) & \cdots & (\Psi_1 | \hat{L} | \Psi_n) \\ \vdots & \vdots & \ddots & \vdots \\ (\Psi_n | \hat{L} | \Phi) & (\Psi_n | \hat{L} | \Psi_1) & \cdots & (\Psi_n | \hat{L} | \Psi_n) \end{vmatrix}}{\begin{vmatrix} (\Psi_1 | \hat{L} | \Psi_1) & \cdots & (\Psi_1 | \hat{L} | \Psi_n) \\ \vdots & \ddots & \vdots \\ (\Psi_n | \hat{L} | \Psi_1) & \cdots & (\Psi_n | \hat{L} | \Psi_n) \end{vmatrix}}, \quad (78)$$

where the set of vectors $\hat{L}^{1/2} |\Psi_1\rangle, \dots, \hat{L}^{1/2} |\Psi_n\rangle$ are linearly independent so the Gram determinant at the denominator is strictly positive. These are all the vectors in the set $\{\hat{L}^{1/2} |\Psi_i\rangle\}$ if they are linearly independent, otherwise they are a subset of n of them which are linearly independent.

We can now immediately prove the general consistence with the thermodynamic principle of entropy nondecrease (H -theorem in Framework B). Indeed, subtracting Eqs. (68), each multiplied by the corresponding β_j from Eq. (67), and then inserting Eq. (75) yields the following explicit expression for the rate of entropy production:

$$\begin{aligned} \Pi_S &= (\Phi | \Pi_\gamma) = (\Phi - \sum_j \beta_j \Psi_j | \Pi_\gamma) \\ &= (\Phi - \sum_i \beta_i \Psi_i | \hat{L} | \Phi - \sum_j \beta_j \Psi_j) \geq 0, \end{aligned} \quad (79)$$

which is clearly non-negative-definite by virtue, again, of the non-negativity that must be assumed for a well defined metric superoperator \hat{G} .

It is interesting to write the expression for the (prescribed) speed $d\ell/dt$ at which the state γ evolves along the SEA path. This amounts to inserting Eq. (75) into the additional constraint

$(d\ell/dt)^2 = \dot{\epsilon}^2 =$ prescribed. We readily find

$$\begin{aligned} \frac{d\ell^2}{dt^2} &= (\Pi_\gamma | \hat{G} | \Pi_\gamma) \\ &= \frac{1}{\tau^2} \left(\Phi - \sum_i \beta_i \Psi_i | \hat{G}^{-1} \hat{G} \hat{G}^{-1} | \Phi - \sum_j \beta_j \Psi_j \right) \\ &= \frac{1}{\tau} \Pi_S = \dot{\epsilon}^2 \end{aligned} \quad (80) \quad (81)$$

so we have the relations

$$\tau = \frac{\sqrt{(\Phi - \sum_i \beta_i \Psi_i | \hat{G}^{-1} | \Phi - \sum_j \beta_j \Psi_j)}}{d\ell/dt} \quad (82)$$

$$= \frac{(\Phi - \sum_i \beta_i \Psi_i | \hat{G}^{-1} | \Phi - \sum_j \beta_j \Psi_j)}{\Pi_S}, \quad (83)$$

from which we see that through the Lagrange multiplier τ we may specify either the speed at which γ evolves along the SEA trajectory in state space or the instantaneous rate of entropy production. Hence, using τ given by Eq. (83) the evolution equation (75) will produce a SEA trajectory in state space with the prescribed entropy production Π_S . These relations also support the interpretation of τ as the ‘‘overall relaxation time.’’ We see this as follows.

In general, we may interpret the vector

$$|\Lambda\rangle = \hat{G}^{-1/2} |\Phi - \sum_i \beta_i \Psi_i\rangle \quad (84)$$

as a vector of ‘‘nonequilibrium affinities’’ or, more precisely, of ‘‘generalized partial affinities.’’ In terms of this vector, Eq. (75) rewrites as

$$\hat{G}^{1/2} |\Pi_\gamma\rangle = \frac{1}{\tau} |\Lambda\rangle. \quad (85)$$

When only some of the partial affinities in the vector Λ are zero, the state is partially equilibrated (equilibrated with respect to the corresponding underlying components of the state γ). When the entries of the vector Λ are all zero, then and only then do we have an equilibrium state or a nondissipative limit cycle. In fact, it is when and only when the entropy production vanishes. $(\Lambda | \Lambda)$, which, with respect to the metric tensor \hat{G} , is the norm of the vector $|\Phi - \sum_j \beta_j \Psi_j\rangle$, represents a measure of the ‘‘overall degree of disequilibrium’’ of the state γ . It is important to note that this definition is valid no matter how far the state is from the (maximum entropy) stable equilibrium state, i.e., also for highly nonequilibrium states.

We have proved in the IQT framework, and the result can be readily extended to all other frameworks, that among the equilibrium states only the maximum entropy one is not unstable (in the sense of Lyapunov [59]). As a result, the maximum entropy states emerge as the only stable equilibrium ones and, therefore, we can assert that the SEA construction implements the Hatsopoulos-Keenan statement of the second law [21,60] at the level of description of everyone of the frameworks we are considering.

Equation (83) rewrites as

$$\Pi_S = \frac{(\Lambda | \Lambda)}{\tau}, \quad (86)$$

which shows that the rate of entropy production is proportional to the overall degree of disequilibrium. The relaxation time

τ may be a state functional and needs not be constant, but even if it is, the SEA principle provides a nontrivial nonlinear evolution equation that is well defined and reasonable, i.e., thermodynamically consistent, even far from equilibrium.

We finally note that when the only contribution to the entropy change comes from the production term Π_S (for example, in Framework B in the case of homogeneous relaxation in the absence of entropy fluxes or in Framework E for an isolated system), i.e., when the entropy balance equation reduces to $dS/dt = \Pi_S$, Eq. (81) may be rewritten as

$$\frac{d\ell}{dt/\tau} = \frac{dS}{d\ell}, \quad (87)$$

from which we see that when time t is measured in units of τ the “speed” along the SEA trajectory is equal to the local rate of entropy increase along the trajectory.

If the state γ moves only due to the dissipative term Π_γ (for example, in Framework E when $[H, \gamma \gamma^\dagger] = 0$), then the overall length of the trajectory in state space traveled between $t = 0$ and t is given by

$$\ell(t) = \int_0^t \sqrt{(\Pi_\gamma | \hat{G} | \Pi_\gamma)} dt, \quad (88)$$

and, correspondingly, we may also define the “nonequilibrium action”

$$\begin{aligned} \Sigma &= \frac{1}{2} \int_0^t (\Pi_\gamma | \hat{G} | \Pi_\gamma) dt = \frac{1}{2} \int_0^t \frac{\Pi_S}{\tau} dt \\ &= \frac{1}{2} \int_0^t \frac{(\Lambda | \Lambda)}{\tau^2} dt, \end{aligned} \quad (89)$$

where for the last two equalities we used Eq. (81) and Eq. (86), respectively.

IV. PICTORIAL REPRESENTATIONS

Let us give pictorial representations of the vectors that we defined in the SEA construction. We consider first the simplest scenario of a uniform metric tensor $\hat{G} = \hat{I}$.

Figure 1 gives a pictorial representation of the linear manifold spanned by the vectors $|\Psi_i\rangle$'s and the orthogonal projection of $|\Phi\rangle$ which defines the Lagrange multipliers β_i in the case of uniform metric, i.e., the orthogonality conditions

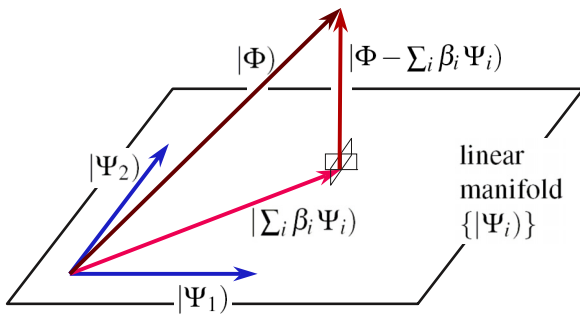


FIG. 1. (Color online) Pictorial representation of the linear manifold spanned by the vectors $|\Psi_i\rangle$ and the orthogonal projection of $|\Phi\rangle$ onto this manifold which defines the Lagrange multipliers β_i in the case of a uniform metric $\hat{G} = \hat{I}$. The construction defines also the generalized affinity vector, which in this case is $|\Lambda\rangle = |\Phi - \sum_i \beta_i \Psi_i\rangle$.

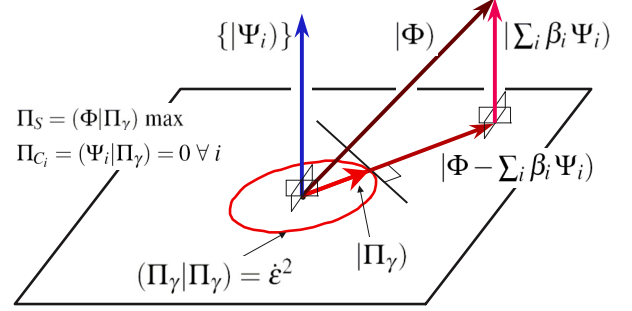


FIG. 2. (Color online) Pictorial representation of the SEA variational construction in the case of a uniform metric $\hat{G} = \hat{I}$. The circle represents the condition $(\Pi_\gamma | \Pi_\gamma) = \dot{\epsilon}^2$. The vector $|\Pi_\gamma\rangle$ must be orthogonal to the $|\Psi_i\rangle$'s in order to satisfy the conservation constraints $\Pi_{C_i} = (\Psi_i | \Pi_\gamma) = 0$. In order to maximize the scalar product $(\Phi - \sum_i \beta_i \Psi_i | \Pi_\gamma)$, $|\Pi_\gamma\rangle$ must have the same direction as $|\Phi - \sum_i \beta_i \Psi_i\rangle$.

$(\Psi_j | \Phi - \sum_i \beta_i \Psi_i) = 0$ for every j , which are Eqs. (77) with $\hat{L} = \hat{I}/\tau$. The construction defines also the generalized affinity vector, which in this case is $|\Lambda\rangle = |\Phi - \sum_i \beta_i \Psi_i\rangle$ and is orthogonal to the linear manifold spanned by the vectors $|\Psi_i\rangle$'s.

Figure 2 gives a pictorial representation of the subspace orthogonal to the linear manifold spanned by the $|\Psi_i\rangle$'s that here we denote for simplicity by $\{|\Psi_i\rangle\}$. The vector $|\Phi\rangle$ is decomposed into its component $|\sum_i \beta_i \Psi_i\rangle$ which lies in the orthogonal subspace and its component $|\Phi - \sum_i \beta_i \Psi_i\rangle$ which lies in the orthogonal subspace.

The circle in Fig. 2 represents the condition $(\Pi_\gamma | \Pi_\gamma) = \dot{\epsilon}^2$ corresponding in the uniform metric to the prescribed rate of advancement in state space, $\dot{\epsilon}^2 = (d\ell/dt)^2$. The compatibility with the conservation constraints $\Pi_{C_i} = (\Psi_i | \Pi_\gamma) = 0$ requires that $|\Pi_\gamma\rangle$ lies in the subspace orthogonal to the $|\Psi_i\rangle$'s. To take the SEA direction, $|\Pi_\gamma\rangle$ must maximize the scalar product $(\Phi - \sum_i \beta_i \Psi_i | \Pi_\gamma)$. This clearly happens when $|\Pi_\gamma\rangle$ has the same direction as the vector $|\Phi - \sum_i \beta_i \Psi_i\rangle$ which in the uniform metric coincides with the generalized affinity vector $|\Lambda\rangle$.

Next we consider the more general scenario of a nonuniform metric tensor \hat{G} . Figure 3 gives a pictorial representation of the linear manifold spanned by the vectors $\hat{G}^{-1/2} |\Psi_i\rangle$ and the orthogonal projection of $\hat{G}^{-1/2} |\Phi\rangle$ which defines the

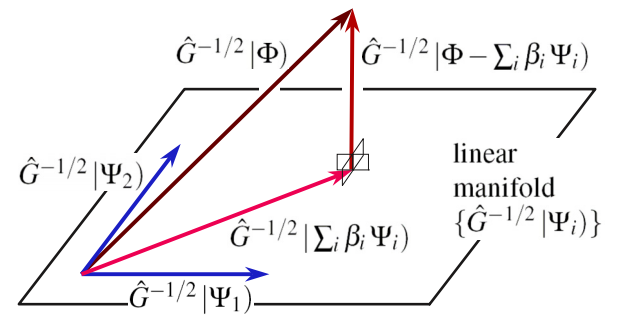


FIG. 3. (Color online) Pictorial representation of the linear manifold spanned by the vectors $\hat{G}^{-1/2} \Psi_i$ and the orthogonal projection of $\hat{G}^{-1/2} |\Phi\rangle$ onto this manifold which defines the Lagrange multipliers β_i in the case of a nonuniform metric \hat{G} . The construction defines also the generalized affinity vector $|\Lambda\rangle = \hat{G}^{-1/2} |\Phi - \sum_i \beta_i \Psi_i\rangle$.

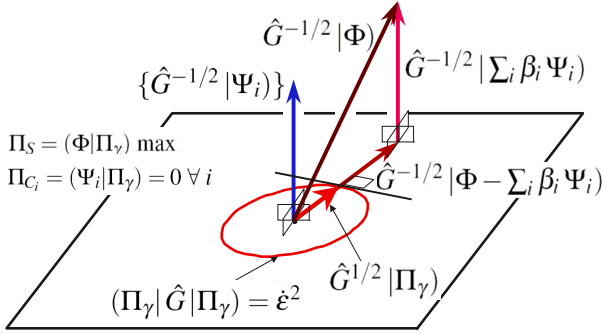


FIG. 4. (Color online) Pictorial representation of the SEA variational construction in the case of a nonuniform metric \hat{G} . The circle represents the condition $(\Pi_\gamma | \hat{G} | \Pi_\gamma) = \epsilon^2$, corresponding to the norm of vector $\hat{G}^{1/2} |\Pi_\gamma\rangle$. This vector must be orthogonal to the $\hat{G}^{-1/2} |\Psi_i\rangle$'s in order to satisfy the conservation constraints $\Pi_{C_i} = (\Psi_i | \Pi_\gamma) = 0$. In order to maximize the scalar product $\Pi_S = (\Phi | \Pi_\gamma) = (\Phi - \sum_i \beta_i \Psi_i | \Pi_\gamma)$, vector $\hat{G}^{1/2} |\Pi_\gamma\rangle$ must have the same direction as $|\Lambda\rangle = \hat{G}^{-1/2} |\Phi - \sum_i \beta_i \Psi_i\rangle$.

Lagrange multipliers β_i in the case of nonuniform metric \hat{G} , where the orthogonality conditions that define the β_i 's are $(\Psi_j | \hat{G}^{-1} |\Phi - \sum_i \beta_i \Psi_i\rangle) = 0$ for every j , which are Eqs. (77). The construction defines also the generalized affinity vector $|\Lambda\rangle = \hat{G}^{-1/2} |\Phi - \sum_i \beta_i \Psi_i\rangle$ which is orthogonal to the linear manifold spanned by the vectors $\hat{G}^{-1/2} |\Psi_i\rangle$'s.

Figure 4 gives a pictorial representation of the subspace orthogonal to the linear manifold spanned by the $\hat{G}^{-1/2} |\Psi_i\rangle$'s that here we denote for simplicity by $\{\hat{G}^{-1/2} |\Psi_i\rangle\}$. The vector $\hat{G}^{-1/2} |\Phi\rangle$ is decomposed into its component $\hat{G}^{-1/2} |\sum_i \beta_i \Psi_i\rangle$ which lies in $\{\hat{G}^{-1/2} |\Psi_i\rangle\}$ and its component $|\Lambda\rangle = \hat{G}^{-1/2} |\Phi - \sum_i \beta_i \Psi_i\rangle$ which lies in the orthogonal subspace.

The circle in Fig. 4 represents the more general condition $(\Pi_\gamma | \hat{G} | \Pi_\gamma) = \epsilon^2$ corresponding in the nonuniform metric to the prescribed rate of advancement in state space, $\epsilon^2 = (d\ell/dt)^2$. It is clear that the direction of $\hat{G}^{1/2} |\Pi_\gamma\rangle$, which maximizes the scalar product $(\Phi - \sum_i \beta_i \Psi_i | \Pi_\gamma)$, is when $|\Pi_\gamma\rangle$ is in the direction of the point of tangency between the ellipse and a line orthogonal to $|\Phi - \sum_i \beta_i \Psi_i\rangle$.

The compatibility with the conservation constraints $\Pi_{C_i} = (\Psi_i | \Pi_\gamma) = 0$ requires that $\hat{G}^{1/2} |\Pi_\gamma\rangle$ lies in the subspace orthogonal to the $\hat{G}^{-1/2} |\Psi_i\rangle$'s. To take the SEA direction, the vector $\hat{G}^{1/2} |\Pi_\gamma\rangle$ must maximize the scalar product $(\Phi - \sum_i \beta_i \Psi_i | \Pi_\gamma)$, which is equal to the entropy production $\Pi_S = (\Phi | \Pi_\gamma)$ since $(\Psi_i | \Pi_\gamma) = 0$. This clearly happens when $\hat{G}^{1/2} |\Pi_\gamma\rangle$ has the same direction as the generalized affinity vector $|\Lambda\rangle = \hat{G}^{-1/2} |\Phi - \sum_i \beta_i \Psi_i\rangle$.

V. CONCLUSIONS

In this paper, we reformulate with a somewhat unusual notation the essential mathematical elements of several different approaches to the description of nonequilibrium dynamics with the purpose of presenting a unified formulation which, in all these contexts, allows us to implement the local SEA concept whereby the dissipative, irreversible component of the time evolution of the local state is assumed to pull the state along the path in state space which, with respect to an

underlying metric, is always tangent to the direction of maximal entropy increase compatible with the local conservation constraints.

The frameworks we consider are the following: (A) statistical or information-theoretic models of relaxation; (B) small-scale and rarefied gas dynamics (i.e., kinetic models for the Boltzmann equation); (C) rational extended thermodynamics, macroscopic nonequilibrium thermodynamics, and chemical kinetics; (D) mesoscopic irreversible thermodynamics and continuum mechanics with fluctuations; (E) quantum statistical mechanics, quantum thermodynamics, mesoscopic nonequilibrium quantum thermodynamics, and intrinsic quantum thermodynamics.

The present SEA unified formulation allows us to extend at once to all these frameworks the SEA concept which has so far been considered only in the framework of quantum thermodynamics. However, a similar or at least closely related set of assumptions underlie the well-known GENERIC scheme [8–10], which developed independently.

In the present paper, we emphasize that, in the SEA construction, a key role is played by the geometrical metric with respect to which to measure the length of a trajectory in state space. The metric tensor turns out to be directly related to the inverse of the Onsager's generalized conductivity tensor. The SEA construction can be viewed as a precisely structured implementation of the MEP principle. The formal relation between the SEA metric tensor \hat{G} and the GENERIC dissipative tensor (usually denoted by M) can be established by means of a detailed technical analysis of the respective underlying mathematical landscapes. We present such discussion in a forthcoming paper, where we discuss the analogies and differences of the SEA and GENERIC approaches and show under what conditions their descriptions of the dissipative part of the time evolution can be considered essentially equivalent.

The formulation discussed here constitutes a generalization of our previous SEA construction in the quantum thermodynamics framework by acknowledging the need of more structured and system-dependent metrics than the uniform Fisher-Rao metric. It also constitutes a natural step towards generalizing mesoscopic nonequilibrium quantum thermodynamics to the far-nonequilibrium nonlinear domain.

We conclude that in most of the existing theories of nonequilibrium the time evolution of the local state representative can be seen to actually follow in state space the path of SEA with respect to a suitable metric connected with the generalized conductivities. This is true in the near-equilibrium limit, where in all frameworks it is possible to show that the traditional assumption of linear relaxation coincides with the SEA result. Since the generalized conductivities represent, at least in the near-equilibrium regime, the strength of the system's reaction when pulled out of equilibrium, it appears that their inverse, i.e., the generalized resistivity tensor, represents the metric with respect to which the time evolution, at least in the near equilibrium regime, is SEA.

Far from equilibrium the resulting unified family of SEA dynamical models is a very fundamental as well as practical starting point because it features an intrinsic consistency with the second law of thermodynamics which follows from the non-negativity of the local entropy production density as well as the instability of the equilibrium states that do

not have the maximum local entropy density for the given local values of the densities of the conserved properties, a general and straightforward conclusion that holds regardless of the details of the underlying metric tensor. In a variety of fields of application, the present unifying approach may prove useful in providing a new basis for effective numerical and theoretical models of irreversible, conservative relaxation towards equilibrium from far nonequilibrium states.

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